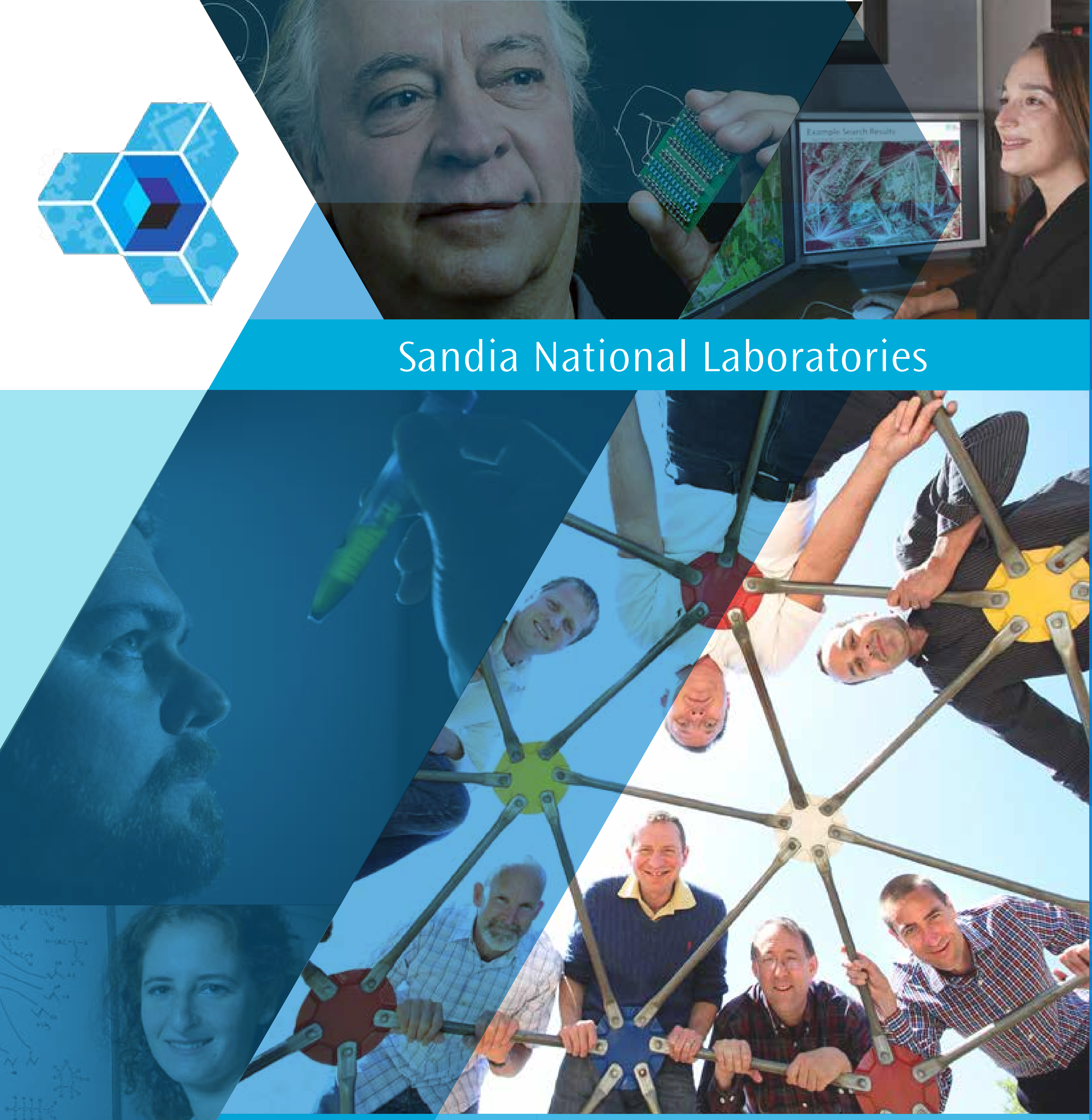


Sandia National Laboratories

Laboratory Directed Research & Development

2015 Annual Report

Twenty-five years of innovation for our nation

Throughout history, imagination and the capacity to dream have always driven great scientific and technological leaps forward. This results from stepping outside the boundaries imposed by mainstream scientific thinking, and partly from an ability to anticipate the future and what it may demand of us.

The Atomic Energy Act of 1954 provided the basis for U.S. Department of Energy (DOE) national laboratories to do just this—respond rapidly to research challenges and developments at the cutting edge of science and technology, all while nurturing the best and brightest minds in science, engineering, and technology.

To help re-energize scientific, technological, and engineering excellence at our national laboratories, the National Defense Authorization Act of 1991 authorized the laboratories to devote a relatively small portion of their research budget to "*work of a creative and innovative nature…for the purpose of maintaining the vitality of the laboratories in defense-related scientific disciplines.*" Since then, this effort has been formally called Laboratory Directed Research and Development (LDRD).

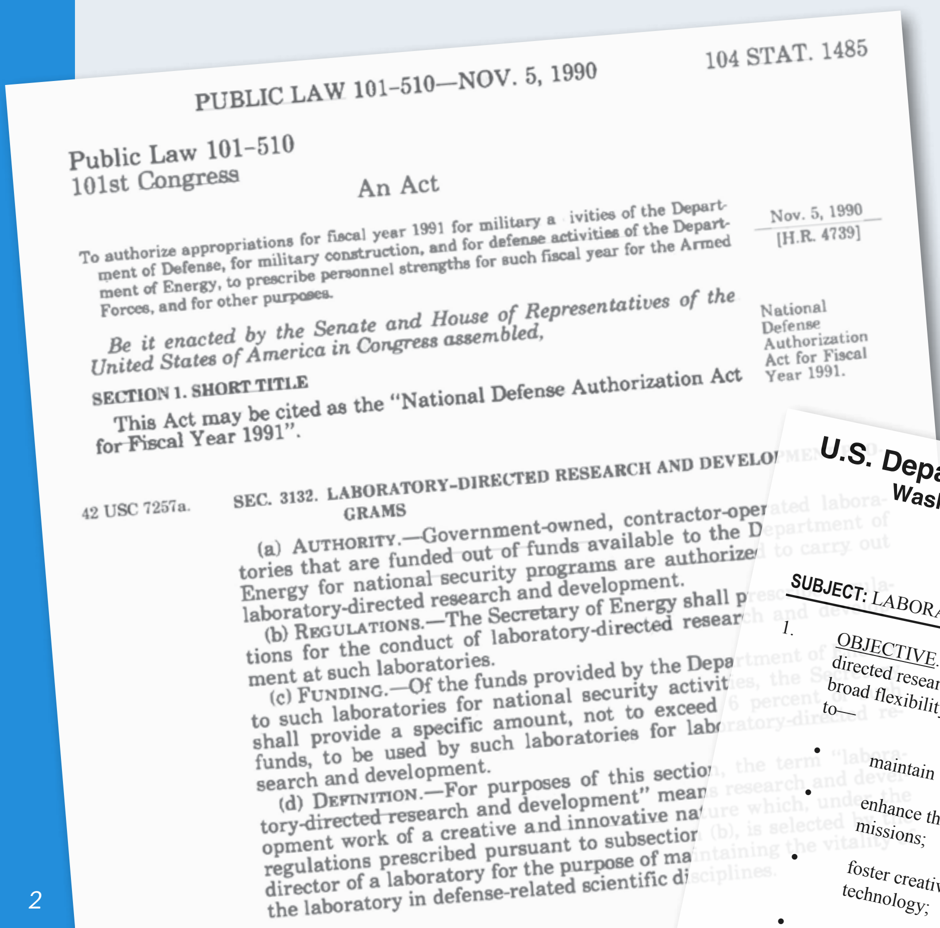
Currently directed by DOE Order 413.2C, LDRD continues to be an important mechanism for our national laboratories to anticipate, innovate, and deliver solutions for the most difficult and significant scientific and technical challenges facing our nation.

For the National Nuclear Security Administration (NNSA) laboratories, such as Sandia, LDRD is the single most important source of internal investment in the future, and allows Sandia to:

- Maintain the scientific and technical vitality of the Laboratories
- Enhance the Laboratories' ability to address current and future DOE/NNSA missions
- Foster creativity and stimulate exploration of forefront science and technology
- Serve as a proving ground for new concepts in research and development
- Support high-risk, potentially high-value research and development

25 YEARS

For 25 years, our national laboratories, through the Congressionally authorized LDRD program, have invested in high-risk, potentially high-payoff research and development to address national security challenges. Some of the nation's most impactful technologies have come from LDRD and allowing researchers to "think outside the box."



PUBLIC LAW 101-510—NOV. 5, 1990 104 STAT. 1485

Public Law 101-510
101st Congress

An Act

To authorize appropriations for fiscal year 1991 for military a ivities of the Department of Defense, for military construction, and for defense activities of the Department of Energy, to prescribe personnel strengths for such fiscal year for the Armed Forces, and for other purposes.

Nov. 5, 1990
[H.R. 4739]

Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled,

National Defense Authorization Act for Fiscal Year 1991.

SECTION 1. SHORT TITLE

This Act may be cited as the "National Defense Authorization Act for Fiscal Year 1991".

42 USC 7257a.

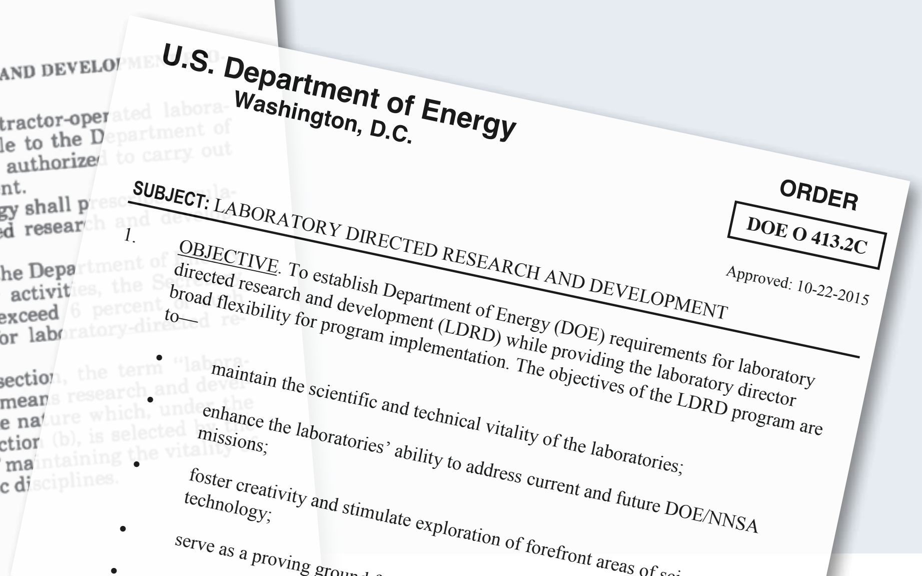
SEC. 3132. LABORATORY-DIRECTED RESEARCH AND DEVELOPMENT PROGRAMS

(a) AUTHORITY.—Government-owned, contractor-operated laboratories that are funded out of funds available to the Department of Energy for national security programs are authorized to carry out laboratory-directed research and development.

(b) REGULATIONS.—The Secretary of Energy shall prescribe regulations for the conduct of laboratory-directed research and development at such laboratories.

(c) FUNDING.—Of the funds provided by the Department of ... to such laboratories for national security activities, the S... shall provide a specific amount, not to exceed 6 percent, ... funds, to be used by such laboratories for laboratory-directed research and development.

(d) DEFINITION.—For purposes of this section, the term "laboratory-directed research and development" means research and development work of a creative and innovative nature which, under the regulations prescribed pursuant to subsection (b), is selected by the director of a laboratory for the purpose of maintaining the vitality of the laboratory in defense-related scientific disciplines.



U.S. Department of Energy
Washington, D.C.

ORDER
DOE O 413.2C

Approved: 10-22-2015

SUBJECT: LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

1. OBJECTIVE. To establish Department of Energy (DOE) requirements for laboratory directed research and development (LDRD) while providing the laboratory director broad flexibility for program implementation. The objectives of the LDRD program are to—
   - maintain the scientific and technical vitality of the laboratories;
   - enhance the laboratories' ability to address current and future DOE/NNSA missions;
   - foster creativity and stimulate exploration of forefront areas of sci... technology;
   - serve as a proving ground...

Table of Contents

On the Cover

Juan Elizondo Decanini holds two compact, high-voltage nonlinear transmission lines. Juan leads a project to exploit nonlinear behavior in materials—behavior that's usually shunned because it's so unpredictable. (173182)

Kristina Czuchlewski is principal investigator for the 26-member PANTHER team, which has accomplished a number of breakthroughs in rethinking how to compare motion and trajectories; developing software to represent remote sensor images, couple them with additional information, and present them in a searchable form; and conducting fundamental research on visual cognition. (165535)

This playground structure represents a larger-than-life nanoporous metal organic framework (MOF) to this Sandia National Laboratories research team of (clockwise from upper left) Michael Foster, Vitalie Stavila, Catalin Spataru, François Léonard, Mark Allendorf, Alec Talin and Reese Jones. The team made the first measurements of thermoelectric behavior in a MOF. (180898)

Judit Zádor's KinBot code looks for 3D structures in chemical reactions to automatically make predictions about behavior of potential reactions in combustion for a given molecule. With these predictions, scientists can identify the rates at which relevant reactions take place, information that is critical to understanding combustion. (153342)

Ryan Davis and Sandia National Laboratories colleagues have developed a method to recycle critical and costly algae cultivation nutrients phosphate and nitrogen. (165714)

A message from Sandia's Chief Technology Officer

On Nov. 5, 1990, President George H.W. Bush signed the National Defense Authorization Act for Fiscal Year (FY) 1991, establishing the Laboratory Directed Research and Development (LDRD) program. The act authorized Department of Energy laboratories to allocate a portion of their budgets toward innovative research and development that serves to maintain their scientific and technical vitality.

At Sandia, LDRD-funded work has been a major contributor to scientific understanding and technological advances. Our researchers work together across a broad spectrum of disciplines, collaborating to advance the frontiers of science and engineering in ways that are critical to Sandia's seven national security mission areas, which range from ensuring the safety, security and reliability of the U.S. nuclear stockpile to securing a sustainable energy future.

LDRD is an essential component of Sandia's strategy for sustaining and developing the world-class science, technology, and engineering capabilities needed to respond rapidly to evolving national security needs as they arise. LDRD research has contributed to scientific and technical advancement at a level that far exceeds what would be expected from a program of its size, less than 6% of Sandia's FY 2015 budget.

Over the past 25 years, Sandia's LDRD program has produced significant advances in areas such as microelectronics, materials science, defense, and advanced radar. These achievements, along with significant intellectual impacts—e.g., highly cited peer-reviewed publications, patents, professional society fellowships and awards, and R&D 100 Awards—demonstrate how Sandia's LDRD investments shape the scientific landscape and impact the state-of-the-art technologies for national security.

The LDRD program has played and continues to play a critical part in Sandia's ability to attract outstanding engineers and scientists, by creating an invigorating and productive research environment. The program has been particularly valuable in recent years as Sandia recruits and trains a new generation of talented scientists and engineers. LDRD is a critical tool in attracting highly sought-after top talent to the Labs.

Each year, researchers across Sandia submit proposals for creative, forward-looking R&D projects that have the potential to greatly benefit our national security mission. In this report, you will find descriptions of each of the projects funded in FY 2015, as well as more information on Sandia's LDRD program.

Rob Leland
Chief Technology Officer
Vice President, Science & Technology

A Snapshot of Sandia's LDRD Program

Sandia National Laboratories, like all DOE/NNSA laboratories, is charged with working on tough technical problems on behalf of the nation. Sandia's LDRD program is an essential element of the Laboratories' intent to provide "exceptional service in the national interest." As Sandia's sole discretionary R&D program, LDRD is foundational, leading-edge R&D that nurtures and enhances core science and engineering capabilities, supports national security missions, and leads to the creation of new capabilities.

PROGRAM GOALS

FY 2015 LDRD Program Statistics

149 [dollars, million] TOTAL LDRD PROGRAM COST

380 [projects] TOTAL LDRD PROJECTS

280 [dollars, K] MEAN PROJECT SIZE

1127 RESEARCHERS THAT CHARGED >10% LDRD

37% LDRD HOURS CHARGED BY NEW STAFF (< 5 YEARS AT SANDIA)

LDRD and Early Career Staff Development

278 — 51% of all Sandia
LDRD-SUPPORTED POSTDOCS
[FY 2011 - 2015]

86 — 62% of all Sandia
LDRD-SUPPORTED POSTDOC CONVERSIONS
[FY 2011 - 2015]

Intellectual Property Resulting from LDRD

1244	803	247	83	14
REFEREED PUBLICATIONS	TECHNICAL ADVANCES	PATENTS ISSUED	SOFTWARE COPYRIGHTS	R&D 100 AWARDS
[CY 2011 - 2014]	[FY 2011 - 2015]	[FY 2011 - 2015]	[FY 2011 - 2015]	[CY 2009 - 2014]
30% of all Sandia	48% of all Sandia	50% of all Sandia	24% of all Sandia	74% of all Sandia

PROGRAM OVERVIEW

Program Structure

Sandia's research strategy arises from its laboratory strategy and is organized through program elements known as Investment Areas, each of which is focused on discipline- or mission-based research priorities set by upper management. The LDRD program elements mirror this structure.

The Research Foundation Investment Areas provide cutting-edge foundational support for all of Sandia's strategic national security missions. Mission Foundation Investment Areas create and nurture the ability to provide innovative solutions for NNSA, DOE, and other Federal agencies.

	Investment Area	Mission Impact and/or Laboratory Capability
Research Foundations	Bioscience	*Analyze, understand, and control the functions of biological systems in order to reduce global chemical and biological dangers and secure a sustainable energy future.*
Research Foundations	Computing & Information Sciences	*Advance the state of the art in computer and computational science and engineering, and information and data science relevant to national security.*
Research Foundations	Engineering Sciences	*Integrate theory, computational simulation, and experimental discovery and validation to understand and predict the behavior of complex physical phenomena and systems.*
Research Foundations	Geosciences	*Perform world-class R&D focused on the properties, structure, phenomena and processes associated with the earth's geosphere, hydrosphere, and atmosphere.*
Research Foundations	Materials Science	*Nurture foundational materials capabilities by developing methodologies to enable new understanding—or create enhanced understanding—of materials issues that are critical to our national security missions.*
Research Foundations	Nanodevices & Microsystems	*Perform creative, leading edge, and high-impact R&D to discover new phenomena at the nanoscale and microscale; and create or prove new concepts, devices, components, subsystems, and systems.*
Research Foundations	Radiation Effects & High Energy Density Sciences	*Advance the state of the art in radiation effects sciences, dynamic material properties, high energy density science, inertial confinement fusion, and pulsed power technology to enable stockpile stewardship and national security missions.*
Research Foundations	New Ideas	*Support pioneering research that may lead to game-changing breakthroughs in science and technology that could eventually impact national security.*
Mission Foundations	Defense Systems & Assessments	*Develop innovative systems, sensors, and advanced science and technology solutions to detect, deter, track, defeat, and defend against threats to our national security.*
Mission Foundations	Energy & Climate	*Develop and create capabilities to contribute to the nation's energy security and resilience, economic viability, and environmental sustainability.*
Mission Foundations	International, Homeland, & Nuclear Security	*Support innovative science and technology that enhances our abilities to provide effective advice, analyses, technologies, and enterprise-level solutions to manage risks from the world's most dangerous events.*
Mission Foundations	Nuclear Weapons	*Nurture a creative and vibrant science, technology, and engineering base to support a deep scientific understanding of current and future NW products.*
	Grand Challenges	*Address bold science, technology and engineering challenges and provide breakthrough solutions to critical national security challenges.*
	Exploratory Express	*Answer a key research question, within a relatively short timeframe, in an area of current or future strategic importance to Sandia.*

Project Selection and Oversight

Each year, the LDRD program issues a Labs-wide *Call for Ideas* organized through the Investment Area leadership teams. In response, staff members generate ideas and proposals that are directed to the appropriate Investment Area selection committee for evaluation.

The Sandia LDRD program is highly competitive. In FY 2015, 866 short idea proposals were submitted; the Investment Area selection committees invited 166 of those to submit full proposals. Ultimately, 71 new projects were funded, with 51 additional projects funded throughout the fiscal year. When added to ongoing projects, 380 projects were active in FY 2015. Each proposal undergoes a rigorous review process, including peer review by subject-matter experts.

NNSA guidance—as well as SNL's internal LDRD processes—provides the framework for review and selection of Sandia's LDRD portfolio. Idea evaluation criteria include: alignment with Sandia strategy and potential impact to Sandia; technical merit and feasibility; and leading edge, high risk R&D character. For each idea selected, the respective Invesment Area appoints a Portfolio/Project Manager who has the appropriate knowledge, experience, and position to leverage the potential impact of the R&D. Multi-year projects are reviewed each year, and must show sufficient technical progress and programmatic alignment in order to receive continued funding.

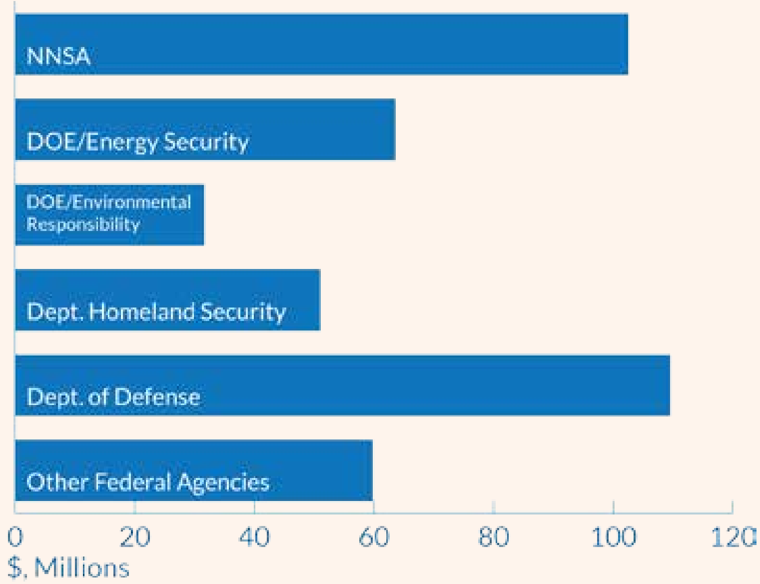
The Grand Challenges portfolio is an important investment for Sandia, and there are special requirements for these larger projects, beyond a longer, detailed proposal and a more rigorous review process. For example, they must form an External Advisory Board (EAB) to guide clarity of project vision and appropriate technical focus. The EAB critically reviews the project's technical progress and planned R&D activities, and provides insight about potential applications throughout the project lifetime.

FY 2015 Idea and Project selection process and statistics.

Mission-Enabling Research

LDRD projects are chosen for their technical quality, their differentiating and programmatic value to Sandia, and their relevance to DOE/NNSA's missions, as well as the national security missions of the Department of Homeland Security, the Department of Defense, and Other Federal Agencies.

The dollar amounts are greater than the FY 2015 program cost, since many projects are expected to benefit more than one mission and are therefore counted more than once.

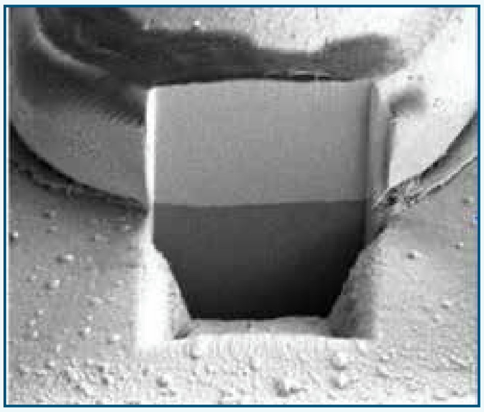


Research Highlights

Predictive Assessment of State of Health and Lifetime of NW Components

Paiboon Tangyunyong, PI

NNSA's stockpile stewardship mission is aimed at ensuring the safety, security, and reliability of weapons in the absence of underground nuclear tests. Understanding how new and existing weapons components will behave throughout the life of the system is critical to maintaining the stockpile. By performing accelerated aging tests on components, researchers can observe device behavior. In the absence of obvious degradation, other techniques must be used to understand and predict aging effects. Researchers are using Sandia-developed power spectrum analysis (PSA) to detect electrical differences in devices and determine whether PSA can detect aging effects when devices—such as commercial-off-the-shelf discrete devices, diodes, and capacitors—are subjected to accelerated life tests at elevated temperatures and voltages. Initial results suggest the method can potentially be used to study aging effects as a standalone technique or as a complementary technique to existing electrical testing methods, providing a useful tool for stockpile assurance.



HIgh-magnification scanning electron microscopy image of a focused ion beam cross-section from a bond-wire area in an unaged diode.

PANTHER: Pattern Analytics to Support High-Performance Exploitation and Reasoning

Kristina Czuchlewski, PI

PANTHER seeks to support high-consequence decision-making by unifying and advancing science across three key technical domains: sensor extraction, big data analytics, and human analytics. The project results will enable analysts to examine mountains of historical and current remote sensing data that would otherwise go untouched, while also gaining meaningful, measurable, and defensible insights into overlooked geospatial-temporal relationships and patterns. Capabilities developed by the PANTHER LDRD team are being used for specific applications in new projects sponsored by various organizations.

This image shows PANTHER's geometric and temporal trajectory analyses of air traffic patterns from 43,000 flights over the continental United States on April 4, 2014. (Credit: Sandia researcher Andy Wilson)

PROGRAM OVERVIEW

Radiography Signature Science of Homemade Explosives

John Parmeter, PI

The ability to accurately screen baggage for explosive materials is critical to aviation security. While considerable research in this area has focused on the detection of traditional explosives, research on the X-ray radiography of homemade explosives (HME) has received less attention. In this project, Sandia researchers used multi-energy computed tomography (CT) measurements and theoretical calculations to investigate the X-ray attenuation properties of various liquid and powder HME, demonstrating excellent agreement between experiment and theory in many cases. Work was also carried out in the development of novel algorithms for the analysis of raw radiography data. The project concluded in September 2015, and the project team will continue research on the X-ray radiography of various explosives as part of the Open Threat Assessment Platform (OTAP) project.

Samples awaiting X-ray.

Sandia's Twistact Technology: The Key to Proliferation of Wind Power

Jeff Koplow, PI

Twistact-based genreator technology will be designed to be a modular drop-in electrical generator for next-generation wind turbines.

Wind power represents a significant renewable energy source—however, traditional wind turbine generator architecture (gearbox-based) is difficult to scale up, often resulting in failure to key components at multi-megawatt (MW) operation. Direct-drive generators, which are less complex and lower maintenance at multi-MW scales, have traditionally relied on rare earth magnets (very high cost, reliable) or high-current slip rings (short operational lifetime, high maintenance) to transmit power. Twistact technology is a new architecture for high-current slip rings, connecting an electrical circuit between moving and non-moving parts. Twistact eliminates the need for rare earth wind turbine magnets, addressing a critical technological vulnerability to US economic security identified by the DOE (2011 Critical Materials Strategy). Twistact consists of an electrically conductive belt and a transmission device that provides a continuous ultralow resistance path for current flow. The technology provides pure rolling contact; direct metallic contact, with negligible voltage drop; a large electrical contact area; two parallel current paths; and extremely effective thermal management. Twistact was selected for participation in the DOE's LapCorp program. LabCorp aims to accelerate the transfer of innovative clean energy technologies from the DOE's National Laboratories into the commercial marketplace. Additionally, the technology recently won an Oustanding Technology Development Award from the Federal Laboratory Consortium for Technology Transfer (Far West Region).

A World-Class Research Community

Sandia's specialized missions require highly motivated, qualified staff with deep expertise, committed to advancing the frontiers of science and engineering through continual growth and development. The LDRD program supports some of Sandia's most accomplished scientists and engineers, as well as many promising early career researchers.

Jon Madison
Black Engineer of the Year
Jon's current NNSA-funded research in 3D materials science is being used to design better high-reliability components and systems for nuclear weapons and other complex engineering systems.

Somuri Prasad
Asian American Engineer of the Year
Somuri has repeatedly broken new ground in the understanding of friction and wear in materials, and made substantial contributions to national security programs.

Pavel Bochev
DOE Ernest Lawrence Award
"I am deeply honored to receive this award, which is a testament to the exceptional research opportunities provided by Sandia and DOE. Since joining Sandia, I've been very fortunate to interact with an outstanding group of researchers who stimulated and supported my work."

Margot Hutchins

Outstanding Young Engineer Award, SME
Margot currently conducts systems analysis for national security, including cyber resilience of critical infrastructure and international engagement on the implementation of nuclear detection architectures.

Steve Slutz
Fellow of the American Physical Society
Steve's MagLIF concept (magnetized liner inertial fusion), proposed in 2010, is currently providing realistic data about neutron production, a key component of nuclear fusion.

Dan Sinars
Fellow of the American Physical Society
Dan's citation reads, "For scientific contributions and leadership in the development of innovative X-ray radiography and spectroscopy diagnostics for the study of z-pinch physics, inertial confinement fusion, and high energy density physics."

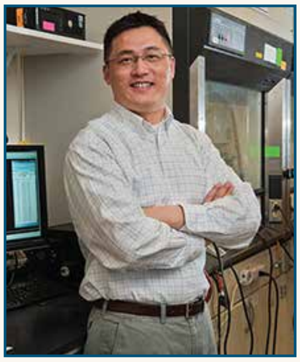
Abraham Ellis
Great Minds in STEM, Outstanding Technical Achievement
Sandia's research on integration of solar and other renewables into the grid has grown considerably, due in part to Abraham's contributions as a researcher, team lead, and deparment manager.

Susan Rempe

New Mexico Women of Influence Award
"LDRD has had a major impact on my career by funding research that helps me and my colleagues find innovative solutions to global problems in cancer drug therapy, water purification, and carbon dioxide capture."

Patrick Feng
Asian American Engineer of the Year
Patrick's work focuses primarily on the luminescence properties of materials, or how light is emitted in response to various stimuli. In several of his projects, Feng and his team develop organic-based materials for the detection of fast neutrons, the signature for a variety of fissionable materials.

Hongyou Fan
Fred Kavli Distinguished Lecture in Nanoscience, Materials Research Society
Hongyou's pioneering research in the field of nanoparticle assembly and integration has supported a paradigm shift from nanoscience discovery to practical nanotechnologies.

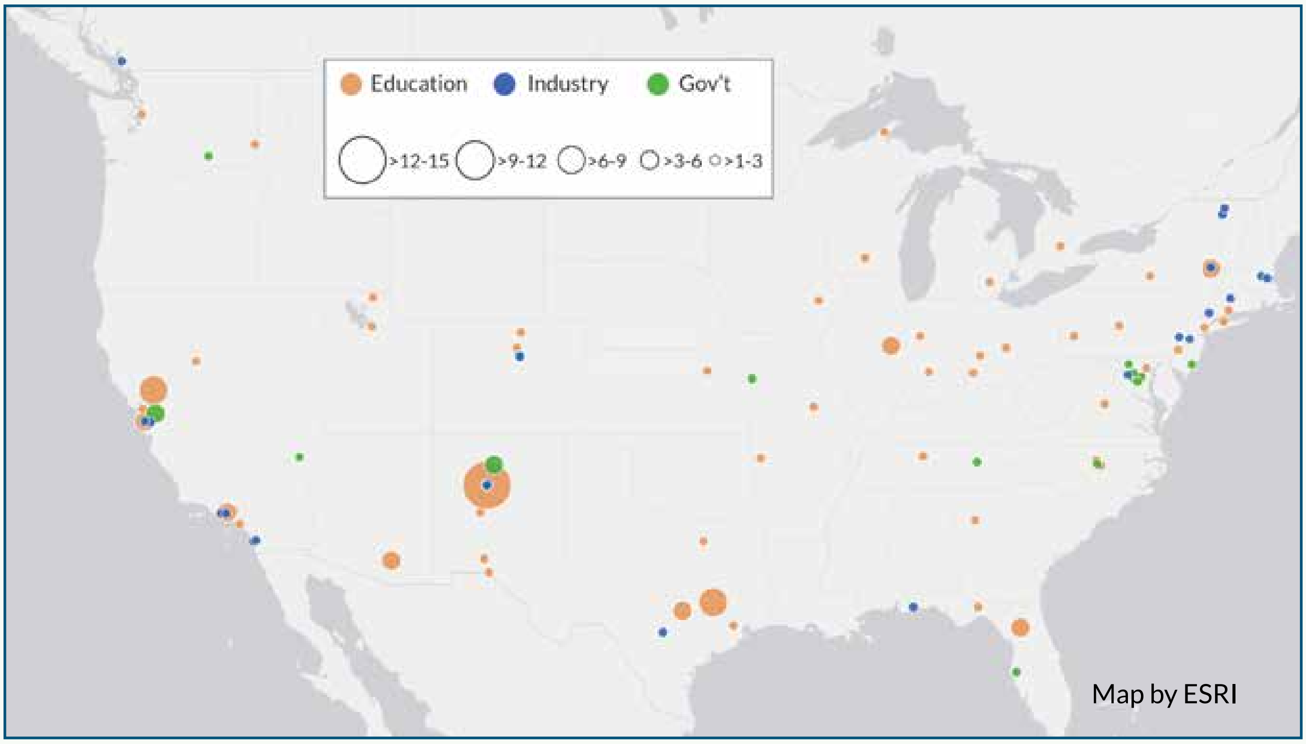


Tamara Kolda
Fellow, Society for Industrial and Applied Mathematics
"Initial funding from Sandia's LDRD program allowed us to develop techniques that are profoundly valuable in scientific and national security data analysis programs."

A Program Rich With Collaboration

Collaborations between Sandia's LDRD researchers and universities, national laboratories, government agencies, and industry enhance Sandia's future capabilities through an influx of knowledge and skills. Sandia's partners also benefit from collaborative research results and interaction with peers from outside their organization. In addition to furthering science, partnerships with academia often provide an important opportunity for Sandia to recruit the world-class scientists and engineers needed for development of mission-critical lab capabilities. Partnerships with industry enable technological breakthroughs developed through the LDRD program to be commercialized under licensing agreements and brought to market for the US public good.

In FY 2015, LDRD researchers at Sandia collaborated with nearly 100 experts across the US, as shown below. Each type of partership is color-coded. The size of each symbol corresponds to the number of unique parterships at an individual institution.



Research Excellence in Service of the Nation

LDRD supports Sandia's mission by investing in leading-edge research that advances the frontiers of science and engineering critical to national security. The program is also instrumental in attracting and developing a world-class workforce of scientists and engineers, the people who make it possible for Sandia to achieve its mission and goals.

To learn more, visit www.sandia.gov/ldrd.

Bioscience

The overarching goal of the Bioscience Investment Area is to develop new competencies in biological science to address two application areas in Sandia's broad national security mission — biodefense and emerging infectious disease, and biofuels.

The research in biodefense includes developing better ways to detect, characterize, and contain harmful pathogens. The strategy integrates advanced technologies with an understanding of human health and immune response. The goal is to improve the response to disease outbreaks and to limit their spread.

The research regarding the nation's reliance on fossil fuels focuses on developing efficient, economical biofuels that can replace or reduce current gasoline, diesel, and aviation fuel consumption. The research includes two sources of energy: lignocellulose, or dry plant matter, and algae. The aim is to find efficient and economical methods to convert lignocellulose into fuels and to understand the factors that govern algal pond stability and identify molecular mechanisms that can be used for lipid/fuel production.

Projects

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Bio-Emulative MOF-Based Lignin Degradation Catalysts

180812 | Year 1 of 3 | **Principal Investigator: M. D. Allendorf**

Project Purpose:

Lignin is the most abundant source of renewable aromatics, with 200-300 Mtons/year projected production by a US biofuels industry, that would process ~1B tons of biomass to meet DOE goals. However, there are currently no efficient processes for extracting these aromatics and converting them to value-added chemicals and drop-in fuels. The technical and economic challenges are staggering, due to the quantities of material involved and lignin's recalcitrance to depolymerization. Conventional lignin degradation processes use aggressive reagents and are energy intensive (400-800°C) and yield complex product mixtures. Milder reaction conditions and narrower product distributions could be achieved using lignin-degrading enzymes, but these are too fragile to be practical for large-scale biorefining. The objective of this project is to develop lignin valorization methods in which oxidative solubilization provides a feedstock for industrially robust catalysts based on metal-organic frameworks (MOFs). MOFs are nanoporous materials with exceptional synthetic versatility arising from a structure comprised of metal ions linked by rigid organic groups. Our strategy is to emulate natural lignin degradation, wherein extra-cellular fungal enzymes generate reactive species to partially degrade lignin. The resulting, low-molecular-weight products are metabolized by lignin-utilizing microorganisms, such as *Sphingobium sp.* SYK-6. We will employ computational biology and in situ diagnostic probes to obtain structural and energetic knowledge of enzyme-catalyzed reactions that we will translate into MOF structures. The lignin pretreatment will employ an inexpensive homogeneous catalyst (e.g., Fenton reaction) or chemical treatment to control the molecular weight distribution of solubilized products, thereby accelerating reaction with the MOF and improving selectivity.

Conventional catalysts for lignin degradation are either costly (e.g., Pt-group metals) or difficult to separate from reaction products (e.g., vanadium complexes). New valorization strategies, combining the best features of enzymes with the robustness of heterogeneous catalysts, require fundamental research to understand reaction mechanisms and develop novel catalyst chemistries.

BIOSCIENCES

Consolidated Bioprocessing and Biofuels Production Platform

165822 | Year 3 of 3 | **Principal Investigator: R. W. Davis**

Project Purpose:

Depleting fossil fuel reserves and environmental concerns are the major catalysts for research into alternatives for transportation energy that are renewable and carbon neutral. To achieve current US renewable fuels goals, approximately 1 billion tons of residual biomass would need to be converted to biofuels. This research aims to reduce biofuel production costs by building a consolidated bioprocessing (CBP) platform, reducing processing steps. We propose to utilize the proteolytic bacterium *Bacillus subtilis* as a chassis to engineer a microbial bioreactor that both degrades biomass feedstocks and produces advanced infrastructure compatible biofuels. We will consolidate biomass pre-treatment and advanced biofuel production to a single bioreactor platform. CBP will reduce unit operations and increase process efficiency by reducing mass transport phenomena and processing steps and costs. Our proposed CBP chassis, *B. subtilis*, produces various enzymes including amylase and various proteases which make it ideal for CBP of high protein biomass, especially microalgae. Although *B. subtilis* accepts a variety of substrates for bioconversion, optimization of amino acid conversion to fuels requires modification of carbon flux pathways and minimization of stress response genes. Therefore, the goal of the research with University of California-Los Angeles is to: 1) investigate combinatorial genetic knock-outs of genes involved in sporulation and 2) use this platform for CBP of protein rich cellulosic biomass to produce advanced biofuels using the amino acid transamination pathway to produce fusel alcohols.

Summary of Accomplishments:

We identified the amino acid consumption profile of *B. subtilis*, including fermentation inhibitors and limiting reagents. It was found that glutamine, cysteine, and proline were completely consumed within 48 hours; asparagine and serine were completely consumed within 96 hours. Within 144 hours, aspartic acid and arginine were completely consumed, while alanine and isoleucine were ~75% consumed. Cysteine was found to be the only essential amino acid required for robust growth of *B. subtilis*. In an effort to emulate the nisin-induced phenotype (i.e., prevent starvation stress), we generated the strain *B. subtilis* Δ*codY*Δ*bkdB*Δ*relA*. Deletion of stringent-response regulator/ppGpp(p) synthase *relA* in *B. subtilis* Δ*codY*Δ*bkdB* led to increased biofuel production. This strain exhibited a delayed response to amino acid starvation as evidenced with the approximately 80% increase in biofuel titers. Furthermore, the strain achieved 60% of the maximum NH_3 yield and 28% of the maximum biofuels yield from amino acids and exhibited a partial-starvation resistance that moves towards complete consumption of protein; maximum conversion titers were achieved within 48 hours. The results indicate that stress gene knockdown should be considered as a general strategy for increasing biofuel yields from bioconversion of biomass

Significance:

The R&D effort and external collaboration bolsters biofuels and renewable energy for the energy security mission and assists with capability development for biomanufacturing with synthetic biology platforms. The results have been key to obtaining follow-on funding from DOE's Office of Energy Efficiency and Renewable Energy-Bioenergy Technologies Office as a part of the Annual Operating Plan portfolio for Algae Biomass and Feedstock Logistics.

Coupling Chemical Energy with Protein Conformational Changes to Translocate Small Molecules across Membranes

180817 | Year 1 of 3 | **Principal Investigator: S. Rempe**

Project Purpose:

All living cells rely on continuous exchange of diverse molecular species (e.g., nutrients, precursors, and reaction products) across cellular membranes for their normal function and survival. Membrane transporters are specialized molecular devices that provide the machinery for selective and efficient transport of materials across the membrane. The biological significance of membrane transporters cannot be overstated, given their central role in a myriad of key cellular processes and their subsequent targeting by a large number of pharmaceuticals. The significance of membrane transporters is also evident from a recent major focus shift of experimental structural biological studies towards characterizing structural states arising during the function of these proteins. Currently, our understanding of active membrane transport is limited. Experimental methods provide only snapshots of the energy-coupled transporter activity. Our goal is to obtain an understanding of the full mechanism. Specifically, we endeavor to understand how chemical energy in a cell couples with the mechanics of protein conformational changes to produce directional translocation of a specific substrate across cellular membranes. To achieve this understanding requires a dynamical description of structural transitions during the transport process and the free energy barriers along the transport pathway. We propose to use molecular simulation to achieve those goals. Upon successful completion, the project will provide, for the first time, a detailed mechanistic description of the entire transport cycle for membrane transporter. The project uses Sandia's high performance computing capabilities, and extensive expertise in molecular simulation of proteins. The work is in collaboration with University of Illinois at Urbana-Champaign.

The research is high-risk due to challenges with determining complex pathways in biological reactions. The result will be new insights for directing transport of specific molecules important to energy and biodefense across membranes.

CRISPR Technology for Biodefense and Emerging Infectious Disease Countermeasure Development

180811 | Year 1 of 1 | **Principal Investigator: O. Negrete**

Project Purpose:

Two urgent problems threaten national and global biosecurity: 1) accelerating emergence of highly virulent, transmissible, and drug-resistant pathogens and 2) globally available, low-cost tools for creating and re-engineering organisms, increasing greatly the odds of the accidental or intentional manufacture and release of deadly pathogens. The hallmark of these biothreats is genetic novelty that evolved naturally or was introduced deliberately to enhance virulence and multi-drug resistance, rendering existing countermeasures ineffective. Traditional drug discovery strategies simply cannot keep up with naturally occurring or potentially engineered antiviral/antimicrobial resistance. New approaches are desperately needed to develop effective countermeasures against a wide variety of infectious diseases. An ideal countermeasure would be easily modified to target different pathogen classes and strains, and require minimal information about the pathogen. Clustered regularly interspaced short palindromic repeats (CRISPR) is a method that can be used for genomic editing, gene inactivation/activation, or suppression of viral RNA replication with a two-component system that consists of a RNA-guided endonuclease Cas9 and a guide RNA (gRNA) complementary to the nucleic acid target. Our main goals for this project were to develop regents and protocols for applying CRISPR-based countermeasures against virus infection.

Summary of Accomplishments:

We first used a host-directed CRISPR countermeasure strategy targeting the Ebola virus (EBOV) receptor with our BSL-2 EBOV virus model (VSV-EBOVGP-GFP). We designed gRNA sequences targeting 600bp, 1200bp and 2100bp into the open reading frame of human NPC1 gene and then used them along with Cas9 to create genome-edited NPC1 knockout cells using VSV-EBOVGP-GFP as a selection pressure. This result demonstrated that targeting NPC1 using CRISPR systems would prevent infection by Ebola GP –VSV. Additionally, we generated CRISPR reporter cells for high-throughput efficiencies measurements. The design of the reporter places a target CRISPR cut site between a red fluorescent protein (RFP) and green fluorescent protein (GFP) genes with the GFP gene out of frame. Endonucleases targeted to the cut site will induce frameshift to move GFP in frame. We have made single cell clones of these constructs in HEK293T and HepG2 cells. Lastly, we have made lentivirus-pooled libraries for CRISPR knockout (KO) screening that can identify host factors involved in virus infection similar to genome-wide RNAi technology. However, CRISPR KO screening is a more robust approach for identifying viral-host interactions due to the fact that RNAi gene silencing is typically incomplete and CRISPR can completely suppress gene expression. We expanded the GeCKO v2 library, verified the coverage of the plasmid expansion using MiSeq Illumina sequencing and have begun screening in HEK293T cells. In all, we developed regents and protocols for CRISPR-based countermeasures using this technology.

Significance:

The proposed research directly addresses the national security mission, specifically in the realm of biosecurity and protection against bioterrorism. The research supports DoD's mission to develop medical countermeasures to ensure robust defense against biological warfare threats.

Discovery of Anti-Viral Inhibitors against the Chikungunya Virus nsP2 Protease Domain

186364 | Year 1 of 3 | **Principal Investigator: B. N. Harmon**

Project Purpose:

Chikungunya virus (CHIKV) is an emerging mosquito borne alphavirus that causes devastating arthritic disease. CHIKV has been responsible for major outbreaks in Africa and Asia leading to serious morbidity and mortality in humans. The first cases of CHIKV were reported in the western hemisphere in late 2013 and nearly 1 million suspected CHIKV infections have occurred in the Americas in the last year. The CHIKV mortality rate has been estimated to be 1:1000. The US National Institute of Allergy and Infectious Disease (NIAID) lists CHIKV as a category C biodefense priority pathogen due to the ability to engineer this pathogen for mass dissemination. At present, there are no licensed vaccines or treatment options to combat CHIKV infection, and research in the development of therapeutics has been limited. To develop timely countermeasures against this biological threat, this project seeks to discover lead compounds for the treatment of CHIKV. Specifically, we will discover drug-like small molecules that are inhibitors of the viral nsP2 protease (nsP2pro) using advanced bioinformatics, cheminformatics and experimental screening methods. Viral nsP2pro is a cysteine protease encoded as part of the viral non-structural polyprotein, and is essential for processing of the polyprotein into functional proteins and for viral reproduction. At the end of the proposed two year project, our goal is to have in hand small molecule inhibitors that meet three criteria: 1) effective inhibition of nsP2pro proteolytic activity, demonstrated *in vitro* and *in vivo*, 2) low inhibition of human proteases and low cytotoxicity, and 3) robustness to resistance due to sequence mutations.

We seek to discover antiviral methods, including the development of a novel FRET-based substrate for high-throughput screening and computer-aided modeling and structural activity relationship for down selection of candidate inhibitors, to allow the identification of compounds that inhibit nsP2pro at nanomolar concentrations in vitro, and inhibit disease in animal models. Unique combined expertise in biodefense, modeling/simulation can accomplish these objectives.

EKSG: A Universal Sample Prep Technology for Multidimensional Bioscience

173020 | Year 2 of 2 | **Principal Investigator: A. Hatch**

Project Purpose:

Systems-level understanding of biological states and disease mechanisms typically requires multidimensional analysis of key samples. Unfortunately, multidimensional analysis is often difficult or impossible using current sample preparation methods, due to inherent challenges purifying multiple analytes from small samples (e.g., human clinical, animal model). Each method generally recovers only certain sub-classes of analyte, yet splitting sample for multidirectional processing is problematic or, for small samples, not feasible. Moreover, treatments of sample and sample-derived analytes can lead to analyte degradation and other undesirable effects (e.g., mixing of intra- and extra-cellular analytes), making interpretation difficult. We aim to address current deficiencies by developing a powerful new sample preparation competency. We will develop a novel electrokinetic step gradient (EKSG) device for continuous processing of blood sample input, enabling precise segregation of different analyte classes (nucleic acids, proteins, nanoparticles, cells) into separate collection reservoirs for downstream analysis. EKSG will be applied to small volumes ($\leq 100\ \mu l$) of healthy whole blood, tuned for simultaneous isolation of informative analytes: 1) mRNA, microRNA, and proteins from white blood cells, 2) microRNA from extracellular vesicles, 3) mRNA, microRNA, and proteins from extracellular RNA/protein nanoparticles, and 4) "free" extracellular DNA, microRNA, and proteins. We will similarly apply EKSG to infected blood for additional isolation of such analytes from viral or bacterial pathogens. Nucleic acid fractions will be analyzed using quantitative polymerase chain reaction (qPCR) and high-throughput sequencing, and proteins using mass spectrometry.

This R&D work explores a novel and significant "disruptive" sample prep technology that could dramatically improve a majority of bioanalytical methodologies. Our novel microdevice configurations facilitate a clever enabling technology solution. The possibility of rapidly isolating the multiple proposed components from a single complex sample is daunting and unprecedented.

Summary of Accomplishments:

We validated a new approach to separating constituents of biological samples. A clear distinction was made between the physical operational principles of the EKSG device and alternative methods reported to date in the scientific and patent literature. We achieved greater than 90% extraction efficiency and greater than 90% purity for isolating multiple key biological analytes including nucleic acids, proteins and blood cells from a continuous sample input. The extraction process occurs within seconds. The ability to separate these multiple sample constituents with the speed and purity in a continuous format is unprecedented.

We designed, built, and tested more than one hundred EKSG microfluidic devices with several iterative design cycles to achieve the high purity and efficiencies demonstrated. We designed and built the imaging, fluidics and electronics control system to operate the devices and image the separation processes. The operational principles and scaling laws were explored by COMSOL, multiphysics modeling, to validate the novelty of our approach, and the overriding physics principles that enable optimization of devices for high efficiency and purity of separation.

The methods were demonstrated with relevant biological samples including blood. The system was also proven to be capable of sorting small microliter volumes important for precious samples and also proven to work for much larger volumes if desired.

Significance:

Many fundamental approaches in the biodefense mission space require sample preparation. The most dangerous pathogens are difficult to study and infectious samples are a precious commodity. Traditional sample processing methods waste sample and limit the extent of analysis that can be performed. This technology enables detailed analysis from these precious samples. The technology is also faster, and leads to more accurate multi-analyte analysis.

In Vivo High-Throughput Transcriptomics to Elucidate the Spatial and Temporal Dynamics of Host-Pathogen Interactions

173021 | Year 2 of 3 | **Principal Investigator: R. Meagher**

Project Purpose:

Transcriptome sequencing (RNA-Seq) has the potential to revolutionize studies of microbial pathogenesis by providing information on the dynamics of gene expression in both the host and pathogen. Although host response to bacterial infection is well studied, the many mechanisms used in concert by pathogenic bacteria to survive and proliferate within a host are poorly understood for many bacteria. A novel Sandia-developed approach called Pathogen Capture can enrich microbial transcripts 100-fold or more, allowing complete recovery and sequencing of the microbial transcriptome without altering host transcripts. However, this technique is low-throughput which is an obstacle to performing large transcriptomic studies.

We propose to develop a high-throughput, automated Pathogen Capture system to enable a host-pathogen interactions study using two model systems: primary cell infection with multi-drug resistant *Klebsiella pneumoniae* (part of an important class of emerging, difficult-to-treat pathogens with associated high mortality and morbidity), and an animal infection model of *Salmonella typhimurium*, in collaboration with the University of Colorado. By enriching for microbial transcripts, we will discover the transcriptional sequence of events by which these pathogens infect the host, overwhelm the immune system, and resist treatment with antimicrobial drugs.

Our proposed pathogenesis investigations will require large sample sets, which are uniquely enabled by the proposed high-throughput platform for Pathogen Capture. The device and methods are broadly applicable to understanding the dynamics of any microbial or viral pathogen in any host system, and the coupled host/pathogen transcriptomic data is a fundamentally new, innovative technique to studying host/pathogen interactions.

The proposed research will generate new knowledge about the pathogenesis of *Salmonella* and *Klebsiella*, which have biodefense relevance (National Institute of Allergy and Infectious Disease (NIAID) Biodefense Categories B and C). The proof-of-concept data and automated system produced by this project will make us attractive partners for collaborations with leaders in microbial pathogenesis.

BIOSCIENCES

Metal Organic Frameworks for Targeted, Triggered, Sustained, and Systemic Delivery of Antibiotics

173493 | Year 2 of 2 | **Principal Investigator: C. E. Ashley**

Project Purpose:

Engineered nanoparticles promise to revolutionize the prevention, detection, and treatment of biological and chemical threats by enabling development of next-generation adjuvants, affinity reagents, and therapeutics. Nanotechnology is especially critical for improving the bioavailability of antibiotics and antivirals through targeted accumulation of nanoparticles at sites of infection and subsequent release of therapeutic payloads in response to an appropriate stimulus. However, many existing nanoparticle delivery vehicles, including liposomes and polymersomes, suffer from limited capacities, uncontrollable release profiles, and complex, specialized synthesis procedures that must be re-adapted for each new cargo molecule, leading to drug- and disease-specific 'one-off' approaches. To address these limitations, we propose to develop mesoporous silica nanoparticles (MSNPs) and metal organic frameworks (MOFs) for targeted delivery of antibiotics to cells, tissues, and organs infected with the Category A biothreat *Francisella tularensis*, which causes the disease tularemia upon inhalation or absorption. MSNPs and MOFs have unprecedented surface areas, synthetic flexibility, and chemical robustness and promise to yield a new, differentiating Sandia capability that enables pre-administration of therapeutics to laboratory, first-responder, or military personnel who are at risk of being exposed to a biological threat. Our proposed effort will also facilitate event recovery by enabling effective decontamination of surfaces or buildings after accidental or intentional release of a biothreat. Furthermore, MSNP and MOF technologies should be easily extendable to delivery of nerve agent countermeasures, treatment of traumatic brain injury, and creation of broad-spectrum vaccine adjuvants. Consequently, this work will help establish Sandia as a leader in the fields of nanotherapeutics and nanoadjuvants. MSNPs and MOFs promise to address many of the limitations of current nanoparticle delivery vehicles. External sponsors typically require *in vivo* evidence of a nanoparticle's potential, however. We will demonstrate *in vivo* proof of concept that MSNPs and MOFs are superior delivery vehicles for small molecule drugs, including antibiotics and antivirals.

Summary of Accomplishments:

Over the course of this project, we synthesized MSNPs and optimized their hydrodynamic diameter, surface area, pore size, and pore chemistry in order to achieve loading capacities for physicochemically disparate antibiotics that exceed those of other nanoparticle delivery vehicles (e.g., liposomes, polymersomes) by 100 to 1000-fold. We then coated antibiotic-loaded MSNPs with biocompatible lipids and tuned properties of the MSNP core and lipid coating to enable long-term retention of encapsulated antibiotics in neutral-pH buffer and blood, as well as tailorable release rates under intracellular conditions. Next, we demonstrated that modifying lipid-coated MSNPs with targeting and endosomolytic ligands promotes highly selective uptake by target cells (i.e., cells that *Francisella tularensis* infects) followed by intracellular release of encapsulated antibiotics, both of which are critical to kill intracellular bacteria in vitro. Finally, we demonstrated that lipid-coated MSNPs, when loaded with antibiotics and targeted to cells and organs that *Francisella tularensis* infects, dramatically improve the efficacy of antibiotics. Impressively, lipid-coated MSNPs increased the survival of mice infected with *Francisella tularensis* from 0% for the 'free' antibiotic to 100%, while also reducing the dose from 40 mg/kg for the free antibiotic to 8 mg/kg, and reducing the dosing frequency from twice per day for the free antibiotic to once every other day. These data are truly revolutionary given the increasing prevalence of drug-resistant bacteria and are under preparation for submission to *Nature*. In addition to our work with MSNPs, we also synthesized MOFs and demonstrated that they have high *in vitro* biocompatibility and colloidal stability and are, therefore, promising as bioimaging agents and delivery vehicles for antibiotics and other medical countermeasures.

Significance:

Our results are the first-ever demonstration that loading antibiotics in nanoparticles and targeting them to sites of infection can reduce the efficacious dose, frequency, and duration of treatment and even recover the effectiveness of antibiotics against which bacteria have developed resistance. These revolutionary data will accelerate Sandia's ability to help respond to outbreaks caused by emerging pathogens or biological weapons in a rapid and cost-effective fashion. They will also establish Sandia as a major player in the field of nanoparticle-based medical countermeasures.

Predictive Pathogen Biology: Genome-Based Prediction of Pathogenic Potential and Countermeasures Targets

180814 | Year 1 of 3 | **Principal Investigator: J. S. Schoeniger**

Project Purpose:

Pathogens with novel genomes arise from emergence of zoonotic agents, anthropogenic selection, or genetic engineering. Understanding molecular mechanisms of pathogens requires years of work, but arresting an outbreak requires rapid assessment of virulence and countermeasure targets. We are grossly unprepared to respond to an engineered biothreat attack: we cannot cope with naturally emerging drug-resistant species. Next-generation sequencing (NGS) technology enables rapid availability of complete genome sequences from outbreak-causing pathogens. Large sets (N>100) of genome sequences from taxonomically related pathogens of differing virulence are now publicly available and the cost for sequencing continues to fall: to apply this revolutionary capability to outbreak response, we urgently need better tools to utilize these data to reliably predict pathogenicity, identify pathogen-lethal targets, and predict countermeasure effectiveness.

Currently, best methods predict correct gene function ~60% of the time, and ~30% of bacterial proteins have no assigned function. While improved annotation is necessary, we propose a more fundamental shift to a data-driven comparative approach. We will implement an analysis pipeline wherein gene and genome features are harvested from large sets of related genomes and statistical and machine learning methods are used to predict drug resistance and virulence phenotypes, similar to a Genome Wide Association Study (GWAS) but with richer feature sets, including horizontal gene transfer descriptors. We will also demonstrate cost-effective sequencing and assembly of hundreds of genomes of common pathogen species directly from clinical samples, and apply our pipeline to predicting observed clinical phenotypes, showing that scaling to ~10,000 genomes will eventually be feasible.

This project will establish proof of principal and software tools for a new approach to predicting pathogen behavior, and demonstration of scaling for sequencing and analysis of thousands of pathogen genomes.

Recombinant Vesicular Stomatitis Virus for Therapeutic Antibody Epitope Mapping and Vaccine Development

170801 | Year 3 of 3 | **Principal Investigator: O. Negrete**

Project Purpose:

Identification and characterization of antibody binding sites (epitopes) are important for the development of novel vaccines, therapeutics, diagnostics, and affinity reagents. Several methods have been established to map epitopes on target antigens, including x-ray co-crystallography of antibody-antigen complexes, array-based peptide scanning, and 'shotgun' mutagenesis mapping. Combinatorial techniques, such as phage display, are less labor- and cost-intensive but are unable to reliably map complex 3D conformational epitopes. Rapid and cost-effective methods of mapping of neutralizing antibodies binding sites at high resolution are currently lacking. This project seeks to develop a novel technology based on recombinant vesicular stomatitis viruses (rVSV) that provides rapid information about the amino acid sequences of therapeutic neutralizing antibody epitopes to aid in vaccine development for priority pathogens of national security concern.

Many priority pathogens classified as potential agents of bioterrorism by the National Institute of Allergy and Infectious Diseases (NIAID) require handling in high-level biocontainment facilities and a complex biosafety infrastructure (e.g., high containment labs, select agent registration/permits). This project seeks to create a rapid capability for the high resolution mapping of antibody epitopes for BSL-3 and BSL-4 biothreat pathogens under BSL-2 containment. We will accomplish this goal by creating libraries of pseudotypical rVSV variants displaying high-complexity randomly mutagenized biothreat antigens. Once the rVSV libraries are developed, we aim to recover detailed information about the amino acid sequences of conformational epitopes recognized by multiple monoclonal antibodies or polyclonal antisera in less than one week using minimal amounts of each antibody.

Our high-risk/high-reward approach for rapid and cost effective epitope mapping of antibodies that recognize biothreat pathogens would have an immediate impact in the development of novel vaccines, therapeutics, diagnostics, and affinity reagents. Our established techniques for creating recombinant vesicular stomatitis virus (VSV) are poised to enable a revolutionary change in epitope mapping of conformational antibodies.

Summary of Accomplishments:

During the course of this project, three major milestones were achieved. First, under BSL-2 containment, we generated a recombinant virus expressing the Ebola virus (EBOV) glycoprotein in preparation for studies of virus entry, antibody response, diagnostic testing and therapeutic inhibitor screening. This recombinant construct is based on the current EBOV vaccine vector in phase III clinical trials known as VSV. We also fused the VSV-P gene with a green fluorescent protein (GFP) in order to easily measure infection using fluorescent microscopy or microtiter plate reader. We rescued the recombinant VSV-EBOVGP-GFP virus in tissue culture cells and confirmed the presence of EBOV-GP on the surface of the virions using an antibody neutralization assay. Our second milestone was met when we performed proof-of-concept studies that tested antiviral strategies targeting the EBOV lipid membrane against our BSL-2 Ebola virus model. Our final milestone was achieved when we characterized the receptor usage of Cedar virus, a new henipavirus (RNA virus). The ability of Cedar virus to use multiple receptors indicates the potential for a broader cellular tropism compared to Nipah virus and Hendra virus. The techniques used to create recombinant VSV reagents and the data obtained from this virus construct will be used in response to future calls on Ebola virus or Nipah related viruses for studies on countermeasures, antibody response, and/or diagnostic testing.

Significance:

NIAID priority pathogens such as Nipah and Hendra viruses are considered potential bioterrorism and agroterrorism agents of national security concern. There are currently no specific therapies or licensed vaccines for many of these highly pathogenic biodefense agents. This project benefits the biosecurity mission through early R&D of a technology that can define the immunodominant structures on viruses, which will facilitate the design and development of improved vaccines against biodefense pathogens. Understanding the full range of viral epitopes targeted by the immune system is vital to designing better vaccines.

Systems-Level Synthetic Biology for Advanced Biofuel Production

170804 | Year 3 of 3 | **Principal Investigator: A. Ruffing**

Project Purpose:

The US is currently reliant upon foreign fossil fuel resources, representing a significant threat to national security. The limited supply of fossil fuels presents a significant challenge for future energy provision, and the accumulation of carbon dioxide from fossil fuel combustion may lead to significant changes in the global climate. The development of a renewable energy source, such as biofuels derived from microalgae, will help lead to energy independence for the US while also addressing concerns of fossil fuels supply and climate change. However, microalgal fuel production is currently limited by the low natural productivities of microalgae. Synthetic biology techniques may be applied to improve the fuel-producing capacity of these microorganisms, yet the impact of this strategy is limited by the one part (or circuit) at a time approach of traditional synthetic biology. To reach the fuel production rates necessary to make this process economically viable, microalgae must be genetically modified at a systems level to optimize the entire genome for fuel production. Hence, new methods and synthetic biology tools must be developed for these microalgal hosts. This project will develop a systems-level synthetic biology approach for targeted genetic manipulation of microalgae. With this technique, multiple genetic targets will be modified in a single transformation step, leading to a significant reduction in the time required for strain development. As an example, consider a strain requiring ten genetic modifications for improved fuel production: the traditional approach would typically require ten months for strain development, assuming a conservative four weeks per genetic modification. The projected systems-level approach would construct the same strain in only one month. Additionally, the systems-level synthetic biology technique would generate variants with different combinations of the ten targeted modifications. Given the inherent non-linearity of biological systems, these combination variants may have unknown synergistic effects, resulting in increased fuel production and informing our basic understanding of fundamental microalgal biology.

Summary of Accomplishments:

This project advances the development of a multiple promoter replacement technique for systems-level optimization of gene expression in a model cyanobacterial host: *Synechococcus* sp. PCC 7002. To realize this multiple-target approach, key capabilities were developed, including a high-throughput detection method for advanced biofuels, enhanced transformation efficiency, and genetic tools for *Synechococcus* sp. PCC 7002. Nile Red and Bodipy based neutral lipid staining methods were developed for characterization and quantification of free fatty acids and alkanes, potential biofuel products. These staining methods may be integrated into high-throughput screening methods for characterizing modified production strains. For modification of our cyanobacterial host *Synechococcus* sp. PCC 7002, we identified and characterized neutral integration sites within the host genome. Parameters used for transformation of *Synechococcus* sp. PCC 7002 were also optimized, including cell concentration and length of homology arms for genome integration. Additionally, exonuclease activity was detected as a potential factor for reduced transformation efficiency in *Synechococcus* sp. PCC 7002, and high genome copy number was identified as an obstacle in generating mutants in this strain. To enable high-throughput characterization of genome integration and gene expression, we characterized fluorescent protein reporters and native promoters in *Synechococcus* sp. PCC 7002. Three fluorescent protein reporters were expressed in *Synechococcus* sp. PCC 7002 and shown to be useful for imaging, flow cytometry, and quantification of gene expression. Twenty-four native promoters were characterized in *Synechococcus* sp. PCC 7002 using a fluorescent protein reporter; these promoters will serve as a toolset for engineering gene expression level and regulatory patterns.

Significance:

The project impacts the DOE's mission to address energy security through the development of transformative science and technology. The development of a systems-level synthetic biology technique for microalgae will reduce the time required to optimize strains for the commercial production of renewable, drop-in replacement fuels. The technique will likely have a broader impact on the field of synthetic biology, advancing other areas of national interest such as renewable replacements to petroleum-based chemical feedstocks. These renewable energy and chemical applications are key focus areas of the DOE's Bioenergy Technology Office and APRA-E.

The Engineering and Understanding of Nanoparticle/Cellular Interactions

165609 | Year 3 of 3 | **Principal Investigator: C. J. Brinker**

Project Purpose:

Stable nanoparticles capable of specific binding to target cells and delivering high doses of therapeutic compounds would be transformational for treatment of disease by making drug delivery into diseased cells more efficient, while reducing toxic side effects in healthy cells and tissues. We recently invented a new composite nanocarrier termed a 'protocell.' Targeted protocells, reported in a 2011 Nature Materials cover article combine the advantages of FDA-approved liposomes (low inherent toxicity, immunogenicity, long circulation times) and porous particle nanocarriers (stability and an enormous capacity for multiple cargos). As recognized in a *Nature Materials News & Views* commentary accompanying our report, "*The properties engineered into this [protocell] system elegantly synergize to approach the goal of an ideal targeted-delivery agent.*" However, it was cautioned that therapeutic efficacy established only in vitro (i.e., in cell culture) "*will need to be tested in animal models, where the complexity of events leading up to encounter of a nanoparticle with its target cell may have a significant impact on the ultimate outcome.*" We completely agree with this assessment; accordingly, the overall purpose of this project is to rigorously engineer nanoparticle characteristics such as size, shape, density, surface charge, and extent of modification with polymers and targeting ligands, and determine the effects on specific and non-specific binding, circulation time, biodistribution, and toxicity in vivo. Our use of state-of-the-art imaging employing an accessible egg embryo model has allowed us uniquely to reveal as yet unrecognized structure-activity relationships needed to achieve efficient targeted delivery *in vivo*.

Summary of Accomplishments:

This project employed a variety of *in vitro* and *in vivo* methods along with modeling and simulation and advanced imaging to explore and quantify nanoparticle/cellular interactions with the goal of establishing needed SARs. A major focus was to use the 'protocell' as a modular platform in order to understand, engineer, and perfect NP/cellular interactions. The *in vivo* behavior, *viz*. the flow characteristics, specific versus non-specific binding, and uptake by the innate immune system, of ENPs was evaluated using an *ex ovo* chick chorioallantoic membrane model or CAM. CAM imaging enabled us to engineer the physicochemical characteristics of ENPs and their in vivo behavior so as to minimize non-specific binding to endothelial and innate immune cells and, therefore, enhance circulation time and binding frequency to target cells. Safer-by-design concepts were developed for silica and rare earth oxide nanoparticles.

Significance:

Engineered nanoparticles (ENPs) capable of specific binding to target cells and delivering high doses of therapeutic compounds could be transformational for treatment of disease by making drug delivery into diseased cells more efficient, while reducing toxic side effects in healthy cells and tissues. ENPs are also of interest for a variety of sensing, diagnostic, and imaging functions that could provide early detection of disease or the onset of infection and enable monitoring of the course of therapy. Underlying these topics and crucial to the safe use of ENPs is development of fundamental structure-activity relationships (SARS) in the context of nanoparticle/cellular interactions *in vivo*. This is essential for advancing the burgeoning field of nanoparticle therapeutics, sensors, imaging agents, and prophylactics for chem/bio defense and other DoD supported areas like traumatic brain injury.

Beyond fundamental science, this project contributed greatly to the protocell intellectual property portfolio where, based on successful responses to office actions, we were issued a second comprehensive US patent on targeted protocells. Additionally, protocell technology was successfully transferred to the biotechnology industry. Aspects of this work also informed a newly funded Grand Challenge project on developing nano-therapeutic platforms for the delivery of clustered regularly interspaced short palindromic repeats (CRISPR) components.

Refereed Communications:

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Understanding and Engineering Lignolysis for Renewable Chemical Production

173019 | Year 2 of 3 | **Principal Investigator: S. Singh**

Project Purpose:
The purpose of this project is to build upon the Sandia expertise in lignin characterization and conversion to develop a microbial chassis capable of converting lignin generated by the biofuel, pulp, and paper industries into targeted renewable chemicals.

Lignin is the only source of renewable aromatics, and utilization of lignin for high value co-products will enable biofuel industries to become cost competitive with petrochemicals. The prospects of macromolecular lignin being utilized as raw materials for fuels and chemicals have been highly touted, but no conversion technologies have been realized. Towards this goal, this project explores two routes: 1) a bio-route based on an engineered organism by borrowing the heterologous enzymes for lignin depolymerization, transportation of the lignin monomers and subsequent modification into value-added chemicals and 2) a hybrid process—a chemical process followed by a bio-based process that utilizes the engineered organism from the first route.

Bacillus subtilis was chosen as a suitable bacterial host for this project as it possesses the ability to secrete the lignolytic enzymes along with other advantages. By performing omics studies on an array of different microbes and substrates, we are aiming to gain knowledge of different transporters involved in lignin uptake, the central metabolism of the lignolytic organism and identify novel enzymes involved in the lignin pathway. We are also evaluating two aromatic transporters for their capability in uptake of a range of oligomeric compounds derived from lignin. Our final product will be a robust synthetic biology toolbox tailored for lignin coupled with an engineered microbial chassis and conversion routes for lignin conversion.

Unknown Pathogen Detection in Clinical Samples: A Novel Hyperspectral Imaging and Single Cell Sequencing Approach

165607 | Year 3 of 3 | **Principal Investigator: B. Carson**

Project Purpose:

Detection of pathogens in pre-symptomatic stages of infection is challenging. Most diagnostic techniques are insufficiently sensitive to detect infection and identify viruses in particular at these early stages. Recently, second-generation sequencing has been applied to this problem. However, despite substantial progress, the signal-to-noise ratio inherent in this technique makes pathogen identification in clinical samples prohibitive, thus leaving treatment decisions dubious. We address this critical problem by identifying spatial and spectral signatures of host response that differentiate uninfected human blood cells from those infected with a pathogenic virus without requiring a priori knowledge of its identity. We will integrate hyperspectral imaging with microfluidic cell sorting to: 1) separate individual infected and uninfected cells and 2) use high-throughput sequencing to analyze individual cells and pools of cells. We envision this will greatly improve the ability to identify pathogens in clinical samples since pathogen-negative cells from the same sample will serve as control. Only single cell analysis can verify the accuracy of this technique, and our success will greatly improve our competitiveness for the National Institutes of Health and other potential sponsors. Moreover, this new capability would transform not only the ability to diagnose infection with unknown pathogens early in disease, but also the identification, characterization, and countermeasure development for emerging and engineered viruses. Finally, the hyperspectral imaging cell sorter we are developing will have countless applications in diverse biological problems including infectious disease, biofuels, and analysis of microbial consortia.

Summary of Accomplishments:

We have designed and tested a laminate microfluidic device capable of axially focusing a stream of cells. A rapid-actuation solenoid valve provides a short burst of pressure to divert a target cell into an adjacent flow stream bound for a sample vial. We have developed image analysis software to select cells that meet user-specified criteria (e.g., color, size, intensity) and have integrated this software with the solenoid valve control software to allow for automated sorting.

We have designed and constructed a prototype of a novel hyperspectral imaging-based cell sorter. Using this instrument, we have demonstrated collection of hyperspectral confocal fluorescence images of individual flowing beads/cells. An invention disclosure has been filed for this technology.

We have identified spectral and spatial biomarkers indicative of viral infection in macrophage cells stained with the vital dye Acridine Orange. The biomarkers are robust and permit classification of infection state as early as six hours post-infection with Adenovirus. Identification and classification are enabled by the development of image analysis algorithms to identify cells and provide cell statistics and by logistic regression classification methods.

We have performed successful sequencing of as few as 10-100 cells with detection of virus. We accomplished single cell sequencing, but this proved to be less robust and sensitive to contamination.

Significance:

The project has provided initial demonstration of a new method for identification and isolation of virus-infected cells from their uninfected counterparts without the use of virus-specific reagents. This method benefits the DOE/NNSA and DHS biodefense missions by facilitating groundbreaking studies on the identification of man-made and emerging pathogens. Further, this capability can benefit DOE/NNSA bioenergy programs since it enables the screening of genetically engineered algal strains and microbial communities for enhanced biofuels production.

Refereed Communications:

S.M. Anthony, A. Carroll-Portillo, and J.L. Timlin, "Dynamics and Interactions of Individual Proteins in the Membrane of Living Cells," *Single Cell Protein Analysis*, A.K. Singh, editor, Springer, 2015.

Computing & Information Sciences

The Computing and Information Sciences (CIS) LDRD Investment Area (IA) champions innovative research and development that advances the state of the art in mathematics, information sciences, and computing relevant to Sandia's national security missions. As these applications continue to technically deepen and broaden (internally and externally), there is an ongoing need to refresh and advance underlying knowledge and capabilities. The scope of the IA includes computer and computational science and engineering, information science (including mathematics and cognitive sciences), and aspects of cyber sciences and data sciences. The IA is pursuing several strategic objectives. First, we want to develop the technologies that will underpin the success of future generations of Sandia computers. These technologies include scalable system architectures, system software and computational methods, and tools for both scientific and data-centric computing. They also include approaches to building future machines out of non-CMOS technologies. Second, we want to develop and exploit synergy between computing and cyber capabilities. Third, we want to advance the science and engineering of trust and resilience in computing and information systems.

Projects

(Active) Learning on Groups of Data with Information-Theoretic Estimators

181061 | Year 1 of 3 | **Principal Investigator: W. P. Kegelmeyer**

Project Purpose:

Machine learning techniques in areas such as classification, anomaly detection, and regression typically focus on single points as the unit of interest; the underlying data is projected into a feature space before the algorithms ever see it. This projection, however, is not always natural, and it may discard key information. In many settings, we wish to perform machine learning tasks on objects that best can be viewed as a set of lower-level objects: for example, images can be successfully viewed as a collection of local patches. In order to use traditional techniques on these set-based objects, we must create a single vector that represents the entire set. Though there are various ways to summarize a set as a vector, we can discard less information and potentially require less work in feature engineering by operating directly on sets of feature vectors.

One method for machine learning on sets is to consider them as samples from some unknown underlying probability distribution over feature vectors. Each example has its own distribution: if we are classifying images as sets of patches, each image is defined as a distribution over patch features; each class of images is a set of patch-level feature distributions. We can then explore kernel methods, based on statistical estimates of distances between probability distributions, to classify samples from these distributions. Because we obtain a kernel, we can exploit the substantial literature of kernel methods to solve many types of learning problems. This research, in collaboration Carnegie Mellon University, is applicable wherever a deeper analysis of sets of things (rather than individual samples) is required.

A Domain-Specific Language for Distributed Tensor Computations

181062 | Year 1 of 1 | **Principal Investigator: T. G. Kolda**

Project Purpose:

The growing complexity of mathematical modeling requires increasingly complex data structures to be partitioned onto massively parallel-distributed computing systems. We are particularly interested in the distribution of multi-way arrays, also known as tensors. A matrix is an example of a two-way array, and much previous work has focused on optimal partitioning schemes to reduce the cost of collective communications (i.e., those operations that involve data exchange between groups of compute nodes). We consider the problem for n-way arrays, which greatly increases the complexity of the problem, but is necessary for facilitating advanced simulations in domains such as computational chemistry, advanced data analysis, and other applications. Each communication pattern has some structure underlying it. Our goal is to provide analysis capabilities for optimizing collective communications.

The goal of this project, in collaboration with University of Texas-Austin, is to create a theory for multilinear computation in distributed-memory environments, which formalizes data distributions, collective communications, and the effect of collective communications, while still being powerful enough to derive high-performance algorithms for multilinear operations. By creating a library that implements the theory, tests can be performed to validate or refute the theory. This project investigates new ways to express distributed objects for n-way arrays.

Summary of Accomplishments:

Large-scale datasets in computational chemistry typically require distributed-memory parallel methods to perform a special operation known as tensor contraction. Tensors are multidimensional arrays, and a tensor contraction is akin to matrix multiplication with special types of permutations. Creating an efficient algorithm and optimized implementation in this domain is complex, tedious, and error-prone. To address this, we have developed a notation to express data distributions so that we can apply automated methods to find optimized implementations for tensor contractions. By considering the spin-adapted coupled cluster singles and doubles method from computational chemistry, we have used our methodology to produce an efficient implementation. Experiments performed on the IBM Blue Gene/Q and Cray XC30 demonstrate both improved performance and reduced memory consumption.

Significance:

Research supporting multiple DOE, DoD, and other government missions often relies on mathematical modeling and advanced simulation, computationally complex operations. Partitioning and executing such processes onto massively parallel distributed computing systems is nontrivial. The success of our results could potentially numerous disciplines reliant on high performance computing.

A Framework for Wind Turbine Design under Uncertainty

173867 | Year 2 of 3 | **Principal Investigator: M. S. Eldred**

Project Purpose:

Wind energy is an increasingly vital component of the electricity generation system in the United States. In 2009, over 3% of the nation's total electricity generation came from wind, and a report by DOE outlines plans to satisfy 20% of the national energy budget with wind power by the year 2030. DOE estimates that as much as a 35% increase in annual wind energy production can be obtained from improvements in wind turbine aerodynamics. Achieving these gains in performance will only be possible by using higher fidelity methods to model the aerodynamics. Therefore, a new framework for wind turbine design under uncertainty, that makes effective use of high-fidelity computational fluid dynamics, tools will be developed in collaboration with Stanford University. The ability to accurately assess the effect of all sources of uncertainty using predictive high-fidelity models will enable businesses to effectively estimate the investment risk in wind energy solutions and promote growth in this energy sector.

Currently, wind turbines are analyzed and designed by low-fidelity tools since they are computationally inexpensive, allowing direct evaluation of quantities of interest (QoI) involving power output and maximum loading for a broad range of input cases. For newer, more aerodynamically aggressive designs, there is little hope of obtaining accurate QoI ranges using the simple low-fidelity models. But, by effectively augmenting a large number of low-fidelity simulations with a smaller number of high-fidelity evaluations within our proposed multifidelity framework, we will accurately and efficiently quantify the uncertainties in our QoIs.

Active Learning in the Era of Big Data

173667 | Year 2 of 2 | **Principal Investigator: W. L. Davis, IV**

Project Purpose:

As the volume of data grows, so does the amount of computational power and the human ingenuity required to harness that power. Processing the data is not the problem. The critical issue is that, while the amount of data is growing, the time it takes a human to answer a question today is the same amount of time it will take the human to answer it tomorrow. And tomorrow, it will cost more. While many tasks have been automated, such as telephone operators, some tasks will always prefer to have a human in the loop. Such tasks may include sensitive, high-risk applications in medical or security areas; they also include areas that require more qualitative assessments of quality: the "I'll know it when I see it" quality that is difficult to automate.

Current active learning research generally neglects the valuable information that can be gained from studying the relationship between the specific machine learning algorithms employed and the active learning heuristics themselves. This project aims to tackle the two major impediments to implementing active learning for big-data in practice: 1) the logistics of query distribution and collection and 2) the lack of efficient algorithms with guarantees. This research, in collaboration with the University of Wisconsin-Madison, will both extend the scalability of active learning approaches and expand the use of active learning techniques by lowering the barrier of complexity. In addition to these practical advancements, this research will advance the science of machine learning by enhancing the theoretical understanding of active learning constraints and guarantees.

Summary of Accomplishments:

To facilitate the development, testing, and deployment of active learning for real applications, we have built an open-source software system for large-scale active learning research and experimentation. The system, NEXT, provides a unique platform for real-world, reproducible active learning research. NEXT enables machine learning researchers to easily deploy and test new active learning algorithms and enables applied researchers to employ active learning methods for real-world applications.

NEXT is accessible through a REST Web API (application programming interface) and can be easily deployed in the cloud with minimal knowledge and expertise using automated scripts. NEXT provides researchers a set of example templates and widgets that can be used as graphical user interfaces to collect data from participants.

In addition to the NEXT software itself, this research produced results that show how experimentation can help expose strengths and weaknesses of active learning algorithms, in sometimes unexpected and enlightening ways.

Significance:

Collecting large-scale datasets for building analytical models for national security can be difficult and time-consuming. NEXT provides a flexible and general-purpose active learning platform that is versatile enough for a large breadth of applications. This allows us to easily replicate past (and future) algorithm implementations, experiments, and applications. This research enables analyst-driven data collection in a much more efficient manner, reducing overall costs for data procurement and increasing the fidelity of our analytical models. This ultimately enhances our ability to utilize analytical models in areas such as cybersecurity and satellite data analysis.

Refereed Communications:

K. Jamieson, S. Katariya, A. Deshpande, and R. Nowak, "Sparse Dueling Bandits," presented at the *Artificial Intelligence and Statistics Conference*, San Diego, CA, 2015.

K. Jamieson, L. Jain, C. Fernandez, N. Glattard, and R. Nowak, "NEXT: A System for Real-World Development, Evaluation, and Application of Active Learning," *Neural Information Processing Systems*, Montreal, Canada, 2015.

Adaptive Bayesian Inference for Prediction

188256 | Year 1 of 1 | **Principal Investigator: T. M. Wildey**

Project Purpose:
Performing rigorous predictive simulation necessitates that any and all available data be incorporated into the modeling process in order accurately quantify uncertainties in the model prediction. Statistical Bayesian inference is the most frequently used approach for incorporating data into uncertainty estimates. Statistical Bayesian inference uses data and an assumed error model to inform posterior distributions of model input variables and model discrepancies. The resulting posterior densities are then propagated forward through the model to quantify the effect of these uncertainties on the model quantities of interest. Markov Chain Monte Carlo (MCMC) sampling (or the special case of Gibbs sampling) is the most popular approach for solving the Bayesian inverse problem. However, MCMC often requires an infeasible number of model evaluations and can fail to converge to the true posterior distribution.

We propose to pursue a new approach for stochastic inversion that:

- Has a solid mathematical foundation
- Does not rely on MCMC sampling to generate samples of the posterior distribution
- Does not require a statistical assumption on the model error
- Leverages the adaptive response surface approximations techniques developed at Sandia

Our approach will utilize a reformulation of a measure-theoretic inversion technique to solve a non-statistical Bayesian inference problem. This reformulation allows us to reduce the computational cost of approximating the posterior distribution using goal-oriented adaptive sampling and approximation methods. Our algorithm will concentrate high-fidelity model evaluations in regions of the parameter space that significantly contribute to the uncertainty in specified quantities of interest and are most informed by the available data.

Summary of Accomplishments:
We compared our new non-statistical Bayesian approach with the standard statistical Bayesian approach and demonstrated that the new approach can easily generate comparable sets of samples from the posterior distribution without relying on MCMC. We also produced numerical results that demonstrate adaptive refinement of a sparse-grid surrogate model based on both the prior and the posterior distributions. Our method demonstrated improvements in the computational cost required to achieve a given error tolerance.

Significance:
Inverse problems are ubiquitous in computational science and engineering. Often, parameters of interest cannot be measured directly and must be inferred from observable data. The approach developed in this project will assist engineers working to understand and quantify the uncertainties for a broad range of national security applications throughout the NNSA and other agencies that require efficient predictive simulation with quantified uncertainty.

Adaptive Multimodel Simulation Infrastructure (AMSI)

166140 | Year 3 of 3 | **Principal Investigator: M. W. Glass**

Project Purpose:
At present, the implementation of a massively parallel multiscale/multiphysics simulation requires expertise, not only in the physical domain of interest, but also in parallel programming and software engineering. While there have been attempts to construct software frameworks to ease the construction of such simulations, these typically require that component codes adhere to certain specific interfaces and data structures. Incorporation of software components used in these simulations can require a great deal of expertise and effort. Through a partnership with Rensselaer Polytechnic Institute, this fundamental research is focused on developing multiphysics code-coupling frameworks for legacy components. We will develop a simulation infrastructure to facilitate the implementation of multimodel adaptive simulations, allowing the incorporation of proven legacy components. This infrastructure will leverage high-level programming techniques and a variation on the typical component-based architectures to facilitate the easy integration of legacy software components for use in the infrastructure. By removing the requirement of low-level programming expertise in order to construct these simulations, domain-specific experts and industry-level users will be able to reuse proven legacy software components in order to simulate the physical phenomena of importance to them.

The design and implementation of a system to facilitate the combination of low-level code components with arbitrary functional interfaces and data structures poses a number of mathematical, logical, and computational challenges, especially in conjunction with the usability goals stated above. The primary foci in the construction of physical simulations are efficiency, performance, and accuracy. Thus, the low-level systems underlying the high-level computation stages pose an entirely different set of challenges to be overcome in their implementation.

Summary of Accomplishments:
We initially focused on designing a set of simulation-state abstractions and implementing mechanisms to model and track them over the life of a simulation. The development of these concepts allowed the initial implementation of the adaptive multiscale simulation infrastructure (AMSI). The primary capabilities of AMSI focused on maintaining the simulation meta-state, as well as planning, managing, and implementing the parallel communication required for multiscale data coupling to occur in a non-intrusive manner. Non-intrusive use of AMSI was a key area of focus, to allow minimal modification to existing single-scale codes for use in general multiscale simulations facilitated by AMSI.

We demonstrated the utility of the initial implementation of AMSI, and applied the method to a test biological tissue problem, coupling together a macroscale finite element code and a microscale quasistatics code. These results were discussed, along with core data structures and algorithms used in the implementation of AMSI, in a talk at the SIAM Conference on Parallel Processing for Scientific Computing 2014. We also demonstrated the use of new capabilities developed for dynamically controlling adaptive multiscale simulations: specifically, for scale-sensitive load balancing operations. These results were presented at the SIAM Conference on Computational Science and Engineering 2015 and included additional discussion on the biological tissue test application.

Significance:
This project saw the implementation of the scale-sensitive load balancing capabilities of AMSI, as well as their inclusion in the biological tissue multiscale simulation. Further exploration of the capabilities of the scale-sensitive load balancing and the optimal methods of use in general multi-scale simulations was then conducted. Initial work is being conducted on 'load-balancing' the execution of individual scales in a multiscale simulation so as to further optimize the time-to-solution and facilitate greater dynamic control over the simulation.

Refereed Communications:
W.R Tobin, D. Fovargue, V.W.L. Chan, and M.S. Shephard, "Load Balancing Multiscale Simulations," presented at the *SIAM Conference on Computational Science and Engineering*, Salt Lake City, UT, 2015.

W.R. Tobin, D. Fovargue, and M.S. Shephard, "Parallel Infrastructure for Multiscale Simulation," presented at the *SIAM Conference on Parallel Processing for Scientific Computing*, Portland, OR, 2014.

Advanced Data Structures for Improved Cyber Resilience and Awareness in Untrusted Environments

180820 | Year 1 of 3 | **Principal Investigator: C. A. Phillips**

Project Purpose:

This project focuses on fundamental research in write-optimized data structures (WODS) with applications to resilient high performance data management. WODS enable systems to ingest and index data faster, by orders of magnitude, than with previous data structures. There are write-optimized data structure replacements for B-trees (for databases) and for Bloom filters (for approximate membership queries). Developed for commercial databases, WODS have not been applied in security settings to their full potential.

We will create WODS to enable network-security-monitoring components to stream high-speed network data to disk and perform complex queries on that data during subsequent analyses. The additional speed of WODS can create new opportunities for cybersecurity monitoring tools to support complex and real-time queries. We will add features to WODS to make them more useful for cyberstream monitoring. These include aging out data and handling significant data repetition. We will quantify performance improvements on realistic cyberstreams.

We will design data structures that combine the speed of WODS with security/resilience (history-independent storage). A snapshot from history-independent data structures would not reveal anything about the past history of the data structure, such as the order that elements were inserted. We will explore fundamental tradeoffs between history independence and data-structure performance in main and external memory.

Finally, we will consider improved efficiency for oblivious RAMs, which hide data-access patterns from intruders and untrusted platform operators. We will investigate improved efficiency and/or security for big data platforms such as Hadoop and Accumulo.

Advanced Uncertainty Quantification Methods for Circuit Simulation

173331 | Year 2 of 3 | **Principal Investigator: E. R. Keiter**

Project Purpose:

This research aims to develop reliability methods for analog circuit simulation, with the goal of mitigating the expense of large ensemble Xyce circuit calculations. The primary output will be discovery of a set of advanced methods to determine time-dependent failure probability of nuclear weapons (NW) circuits. Historically, NW circuit designers and analysts rely almost exclusively on brute-force nested sampling methods, requiring expensive numbers of Xyce simulations. To address this, our research is focused on aspects of uncertainty quantification (UQ) that can be used to mitigate this computational expense. We have recently included the addition of analytical parameter sensitivities in Xyce for steady state and transient analysis, and surrogate modeling via principal component analysis on field data.

In the final year of the project, we plan to focus on two main areas: 1) hierarchical uncertainty quantification and 2) the use of analytic parameter sensitivities in calibration and UQ. Research Area 1 involves decomposing a circuit into subcircuit or device models, where each submodel may be characterized with a lower-dimensional representation, such as a polynomial chaos expansion or a surrogate model, as mentioned above. The hierarchical approach has the potential to make UQ more feasible for complex circuits that are computationally expensive. Research Area 2 focuses on the adjoints that Xyce now produces, which can be used to reduce the number of function evaluations both for UQ and calibration methods. We plan to investigate this in the context of compact models and the construction of derivative-enhanced surrogates.

The successful development of this research will reduce the number of simulations required to assess NW circuit failure due to hostile radiation. It is anticipated that this will impact weapons qualification activities (e.g., Qualification Alternatives to the Sandia Pulsed Reactor), enhanced surveillance programs, and various NW life extension programs. Advanced UQ methods have not been previously attempted for production-level circuit simulation. This project addresses several issues that will render uncertainty quantification and failure analysis more feasible for large-scale NW radiation-hardness circuit problems.

Analyst-to-Analyst Variability in Simulation-Based Prediction

173028 | Year 2 of 3 | **Principal Investigator: M. R. Glickman**

Project Purpose:

Despite the tremendous number of compute cycles devoted to computer-based simulation, the value of all this computation is only realized when coupled with a different kind of computational process that is performed by human beings seeking to refine their understanding and make predictions. Moreover, from informal observation and discussions with analysts, we have become aware that, even when provided the same problem, source data, simulation tools, and specific questions, it is unlikely that two analysts will arrive at precisely the same predictive judgments.

Analyst-to-analyst variability is an indicator of potential uncertainty in simulation-based assessment. What impact might such uncertainty have on our national security mission? Are there effective ways to mitigate associated risk and/or improve decision-making? We don't know because there have been few, if any, formal studies of analyst-to-analyst variability in simulation-based assessment. In lieu of such studies, analyst judgment is developed through professional training and mentoring and subjected to peer review. Despite these wise practices, there remains a large disparity between our relatively intuitive approach to analyst judgment and our formal treatment of other stages of the simulation-based assessment pipeline such as hardware architectures and numerical algorithms. More alarmingly, psychological research continues to reveal consistent biases in human judgment and decision-making, biases that were only divined via formal analysis.

We are conducting both: a) in situ observational studies of simulation-based judgment as practiced at Sandia and b) formal, controlled experiments in which subjects are given carefully chosen data and tools and asked to derive their best assessment. The goal of this project is to identify and document significant factors that underlie variability in simulation-based assessment to prepare for investigating how this understanding might be leveraged to boost predictive performance. This novel project leverages psychological findings within the already highly interdisciplinary enterprise of predictive computer simulation of physical processes.

APEX: Application Characterization for Exascale Systems

173031 | Year 2 of 2 | **Principal Investigator: S. D. Hammond**

Project Purpose:

Scalable parallel applications and computer architectures are a critical capability for DOE and NNSA missions, NNSA's Advanced Simulation and Computing Program, and many other national security related programs. As the community continues to pursue significant increases in the performance of supercomputing hardware, we are quickly finding that the mapping of existing algorithms and programming models to leading-edge hardware is becoming highly strained. This is, in part, a result of the changing approach to delivering hardware performance–parallelism is offered instead of increased core clock frequency–as well as implicit assumptions regarding the behavior and structure of machines that no longer continue to hold. When combined with the challenges of lowering power consumption and the reduced reliability of future hardware systems used at scale, the use of existing production codes on future supercomputers without modification now seems unlikely. Application developers are, therefore, facing the prospect, for perhaps the first time in two decades, of needing to fundamentally rearchitect, and in some cases rewrite, large sections of key production code. Whilst a full application rewrite may seem an appealing route, the cost and time associated with this activity alone means it cannot be undertaken for more than a handful of codes or libraries before it becomes prohibitive. An alternative approach is to evolve applications through the identification of key kernels and libraries addressing performance, power, and reliability concerns in a step-wise manner.

We are proposing a suite of binary analysis and instrumentation tools to support developers in characterizing their existing applications, with a specific focus on identifying areas of concern relating to performance, data motion, and reliability. The output of these tools will relate program level objects such as data structures, functions, loops, or even code segments, to specific program metrics of interest in exascale systems. These metrics are being identified by research using the Sandia-led NNSA/ASC future architecture test bed program and collaborations with leading industry vendors.

Summary of Accomplishments:

The tools produced in this project, the first of any national laboratory, have been used to provide specific and accurate calculation of achieved levels of floating point and integer vectorization. Our research was able to demonstrate that vectorized floating point calculations, as expected by the developer, show poor correlation with hardware-reported performance counters, indicating that tools built upon these counters are likely to be provide incorrect information to NNSA/ASC code teams. Collaboration with Intel persuaded the Advisor-XE tools group to develop a vectorization analysis extension based largely on the approach illustrated in this project. Further, through the development of methods for assessing application structure, we provided insight into where large scientific codes spend the most significant amount time executing instructions. The demonstration of this analysis on the SIERRA ADAGIO and ALEGRA Albany codes show the ability of this research to scale to production-class workloads. Extensions of this work to multi-threaded applications has since been employed on a number of research problems including analysis of kernels for Trilinos, Albany, SIERRA, and Kokkos–many of which are actively targeting the ASC Trinity and other platforms. We also extended the analysis methods to the Xeon Phi Knights Corner platform and then, with collaboration from Intel, limited initial analysis of program structures for the Xeon Phi Knights Landing instruction-set architecture (ISA) to be used in Trinity. The project provided the first assessment of program instruction behavior for these platforms and was reported to several ASC projects to help guide application porting and optimization activities.

Significance:

The project has provided significant insight into program behavior for production-class algorithms, and in some cases, full production codes. The assessment of this behavior is enabling production code developers to understand weaknesses in code performance and areas where optimization may need to be considered. The instruction profile data is being provided to industry vendors to help improve processor/ISA design for future products that may be selected for NNSA/ASC production computing platforms. The project, therefore, is helping to improve algorithm performance on both contemporary and future systems.

Cognitive Computing for Security

165613 | Year 3 of 3 | **Principal Investigator: E. Debenedictis**

Project Purpose:

The original project purpose was to study applications of memristor-based neural networks to security systems, but the scope changed over its lifetime. These "new" security systems were to have had two features: they would have a novel physical security feature that stores critical information in memristors, which could be quickly erased or otherwise used for information protection. The cognitive features would also be able to learn certain security relevant tasks on the fly, such as identification of malware. These objectives changed and expanded over time.

The project identified that the original direction was not practical based on current memristor technology, which led to development of a comprehensive theory on when certain new transistor-replacement device could outperform conventional complementary metal oxide semiconductors (CMOS). The original idea of malware detection also expanded over time to an understanding of how to embed a general-purpose computer into a neural network–leading to a reconciliation of the current "Turing machine" class computer that is a ubiquitous office machine and the other main class of computer in the world, which are the brains of animals.

Based on our new research direction, we sought to identify the scaling limits of artificial neural networks built from analog electronics, applying the resulting know-how to a security application as a demonstration. There has been science fiction-class vision for many decades that mankind would make artificial neurons that can duplicate the human brain. While realizing this vision is likely far off, there is a reasonable intermediate goal of having artificial neurons and related brain-inspired techniques address useful problems at smaller scale. In fact, there is a good possibility that artificial neural networks could fill a role as a "Beyond CMOS" or "Beyond Moore" computing system.

To make progress toward such an intermediate goal requires a clear understanding of the capabilities and limitations of artificial neurons as engineered subsystems, with an ultimate goal of understanding how to make reliable, manufacturable artificial neural networks at appropriate scale. This includes developing CMOS analog electronics in Sandia's MESA facility that fill the equivalent role of neuron cell bodies. The CMOS analog electronics will be integrated with evaporatively deposited memristors to fill the role of synapses and accompanied by the neural network learning theory to learn/program suitable applications.

We identified a security application that would create a useful neural network at a manufacturable scale, which is essentially an encryption device implemented with artificial neurons. The device is physically constructed so it is encased in its neurons. Disassembly would damage the encryption parameters, so the system would neither encrypt again nor reveal the keys.

Summary of Accomplishments:

The project began with extensive characterization of memristors. The activity began in an environment when memristors were believed to have "figure 8" curve traces–there was heavy debate about the precise shape of the figure 8. The noteworthy result is that we characterized memristor more comprehensively than other organizations (at the time), discovering that memristors actually had additional internal state and "noise," both factors invalidating the entire concept that the device could be characterized by a curve of any sort. This did not mean memristors were less useful, but rather that they would only work in different circuits than had been studied by that time.

A second development was a theoretical framework for energy efficiency of these new non-CMOS devices. Essentially, CMOS is widely believed to have a theoretical energy minimum of $kT \ln(2)$ per gate operation. Analysis of memristor circuits showed a minimum, also in units of kT, but instead of the coefficient being the constant $\ln(2)$, it scaled with N and the amount of precision. In other words, it is not a bad device in terms of energy efficiency, but its behavior is quite different than transistors.

This led to an exploration of computer architectures that would be compatible with memristors– a host of other devices with unrealized R&D potential. The overarching result from this research is the discovery of a way to make general-purpose computers, which is an important development. With this discovered, we noted, interestingly that the circuits scaled up the number of small neural networks whereas most of the research community expected a single neural network to scale up in size.

Significance:

As this project concludes, it is contributing to the national dialog on new computers. The project developed a new computing model incorporating aspects of the von Neumann computer architecture and neuromorphic computers (or brains), accompanied by an energy and power model and experimental and theoretical validation. These ideas were adopted internally and influenced ongoing research in adaptive neural algorithms for threat detection. The results, in collaboration with insights from Hewlett-Packard Laboratories' Fellow Stan Williams, were developed into whitepapers for the Office of Science and Technology Policy (OSTP), with the combined set of ideas being announced as an OSTP Nanotechnology-Inspired Grand Challenge for the Next Decade on the "Sensible Machine." OSTP is essentially using this set of ideas to set an R&D agenda for the National Strategic Computing Initiative's fundamental research arm at the national level.

Refereed Communications:

F. Rothganger, B.R. Evans, J.B. Aimone, and E.P. Debenedictis, "Training Neural Hardware with Noisy Components," in *Proceedings of the International Joint Conference on Neural Networks*, pp. 1-8, 2015.

A.J. Lohn, P.R. Mickel, J.B. Aimone, E.P. Debenedictis, and M.J. Marinella, "Memristors as Synapses in Artificial Neural Networks: Biomimicry Beyond Weight Change," in *Cybersecurity Systems for Human Cognition Augmentation*, pp. 135-150, September 2014.

M. Marinella, et al., "Development, Characterization, and Modeling of a TaOx ReRAM for a Neuromorphic Accelerator," presented (invited) Meeting Abstracts. No. 42, *The Electrochemical Society*, vol. 64, pp. 37-42, 2014.

Coupling Computational Models: From Art to Science

173025| Year 2 of 3 | **Principal Investigator: P. B. Bochev**

Project Purpose:
The purpose of this project is to formulate, develop, and demonstrate new and mathematically rigorous approaches for the coupling of disparate numerical models.

For many mission-critical DOE applications, accurate and efficient coupling of trusted simulation codes could expand scope, and deliver new modeling capabilities for a fraction of the time and cost of new development. Of particular importance to DOE/NNSA, and the main focus of this project, are coupled computational models (CCM) for high-consequence analyses of impact fuzes and asset protection. Current state-of-the-art CCM poses the coupling as a "hard" constraint on the models. Mathematically correct implementation of such couplings can be difficult, and is often substituted by simpler ad hoc solutions. Such tactics, while expedient, are frequently mathematically questionable (e.g., regarding stability), physically inconsistent (e.g., regarding conservation), and sometimes computationally catastrophic (e.g., leading to clearly inadmissible results). We propose to significantly improve the robustness, accuracy, and physical fidelity of CCM by developing a new mathematically rigorous, yet adaptable, coupling strategy that casts the coupling into a constrained optimization problem.

Posing CCM as a constrained optimization problem—to minimize the mismatched "energy" between states subject to physical constraints—enables a reversal of roles, where the coupling adapts to the physical models. Furthermore, since the basic approach relies on generic optimization ideas, adaptable optimization-based couplings have significant potential for other multi-physics problems, and for informing future research directions in solving such problems.

The proposed adaptable coupling strategy is a first-of-its-kind application of optimization ideas to CCM that aims to deliver an advanced simulation capability.

Data-Driven Optimization for the Design and Control of Large-Scale Systems

180822 | Year 1 of 2 | **Principal Investigator: D. P. Kouri**

Project Purpose:

This project will fuse data, uncertainty, and simulation in novel algorithms and discretizations for the rapid and robust solution of mission-critical optimization problems.

Decisions are often formulated as optimization problems. In many applications, these problems are simulation-based and involve partial differential equations, ordinary differential equations, or differential algebraic equations. Such problems are often large-scale and the governing simulation typically involves uncertain input parameters. An example application is the reliability testing of components using direct field acoustic testing (DFAT). In DFAT, one must determine the speaker output that reproduces target vibration profiles through the component while accounting for material uncertainties. Another application is to design “off-normal tests” in which one interrogates a hardware or software system to discover vulnerabilities. To design a robust, off-normal testing harness, one must account for uncertainty in system components. For such problems, using data to reduce uncertainty is crucial.

A common solution approach for these problems is to assume a known probability distribution for the uncertain parameters, discretize the governing dynamics using standard numerical approximation schemes, and solve the resulting finite-dimensional optimization problem. In many applications, such as reliability engineering, assuming a known probability distribution can lead to unreliable system performance with potentially catastrophic outcomes. To circumvent this issue, we propose novel discretizations and optimization formulations that do not assume a known probability distribution, but rather use data to determine an optimal solution that is robust to our ignorance of the true probabilistic characterization of the uncertain inputs. The expected outcome of this project is a rigorous and broadly applicable framework for optimal design, control, and decision making in the presence of uncertainty that combines data, simulation, and optimization.

COMPUTING & INFORMATION SCIENCES

Decision Analytics for Complex Supply Chain Networks

178670 | Year 2 of 2 | **Principal Investigator: G. K. Kao**

Project Purpose:

The purpose of this project is to develop decision-support technologies to enable decision makers to perform risk-based cost-benefit prioritization of security investments to manage supply chain integrity and risk. We propose a new systematic approach to examine the lifecycle phases (e.g., design, implementation, testing, deployment, maintenance, retirement) of supply chains by leveraging a new security risk metric based on the degree of difficulty adversaries will encounter to successfully execute the most advantageous attack scenario. The key challenge is that the scale of the end-to-end supply chain lifecycle problem is too large and complex. To manage this complexity, we propose a hierarchical decomposition methodology in modeling the supply chain lifecycle. Our framework consists of: 1) hierarchical representation, 2) macro state-of-health assessment, 3) adversary action evaluation, 4) difficulty and consequence evaluation, and 5) optimization. The hierarchical representation modeling enabled us to decompose the supply chain problem into manageable pieces, such that risk and state-of-heath evaluation can be performed. High-level metrics will enable decision makers and analysts to identify critical areas for further deep dives. The macro state-of-health assessment is analogous to measuring vital signs before administering any diagnoses. Data analytic techniques will address data integrity issues, where deep dive analysis will consist of generating adversary scenarios based on functional grammars. Difficulty and consequence metrics will enable decision makers to overcome complexity of quantifying security risk, and will be suited for cost-benefit optimization. New optimization techniques, such as multilevel optimization methods, will be explored. By design, the hierarchical and recursive approach will address the supply chain problem comprehensively at various depths. Our methodology will help manage the complexity of the problem, such that analysts can understand and gain insights into the end-to-end supply chain to make risk-informed, effective decisions.

Summary of Accomplishments:

We designed a new holistic supply chain lifecycle decision analytic framework that enables decision makers to perform risk-based cost-benefit analyses to optimally apply mitigation options to address vulnerabilities in supply chains. The framework is demonstrated by a tool chain consisting of four major components:

1. Hierarchical Supply Chain Representation
2. Sandia's Difficulty and Consequences Risk Based Assessment
3. Semi-Automatic Grammar Based Vulnerability and Mitigation Assessment
4. Optimization Based Decision Analytics

Two data representation models, leveraging graph databases, and traditional relational databases, were developed to capture the hierarchical lifecycle supply chain. These representation models enabled high-level state-of-health evaluation based on our newly developed supply chain risk metrics. We then developed a set of context free grammar, which were applied to our representation models to generate an attack surface. Our method generated attack graphs that were not bounded by subject matter experts' input, and provided a more comprehensive attack surface for assessment. Bi-level optimization problems were formulated for attack graph assessment. These optimization techniques enabled analysts to identify attractive attack paths based on adversary's difficulty, defender's consequences, and other constraints.

A patent, *Framework and Methodology for Supply Chain Lifecycle Analytics*, was also submitted, and is currently under review. Furthermore, we demonstrated this framework on multiple-use cases. We applied our framework to real life processes and electronic components, which also resulted in publication demonstrating applications.

Significance:
Our research builds the capabilities to help strengthen the foundation of the nation's information and communication technologies critical infrastructure supply chain. This problem addresses issues that will not only have a national impact, but will also have a global impact. We have developed new assessment methodology that advances the science in supply chain risk management. The models developed will help federal agencies (e.g., DOE, DoD, DHS) to evaluate security impact in designing and developing a viable and secure global supply chain. This research will, no doubt, provide insights to the national security risk on the reliance of the global supply chain.

Refereed Communications:
G. Kao, J. Hamlet, R. Helinski, J. Michalski, and H. Lin, "Macro Supply Chain Security Decision Analytics," presented at the *Annual Computer Security Applications Conference* (ACSAC), 2015.

G. Kao, H. Lin, B. Eames, J. Haas, A. Fisher, J. Michalski, J. Blount, J. Hamlet, E. Lee, J. Gauthier, G. Wyss, R. Helinski, D. Franklin, and L. McLay, "Supply Chain Lifecycle Decision Analytics," in *Proceedings of International Carnahan Conference on Security Technology* (ICCST), pp. 1-7, 2014.

G. Kao, J. Hamlet, R. Helinski, J. Michalski, H. Lin, and M. Shakamuri, "Supply Chain Security Decision Analytics: Macro Analysis," in *Proceedings of IAEA Computer Security in a Nuclear World*, 2015.

M. McCrory, G. Kao, and D. Blair, "Supply Chain Risk Management: The Challenge in a Digital World", in *Proceedings of IAEA Computer Security in a Nuclear World*, 2015.

Detecting Lateral Movement on Internal Networks

188321 | Year 1 of 1 | **Principal Investigator: S. Martin**

Project Purpose:

After gaining access to a network (via phishing, drive-by-downloads, etc.), attackers attempt to move laterally within that network, with the goal of stealing credentials, gaining access to additional computers, and ultimately compromising servers and stealing secrets. Currently, there are limited methods for detecting lateral movement within a network, and it is unknown to what degree intruders can be detected using authentication data. Authentication is difficult to obtain and parse, and it is not known to what extent existing algorithms will uncover lateral movement in networks. We propose to develop automatic lateral movement detection methods by applying machine learning algorithms to authentication data.

One source of user-based data relevant to detection of lateral movement is authentication data, as might be found in Kerberos logs, or even packet capture data. Researchers at LANL have assembled a new unique dataset containing authentication data. The data includes red team activity as ground truth. This dataset is ideal for developing and refining our algorithms.

We will investigate the use of machine learning algorithms (anomaly detection and/or supervised learning) to automatically identify lateral movement within a network. We will apply our algorithms to LANL's augmented authentication dataset; if successful, our approach will greatly benefit cybersecurity personnel, improving the chances of detecting targeted attacks in a timely manner.

Summary of Accomplishments:

In order to establish the feasibility of using authentication data to detect lateral movement within internal networks, we utilized two datasets collected at LANL. One dataset spanned a nine-month period with very few details per event, and the other spanned a two-month period with many details per event, including red team activity. We analyzed the data using simple statistics and various machine learning algorithms, including graph layout, dimension reduction, supervised learning, and anomaly detection algorithms. For both datasets, our results were encouraging, and pointed the way towards further analysis and eventual application.

For the nine-month dataset, we constructed both a bipartite user-computer graph and user activity profiles for each user over time. The user-computer graph showed definite groups of users and their computers on the LANL network, and how these groups were connected.

For the two-month dataset, we constructed personal authentication subgraphs (PASs), which are user-computer graphs for a given user. Simple graph statistics were computed for each user on that user's PAS, including: number of nodes, number of edges, diameter, max in degree, max out degree, and number of user changes. We then used these statistics as input features for support vector machines (SVMs) and anomaly detection algorithms in order to detect red team activity. The SVMs were able to detect red team activity with up to 77.5% accuracy, with the area under the receiver-operating-characteristic (ROC) curve scores up to 0.81. The best anomaly detection algorithm was able to achieve an area under the ROC curve of 0.85 on the same task.

Significance:

Once an attacker gains access to a single computer on a network, he/she will attempt to move laterally within the network. The goal is to steal credentials, gain access to additional computers, and ultimately compromise servers and obtain data. Sometimes this sequence of events can happen very quickly. A system that automatically alerts cybersecurity personnel would significantly impact multiple security and consumer domains..

Efficient Probability of Failure Calculations for QMU using Computational Geometry

165617 | Year 3 of 3 | **Principal Investigator: S. A. Mitchell**

Project Purpose:

This project focuses on new algorithms for uncertainty quantification (UQ) and optimization (Opt), as well as mesh generation. These algorithms are of general use for a broad variety of reliability and design questions related to NNSA's stockpile stewardship mission.

The key technical challenge is improving the efficiency of UQ and Opt methods (i.e., the accuracy that can be obtained in a given computational time). In realistic applications, the computational time is dominated by function evaluation calculations, which are typically large scale. Thus, efficiency is increased if we can obtain the same information using fewer function evaluations, where each function evaluation is a sample point in our approach. Hence, efficiency translates into innovative, adaptive sampling approaches that place samples at locations where the most overall information can be gained. There are both challenges and benefits related to the use of surrogates, which are explicit functions constructed from prior samples. What is unique to our algorithms is the heavy use of geometric concepts. Instead of boxes, our sample's neighborhoods are spheres or Voronoi cells. The size of these neighborhoods is adapted, based on information gained from new samples. Further, instead of sample points, we consider sample lines, planes, hyperplanes, etc. Sometimes this recursive-by-dimensions organization must be handled numerically; other times, we gain immense efficiency by exploiting the analytic form of a sphere or surrogate. The general-purpose algorithms developed in this project will be included in Sandia's publically available Dakota optimization and UQ toolkit, as well as in stand-alone meshing software.

Summary of Accomplishments:

The intent of the project was to utilize computational geometry and computer graphics techniques to develop new algorithms for quantified margins of uncertainty, a form of uncertainty quantification. Algorithm development focused on using sampling techniques—notably hyper-line sampling and sphere packing sampling—together with Voronoi diagrams and surrogate functions. These new algorithms are ideal for applications involving the use of numerical integration and surrogate functions of some form. Additionally, algorithm development yielded a number of mesh-generation applications that utilize the same core sampling techniques and Voronoi diagrams. Many of the techniques developed in this project were deployed in stand-alone demonstration software. Some of the more practical capabilities—notably some uncertainty quantification and optimization algorithms, together with a library for analytic surrogate functions for interpolating data—were deployed in the Dakota optimization toolkit.

Significance:

Our results strengthened our external visibility, which helps enhance the vitality of the workforce (e.g., for recruiting talented new researchers). Partnering with academia during algorithm development also allowed us to gain insight into the techniques of other fields (e.g., computer graphics and geometric modeling), and enabled the application of our core algorithms to other fields. Our results advanced mathematical and computer science capabilities for conducting science and engineering activities by providing more efficient and new meshing and opt/UQ algorithms, with enhanced understanding of the key mathematics underlying these techniques. The methods were vetted on problems with the same structure as mission-relevant applications. The project also had a strong cross-disciplinary approach, integrating efforts from computational and engineering sciences, so as to consider method applications. A number of natural follow-on projects emerged based on the research outcomes, and several of these were funded. Finally, the project spawned technical achievements and numerous published papers, and spanned general sampling techniques, giving rise to uncertainty quantification, global optimization, modeling, and meshing techniques.

Refereed Communications:

A.A. Rushdi, S.A. Mitchell, C.L. Bajaj, and M.S. Ebeida, "Robust All-Quad Meshing of Domains with Connected Regions," presented at the *International Meshing Roundtable*, Austin, TX, 2015.

M.S. Ebeida, S.A. Mitchell, A. Patney, A.A. Davidson, S. Tzeng, M.A. Awad, A.H. Mahmoud, and J.D. Owens, "Exercises in High-Dimensional Sampling: Maximal Poisson-Disk Sampling and k-d Darts," Series: Mathematics and Visualization, *Topological and Statistical Methods for Complex Data*, pp: 221-238, 2015.

S.A. Mitchell, M.A. Mohammed, A.H. Mahmoud, and M.S. Ebeida," Delaunay Quadrangulation by Two-coloring Vertices," presented at the *International Meshing Roundtable*, London, England, 2014.

Enabling Bidirectional Modality Transitions in Collaborative Virtual Environments

166537 | Year 3 of 3 | **Principal Investigator: K. M. Mahrous**

Project Purpose:

Due to the time and cost of manufacturing, nearly all items—from metal casings to weapons to buildings—are first designed virtually. Most collaborative engineering environments allow for the manipulation and visualization of these virtual designs through a 2D interface (e.g., computer monitor), which is an insufficient substitute for interacting with the model in 3D (regardless of scale). In a collaborative design process, this often makes it difficult to thoroughly review and discuss designs, a problem exacerbated by geographically distributed teams. This research aims to address this problem by enhancing the work done in collaborative virtual environments (CVEs). Current CVEs focus on visual (2D or 3D) interactions with the design; enhanced CVEs incorporate haptic feedback via devices such as force-feedback gloves. We propose to explore this research direction further, but also to take an entirely novel approach by introducing 3D materializers into the environment, so that we can interact with cheap, quickly made, but still geometrically identical copies of objects. Furthermore, the ability of current CVEs to transform physical objects into virtual ones via 3D scanning algorithms will be extended to form a bidirectional pipeline that allows for a physical-to-virtual-to-physical sequence where the object can be modified in both forms; we deem this novel procedure the multimodal collaboration pipeline (MCP). Current CVEs only allow for 3D scanning to convert physical objects into virtual ones, which necessitates that the engineer do most of the work in one of the two domains. By closing the gap and allowing for bidirectional modality transitions between the physical and virtual domains, we are creating a cutting-edge CVE with the potential to reduce manufacturing costs and design time. As with any novel system utilizing new technology, there is a risk that the system will not be measurably better for users. This work is in collaboration with the University of California at Davis.

Summary of Accomplishments:

The project was intended to provide an integrated, cyclical system that allows users to work on designs in both the physical and digital modalities. Current physical-to-digital acquisition methods still lack both the accuracy and density required for the high-fidelity sampling and reconstruction necessary for mission-critical work. As a result, we pivoted to focus the research on performing object reconstruction from a fresh perspective that keeps in mind additive manufacturing and advances in sensors, such as depth sensors. The final result explores the impact of sensors and additive manufacturing on problems in computer vision, primarily object and scene reconstruction. First, it introduces a novel method for object reconstruction, based on additively embedded sensors, and verifies it with synthetic data. Second, it introduces a hybrid structure-from-motion (SFM) pipeline that uses surface-level sensors to achieve more accurate photogrammetry data than photography alone. Third, it discusses a depth-based error metric for use as a cost function in optimization during the last phase of a traditional SFM pipeline. Fourth, it discusses an efficient SFM pipeline that produces denser reconstructions from initial reconstructions via progressive image consistency constraints and interpolation. Fifth, it introduces a novel paradigm for evaluating object reconstruction algorithms by utilizing datasets consisting of reproducible and customizable additively manufactured objects.

Significance:

The fundamental research that went into developing a robust, MCP-advanced imaging and image-processing theory is anticipated to benefit intelligence gathering and surveillance domains. For example, multiple new sensor-fusion paradigms and algorithms are immediately useful and may change future additive manufacturing processes. Furthermore, a new 3D-datasets paradigm, utilizing additive manufacturing, enables new intra-algorithm comparisons and research. Investigations into sensor fusion yielded future ideas about Near Field Communication, embedded sensors, and their roles in future datasets and their acquisition. This has an impact on first responders other active personnel.

Refereed Communications:

S. Recker, C. Gribble, M.M. Shashkov, M. Yepez, M. Hess-Flores, and K.I. Joy, "Depth Data Assisted Structure-from-Motion Parameter Optimization and Feature Track Correction," in *Proceedings of IEEE Applied Imagery Pattern Recognition Workshop*, pp. 1-9, 2014.

Game Theory for Proactive Dynamic Defense and Attack Mitigation in Cyber-Physical Systems

177965 | Year 2 of 3 | **Principal Investigator: J. Letchford**

Project Purpose:

Malicious attacks on cyber-physical systems, such as nuclear weapons systems or the electric power grid, are orchestrated by human attackers whose decisions are influenced by personal incentives. Current systems take into account that the value of a security system or policy is not only in the attacks that it successfully foils, but also in the way that potential attackers' actions are changed. However, there are many other (currently non-accounted) decisions already being made in these systems that also have the potential for deterring attacks. For example, strategies for mitigating the extent of system failure or backup systems ignore this deterrence effect, and are not included in current security models. When our security and resilience models ignore the changes in attacker incentives due to other investment areas, we are less effective in allocating our limited resources. Our goal is to develop models and algorithms that manage the computational issues that arise when we consider a wide range of potential deterrence effects and attack vectors to enable more efficient planning for investments in security, resiliency, and mitigation, both exploiting potential synergies and avoiding costly redundant investments.

This project will give us the potential to consider a wide range of cyber-physical security domains, with the hope that we will be able to find interesting parallels between these domains that allow us to extend the techniques we develop for one domain to other domains.

We will use adversarial game theoretic analysis to develop new models and algorithms for cyber-physical systems that characterize the deterrence factor of infrastructure investments that make attacks impossible, and of investments that reduce the impact of system failures. We will also develop the first models that take into account the interconnected nature of these investment areas.

Graph Learning in Knowledge Bases

183780 | Year 1 of 3 | **Principal Investigator: A. Pinar**

Project Purpose:
Data science is a foundational pillar to many research areas. Current science and technology approaches to data science focus on post-acquisition analysis. Very few analysis techniques support the data acquisition process itself. The purpose of this project is to discover a framework that allows for quantitative assessment of the value of data to the problem being solved; this process is known as data valuation.

This problem is trivial if all data are equally valuable and useful, but this is not the case in practice. Data elements can have complex relational dependencies where some aspects of the data can be inferred, making its physical acquisition redundant. This inference is inherently probabilistic; maintaining inferred data requires a knowledge-base structure that can handle non-deterministic queries. Because traditional database queries return a single answer (requested data or null), in absentia use of inferred data is hampered. Addressing this problem requires advances in probabilistic knowledge-base design and utilization.

In collaboration with the University of Florida, the proposed research will leverage state-of-the-art machine learning techniques for performing inference on a large-scale, probabilistic knowledge graph. Specifically, probabilistic knowledge bases report, per cell, a probability that indicates the likelihood that the element is a particular value. The techniques developed in this research will focus on addressing issues and opportunities created with human-in-the-loop analysis patterns and techniques. It is conceivable these data valuation frameworks (if quantitative) could replace current, mostly arbitrary, data collection and retention policies.

HostWatch: Situational Awareness of Machine State for Cybersecurity

165614 | Year 3 of 3 | **Principal Investigator: J. B. Ingram**

Project Purpose:

There are two behaviors that are common to most malware (malicious software): persistence and communication. To date, most research and tool development for intrusion detection has been focused solely on communication, presumably because mature collection tools for network traffic have existed for some time. Recently, tools to collect host state data have matured enough to allow large-scale collection. However, tools to analyze this voluminous data are very rudimentary.

We propose to increase situational awareness of cyberspace by using machine learning to automatically detect compromised hosts via analysis of host state. The successful application of machine learning to cybersecurity problems has been largely unproven, and to our knowledge, no other research has attempted a large-scale analysis of host state. This analysis is accomplished by combining two types of machine learning algorithms: anomaly detection and supervised/semi-supervised learning. Anomaly detection is an unsupervised strategy, which is used to identify potentially unknown threats. Supervised learning is used to detect known threats, which remain unidentified on the network.

Both strategies are necessary. Anomaly detection may identify new malware, but it may also identify unusual but harmless entries. Supervised learning can differentiate good and bad software, but it may miss new malware, which is substantially different from previously encountered instances. Together, the two approaches can highlight potentially new, previously unseen threats, as well as new instances of previously seen threats.

An automated analysis workflow automatically ingests and analyzes new data. Both host data and model output are intuitively visualized in a web interface to reduce cognitive load and allow analysts to provide feedback, which is used to evaluate and improve models. The intent of such an interface is to demonstrate the potential for providing results to cyber incident responders in near real-time.

Summary of Accomplishments:

Currently, Windows is the most common operating system, which makes it a highly sought target for exploits. The most common persistence mechanism on Windows is the Registry, a hierarchical key-value system database that stores configuration and program settings, user profiles, and is even capable of storing commands to execute when the system is loaded. We performed an extensive analysis of approximately 20 million Registry keys collected since October 2012. We developed techniques to convert the data into a format amenable to machine learning, while significantly reducing the number of instances to analyze. We established an initial performance baseline of various state-of-the-art machine-learning techniques on this data, demonstrating the efficacy of machine learning for detecting compromised hosts on a network. We anticipate that, with our best-supervised model, a cyber analyst could find roughly 83% of known malware after viewing only a small fraction of the total list.

We also made several algorithmic and programmatic contributions. Our algorithmic contributions include: generating features for anomaly detection based on bipartite graph analysis, monitoring the performance of classification models without labeled data, and developing novel multivariate anomaly detection techniques. Additionally, most popular multivariate anomaly detection techniques are heuristic-based and produce a score instead of a probability or density estimate. These score distributions are generally difficult to compare among algorithms, which makes combining them to improve accuracy more difficult. We developed novel non-parametric techniques to combine these scores into an overall score. Initial experiments indicate that our technique doubles in performance when compared to the average performance of the individual algorithms. Our programmatic contributions include the implementation and deployment of several automated analysis workflows: one for automatically ingesting and analyzing host state and the other for performing streaming anomaly detection.

Significance:

Most current research in intrusion detection has focused solely on detecting the communication aspect of intrusions, typically via collection and analysis of network traffic. Being able to effectively represent and model host-state data allows for more advanced enterprise-wide monitoring, providing a more complete picture of events and changes that are occurring on machines within a network. Over the course of this project, we have demonstrated the feasibility and efficacy of collecting and analyzing host state across an enterprise, a capability that most organizations do not currently possess.

Refereed Communications:

M. Solaimani, M. Iftekhar, L. Khan, B.M. Thuraisingham, and J.B. Ingram, “Spark-Based Anomaly Detection over Multi-Source VMware Performance Data in Real-Time,” in *Proceedings of the IEEE Computational Intelligence* (IEEE SSCI), pp. 66–73, 2014.

E. Goodman, J. Ingram, S. Martin, and D. Grunwald, “Using Bipartite Anomaly Features for Cyber Security Applications,” to appear in *Proceedings of the 14th IEEE International Conference on Machine Learning and Applications* (ICMLA), 2015.

Identification of Markers of High RANS Uncertainty for Model Improvement in Engineering Flows

180823 | Year 1 of 3 | **Principal Investigator: J. Ling**

Project Purpose:

The purpose of this Truman Fellow project is to develop and apply machine-learning techniques for the detection of regions of high model form uncertainty in Reynolds Averaged Navier Stokes (RANS) flow predictions. RANS simulations rely on empirical transport equations to model transport due to turbulence. These simulations are susceptible to high uncertainty when the underlying model assumptions are violated. Current methods for validating RANS simulations rely on validation experiments or high fidelity simulations, both of which can be costly or infeasible to perform for many flows of engineering relevance (for example, in areas within nuclear security and energy security domains). Therefore, there is significant demand for computationally efficient methods that can detect regions of high model form uncertainty in RANS simulations.

Machine learning algorithms are data-driven methods that can leverage the big data generated by computational fluid dynamics simulations to learn when RANS model assumptions are violated. These algorithms are trained on a database of canonical flow configurations for which both high fidelity and RANS results are available. These detectors for elevated RANS uncertainty have a range of potential applications. They are immediately useful for post-processing simulation results because they enable users to know in which regions of the flow their simulations have increased uncertainty. Furthermore, they could be used to trigger adaptive corrections during run-time. They are also informative in experimental design to designate the regions of the flow that should be probed to provide the strongest validation for the simulation results.

In Situ Compressed Sampling and Reconstruction of Exascale Unstructured Mesh Datasets

180818 | Year 1 of 3 | **Principal Investigator: M. Salloum**

Project Purpose:

Post-Moore and exascale platforms are expected to generate datasets that are too large to be reliably stored or transferred across networks, thus impeding data exploration and knowledge discovery. In situ data compression can address this problem, but current efforts are overwhelmingly targeted at data defined on regular lattices. These efforts are not suitable for data defined on irregularly spaced points ("point-clouds") (e.g., unstructured meshes).

We will develop a fast data compression method for time-dependent fields defined on point-clouds, based on the theory of compressive sensing (CS) of videostreams. Conventional CS theory, developed for image compression, is based on the representation of lattice data using first generation wavelets. We will extend the theory to encompass second-generation wavelets (SGW) that can be described on point-clouds. This extension requires designing random matrices that are incoherent with SGW and establishing the restricted isometry required for unique inflation of compressed samples. Time-series modeling of wavelet representations of datasets will be used to reduce the temporal reconstruction cost. We will also investigate scalable reconstruction algorithms and error metrics to be combined into a practical framework for analysis and knowledge discovery.

Our method will be implemented as a parallel codec (coder/decoder) and demonstrated in compressing/inflating a time-dependent, 10-billion-node dataset from a turbulent jet simulation running on petascale capability computing platform Cielo. Such data compression capability will be of relevance to exascale engineering simulations conducted for nuclear weapons and energy efficiency applications. The cloud-of-points data representation will also make the codec applicable to particle-based simulations.

Kernel and Meshless Methods for Partial Differential Equations

166141 | Year 3 of 3 | **Principal Investigator: R. B. Lehoucq**

Project Purpose:

Efficient methods for solving integral and partial differential equations are at the core of a multitude of engineering and science problems, which are critical to national security missions. For example, simulations often use partial differential equations (PDEs). In order to obtain a high fidelity model, the ensuing simulations can take an inordinate amount of time to compute. Improved methods for solving PDEs, and approximating them with integral equations, will allow for more timely and rapid simulations, which are critical to many projects. We anticipate that our results will offer new methods that will ultimately improve the computation of solutions to numerical PDEs. This project is in collaboration with Texas A&M University.

The approximation of integral and PDEs with mesh-free techniques are a non-conventional approach. The proposed work attempts to design the theoretical background for an application of novel “small-footprint” bases to numerical PDEs. We will then develop and implement algorithms for this technique and compare/quantify computational benefits to current techniques.

Summary of Accomplishments:

We introduced a mesh-free discretization for a nonlocal diffusion problem using a localized basis of radial basis functions. Our method consists of a conforming radial basis of local Lagrange functions for a variational formulation of a volume-constrained, nonlocal diffusion equation. We also established an L2 error estimate on the local Lagrange interpolant. The stiffness matrix is assembled by a special quadrature routine unique to the localized basis. Combining the quadrature method with the localized basis produces a well-conditioned, sparse, symmetric positive definite stiffness matrix. We demonstrated that both the continuum and discrete problems are well-posed and present numerical results for the convergence behavior of the radial basis function method. We explored approximating the solution to inhomogeneous differential equations by solving inhomogeneous nonlocal integral equations using the proposed radial basis function method.

Significance:

The collaboration between Sandia and Texas A&M was a synergistic fusion of applying the sophisticated techniques of kernel based methods of the latter to the interesting problem of nonlocal diffusion of the former. The collaboration also opens the door to extended applications with DOE/NNSA mission areas.

Refereed Communications:

S.D. Bond, R.B. Lehoucq, and S.T. Rowe, “A Galerkin Radial Basis Function Method for Nonlocal Diffusion,” Mesh-free Methods for Partial Differential Equations VII, *Lecture Notes in Computational Science and Engineering*, vol. 100, pp. 1-21, November 2014.

Modeling Information Multiplexing in the Hippocampus

178470 | Year 2 of 3 | **Principal Investigator: F. S. Chance**

Project Purpose:

Modern computers face the challenge of processing ever-growing quantities of data that span a wide range of modalities. Of particular relevance to national security interests is the ability of sensor systems to integrate multimodal data for the purpose of fast and automated decision making. The brain is a biological system that is specialized for high performance at this task, suggesting that understanding the mechanisms by which neural circuits integrate multimodal data may lead to improved automated detection systems. This research project will develop and test a novel theory of how neurons in the hippocampus integrate, process, and transmit different information streams. Our goals are to: 1) test the hypothesis that hippocampal neurons multiplex information from two different input streams and 2) generate a description of this multiplexing algorithm that will be implementable in computer systems. If this hypothesis is verified, this research will be the first demonstration (to our knowledge) of multiplexing in any nervous system. Successful outcomes could aid the development of new brain-inspired algorithms for multimodal data integration. These algorithms could significantly impact brain-inspired Beyond Moore computing research and enhance data-processing systems vital for the national security missions of the DOE.

Operationally Relevant Cyber Situational Awareness Tool Development

165611 | Year 3 of 3 | **Principal Investigator: R. G. Abbott**

Project Purpose:
There have been substantial investments in algorithms/tools to benefit situation awareness of cyber personnel. However, the return on investment has been marginal with respect to operational performance. It is pertinent to ask, why have there not been greater returns on investment? There are existing business practices that are highly successful within the operational cyber community; inertia often surrounds these practices due to the costs and risks associated with adopting new technologies. Furthermore, cyber personnel have been asked to accept on faith that the promised benefits of new software tools justify their associated costs/risks.

Improving adoption of new tools by the cyber community involves addressing two critical needs. First, there is need for an empirically based model of operational practices, with particular focus on the human component. Given such a model, algorithm development may target specific opportunities to improve performance (e.g., recognizing patterns in disparate data). More importantly, tools may be designed that readily mesh with operational practices. Second, there is a need for capabilities to quantitatively assess the utility of tools so there is a rational basis for making trade-offs relative to operational benefits.

This project builds upon existing capabilities: 1) Tracer FIRE (Forensic and Incident Response Exercise), a tool that presents cyber personnel realistic threat situations within a laboratory instrumented for collecting data regarding performance, and (2) automated knowledge-capture tools for modeling and assessing human performance during operational tasks. The proposed project combines these capabilities within the Cyber Engineering Research Institute to develop a test bed to support all phases of tool development to help assure eventual adoption and positive returns on investment.

The human-in-the-loop component of cyber has only recently become the subject of scientific study. Consequently, there has been insufficient scientific study to understand the contributing factors for technologies to measurably enhance the individual and team performance of cybersecurity analysts. This project provides the essential science necessary to apply modeling and simulation capabilities to cybersecurity.

Summary of Accomplishments:
Using survey input from 70 cyber professionals, we identified a set of 70 factors that determine tool utility. Our objective in this initial survey was to cast a broad net so that our subsequent inquiries would not overlook any important factors. Then, we focused on the Sandia-specific cyber workflow (tools, workflow, and cyber-tool adoption process) by performing interviews and limited work observations of Sandia cyber professionals.

Next, we developed an event-based computational model of incident response using MicroSaint, a discrete event-modeling tool. In this model, simulated cyber incidents were inserted into a simulation of the Sandia Cyber Omni Tracker system, and the process of dispatching the incident to the correct analyst–and the analyst's process for assessing and resolving the incident–was simulated. We found close agreement between the model and statistics gleaned from Sandia operational data in terms of the time taken to resolve an incident.

After that, we instrumented Sandia's Tracer cyber-training lab to collect human performance data, with a particular focus on cyber tool usage. This allowed us to capture user actions down to the level of individual keystrokes. We collected data at two different Tracer exercises.

Analysis of the data initially focused on groups of cyber tools that are complimentary (i.e., used in succession)—a key finding showed that even the most sophisticated tools are used in combination with simple, general-purpose tools such as web browsers and text editors.

Finally, we developed code to analyze the behavior traces by grouping fine-grained actions together into logically contiguous "blocks" of activity. This is an important step in understanding cyber-analysis techniques from log-level data.

Significance:

Sandia, DOE, and the wider US government expend significant resources to hire, train, and equip cybersecurity professionals. The results of our study analyzed a tool-centric approach to cyber defense, in which training on a single tool (or small set of tools) takes the place of a broader technical background in hardware and software and expertise with a wide variety of tools. Our conclusion is that tools should be evaluated not only in terms of the features provided, but also with a strong emphasis on data exchange and compatibility with other best-of-breed tools.

Refereed Communications:

G.A. Radvansky, S. D'Mello, R.G. Abbott, B. Morgan, K. Fike, and A. Tamplin, "The Fluid Events Model: Predicting Continuous Task Action Change," *Quarterly Journal of Experimental Psychology*, vol. 68, pp. 2051-2072, 2015.

R.G. Abbott, J. McClain, B. Anderson, K. Nauer, A. Silva, and C. Forsythe, "Log Analysis of Cyber Security Training Exercises," presented at the *6th International Conference on Applied Human Factors and Ergonomics*, Las Vegas, NV, 2015.

R.G. Abbott, J. McClain, B. Anderson, K. Nauer, A. Silva, and C. Forsythe, "Automated Performance Assessment in Cyber Training Exercises," accepted at *I/ITSEC*, Orlando, FL, 2015.

T. Reed, R.G. Abbott, B. Anderson, K. Nauer, and C. Forsythe, "Simulation of Workflow and Threat Characteristics for Cyber Security Incident Response Teams," presented at *HFES 2014*, Chicago, IL, 2014.

A. Silva, J. McClain, T. Reed, B. Anderson, K. Nauer, R.G. Abbott, and C. Forsythe, "Factors Impacting Performance in Competitive Cyber Exercises," presented at *I/ITSEC 2014*, Orlando, FL, 2014.

PIMS: Memristor-Based Processing-in-Memory-and-Storage

180819 | Year 1 of 3 | **Principal Investigator: J. Cook**

Project Purpose:

Continued progress in computing has augmented the quest for higher performance with a new quest for higher energy efficiency. This has led to the reemergence of processing-in-memory (PIM) architectures that offer higher density and performance, with some boost in energy efficiency. Past PIM systems either integrated a standard CPU with a conventional dynamic random access memory to improve the CPU-memory link, or used a bit-level processor with single instruction multiple data control, but neither matched the energy consumption of the memory to the computation. We propose to develop a new architecture derived from PIM that more effectively addresses energy efficiency for high performance scientific, data analytics, and neuromorphic applications. Our PIM innovation uses intermediate-sized multiple instruction multiple data arithmetic/logic units (ALUs) that match the power consumption of an advanced storage array to maximize energy efficiency. By augmenting storage (instead of memory), the system can address both in-memory computation and applications that access larger datasets directly from storage, hence processing-in-memory-and-storage (PIMS).

We will design the PIMS architecture and evaluate the performance/energy tradeoffs for DOE/NNSA-relevant applications by developing: 1) a high-level abstraction of PIMS for implementation within existing codes to functionally evaluate performance, 2) an analytic and/or functional PIMS model to investigate architecture performance/power tradeoffs, and 3) a low-level hardware model that provides latency and power data to inform the architecture model. The key challenge will be defining ALU functions (e.g., matrix operations, searching) that adequately support applications, balance memory array and computational energy, and raise system performance.

Few examples of revolutionary new architectures exist in the mainstream due to the challenge, cost, and time required for hardware and software development and community adoption. This prohibits industry from making investments in such new technology. Our novel approach will potentially shorten the path to industry adoption of PIMS.

Reducing Computation and Communication in Scientific Computing: Connecting Theory to Practice

173882 | Year 2 of 3 | **Principal Investigator: G. Ballard**

Project Purpose:

The gap between the peak capabilities of computer hardware and the achieved performance of numerical computations is caused in large part by the high cost of communication (i.e., the movement of data between processors and throughout the memory hierarchy of a single processor). "Standard" O(n3) matrix multiplication is the most fundamental dense matrix computation. "Fast" [O(np) with p < 3] matrix multiplication algorithms have been identified for over 40 years and are starting to become practical as communication costs dominate. The primary objective of this research is to find an algorithm that is both theoretically and experimentally faster than current implementations {i.e., O(np) with p < 2.81]. The secondary objective is to pursue several complementary tasks that involve developing other communication-optimal algorithms.

Many researchers have tried to improve the exponent of matrix multiplication, though they were not as concerned with finding a practical algorithm. We propose to use computer-aided search to find a practical algorithm by formulating the problem as an integer-valued tensor decomposition problem. However, the main difficulty is that the problem to solve is NP-complete.

If this Truman Fellow project is successful, the immediate reward will be improvement in applications like the coupled cluster method, a quantum chemistry computation where nearly all the computational time is spent in dense matrix multiplication. In addition, many efficient numerical linear algebra and combinatorial algorithms have been reduced to matrix multiplication, thereby inheriting the best-known complexity. By delivering a fast, practical matrix multiplication algorithm, we can connect all those theoretical results to practical implementations.

Scaling up Semiconductor Quantum Computers through Multiscale Analysis

173883 | Year 2 of 3 | **Principal Investigator: J. K. Gamble, IV**

Project Purpose:

Quantum computers have the capability to revolutionize the computation landscape in ways that incremental improvements to conventional computers cannot achieve. Although researchers have had recent success with small-scale devices in many architectures, the largest universal quantum computer demonstrated to date consists of 14 qubits, compared to the billions of bits found in classical computers. It is clear that, for quantum computers to have an impact, they must be massively scaled up.

In this project, we propose a plan for scalable quantum computation in semiconductor systems. By completing this course of research, silicon-based quantum computing technologies will be brought closer to the level of gallium arsenide (GaAs) in terms of device reliability, while sidestepping the decoherence problems intrinsic to GaAs. This project consists of three principal stages. Stage 1 will begin by continuing to clarify the role that disorder plays in quantum control of semiconductor qubits. Multiscale effective mass models that phenomenologically incorporate disorder will be developed and validated. Stage 2 will incorporate the results from Stage 1 into large-scale models, which are capable of simulating entire devices, and have not yet been able to capture such small-scale features. Finally, Stage 3 will optimize device designs in order to mitigate the role of disorder. In doing so, this research will help to overcome one of the major obstacles to scalable quantum computing.

The focus of this Truman Fellow project is to understand the fundamental science of disordered semiconductor systems. Once the basic science is understood, the knowledge gained will be used to facilitate engineering advances in semiconductor qubit development, which will help advance research in nuclear security, quantum science, and high performance computing.

Simulation Capability and Computational Assessment of Memristors as Beyond-CMOS Logic and Memory Devices

173024 | Year 2 of 3 | **Principal Investigator: D. Mamaluy**

Project Purpose:

Transition metal oxide (TMO) memristors have recently attracted special attention from the semiconductor industry and academia. Memristors are one of the strongest candidates to replace flash, possibly dynamic random-access memory and static random access memory in the near future.

The purpose of this project is to create a memristor charge transport simulator that will facilitate understanding of switching mechanisms, predict electrical characteristics, and aid experimentalists in device optimization for different applications. Switching in these devices involves a complex process of oxygen vacancy motion in the TMO film, governed by thermally and electrically driven processes intertwined temporally and spatially. Computational simulation of these phenomena requires a new method that captures effects of many species (ions/vacancies/electrons/holes) transport properties, changes in material composition, Fickian diffusion, thermophoresis, and field drift. The simulator will greatly assist in evaluating novel memristor-based designs and will potentially benefit high performance computing systems for scientific computing and informatics.

This year, we have succeeded in overcoming one of the main challenges for the project, which involves solving five highly nonlinear and strongly coupled partial differential equations (PDEs) that describe continuum self-consistent transport for multiple charged species as well as self-heating (Joule, Soret-type) effects. We were able to identify and modify key Rhythmos parameters to guarantee the convergence for the PDE system of interest. The device operating temperatures can now be modeled up to 1000K values (previously 650K was the maximum, with no ability to reach steady state). We have also identified and implemented physical models for oxygen ion/vacancy mobility, diffusion, and Soret coefficients, and calibrated the necessary parameters based on available experimental data. As a result, for the first time, we were able to perform realistic, fully converged transient simulations for different filamentary tantalum oxide memristor devices from sub-nanosecond regimes to full steady-state (micro to millisecond) regimes for a range of applied voltages.

Strong Local-Nonlocal Coupling for Integrated Fracture Modeling

165616 | Year 3 of 3 | **Principal Investigator: D. J. Littlewood**

Project Purpose:

Peridynamics is a nonlocal extension of continuum mechanics that seeks to unify the mechanics of continuous media, cracks, and particles. Unlike classical approaches based on partial derivatives, the peridynamic governing equations utilize integral expressions that remain valid in the presence of discontinuities. The result is a consistent framework for capturing a wide range of constitutive responses in combination with material failure. The application of peridynamics for system-level analyses is challenging, largely due to computational expense and the need to specify constraints over nonlocal volumetric boundary regions. Additionally, characteristics of nonlocal models, such as wave dispersion, are desirable in some cases but undesirable in others.

The goal of this project is to develop mathematically consistent formulations for local-nonlocal coupling that allow for full integration of peridynamics with classical finite element analysis. We focus on two distinct strategies. The first is an extension of peridynamics to facilitate a variable nonlocal length scale. This approach improves the compatibility of local and nonlocal models by selectively reducing the nonlocal length scale. The second strategy is a blending-based approach that is distinct from general blending methods (e.g., the Arlequin approach) in that it is specific to the coupling of peridynamics and classical continuum mechanics. This specialization manifests as an additional coupling term that mitigates so-called ghost forces at local-nonlocal interfaces. Facilitating the coupling of peridynamics and classical continuum mechanics also requires innovations aimed directly at peridynamic models–for example, the treatment of peridynamic constitutive laws near domain boundaries. To be effective as engineering tools, coupling strategies and improvements to peridynamic models must be efficient and amenable to implementation in production analysis codes. An open-source, collaborative software framework allows for prototype constructions via Trilinos agile components and mitigates risk by providing a proving ground for algorithm development.

Summary of Accomplishments:

A number of challenges inherent to coupling local and nonlocal models have been addressed. A primary result is the extension of peridynamics to facilitate a variable, nonlocal length scale. This approach, termed the peridynamic partial stress, can greatly reduce the mathematical incompatibility between local and nonlocal equations through reduction of the peridynamic horizon in the vicinity of a model interface.

A second result is the formulation of a blending-based coupling approach that may be applied either as the primary coupling strategy, or in combination with the peridynamic partial stress. This blending-based approach is specialized for the coupling of peridynamic models and classical continuum mechanics models through inclusion of a coupling term that addresses artifacts in the nonlocal model that can manifest in the coupling region. Facilitating the coupling of peridynamics and classical continuum mechanics has also required innovations in peridynamic modeling. Specifically, the properties of peridynamic constitutive models near domain boundaries and shortcomings in available discretization strategies have been addressed. The results are a class of position-aware peridynamic constitutive laws for dramatically improved consistency at domain boundaries, and an enhancement to the mesh-free discretization applied to peridynamic models that removes irregularities at the limit of the nonlocal length scale and dramatically improves convergence behavior.

Finally, a novel approach for modeling ductile failure has been developed, motivated by the desire to apply coupled local-nonlocal models to a wide variety of materials, including ductile metals, which have received minimal attention in the peridynamic literature. Software implementation of the partial-stress coupling strategy, the position-aware peridynamic constitutive models, and the strategies for improving the convergence behavior of peridynamic models was completed within the Peridigm and Albany codes, developed at Sandia, and made publicly available under the open-source BSD 3-Clause license.

Significance:

The development of local-nonlocal coupling schemes, and the integrated fracture modeling capability that they enable, will benefit multiple DOE security missions. Advancing the state of the art in modeling material failure and fracture has application to a broad class of problems in the areas of nuclear and conventional weapon safety and surety. Broader impact to Sandia's role as a national leader in scientific innovation results from the integration of expertise in mathematics, computational mechanics, and scientific computing for the solution of a foremost challenge in computational science.

Refereed Communications:

J. Mitchell, S. Silling, and D. Littlewood, "A Position-Aware Linear Solid (PALS) Model for Isotropic Elastic Materials," to be published in the *Journal of Mechanics of Materials and Structures*.

P. Seleson and D. Littlewood, "Convergence Studies in Meshfree Peridynamic Simulations," to be published in *Computers and Mathematics with Applications*.

S. Silling, D. Littlewood, and P. Seleson, "Variable Horizon in a Peridynamic Medium," to be published in *Journal of Mechanics of Materials and Structures*.

M. D'Elia, M. Perego, P. Bochev, and D. Littlewood, "A Coupling Strategy for Nonlocal and Local Diffusion Models with Mixed Volume Constraints and Boundary Conditions," to be published in *Computers and Mathematics with Applications*.

P. Seleson and D. Littlewood, "Convergence Studies of Meshfree Peridynamic Simulations," presented (invited) at the *8th International Congress on Industrial and Applied Mathematics*, Beijing, China, 2015.

P. Seleson, "A Blending Approach to Concurrently Couple Peridynamics and Classical Continuum Mechanics," presented (invited) at the *8th International Congress on Industrial and Applied Mathematics*, Beijing, China, 2015.

D. Littlewood, S. Silling, P. Seleson, and J. Mitchell, "Coupling Approaches for Integrating Meshfree Peridynamic Models with Classical Finite Element Analysis," presented (invited) at *13th US National Congress on Computational Mechanics*, San Diego, CA, 2015.

P. Seleson and D. Littlewood, "Convergence Studies of Meshfree Peridynamic Simulations," presented (invited) at *Conference on Recent Developments in Continuum Mechanics and Partial Differential Equations*, Lincoln, NE, 2015.

J. Mitchell, "On a Position-Aware Viscoelastic (PAVE) Model for Peridynamics," presented (invited) at *1st Pan-American Congress on Computational Mechanics*, Buenos Aires, Argentina, 2015.

P. Seleson, D. Littlewood, and S. Silling, "A Blending Approach to Concurrently Couple Peridynamics and Classical Continuum Mechanics," presented (invited) at *1st Pan-American Congress on Computational Mechanics*, Buenos Aires, Argentina, 2015.

P. Seleson, Y.D. Ha, S. Beneddine, and S. Prudhomme, "A Concurrent Multiscale Blending Scheme for Local/Nonlocal Coupling," presented (invited) at *AMS Spring Southeastern Sectional Meeting*, Huntsville, AL, 2015.

P. Seleson and D. Littlewood, "Convergence Studies of Meshfree Peridynamic Simulations," presented (invited) at *13th US National Congress on Computational Mechanics*, San Diego, CA, 2015.

Sublinear Algorithms for In Situ and In-Transit Data Analysis at Exascale

165615 | Year 3 of 3 | **Principal Investigator: J. C. Bennett**

Project Purpose:

Steady improvements in computing resources enable increasingly enhanced simulations, but data input/output (I/O) constraints are impeding their impact. Despite increases in temporal resolution, the gap between time steps saved to disk keeps increasing as computational power continues to outpace I/O capabilities. Consequently, we are seeing a paradigm shift away from the use of prescribed I/O frequencies and post-process-centric data analysis, towards a more flexible concurrent paradigm in which raw simulation data is processed as it is computed.

This paradigm shift introduces an enormous research challenge: the need for efficient, data driven control-flow mechanisms. Specifically, scientists need techniques to automatically and adaptively determine I/O and in situ data analysis frequencies, based on the current simulation state. Furthermore, these techniques must adapt to machines with extreme concurrency, low communication bandwidth, and high memory latency, while operating within the time constraints prescribed by the simulation.

The study of sublinear algorithms is a recent development in theoretical computer science and discrete mathematics that shows significant promise in its potential to provide solutions to some of these fundamental issues. Sublinear algorithms are designed to estimate properties of a function over a massive discrete domain while accessing only a tiny fraction of the domain. The study of sublinear algorithms is a recent development and there is no precedent in applying these techniques to large-scale, physics-based simulations. Any success in applying sublinear approaches for a tool-like feature-based statistical summaries would likely lead to algorithmic improvements for many scientific high performance computing problems, particularly in areas reliant on extreme-scale (exascale) computing (e.g., nuclear security, energy security).

Summary of Accomplishments:

This project has made several key contributions in mitigating high performance computing challenges posed by next generation computing platforms through the use of sublinear algorithms. In particular, this research has focused on addressing several fundamental issues posed by the shift to in situ, concurrent workflows. First, we examined how sublinear algorithms could be leveraged to increase efficiency of the analysis algorithms themselves. Towards this end, we developed a sampling-based method to generate colormaps. Our algorithm identifies important values in the data, provides a provably good approximation of the cumulative density function of the remaining data, and uses this information to automatically generate discrete and/or continuous colormaps. Our experiments showed the new colormaps yield images that better highlight features within the data. The proposed approach is simple and efficient, yet provably robust. Most importantly, the number of samples required by the algorithm depends only on the desired accuracy in estimations and is independent of the dataset size. This provides excellent scalability for our algorithms, as the required preprocessing time remains constant, despite increasing data as we move to exascale computing. The algorithms are also efficiently parallelizable and yield linear scaling. We have made these algorithms available to the broader scientific community in Paraview and VTK, both open-source Kitware, Inc., products.

We also developed an approach for enabling dynamic, adaptive, exascale scientific computing workflows. The approach introduces the notion of indicators and triggers—computed in situ—that support data-driven control-flow decisions based on the simulation state. For those indicators and triggers computationally prohibitive to compute, we demonstrate how sublinear algorithms enable their estimation with high confidence while incurring extremely low computational overheads. In the context of our adaptive workflow research, we demonstrated our approach in practice on a large-scale combustion simulation.

Significance:
The impact of our research is twofold. From the applications' perspective, we have introduced important tools that enable feature detection and adaptive workflows in their simulations. Our proposed methods enable the controlling of identification of features, mesh granularities, and adaptive I/O frequencies. It is already becoming critically important to have adaptive control over these quantities, but will be crucial as we look ahead to exascale computing. From an algorithmic perspective, our efforts showcased how sublinear algorithms can be applied to mitigate exascale research challenges. We believe these algorithmic techniques will be adopted widely in the future.

Refereed Communications:
J.C. Bennett, A. Bhagatwala, J. Chen, C. Seshadhri, A. Pinar, and M. Salloum, "Trigger Detection for Adaptive Scientific Workflows using Percentile Sampling," to be published in *SIAM Journal on Scientific Computing*.

J.C. Bennett, "Extreme-Scale In Situ Data Analysis," presented (invited) at the Broader Engagement Panel, *Supercomputing 2014*, New Orleans, LA, 2014.

M. Salloum, J. Bennett, A. Pinar, A. Bhagatwala, and J. Chen, "Enabling Adaptive Scientific Workflows via Trigger Detection," to be published in *In Situ Infrastructures for Enabling Extreme-Scale Analysis and Visualization.*

Topological Design Optimization of Convolutes in Next-Generation Pulsed Power Devices

180821 | Year 1 of 3 | **Principal Investigator: E. C. Cyr**

Project Purpose:

We propose novel topology optimization approaches for electromagnetic and plasma systems. If successful, this project would be a first-of-its-kind capability to design the "convolute" structure that couples pulsed power generators to the fusion target in Sandia's Z machine. To date, convolute designs suffer from substantial (20%) power loss, an issue that is aggravated with increasing voltage, current, and load impedance. An improved convolute design is desired. Already, progress has been made in understanding and improving physical models of the convolute. In addition, modelers have attempted to reduce power loss through parameterized shape optimization of the convolute and concluded that simultaneous investments in modeling, simulation, and optimization are required.

Our differentiating approach is to develop computational techniques for topology optimization capable of designing a convolute structure that minimizes current loss. The complexity of the convolute physics, dominated by plasma models, will require substantial development of: 1) optimization formulations that support complex 3D topologies, 2) nonlinear programming techniques that improve the convergence of topology optimization algorithms, and 3) multiphysics solution methods that support large jumps in material coefficients. Each of these topics is a substantial challenge in its own right, and designing the convolute will require concurrent development of these technologies. If successful, the proposed technologies will lead to an improved convolute design. The algorithmic technology developed by this project will extend beyond convolute design with implications in a number of science and technology areas critical to DOE and NNSA.

Towards Rigorous Multiphysics Shock-Hydro Capabilities for Predictive Computational Analysis

173026 | Year 2 of 3 | **Principal Investigator: J. N. Shadid**

Project Purpose:

A number of critical science and weapons applications require predictive analysis of complex shock-hydrodynamics with electromagnetics. The physical mechanisms include wave phenomena, material transport, diffusion, chemical reactions, and electromagnetics. The highly nonlinear multiple-time and length-scale response of these systems includes discontinuities formed from shocks, contact surfaces, and complex tabular equations of state. Current computational solution strategies use ad hoc combinations of operator-splitting, semi-implicit and explicit time-integration methods, and decoupled nonlinear solvers. The mathematical structure of these methods has not provided stability, accuracy, and efficiency to resolve all the dynamical time scales of interest, nor has it enabled integrated fast sensitivity analysis and uncertainty quantification (UQ).

Our goal is the development of a unique, modern, mathematical/computational approach for multiphysics shock-hydrodynamics that integrates efficient sensitivity and UQ analysis techniques for specific scientific quantities of interest (QoI) that are required outputs from the forward simulation. Our approach is to develop a well-structured high-level mathematical model employing recent Implicit-Explicit time-integration methods and new robust arbitrary-Lagrangian-Eulerian spatial discretizations. This will enable development of fast adjoint-enhanced integrated sensitivity and UQ methods. Achieving this will require developing: 1) a new general space-time discretization algorithmic framework for stable, accurate, and efficient multiphysics shock-hydrodynamics forward solutions that provides for adjoint-enhanced sensitivity and UQ and 2) robust adjoint-based techniques for: s sensitivity analysis, surrogate model creation for UQ, numerical error-estimation, and methods to detect and handle discontinuities in QoI over parameter space. To guide and challenge this effort, we will utilize the exploding wire as our focus multiphysics shock-hydrodynamics application.

User-Accessible Unified Manycore Performance-Portable Programming Model

173029 | Year 2 of 3 | **Principal Investigator: H. C. Edwards**

Project Purpose:

Rapid and disruptive changes in computing architectures (i.e., the manycore revolution) impact DOE/NNSA mission-critical computational science and engineering codes. The diversity and ongoing evolution of architectures undermines portability of these codes, and code teams typically lack resources and expertise to migrate their codes to multiple, changing manycore architectures (e.g., terascale workstations, petascale clusters, and exascale supercomputers). Migrating applications to manycore architectures currently requires scientists and engineers to have detailed knowledge of vendor-specific performance characteristics and constraints, obfuscate essential mathematics in their codes with parallel processing directives, and generate and maintain multiple versions of codes to meet vendor-specific performance requirements. Even vendor-neutral programming models (OpenMP, OpenACC, OpenCL) require architecture-specific knowledge to achieve acceptable performance and pollute mathematical code with parallel processing directives.

Two key Sandia R&D products are addressing independent facets of manycore parallelism. Qthreads addresses task parallelism with highly efficient task scheduling algorithms. Kokkos addresses data and vector parallelism through a performance-portable interface that minimizes users' exposure to architecture-specific details. We plan to integrate these R&D efforts to create a unified, user-accessible manycore performance-portable programming model for the complete range of manycore parallelism: task, data, and vector. Our qualitative user accessibility goal is to allow scientists and engineers to program emerging manycore architectures with neither extensive architecture-specific knowledge nor ubiquitous parallel processing directives.

Merging these disparate and cutting-edge tracks of R&D into a programming model that minimizes teams' demand for manycore expertise (user accessible), minimizes codes' need for architecture-specificity (performance portable), and maximizes opportunities for manycore scalability (task-data-vector parallelism) is an extreme challenge unmet by any past and current R&D efforts. If successful, the new programming model will provide a clear and cost-effective path forward for our broad set of mission-critical analysis codes to meet the disruptive, ongoing manycore revolution in computer architectures.

Versatile Formal Methods Applied to Quantum Information

188255 | Year 1 of 1 | **Principal Investigator: W. Witzel**

Project Purpose:

Cutting-edge research is fraught with uncertainty, fallibility, and doubt. Negative consequences are two-fold. On one hand, errors can propagate, wreak havoc, and lead to waste. On the other, skepticism of an idea delays its adoption, investment, and the benefit it would provide. Skepticism of quantum information is warranted because technology greatly lags theory and the theory is complicated and nuanced. A leap of faith is required when investing in this technology. Are promising quantum algorithms valid, and under what assumptions? How can we be certain that an implementation of the algorithm is correct? How can we efficiently explore the vast space of algorithm and application possibilities?

While many formal tools are available, their practical utility is limited. Transforming a problem of interest to be amenable to analysis with these tools and working through the steps of a proof is an art form that requires much expertise. One must surrender to the preferences and restrictions of the tool regarding how mathematical notions are expressed and what deductions are allowed. When a proof is already understood at the human level and we simply need to confirm and communicate its validity, this approach is unnecessarily cumbersome and limiting. We are developing a theorem-proving system specifically designed to allow limitless expression and freedom in deriving mathematical knowledge from base axioms. We should be able to mirror and verify any sound mathematical reasoning. In particular, our system will enable verification of the correctness of quantum algorithms and the correctness of their implementation.

Our approach is untested and very different from traditional formal methods. Traditional methods are very constrained, deliberately imposing limitations (e.g., type theory) to make it feasible for the computer to automatically search for proofs. We opt to trade power in blind automation for the ability to follow any line of reasoning. We hope to demonstrate advantages in this approach.

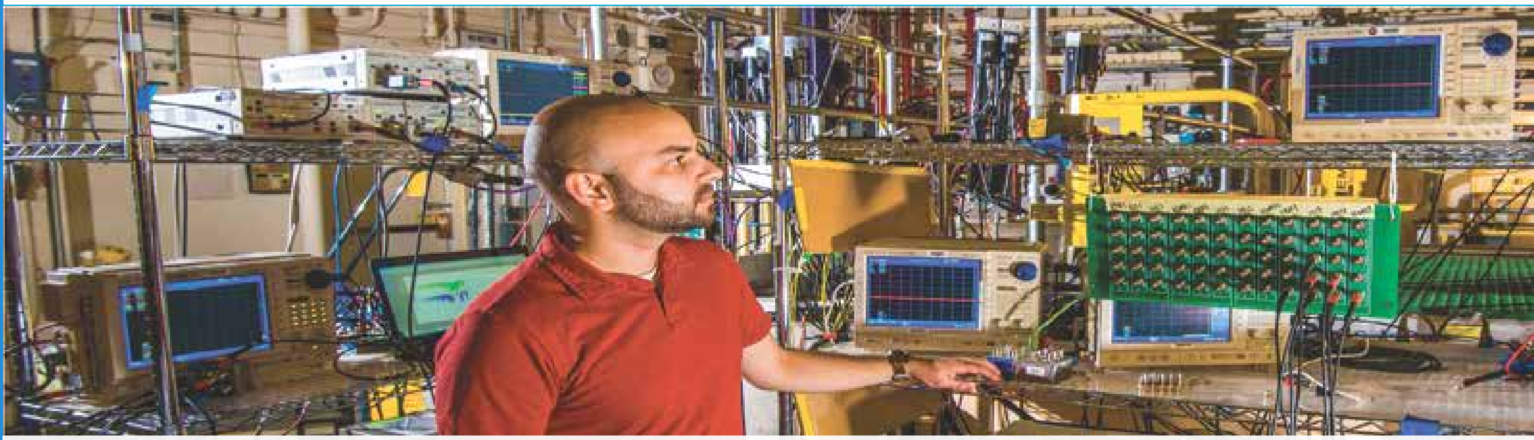
Summary of Accomplishments:

Our ultimate goal was to generate a proof, in our own theorem-proving system called Prove-It, of the validity of the quantum phase estimation algorithm. This algorithm is a critical component of Shor's factoring algorithm, which promises exponential speed-up over all known classical algorithms and has significant national security implications. Our proof would show that the algorithm produces the correct result with the claimed time and space complexity. In this one-year project, we did not intend to produce a complete proof down to the level of axioms, but rather employ, by fiat, high-level theorems of well-known facts in mathematics and quantum physics.

We were able to accomplish much of this ambitious goal. As a guide, we followed a proof in a well-known textbook, Quantum Computation and Quantum Information by Isaac Chuang and Michael Nielsen. Much of their emphasis is on proving that the outcome measuring the quantum circuit, which describes the algorithm, does indeed give an estimate of the desired quantum phase to the desired bits of precision. The time and space scaling of the algorithm is inherent in the quantum circuit description. We focused our effort on the more difficult parts of the proof. We split the proof into three critical pieces to work on independently and we added these into our system. We also laid out a skeleton for connecting these pieces through a series of easier theorems, but did not finish gluing the pieces together. In the process, we found three minor mistakes in the textbook proof. In the process of accomplishing this goal, we added quite a number of basic mathematical facts in the system, which will be useful for future work. Examples are factoring, distributing, and number set closure under arithmetic operations.

Significance:

Our work demonstrates that our Prove-It theorem-proving system is capable of validating fairly sophisticated proofs. It does so with great flexibility that broadens the accessibility of formal proof generation. This is not only useful for confirming the validity of quantum algorithms of interest to national security, but can have a wide range of applications relevant to other areas, such as energy security. Additionally, the algorithm will broaden the use of formal methods verification and validation of weapons systems, greatly enhancing the safety and reliability of critical systems.



Engineering Sciences

The Engineering Sciences Research Foundation (ESRF) drives understanding and innovation by integrating theory, computational simulation, and experimental discovery and validation to understand and predict the behavior of complex physical phenomena and systems. The ESRF Investment Area supports innovative, leading-edge R&D that 1) advances the scientific understanding of physical phenomena underlying problems of interest to Sandia, 2) drives innovation and broad usage of state-of-the-art, validated computational modeling and simulation tools, and 3) accelerates the development of experimental diagnostics for discovery, model validation, and enhancement of our test and evaluation capabilities.

Projects

A Galerkin Least Squares Approach to Viscoelastic Flow Modeling

186870 | Year 1 of 1 | **Principal Investigator: R. R. Rao**

Project Purpose:

Many defense program manufacturing applications, including 3D printing, mold filling, and foam encapsulation involve coupled free surface flows of complex fluids. Simulating the behavior of these fluids (e.g., polymers, suspensions, and foams/emulsions) requires complex material models. Specifically, we must use a viscoelastic constitutive equation that takes into account the history dependence of the material, including effects such as shear thinning and time-dependence, which can modulate the behavior from solid-like to fluid-like.

In Goma 6.0, the 2014 R&D 100 Award-winning open source software, we developed a viscoelastic flow formulation based on the Elastic Viscous Stress Splitting Method. This method works well for 2D and small, 3D steady-state problems, but it requires a direct solver due to the ill-conditioned matrices formed during discretization. Topical at Sandia are 3D and time-dependent viscoelastic flows, which press Goma to be expanded to accommodate new solver algorithms and methods that are more scalable and allow for faster solution times while using more refined meshes. In this project, we will develop computational formulations for viscoelastic flows using a Galerkin least-squares (GLS) finite element approach. This approach allows for the use of equal order interpolation, and it could allow for the use of fast, scalable Krylov-based iterative solvers/preconditioners from the Trilinos library, thereby making Goma a viable tool for these applications. The work will research and investigate preconditioners and algorithmic pairings, including the possibility of a fully explicit stress implementation decoupled from the flow equations.

Summary of Accomplishments:

During this project, we have implemented a Galerkin least-squares method for viscoelastic flow in Goma. Our GLS formulation uses a discrete Elastic Viscous Stress Splitting formulation. From this, a possible new stress formulation was developed. This technique was tested on the flow of an Oldroyd-B fluid past a rigid cylinder, where it is found to produce inaccurate drag coefficients. Furthermore, it fails for a relatively low Weissenberg number, indicating it is not suited for use as a general algorithm. In addition, a decoupled approach is used to separate the constitutive equation from the rest of the system. A Pressure Poisson equation was first attempted, to decouple the velocity and pressure, but we had issues with the pressure field for problems where inflow/outflow boundaries were considered. However, a coupled pressure velocity equation with a decoupled constitutive equation proved successful for the flow past a rigid cylinder and for the four-to-one contraction problem. Decoupling the matrices has several advantages: 1) it creates smaller, better-conditioned matrices compared to the monolithic solver since the Stokes matrix usually has the highest condition numbers due to the incompressibility constraint and 2) it allows for special treatment of each matrix system–thus, a direct solver can be applied to the Stokes system, an algebraic method can be applied to the velocity gradient projection, and the stress equations can be solved with an iterative solver/precondition pair that is scalable. A new Stratimikos interface to Trilinos was added to Goma to expand the preconditioners available for the iterative solvers. We had intriguing success using a SIMPLEC algorithm, which uses ideas from pressure projection to precondition the velocity-pressure matrix. We were successful with this formulation using a Krylov-based iterative solver. Thus, this method seems to be suitable as a general use algorithm, though we are working on improving solve time.

Significance:

This research will open doors for modeling soft solids, whose behavior is neither fluid nor solid and will lead to publishable results. Currently, no scalable viscoelastic flow solver is available to understand manufacturing flows of polymers, especially for flows involving free surfaces such as injection molding and extrusion. With the ongoing life extension programs, manufacturing of many new polymeric materials, including foam parts, encapsulants, and pads is under way. A scalable computational modeling approach for viscoelastic polymer flows will allow us to improve the design of new processes and troubleshoot existing processes, thereby increasing yields and decreasing costs.

A Mesh-Free Method to Predictively Simulate Solid-to-Liquid Phase Transitions in Abnormal Thermal Environments

173194 | Year 2 of 3 | **Principal Investigator: J. A. Templeton**

Project Purpose:

Metal melting and encapsulant decomposition significantly impact weapon systems' safety in abnormal thermal environments. Currently, Sandia has no production-ready simulation capability to predict system failure due to complex thermal-mechanical processes or provide the computational verification and validation required to confidently assess associated nuclear safety issues. Most existing finite element codes are also unable to adequately capture massive geometry changes and liquid relocation. Alternatively, smooth-particle hydrodynamics has been applied to molten aluminum flows, but its formulation precludes phase changes and uncertainty quantification. Other particle formulations, such as the reproducing kernel particle method, are amenable to rigorous error analysis and preserve physical quantities (e.g., viscosity, by retaining the integral form) but have difficulties maintaining high-order numerical quadrature as particles advect. Given the promise of mesh-free methods to accurately model melting and relocation, we propose developing a novel mesh-free formulation with error estimation and validation incorporated from inception by resolving the key technological barriers impeding these methods: minimizing integration error as quadrature points move and resolving processes at the solid/liquid and liquid/air interfaces. To the best of our knowledge, these challenges remain unresolved in the literature and solutions are needed to meet the requirements of the nuclear weapons program. Specifically, the former is necessary for solution verification, while the latter is required to validate the complex physics. This project will provide a high-order quadrature mesh-free scheme implemented in a scalable software package. To understand interactions among all relevant processes, models for aluminum melting, oxidation, and flow will be included.

We are exploring mesh-free strategies for simulating metal melt and relocation, which is currently a unique capability at Sandia. Because particle methods can model large deformations and surface effects arising in many lab-relevant problems, this project has the potential for significant and broad impact.

A PDE Constrained Optimization Approach for Crack Identification Based on Phase-Field Regularization

180879 | Year 1 of 2 | **Principal Investigator: M. R. Tupek**

Project Purpose:

The purpose of this project is to develop a computational capability for solving inverse problems involving cracks and fracture propagation. Computational simulations of the failure of engineering materials based on numerical solutions of systems of partial differential equations (PDEs) to determine the evolution of cracks and damage have been commonplace for decades. These so-called forward-problem approaches have proven their utility in engineering design and analysis for many Sandia and DOE applications. However, what is often truly desired is a solution to the corresponding inverse problem, which asks, for example, "Given experimental observations of a fractured material, what were the mechanical loadings and crack propagation histories which led to the current material state?" We call this the crack forensics problem. A related inverse problem, which we call the crack identification problem, answers the question, "Given experimental observations of a mechanical structure, does it contain cracks and if so, what are their sizes, shapes and locations?" We propose to develop simulation capabilities to efficiently solve these inverse problems using partial differential equation constrained optimization techniques combined with a modern phase-field regularization approach to model the crack features.

What distinguishes our proposed approach with many related approaches in the field of structural health monitoring is the ability to reconstruct full field representations of the existing cracks. An additional advantage of our approach is that it is indifferent towards the experimental techniques used to measure the structural response. This work will be designed initially to take advantage of structural frequency response measurements, as well as surface displacement measurements coming from experiments using digital image correlation. A final advantage of the proposed approach is its use of phase-field models for fracture, which have been shown to be well posed and convergent, a presumed prerequisite for inverse analysis.

A Process and Environment Aware Sierra/SM Cohesive Zone Modeling Capability for Polymer/Solid Interfaces

165649 | Year 3 of 3 | **Principal Investigator: E. D. Reedy, Jr.**

Project Purpose:

The purpose of this project is to create a unique capability to predict the performance of polymer/solid interfaces. This requires an innovative approach that is based on the hypothesis that the complex nature of interfacial fracture can be predicted by combining nonlinear viscoelastic material response with a new type of interfacial separation model. The performance and reliability of many mechanical and electrical components depend on the integrity of polymer-to-solid interfaces. Such interfaces are found in adhesively bonded joints, encapsulated or underfilled electronic modules, protective coatings, and laminates. This project focused on improving Sandia's finite element-based capability to predict interfacial crack growth by: 1) using a high-fidelity nonlinear viscoelastic material model for the adhesive in fracture simulations and 2) developing and implementing a novel cohesive zone fracture model that generates a mode-mixity dependent toughness as a natural consequence of its formulation (i.e., generates the observed increase in interfacial toughness with increasing crack-tip interfacial shear). Furthermore, molecular dynamics simulations were used to study fundamental material/interfacial physics so as to develop a fuller understanding of the connection between molecular structure and failure. Also reported are test results that quantify how joint strength and interfacial toughness vary with temperature.

Summary of Accomplishments:

We developed a simple, cohesive zone model that generates a mode-mixity dependent toughness (mode-mixity is a measure of shear-to-normal stress at the crack tip). We analyzed a test geometry similar to that used to measure the dependence of interfacial toughness on crack-tip mode-mixity. In such tests, a thin adhesive bond with a long interfacial edge crack is sandwiched between rigid grips that can be translated to induce normal and shear loads. Our calculated results for a glass/epoxy interface are in good agreement with published data and display a rapid increase in toughness with increasing crack tip interfacial shear. To our knowledge, we are the first to quantify the increase in interfacial toughness of an epoxy/aluminum interface with decreasing temperature (85% increase in toughness when the temperature is reduced from 23°C to -65°C). This helps to explain the paradox of why joint strength increases with decreasing temperature. We developed a new coarse-grained model for highly cross-linked polymer networks to more accurately represent molecular packing at the interface of bond failure. The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) molecular dynamic code was used to perform simulations of an adhesive layer sandwiched between two solid surfaces. These simulations showed crack initiation in the corners adjacent to the stress-free edge. The failure strain decreased rapidly as the system size increased. Extrapolating our results to larger bond thickness suggests that adhesive bonds with a thickness of about a few microns will have failure strains similar to those observed in experiments. This explains the large difference in failure strains predicted by our simulations and those measured in engineering scale experiments. At some size, the decrease in failure strain must halt. This suggests an important, but poorly understood, length scale that governs fracture in the polymer adhesive systems.

Significance:

The performance and reliability of many critical NNSA and DoD components depend on the integrity of polymer/solid interfaces. Such interfaces are found in adhesively bonded joints, bonded assemblages, encapsulated or under-filled components, protective coatings, and microelectronics. Interfacial failure can severely impact a component's electrical and structural integrity. The new cohesive zone fracture model we developed enables an improved finite element-based simulation capability to predict how variations in processing, environment, geometry, and loading affect the performance and reliability of polymer/solid interfaces. This capability can be used to design components as well as to quantify process sensitivities and guide processing improvements.

Refereed Communications:

E.D. Reedy, "A Simple, Mixed-Mode Dependent Cohesive Zone Model," presented (invited) at *38th Annual Meeting of The Adhesion Society*, Savannah, GA, 2015.

Advanced Computational Methods for Thermal Radiative Heat Transfer

186367 | Year 1 of 2 | **Principal Investigator: J. Tencer**

Project Purpose:

Assessing weapons safety in abnormal thermal environments using numerical modeling plays an extremely important role in assuring the safety of both the existing stockpile and ongoing life extension programs. Participating media radiation (PMR) is routinely neglected in full-system simulations because, to date, it has been prohibitively computationally expensive. The methods investigated here have potential to reduce this computational resource constraint, improving simulation fidelity and increasing confidence in a number of high-consequence applications of interest to the DOE (i.e., within the fire, weapon safety, and satellite communities).

In weapons safety assessments involving abnormal thermal environments, radiation heat transfer is frequently a dominant energy transfer mechanism. Radiation heat transfer can often dominate computational resource requirements (by several orders of magnitude) in these studies due to the nonlinear coupling between radiation and the other heat transfer modes and the dependence of the radiative intensity on direction. Presently, such analyses are impractical, even with current high performance computing resources. Consequently, analysts have often ignored participating media or have applied approximate models and other simplifications to reduce the computational expense to an acceptable level, at the expense of severely compromising the underlying physics. Organic encapsulants are widely used in weapon systems and they decompose at high temperature. This produces products that absorb, emit, and transmit significant thermal radiation. The goal of this work is to make modeling of PMR tractable by applying more efficient computational methods. We will investigate novel approaches to improve the computational efficiency of PMR calculations, including data-driven reduced-order modeling approaches.

The purpose of the project is to demonstrate the application of reduced order modeling approaches to radiation heat transfer applications in order to significantly reduce the computational cost associated with these simulations. In the first year, this approach has been demonstrated to be applicable to 1D and 2D radiation heat transfer problems.

Determination of Surface-Mediated Degradation Products in Energetic Materials at Critical Interfaces

170974 | Year 3 of 3 | **Principal Investigator: C. L. Beppler**

Project Purpose:

Degradation of energetic materials at the powder/bridgewire interface can cause significant changes in the component up to and including failure to function. Just 1% or less degradation of the total material, if present at the critical energetic material (EM)/bridgewire interface, can cause function changes and is a limiting factor in the lifetime of energetic components in the aging stockpile. However, the long-term behavior of these materials inside a component microenvironment is still not well understood. In this project, we propose a new approach for determining the types of chemical degradation products forming at interfaces in EMs and provide more insight into why surface-mediated degradation is occurring in the energetic component.

The main methods used to detect degradation are visual inspection and gas analysis. These methods indicate degradation has occurred, but cannot determine how or why degradation occurred. In addition, the focus of previous work has been on understanding the degradation behavior of the homogenous bulk material. However, bulk material behavior may not be representative of the EM's behavior at the critical bridgewire surface. Thus, this study will provide a greater understanding of the surface-mediated chemical degradation products that form in these fundamentally reactive materials through the use of state-of-the-art analysis methods.

This study is the first to apply recently available, more sensitive tools to better understand how surface-mediated EM degradation occurs at the powder/bridgewire interface inside components. These tools will probe the previously under examined non-volatile degradation products in EM, a key deficiency in our knowledge of EM degradation. This knowledge will enable new and more accurate experimental and computational methods to predict critical aging parameters in energetic materials. The knowledge of these key aging parameters can then enable more accurate component lifetime predictions and be applied to benefit the design and production of EM components for the stockpile by providing better criteria for selecting component materials.

Summary of Accomplishments:

We developed a novel method to detect non-volatile energetic material degradation products in reactive organic materials. This novel approach to analyzing organic materials for degradation also showed that the amount of time and temperature of the accelerated aging regime influenced the extent of degradation, and possibly the type of degradation products formed. Clear trends were observed when pristine energetic materials were aged versus when they were aged with chemically incompatible materials. These trends indicated that one or more chemical degradation mechanisms are taking place in these systems. This technique may also be useful as an early warning diagnostic to find evidence of EM degradation before changes in bulk material are evident. We identified potential 'markers' of EM degradation, which can be used to better understand how and why an EM can degrade at a material interface. Eventually, this data can be used to help discover mechanistic information regarding how and why certain materials accelerate degradation of energetic materials. We also designed a new, hermetically sealed sample creation system to modernize EM compatibility and aging studies.

Significance:

This study expanded scientific boundaries by creating a novel method for detecting EM degradation, which was not previously available. This new method can now distinguish between EM degradation and surface-mediated degradation of EM, which may cause the EM to degrade by a different chemical mechanism. This study produced benchmark data that may eventually be used for ab initio molecular dynamics simulations probing why EMs degrade at critical interfaces. This technique has the potential to provide mechanistic information to probe how and why certain surfaces cause EM degradation.

Developing Strong, Concurrent, Multiphysics, Multiscale Coupling to Understand the Impact of Microstructural Mechanisms on the Structural Scale

180877 | Year 1 of 3 | **Principal Investigator: J. W. Foulk, III**

Project Purpose:

The mechanical performance of metallic structures is driven by microstructure. Strongly coupled processes can localize grain deformations through deformation twinning and void nucleation. We cannot observe, understand, or simulate the high-rate behavior of tantalum for the nuclear weapons complex or hydrogen embrittlement of austenitic stainless steels for gas transfer systems with phenomenology. Our ability to make engineering decisions hinges on our ability to resolve and couple microstructure to the structural scale.

The dominant dissipative mechanisms for candidate face-centered cubic and body-centered cubic metals result from intimately coupled processes evolving over many grains (~millimeters) embedded within a structure (~meters) subjected to abnormal or aging environments. We are required to invoke strong multiphysics at concurrent multiscales to resolve failure processes. We are also required to move beyond crystal plasticity and develop discrete models for deformation twinning (~nanometers) and void nucleation (~nanometers). The ability to enrich structural models with resolved microstructure creates a new computing paradigm that can only be realized with new computer architectures.

We propose to relate the inherent variability of microstructure to the performance of structures through significant contributions in coupling, adaptivity, grain-scale physics, and extensions to many core environments. We stress that these developments have general applicability to hierarchical systems (~meters) composed of many components (~centimeters) having design details (~millimeters) with defects (~micrometers) that drive failure processes. The ability to assess system reliability through the resolution of flaws in forgings, cracks in glass, and debonding along interfaces will move Sandia from a reactive to a proactive approach for stockpile design, certification, and surveillance. Moreover, our open-source approach contributes to the community and provides avenues for future collaborations with academia and other laboratories.

Development of a Spatially Resolved Microwave Interferometer (SRMI)

173881 | Year 2 of 2 | **Principal Investigator: P. E. Specht**

Project Purpose:

This project focused on the development of a spatially resolved microwave interferometry capability to non-invasively monitor the internal transit of a shock, detonation, or reaction front in energetic media. Standard optical interferometry techniques only measure surface or interface velocities. Without a direct, internal measurement, it is necessary to infer the material's state. Alternate diagnostics embedded in the sample inherently disrupt the state of the shock or reaction front measured. The only method to obtain a non-invasive internal velocity measurement in energetic media is with microwave interferometry. Most energetic media is transparent in the microwave regime, but the dielectric discontinuity at a shock, detonation, or reaction front generates a back reflection, enabling an interferometric measurement. Current microwave interferometers only provide a continuum measurement, averaging out the spatial characteristics. Spatial information is necessary for understanding the complex wave and material interactions affecting the thermal, mechanical, and chemical response of heterogeneous energetic materials. Bridging this experimental gap by obtaining spatial information in the microwave regime requires a new interferometer configuration. By coupling laser and microwave interferometry techniques with terahertz spectroscopic methods, a novel multipoint microwave interferometry (MPMI) concept was developed. The concept relies on the phase lag generated by an electro-optic (EO) crystal and polarization optics to impart a microwave frequency onto a laser. This eliminates the technical challenges associated with collimating a microwave beam over large distance and recording it on time scales necessary for shock physics experimentation. The MPMI design uses a standard heterodyne interferometer and established fast Fourier transform methods to extract the microwave frequency and detect any Doppler shift present. Imaging the reflected microwaves onto the EO crystal and the laser exiting the EO crystal onto a fiber array allows for recording the velocity at multiple locations over the measurement surface.

Summary of Accomplishments:

A 35.2 GHz single-point microwave interferometry capability was established at Sandia. Its application was verified through the recording of a known surface velocity. A graphical user interface-based analysis program was written in MATLAB for quickly analyzing the data through peak counting, quadrature analysis, and a simple fast Fourier transform. The knowledge gained from the implementation of the single-point interferometer was applied to the generation of a novel MPMI concept that integrates technologies from laser and microwave interferometry with terahertz spectroscopy. A simplified version of the MPMI concept was constructed and used to measure a microwave frequency through the EO modulation of a laser beam. These experiments proved the underlying physical concept of the MPMI design and illustrated the practical limitations imposed by the longer microwave wavelength. Given the equipment available, the recorded experimental results contained too large a frequency error to adequately measure a velocity. Several alterations to the current experimental setup were suggested for future implementations of the diagnostic to enable the accurate measurement of multiple velocities.

Significance:

The successful implementation of the single-point microwave interferometer established this new and novel capability at Sandia and provided a new diagnostic for studying the reaction and detonation behavior of energetic media. The experimental results obtained using MPMI proved it is a viable interferometric method capable of providing an unparalleled diagnostic for further understanding the thermal, chemical, and mechanical interactions present in heterogeneous energetic media.

Experiments and Computational Theory for Electrical Breakdown in Critical Components

173097 | Year 2 of 3 | **Principal Investigator: F. J. Zutavern**

Project Purpose:
Electrical breakdown is a key issue for many electrical components, either in the need to control it or prevent it from occurring entirely. For example, lightning arresters are designed to protect electrical systems by breaking down when struck by lightning. Alternatively, insulators in high energy density storage, switching, and transmission systems are designed to avoid breakdown using the minimum required volume. Predicting the performance and characteristics of these devices in extreme environments for stockpile and other critical applications is a key issue of national importance. For over a century, component designers have used the breakdown strength of bulk materials as a design guide in many different environments, conditions, and configurations. Science-based modeling of this important phenomenon has had limited success in predicting many of the observed characteristics (such as component breakdown strengths, location and size of primary current channels, damage on solid surfaces and in bulk insulating and multiphase materials, the generation and relative roles of ion and electron distributions in initiating and growing an electrical discharge, and the interaction with solid interfaces near breakdown events) without the help of well-diagnosed discovery experiments.

This project is applying a new experimental technique to the study of electrical breakdown, using ultra-short pulse laser-induced terahertz imaging of electron distributions, to provide more information about electrical breakdown than optical imaging. In the past, optical radiation from the recombination of electrons and ions during electrical breakdown has provided a wealth of information about the plasma distribution in regions where both electrons and ions are present. However, this will be the first diagnostic to provide sub-nanosecond images of the highly mobile electron-rich (ion-depleted) regions of the plasma. Other discovery experiments and advanced diagnostics that will also provide new insight into electrical breakdown are being analyzed to understand their scientific issues and potential impact on advance breakdown theory to improve physics-based simulations.

Experiments to Elucidate Fundamental Breakup Mechanisms of Molten Components in Shock-Driven Flows

180876 | Year 1 of 3 | **Principal Investigator: D. R. Guildenbecher**

Project Purpose:

High-speed, molten metal particulate is found in many applications of interest to Sandia, DOE, and other government agencies. Current predictive capabilities suffer from limited physical understanding of the complex interfacial phenomena associated with liquid metals. While significant knowledge exists on the interfacial instabilities which lead to the breakup of ordinary liquids, such as water, the breakup of liquid metals is much more complex due to substantially higher density and surface tension, oxide skins, potential phase change, and reactivity. New data and novel diagnostics are needed to understand these phenomena and derive next-generation models.

Towards this end, we propose to develop a unique experimental capability. Molten drops, generated using an innovative electrical heater design, will be subjected to shock-induced breakup in a shock tube. Quantitative measurements of the breakup process are made possible with Sandia's state-of-the-art digital in-line holography (DIH) capabilities. Previously, we have demonstrated DIH for 3D measurements of fragment sizes, velocities, and morphologies in low-speed flows. However, in the proposed work, measurement uncertainty arising from thermal gradients, shock waves, and dense particulate clouds will challenge the DIH technique. To overcome this, we will combine nonlinear optical techniques, including phase conjugation and ballistic imaging, with the DIH diagnostic to yield revolutionary measurement capabilities. Successful development will allow for improved diagnostics of propellant fires, particle behavior in igniters, and additive manufacturing using molten metal sprays.

Exploring the Influence of Microstructural Properties of Heterogeneous Explosives on Performance

180880 | Year 1 of 2 | **Principal Investigator: T. Reedy**

Project Purpose:

Conventional detonators (exploding bridgewire and exploding foil initiator) rely on the bursting of an electrically conductive bridge element to deliver an impulse to the explosive, which initiates detonation. However, the transfer of energy to the explosive and the physical processes, which govern the initiation of chemical reactions and build-up to steady detonation within the explosive are not fully understood. The complicated physics of explosive initiation are assumed to include subsonic bed compaction, particle-to-particle interactions, development of hotspots, onset of chemical reactions, formation of a highly dense "plug" of explosive material, strong shock formation, and finally, transition of the shock wave to detonation. It is postulated that these processes are linked to the internal microstructural properties of the heterogeneous explosive pellet. New diagnostic capabilities allow for the interrogation of the pellet's internal microstructure (such as pore size and interface area), providing a more detailed and accurate description of the end-use form of the explosive than the loose, raw explosive powder. Moreover, CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane), the explosive to be examined within this investigation, is a new high-performance energetic material that has not been fully characterized in this manner.

This project will address the current inability to predict detonator performance and further basic understanding by experimentally determining how explosive microstructure influences performance. Validation-quality material properties, initiation threshold, and performance data are key deliverables, critical for future model development. Using novel diagnostic techniques, including multipoint photonic Doppler velocimetry and multi-view streak camera imaging, the explosive build-up to detonation will be characterized, providing reaction front trajectory, run distance, and detonation velocity. In total, these spatially and temporally resolved data will correlate explosive microstructure to performance and be used to develop predictive models, enabling the optimization of microstructure and component design.

Fully Coupled Simulation of Lithium-Ion Battery Cell Performance

173655 | Year 2 of 2 | **Principal Investigator: S. A. Roberts**

Project Purpose:

Lithium-ion batteries are commonly modeled using a volume-averaged formulation (porous electrode theory) in order to simulate battery behavior on a large scale. These methods utilize effective material properties and assume a simplified spherical geometry of the electrode particles. In contrast, a particle-scale simulation applied to real electrode geometries predicts localized phenomena. The purpose of the project is to develop a fully coupled finite volume methodology for the simulation of the electrochemical-thermal equations in a lithium-ion battery cell. Due to highly complex electrode geometries, these models will operate on any unstructured computational mesh and, therefore, will be implemented within the MEMOSA software framework of Purdue's PRISM center. Fully coupling the nonlinear species transport, electrostatics, temperature, and Butler-Volmer kinetics in a stable, efficient, and parallel/scalable computational algorithm for arbitrary geometries is a significant technical challenge that could lead to better-informed decisions on electrode design. The second thrust of the project will investigate 3D electrode architectures that offer potential performance improvements over traditional 2D battery geometries. In addition to simulating possible 3D architectures using the particle-scale model, a volume-averaged formulation will be developed for these unique geometrical conditions. It will be necessary to average all three material domains (anode, cathode, and electrolyte) together, which deviates from the traditional two material volume-averaging method. This method, along with information from our particle-scale models, will enable battery-level simulations of 3D architectures, thus quantifying their ability to advance the field.

The proposed model will take into account the geometry of the battery microstructure and yield more physically accurate simulations that would be used to develop improved constitutive models for use in full-battery reduced-order transport simulations, potentially leading to better battery design and performance. This project with the University of Texas at Austin enhances collaborative research efforts between Sandia and academia.

Summary of Accomplishments:

We implemented a particle-scale electrochemical lithium-ion battery model using a finite volume discretization method and used it to simulate discharge performance of both traditional particle bed geometries, as well as novel interpenetrating 3D battery electrode geometries. The simulations indicate that when a uniform surface area to volume ratio is applied across microstructures, an alternating plate type of geometry provides the best performance among the structures considered. All 3D battery designs perform significantly better than the particle bed geometry, with energy density improvements of 3.7–6.9x observed at the highest power density simulated. The double gyroid geometry performs best, and both it and the Schwarz P geometry significantly outperform the more simplistic 3D battery architectures of inter-digitated plates and cylinders. Overall, the electrochemical simulations suggest that interpenetrating 3D microbatteries outperform traditional particle bed electrodes and that a double gyroid microstructure is superior when considering the realistic manufacturing constraint of feature size resolution.

A 3D battery volume-averaged model has been developed and numerically implemented in the Portable, Extensible Toolkit for Scientific Computation using the finite volume method (FVM). By comparing to particle-scale simulations, we show that the model is quite accurate for simple geometries, such as plates and cylinders, when analytically derived diffusion length relationships are used. For discharge rates up to 160 A/m^2 (~9°C), relative energy density errors remain within 6% for small electrode feature sizes (4.4–11 m) and within 22% for large electrode feature sizes (19–54 m). For smaller feature size (7.5–10.5 m) minimal surface geometry batteries, we observe that a single diffusion length value can be used without introducing significant error (<7%) for discharge rates up to 160 A/m^2. We observe no such consistent value for the larger feature size (17–24 m) structures, and conclude that the limitations of the volume-averaged diffusion length model may be surpassed by these larger geometries.

Significance:
This project focused on developing robust capabilities to numerically simulate lithium-ion battery particle-scale electrochemistry and utilize such capabilities to gain valuable insight into the effect of electrode microstructure on battery performance. Such capabilities are critical to capturing localized transport phenomena within an electrode particle bed to lead to a better understanding of the microscale geometric effects on battery performance. This advance in technical capability will enable battery designers to improve performance, power density, and lifespan of batteries, which is critical to multiple DOE/NNSA missions.

High Fidelity Coupling Methods for Blast Response on Thin Shell Structures

173095 | Year 2 of 3 | **Principal Investigator: M. W. Heinstein**

Project Purpose:
Modeling blast loading on thin shell structures, including initial structural failure and fragmentation through late-time over-pressure within the structure, is proving to be difficult. It is a multidiscipline problem involving a Lagrangian shell finite element description of the structure coupled with a Eulerian volume of fluid description of the air blast. Traditional approaches, including in-house solutions based on the Sandia codes CTH, ALEGRA, and Presto, have coupled Eulerian hydrocodes with Lagrangian structural dynamics codes using a staggered pressure-velocity mapping. Numerical experience has supported the theoretical view that such staggered coupling schemes can be numerically noisy and often unstable. Experience also shows that greater mesh resolution and pressure smoothing in the Eulerian domain can help, but at great computational expense.

We propose to explore fluid-structure interaction methods to accurately capture the internal dynamic structural boundary condition in the Eulerian hydrodynamics method, and the conservative transfer of mass, momentum, and energy constraints to the Lagrangian structural dynamics method. The proposed work centers on creating a shock physics/solid mechanics coupling test bed to develop a coupling technique, which is conservative and restores smoothness and stability. We anticipate embedding level sets in high-resolution Eulerian shock physics stencils, which can both represent the Lagrangian thin-shell structure and provide a split-cell topology with appropriate data needed for the coupling. The potential of this approach is to dramatically improve the accuracy over current fluid-structure iteration (FSI) methods. The approach would be applicable to both solid and shell/membrane structures responding to any fluid medium.

High Precision Testing and Structural Analysis of Li-ion Batteries

166152 | Year 3 of 3 | **Principal Investigator: S. R. Ferreira**

Project Purpose:

In collaboration with the University of New Mexico, we will investigate high precision testing combined with materials characterization of battery cells. We aim to advance capabilities in materials screening and in improving prognostics in lifecycle expectancy. Advances in current testing techniques and methodologies are becoming crucial; as the market for energy storage is moving beyond one- to two-year batteries for consumer goods, such as laptops and cellphones, into large-scale, long-term advanced technologies for electric vehicle and stationary storage applications. Current battery testing methods use low precision testers, where long-term cycling is currently the only reliable way to determine life. Long-term validation testing far exceeds the development cycle for battery technologies and is prohibitively expensive. A transformative way of quickly and reliably validating battery materials and battery life is critical to enabling advances in stationary storage technology. Rapid, reliable battery evaluation, facilitated by high precision testing, will be coupled with materials characterization techniques. This will be used to understand and predict battery performance and life to better enable adoption for stationary storage applications.

Summary of Accomplishments:

The use of principal component analysis simplifies the work required to develop a structure activity relationship for carbon-based battery electrode materials. The ability to conduct a multivariate study with variables that typically do not relate to each other provides a more thorough understanding of factors that contribute to battery failure. This project shows the practicality of applying to structural characteristics of the anode and cycle life and the results agreed with trends observed with the raw values collected on the scanning electron microscope (SEM) images through digital image processing.

It is important to realize this work represents, at best, a proof of concept of the use of digital image processing, as the image collection took place under variable operating conditions. These conditions affect the roughness and texture parameters of the images and leads to an overall obscuring of data. In addition, the available images for data analysis varied greatly for each sample. This made it difficult to compare the structural changes in the four samples over time, which limited the amount of publishable results possible for this project. This is especially true for the data available on the graphitic carbon control. Without a control for comparison, results within this report are qualitative instead of quantitative.

In order to obtain a precise and accurate view of structural changes over time, collection of sample images must take place within the same day by one operator under the same microscope settings, such as focus and brightness. Other factors that need to be consistent are acceleration voltage, and current. The fact that processing these images, which were collected under less than ideal conditions, still yielded data with recognizable trends speaks to the powerful capabilities of this tool.

Significance:

Since both lead acid and lithium-ion batteries utilize carbon-based electrode materials, the image analysis used during this project is suitable for studying the phenomena of the formation of the solid electrolyte interface (SEI). The primary source of performance limitations in lithium-ion batteries involves defects within the SEI. Future research involves the cycling of lithium-ion batteries over time and collecting SEM images of the anodes at various points in testing. Analyzing newer carbon anode materials for lithium-ion batteries through this method allows for a more thorough overview of how the SEI performs over time.

Magnetic Sensing to Determine Material Flows within Opaque Vessels

180875 | Year 1 of 3 | **Principal Investigator: M. Nemer**

Project Purpose:

The purpose of this project is to create and demonstrate a magnetic field measurement technique for visualizing flow within high-temperature high-pressure opaque vessels where traditional optical methods are not possible. Many national security applications have a critical need for flow diagnostics that can be applied to high-temperature high-pressure (HTHP) opaque vessels and materials. Examples include liquefaction of organic materials (i.e., encapsulating foam), potting of components with encapsulant, porous-media flows, thermal decomposition of explosives, shock-wave propagation, and heat-exchanger optimization. Assured safety requires characterization and understanding fluid behavior under HTHP conditions. Our concept borrows ideas from both magnetic resonance imaging and optical particle imaging velocimetry/particle-tracking methods. Our concept involves seeding the fluid with magnetic dipole particles, applying time-varying fields to rotationally induce dipole alignment within well-defined regions, and then observing the flow-induced particle-driven time-varying magnetic field outside the vessel using small, low-cost, highly sensitive, commercially available magnetometers that are mass produced for consumer applications. The magnetic field observations will subsequently be matched with numerical predictions through the application of efficient inversion techniques, and propagation of sensor and other sources of uncertainty through these inversion techniques.

Mechanics of Battery Degradation through Stress-Driven Rearrangement of Percolated Conductive Networks during Discharge and Cycling

173098 | Year 2 of 3 | **Principal Investigator: A. Grillet**

Project Purpose:

Mesoscale battery electrode structure and dynamics control electron and ion transport and determine the performance and capacity of rechargeable batteries. We will develop an understanding of the impact of changes in the electrode structure of lithium ion batteries, focusing specifically on the ionic and electronic percolation pathways. Building on research at the single particle level, we will examine how mechanical changes during cycling cause capacity fade through particle deformations and rearrangements, localized over-potentials, electronic isolation of particles, and lithium ion flux limitations. This project will develop new experimental techniques to study battery electrodes, by examining the connectivity of both the particles and porosity as a function of internal (lithiation) and external (applied) stresses. We will drive new methods of computationally coupling mechanics and electrochemical changes, including anisotropic particle swelling and changes in modulus and porosity/tortuosity of the electrodes. In particular, we will explore how structural heterogeneity coupled with anisotropic changes at the grain scale cause changes in the electronic conductivity of the percolated network. To date, this level of sophistication in developing coupled mechanics and performance models of the complex percolated structure of battery electrodes has not been developed, and represents a new way of looking at degradation mechanisms during cycling. Understanding capacity fade and reliability of rechargeable batteries will significantly impact on our nation's ability to field advanced chemistries for electronics, munitions, and energy storage for renewable sources.

This project will develop new fundamental mechanistic understanding, experimental characterization, and modeling capabilities to explain lithium ion battery capacity fade during cycling. These new foundational capabilities in battery performance and characterization of electrode structure evolution will help Sandia support nuclear weapons and other missions in the future.

Modeling Primary Atomization of Liquid Fuels using a Multiphase DNS/LES Approach

173096 | Year 2 of 3 | **Principal Investigator: M. Arienti**

Project Purpose:

The purpose of this project is to study the injection dynamics of dense sprays in the context of large eddy simulation (LES) of turbulent combustion. An existing LES framework at Sandia (the code RAPTOR) can treat the full range of scales in turbulent reacting flows in a computationally feasible manner (large energetic scales are resolved and the small sub-grid scales are modeled), but requires the correct initial spray information. The high-fidelity simulation of spray atomization by a second computer code (CLSVOF) is used in this project to develop a model-free database for generating new closure terms for LES.

The semi-Lagrangian framework developed in RAPTOR (Rapid Threat Organism Recognition) has been tested and challenged in a realistic fuel injection configuration by the simulation of "spray A," one of the Engine Combustion Network suite of industry-relevant diesel injectors that is being experimentally characterized at Sandia and Argonne National Laboratories. The framework is sufficiently robust that we are moving, ahead of schedule, toward the simulation of auto-ignition of a spray flame. Progress was also made in the sub-grid description of flow turbulent effects on droplet spatial distribution. Remaining challenges for the final year are the excessive compressibility of the liquid phase from the new method and a way to introduce inlet flow perturbations.

Regarding the model-free spray database with CLSVOF, a self-consistent, realistic equation of state for n-dodecane was used to demonstrate the occurrence of thermal effects in the liquid phase above 1500 bars of injection pressure. CLSVOF was chosen by the Spray Combustion Consortium (SCC) to study—in concert with other experimental and numerical capabilities—the fuel injector's internal flow, and is expected to garner interest from industry as the code matures. The contributions to LES will aid in ultimately enabling increased efficiency and reduced emissions in internal combustion engines and gas turbines.

ENGINEERING SCIENCES

Multiscale Now! A Novel Hierarchical Approach for Multiscale Structural Reliability Predictions of Ultra-High Consequence Systems

180878 | Year 1 of 3 | **Principal Investigator: J. M. Emery**

Project Purpose:

This project will impact DOE's nuclear safety mission through development of robust, yet tractable, multiscale structural reliability capabilities for uncertainty quantification. The primary purpose of this project is not to create another multiscale numerical method (MNM). It's about what comes next. This work spans a gap in research with innovative thinking to create game-changing tools that uniquely combine Sandia's current investments in MNMs. Prediction of structural failure due to strain localization or fracture is essential to nuclear safety, where ultra-high reliability (e.g., failure probability <1e-06) is required. Heterogeneity at the fine scale contributes to significant uncertainties in performance. Practical applications cannot include fine-scale details throughout the problem domain due to exorbitant computational demand. A concurrent MNM is necessary but not sufficient.

For example, a multiscale finite element analysis coupling a polycrystalline subdomain to one hotspot in a component typically requires the solution to 100s of millions of equations for one realization of the microstructure—a very computationally expensive endeavor. This represents only one data point for the conditional probability of failure, assuming failure occurs at that hotspot; there are presumably many hotspots. To complete the reliability assessment, Monte Carlo simulation (MCS) is necessary at each hotspot, requiring many thousands of such analyses–this is intractable.

We propose a novel hierarchical solution that will: 1) systematically focus computational resources at requisite hotspots, 2) combine analyses of variable fidelity to maximize efficiency, 3) make MCS tractable using stochastic reduced-order models, and 4) be validated with a first-of-its-kind multiscale experimental technique.

This project advances a new concept for multiscale structural reliability prediction and will provide proof-of-principle application to ductile alloys. It uses an innovative hierarchical scheme that combines predictions of varying fidelity to compute the probability of failure of a component. There are significant risks, but if successful, will benefit a broad range of structural reliability applications.

Novel Method to Characterize and Model the Multiaxial Constitutive and Damage Response of Energetic Materials

180883 | Year 1 of 3 | **Principal Investigator: M. J. Kaneshige**

Project Purpose:

This study, in collaboration with the University of Texas at El Paso, aims to create a scientific breakthrough in the ability to predict the mechanical behavior of energetic materials through the design of a new multiaxial testing method using 3D digital image correlation and the development of a novel continuum damage mechanics (CDM)-based constitutive model for the volumetric and deviatoric response of energetic materials. Traditional methods to elucidate the volumetric and deviatoric response of energetic materials require the use of complex load frame configurations, which apply hydrostatic pressure and uniaxial loads independently. This new method will utilize a variation of the Bridgman notched specimen method, and through 3D optical strain measurements, will elucidate the multiaxial constitutive and damage behavior through comparison to the analytical (skeletal stress) or elastic finite element solution. This work will be extended to deal with effects of strain rate (0.001 to 1 s^{-1}) and temperature (ambient to 75 °C). The primary challenge of this effort is transforming the Bridgman method that was originally developed for metals under tension towards energetic materials under compression. An outcome of this novel characterization method is the development of a CDM-based constitutive model for the prediction of the "batch-to-batch" mechanical behavior of energetic materials. This model will be used to simulate the service conditions of mock plastic bonded explosive material, including uniaxial and multiaxial states of static and dynamic loading.

Mechanical response of energetic materials has a crosscutting impact on diverse programs and problems; development and validation of predictive models entails additional technical challenge and risk. Structural material models are often adapted, but are generally inadequate. Novel approaches to mechanical response modeling are needed and will benefit multiple programs (weapons design, surety) and business areas with the engineering sciences.

ENGINEERING SCIENCES

Numerical Methods for Efficient Simulations and Analysis of Circuits with Separated Time Scales

171117 | Year 3 of 3 | **Principal Investigator: M. N. Hsieh**

Project Purpose:

The purpose of the project is to develop novel numerical methods for efficient modeling of complex fast/slow circuits (i.e., small circuits with strong, nonlinear oscillations and separated fast/slow time scales). Circuit-level weapon simulation and analysis can support electrical interface characterization and predict functional performance limits under untestable environments or scenarios. However, fast/slow circuits can make the computation time of even a single simulation unmanageable. Parallel simulation cannot improve the computation efficiency because these circuits are small. These types of circuits are common in both legacy and new weapons, such as charging circuits in firing sets. Many numerical methods are proposed to speed up such simulations by utilizing multiple time variables to efficiently represent circuit signals with widely separated rates of variation. However, weapon circuits possess complex behaviors, which present outstanding challenges in this research field. Our goal is to develop novel numerical methods for fast/slow weapon circuit simulations and deliver significant simulation speedups to facilitate efficient weapon assurance.

The multi-time partial differential equation (MPDE) methods can provide large simulation speedup for modeling circuits with simple fast/slow behaviors. This research will explore novel numerical methods for efficient modeling of a broader class of fast/slow circuits and overcome the outstanding challenges in the field. If successful, this project will provide capabilities to simulate and analyze the entire operation cycles of fast/slow weapon circuits with high fidelity in manageable time, which is impossible using existing technologies.

Summary of Accomplishments:

We improved MPDE methods for efficient simulations of fast/slow weapon circuits. The key R&D accomplishments of this work are as follows:

We characterized the behaviors of all available fast/slow weapon circuits. Circuits are actually periodic with changing frequency of oscillations during the circuit charging process. This analysis suggested warped MPDE (WaMPDE) should be used for fast/slow weapon circuit simulations.

We improved the discretization methods in Sandia's high-performance analog circuit simulator, Xyce

We developed novel initial condition strategies for WaMPDE in Xyce that can skip an aperiodic phase and work directly with the next more periodic phase

We also developed novel phase condition strategies in Xyce that can automatically determine a good initial condition for WaMPDE and accurately detect phase change of the fast varying signals

We derived the Jacobian matrix of MPDE systems that supports voltage limiting and implemented it in Xyce

We achieved 30x simulation speedup by applying our methods to a charging circuit.

Significance:

Our circuit analysis suggests weapon circuits are actually periodic enough for the warped MPDE methods to work consistently. We improved numerical algorithms and voltage limiting in Xyce's MPDE package, which enables efficient simulations of fast/slow weapon circuits. Our results show that the proposed methods speed up the simulation of a weapon charging circuit by 30x. Our results and methods provide a strong foundation to simulate and analyze the entire operation cycles of fast/slow weapon circuits having high fidelity in manageable time.

Refereed Communications:

M. Hsieh, "Numerical Methods for Efficient Simulations and Analysis of Circuits with Separated Time Scales," *Design Automation and Test in Europe* (DATE 2015), Grenoble, France, 2015.

Prediction of Spark Discharge Paths and Voltages

165652 | Year 3 of 3 | **Principal Investigator: L. K. Warne**

Project Purpose:

A fundamental problem is how a spark discharge path selects candidate conductors in proximity to an electrode (or plasma) at high voltage, and the statistics associated with such spark attachments. The spark discharge path determines whether penetrant energy is diverted to chassis or leads. This problem pertains to penetrations associated with metallic burnthrough by lightning continuing current, to phenolic blastthrough events driven by lightning return strokes, and to other penetrations. A semi-empirical static breakdown criterion, developed in past research, does not answer fundamental, technically challenging questions arising from the transient development of the spark, particularly: (1) Discharge timing (lightning-driven voltages are time limited); (2) Conductor impedance (floating electrodes and dielectrics); and (3) Probability of path and statistics of attachment.

The extensive literature on sparkover is mostly empirical and not easily generalized to geometries and conditions (target electrode impedance, drive waveform, etc.) of interest to NNSA missions. Furthermore, these models and experiments present no clear picture of how sparkover presents with non-uniform geometries. Our objective is to develop rigorous sparkover criteria and tools for determining discharge path in arbitrary gap geometries, as applied to components subjected to high voltage in gaseous environments. We propose that the intermediate stage of spark development–bridging the initial gas ionization stage with the final heating stage, and involving interactions of the discharge with the electrodes–sets the sparking condition. This has been somewhat ignored in the literature. If successful in understanding how the spark occurs, our first-principles model will greatly advance the state of the art.

Summary of Accomplishments:

The behavior of breakdown voltage exhibits a bifurcation when the field becomes sufficiently non-uniform, separating into corona and spark branches. In order to describe the underlying physics of these branches, the breakdown threshold problem was framed as two conditions: 1) a replacement condition, guaranteeing that the gap is bridged by an ionized channel and 2) an instability condition, guaranteeing that the channel transitions into a highly conductive filament. With limited non-uniformity, only a spark occurs and the replacement condition (Townsend or Meek criterion) is sufficient to predict breakdown. Alternatively, in the bifurcated region, the replacement condition predicts the corona branch; the instability condition–identified here as the minimum field of the gap compared to the streamer-sustaining field–predicts the spark branch.

We examined issues related to streamer current characteristics at both the region of inception (the stressed anode region) and the terminating (plane cathode) region. It is believed that streamer spatial branching leads to saturation of streamer charge as the ionization wave progresses into the low field region of a gap. We proposed a kinetic trigger for streamer branching by generalizing the Palmer criterion for avalanche overlap (from uniform laser cavities) to the non-uniform field associated with the streamer head region. The narrow cathode fall region was modeled to examine the current emission following streamer crossing.

We showed that the physics behind the instability condition results from a nonlinear jump in the energy delivered to the streamer channel when the minimum drive field level exceeds the sustaining field level. When neutral dynamics is taken into account, this sudden increase in delivered energy results in renewed ionization. Experiments have been conducted in both triggered-uniform and non-uniform gaps to elucidate the instability with respect to streamers and capture the voltage threshold levels.

Significance:

Our research now enables prediction of spark breakdown thresholds in non-uniform geometries, allowing for judgments on the reliability of gas insulation in critical components and systems subjected to high voltage environments, such as lightning. Results provide the underpinning for the prediction of spark breakdown in non-uniform geometries, which was previously unavailable.

Process Modeling for Additive Manufacturing

180881 | Year 1 of 2 | **Principal Investigator: L. L. Beghini**

Project Purpose:

Additive Manufacturing (AM) provides a new avenue to design innovative materials and components that cannot be created using traditional machining operations. With current AM capabilities, complex designs (such as those required in weapon systems) can be readily manufactured with laser powder forming (or Laser-Engineered Net Shaping [LENSTM]) that would be otherwise cost prohibitive or impossible to produce. However, before an AM product can be qualified for weapon applications, the characteristics of the metals produced by additive manufacturing processes need to be well understood. This project focuses on the development of computational simulation tools to model metal additive manufacturing processes. This proposed work would extend and integrate existing Sandia tools to accomplish the following:

- Be able to better predict residual stresses in AM product
- Extend high-fidelity material models to capture material evolution during the formation process, leading to prediction of end-state material properties
- Provide a basis for engineering tools to propose improvements to additive manufacturing process variables, including those that minimize process variation

While this work would be directly applicable to AM processes, the tools developed would also help enable modeling welding processes such as gas tungsten arc, electron beam, and laser welding.

This project aims to develop a new modeling tool/capability, which has not been previously attempted nor documented in the literature. Once such a tool is created, additional enhancements or extensions could include optimization of the process variables for specific components.

Quantitative Imaging of Turbulent Mixing Dynamics in High-Pressure Fuel Injection to Enable Predictive Simulations of Engine Combustion

165646 | Year 3 of 3 | **Principal Investigator: J. H. Frank**

Project Purpose:

We have developed a capability for quantitative imaging measurements of high-pressure fuel injection dynamics that will transform our understanding of turbulent mixing in transcritical flows, ignition, and flame stabilization mechanisms, and will provide essential validation data for developing predictive tools for engine combustion simulations. Advanced, fuel-efficient engine technologies rely on fuel injection into a high-pressure, high-temperature environment for mixture preparation and combustion. However, the dynamics of fuel mixing and combustion are not well understood and cannot be accurately predicted. Quantitative measurements for model validation are lacking because spatially and temporally resolved measurements of turbulent mixing and combustion dynamics in multiphase, high-pressure, high-temperature flows pose significant diagnostic challenges.

The development and application of high-fidelity imaging diagnostics for understanding fuel injection dynamics is ambitious considering the complexity of the experiments and the demanding temporal and spatial resolution requirements. This newly developed capability will transform our understanding of fuel injection dynamics, which affect engine combustion processes such as flame lift-off, soot formation, and cycle-to-cycle variations. To attain high data rates for tracking the motion of turbulent mixing (~100kHz), we developed a unique pulse-burst laser for high-speed planar laser imaging of fuel vapor mixing, velocity, and ignition. Quantitative interpretation of high-pressure measurements was advanced by innovative treatment of laser-based imaging measurements. Results will be used for testing turbulent mixing models that are central to Sandia's efforts to develop predictive simulations of fuel injection. This diagnostics capability has broad applicability for high-repetition rate imaging of motion in areas such as energy surety and defense.

Our measurements have captured key physical processes in high-pressure, high-speed fuel injection. This interdisciplinary project involved taking significant risks to develop high-speed imaging diagnostic capabilities that will transform our understanding of high-pressure fuel injection. The project enabled collaborative effort between researchers with expertise in imaging diagnostics, laser development, and internal combustion engines.

Summary of Accomplishments:

We designed, developed, and constructed a custom mobile pulse-burst laser for imaging the dynamics of transient fuel injection. We performed 100 kHz scalar and velocity field imaging of high-pressure injections. Experiments were conducted in two different facilities to address different aspects of the project. We constructed a constant volume high-pressure vessel and used it for high-speed Rayleigh scattering measurements in a pulsed gas-phase jet. We used this canonical configuration for fundamental studies of turbulent mixing dynamics at different pressures as well as for the development of methods to correct for laser beam-steering effects in imaging measurements at elevated pressure. An existing high-pressure, high-temperature constant volume vessel was used for studying dynamics of fuel injection for a Diesel injector and a gasoline injector at conditions relevant to internal combustion engines.

We performed the first high-speed planar imaging measurements in Sandia's high-pressure fuel injection chamber, capturing the dynamics of the entire injection event. Our new high-speed capability not only enabled spatially and temporally resolved studies of injection dynamics, but also increased the previously available data rate in this facility by orders of magnitude, enabling statistical analysis of mixing dynamics and setting the stage for many new insights and further studies in the dynamics of fuel injection under different conditions and injector types. For example, our high-speed particle image velocimetry measurements captured, for the first time, the flow reversal in the central region of a multi-plume gasoline injection. This reversal is associated with an important, but poorly understood, dynamic in which the initially separated plumes collapse into a single plume towards the end of injection. We expect that ongoing studies using this new capability will capture more processes that need to be better understood in order to develop physically accurate models for simulations.

Significance:

The results of this work will advance understanding of key physical processes in high-pressure, high-speed fuel injection and will provide input for developing predictive simulation capabilities in mission-critical areas, such as energy surety. The approach develops fundamental understanding through innovative experimental methods in a manner that will strengthen predictive capabilities in areas of critical importance. With high-pressure reacting and non-reacting flow dynamics as our target application, the proposed research has high relevance in a wide range of problems relevant to the defense and energy areas.

Reducing the Adverse Effects of Boundary-Layer Transition on High-Speed Flight Vehicles

173878 | Year 2 of 3 | **Principal Investigator: K. M. Casper**

Project Purpose:

During boundary-layer transition, high-pressure fluctuations are generated on reentry vehicles, which can create significant vibration of internal components. Ongoing research efforts are focused on better predicting these fluctuations and understanding how they couple to the vibration of the structure. Modern computational capabilities now allow modeling of the fluid-structure interactions in these hypersonic vehicles. These models must be developed from experimental data; however, current structural testing of hypersonic vehicles relies on static tests that do not provide an accurate representation of the fluid-forcing environment in flight. We propose to make novel measurements of this coupling by introducing controlled pressure disturbances over a flexible panel in hypersonic flow. The flow field and panel response will be characterized using high-frequency pressure and vibration measurements as well as flow-field visualization. High temporal resolution is required to resolve the unsteady flow field at hypersonic speeds, but these diagnostics have only recently attained the frequency response necessary to study this problem.

This work has never been attempted because of its complexity: the design of the model, flow perturber, and thin panel all require significant research to develop. The subsequent experiments and data analysis describing the fluid-structure interactions are expected to impact DOE's nuclear weapons mission.

Solving the Big Data (BD) Problem in Advanced Manufacturing

184022 | Year 1 of 1 | **Principal Investigator: B. W. Clark**

Project Purpose:

The purpose of the project is to understand the error in 3D printed objects associated with the shape of the object and the print direction, in order to develop approaches for mitigating this error. 3D printing, originally known as additive manufacturing, is the process of making 3D solid objects from a CAD file. This groundbreaking technology is widely used for industrial and biomedical purposes (e.g., building objects, tools, body parts and cosmetics). An important benefit of 3D printing is the cost reduction and manufacturing flexibility; complex parts are built at a fraction of the price. However, layer-by-layer printing of complex shapes adds error due to the surface roughness. Any such error results in poor quality products with inaccurate dimensions. The main purpose of this research is to measure the amount of printing errors for parts with different geometric shapes and to analyze them in order to determine optimal printing settings to minimize the error. We use a Design of Experiments framework, and focus on studying parts with cone and ellipsoid shapes. We found that the orientation and the shape of geometries yield significant effects on the printing error. From our analysis, we also determined the optimal orientation that gives the least printing error.

Summary of Accomplishments:

We identified and characterized sources of error related to build orientation and part geometry when using layer-by-layer additive manufacturing processes. In this research, we showed a critical deficiency of 3D printers in terms of surface roughness (or error) and explained the adverse effects. We designed an experiment to analyze the effects of design and process parameters on the printing error. We performed the experiment on cones and ellipsoids and tested their shape (design) and orientation (process) parameters. We discussed the significant effects and recommended optimal printing settings for minimal error.

Significance:

This study helped identify and characterize two sources of error (build orientation and part geometry) when using layer-by-layer additive manufacturing processes. As additive manufacturing continues to enter mainstream production and parts start to be included in the NW stockpile, these types of studies will be crucial for understanding the sources of error and improving the processes. This study was a start toward characterizing basic sources of error on simple primitive shapes. A better understanding of these errors will be a catalyst for improving the additive manufacturing machines themselves to eliminate these sources of error.

Time-Resolved Optical Measurements of Shock-Induced Chemistry in Energetic Materials

165656 | Year 3 of 3 | **Principal Investigator: R. R. Wixom**

Project Purpose:

State-of-the-art models for shock initiation of explosives are not predictive and thus have limited utility for engineering design, analysis, and quantification of margins and uncertainty for energetic components. The development of physically based predictive tools is severely limited by a lack of knowledge of reaction chemistry and a poor understanding of the physics of chemical energy release at hotspots. The reactive processes occurring during shock initiation are poorly understood due to the inherent difficulty of making measurements over the very fast timescales, short length scales, and extreme conditions that are typically encountered.

Direct observation of thermodynamic states and shock-induced reactions in heterogeneous, condensed-phase solids is difficult due to the technical challenge of obtaining sufficient signal-to-noise ratio while maintaining sufficiently high temporal and spatial resolution. When resolution is sacrificed, the measurements become averaged over time or space in the heterogeneous material and the observation of local non-equilibrium phenomena is compromised. However, newly available optically thin, homogeneous samples may allow us to probe reactions occurring within the material during shock initiation.

We will use these unique vapor deposited films of explosives, including hexanitrostilbene (HNS), which are relatively transparent and allow for measurement of optical emission from within the shocked material. The emission spectrum will be used to determine both temperature of the sample and the presence of chemical species that evolve over time–information that will validate equation of state predictions and provide data for inserting accurate chemical reactivity into hydrocode simulations of explosive components.

The ultimate goal is to develop a fundamental understanding of chemical reaction mechanisms and kinetics, and their relationship to the local thermodynamic state of the material. We are using untested techniques and samples to perform a rigorous study.

Summary of Accomplishments:

Access to unique vapor-deposited films of PETN (Pentaerythritol tetranitrate), HNS (hexanitrostibene), and HNAB (hexanitrobenzene) allowed for the collection of light emitted from detonating and shock-loaded films. We observed molecular and atomic emissions having features similar to those observed by other researchers. The most prominent features in the HNS spectra were from C2 and CN. The PETN spectra were dominated by a broad NO2 peak; this seems to confirm molecular dynamics predictions that suggest NO2 is one of the first intermediates to form. Identifying these intermediate and product species and their rotational-vibrational-electronic quantum state distributions can be used to infer details about the potential energy surfaces that govern reaction processes during initiation and detonation. Our current analysis of some of the results may indicate observation of states not in thermal equilibrium with expected detonation temperatures.

Optimization of the deposition parameters for HNS enabled growth of films of varying thickness with controlled microstructure. These films were used in velocimetry experiments that capture the build-up to detonation on an extremely small scale. This represents the first measurement of shock-induced run-distance in these detonator materials to exhibit such a quick shock-to- detonation transition. This was accomplished using planar Doppler velocimetry to record particle velocity histories at the interface between the flyer-impacted explosive film and a transparent substrate. These data were used to parameterize history variable reactive burn and Arrhenium reactive burn models for HNS. While additional experiments are needed for better parameterization, this method demonstrates the use of this new method of obtaining data for building reaction models of explosives.

Significance:

Accurate predictive simulations of the initiation and build-up to detonation in explosives will transform how we approach explosive component design, stewardship, and surveillance. One of the main roadblocks for achieving this paradigm is the inability to measure and describe the chemical reactions occurring during this process. The state of the art has been empirical parameterization of engineering models. This project resulted in new knowledge of the chemistry occurring during initiation and new methods of measuring the transient thermodynamic state of the explosive with nanosecond accuracy.

Refereed Communications:

J.J. Kay, "Mechanisms of Shock-Induced Reactions in High Explosives," presented at the *APS Topical Group on Shock Compression of Condensed Matter*, SCCM, Tampa, FL, 2015.

Understanding Hot Spot Initiation using Electronic Ultrafast Sum Frequency Spectroscopy

180874 | Year 1 of 3 | **Principal Investigator: J. J. Kay**

Project Purpose:

Although shock initiation of explosives has been studied for decades, it is still not clear how shock waves initiate chemical reactions that lead to detonation. Understanding the sequence of reactions involved in initiation is critical to predictive understanding of energetic material performance. At present, we have little predictive understanding of the shock sensitivity of energetic materials and, therefore, limited capacity to predict initiation thresholds and uncertainties in explosive components.

"Hot spot" initiation is one key aspect of the problem that remains unanswered. It is empirically well known that material porosity enhances shock sensitivity, and it is often assumed that localized heating initiates reactions at defect sites. However, a wealth of evidence indicates that the mechanism may not be thermal heating, but rather spontaneous pressure-induced decomposition. This alternate mechanism is postulated to involve shock-induced changes in the electronic structure of the material, in which instantaneous reactions occur at the shock front, assisted by local distortion of electronic structure at defect sites. At present, no definitive measurement or calculation has proven or disproven this mechanism.

We are interrogating this energy localization mechanism in explosives using interface-specific ultrafast spectroscopy. We will perform a series of spectroscopic measurements to determine whether this pressure-induced reaction mechanism can properly explain hot spot initiation. The measurements we propose will answer, once and for all, whether pressure-induced reactions are important in shock initiation. Answering this pivotal question will assist predictive modeling of shock initiation in energetic materials, which ultimately assists development and certification of explosive components at Sandia.

Upscaling Ab-Initio Quantum Chemistry Models for Nonequilibrium Reacting Flow Simulations

166153 | Year 3 of 3 | **Principal Investigator: D. J. Rader**

Project Purpose:

Many advanced engineering technologies that support national security involve nonequilibrium reacting flows. Such flows are generated by reentry vehicles, plasma environments, and detonations. During Earth reentry, gas temperatures in the shock region exceed 10,000K, which leads to air dissociation. The flow in the shock layer is highly nonequilibrium and chemical kinetics there cannot be characterized by single-temperature Arrhenius rates. Since characterizing such flows in ground or flight experiments is prohibitively expensive, there is currently a lack of high fidelity, nonequilibrium chemistry models that could account for internal energy-specific chemical processes. The proposed research, in collaboration with Purdue University, focuses on the development of a state-specific air chemistry model by performing quasi-classical trajectory simulations using potential energy surfaces obtained from ab initio quantum chemistry calculations. This methodology allows construction of nonequilibrium collision, energy exchange, and reaction models for systems for which little or no experimental data exist. These models will then be used in rarefied-flow simulations to more accurately predict gas drag and thermal load to reentry vehicles. In particular, this work focuses on O2+O processes that can affect high-speed flow field structures and surface oxidation. Methods developed in this work can be expanded to other chemical systems. The resulting non-equilibrium chemistry models will be applied in Sandia Computational Fluid Dynamics (CFD) and Direct Simulation Monte Carlo (DSMC) codes to improve their fidelity. The purpose of this work is to develop a methodology and computational framework for replacing phenomenological elastic collisions, energy relaxation, and chemical reaction models, which are found in most CFD and DSMC codes, with high-fidelity ab initio physics-based models. This will make it possible to simulate flow fields in non-equilibrium regimes with a high degree of confidence, even when few experiments exist.

Summary of Accomplishments:

This project demonstrated that ab initio calculations of potential energy surfaces can be used to develop non-equilibrium chemistry models that can be applied in DSMC and CFD simulations of flow fields. A quasi-classical trajectory (QCT) code was developed and used to calculate O_2+O collision at temperatures up to 20,000K. These calculations produced state-specific dissociation cross-sections and state-to-state rotational-vibrational energy exchange cross sections that can now be used as input to DSMC simulations. The cross sections can also be integrated to produce rates that are needed for CFD calculations. A major challenge was identified in linking ab initio calculations to flow field simulations for any general chemical system: ab initio surfaces are not available for all combinations of species found in non-equilibrium flows and the quality of available surfaces are not well known. Therefore, the sensitivity of rates and cross sections was studied in this work by comparing calculations with ab initio potentials to calculations with Morse additive pairwise (MAP) potential based on spectroscopic measurements. The equilibrium rates calculated via MAP and ab initio potentials agree within 12%, for temperatures between 2,500 K and 5,000 K. The agreement in dissociation rates improves at temperatures up to 10,000 K. In contrast, the difference between O_2+O experimental equilibrium rate measurements is 300% at 10,000 K. Under nonequilibrium conditions, the QCT calculations based on the two potentials match within 70%, while the current phenomenological models disagree by over two orders of magnitude. The simpler MAP potential predicts higher vibrational and rotational de-excitation at low collision velocities, but this agreement also improves as collision energies increase. The excitation and de-excitation rates calculated via the two potentials may differ by up to a factor of three.

Significance:

The methods developed under this project for predicting chemical reaction rates under conditions of thermodynamic nonequilibrium will greatly improve Sandia's ability to simulate flow fields and to predict thermal and structural loads for reentry vehicles. The need for accurate, validated, predictive tools for simulating flow about reentry vehicles is critical to NNSA's nuclear weapons mission and continues to be an area of active research and investment. This project identifies several new methods and technologies for advancing our simulation capabilities in these areas.

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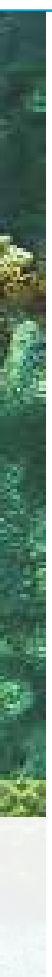
Geoscience

The Geoscience Investment Area seeks to expand the frontiers of knowledge in the following areas: 1) the properties, structure, phenomena and processes associated with the earth's subsurface, surface, and atmosphere and 2) how engineered systems interact with the earth and the earth system. These earth systems and properties impact Sandia national security missions, including energy security, defense, nonproliferation, disaster response, and climate security.

Projects



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Appraisal of Hydraulic Fractures Using Natural Tracers

165670 | Year 3 of 3 | **Principal Investigator: J. E. Heath**

Project Purpose:

We will develop new in situ natural tracer testing methodologies to evaluate local well-to-reservoir-scale hydraulic fracturing efficiency and matrix-to-fracture transport mechanisms, focusing on application to shale hydrocarbon production. Maximizing fracturing efficiency improves producible reservoir volumes and can mitigate risk to groundwater resources. Current fracture characterization with production decline analysis only poorly constrains fracture geometries and connectivity. Key hydro-mechanical reservoir characteristics control natural tracer release during fracturing and production, including: 1) the number, connectivity, and geometry of fractures, 2) the distribution of fracture surface area to matrix block volume, and 3) phase behavior of reservoir fluids. We will characterize a shale reservoir using natural noble gas tracers sampled at the wellhead. Favorable attributes of noble gas tracers include: 1) the suite of natural tracers will display a large range of diffusion coefficients and 2) diffusive mass transfer out of the matrix into fractures may cause elemental and isotopic fractionation, providing additional insight into dominant mass transfer mechanisms.

Natural tracer data may characterize fracture surface area and transport velocities. However, existing techniques have never been applied in shale systems, nor have natural tracer studies considered multirate mass transfer theory. The existence of multiple phases and matrix heterogeneity in shale formations complicates tracer interpretation, increasing possible non-uniqueness of underlying fracture-reservoir parameters generated through our improved breakthrough curve interpretation. By considering data from multiple naturally occurring tracers, our project promises techniques for greatly improved fracture and fluid flow characterization, utilizing data easily collected at the wellhead.

This project develops cutting-edge methodologies using natural tracers to determine reservoir transport mechanisms. Time-series of natural noble gas tracers have not been previously collected from hydraulically fractured wells in shale, much less used to improve reservoir parameter identification. The outcomes of this project will position Sandia as a leader in shale fracture characterization, and contribute to DOE's mission in energy security and environmental protection.

Summary of Accomplishments:

This project developed the novel use of in situ naturally occurring noble gas tracers to evaluate transport mechanisms and deformation in shale hydrocarbon reservoirs. This project included field and laboratory studies of noble gas tracers, combined with other standard data types. Also included is work on methods for hydrocarbon production forecasts that borrow statistical strength from production data of nearby wells to reduce uncertainty in the forecasts. The field study included collection of a 1.5-year time-series of wellhead fluid samples immediately following the first gas production from two hydraulically fractured wells. The noble gas compositions and isotopes of the samples suggest a strong signature of atmospheric contribution to the noble gases that mix with deep, old reservoir fluids. Complex mixing and transport of fracturing and reservoir fluids occurs during production–knowledge of which may be useful to help understand and improve production. Access to actively producing wells was important to demonstrate actual characterization with noble gases of a non-theoretical site. Real-time laboratory measurements were performed on triaxially deforming shale samples–core samples from the same shale field site–to link deformation behavior, transport, and gas tracer signatures. The statistical methods used Bayesian techniques to investigate production data reported for horizontal Barnett gas wells in Texas. Three different examples were used to show the approach. Production forecasting was performed for 197 wells with the Arps and Duong models; six nearby wells were used to demonstrate the process of borrowing statistical strength to better characterize model uncertainty. Predictions of estimated ultimate recovery were also made, considering the uncertainty associated with the fit between the model and reported data. The Bayesian methods allow for better forecasts with less production data.

Significance:

This project benefits DOE's energy security and environmental protection missions. Shale hydrocarbon reservoirs play an increasingly key role in providing clean and reasonably priced domestic energy. Our project developed techniques for fluid flow characterization in shale with data that can be collected at wellheads. Evaluation of shale hydraulic fracture and flow systems may result in more cost-effective production from shale. Environmental protection may be simultaneously achieved with the ability to identify hydraulic fracture designs that minimize impacts to underground sources of drinking water.

Refereed Communications:

K.L. Kuhlman, B. Malama, and J.E. Heath, "Multiporosity Flow in Fractured Low-Permeability Rocks," *Water Resources Research*, vol. 51, pp. 848-860, February 2015.

S.J. Bauer, M.Y. Lee, and W.P. Gardner, "Helium-Mass-Spectrometry-Permeameter for the Measurement of Permeability of Low Permeability Rock with Application to Triaxial Deformation Conditions," presented at the ARMA 15-376, *49th US Rock Mechanics/Geomechanics Symposium*, San Francisco, CA, 2015.

Detecting Seasonal Changes in Permafrost using In Situ Seismic Velocities, Near-Field Soil Moisture Monitoring, and Remote Sensing

171381 | Year 3 of 3 | **Principal Investigator: R. Abbott**

Project Purpose:

The Arctic is important to Earth's climate system. In 2012, Arctic sea ice retreated the furthest in recorded history, opening the Arctic to commerce, resource exploration, and national security threats. The melting of Arctic ice also increases sea surface temperatures, which then leads to increased storm severity around the globe. The melting of permafrost releases methane, which has been locked in the frozen layers, potentially causing further increases in Earth's temperature. Current climate models do not have sufficient data to predict the impact these factors will have on climate. The Arctic is not a homogeneous area in terms of precipitation, depth to permafrost, distance from the sea, etc. Therefore, data need to be collected from a variety of areas (coastal, inland, high and low precipitation, etc.). To effectively capture these data, remote sensing methods that can collect accurate data over multiple scales are needed. These methods do not currently exist. Similarly, precipitation in the Arctic is difficult to measure. Differentiating between falling snow vs. snow that is being moved by the wind is essential for accurate water balances, but difficult to achieve in practice.

This project will apply recent advances in seismic research and soil moisture monitoring to the Arctic for the first time. The data from those efforts will be coupled with remote sensing data originally collected for national security purposes to determine if remote methods can be used to accurately collect data for use in climate models. Although Sandia has performed research in each of these areas in the past, this will be the first time that we will apply them to the climate arena. Since none of these techniques have been deployed in the Arctic, there is a high level of risk for the project. Results from this effort will contribute to a DOE Office of Science goal of improved understanding of Arctic water budgets.

Summary of Accomplishments:

- The project successfully installed a seven-element seismic array at Poker Flat Research Range, Alaska. The array was designed for near-autonomous data collection and telemetry. The harsh conditions dictated engineering for cold, dark (no solar power), deep snow in winter, under water in summer, and animal (large and small) activity. Site visits confirmed six of seven stations weathered the winter seasons with no adverse effects. The seventh station suffered a power failure unrelated to harsh conditions.
- Successfully acquired and analyzed three "ground truth" datasets: one Refraction-Microtemor survey, one cross-borehole seismic survey, and multiple tile-probe surveys
- Successfully acquired and analyzed multiple satellite remote sensing data sets
- Acquired over 460 days of continuous seismic data
- Created or modified algorithms to compute horizontal-to-vertical spectral ratios (HVSR) and compute seismic ambient noise cross-correlations
- Demonstrated that active layer thickness can be determined using HVSR. The HVSR can be computed daily without costly site visits.
- Demonstrated that seasonal freezing and thawing signals can be seen in ambient noise cross correlations
- Demonstrated that remote sensing data products (such as normalized difference vegetation index and normalized difference snow index) are correlated with ambient noise and HVSR results
- Determined that satellite image segmentation techniques can identify zones with potentially similar permafrost characteristics
- Determined that the ambient noise at the recoding site is "diffuse," a requirement for accurate inversion results
- Successfully inverted HVSR data for active layer depth. Results were consistent with ground truth measurements, but suffered from a non-uniqueness problem.

- Determined that ambient noise cross-correlations, while promising, do not have the time resolution necessary during rapid freezing and thawing

Significance:
This project has shown that one can use seismometers to track seasonal signals caused by permafrost freezing and thawing. No active source is needed, as the techniques work on everyday ambient seismic noise. Commercial off the shelf equipment (digitizers, seismometers, etc.), as long as installed in proper enclosures, can survive multiple seasons with few site visits, making the technique cost-effective relative to current techniques. Satellite remote sensing was shown to be a promising adjunct method to increase the footprint of the measurements to beyond just the seismic array aperture. The results are anticipated to benefit multiple DOE missions as well as NOAA and the EPA.

Determination of Aerosol Scattering Characteristics for Atmospheric Measurements

165669 | Year 3 of 3 | **Principal Investigator: M. Arienti**

Project Purpose:
This project targets some of the uncertainties in optical remote atmospheric measurements caused by the inherently incomplete information on aerosol particles. We consider, in detail, two scenarios: 1) the scattering bias due to the preferential orientation of medium to large particles in flow with gradients and 2) the inclusion of soot in ice crystals, which form a heterogeneous aerosol having a large difference in the components' refractive indices.

Preferential orientation of non-spherical particles is a previously unexplored topic from a scattering perspective: we found a significantly different participation in radiative energy exchange depending on preferential orientation, which therefore may bias remote sensing readings. We are also addressing the mixing state of black carbon (BC) from soot with non-BC particles. As an individual particle, BC is well known to be the major contributor of positive radiative forcing (warming). However, since ice can act as a lens for BC, the role of BC-contaminated crystals is of growing interest, particularly in the Arctic region.

We are also using state-of-the-art computational tools in a numerical hybrid approach. The discrete dipole approximation (DDA) method is used to compute scattering and absorption of electromagnetic waves by discretized particles of arbitrary geometry and composition. The calculations are parametrized by crystal shape, percentage of BC inclusion, and type of BC aggregate. Because DDA applicability is limited to very small particles, calculations are repeated in the geometric optics limit (amenable to a ray-tracing approach) to identify trends common to the two size domains.

Summary of Accomplishments:
We have developed and published a four-channel polarization lidar concept for the detection of preferential orientation of atmospheric particulates. There is evidence of preferential orientation of aerosols depending on their size and the local turbulence intensity. We have developed an optimum optical configuration for linear and circular polarized incident laser beams based on considerations of data inversion stability and propagation of measurement uncertainties: the accuracy (theoretical) in the retrieval of backscatter cross-sections and depolarization ratios is similar to conventional two-channel configurations, but the bias due to particulate preferential orientation can be detected and corrected.

After modifying a ray-tracing algorithm for modeling the optical properties of composite particles of arbitrary shape, the study of the optical properties of ice crystals grown on soot was expanded with backscatter measurements from the Cloud and Aerosol Spectrometer with Polarization. The measurements, taken in the ice nucleation chamber at Texas A&M University, were used to validate the predictions of the computer codes used in this project. The data set and numerical calibration procedure that was developed are a first for this type of composite particle, by accounting for the shape variability of the particles, a satisfactory qualitative agreement of calculations with measurements was found.

An extensive parametric study over a broad variety of crystal shapes recovered the well known "lens effect," which magnifies the soot absorption cross-section even in very small volume percentages. The study also found that this effect is over-estimated by internal mixing models that use the refractive index of a homogenized sphere. This is an important finding, since this type of internal mixing model is often used in climate prediction codes to calculate the radiative budget of the atmosphere.

Significance:
This project's results contributed to a better understanding of the effects of cloud turbulence on remote optical sensing and proposed a relatively simple optic augmentation (to four channels) of the lidar sensors deployed by Sandia. The project also studied the optical properties of soot captured in the atmosphere to form ice crystals: this element factors in the atmosphere's radiative forcing by soot and it is relevant to Sandia's remote monitoring activity of atmosphere in the Arctic region. Additionally, the results and methods are anticipated to benefit DOE's missions in nuclear and energy security, EPA mission areas, and DoD missions related to remote sensing.

Fundamental Study of Disposition and Release of Methane in a Shale Gas Reservoir

173102 | Year 2 of 3 | **Principal Investigator: Y. Wang**

Project Purpose:
The boom in shale gas production through hydrofracturing may reshape the energy production landscape in the US. However, one troubling issue related to shale gas extraction is the decline in wellbore production by up to 95% over the first three years, with a recovery rate less than 10%. Maximizing wellbore production and extending the production lifecycle are crucial to realize the energy security benefits of shale gas. This effort has been hindered by a lack of mechanistic understanding of gas disposition and release in shale gas reservoirs. Existing knowledge drawn from conventional gas-oil reservoirs is not applicable to shale formations characterized by nanometer-scale pore sizes and extremely low permeability. Gas in shale (mainly methane) exists as a compressed gaseous phase or an adsorbed phase in nanopores, with the latter accounting for up to 85% of total gas in place (GIP). We will perform an integrated experimental and modeling study to fundamentally understand two important processes that directly control GIP in a reservoir and wellbore production: methane partitioning in the nanopores of mudstone matrices and methane transport from low-permeability matrices to fractures. We will first carefully characterize pore geometry and pore-size distributions of representative shale samples. We will then measure methane sorption isotherms, desorption kinetics, and transport properties on selected shale samples, either crushed or intact, under simulated reservoir conditions, using our newly developed high temperature/high pressure (HTHP) systems and microanalysis techniques. The data will be synthesized, using novel nanogeochemistry and nanofluidics concepts and molecular dynamic simulations to establish needed constitutive relationships for predicting and optimizing shale gas wellbore production. The project will leverage Sandia's unique expertise in material science, nanogeochemistry, HTHP geochemistry, and high-performance computation capability. If successful, this work will advance research of shale gas, particularly in areas related to nanogeoscience, as well as prediction of material behaviors in extreme environments, greatly impacting DOE's energy security mission.

Imaging the Subsurface with Upgoing Muons

173101 | Year 2 of 3 | **Principal Investigator: N. Bonal**

Project Purpose:

The purpose of this project is to develop subsurface imaging using upgoing muons. Subsurface imaging of underground structures, such as tunnels and caverns, is important to DOE missions related to energy surety, nonproliferation, and border and infrastructure security. Muons are subatomic particles produced in the upper atmosphere, which penetrate the earth's crust up to few kilometers. Their absorption rate depends on the density of the materials, including fluids, through which they pass. Measurements of muon flux rate at differing directions provide density variations of the materials between the sky and detector from those directions, much like a CAT scan. Traditional muon imaging focuses on more prevalent downgoing muons, but requires below-target detectors—a major obstacle to widespread use.

Exploratory work in the project's first year demonstrated that upgoing muon fluxes appear sufficient to achieve target detection within a few months. Work in the second year demonstrated that low-density objects can be detected by muons—even when enclosed in high-density material like lead—and even small changes in density (e.g., changes due to fracturing of material) can be detected. Additionally, simulations show that muons can be used to image void space (e.g., tunnels) within rock.

Currently, muon tomography can resolve features to the sub-meter scale. However, their practical use is uncertain because dependencies among resolution, duration of acquisition, density contrast, size of the target, and distance between target and detector remain undefined. To widen the performance envelope of muon technology, these parameters are being addressed through a combination of modeling and experimental verification.

Methane Hydrate Formation on Clay Mineral Surfaces: Thermodynamic Stability and Heterogeneous Nucleation Mechanisms

165668 | Year 3 of 3 | **Principal Investigator: R. T. Cygan**

Project Purpose:

We will develop a comprehensive understanding of the heterogeneous nucleation of methane hydrates and their subsequent thermodynamic properties. This will lead to more effective methods to extract subsurface methane (natural gas) from hydrates, and better control hydrate formation associated with oil extraction (pipeline flow assurance, Gulf oil disaster). Methane hydrates, ice-like water cages surrounding methane molecules, have the potential to play a huge role in our nation's energy security. Large untapped hydrate reserves exist in seafloor and Arctic sediments. A recent US Geological Survey estimates 590 trillion cubic feet of methane hydrate—more than three times the amount of natural gas—is located on the north slope of Alaska. The ability to utilize and control hydrate reserves is currently hindered by a lack of fundamental understanding of the natural environment's impact on the stability and formation of methane hydrates, which are often found in areas of clay-rich sediments. Most studies on hydrate nucleation and thermodynamic stability have focused on homogeneous systems, whereas heterogeneous systems are found in nature and in technical settings. The addition of nucleating mineral surfaces will impact the outcome of any study performed, and will advance this field towards an improved knowledge base furthering our ability to utilize hydrate-based fuel resources.

Heterogeneous nucleation and thermodynamic stability of methane hydrates is an understudied phenomenon despite its critical energy security importance. Cutting-edge simulation methods using Sandia's supercomputers are required to address this challenge. Strategic experiments will both validate and inform the simulations. The outcome of this project is a foundational and comprehensive molecular and macroscopic understanding of heterogeneous hydrates, supporting DOE's energy security mission.

Summary of Accomplishments:

Heterogeneous nucleation of methane hydrates was examined using molecular simulation, experimental bulk synthesis, and scanning-probe microscopy. Theoretical nucleation rates were determined, using molecular dynamics simulations as a function of clay surface, represented by hydrophobic and hydrophilic systems. Surface effects were quantified by monitoring cage formation and induction time for nucleation events, as a function of distance from the surfaces. We have completed ten independent simulations for each system in this study, representing sixty 1 μs-long simulations. Various water potentials were evaluated using clay mineral-water simulations to compare water structure and water diffusion behavior at the interface.

Controlled syntheses of methane hydrates were performed at 265-285K and 6.89 MPa to examine the impact of montmorillonite surfaces in clay-ice mixtures to nucleate and form methane hydrate. Results suggest that the hydrophilic and methane-adsorbing properties of Na-montmorillonite reduce the nucleation period of methane hydrate formation in pure ice systems. X-ray diffraction and Raman spectroscopy confirm the nucleation and growth of the synthesized hydrates. Methane hydrates were also synthesized in a Raman spectroscopic cell that maintains the required pressure and temperature for methane hydrate stability throughout the synthesis and Raman analysis. This capability is crucial for characterizing temperature- and pressure-sensitive hydrates in situ. Raman spectra collected confirm the presence of methane hydrates. A time-series scan, while warming the cell, evaluated the melting of remnant ice in the cell, followed by methane hydrate decomposition, demonstrating the sensitivity of the instrument and utility of this cell. Various kinetic pathways were explored to produce methane or isobutene clathrates in an ultra-high vacuum apparatus at very low temperatures. But, scanning probe microscopy indicates the formation of only ice.

Significance:

Development of the foundational science underlying methane hydrate formation and stability directly impacts DOE's energy security mission. Researchers and engineers in the field can leverage this information to design methods, catalysts, and inhibitors to more effectively, economically, and safely extract methane as a cleaner fuel source alternative to crude oil. Knowledge of methane hydrate stability impacts flow assurance in the extraction of oil resources, particularly in the Gulf of Mexico, and understanding hydrate behavior is important for the safety of oil production facilities, which tragically played out in the Macondo disaster in April 2010.

Refereed Communications:

K. Thürmer, C.Yuan, G.A. Kimmel, B.D. Kay, and R.S. Smith, "Weak Interactions between Water and Clathrate-Forming Gases at Low Pressures," *Surface Science*, vol. 641, pp. 216-223, November 2015.

Monitoring, Understanding, and Predicting the Growth of Methane Emissions in the Arctic

173100 | Year 2 of 3 | **Principal Investigator: H. A. Michelsen**

Project Purpose:

Concern over Arctic methane (CH) emissions has increased following recent discoveries of poorly understood sources and predictions that methane emissions from known sources will grow as Arctic temperatures increase. Methane has a 25-fold higher global warming potential than carbon monoxide (CO) and is believed to cause ~50% of the net radiative forcing of CO. The calculated capacity of the warming Arctic to produce methane is enormous, and the warming effect of CH could surpass that of CO. Methane sources predicted to increase include: thawing terrestrial permafrost, shallow oceanic methane hydrates, and submerged permafrost. Recent studies revealed an unexplained methane source associated with cracks in sea ice and a potentially important open ocean source. A few incomplete datasets are available to study. Arctic methane emissions, and new efforts, are required to detect increases and explain sources without being confounded by the multiple sources. Methods for distinguishing different sources are critical. We plan to conduct measurements of atmospheric methane and source tracers and couple these measurements with global atmospheric modeling and back-trajectory analysis to identify, characterize, and assess the climate impact of Arctic methane sources. The unique data and analysis will address a timely and high profile scientific question. Understanding Arctic methane sources will help inform decisions related to human activity (such as oil and gas exploration) at high latitudes.

We will address uncertainties in Arctic methane sources and their potential impact on climate. We will characterize methane sources using high-resolution atmospheric chemical transport models and tracer measurements and will model the Arctic climate using the state-of-the-art high-resolution Sandia's Spectral Element Community Atmosphere Model. We propose leveraging the Sandia-managed atmospheric research station in Barrow, Alaska to deploy newly developed trace gas analyzers. This project incorporates inherent risk associated with the uncertainties in the novel use of tracers and the complexity of inversions on multiple tracers in the Arctic. The results are expected to benefit DOE energy and environmental missions, as well as government agencies such as NOAA and the EPA.

Polyfunctional Desorption of Oil from Shales

171069 | Year 3 of 3 | **Principal Investigator: P. V. Brady**

Project Purpose:

The objective of the project is to develop a first principles-based approach to predicting oil adhesion to shales.

The S&T challenge is to understand the specific molecular adhesion mechanisms that control oil movement in hydrofracked shales. Specifically, we need to identify the oil and solid surface groups that control adhesion, and work out exactly how they respond to changes in fluid chemistry.

The key technical challenge is developing a mechanistic model linking electrostatic attraction and oil wettability. This has not been done before because: 1) the industry had a poor understanding of oil and mineral surface chemistry, 2) industry has instead focused on measurements that give non-unique solutions and are plagued with artifacts—contact angle measurements and corefloods, and 3) corefloods/contact angle measurements on low permeability, high surface area shales are particularly difficult to perform/interpret. Also, corefloods conflate physical and chemical processes, obscuring both.

We expect to get around the existing problems by developing the first-ever measurement technique that unambiguously quantifies the chemical controls over adhesion, allowing us to then isolate the contribution of physical processes. If successful, it will allow us to design hydrofracking fluids that produce more oil from shales.

Summary of Accomplishments:

We developed a new way to measure oil adhesion and calibrated it against field cores from the middle Bakken. We then used these measurements to test and refine a new model of wettability in tight sandstones. In parallel, we designed a thermochemical analysis of fluid-mineral equilibrium in tight formations, allowing us to predict pH and salinity evolution during hydrofracking. Combining the wettability model and the thermochemical analysis allowed us to refine a method for altering frack fluid compositions to recover more oil from tight formations.

Significance:

If our field test(s) succeed and we are able to commercialize the process, we should be able to substantially increase the booked reserves of US oil companies that are fracking shales. This will advance US energy security. It should also open up a whole new science of shale oil geochemistry and put the US squarely in the lead this new research area.

Refereed Communications:

P.V. Brady, N.R. Morrow, A. Fogden, V. Deniz, and N. Loahardjo, "Electrostatics and the Low Salinity Effect in Sandstone Reservoirs," *Energy & Fuels*, vol. 29, pp. 666-677, February 2015.

Predicting the Occurrence of Mixed Mode Failure Associated with Hydraulic Fracturing

173662 | Year 2 of 2 | **Principal Investigator: S. J. Bauer**

Project Purpose:

The objectives of this study are to 1) understand the nature of the extension to shear fracture transition in fine-grained unconventional reservoir rocks and (2) develop a universal failure criterion that is scalable by easily measured rock properties such as tensile strength, uniaxial compressive strength, porosity, grain size, and composition. Using these properties and the in situ reservoir stress state, the failure criterion can be combined with fracture mechanics to predict the mode of off-crack failure, fracture orientation, and small-scale damage likely to occur during hydraulic fracturing.

In the project's second year, seven water-saturated triaxial extension experiments were conducted on four sedimentary rocks, making use of Sandia's unique high-pressure geomechanics laboratory. This experimental condition was hypothesized as more representative of downhole hydrofracture than previously existing research, and thus it may improve our understanding of the phenomena. In all tests, the pore pressure was 10 MPa and confining pressure was adjusted to achieve tensile and transitional failure mode conditions. Using previous work in this project for comparison, the law of effective stress is demonstrated in extension using this sample geometry. In three of the four lithologies, no apparent chemo-mechanical effect of water is apparent, and in the fourth lithology test, results indicate some chemo-mechanical effect of water.

Development of multi-physics models validated by sophisticated experiments and observations presented a significant technical challenge; the complexity and integration of this approach to develop a universal failure criteria provides the framework for this effort is used in the development of a physics-based understanding/assessment of the rock failure process. The integrated experiment/observation/analysis approach lays the foundation for improved understandings of the flow and transport in rock response to stimulation, leading to increased resource production and recovery. The work is in collaboration with Texas A&M University.

Summary of Accomplishments:

The stress-strain behavior and observations of deformed wet and dry Berea Sandstone indicate similar material response (strength and ductility) and fracture characteristics; no chemical effect of water is evident at these test conditions, and in this highly porous and permeable rock, the effective stress principle appears to work.

The stress-strain behavior and observations of deformed wet and dry Carrara Marble indicate the wet rock to be stronger than the dry rock, and for the wet rock to experience more strain at failure than the dry rock. Here, in water-saturated extension conditions, we demonstrated experimental evidence of "dilatancy hardening." The water in the cracks and pores was unable to flow fast enough during the imposed deformation rate to maintain an effective confining pressure as outwardly monitored. Rather, as cracks were forming, the absence of a uniform pore pressure resulted in a strengthening of the rock. This again supports documentation of the effective stress principal, but in a negative way.

The stress-strain behavior and observations of deformed wet and dry Indiana Limestone indicate very similar material response (strength and ductility) and fracture characteristics; no chemical effect of water is evident at these test conditions, and in this highly porous and permeable rock, the effective stress principle is again clearly demonstrated.

The stress-strain behavior and observations of deformed wet and dry Kansas Chalk indicate very different material response (strength and ductility) and deformation/fracture characteristics. There is the potential for chemical of water at these test conditions, and in this highly porous and low permeability rock, the effective stress principle may come into play. The isopropanol test–being most likened to the dry test in terms of strength, ductility, and fracture characteristics–indicates that the water wet test results may be chemo-water impacted. The few wet tests on this rock beg for more testing of this lithology.

Significance:

This study documents test results upon water-saturated counterparts of a dry suite of tests in extension. The experimental suite used advanced instrumentation and experimental methods, wherein a specific sample geometry was used to measure the material behavior of a suite of lithologies in extension. The lithologies chosen were representative of rock strengths of differing strengths and ductility. The work provides rock-property characterization at in situ conditions, demonstrating ways to manipulate material response. The work provides insight to in situ permeability modification through fracture initiation. Finally, this study provides a glimpse of the impact of pore-water and pore pressure upon rock behavior in extension.

Self-Tuning Seismic Sensor Data Processing

180882 | Year 1 of 2 | **Principal Investigator: T. J. Draelos**

Project Purpose:

Data from seismic sensor networks are automatically processed to detect a variety of sources such as underground explosions, volcanic eruptions, induced microfractures, road usage, footsteps, etc. The quality of automatic detection depends on a large number of data processing parameters that interact in complex ways. Researchers routinely perform studies to determine the optimal parameters. This largely manual process is painstaking and does not guarantee that the resulting controls are the optimal configuration settings. Yet, achieving superior automatic detection of seismic events is closely related to these parameters.

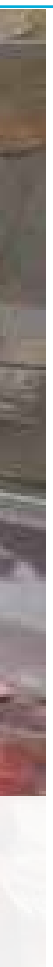
We propose automated data processing parameter tuning by representing the problem as an optimal control problem and solving it with machine learning (ML). We propose to develop automated sensor tuning (AST) software that learns near-optimal parameter settings for each event type, using neuro-dynamic programming (reinforcement learning) trained with historic data. AST learns to test the raw signal against all event settings and automatically self-tune to an emerging event in real time. The overall goal is to reduce the number of missed legitimate events and the number of false event detections. Reducing false alarms early in the seismic pipeline processing will have a significant impact on this goal. Applicable both for existing sensor performance boosting and new sensor deployment, the completed project will provide an important new method to automatically tune complex remote sensing systems. Systems tuned in this way will achieve better performance than is currently possible by manual tuning, and with much less time and effort devoted to the tuning process.

This project addresses the difficult problem of seismic sensor deployment. The innovative solution to sensor self-tuning, posed as an optimal control problem, will extend current state of the art in both seismology and ML. The project will have a fundamental impact on remote sensing and event detection with a wide-reaching impact for many national security remote sensing applications, including seismic, space, and imaging.

Materials Science

R&D sponsored by the Materials Science Investment Area strives to discover new phenomena, to create new classes of materials with novel synthesis techniques and processing approaches, and to understand and control materials' structures and properties. The goal is to foster a bold, vibrant, ground breaking, materials science base of world-renown, which serves as the foundation for developing the critical and differentiating technical capabilities that will be needed in the future to support our national security missions.

Projects



Additive Manufacturing: Predicting the Performance and Reliability of Laser Engineered Materials

180901 | Year 1 of 3 | **Principal Investigator: J. D. Sugar**

Project Purpose:

The purpose of this project is to understand the relationship between the thermal history of an additively manufactured component and its shape, microstructure, and properties. Our approach is to use thermal imaging cameras during additive manufacturing (AM) builds to make in situ temperature measurements that can then be used in multiphysics models to predict the final properties of a part. AM processes are fundamentally different than conventional subtractive manufacturing techniques because both the material fabrication and the final shaping process happen simultaneously. Conventional subtractive manufacturing begins with a billet of material of known properties and then removes material to obtain the appropriate shape. Because the near-net shaping processes associated with AM rely on rapid solidification and large thermal gradients, AM parts are inherently non-uniform in microstructure and properties and also contain residual stresses that cause undesired variations in final dimensions. Our hypothesis is that the thermal history, measured at each point in a part during manufacturing, and the resultant microstructural and property variations are highly correlated; knowledge of one is predictive of the other. Thus, the thermal history measurements and their associated variations with AM processing parameters provide the necessary information needed to predict performance and optimize processing parameters for the design and function of any AM-fabricated part. We are using: 1) diagnostic sensors that measure the thermal history during manufacturing, 2) analytic microscopy and mechanical testing to characterize microstructure and properties, and 3) finite element to mesoscale modeling to predict the evolution of properties, residual stress, and microstructure during AM processing. Our ultimate goal is to deliver multiphysics process models that can be used to optimize processing parameters and thermal history of AM parts for their intended function. This study provides the first steps towards a fundamental understanding of the immediate and long-term performance of AM parts, which is required for their use in high consequence environments.

Compliant Nanoepitaxy: The Next Materials Revolution

180899 | Year 1 of 3 | **Principal Investigator: S. R. Lee**

Project Purpose:

Sandia's pioneering contributions to lattice-mismatched semiconductor materials have seeded a ~40-year-long technology revolution in strained-layer-heteroepitaxial devices–devices that now underpin optoelectronics-based telecommunication technology, strained-Si-based microprocessors, and light emitting diode-based solid state lighting (SSL). While these achievements might suggest that the zenith of strained-layer-materials R&D has passed, the cover-article of the February 2014 MRS Bulletin asserts exactly the opposite: the confluence of elastic-strain engineering and nanotechnology places us instead at the beginning of a new era where nanostructured manipulation of strain in 3D will yield revolutionary new materials solutions. However, emerging research in this area often focuses on rapid application to devices, and not the fundamental materials science understanding needed to fulfill this concept. We seek to fill this knowledge gap via in-depth experimental and theoretical studies of compliant nanoepitaxy, focusing on nanostructure shape, composition, strain, and defect content. The model system proposed for study comprises In(x) Ga(1-x)N alloys grown on nanopatterned GaN. While these alloys promise efficient light emission and absorption spanning all visible wavelengths, high-energy-efficiency materials operating at green wavelengths and longer remain outside the reach of planar epitaxy because of extreme lattice-mismatch strains on GaN substrates (dl/l=2.1-9.8% for x=0.2-1.0). Compliancy-based control of strain enabled by nanoepitaxy could unleash the full energy-efficiency promise of these alloys by raising indium compositions in the alloys while simultaneously eliminating materials defects. Project success would advance our knowledge of nano-enabled strain engineering, thereby creating innovative materials for applications in power electronics, photovoltaics, SSL, and beyond. The proposed compliant-nanoepitaxy research is very low-technology-readiness work not addressed in existing advanced-device development or systems-development programs elsewhere at Sandia. The research is particularly well suited to Sandia because of its reliance on diverse scientific expertise and facilities (Mesa-Fab, Mesa-Labs, and Redsky) rarely available within a single institution. The proposed work will accelerate discovery in the emergent field of compliant nanoepitaxy.

Creating a Novel Silicon Substrate for the MOCVD Growth of Low Defect GaN

168763 | Year 3 of 3 | **Principal Investigator: A. A. Allerman**

Project Purpose:

Conventional c-plane wurtzite gallium nitride (GaN) light emitting diodes (LEDs) suffer from many problems, including wavelength shift, poor efficiencies at long wavelengths, and efficiency droop. Strong piezoelectric polarization leads to poor carrier overlap and, thus, low recombination rates. To counter this effect, narrow quantum wells (QWs) and high carrier concentrations are required. These together are also thought to cause enhanced non-radiative Auger recombination, which could explain performance droop. One solution is to grow along the non-polar m- or a-axes of wurtzite. However, for decent quality, such orientations require rare and expensive bulk GaN. Instead, we opt to develop GaN in its non-polar cubic phase. We use micropatterned conventional Si (001) substrates to grow cubic GaN by metalorganic vapor phase epitaxy. The bandgap of cubic GaN being less than wurtzite should allow for longer wavelengths with less indium. We have successfully grown and fabricated a first set of cubic LEDs using wurtzite device structures. In the absence of polarization, we propose to develop wide, single QW LED structures. To characterize the LED, we will remove the opaque Si substrate and device-fabricate using a flip-chip method we developed for this purpose. Ray trace modeling of the structures suggests increased light extraction efficiency. We have evidence that higher indium incorporation will be possible in such structures also, and we will employ it to achieve longer wavelength LEDs in the yellow and red. To monitor progress towards dislocation avoidance at long wavelengths, we will characterize stress and strain evolution of the microstructured system.

Theoretically, cubic GaN should be an ideal material for LEDs, but little has been verified experimentally. It is our goal to test the theory in the methods described above. This will vet cubic GaN as a viable alternative for non-polar GaN LEDs.

Summary of Accomplishments:

GaN and gallium indium nitride (GaInN) has successfully been grown by metal organic vapor phase epitaxy (MOVPE) on micropatterned Si, including stripes with up to 1 μm width with reduced size of parasitic polycrystalline GaN grains. Cubic GaN with wide GaInN (3, 6, 9, 12, 15, 30 nm) single quantum well (SQW) structures have successfully been grown and peak wavelengths via photoluminescence (PL) of 520 to 570 nm have been achieved.

Cathodoluminescent (CL) studies show that the cubic GaInN contributes the highest intensity emission and dominates the PL signal. Furthermore, we compare photoluminescence intensity at 77 K and 296 K to arrive at an upper limit of the internal quantum efficiency (IQE) that we estimate to be 50%. The high IQE combined with mode confinement within the stripe motivate the use of cubic GaInN micro stripes for lasers diode structures. CL also shows that the cubic GaInN emits, on average, at wavelengths 26 nm longer than wurtzite (1-101) and 40 nm longer than polycrystalline GaInN grown under the same conditions. Associating peak PL and CL wavelengths with bandgap energy and applying bowing parameter theory and experiments from literature we estimate the InN fraction in our cubic GaInN to between 0.00 and 0.48. Cubic LED fabrication has proceeded with a thin-film flip-chip model and green, wavelength stable electroluminescence has been recorded.

X-ray diffraction (XRD) studies revealed that the cubic GaN is under asymmetric biaxial tensile stress due to the growth confinement within the 1D stripe geometry. The cubic cell is strained nearly 30 times more in the direction of the grooves than across the grooves. This strain is thought to cause polarized light emission from the GaInN SQW by strain induced valance band splitting. A polarization ratio between 0.2 and 0.4 has been measured for the cubic GaInN emission.

Significance:
The cubic phase of GaInN grown on micropatterned Si (001) offers the ability to integrate LEDs, lasers, or power electronics on the same wafer as silicon complementary metal oxide semiconductor technology. Asymmetric biaxial strain causes a break in degeneracy within the valance band that should result in lower inversion thresholds for the achievement of stimulated emission in a laser diode. This break in degeneracy combined with high IQE, long wavelength emission, and easy cleaving of the stripes to form mirror facets make cubic GaInN microstripes an optimal platform for laser development. Such lasers could offer full spectrum illumination with high frequency switching capabilities.

An inexpensive, easily processed Si substrate for GaN LEDs would allow solid state lighting to compete with incandescent lighting. For the Department of Defense, LED lighting would reduce the weight carried by personnel as well as their vehicles. This work may benefit DOE energy security and DoD national security missions.

Engineered Reliability via Intrinsic Thermomechanical Stability of Nanocrystalline Alloys

180900 | Year 1 of 3 | **Principal Investigator: B. Clark**

Project Purpose:
Nanocrystalline metals have demonstrated clear advantages in strength, wear resistance, and fatigue tolerance over commercially available structural alloys. However, existing nanostructured alloys remain impractical for mission critical applications primarily due to their propensity to undergo rapid microstructural evolution upon application of thermal or mechanical load (even at room temperature). This microstructural evolution renders them unreliable and precludes fabrication in bulk forms.

We have identified a novel approach to alloy design that renders certain binary alloys intrinsically stable, resulting in a new class of alloys inherently impervious to abnormal thermal environments, large cyclic thermal stresses, and loss of wear-resistance in electrical-tribological components. Recently, several groups have proposed models for stabilization of binary nanocrystalline alloys, and they have independently confirmed profound thermal stability: nanocrystalline grain size is maintained after weeks at 1100 °C (Massachusetts Institute of Technology, W-Ti), or after hours at 97% of melting (Army Research Lab, Cu-Ta)! In the MIT model, grain boundary stabilization via segregation of immiscible solute creates a localized thermodynamic equilibrium that eliminates the driving force for grain growth. While there are important energetic distinctions between the different models for stabilization, they all disregard the destabilizing role of mechanical loading. The remaining scientific mystery to be unraveled is the interplay between mechanical stress/strain and grain boundary motion in the context of a segregation-stabilized nanocrystalline alloy. We propose to establish this link, initially focusing on alloys for electrical contacts (applicable to many components of interest). Such permanently stable alloys are broadly transformative, potentially addressing problems from transportation lightweighting to power electronics.

MATERIALS SCIENCE

Engineering Bioelectronic Signal Transduction using the Bacterial Type III Secretion Apparatus

173670 | Year 2 of 3 | **Principal Investigator: D. Y. Sasaki**

Project Purpose:

Engineering efficient methods for living systems to transfer electrical energy to non-living systems, at relevant size scales, continues to challenge our knowledge of materials and biology. Our goal is to enable signal transduction between cells and inorganic materials, using controlled electron transport as the energy transfer mechanism. We envision using the cell as a living battery, providing a set of environmental signals to trigger synthetic biological networks that divert intracellular electron transport pathways to inorganic extracellular structures. Conversely, changing electron influxes could guide cellular responses. It is challenging, however, to precisely engineer nanostructured materials to achieve controllable catalytic or electronic properties and connect them with biological energy sources. Our approach to this problem is to engineer protein scaffolds, taking advantage of the native recognition, selectivity and self-assembly properties of these nanoscale building blocks as well as their native intracellular localization patterns. We are using a type III secretion system (T3SS) needle protein from Salmonella enterica, PrgI, as a template for metal nanowire synthesis for biosensing and bioenergy applications. Our strategy is transformative as there are few examples of devices that interface live cells with micro/nanocircuitry to extend the native functionality of biological systems. The work is in collaboration with University of California-Berkeley.

We seek to develop the groundwork for directly interfacing living cells with microsystems as potential areas of interest for external agencies (e.g., DTRA, EPA, BES). Successful research could revolutionize the integration and electrical connectivity of biological tissue with synthetic materials, directly impacting Sandia research missions in biodefense and remote surveillance.

Harnessing Multiscale Periodicity of 2D-Crystals for Flexible Adaptable Broadband Optics

173124 | Year 2 of 3 | **Principal Investigator: T. E. Beechem, III**

Project Purpose:

The library of isolated 2D crystals grows daily. Beyond graphene, atomically thin nitrides, oxides, and transition metal dichalcogenides (e.g., MoS_2), along with many others are now available and routinely stacked to create hybrid 2D-solids. Importantly, when 2D crystals are combined, properties change. The mobility of graphene, for instance, is greatly improved when overlaid on hexagonal boron nitride (hBN). Similarly, arbitrarily stacked graphene transforms from a broadband to bandpass optical absorber. Such changes occur because of interactions between atomic layers. These interactions take place over a new, larger scale (100s of Å), periodicity manifested by the moiré superlattice that evolves between the layers. Combined with the intrinsic atomic periodicity (~1Å), a moiré potential hybridizes the electronic bandstructure of the entire system. Leveraging the interlayer interactions and the resulting multiscale periodicity provides, therefore, a means to create new 2D solids having tailored and engineered properties. Realizing this possibility, however, rests on fundamental understanding linking interlayer interactions, the interplay of differing length scales of periodicity, and the original properties of each 2D crystal. We pursue this fundamental understanding to develop new optical materials impacting a broad spectral range that exhibit operational adaptability and mechanical flexibility. Specifically, while understood theoretically and demonstrated experimentally, the interplay of 2D-solids, interlayer interactions and multiscale periodicity, has neither been examined systematically nor leveraged purposely. This is our objective. Specifically, we seek to demonstrate new interlayer 2D phenomena in order to highlight its potential for application.

High Fidelity Modeling of Ionic Conduction in Solids

173121 | Year 2 of 3 | **Principal Investigator: F. P. Doty**

Project Purpose:

Our purpose is to develop a hybrid transport model to understand aging in the semiconductor, TlBr. This material is a high atomic number semiconductor, which could enable an order of magnitude improvement in photopeak sensitivity over CdZnTe gamma spectrometers if aging of the material can be mitigated.

Prior ionic conduction models for TlBr are restricted to point defect diffusion in perfect crystals, and fail to predict observed macroscopic changes under electric fields (aging). This work is the first to consider field-driven migration mechanisms, interaction of mobile charged defects with extended defect networks, and the evolution of these networks causing permanent changes in structure and properties.

The approach combines high fidelity interatomic potentials with an electrostatic force model derived from density functional theory (DFT). Ion transport and structure evolution will be directly studied with molecular dynamics (MD) simulations using a novel variable charge model that captures the electric field induced forces on atoms. Innovative, enabling concepts include: 1) dedicated models to independently treat interatomic potential and variable charge effects both simplifies the method and improves accuracy, 2) use of electrostatic forces, rather than charges, solves the problem in previous models that atomic charges are ill-defined in DFT due to distributed electron density, and 3) our novel analytical variable charge model significantly improves calculation efficiency over literature numerical variable charge models.

This project develops tools to understand aging of ionic conductors. Prior work focused on atomic-scale defect diffusion, and addressed neither ion drift, nor interactions with large-scale disorder, which can evolve and cause permanent changes in material properties. The new approach will enable realistic understanding of transport and aging, and will be applicable to a range of important systems.

Improved Mechanical Performance and Reliability of Radical-Cured Thermosets

180902 | Year 1 of 2 | **Principal Investigator: E. M. Redline**

Project Purpose:

This research uses a novel approach to improve mechanical and fracture properties of chain-polymerized thermosets by increasing network homogeneity. Typically, enhancement of mechanical/fracture properties of these materials is achieved using additive particles. However, recent research suggests that this particular class of thermosets is less receptive to additive toughening because of a poorly developed network structure–a result of the crosslinking chemistry. Thus, we propose by improving network homogeneity, we can improve mechanical and fracture performance of the neat materials and also those toughened using traditional additive strategies.

Controlled radical polymerization (CRP) has been demonstrated to reduce heterogeneity in chain-polymerized thermosets and will also be utilized in this research. However, the amount of heterogeneity has not yet been quantified and the degree to which this parameter contributes to desired mechanical and fracture properties are unknown. We will take a two-pronged approach to this problem by experimentally measuring network homogeneity as well as glass transition temperature, elastic modulus, fracture toughness, and crack speed in filled and unfilled materials. Models will be correlated to the measured properties and used as guidance to create materials where enhanced mechanical stability and reliability are important. Further, the success of this project will allow UV-curable thermosets to be used in place of thermally cured/post-cured epoxies, thereby eliminating problems from thermal expansion mismatch. UV-curable systems could also facilitate manufacturing/production ease and reduction in cure time, opening these thermosets to new applications and existing needs in nuclear weapons, coatings, encapsulants, potting materials, and/or underfills.

We propose to develop tough, reliable, radical-cured coatings/encapsulants that do not require long-time or elevated temperature curing/post-curing. This project will create novel materials based on fundamental polymer science. The relationship between network heterogeneity and fracture properties is poorly understood; the combined experimental and computational work proposed herein can be leveraged to foams and polymer degradation.

In Situ Study of Surface-Mediated Explosive Degradation using Surface-Enhanced IR-Vis Sum Frequency Generation

173118 | Year 2 of 3 | **Principal Investigator: D. Farrow**

Project Purpose:

Degradation of explosives at the bridgewire/explosive interface, where the bridgewire initiates detonation by plasma induced shock, is known to change component performance. It has been observed that losses of <1% of total material in a bridgewire detonator can change function time and substantially reduce component lifetime. Two proposed mechanisms are: 1) low levels of ionizing radiation generate free electrons in the bridgewire that cleave a N-O bond in the explosive at the bridgewire interface and 2) chemical reactions at the metal interface (e.g., corrosion) bringing reactive species in contact with the explosive. Furthermore, products of explosive degradation may also corrode the bridgewire. No tool currently exists for in situ identification of short-lived intermediates at a buried interface. Current methods are only sensitive to bulk material (Raman), cannot access the organic/metal interface (mass spectroscopy), or cannot detect species in low concentration (IR-Vis) sum-frequency generation (SFG).

We will build a novel platform to directly observe low concentrations of reactive species at buried organic/metal interface for the first time. We will improve on the state of the art by: 1) using heterodyne SFG to increase detection sensitivity, 2) using the nanostructure/film interface as a model for the explosive/bridgewire interface, and 3) exposing it to reactive stimuli and then probing surface mediated reactions in situ. If successful, we will make the first direct observation of reactive intermediates driving ionization and corrosion-mediated aging at the explosive/bridgewire interface.

This project will create a novel capability for in situ characterization of organic material aging within a few monolayers of a metal interface to identify intermediate species with life times of a few picoseconds at room temperature. If successful, we would be one of a handful of groups worldwide using this technique to explore the surface chemistry of energetics.

Ion-Conduction Mechanisms in NaSICON-Type Membranes for Energy Storage and Utilization

165694 | Year 3 of 3 | **Principal Investigator: A. H. McDaniel**

Project Purpose:

Next-generation metal ion-conducting membranes are key to developing technologies like batteries, fuel cells, and even technologies for remediating radioactive waste. Metal-air batteries will enable grid-scale electrical energy storage, and thus facilitate the integration of renewable sources into the US energy infrastructure. NaSICON-type materials (sodium super ionic conductor) are a class of compounds with $AM_1M_2(PO_4)_3$ stoichiometry where the choice of "A" and "M" cation varies widely. This work is focused on Al and Si derivatives of $NaZr_2P_3O_{12}$. Other than stoichiometry, the defining feature of NaSICON is a 3D crystallographic framework containing interconnected channels within which mobile ions are transported. Progress in the design of NaSICON with optimal ion mobility and chemical stability is currently mired by heuristic approaches that probe the enormous array of possible material compositions available to NaSICON. A comprehensive molecular-level picture of the factors that influence ion conduction is missing.

The objective of this project is to analyze transport chemistry using a combination of operando studies of structure, composition, and bonding, combined with first principles theory and modeling, to develop an atomistic understanding of mechanisms that give rise to and influence ionic conductivity. Synchrotron-based x-ray diagnostics will probe the electronic structure of well-controlled, model NaSICON films while in operation (i.e., conducting Na ions under an applied field). First principles theory and modeling will be used to interpret the experimental observations and enhance understanding of atomistic processes. This combination of novel experimental methodology and theory is innovative and represents a holistic approach to understanding ion conduction in NaSICON.

Summary of Accomplishments:

The objective of this project was to analyze transport chemistry in NaSICON materials using in situ, synchrotron-based x-ray diagnostics and density functional theory (DFT). We devised a method for synthesizing NaSICON thin films using chemical solutions. Depending on the stoichiometry and annealing temperature, various film textures, ion conductivities, and phase impurities were obtained. In general, Na+ ion conductivity in the Al- and Si-substituted variants of $NaZr_2P_3O_{12}$ (NZP) was much higher than the baseline material.

We deployed an experimental platform for x-ray Raman measurements at Stanford Synchrotron Radiation Lightsource (SSRL) and a custom fluorescence yield detector at the Advanced Light Source (ALS). We tested the feasibility of using hard x-ray Raman spectroscopy to overcome spectral interference from molecular O_2 and H_2O, we collected in situ soft X-ray absorption spectroscopy (XAS) on O and Na atoms for $NaZr_2P_3O_{12}$, $Na_{1.25}Al_{0.25}Zr_{1.75}P_3O_{12}$, and $Na_{1.5}Zr_2Si_{0.5}P_{2.5}O_{12}$ thin films under partial pressures of O_2 and H_2O at elevated temperature. We tested the efficacy of using transmission electron microscopy high resolution electron energy loss spectroscopy (TEM HREELS) to supplement the information provided by XAS, and ultimately discovered that Al and Si substitution into NZP has a significant effect on the local bonding environment for Na and O atoms in the lattice.

We applied DFT to interpret the experimental observations and provide a critical link to atomistic processes that underpin and influence ion transport. Electronic structure models for our NaSICONs were derived from alloying and relaxing known structures. We formulated a methodology for applying a parameter-free, *ab initio* physics code for predicting XAS in heterogeneous systems and used this to validate DFT models. We found agreement between DFT and experiment for Na+ conduction energetics (i.e., activation energies), and that the diffusion barrier is very sensitive to lattice constant and ion channel size. Given this, we now have the ability to theoretically formulate appropriately chosen substitutional defects that could considerably increase ion conductivity in NaSICON.

Significance:

The development of highly functional, high-performance materials having novel properties that enable efficient energy storage, energy utilization, or sustainable manufacturing directly supports DOE missions to transform energy technologies by 2020. Specifically, improved sodium air batteries that are scaled appropriately for grid-level storage can facilitate the expansion of renewable power generation. NaSICON can also be used to develop technologies for recovering metal ions from low activity waste. DOE's science mission was enhanced by the close coupling of theory to novel enhanced diagnostics, as well as supporting research directed toward discovering new materials using laboratory facilities such as the synchrotron centers.

LEEM-PEEM Studies of Localization Mechanisms in InGaN-Based Heterostructures

165692 | Year 3 of 3 | **Principal Investigator: T. Ohta**

Project Purpose:

Scientific insight is crucial for improving the efficiency of optoelectronic devices that target energy mission needs. An example is InGaN light-emitting diodes (LEDs) for energy efficient solid state lighting (SSL). A key fundamental question is: why do blue emitting InGaN alloys have high radiative efficiency despite having threading dislocation (TD) densities that quench light emission in traditional semiconductors? It is hypothesized that structural and compositional inhomogeneities localize carriers away from crystalline defects, but the nature and degree of localization, its correlation with defects, and its dependence on composition are controversial. The nanoscale properties that influence carrier localization may also contribute to long-standing (~15 year) roadblocks to high-efficiency SSL, including the "green-yellow gap" in LED efficiency (where the efficiency of InGaN degrades at longer wavelengths) and the "efficiency drop" observed for InGaN LEDs operated at high currents. To circumvent these roadblocks, we propose the implementation of spectroscopic low-energy electron microscopy–photoemission electron microscopy (LEEM-PEEM) on test device structures as a new approach to reveal key structure-property relationships vital for understanding the carrier localization mechanisms impacting efficiencies.

We will use spectroscopic LEEM-PEEM to probe the surface potential, occupied electron density of states (DOS), and alloy composition of InGaN alloys with micro- to nano-meter spatial resolution. Combined with controlled growth studies, time-resolved optical spectroscopy, and detailed modeling of as-grown surface morphology/composition, these studies will enable unprecedented insight into the connection between microscopic/nanoscale materials properties and efficiency limitations of InGaN LEDs. An elusive correlation among defect density, structural and compositional inhomogeneities, and carrier localization is a long-lasting fundamental question.

Summary of Accomplishments:

We examined the surface electronic structure and its local variation in the vicinity of TDs in InGaN multi-quantum wells capped with a thin GaN layer using low energy and photoemission electron microscopy in our approach to understanding the high radiative efficiency in blue emitting InGaN heterostructures.

Significance:

Our goal was to discover fundamental relationships between submicron/nanoscale structure and optoelectronic properties in InGaN. The insights and advanced capabilities gained from this project would enable multiple national security and energy security technologies that employ III-nitride materials. We demonstrated the use of LEEM-PEEM in a non-traditional approach for understanding energy mission related materials and devices. We anticipate that this approach has further adaptability for improving the understanding of photovoltaic device efficiency limitations.

Microsensor Arrays for Energy Efficiency, Emission Monitoring and Explosives Detection

180835 | Year 1 of 2 | **Principal Investigator: F. H. Garzon**

Project Purpose:

The purpose of this project is to develop ceramic electrochemical multi-sensors, integrated on a chip, which will sense gases such as carbon monoxide, hydrocarbons, sulfur dioxide, and nitric oxide emissions. These gases are emissions that result from the combustion of hydrocarbon fuels and are regulated by the US EPA and other international regulatory organizations with more stringent standards being enforced in the 2017 Europe and EPA Tier III regulations. Dynamic measurement of emissions is essential feedback for optimizing combustion efficiency while minimizing emissions. Cost-effective control and monitoring of these species requires new sensing technologies as traditional spectroscopic and/or chromagraphic methods are expensive, and are often unsuitable for continuous unattended operation. The aforementioned molecules are also decomposition products of most explosives and provide unique signatures for their identification. The solid state electrochemical devices generate a signal that is proportional to the concentration of the gas species. Unlike liquid electrolyte based sensors, they exhibit excellent stability and solid electrolyte sensors can operate at elevated temperatures (400-800 °C), thus making them excellent candidates for in situ applications. The multi-sensor arrays detection principle is based on differential electrocatalysis and will produce a voltage signal proportional to concentration. The devices will measure combustion emission gases and the decomposition products of the pyrolysis of nanoparticles and molecules of explosives. The development of these devices will require significant cross disciplinary expertise in electrochemistry and materials science, the lithography of mixed conducting oxides and solid electrolytes, and the successful design of robust microsensor arrays.

Molecule@MOF: A New Class of Optoelectronic Materials

180898 | Year 1 of 3 | **Principal Investigator: A. A. Talin**

Project Purpose:

The principal purpose of this project is to determine the factors controlling charge and energy transport in a new class of hybrid organic-inorganic materials called metal-organic frameworks (MOFs) and how can they be manipulated to create materials with unique and/or record performance. Achieving this goal will enable future generations of mission-specific conducting MOF materials to be developed. New insights into the broader problem of conductivity in organics will also be gained, which lacks scientific consensus. Synthetically tunable optoelectronic materials are a long-standing, but elusive, technological goal. Inorganic semiconductors have outstanding properties, but limited synthetic flexibility; organic polymers offer chemical tunability and low-cost fabrication, but have poor mobility and long-term stability. In this project we are probing the fundamental mechanisms of charge and energy transport in MOFs, as well as exploring applications such as room temperature thermoelectrics, that can take advantage of the unique properties of these novel materials.

Multi-Resolution Characterization and Prediction of Environmentally Assisted Intergranular Fracture

173116 | Year 2 of 3 | **Principal Investigator: R. A. Karnesky**

Project Purpose:

The purpose of the project is to create a multiscale/multi-physics model in order to predict environmentally assisted intergranular fracture.

Material fracture in the US costs over $119 billion annually. Environmental influences such as hydrogen, irradiation, and high temperatures render ductile alloys susceptible to brittle fracture. Unexpected component failures lead to unacceptable consequences such as the release of hazardous chemicals. These failures impact gas transfer systems, hydrogen for transportation, and nuclear power generation and waste storage.

At present, however, most procedures for managing materials in harsh environments rely on extensive experimental databases in the form of empirical crack growth equations and are implemented into structural analysis codes. These procedures cannot be reliable without thorough experimental data because of complex interactions of environmental influences with deformation mechanisms and microstructure. Our validated computational capability will move us beyond the empiricism of current methods.

Our framework couples simulations and unique experimental techniques at multiple length scales. Applying this coupling to a thoroughly understood material, the resulting model can predict transient fracture resistance. Deliverables open new core capabilities needed by Sandia and the DOE for interpreting effects of environmental variables and their interactions with microstructure.

Our grain-level model, validated by mechanical tests, is based on the Material Point Method, and integrates features from kinetic Monte Carlo and phase-field coupled with crystal plasticity. It is informed by atomistic models and experiments. Modeled grain boundary chemistry and cohesion will be validated by transmission electron microscopy (TEM) and atom-probe tomography. Active mechanisms observed during in situ TEM will be compared to molecular dynamics. This coupled approach is needed for predictive capabilities.

There is no successful predictive fracture model and additional basic science is needed to achieve this. Further, we leverage a well-understood face-centered metal rather than the complex materials engineers are using now. When successful on this model system, engineering groups will extend our results to tackle other alloys.

Multiscale Modeling of SMA Materials

166636 | Year 3 of 3 | **Principal Investigator: T. E. Buchheit**

Project Purpose:

Shape memory alloys (SMAs) have the unique ability to recover a remembered shape via a temperature induced phase transformation. This phase transformation in this class of materials can be exploited in different ways to produce several unique and useful behaviors. To pursue research of mutual interest to both Texas A&M and Sandia, we propose to focus on two areas for SMA investigations: 1) a general purpose SMA constitutive model development and implementation into Sandia's Sierra/Solid Mechanics finite element code framework and 2) investigation of nano- and microscale phenomena and hybrid SMA composites currently under investigation at Texas A&M. The constitutive model development at Sandia addresses short-term needs regarding development and use of wide hysteresis Ni-Ti-Nb SMA and longer-term needs regarding development of high temperature SMAs. The hybrid SMA–MAX phase ceramic (e.g., Ti_2AlC, Ti_3SiC_2) composite will be used as an example material system for the nano- and microscale phenomena portion of the project conducted primarily at Texas A&M University. The focus of the two-part research effort addresses the broader objective of developing a framework applicable range of high-performance material systems whose deformation behavior is governed by complex micromechanical mechanisms. Such tools are needed to address both current and future engineering problems facing both institutions.

Aside from the Ni-Ti-Nb locking ring application, SMAs are still under development for national security applications. Fundamental research, particularly on the high temperature version of these alloys, is still required before devices using these materials can be developed.

Summary of Accomplishments:

Accomplishments through this effort have been made in two key areas: constitutive modeling and composite micromechanics. First, with regard to constitutive efforts, SMA models have been successfully added to the Sierra/SM LAME materials library. The developed implementations have been verified through different test problems and used to analyze various experiments and structures of interest to Sandia. Secondly, a MAX phase constitutive model has been developed capable of capturing three distinct mechanisms: recoverable kinking, irrecoverable deformations and damage associated with permanent kink band formation, and plastic slip in non-aligned grains. Such a coupled formulation is the first model capable of describing all of the observed characteristics of the macroscopic response. This theoretical model was implemented in a 3D subroutine using an implicit return mapping approach considering the coupling between the multiple yield surfaces associated with each mechanism. The developed model was used to analyze recent experimental results. Predictions of these experiments showed good agreement. Importantly, by considering the contribution of different mechanisms, it was demonstrated that both the permanent kinking and plastic slip mechanisms were needed to produce open hysteric first cycles experimentally observed.

In addition to the constitutive efforts, the micromechanics of inelastic SMA-based composites have also been studied. Two approaches were undertaken–analytical investigations using mean-field micromechanical approaches and simulation of realistic microstructures. These two tracks were used in conjunction to consider the effect of different inelastic mechanisms (and combinations thereof) on the effective response. Special attention was paid to identifying changes in the thermal cycling behavior and the interaction of recoverable and irrecoverable mechanisms in developing residual stresses in the composite. The impact of different microstructural features and inelastic properties were considered. In the case of SMA-MAX phase composites, it was shown that the permanent deformations of the latter dominated the effect of the recoverable.

Significance:
First, the implemented SMA model has been used to support the analysis of various Sandia engineering parts. Continued development of those models provides a unique capability for subsequent efforts. The formulation and implementation of the MAX phase model represents a new capability both at Sandia and in the broader scientific community. Efforts toward understanding the theoretical and numerical coupling aid the development of other models. Finally, the composite studies have studied the interactions of multiple complex constituents and sought ways to develop structure-property correlations for this and other novel multiphase inelastic materials and composites.

Successful development of modeling tools through this work will allow for new material systems (specifically systems utilizing SMAs) to be designed and optimized to meet the needs of various challenging engineering and materials reliability problems.

Refereed Communications:
B.T. Lester, T. Baxevanis, Y. Chemisky, and D.C. Lagoudas, "Review and Perspectives: Shape Memory Alloy Composite," *Acta Mechanica*, vol. 226, pp. 3907-3960, 2015.

Novel Cathode Materials for Large-Scale Electrical Energy Storage

177964 | Year 2 of 3 | **Principal Investigator: D. F. Sava Gallis**

Project Purpose:

The purpose of the project is to develop novel materials for large-scale electrical energy storage. Alternative approaches are needed to address the limitations of state-of-the-art materials, which have modest cycle life and efficiency (lead acid batteries), low charging rates and efficiency (Na-S, Na-metal halide), and prohibitive costs (Li-ion batteries). In order to attain both fast cycling and enhanced storage capabilities, we are focused on implementing metal-organic frameworks (MOFs), a class of materials virtually unexplored in the large-scale energy storage arena. MOFs are inherently highly porous, and therefore, fast ion insertion and removal during cycling can be achieved. Additionally, multi-electron transfer is possible due to the hybrid inorganic-organic nature of these materials. Since both the metal and organic ligand can be redox-active, this can lead to higher energy storage per gram of material. Emphasis is placed on establishing: 1) a methodology to successfully fabricate MOFs-based coin cells batteries capable to run over hundreds of cycles and 2) the structure-function relationship in these systems through the fundamental understanding of the mechanism for ion insertion/extraction, correlated with the electrochemical performance. This project is uniquely designed to be successful via a multidisciplinary approach of materials synthesis and characterization and battery design and testing expertise.

Phonon Scattering at Mobile Ferroelastic Domain Walls: Toward Voltage Tunable Thermal Conductivity

173117 | Year 2 of 3 | **Principal Investigator: J. Ihlefeld**

Project Purpose:

The challenge addressed in this project is an ability to actively modify thermal conductivity in a solid state material over a broad temperature range using non-mechanical stimuli, which has been an elusive technological goal. If successful, this will enable active and low-power thermal emission and heat control. To date, altering thermal conductivity in a material at non-cryogenic temperatures has only been achieved by applying a mechanical strain, by traversing a narrow phase transition, or by changing the physical dimensions of the material itself. The solution proposed in this project is to develop a means to achieve voltage tuning of thermal conductivity by harnessing mobile coherent interfaces (domain walls) in ferroelectric materials to scatter heat-carrying phonons. By adjusting domain wall spacing to be smaller than the phonon mean free path through preparing thin films, phonon-domain wall scattering becomes the dominant mechanism leading to manipulation of thermal conductivity. Electric fields can alter the configuration and density of these interfaces and will result in tuning of thermal conductivity. We will study $Pb(Zr,Ti)O_3$ thin films where domain wall type and density can be deterministically controlled. We will develop the underlying science and technology of this approach for tuning thermal conductivity by understanding the fundamental variables controlling phonon scattering at domain boundaries, which are poorly understood–and not at all understood at non-cryogenic temperatures. Utilizing empirical results and phase field modeling, the necessary understanding to harness this effect will enable the first-ever demonstration of field-tunable thermal conductivity at non-cryogenic temperatures.

Demonstration of altering thermal conductivity at room temperature in a non-moving solid state material has not previously been accomplished. To be exploited for applications, this phenomenon of variables controlling phonon scattering at domain boundaries must be demonstrated and understood.

Predicting Growth of Graphene Nanostructures using High-Fidelity Atomistic Simulations

165698 | Year 3 of 3 | **Principal Investigator: N. C. Bartelt**

Project Purpose:

Graphene continues to attract widespread attention due to its outstanding electronic and optical properties for next-generation electronics. In future applications, device functionality critically depends on producing graphene nanomaterials with high quality and uniformity (with few or no defects). Inserting these novel electronic materials into real world devices requires discovering improved understanding to better control growth. Among the numerous methods for graphene synthesis, chemical vapor deposition (CVD) growth on transition metal substrates stands out for producing large-area films amenable to commercial applications. In particular, large-area graphene growth on copper (Cu) foils (the most commonly used substrate) shows the greatest promise because low solubility of carbon in Cu inherently favors single-layer graphene growth. However, despite its potential, the detailed mechanisms or conditions for controlled graphene growth are unknown or very poorly characterized, often leading to a wide variety of nanostructures. Specifically, how graphene grows on different Cu facets, what controls its in-plane orientation, and how intrinsic Cu defects affect nucleation and defect formation remain inadequately understood. Indeed, even how graphene is aligned, in terms of its crystallography, with Cu itself remains an open question. Consequently, it is extremely difficult to design experimental procedures that will lead to reproducible, controlled growth of optimal nanostructures. A theoretical understanding of the detailed mechanisms of graphene growth is needed to help tailor the experimental conditions to generate high-quality graphene nanostructures. The aims of this project are to: 1) develop a paradigm-changing computational capability for predicting the growth of graphene nanostructures on a metallic substrate, 2) validate the capability through comparison to experimental observations of graphene growth on Cu, 3) use this predictive tool to understand the fundamental mechanistic processes and conditions (temperature, pressure, deposition rate, and substrate orientation) that govern high-quality growth, and 4) perform a proof-of-concept demonstration to down select a subset of candidate growth experiments for graphene nanostructures to be carried out under specific conditions.

Summary of Accomplishments:

To enable the creation of higher quality graphene for novel electronics applications, we have developed a molecular dynamics (MD) simulation tool that can predict graphene growth quality on metal surfaces. We have performed extensive molecular dynamics of graphene growth from deposited carbon atoms and have validated our understanding by comparing our predictions to experiments of graphene growth on Ir, Cu and Ge.

Previous experimental work has established that graphene growth does not occur by the simple attachment of single carbon atoms. Instead it involves a complex series of events that involve as many as five atoms. To use MD simulations to probe this process, we needed to develop empirical potentials that can be evaluated with little computational effort, but describe both the carbon-carbon bonding and the carbon-substrate bonding. We used the bond order potential formalism to do this. We used density functional theory (DFT), to calibrate the potential. Its validity was verified by successfully performing simulations of graphitic- and diamond-like carbon. Combined with previously determined potentials for substrate interactions, this enables the simulations of growth we have performed.

The interaction of graphene with a substrate, because of its inherent 2D nature, is quite weak–determined mostly van der Waals (vdW) interactions. A crucial question in modeling vdW epitaxy and predicting graphene quality is whether this interaction is strong enough to allow epitaxy to occur. To answer this question, we performed experiments to determine graphene energies on Ir as a function of in-plane graphene orientations. We find these energies compare well with estimates derived from our vdW DFT calculations. Further, we developed a way of parameterizing the orientation dependence of the vdW interaction with only two easily computed parameters.

Significance:
Our quantitative description of how graphene grows will allow a faster and more systematic approach to choosing optimal substrates for graphene growth. Ongoing applications of our simulation technique to other 2D electronic materials will also help determine how these materials grow. This comprehensive modeling capability will facilitate novel devices for future defense and nuclear weapons needs.

Refereed Communications:

X.W. Zhou, D.K. Ward, and M.E. Foster, "An Analytical Bond-Order Potential for Carbon," *Journal of Computational Chemistry*, vol. 36, pp. 1719-1735, September 2015.

P.C. Rogge, K. Thuermer, M.E. Foster, K.F. McCarty, O.D. Dubon, and N.C. Bartelt, "Real-Time Observation of Epitaxial Graphene Domain Reorientation," *Nature Communications*, vol. 6, Article 6880, April 2015.

P.C. Rogge, S. Nie, K.F. McCarty, N.C. Bartelt, and O.D. Dubon, "Orientation-Dependent Growth Mechanism of Graphene Islands on Ir(111)," *Nanoletters*, vol. 15, pp. 170-175, 2015.

P.C. Rogge, J. Wofford, K.F. McCarty, N.C. Bartelt and O.D. Dubon, "On the Rotational Alignment of Graphene Domains Grown on Ge(110) and Ge(111)," *MRS Communications*, vol. 5, pp. 539-546, September 2015.

Predicting the Multiscale, Mechanical Response of Additively Manufactured Materials across a Wide Spectrum of Loading Conditions

178667 | Year 2 of 3 | **Principal Investigator: D. P. Adams**

Project Purpose:

Developing a fundamental understanding of a material's mechanical behavior has traditionally relied on time-consuming and costly experimental characterization; however, as microstructures and interfaces become more exotic due to advanced design and novel fabrication techniques (e.g., additive manufacturing), assuring performance will come to rely on strong coupling between experiments and modeling of material behaviors. Predictive modeling must now incorporate the detailed microstructural 'elements' present in a starting material. Furthermore, modeling must be able to predict mechanical properties for a wide range of loading conditions in order to assure that novel microstructures will have acceptable responses.

Toward this end, we will build a framework to model deformation of inhomogeneous, anisotropic alloys. Building from Sandia's crystal-plasticity models and fed by experimental evaluations, grain-scale behavior will be determined and then coupled to larger-scale models predicting structural response to a range of strain rates. This problem could not be addressed previously, because the requirements were computationally taxing and cost prohibitive.

This project will: 1) develop a new understanding of whether homogenization and multiscale theory can predict the dynamic mechanical behaviors of additively-manufactured materials and 2) elucidate how their complex microstructures give rise to mechanistic transitions between quasi-static and inertial strain rates, possibly through stress-wave-amplified dislocation movement and shock-induced, adiabatic shear banding.

Programmable Nanocomposite Membranes for Ion-Based Electrical Energy Storage

165696 | Year 3 of 3 | **Principal Investigator: E. D. Spoerke**

Project Purpose:

Controlled transport and storage of ions are central to the effective operation of modern electrical energy storage (EES). High volume, rate-limited ion intercalation in batteries yields high energy density but limited power; conversely, fast ion transport restricted to electrode surfaces facilitates high power densities with reduced capacity in ultracapacitors. Mating high energy density and high power density will require innovative new strategies for ion transport and storage. We present a new approach to ion-based EES, inspired by organisms such as the electric eel, which generate large voltages and currents using energy-dissipative ion pumps and gated ion-selective channels to manipulate large ion concentration gradients across biological membranes. We propose to translate the scientific concepts behind this scheme to a synthetic system utilizing ion pumps and programmable ion channels in engineered materials to control the transport, accumulation, and dissipation of ions for EES. Until now, mimicking this multifunctional, bio-inspired materials system has vexed researchers unable to assemble the necessary advanced tools and expertise in nanomaterials chemistry, biointegration, and electrochemistry. Combining our expertise in these areas with advanced characterization and computation, we aim to create and understand materials to programmably regulate ion concentration gradients. Our studies will focus on the cooperation of a "pump membrane," comprising light-powered ion pumps (bacteriorhodopsin), with a nanoporous "gate membrane," functionalized with novel programmable ion gating chemistries, to explore controlled ion transport in this bio-inspired synthetic system. Insights gained will facilitate improvements in existing technologies (e.g., battery separators, water treatment) and enable development of novel bio-inspired energy storage.

This work involves the development of a new type of bio-inspired electrical energy storage, a project balancing high technical risk of an unknown system with the potential for significant technical impact of a new type of electrical energy storage.

Summary of Accomplishments:

This project advanced several fronts towards understanding and learning to control transmembrane ion transport in biomimetic, synthetic systems. In the context of active ion transport, we successfully grew and harvested the biological ion pump bacteriorhodopsin (BR) and demonstrated its integration into synthetic lipid and polymer-based membranes. We further showed that, powered by light, these integrated biomaterials could be used to create ion concentration gradients (electrochemical potentials) in synthetic environments. Moreover, through tailored modifications in protein composition, we introduced chemical "handles" that allowed us to simultaneously attach and orient BR on synthetic nanoporous membrane surfaces, an important potential attribute for ultimate device integration. Toward effective ion gating, we first utilized computational models to better understand, from a free-energy standpoint, how the influences of critical variables such as ion hydration, ion-ligand interactions, ion/channel size ratios, and ion position in a channel can be used to predict ion reject, permeation, or blocking in functional nanopores. In addition to providing a better understanding of ion transport in natural systems, these studies also informed a number of synthetic designs. We utilized several materials chemistry approaches to show that variations in charged nanopore morphology (e.g., conical versus cylindrical nanopores) as well as changes in pore surface charge can be used to control ion rectification through synthetic membranes. Of particular note was the development of novel electrochemically programmable surface-modifying chemistries that could be used to change the charge state of a nanopore. This tunability enabled us to turn on and off rectified ion current through nanoporous membranes, another central requirement to controlling transmembrane charge transport. Collectively, these research efforts provided key insights and developed new capabilities required to regulate both active transport and controlled ion gating, both important elements needed for the ultimate development of a biomimetic ion-based energy storage system.

Significance:

These efforts provide key insights that not only inform the potential development of a new biomimetic energy technology, a clear national priority, but they also provide technical depth relating to ion-based technologies in general as well as molecular manipulation of materials. Collectively this technical growth may impact biomedical fields through improved understanding of biological function/dysfunction, advances in biomedical testing, and the development of new therapeutic materials. The ability to selectively control ion transport has considerable added potential to impact energy storage, chemical separations, information management, chemical sensing, and other applications spanning both civilian and defense-related technology space.

Refereed Communications:

E.D. Spoerke, L.J. Small, A.M. Martinez, D.R. Wheeler, V. Vandelinder, G.D. Bachand, and S. Rempe, "Electric Eels: Bizarre Natural Phenomena or Inspiration for Novel Nanocomposite Energy Storage?" presented at *Composites* at Lake Louise, Alberta, Canada, 2015.

M.I. Chaudhari, M. Soniat, and S.B. Rempe. "Octa-Coordination and the Aqueous Ba2+ Ion," *The Journal of Physical Chemistry* B, vol. 119, pp. 8746-8753, June 2015.

V.S. Vandelinder, D.R. Wheeler, L.J. Small, M.T. Brumbach, E.D. Spoerke, I.M. Henderson, and G.D. Bachand, "Simple, Benign, Aqueous-Based Amination of Polycarbonate Surfaces," *ACS Applied Materials and Interfaces*, vol. 7, pp. 5643-5649, March 2015.

L.J. Small, D.R. Wheeler, and E.D. Spoerke,"Nanoporous Membranes with Electrochemically Switchable, Chemically Stabilized Ionic Selectivity," *Nanoscale*, vol. 7, pp. 16909-16920, October 2015.

M. Soniat, D.M. Rogers, and S.B. Rempe, "Dispersion- and Exchange-Corrected Density Functional Theory for Sodium Ion Hydration," *Journal of Chemical Theory and Computation*, vol. 11, pp. 2958-2967, June 2015.

P.E. Mason, S. Ansell, G.W. Neilson, and S.B. Rempe, "Neutron Scattering Studies of the Hydration Structure of Li," The *Journal of Physical Chemistry* B, vol. 119, pp. 2003-2009, January 2015.

S.B. Rempe, "Biomimetic Membranes," presented (invited) Vogel Research Group ETH, Zurich, Switzerland, 2014.

S.B. Rempe, "Biomimetic Membranes," presented (invited) IEEE Nanotech Materials and Devices, Sicily, Italy, 2014.

Room Temperature Solid State Deposition of Ceramics

177962 | Year 2 of 3 | **Principal Investigator: P. Sarobol**

Project Purpose:

The ability to integrate ceramics with other materials is limited by high processing temperatures (>800 °C). A process to fabricate ceramic films at room temperature (RT) in solid state, aerosol deposition (AD) has been demonstrated in literature. High velocity ceramic particles impact on substrates, deform, and form films under vacuum. AD eliminates high processing temperatures, enables materials integration, where ceramics are deposited on metals, plastics, and glass at RT. AD films are reported to have excellent properties, equivalent to or exceeding conventional pressed/sintered ceramics. Future impacts on Sandia's mission include improved ceramic integration, miniaturized magnetic circulators in radar applications, conformal capacitors, thin batteries, glass-to-metal seals, and transparent electronics.

The fundamental mechanisms for ceramic particle deformation and bonding in AD are not understood and are needed to advance this technology. This project will leverage Sandia's existing experimental equipment and simulations capabilities to establish processing mechanisms and knowledge of the microstructure properties relationship needed for future technological maturation. Thus far, we have established that AD involves a balance between particle size, particle plastic deformation, particle velocity (impact energy), and traversing. In FY 2016, particle-particle bonding mechanisms will be determined and ceramic integration with other materials will be demonstrated.

Scanning Ultrafast Electron Microscopy for Charge Carrier Lifetime Imaging with High Spatial Resolution

173119 | Year 2 of 3 | **Principal Investigator: J. R. Michael**

Project Purpose:

There are many applications of materials that rely on modifications of the electrical properties of small regions to obtain useful properties. For example, modern integrated circuits are dependent upon the small size, down to 22 nm, and low dopant concentrations of active regions to achieve the needed performance levels. It is important to visualize the modified regions and to determine the local concentration of impurities to understand device performance and failure modes. Currently, this is not possible. Scanning electron microscopy (SEM) and low energy electron microscopy (LEEM) are limited to 100 nm about 10 times worse than the new and innovative scanning ultrafast electron microscope (SUEM) dedicated to materials science proposed in this work.

The purpose of this work is to develop, build, and use an innovative new SUEM dedicated to probe active regions of semiconductor devices to determine the carrier lifetimes and infer the doping concentrations. SUEM will allow ultrashort time resolved imaging through the use of an electron beam that is pulsed in synchronicity with a laser beam used to excite the sample. Thus, dynamic processes can be imaged with high spatial resolution (1 nm) and high temporal resolutions (ps to fs). This SUEM will, for the first time, be used to answer important questions about impurity (dopant distributions) and charge in semiconductor devices providing semiconductor design and performance information that was previously impossible to obtain.

A high degree of risk accompanies this work due to the unknowns of laser interactions with semiconducting materials and the resulting electronic excitations and secondary electron imaging. Success will produce a system that can probe the electronic properties of materials at short length scales for analysis of semiconductor structures.

Science-Based Design of Stable Quantum Dots for Energy-Efficient Lighting

165697 | Year 3 of 3 | **Principal Investigator: J. E. Martin**

Project Purpose:

Fluorescent and solid state lighting rely on rare earths (yttrium, europium, terbium, and cerium) for which shortages are expected. We propose to replace these rare earths with photoluminescent quantum dots (QDs). To meet the extreme demands of lighting requires that QDs have greatly improved photo and thermal stability. Increased stability can be achieved by coating the QDs with suitable shell materials, but these lead to stresses that generate defects both at the heterojunction and within the lattice. Such defects serve as non-radiative recombination centers that greatly reduce the quantum yield. To design QDs that have both high stability and quantum yield, we propose to use alloying of both the cores and the shells. Continuum calculations show that alloying will greatly reduce the strains that lead to defect formation. We will use atomistic modeling to predict those graded compositions that have the highest stability to defect formation. Defect formation will be identified through photophysical characterization and with Sandia's unique Z-contrast aberration-corrected scanning electron transmission microscope (AC-STEM).

Summary of Accomplishments:

We have developed a fundamental atomistic modeling capability, based on Stillinger-Weber and Bond-Order potentials we developed for the entire II-VI class of compounds. These pseudo-potentials have enabled us to conduct large-scale atomistic simulations that have led to the computation of phase diagrams of II-VI QDs. These phase diagrams demonstrate that at elevated temperatures the zinc blende phase of CdTe with CdSe grown on it epitaxially becomes thermodynamically unstable due to alloying. This is accompanied by a loss of hole confinement and a severe drop in the quantum yield (QY) and emission lifetime, which is confirmed experimentally for the zinc blende core/shell QDs prepared at low temperatures. These QDs have QYs as high as 95%, which makes them very attractive for lighting. Finally, to address strain relaxation in these materials, we have developed a continuum model for misfit dislocation formation that we have validated through atomistic simulations.

Significance:

We have demonstrated that Wurtzite core/shell QDs synthesized by conventional high temperature reactions have shells that are subject to surface reconstruction, creating hole traps that enable dark exciton recombination and thus reduce the photoluminescence (PL) quantum yield (QY). We have synthesized zinc blende core/shell QDs at low temperatures that are metastable to surface reconstruction and thus have exceedingly high QYs, as high as 95%, even for thick shells. These QDs are good candidates for red downconverters in solid state lighting. The availability of rare earth-free luminescent materials that meet the requirements of fluorescent and solid state lighting would greatly reduce our dependence on four of the most critical materials in DOE's Critical Materials report (yttrium, europium, terbium, and cerium). The quantum dots that we propose to develop are currently the best alternative to rare earth lighting phosphors.

Refereed Communications:

F. van Swol, X.W. Zhou, S.R. Challa, and J.E. Martin, "Thermodynamic Properties of Model CdTe/CdSe Mixtures," *Molecular Simulation*, vol. 42, pp. 14-24, February 2015.

X.W. Zhou, M.E. Foster, F. B. van Swol, J.E. Martin, and B.M. Wong, "Analytical Bond-Order Potential for the Cd-Te-Se Ternary System," *The Journal of Physical Chemistry* C, vol. 118, pp. 20661-20679, August 2014.

K.E. Gong, J.E. Martin, L.E. Shea-Rohwer, P. Lu, and D.F. Kelley, "Radiative Lifetimes of Zincblende CdSe/CdS Quantum Dots," *The Journal of Physical Chemistry* C, vol. 119, pp. 2231-2238, January 2015.

F. van Swol, X.W. Zhou, S.R. Challa, and J.E. Martin, "Heterojunctions of Model CdTe/CdSe Mixtures," *Modelling and Simulation of Materials Science and Engineering*, vol. 23, p. 035007, March 2015.

The Development of a Novel AlGaN Defect Detection, Localization, and Analysis Methodology

176400 | Year 2 of 2 | **Principal Investigator: M. A. Miller**

Project Purpose:

This project develops an approach to characterize material defects in wide bandgap AlGaN-based devices by coupling laser-based failure analysis techniques with deep-level optical spectroscopy (DLOS). Understanding the source and effects of active defects is crucial to understanding mechanisms that limit device lifetime, efficiency, and reliability. AlGaN has great potential in light-emitting diodes, laser diodes, and high electron mobility transistors. Improvements in efficiency and reliability would benefit applications in biosensing, secure local communications, high frequency power amplifiers for radar, and high voltage switching for power electronics. AlGaN-based device performance is limited by lack of commercially available lattice-matched substrates, resulting in devices with high crystalline defect densities or threading dislocations. Often, one device is comprised of multiple AlGaN compositions and doping densities yielding poor p-type doping efficiency, spatial non-uniformities and non-radiative point defects as additional materials challenges. Information from conventional defect characterization techniques can be both difficult to collect and interpret due to poor spatial or depth resolution, threading dislocation densities, the wide-bandgap itself, or limited access to the active region. We will develop a new defect characterization methodology for AlGaN-based devices comprised of laser-based localization techniques and DLOS. This approach will localize electrically active defects in AlGaN-based devices and provide information on deep level defect states associated with those defects. If successful, the approach will become a comprehensive tool for defect characterization of III-nitride material systems. The developed methodology will bolster in-house AlGaN material system optimization and provide leverage for future industrial collaborations.

We are developing a fundamental science understanding of the defects that directly impact device efficiency/reliability as well as developing an approach that combines deep level optical spectroscopy and laser-based failure analysis techniques to characterize defects.

Summary of Accomplishments:

We successfully correlated laser scanning microscopy (LSM) defect signals to DLOS signatures in UV light emitting diodes (LEDs). Since LSM is primarily an extended defect localization tool and DLOS a point defect characterization tool, this goal had inherent risk. A large number of parts were necessary to obtain few parts with LSM defect signals. This altered the timeline as significant effort went into LSM analysis and fewer parts than expected were examined by DLOS.

The DLOS signature of an LED with an LSM defect signal showed strong defect density depth dependence and strong response to the Ec-2.45eV midgap state (3.3eV illumination). This nicely correlated to the clear LSM defect signal response at 532nm and in newer results at 375nm. Laser-spotted IV curves also gave direct indication that increased leakage current (prior to LED turn-on) responded strongly to the shorter wavelength lasers.

Local-illuminated differential capacitance mapping (LIDCM) was developed, a marriage of point defect depth profiling capability of DLOS in an x-y defect mapping capability of LSM. We could spatially map changes in capacitance as a function of bias (depth into the sample) and wavelength (point defect energy level). The LIDCM technique suggests that a combination of thermal and e-h pair effects contribute to the large-scale capacitance changes in UV LEDs.

Materials characterization of the UV LEDs indicated dislocation clusters at the LSM defect signal site, consistent with previous work. The dislocations stemmed from a large misaligned grain originating near the AlN/AlGaN interface. Non-ideal semiconductor junctions at the pn interface, the cluster of dislocations and the point defects that decorate them could contribute to the leakage at the center of the LSM or LIDCM defect signal. LSM and LIDCM analysis can localize macroscopic defects impacting device leakage and can characterize their electrical behavior.

Significance:

The LSM and LIDCM techniques can be applied to other wide bandgap optoelectronics, power electronics and template growth optimization. LIDCM is not yet commercially available. Defect characterization will suggest subsequent processing modifications for targeted defect reduction, leading to increased lifetimes and efficiencies. The potential for use includes solid state lighting (DOE), biosensing (DHS), water and air purification (DOE and DHS), polymer curing, medical applications, and various nuclear weapons and defense applications.

Tunable Quantum Dot Solids: Impact of Interparticle Interactions on Bulk Properties

165700 | Year 3 of 3 | **Principal Investigator: M. B. Sinclair**

Project Purpose:

We will develop a fundamental understanding of the relationship between nanoparticle interactions and the different regimes of charge and energy transport in semiconductor quantum dot (QD) solids. QD solids comprising self-assembled semiconductor nanocrystals such as PbSe are currently under investigation for use in a wide array of applications including light emitting diodes, solar cells, field effect transistors, photodetectors, and biosensors. These unique materials exist at the crossover between isolated particles and bulk materials. They retain many of the attractive features of the isolated particles such as size-tunable bandgaps, but interparticle interactions modify their behavior and cause charge and energy delocalization. At present, the relative contributions of charge and energy transport to device performance are not understood. Device optimization requires a quantitative fundamental understanding of the means by which interparticle interactions lead to collective bulk behavior. The current state of the art in the study of interparticle effects relies on the utilization of different capping ligands to control the interparticle separation. However, the interpretation of experimental results is clouded by the large number of other variables that change as the ligand is varied. We propose to use a Sandia developed mechanical compression method, in conjunction with nanoparticle self-assembly, to fabricate QD solids with precisely controllable interparticle spacing. State-of-the-art optical probes, including ultrafast spectroscopy and non-contact photoconductivity will be used to characterize QD solid behavior spanning the range from widely separated nanoparticles to sintered nanoparticle superlattices. This approach allows for an unambiguous unraveling of the behavior of this unique class of solids.

This is research project seeks to obtain very fundamental information about the interactions between nanoparticles in quantum dot solids. It is hoped that fine-tuning of the interactions can eventually lead to enhanced properties for device applications.

Summary of Accomplishments:

We developed the capability to fabricate high quality QD solids and also developed techniques for in situ optical and structural characterization of the solids under hydrostatic pressure. Small angle and wide-angle x-ray (SAX and WAX) scattering studies as a function of pressure were performed at the synchrotron facilities at Cornell. The combination of WAX and SAX data allowed us to simultaneously determine the crystal structure and lattice constants of the QD solid as well as the crystal structure of the underlying QDs. We found that, for the CdSe system: 1) reversible control of the interparticle spacing is possible, provided the applied pressure does not exceed ~7GPa, 2) the degree of ordering of the face-centered cubic (FCC) crystal improves upon initial application of pressure to ~3GPa, 3) above a pressure of ~6GPa, the crystal structure of the CdSe dots undergoes a transition from a wurtzite to rock salt structure, and 4) above a pressure of ~ 7GPa sintering of the QDs along the out of plane direction occurs to form quantum wires (QWs) with lengths of up to ~10 microns. These quantum wires were successfully transferred to transmission electron microscopy (TEM) grids for structural measurements and for hyperspectral confocal microscopy. We also performed in situ optical spectroscopy on the QD solids as a function of pressure. Our results showed a gradual shifting of the QD absorption edge and emission maximum as the pressure is increased, and then a sudden loss of photoluminescence efficiency at ~6GPa. This loss of photoluminescence is consistent with the observed direct bandgap wurtzite to indirect bandgap rock salt lattice transformation. We also performed a first-ever in situ ultrafast optical spectroscopy on the QD solids as a function of pressure. Both our ultrafast fluorescence and ultrafast photo-induced absorption measurements showed a two-component exponential decay, with the decay constants becoming shorter with increasing pressure.

Significance:
Our work advances the science of synthesis of nanostructures. The newly developed pressure directed synthesis provides a new route for the synthesis of semiconductor quantum wires. We anticipate that with further optimization the new synthesis route could lead to highly monodisperse quantum wires that exhibit good quantum yield for fluorescence emission. Furthermore, we anticipate that the pressure directed synthesis can be adapted to other semiconductor quantum dot systems and other materials systems in general. In addition, our first-ever in situ ultrafast studies of the photodynamics of quantum dot solids under pressure will lead to new understandings of quantum dot interactions.

This project developed a fundamental new understanding of the complex interplay of charge and energy delocalization in QD solids, which could ultimately be used to design improved light emission devices, solar cells, infrared photodetectors, and low-cost field effect transistors. As such, this technology could have an impact on DOE energy missions, and national security missions including, space missions, surveillance, and nonproliferation.

Refereed Communications:
H. Fan, "Nanomaterials under Stress: A New Opportunity for Nanomaterials Synthesis and Engineering," 2015 Fred Kavli Distinguished Lecture on Nanoscience, *2015 MRS Spring Me*eting, San Francisco, CA, 2015.

Understanding and Overcoming Materials Challenges for AlN: A Scientific Foundation for Next-Generation Power Electronics

173122 | Year 2 of 3 | **Principal Investigator: A. Armstrong**

Project Purpose:
The proposed research will lay the foundation for ultra-wide bandgap (UWBG) semiconductor material science by transmuting AlN with bandgap energy (Eg) of 6.2 eV from an electrical insulator to an electrically conductive material with fully tunable conductivity type. This will enable a revolution in power electronics because the breakdown voltage (Vbr) grows rapidly with Eg. UWBG-based power switches with Vbr upwards of 100 kV becomes plausible for enabling energy technology revolutions such as DC electrical grids with greatly improved efficiency. AlN is attractive due to its large Eg and compatibility with existing semiconductor technology. However, AlN is electrically insulating and must be made conductive to function as an electronic material. Typical methods of controlling electrical conductivity for semiconductors (e.g., impurity doping and minimizing crystal defects) fail for AlN because thermodynamics drives spontaneous defect formation that completely compensates dopants. New methods must be discovered to control the electrical conductivity of AlN.

This project seeks to demonstrate controllable electrical conductivity for AlN for the first time using the strong piezoelectricity and non-centrosymmetric lattice to produce electrical conductivity without dopants. We will employ advanced defect spectroscopy to understand the physical origin and properties of defects in AlN and mitigate their impact on electrical properties. Quantum kinetic theory will be developed to assess electrical transport phenomena in AlN by treating the largely unexplored physics of carrier scattering in AlN including strong electron-phonon coupling and quantum memory effects.

We anticipate future mission needs by addressing scientific problems that will arise when AlN becomes the focus for next-generation power electronics. Making AlN a functional electronic material requires surmounting new challenges attendant with large band gap that makes otherwise simple tasks difficult (e.g., doping).

Understanding Membrane-Nanoparticle Interactions: Implications for Developing Novel Medical Therapeutics and Functional Materials

165824 | Year 3 of 3 | **Principal Investigator: C. Ting**

Project Purpose:

Membrane-nanoparticle interactions are a common motif underlying a number of important phenomena in biology, ranging from cytotoxicity to viral cell entry. Inspired by nature, membrane-nanoparticle composites are a class of functional materials comprised of nanoparticles and diblock co-polymers. The versatility of polymer chemistries offers controllable design of diverse vesicle properties and morphologies beyond the range achievable through lipids. The nanoparticles, in turn, impart novel functionalities (e.g., magnetic, optical, or fluorescence) to these materials. Thermal fluctuations are important in these systems and many interesting processes involve thermally activated (rare) events.

More generally, many soft matter systems undergo collective dynamics, which fall under the category of a rare event. We will address the difficult problem of activation in soft matter. Besides the long time scales associated with these rare events, a significant challenge arises in simulating the complex molecules, which undergo collective dynamics and exhibit emergent properties. We combine self-consistent field theory and the string method to overcome these challenges. To directly study the dynamics, we use coarse-grained molecular simulations.

While method development is ongoing, we will continue to explore a wide range of self-assembly problems in biological and synthetic soft matter systems. Molecular self-assembly is an elegant and efficient bottom-up approach to control the nanostructure of novel, functional materials. However, understanding how to design the molecular components to achieve a desired structure is not well understood for systems beyond simple molecules. Modeling and simulation are ideal tools to bridge the gap between experimental observations and theoretical understandings. In particular, modeling and simulation provide a molecular picture of the interactions that control the thermodynamics and kinetics of self-assembly, and how this relates to emergent macroscopic, collective properties of the material.

Summary of Accomplishments:

This work explores several examples of bottom-up approaches to designing functional materials. Results are used to interpret experimental observations and to make predictions to guide future experimental studies.

We have explored the directed insertion of asymmetric nanoparticles into functional polymer vesicles. Here, we have computed various transition pathways to understand how to use kinetics to control the final state of the polymer nanoparticle composites.

We have developed a theoretical understanding of experimental studies exploring the self-assembly of peptide amphiphiles into structures such as fibers, vesicles, and sheets. We have proposed a novel triblock architecture, which was later experimentally demonstrated to self-assemble into desired nanotubes.

We have simulated coarse-grained model ionomers under external electric fields to understand their structural and dynamical properties for battery applications. We are learning to correlate molecular dynamics with dielectric spectroscopy experiments.

Self-assembly of polymer-grafted nano rods is being explored for Surface Enhanced Raman Spectroscopy for single molecule sensing applications.

Significance:
Molecular self-assembly is an elegant and efficient bottom-up approach to control the nanostructure of novel, functional materials. It is a scalable and cost-efficient alternative to conventional top-down techniques such as lithography. The results from our modeling and simulation studies are ideal tools to bridge the gap between experimental observations and theoretical understandings. This work is in collaboration with experimental studies at Sandia and in academia, and provided the insights necessary for a molecular-based design of functional materials with novel properties.

The results from this Truman Fellow work will help enable the rational design of innovative medical therapeutics and functional membrane-nanoparticle composites based on an understanding of the molecular interactions. This work is relevant to the biodefense missions of DHS, and DARPA. More generally, these new methods will lead to insights into a variety of nucleation phenomena in soft matter systems, and will thus enable fundamental science beneficial to the nanoscience, soft matter, and bioscience communities, including DOE's Office of Science.

Refereed Communications:
C.L. Ting, M.J. Stevens, and A.L. Frischknecht, "Structure and Dynamics of Coarse-Grained Ionomer Melts in an External Electric Field," *Macromolecules*, vol. 48, pp. 809-818, January 2015.

C.L. Ting, B.H. Jones, A.L. Frischknecht, E.D. Spoerke, and M.J. Stevens, "Amphiphilic Triblocks to Control Assembly of Mixed or Segregated Bilayers and Monolayers," *Soft Matter*, vol. 11, pp. 6800-6807, July 2015.

Utilization of Reactive Metal Films for Self-Healing Metal Matrix Composites

173653 | Year 2 of 2 | **Principal Investigator: D. P. Adams**

Project Purpose:

Failures involving fatigue, creep, and fracture can readily occur in service if materials are designed and used inappropriately. The traditional approach to mitigate failure is to increase strength, which delays the inevitable without solving the problem. In collaboration with University of Florida, the focus of this research is to investigate techniques that can ultimately heal and repair damage through the combination of heat-emitting reactive materials and self-healing metal matrix composite technology. Specifically, this project investigates how reactive metal foils emit heat and modify neighboring materials. This approach has not been previously studied and provides the opportunity to: 1) understand and characterize the fundamental relationships between heat flow produced by the reactive foils and matrix liquidation, 2) optimize matrix melting behavior, composite properties, and exothermicity of the reactive foil, and 3) develop fabrication techniques that meld the properties of self-healing and reactive materials. The research includes development of predictive models that estimate the effects of reactive metal foil heating on neighboring materials. Model predictions of heat-affected zone dimension, microstructure, and phase are validated by experimental tests of several low melting point alloys (Sn-Zn and Sn-Bi).

Summary of Accomplishments:

Predictive models were first developed to evaluate the effects of reactive metal foils (RMF) on heating and modifying the microstructure of different, neighboring substrate materials. Initial models leveraged a 1D finite difference approximation of the heat equation in conjunction with phenomenological estimations of the physical properties of a substrate to predict heat flow and resultant heat affected zone (HAZ) depth. Experimental validation of these model predictions was conducted using four Sn-Bi alloys with different thermal properties and initial microstructures, specifically having different phase morphologies and distributions. The best agreement between the predicted and measured HAZ dimensions occurred when the variations due to foil distortion during the reaction were included in the simulation. With a second study, 2D models were developed to estimate HAZ dimensions for Sn-Zn alloys affected by heat released from adjacent reactive metal (Ni/Al) foils. The effect of the initial substrate microstructure on microstructural evolution within the heat-affected zone was evaluated experimentally and confirmed using two Sn-Zn alloys. The results of this work indicate that initial substrate microstructure can play a large role in the heat flow, and consequently, the microstructure evolution that results from adjacent RMF reactions. Therefore, initial substrate microstructure and phase should be accounted for in examinations of this approach going forward.

Significance:

This collaborative research with the University of Florida has provided key scientific insight into the potential of reactive multilayers for intrinsic material repair. Our combined model and experimental study has advanced the understanding of how heat evolved from reactive multilayers changes the microstructure in neighboring materials. This should enable new applications, such as material self-repair, while benefiting commercial joining technology that relies on a local heating approach to preserve material structure and functionality.

A method to restore the properties of damaged metal components in service through self-healing technology will advance materials reliability and allow new design paradigms. The envisioned self-healing system allows for greater autonomy, as the damaged component will no longer have to be taken out of service to repair. It is envisioned that reactive films can be placed on a damaged component and the repair can be initialized by simple ignition sources, as opposed to heat treatment. This type of new technology may make a significant contribution to the energy, environment, and security missions of DOE as well as supporting the national infrastructure.

Refereed Communications:

R.J. Hooper, D.P. Adams, D. Hirschfeld, and M.V. Manuel, "The Effect of Substrate Microstructure on the Heat-Affected Zone Size in Sn-Zn Alloys due to Adjoining Ni-Al Reactive Multilayer Foil Reaction," *Journal of Electronic Materials*, DOI: 10.1007/s11664-015-3941-z, August 2015.

R.J. Hooper, C.G. Davis, P.M. Johns, D.P. Adams, D. Hirschfeld, J.C. Nino, and M.V. Manuel, "Prediction and Characterization of Heat-Affected Zone Formation in Tin-Bismuth Alloys due to Nickel-Aluminum Multilayer Foil Reaction," *Journal of Applied Physics*, vol. 117, p. 245104, 2015.

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Nanodevices & Microsystems

The Nanodevices and Microsystems Research Foundation supports Sandia's mission by performing creative, leading edge, and high-impact R&D. This R&D strives to discover new phenomena at the nanoscale and microscale; and create or prove new concepts, devices, components, subsystems, and systems. Its objective is to foster a bold, vibrant, ground-breaking, science and technology base of world-renown as a means to developing the critical and differentiating technical capabilities that will be needed in the future to support our national security missions. The Nanodevices and Microsystems Investment Area seeks to 1) increase our understanding of physical phenomena across the nanoscale to microscale, 2) develop innovative nanoscale and microscale devices, 3) achieve new methods of integration, and 4) realize novel microsystems-based complex systems.

Projects

A New Approach to Entangling Neutral Atoms

173130 | Year 2 of 3 | **Principal Investigator: G. Biedermann**

Project Purpose:

We propose a new technique for entangling neutral atoms that will show feasibility of significant metrological gains. A successful outcome will directly impact the emerging field of "quantum sensing" and position us to lead future work. The motivation for harnessing entanglement in the context of quantum sensing is the superior scaling of sensitivity with atom number, N, when compared with classical sensing (e.g., N versus $\sqrt{N}$ respectively). While the advantage with a small number of atoms is moderate, it reaches an order of magnitude improvement with only 100 atoms. Neutral atoms are the most compelling candidates for quantum sensing with entangled systems because they have been broadly shown to make exceptional sensors. However, the fidelity of entangling two atomic qubits was previously limited to 75%, a number unsuitable for many-atom entanglement.

The most established approach to entangling neutral atoms currently uses resonant excitation to a Rydberg level, whereby atoms interact via electric dipole-dipole coupling. The limit to fidelity is thermal motion of the atoms that causes the exciting laser beams to imprint random phases on the quantum states and degrade the coherence of the entangling interaction. However, by employing adiabatic evolution induced by a laser tuned off-resonance from a high-lying Rydberg level, the coherence can be much more robust. With our new approach, we predict two-qubit entanglement with fidelities near 99%. In addition, we will explore unique entangling operations beyond two qubits that are not easily accessible in other technologies. We anticipate multi-faceted impacts in both quantum sensing and computation.

A Space-Like Low-Energy Proton Test Environment to Rapidly Qualify Advanced Microelectronics for Flight Readiness

173134 | Year 2 of 2 | **Principal Investigator: N. A. Dodds**

Project Purpose:

For the past 30 years, space programs have predicted the rate of occurrence of radiation-induced errors in microelectronics using the same general set of testing and modeling methods. These methods have broken down in the past few years because, unlike older technologies, new highly scaled (sub 100 nm) technologies are so susceptible to charged particle strikes that now even low energy protons are able to trigger errors through direct ionization. These protons are the most abundant particles in most space environments and, therefore, might dominate on-orbit error rates. New error rate prediction methods have been proposed to deal with this new mechanism, but they are impractical because implementing them can require over one year per integrated circuit (IC). To enable the reliable usage of cutting-edge ICs in space, we propose that an error rate prediction method be developed that can accurately predict the error rate in just a few hours. If successful, this work will produce a dramatically simplified rate prediction method, enabling spacecraft designers to reliably use advanced ICs.

Summary of Accomplishments:

Three publications resulted from this project. The three publications address a recently emerging reliability issue–namely, that low-energy protons (LEPs) can cause single-event effects (SEEs) in highly scaled microelectronics. In the first, novel experiments were used to prove that proton direct ionization is the dominant mechanism for LEP-induced SEEs. In the second, a simple method was developed to calculate expected on-orbit error rates for LEP effects. This simplification was enabled by creating (and characterizing) an accelerated space-like LEP environment in the laboratory. In the third publication, this new method was applied to many memory circuits from the 20-90 nm technology nodes to study the general importance of LEP effects, in terms of their contribution to the total on-orbit SEE rate. The results show that LEPs can more than double the total on-orbit SEE rate, demonstrating that LEPs are an important new reliability issue that cannot be ignored.

Significance:

Hardness assurance for low-energy proton effects is now much simpler and more accurate than it was two years ago, allowing us to better predict the reliability of highly scaled circuits in space. This empowers spacecraft designers to reliably use advanced circuits that might otherwise have been disqualified by excessive testing requirements and/or unquantifiable risks. Therefore, this research will benefit all programs that desire to use circuits from sub-90-nm technology nodes in proton rich environments. This includes satellites with high bandwidth requirements, especially telecommunication or earth-observing satellites used for reconnaissance or nonproliferation treaty verification, for example.

Refereed Communications:

N. A. Dodds et al., "The Contribution of Low-Energy Protons to the Total On-Orbit SEU Rate," to be published in *IEEE Transactions on Nuclear Science*.

N.A. Dodds, P.E. Dodd, M.R. Shaneyfelt, F.W. Sexton, M.J. Martinez, J.D. Black, P.W. Marshall, R.A. Reed, M.W. McCurdy, R.A. Weller, J.A. Pellish, K.P. Rodbell, and M.S. Gordon, "New Insights Gained on Mechanisms of Low-Energy Proton-Induced SEUs by Minimizing Energy Straggle," to be published in *IEEE Transactions on Nuclear Science*.

N.A. Dodds, J.R. Schwank, M.R. Shaneyfelt, P.E. Dodd, B.L. Doyle, M. Trinczek, E.W. Blackmore, K.P. Rodbell, M.S. Gordon, R.A. Reed, J.A. Pellish, K.A. LaBel, P.W. Marshall, S.E. Swanson, G. Vizkelethy, S. Van Deusen, F.W. Sexton, and M.J. Martinez, "Hardness Assurance for Proton Direct Ionization-Induced SEEs using a High-Energy Proton Beam," *IEEE Transactions on Nuclear Science*, vol. 61, pp. 2904–2914, December 2014.

N.A. Dodds et al., "The Contribution of Low-Energy Protons to the Total On-Orbit SEU Rate," presented at the *Nuclear and Space Radiation Effects Conference*, Boston, MA, 2015.

N.A. Dodds, P.E. Dodd, M.R. Shaneyfelt, F.W. Sexton, M.J. Martinez, J.D. Black, P.W. Marshall, R.A. Reed, M.W. McCurdy, R.A. Weller, J.A. Pellish, K.P. Rodbell, and M.S. Gordon, "New Insights Gained on Mechanisms of Low-Energy Proton-Induced SEUs by Minimizing Energy Straggle," presented at the *Nuclear and Space Radiation Effects Conference*, Boston, MA, 2015.

Active Plasmonics from the Weak to Strong Coupling Regime

165702 | Year 3 of 3 | **Principal Investigator: G. A. Keeler**

Project Purpose:

Plasmonics focuses on the manipulation of light using metallic nanostructures and promises to transform the field of optoelectronics which has traditionally relied upon light guiding in dielectrics and semiconductor-based devices. Most nanoplasmonics efforts have examined passive structures with static, geometry-defined responses. This activity seeks to demonstrate a range of active plasmonic devices based on guided surface plasmons coupled with electrically controlled compound semiconductor structures operating at near-infrared (NIR) wavelengths. We expect these active devices to fundamentally alter the photonics landscape and push the frontiers of nanoscale optics.

The primary scientific question examined in this project is how light-matter coupling changes when light is confined to the nanometer scale in the form of plasmons. Experimental tests of our theoretical understanding will be performed using test devices such as modulators and emitters that bring about various degrees of plasmon coupling with matter. Devices under investigation include plasmonic modulators and nanocavity emitters based on semiconductor quantum wells that can be forward or reverse biased to achieve gain or loss. We intend to analyze a range of these active plasmonic devices experimentally and theoretically, thereby building a comprehensive foundational capability that can sustainably impact future mission areas with new nanophotonic device concepts.

To date, there have been no demonstrations of efficient electrical modulation and amplification techniques for NIR guided plasmons using traditional semiconductor materials. Nanocavity emission represents another exciting new area of study, with significant complexity arising due to nanoscale effects. Active plasmonic devices have the potential to impact a wide range of applications. Sandia is uniquely positioned to fully explore active plasmonics technologies and rapidly resolve fundamental scientific and technological uncertainties, thereby enabling mission customers to leverage the technology through follow-on activities.

Summary of Accomplishments:

This project focused on the theoretical simulation and experimental demonstration of photonic devices using three key concepts: active plasmonic devices based on compound semiconductors, nanophotonic devices that leverage near-zero permittivity effects, and semiconductor nanocavity emitters. As an example of the accomplishments in the first thrust, we designed, fabricated, and characterized the first plasmonic modulator based on quantum well electroabsorption. The modulator operates at 1550 nm for compatibility with optical communications systems, and uses plasmonic confinement to enable a reduction in length to around 10 microns. This is about 20x smaller than conventional InP devices and should enable far greater integration density, lower power dissipation, and higher modulation rates.

Near-zero permittivity effects, sometimes combined with plasmonic confinement, allowed the demonstration of multiple compelling nanophotonic concepts. This thrust focused on using conducting ceramic materials whose carrier density is higher than typically achievable in semiconductors. Through deep subwavelength confinement, we demonstrated enhanced nonlinear optical harmonic generation in ultrathin films of indium tin oxide. We also studied ways to achieve ultracompact free-carrier absorption modulators for silicon photonics by incorporating various conducting ceramic films, developed models, and created material deposition processes for high-mobility oxides.

Nano-emitters represent the third focus area of our work. We performed extensive microscopic modeling of nanocavity lasers to understand the implications of shrinking to the nanoscale, describing the photon statistics of nanolasers in the threshold-less and few-emitter regimes. Experimentally, we studied the effects of Purcell lifetime enhancement in metallic nanocavity light-emitting diodes, demonstrated electrically pumped plasmonic amplifiers using quantum well active regions, and investigated the impact of sidewall recombination in GaAs-based nano-emitters. Results from this work collectively led to numerous papers, presentations, and intellectual property and created an enduring infrastructure for plasmonic device design, modeling, nanofabrication, and optical testing.

Significance:

The development of active plasmonic modulation, amplification, and nanoscale emission technologies through this project could enable revolutionary improvements in DOE-relevant mission areas that include high-performance computing, optical communications within data centers, high-efficiency lighting, and high-sensitivity detection and sensing. New insights on plasmon-matter interactions gained through our efforts represent a strengthened connection between fundamental science and technology innovation and will lay the groundwork for emerging applications such as millimeter-wave to optical frequency conversion, RF optical remoting, analog-to-digital conversion for signal processing, and single photon sources for quantum computing.

Refereed Communications:

T S. Luk, D. de Ceglia, G.A. Keeler, R.P. Prasankumar, M.A. Vincenti, S. Liu, M. Scalora, M.B. Sinclair, and S. Campione, "Third Harmonic Generation in Ultrathin Epsilon-Near-Zero Media," presented at *CLEO* 2015, San Jose, CA, 2015.

G.A. Keeler, et al., "Plasmonic Modulators using Quantum Well Electroabsorption," presented at *Nanometa* 2015, Seefeld, Austria, 2015.

W.W. Chow, "Nanolasers as Solution to Efficiency Droop in Solid-State Lighting," presented at *SPIE Photonics West 2015*, San Francisco, CA, 2015.

T.S. Luk, D. de Ceglia, S. Liu, G.A. Keeler, R.P. Prasankumar, M.A. Vincenti, M. Scalora, M.B. Sinclair, and S. Campione, "Enhanced Third Harmonic Generation from the Epsilon-Near-Zero Modes of Ultrathin Films," *Applied Physics Letters*, vol. 106, p. 151103, 2015.

W.W. Chow, "First Principle Study of Nanolasers: Photon Statistics and Laser Threshold," presented (invited) at *OSA Asia Communications and Photonics Conference* (ACP), Shanghai, China, 2014.

W.W. Chow and M.H. Crawford, "Analysis of Lasers as Solution to Efficiency Droop in Solid State Lighting," *Applied Physics Letters*, vol. 107, p. 141107, 2015.

W.W. Chow, F. Jahnke, and C. Gies, "Emission Properties from Nanolasers during Transition to Lasing," *Light: Science & Applications*, vol. 3, p. e201, August 2014.

Atom Traps on a Microfabricated Optical Waveguide Platform for Quantum-Limited Spin-Squeezed Magnetometry and Quantum Information Applications

180919 | Year 1 of 3 | **Principal Investigator: Y. Jau**

Project Purpose:

The purpose of the project is to develop a new neutral-atom platform that utilizes optical evanescent fields from the light transmitted in a fabricated nano-waveguide to optically trap atoms in the well-defined locations. In this way, we can avoid complex free-space alignments for optical access of atoms, and this platform can be scalable and flexible. In addition, photons traversing the waveguide are confined to a region of space comparable to the absorption cross section of an atom, naturally making a very strong photon-atom interaction, which is of fundamental importance to photon-assisted quantum controls with atoms. Furthermore, this waveguide configuration, when combined with the ability to incorporate photonic-crystal optical elements, leads to exciting opportunities, such as cavity quantum electrodynamics with record-setting atom-photon coupling and long-range atom-atom interactions mediated by photons. The ability to create complex structures on this "optical atom chip" would have important application to precision measurement (quantum sensing) and to quantum computing and communication technologies. In order to succeed in this optical atom chip, evanescent fields from the waveguide structure and the physics of near the surface atom trapping will be carefully modeled. We will carry out investigations in microfabrication to ensure that waveguide can handle required optical power and generate clean evanescent fields. For efficient atom loading, we will research in producing a constantly cooled atomic ensemble at the small-scaled waveguide location. We will also study the effect of neutral-atom adsorption on the waveguide, which may significantly modify the atom trapping potentials. Following the demonstration of trapping atoms at the waveguide and the strong photon-atom interaction, as a first high-consequence application of the optical atom chip, we plan to demonstrate spin squeezing on chip for magnetometry beyond the classical limit by incorporating additional microfabricated structures. From the new studies carried out in this project, we anticipate bringing significant impacts to the field of neutral-atom quantum controls.

Beyond Graphene: BN-Based Semiconductor Alloys for Next-Generation Optoelectronics

180920 | Year 1 of 3 | **Principal Investigator: A. A. Allerman**

Project Purpose:

Hexagonal boron nitride (hBN) has great promise for circumventing fundamental materials challenges of AlGaN alloys that limit the performance of present-day ultraviolet (UV) optoelectronics. The principal objective of this project is to discover and exploit novel optical and electronic properties of hBN-based heterostructures, enabled by a distinct, 2D, layered crystal structure, to realize a new class of UV emitters and photodetectors.

We propose to explore and exploit novel properties of hBN to enable next generation UV-LEDs and photodetectors. First, we will apply our in-depth experience in III-nitride material growth to extend beyond hBN to hB(Al,Ga)N alloys, achieving heterostructures for high-performance optoelectronic devices for the first time. Second, we will leverage our atomic-layer growth control to explore the potential for hB(Al,Ga)N heterostructures employing monolayer constituents. Analogous to graphene and van der Waals heterostructures, we anticipate devices with highly tailorable properties yet fabricated with modern semiconductor technology rather than layer-transfer methods. The fusion of 2D-crystal properties and UV semiconductors may enable covert communications, compact, robust bio-agent and neutron detectors, and other devices relevant to the nuclear weapons mission and the DoD.

Beyond Moore's Law through 3D-IC Fabrication

173129 | Year 2 of 3 | **Principal Investigator: D. B. Burckel**

Project Purpose:

The goal of the proposed research is to develop 3D integrated circuits (3D-ICs) at both the device and system levels. Today's ICs are fabricated using top down techniques on planar surfaces. Scaling areal transistor density has continued to increase IC performance, but requires increasingly expensive lithography equipment. Recently, we invented and demonstrated membrane projection lithography (MPL), a microfabrication technique where directional deposition through a suspended, patterned membrane was used to create micron-scale 3D metamaterials. By generalizing this fabrication approach to include patterned etch and patterned ion implantation, combined with blanket processes such as oxidation and planarization, we will provide a first-of-its-kind approach to 3D-IC fabrication.

Creation of 3D circuits will transform devices, systems and technologies. Regarding devices transformation, fabrication in 3D enables higher transistor packing density, new geometries for devices such as power metal-oxide-semiconductor field-effect resonators (MOSFETs), and the possibility of making radiation hardened complementary metal-oxide-semiconductor (CMOS) on non-silicon-on-substrates (SOI) substrates. At the systems level, 3D-ICs will be more difficult to reverse engineer while providing new topologies for interconnect/signal routing, improving signal integrity and RC delay. Finally, for the first time, hybrid technologies are possible with a mature 3D-IC platform, where biological cells or photons are interfaced directly to CMOS control/sensing electronics. In order to realize these benefits, we need an entirely new fabrication paradigm like the one proposed here–capable of creating complex 3D structures in a sub-micron CMOS compatible platform and addressing issues of thermal budget, device isolation, interconnect strategies, and 3D topography-induced stress.

Chemical Vapor into Liquid (CViL) Encapsulation of Microorganisms for Hazardous Agent Detection

173339 | Year 2 of 3 | **Principal Investigator: J. C. Harper**

Project Purpose:

To detect chemical and biological threats both on and off the battlefield, development of portable, robust detection systems capable of real-time identification of these threats is essential. Living cell–based sensors have proven effective as sensitive and specific detectors, capable of near real-time detection. However, living cell-based sensors require frequent replenishment with new cells due to cellular sensitivity to the ex-vivo environment. To make cell-based devices practical for implementation, cells can be encapsulated in a biocompatible matrix, which protects cells from environmental stresses, maintains biological sensing functions, and allows cellular interaction with the external environment. Silica materials are promising for use as encapsulation matrices, with advantages including biological inertness, mechanical stability, simple room temperature processing, and tunable material and chemical properties. However, traditional, aqueous sol-gel routes are cytotoxic to cells, limiting their use for cell-based biosensing.

To generate stable biosensing components, living cells need to be encapsulated in matrices that allow cellular interaction with molecules of interest, while maintaining cell viability. The purpose of this project is the encapsulation and stabilization of genetically engineered S. cerevisiae, E. coli, and B lymphocyte cells in porous, nanostructured silica shells to serve as model biosensing components. Our approach utilizes a novel sol-generating chemical vapor into liquid (SG-CViL) process. This process minimizes cell contact with cytotoxic reaction constituents, allows precise control of reaction parameters, and facilitates incorporation of components that enhance silica gel biocompatibility, such as polyethylene glycol. These factors make SG-CViL attractive as an encapsulation strategy for living cell-based biosensor design. This work focuses on characterizing cell-silica biocomposites, assessing encapsulated cell activity, and optimizing cell-silica biocomposites for particular sensing functions. Successful development of SG-CViL will be a significant step in designing biosensors that use living cells as the sensing unit, potentially leading to devices capable of detecting multiple threats at very low concentrations. This project is in collaboration with New Mexico Tech.

Decoupling Superconducting Transmon Qubits from their Quantum Bus/Readout Resonators to Enable Scaling

172334 | Year 3 of 3 | **Principal Investigator: R. M. Lewis**

Project Purpose:

Superconducting qubits have made great strides in coherence time, gating, and algorithms. However, to achieve real scalability, more is required. We propose to study the problem of coupling and decoupling a transmon, a popular type of superconducting qubit, from its host resonator, which serves the dual role of as a bus connecting qubits together and a readout channel. The transmon couples to its host resonator via its electric-dipole moment. We plan to use a trick of quantum mechanics to null the dipole moment and decouple the transmon. In doing so, we hope to study a variety of physics associated with multi-qubit operation, control, and readout.

Coupling superconducting qubits, such that their electric dipole moments cancel, creates a subspace where the first excited state of the paired qubits doesn't couple to nearby electric fields. This subspace provides a means of protecting qubits against local perturbations caused by operations and reads on neighbors. We seek foundational understanding of decoupling such subspaces, key to integrating larger quantum networks.

Summary of Accomplishments:

We demonstrated gallium-focused ion beam nanopatterning of niobium (Nb) films. This work points the way towards nanopatterning of Nb constriction junctions and perhaps multilayer junctions stacks for higher Josephson junction integration densities and more complex circuits.

We demonstrated microwave resonances in a variety of Nb resonator structures designed to house superconducting qubits, show multi-qubit layouts, and enable high qubit integration. These results validate earlier modeling, and show a path forward to more complicated devices.

We succeeded in combining the three scales of lithography needed to create superconducting qubits. This involves aligning photo and e-beam lithography patterns at the chip size, 100 μm, and 100 nm scales.

Modeling of complex layouts was achieved which agrees well with analytical expressions for our qubits. This enables complex designs to be pursued and evaluated and then fabricated with confidence.

Significance:

Quantum computation has the potential of enabling advanced algorithms for multiple applications. It is essential to national security that the US be the world leader in this field. By pursuing quantum computing in superconductivity, Sandia is ensuring competence in this area.

Defect Characterization in Low Bandgap Materials

173665 | Year 2 of 2 | **Principal Investigator: E. A. Shaner**

Project Purpose:

The purpose of this effort is to conduct research into specific generation recombination and dark current producing mechanisms of modern III-V material systems to aid in minimizing their impact on device performance. The fundamental dark current generated in type II absorber material limits its performance. We will utilize deep level transient spectroscopy (DLTS) to quantify the defects existing in these materials. Under the proposed effort, we will study defects in type II superlattices, such as GaSb/InAsSb and InAs/InAsSb SLS material systems, and correlate measurements with growth conditions and crystal structure.

Sandia has significant expertise in deep level transient spectroscopy (DLTS). Combined with the outstanding infrared material growth and detector experience, we are the ideal facility to perform this research. We anticipate significant improvements in the knowledge of device physics and material science that will enhance performance of infrared sensors beyond levels attainable with current technologies. If successful, we will characterize defects in InAs/InAsSb material that should show paths to improvement in material quality.

Summary of Accomplishments:

Overall, DLTS on low bandgap materials is challenging and we made significant progress on admittance spectroscopy of Type II superlattices. In particular, through collaboration with the University of Illinois Urbana-Champaign, we tested superlattice systems embedded in p-n junctions that appear to allow defect analysis.

Significance:

Understanding type II materials, in particular the defects in such systems, is important for next-generation detector development.

Development of a MEMS Dual-Axis Differential Capacitance

165823 | Year 3 of 3 | **Principal Investigator: B. Griffin**

Project Purpose:

This work is in collaboration with the University of Florida. Reduction of drag over a surface, due to both viscous skin friction and pressure separation effects, is an essential component of the effort to increase vehicle efficiency. Currently there is no method for time resolved, direct measurement of wall shear stress at the spatial and temporal scales of turbulent flow structures inside model testing facilities. Indirect methods require extensive in situ calibration, and rely on inferred relations to produce a measurement. Direct sensors can circumvent these issues. Direct sensors based on microelectromechanical system (MEMS) technology benefit from many favorable scaling effects which reduce overall measurement error, and retain spatial resolution while measuring small-magnitude forces. To prevent spatial averaging, the sensor length scale needs to remain under 20 viscous wall units, where a typical wall unit can be on the order of 10 μm for a turbulent boundary layer. This scale sensor is achievable with MEMS. Previous single axis sensors have concerns over accuracy due to alignment in testing and multi-directional flow effects. A unique MEMS-based differential capacitance floating element shear stress sensor capable of sensing force inputs in two orthogonal in-plane directions will be developed. Differential capacitance sensing schemes using interdigitated multi-finger designs have been found able to achieve suitable levels of minimum detectable shear stress and dynamic range. By allowing for compliance, and subsequent detection, in two directions, a vector measurement of shear forces tangential to the surface will be produced.

There is currently no commercially available sensor for the direct measurement of fluid induced shear stress, despite the implications on drag for aerospace vehicles and thus fuel efficiency. This research attempts to fill this gap by using MEMS microfabrication techniques to create dual axis shear stress sensors.

Summary of Accomplishments:

Full-scale wind tunnel measurements were made with the wall shear stress sensor at the University of Florida (UF), and at external locations including California Institute of Technology and NASA Langley Research Center. These are the only publically disclosed measurements of microscale wall shear stress in full-scale wind tunnel conditions. Using a hotwire as a secondary measurement tool, signal processing of correlation levels between wall shear stress and free-stream velocity fluctuations was carried out. These results helped to shape a more complete understanding of turbulent structure development and propagation in near wall conditions. A unique calibration rig to determine relative phase lag between the wall shear stress sensor, hotwires, and pressure transducers was constructed.

Sensitivity to environmental changes has been identified as a major culprit in mean wall shear stress measurement error. During tests at NASA's Langley Research Center, where wind tunnel air was non-conditioned, changes in tunnel temperature mapped closely with changes in sensor output. It is expected to be directly related to the coefficient of thermal expansion (CTE) mismatching in device packaging, as tests in a controlled environmental chamber yield similar results. A printed circuit board substrate from the Arlon Corporation, made of woven Kevlar with a laminated epoxy inter-layers, was identified with CTEs nearly matching Silicon. New sensors using the Arlon PCBs were packaged, with additional environmental testing to follow. The final packaging of wall shear stress sensors with integrated through silicon vias (TSVs) was completed. These were the first devices of this type to present a hydraulically flush front surface to the flow. Initial die level testing showed performance identical to the standard wire-bonded sensors described elsewhere in this work. The prototype devices were calibrated prior to testing in full-scale wind tunnel experiments.

Significance:

These results continue to open up pathways of microscale wall shear stress measurement as a viable tool option for experimentalists. Transition to a commercially available product is achievable within the next few years. Because the sensors are direct transducers, requiring no in situ calibration, they can be applied to situations, which differ greatly from canonical flow profiles. With the continuing move towards miniaturized aerodynamic vehicles (e.g., drones) an accurate measurement of wall shear stress can be useful both in design, and as an active feedback tool integrated with drone hardware for aerodynamic stability.

Efficient Heat Removal from Power Semiconductor Devices using Carbon Nanotube Arrays and Graphene

165705 | Year 3 of 3 | **Principal Investigator: M. P. Siegal**

Project Purpose:

Heat removal from semiconductor-based power electronics is becoming increasingly important, especially with the growing investment in renewable energy sources that require advanced power electronics to interface with the electric grid. This problem exacerbates as voltage, current, and switching-frequency scale to increase grid efficiency. This led to using wide-bandgap SiC and GaN for next-generation power electronics. However, these advantages are obscured by reduced performance and lifetime that occur with increased temperature. To fully achieve these material gains, the thermal resistance of the system must be reduced. Therefore, this project targets the large thermal resistance at the device die/package boundary where standard thermal interface materials (TIM) (e.g., metal-loaded epoxies with thermal conductivity ~1 W/m^{-K}) act as a thermal bottleneck that can mitigate performance or cause failure.

We seek to eliminate the TIM heat-transfer bottleneck from high-power devices to enable efficient cooling for improved device performance and reliability by creating all-carbon TIM cooling strategies to meet present/future needs. Carbon nanotubes (CNTs) and graphene can have thermal conductivities >10x that of metals. We propose synthesizing high-quality, vertically aligned CNT arrays directly onto a metal package that directly bonds to the device die in order to reduce TIM resistance by 10–100x. While this alone will reduce the existing thermal bottleneck, we further propose incorporating highly oriented pyrolytic graphite (HOPG) to the top of device surfaces to act as an ultimate heat spreader. By making thermal contact between the heat spreader and CNT-TIM in a flip-chip architecture, 10–400x improvements over state-of-the-art TIMs are obtainable, potentially rendering irrelevant the device substrate thermal conductivity, and lead to a new paradigm for high-power device performance.

This work is exploratory in nature, involving the use of nano carbon materials for device thermal packaging. While both CNTs and HOPG are known to have high thermal conductivity when highly crystalline, achieving such crystalline-quality reproducibly and over large areas has been problematic. In addition, the fundamental thermal conductance is not well understood a priori between CNTs and planar carbons like HOPG or graphene.

Summary of Accomplishments:

This project took on an extremely difficult set of scientific and technical goals that numerous groups had earlier failed and given up. Our progress has been remarkable and been well received at major conferences such as Materials Research Society and Electrochemical Society, as well as at Cambridge University, a world leader in the development and application of carbon nanomaterials, and Georgia Tech which has a premier facility for measuring thermal properties; each has led to new, ongoing collaborations. This work involved developments in three separate technical areas.

We made great progress toward developing CNT based TIMs. We report the first demonstration of:

- High-density, untangled arrays of high-quality CNTs with ~ 40% surface area coverage—critical to achieving high thermal conductance
- Planarized CNT arrays (every CNT cut to the same height), critical to achieving high thermal contact areas

These accomplishments result in a strong likelihood to ultimately improve the thermal conductivity of TIMs by 1-2 orders of magnitude over the state-of-the-art Ag-pastes.

Modeling and experimental work demonstrated that carbon-based planar heat spreading materials can greatly improve TIM performance. In particular, we've learned that:

- HOPG has better thermal conductivity than a graphene stack with a similar thickness due to better registry between adjacent layers in HOPG than in multilayer graphene
- A heat-spreading layer must be sufficiently thick, approaching 1 micrometer, to enable the removal of a high density of phonons
- Cooling can be greatly improved whenever "blanket" coverage directly over a heat-producing element is allowable

Lastly, we developed and fabricated a unique TIM test platform to compare the effectiveness of various TIMs with respect to power-device performance. The utility of this platform was demonstrated by testing a SiC metal-oxide-semiconductor field-effect transistor power device using a state-of-the-art Ag-paste TIM.

Significance:

This work bridges the nanoscale nature of carbon nanotubes and graphene with microsystem performance. Subsequent fine-tuning and successful implementation advanced TIMs and heat spreaders will support Power on Demand by enabling higher efficiency power conversion architectures via novel TIM devices for integrated microsystems. CNT-TIMs developments improve the safety and performance of electro-explosive devices for thermal battery operations, and the use of infrared thermography and modeling capabilities developed here are a useful diagnostic tool, both important to the Nuclear Weapons mission. The development of nanopore templates may be explored as platforms in chem-bio advanced sensing applications.

Refereed Communications:

C. Rochford, S.J. Limmer, S.W. Howell, T.E. Beechem and M.P. Siegal, "Planarized Arrays of Aligned, Untangled, Multiwall Carbon Nanotubes with Ohmic Back Contacts," *Journal of Materials Research*, v. 30, pp. 315-322, January 2015.

Electrically Injected UV-Visible Nanowire Lasers

165704 | Year 3 of 3 | **Principal Investigator: G. T. Wang**

Project Purpose:

There is strong interest in minimizing the volume of lasers to enable ultracompact, low-power, coherent light sources. Nanowires represent an ideal candidate for such nanolasers as stand-alone optical cavities and gain media, and optically pumped nanowire lasing has been demonstrated in several semiconductor systems. Electrically injected nanowire lasers are needed to realize actual working devices but have been elusive due to limitations of current methods to address the requirement for nanowire device heterostructures with high material quality, controlled doping and geometry, low optical loss, and efficient carrier injection. We propose to demonstrate electrically injected nanowire lasers emitting in the important ultraviolet (UV) to visible wavelengths. Our approach to simultaneously address these challenges is based on high quality III-nitride nanowire device heterostructures with precisely controlled geometries and strong gain and mode confinement to minimize lasing thresholds, enabled by a unique top-down nanowire fabrication technique developed at Sandia that provides maximum design flexibility. Our approach applies novel strategies for addressing these issues and leverages our combined expertise in III-nitride nanowire fabrication and characterization, nanodevices, and semiconductor laser modeling. Theory and modeling will be closely integrated with experiments to help design and demonstrate nanowire heterostructures with minimal lasing thresholds and to understand and predict the properties and physics from these nanolasers. Successful demonstration of a working III-nitride nanowire laser would enable diverse new functionalities in the integration of electronics and photonics, chem-bio sensing, imaging, ultra-high density storage, nanolithography, lighting, and quantum information.

Development of electrically injected nanowire lasers, while highly desirable, has been difficult due to a number of technical challenges. A proof-of-concept demonstration is lacking and is a goal of this project.

Summary of Accomplishments:

This project resulted in a number of technical accomplishments and successes towards the realization of electrically injected single nanowire lasers, although electrically injected lasing itself was not ultimately achieved. Some highlights include:

- Advanced the state of the art in controlled III-nitride nanowire fabrication using e-beam patterning and optimized dry and wet etch processes
- Demonstrated processes for nanowire cross-sectional shape control and resulting ability to manipulate nanowire laser properties, such as beam shape and polarization
- Analyzed and gained an understanding of the pros and cons of axial versus radial nanowire laser designs
- Achieved optically pumping lasing from nonpolar core-shell III-N nanowires, demonstrating its viability for electrically injected lasing
- Achieved electrically injected axial and radial InGaN/GaN nanowire LEDs
- Showed impact of metal contacts on optical loss
- Preliminarily explored new horizontal nanostripe geometry, which may have a better chance at electrically injected lasing than radial nanowire geometry

Additionally, this project contributed to the publication of ten journal articles (eight published, two in preparation), 28 invited talks, and 4 patent applications.

Significance:

Over the course of this project, we made several technical advancements, which greatly enhance Sandia's capabilities and expertise in the area of III-nitride nanostructures and UV-visible nanophotonics. Several new scientific understandings of light-matter interactions in nanostructures and nanodevices were obtained, such as the ability to manipulate optical properties based on cross-sectional shape control. Building off these advancements can enable future solutions that can significantly impact the DOE and national security missions (e.g., on-chip ultracompact low power optical sources, solid state lighting and displays, visible light communications, and high resolution imaging and lithography).

Refereed Communications:

C. Li, S. Liu, A. Hurtado, J.B. Wright, H. Xu, T.S. Luk, J.J. Figiel, I. Brener, S.R. Brueck, and G.T. Wang, "Annular-Shaped Emission from Gallium Nitride Nanotube Lasers," *ACS Photonics*, vol. 2, pp. 1025-1029, July 2015.

W.W. Chow, F. Jahnke, and C. Gies, "Emission Properties of Nanolasers during Transition to Lasing," *Light: Science & Applications*, vol. 3, p. e201, August 2014.

G.T. Wang, "III-Nitride Nanowires for Future Optoelectronics, presented at *International Symposium on Materials for Enabling Nanodevices*, (ISMEN2014), Tainan, Taiwan, 2014.

G.T. Wang, "III-Nitride Nanowires: Novel Materials for Future Optoelectronics," *International Symposium on Materials for Enabling Nanodevices* (ISSLED) Kaohsiung, Taiwan, 2015.

S. Liu, C. Li, J.J. Figiel, S.R. Brueck, I. Brener, and G.T. Wang, "Continuous and Dynamic Spectral Tuning of Single Nanowire Lasers with Subnanometer Resolution using Hydrostatic Pressure," *Nanoscale*, vol. 7, pp. 9581-9588, April 2015.

G.T. Wang, "III-Nitride Nanowires for UV-Visible Optoelectronics," presented at *IEEE Photonics Society Summer Topicals Meeting Series*, Nassau, Bahamas, 2015.

W.W. Chow, F. Jahnke, and C. Gies, "Nanolaser Emission under Few-Emitter or Unity-Spontaneous-Emission-Factor Conditions," presented at the 12th *Conference on Nonlinear Optics and Excitation Kinetics in Semiconductors* (NOEKS), Bremen, Germany, 2014.

W.W. Chow, F. Jahnke, and C. Gies, "First Principle Study of Nanolasers: Photon Statistics and Laser Threshold," presented at the *Asia Communications and Photonics Conference* (ACP 2014), Shanghai, China, 2014.

Electrochemical Detection of Single Molecules in Nanogap Electrode Fluidic Devices

180907 | Year 1 of 3 | **Principal Investigator: R. Polsky**

Project Purpose:

The purpose of this project is to gain fundamental understandings of molecular diffusion in nanogap electrodes and the diffusive behavior of single molecules undergoing electron transfer. The molecules to be studied here are commonly used as detection tags for biological labeling. Therefore, electrochemical detection of single molecules undergoing redox cycling would enable detection of single enzymes, proteins, and DNA strands resulting in new and improved ultrasensitive sensing devices, supporting needs in DHS and DoD. We propose to integrate orthogonal validation techniques, total internal reflection fluorescence microscopy (TIRF), and molecular simulation to clarify: 1) the mechanism leading to current build up due to redox cycling and 2) diffusion and adsorption of single molecules undergoing redox reactions. This project leverages key Sandia capabilities: 1) Microsystems and Engineering Sciences Applications Facility (MESA) has unique experience in fabricating large-area nanogaps to create nanogap electrode fluidic designs, 2) through simultaneous electrical and optical monitoring, Sandia's TIRF capability can unequivocally confirm measurements of a single molecule undergoing redox reactions, and 3) standard molecular dynamic simulations can determine diffusion behavior while ab initio molecular dynamic simulations can interrogate electron transfer as a function of electrode material. Such orthogonal monitoring coupled with innovative new device designs aided by atomistic simulations will provide an unprecedented insight into redox cycling mechanisms and fundamental information on the diffusive behavior of single molecules undergoing electron transfer. Results will be used to design basic research tools to study extracellular signaling, molecular-scale processes, internal dynamics, and intermolecular interactions and ultrasensitive chem-bio sensors.

In order to understand how redox cycling can be used for single molecule detection, the variability in measurements associated with the multitude of diffusion paths the molecule can traverse in the channel, varying residence times, and electrostatic molecule-electrode interactions need to be understood. These molecules can then be used as biological tags for detection of single enzymes, proteins, and DNA.

Fabrication and Characterization of a Single Hole Transistor in p-type GaAs/AlGaAs Heterostructures

165706 | | Year 3 of 3 | **Principal Investigator: L. A. Tracy**

Project Purpose:

One of the leading candidates for a solid state quantum bit is the spin of a single electron confined in a semiconductor. Coherent control of individual electron spins has already been demonstrated in quantum dots. These groundbreaking experiments utilized high-mobility 2D electron systems in GaAs/AlGaAs heterostructures grown via molecular beam epitaxy. The major source of decoherence in such experiments is coupling between electron spins and nuclear spins in the host GaAs semiconductor. It has been proposed that hole spins in GaAs would be better suited for such experiments due to a lesser coupling between hole and nuclear spins. Recent experiments already show that the coherence time for hole spins in GaAs quantum dots is at least one order of magnitude longer than that of the electron spin.

To date, experiments looking at the possibility of using spins in semiconductors as quantum bits have primarily focused on electron spins. One of the main reasons that there are relatively few experiments on holes in GaAs, as compared to electrons, is the difficulty of growing high-quality 2D-hole systems (2DHS) that can be used to fabricate stable hole nanostructures (such as quantum dots). Building on recent successes in the growth of 2DHS in GaAs/AlGaAs heterostructures at Sandia, we propose to fabricate and characterize single-hole transistors, looking towards eventual applications in the area of quantum computing. This work will leverage Sandia's unique, world-class capabilities in molecular beam epitaxy (MBE) growth of GaAs/AlGaAs heterostructures and expertise in low-temperature measurements. The physics of hole nanostructures is largely unexplored due to previous difficulties with fabrication of devices that are electrically stable. We hope that this project will demonstrate the viability of p-type nanostructures in GaAs, with potential application in quantum information.

Summary of Accomplishments:

In this project, we demonstrated the world's first few-hole double quantum dot in GaAs. Using charge sensing, we showed the ability to completely empty the dot and control the occupation at the few-hole level. The double quantum dot interdot coupling is tunable over a wide range, from formation of a large single dot to two well-isolated individual dots. These devices should provide a path for controlling and coupling individual hole spins in GaAs. A past hurdle facing hole nanostructures in GaAs was the ability to form devices with surface depletion gates that are stable. The mechanism behind the conductance drift and/or noise was not well understood. By using undoped heterostructures, we have achieved a very high level of device electrical stability, which appears to be limited by the voltage source used to control the device gates rather than the intrinsic properties of the device.

To form nanostructures with sharp electrostatic confinement in the 2D layer, it is necessary to use a relatively shallow 2D layer. We were able to achieve a shallow 2D hole layer with 50 nm depth while maintaining very low disorder. Our 2D layer mobility is ~105 cm2/Vs and has a mean free path of ~1 µm, which is larger than typical nanostructure dimensions. This aids in the formation of low disorder few-hole nanostructures, where hole transport and control over the confining potential is not hindered by defects. The high quality of our nanostructures is also indicated by the performance of a quantum point contact (QPC) fabricated in this material. As the QPC channel is gradually depleted, the conductance drops in discrete steps, quantized at multiples of 2e2/h, as expected for ballistic transport through a channel, indicating that the motion of holes in this device is not impeded by defects.

NANODEVICES & MICROSYSTEMS

Significance:

Hole spins in GaAs are predicted to have some advantages over electron spins, such as reduced coupling to host semiconductor nuclear spins and the ability to control hole spins electrically using the large spin-orbit interaction. Our double quantum dot (DQD) devices will allow investigation of all-electrical control of individual hole spins and coupling between hole spins in GaAs quantum dots and experiments investigating the role of spin orbit coupling and nuclear spin effects in p-type nanostructures in GaAs. Our advances in fabrication of shallow high mobility 2D layers may also provide a route for low temperature amplifiers for other quantum projects.

Refereed Communications:

L.A. Tracy, J.L. Reno, and T.W. Hargett, "Few-Hole Double Quantum Dot in an Undoped GaAs/AlGaAs Heterostructure," *Applied Physics Letters*, vol.104, p. 123101, 2014.

Fluid Polymer Bilayer Matrices: Toward Robust and Field-Deployable Biosensors

180909 | Year 1 of 1 | **Principal Investigator: W. F. Paxton**

Project Purpose:

In bionanotechnology, many biomimetic materials are being discovered for the use in medical imaging, therapeutics, and electronics. Block copolymers have been given much attention for their unique properties, ability to self-assemble and the countless chemical modifications they can undergo. Spherical structures made from these block copolymers, known as polymersomes are ideal for drug delivery applications and have been studied as such. Their ability to encapsulate hydrophilic molecules within their interior aqueous solution as well as incorporate hydrophobic molecules into the hydrophobic core are key factors in creating a cargo delivery system. Within this thesis, we have used polymersomes for transporting reagents and as the alternative environment for a trans-membrane to incorporate for proton transport.

Summary of Accomplishments:

We have found that bacteriorhodopsin (bR) can be integrated into hybrid vesicles that fully retain their functionality as measured by the pH of the bulk solution. We also know that over the course of several days either more bR monomers integrate into the membrane or oligomers are formed on top of pre-integrated bR molecules. As for integrating bR into giant unilamellar vesicles, we can visually say bR is present in the membrane, but more work needs to be done in order to determine the functionality and stability of these giant vesicles.

Significance:

One of the important outcomes of this work that will need to be repeated prior to publication is the longevity of BR in hybrid membranes. The ability to integrate functional biomolecules into synthetic matrices that preserve rather than destroy bioactivity is incredibly valuable for integrating such molecules into devices (e.g., biosensors). If this important result can be extended to other transmembrane proteins, such as potassium and sodium channels in nerve synapses, it would have huge implications for developing a wide range of more robust biosensors that mimic the response of biological cells.

This work greatly supported the efforts of developing robust, sensitive sensors that detect chemical and biological threats based on their biological function rather than their chemical form. The proposed work to create supported hybrid polymer/lipid bilayer systems with reconstituted functional biomolecules will greatly expand our understanding of the principles that enable biomolecules to function in non-native matrices.

Fundamental Scaling of Microplasmas and Tunable UV Light Generation

173131 | Year 2 of 3 | **Principal Investigator: R. P. Manginell**

Project Purpose:

This project seeks to fundamentally understand microplasma devices (MD), their scaling into the microdomain, and their ultraviolet (UV) emission physics. We hypothesize that the UV emission spectrum of MD can be manipulated real-time (sub-millisecond timescale). Applications of modulated UV emission from MD include tunable probing of quantum systems, such as atomic clock transitions, and selective chemical sensing. This work impacts basic science, national and homeland security, and other applications.

We have, to date, obtained current-voltage (I-V) characteristics and light spectrum (using a commercial Maya Pro spectrometer) of our microplasma devices as function of pressure for He, Ne, and Ar. We have tested with direct current (DC) and pulsed DC driving and are studying UV emission characteristics under these circumstances. We are now set up to test fast driving pulses and their effect on UV emission.

We have transitioned this year to studies using a calibrated McPherson monochromator for spectral measurements ranging from 300 nm to about 120 nm. This range is suitable for atomic physics and chemical sensing applications of ultimate interest.

We have made great progress in modeling and simulation of our microplasmas. Our model is now 3D sector, fully kinetic, capable of non-direct-current (non-DC) simulations, and includes double ionization processes, three excitation processes, and elastic collision terms. We have successfully simulated IV curves from an operational MD and compared those favorably to our experiments.

In Situ Techniques to Characterize Creep and Fatigue in Freestanding Metal Thin Films

166154 | Year 3 of 3 | **Principal Investigator: B. Boyce**

Project Purpose:

In collaboration with Carnegie Mellon, we will develop powerful in situ techniques to study thin film creep and fatigue using microelectromechanical systems (MEMS) design, processing, and test methods. We will work with a standard material (Aluminum) to prove out the methods. Once established, we aim to apply these tests to develop high strength multilayer thin-film metal stacks. Diverse applications for these materials are possible: 1) as low creep/fatigue materials in microrelays and micromirrors, 2) as damage-tolerant materials in extreme radiation environments (e.g., in nuclear reactor walls), 3) as high-temperature, high-strength materials, and 4) for x-ray focusing.

This research is high-risk advanced development of mechanical test techniques for the fatigue and wear behavior of metallic thin films that are ~100 nm in thickness.

Summary of Accomplishments:

An initial thermal experiment to test the experimental setup has led to the development of a novel approach for determining the coefficient of thermal expansion (CTE) of free standing thin film (Pocratsky and De Boer, *J. Vac. Sci. Tech. B*, 2014). This method allows the CTE of a film to be determined locally to other devices of interest since the test structure is a fixed-fixed beam. The difference in CTE between the free standing thin film and the substrate is critical to the self-actuation method utilized in the designed MEMS creep test platform.

The creep test platform was designed to give an approximately constant load versus displacement to accurately reflect the testing method of bulk materials. This unique feature was achieved by designing thermal actuators legs to buckle. Typically, the buckling instability is avoided to get an approximately linear load versus displacement. Finite element analysis was performed to design a set of thermal actuators with a wide range of leg length, leg offset, and number of legs that provide a wide range of output force. The creep test platform utilized a load cell to optically determine the displacement across a load spring with calculated stiffness and the axial displacement of a microtensile specimen. The test platform has the capability of analyzing any thin film of interest over multiple orders of magnitude in strain rate on a single chip in a single experiment. The MEMS device can also be used to analyze creep during in situ transmission electron microscopy (TEM) experiments to observe the creep mechanisms. The fabrication process of the device was developed at the Carnegie Mellon University nanofabrication laboratory.

Significance:

The use of MEMS test platforms coupled with in situ TEM to investigate the mechanical properties of nanocrystalline metals as well as other materials will prove to be extremely fruitful. We focused on the study of creep in this report. However, the process flow under development will be of broad use for mechanical property testing under a wide range of load and temperature and for many different materials and under different environmental conditions.

Refereed Communications:

R.M. Pocratsky and M.P. de Boer, "Determination of Thin Film Coefficient of Thermal Expansion and Residual Strain from Freestanding Fixed-Fixed Beams," *Journal of Vacuum Science & Technology* B, vol. 32, p. 062001, 2014.

Magnetic Josephson Junction Memory and 3D Integration for Scalable, High Performance, Low Power Computing

180906 | Year 1 of 3 | **Principal Investigator: N. A. Missert**

Project Purpose:

Superconducting electronics (SCE) is one of the leading technology candidates for high performance, ultra-low power computation needed by Sandia's national security customers. Although high-speed, digital superconducting circuits have been demonstrated, the promise of extending these devices to high performance computing has been severely hindered by the lack of a fast, low energy, high capacity, integrated memory cell and scalable 3D active device structure. This proposal addresses each of these issues by employing novel, tailored, ferromagnetic thin films for memory cells integrated with a Josephson junction (JJ) structure that can be fabricated in 3D by using an alternative superconducting layered system. In contrast to the Nb/AlO_x/Nb JJ technology currently employed for SCE, where degradation issues do not allow 3D stacking of the active JJ layers, our approach exploits the relative stability of Nb and Ta nitrides for the logic gates and Cr-doped Al and Ga nitrides for ferromagnetic memory elements. The technical challenges include understanding and optimizing Cooper-pair transport across both the Ta_xN layer near the metal-insulator transition and the single-domain Cr:AlN and Cr:GaN soft ferromagnetic layers, as well as ultimately demonstrating an integrated working memory cell in a 3D stack. If successful, this work will provide the foundation for the next generation of truly scalable SCE for high performance, low power computing.

There are forefront materials science and device physics challenges that need to be addressed in order to create JJs and memory elements with the required performance, and also considerable technical challenges associated with their integration in 3D.

Metal-Organic Framework Thin Films as Gas-Chromatography Stationary Phases for the Detection of Toxic Industrial Chemicals

173133 | Year 2 of 2 | **Principal Investigator: D. Read**

Project Purpose:

The purpose of this project is to integrate metal-organic framework (MOFs) materials with Sandia's current microfabricated-gas-chromatography (μGC) columns to enable the portable detection of high-volatility analytes such as toxic industrial chemicals (TICs). TICs represent a large class of ubiquitous, highly volatile chemicals, which pose a threat to human life and the environment through accidental or terrorist release. Example TICs include chlorine gas, hydrogen cyanide, hydrogen sulfide, sulfur dioxide, and formaldehyde. The Department of Homeland Security, Defense Threat Reduction Agency, and National Counterterrorism Center have all identified TICs as a major area of concern for possible chemical attack. μGC columns are necessary to meet the power and size requirements of a portable GC system, but are not presently suited to the detection of TICs due to the poor retention characteristics of the traditional polymer sorbent materials which are currently employed. A need exists for a material that can fill this gap in chem-detection capabilities. One such class of candidate materials is that of MOFs. MOFs are crystalline materials containing inorganic clusters crosslinked by a rigid organic network, and have been demonstrated to be well suited for small-molecule absorption, in general. MOFs are highly porous, thermally stable, and possess tunable chemical sorption affinity through modification of their chemical functionality and pore structure.

The use of MOFs as μGC-column stationary phases has not yet been demonstrated in the literature, constituting a new approach to address these challenging chromatographic separations. The successful integration of MOFs and μGCs would not only offer a valuable and innovative solution to this chem-detection crux, but would also further knowledge in the field of MOF research through the development of a method for quickly determining sorption thermodynamic constants using gas chromatography instrumentation.

Summary of Accomplishments:

We have successfully grown conformal thin films (25–300 nm) for two MOFs: ZIF-8 and HKUST-1 (Hong Kong University of Science and Technology) using layer-by-layer (LBL) deposition techniques within high-aspect-ratio, μGC column channels (30 μm x 685 μm x 90 cm), as well as within fused-silica capillary, known as traditional GC substrates. LBL HKUST-1 film growth kinetics were characterized on silicon-oxide coated quartz crystal microbalance (QCM) for in situ monitoring of MOF growth. We demonstrated the ability to tailor the chromatographic retention time of an analyte by varying the number of layer-by-layer, MOF thin-film deposition cycles. This will be of great interest to the analytical chemistry community. We have achieved the principal project milestone by demonstrating the first μGC retention of natural gas components and select TICs including chlorine gas. As a corollary, we have established a thermodynamic sorption model by using scanning electron microscope (SEM) micrographs to determine film thickness and chromatographic retention data. This model not only yielded the fundamental/intensive sorption constants (i.e., partition coefficients) of HKUST-1 for natural gas as well as select TICs, but also yielded phenomenological insight into the deposition kinetics of HKUST-1 on silicon-oxide. Specifically, we showed that HKUST-1 growth occurs only in nucleation islands until ~17 layer-by-layer deposition cycles at which point the film is conformal and the deposition rate reaches a steady-state value of 1.8 nm/cycle. This high degree of regulation over MOF film thickness has enabled extraordinary control over chromatographic performance, thereby allowing us to tune these MOF thin films for specific chemical detection applications. We have now successfully demonstrated the first-ever μGC x μGC (2-D GC) separation of extreme high-volatility analytes, which requires two separate GC columns with disparate-polarity stationary phases. This work has also led to the quantification of the polar nature of HKUST-1, something that has been subjectively eluded to in the literature, but never proven.

Significance:
Simply stated, these MOF films are outperforming any commercially available GC stationary phase coating for polar, small molecule retention. We have used the data generated in this project for three separate external funding proposals (DTRA, DHS, and Aquila Group), as well as the work being incorporated in five additional funding presentations. This research has proved to be rich in novel developments, has furthered basic scientific understanding of MOF thin films, and is garnering the interest of potential internal and external customers alike (both government and private) for previously impractical chem-detection applications.

Minority Carrier Lifetime Characterization and Analysis for Infrared Detectors

165703 | Year 3 of 3 | **Principal Investigator: E. A. Shaner**

Project Purpose:

Minority carrier recombination times in infrared detector materials, such as mercury cadium telluride (MCT) and InAs/GaSb systems, are important for quantifying and improving material quality as well as key device parameters such as dark current. Unfortunately, the relevant lifetimes for these materials are in the nanosecond to microsecond regime. Standard instruments for lifetime characterization are ultrafast pump-probe measurements (sub-picosecond to nanosecond, high carrier densities) and RF characterization that has been developed for silicon (typically microsecond and longer). Neither approach is valid for our timescales. One must also measure under low incident pump flux in order to capture the relevant recombination dynamics (requiring high sensitivity) while also having the ability to perform Fourier transform infrared (FTIR) spectroscopic analysis all in a cryogenic environment.

We have developed lifetime measurement capability based on time-resolved photoluminescence (PL) for moderate carrier densities (~1015/cm^3), along with a frequency domain PL approach for lower carrier densities. Under this effort, we will develop a time-resolved microwave probed lifetime measurement that is more sensitive than any PL technique. Perhaps more importantly, we will develop models and understanding of acquired data in order to accurately define Auger, radiative, and defect (Shockley-Read-Hall, and surface states) contributions to minority carrier lifetimes in detector material. One must keep in mind that in real devices, the doping level of certain layers (such as absorbers) impacts lifetimes and diffusion profiles. To fully understand an immature material system, many different structures with varying layer composition and doping must be characterized over a wide range of temperatures.

Summary of Accomplishments:

We developed highly sensitive microwave techniques for characterizing minority carrier lifetimes in semiconductor materials. In addition, we made significant progress on understanding the physics of defects in type II materials. In particular, as documented through multiple publications, we furthered the understanding of InAs/InAsSb superlattices.

Significance:

The understanding of type II materials, and defects in particular, is important for furthering advances in detectors.

Refereed Communications:

M.R. Wood, K. Kanedy, F. Lopez, M. Weimer, J.F. Klem, S.D. Hawkins, E.A. Shaner, and J.K. Kim, “Monolayer-by-Monolayer Compositional Analysis of InAs/InAsSb Superlattices with Cross-Sectional STM,” *Journal of Crystal Growth*, vol. 425, pp. 110-114, 2014.

H.J. Haugan, G.J. Brown, B.V. Olson, E.A. Kadlec, J.K. Kim, and E.A. Shaner, “Demonstration of Long Minority Carrier Lifetimes in very Narrow Bandgap Ternary InAs/GaInSb Superlattices,” *Applied Physics Letters*, vol. 107, p. 131102, 2015.

B.V. Olson, E.A. Kadlec, J.K. Kim, J.F. Klem, S.D. Hawkins, and E.A. Shaner, “Intensity- and Temperature-Dependent Carrier Recombination in InAs/In As1-x Sbx Type-II Superlattices,” *Physical Review Applied*, vol. 3, p. 044010, April 2015.

D. Zuo, R. Liu, D. Wasserman, J. Mabon, Z-Y. He, S. Liu, Y-H. Zhang, E.A. Kadlec, B.V. Olson and E.A. Shaner, “Direct Minority Carrier Transport Characterization of InAs/InAsSb Superlattice nBn Photodetectors,” *Applied Physics Letters*, vol. 106, p. 071107, 2015.

J. Aytac, B.V. Olson, J.K. Kim, E.A. Shaner, S.D. Hawkins, J.F. Klem, M.E. Flatte, and T.F. Boggess, “Temperature-Dependent Optical Measurements of the Dominant Recombination Mechanisms in InAs/InAsSb Type-2 Superlattices,” *Journal of Applied Physics*, vol. 118, p. 125701, 2015.

Multifunctional Integrated Sensors (MFISES)

173269 | Year 2 of 2 | **Principal Investigator: B. D. Homeijer**

Project Purpose:

Self-powered autonomous sensor systems would be a great benefit for many national security applications, including border and infrastructure security, soldier health monitoring, and clandestine operations. Large channel count wireless arrays on structures such as pipelines and autonomous sensors for clandestine applications are just two applications where replacing a battery is either impractical or dangerous. The applications are vast and most proposed solutions are specific to the given application. This work, in collaboration with Stanford University, is focused on developing self-powered multifunctional sensor nodes to achieve generic sensing platforms suitable for wireless network integration and real-time monitoring in a range of applications. The architecture of the node includes: 1) devices and electronics to harvest, manage, and store electrical energy, 2) a multifunctional sensor, 3) a low-power microcontroller, and 4) low-power communications. This research is focused on the sensor and energy harvester components.

The proposed sensor nodes will provide pivotal enabling technology in the emerging technologies of autonomous wireless sensor networks. Current sensor node technologies are cumbersome by wiring requirements to meet power demands, limited in deployment duration by expendable power sources, and are designed to measure only a single parameter. Incorporating on-board multi-functional energy scavenging with a multi-functional sensor would greatly increase the utility and potential deployment space of the sensing networks.

Summary of Accomplishments:

A low power wireless sensor system consisting of various types of sensors and energy harvesting devices, coupled to power management, low power microcontroller and a low power transceiver was developed. This effort completed fabrication of two generations of multifunctional integrated sensors and has demonstrated the capability of measuring ten parameters (temperature, humidity, air speed, air flow direction, light intensity, pressure, magnetic field strength, three-axis acceleration) using a single chip. To our knowledge, this represents the highest degree of functional integration demonstrated in a MEMS sensor. The concept was to build a “Swiss Army Knife” sensor: a compact device useful in many different applications. This design requires lower power, reduces package size, and decreases the cost of the sensors compared to ten individual devices. Extensive cross-sensitivity testing has been conducted to be able to deploy the sensors and our fundamental findings are applicable to general sensor design and operation. Stanford is currently fabricating a next-generation sensor that reduces the chip size 25 times and encapsulates the inertial sensors in a hermetically sealed chamber. The second next-generation sensors add additional sensing capability, will be more stable in operation, and require less power than the first generation devices.

Significance:

Currently, there are no platforms that are available with the vast capabilities we have proposed. Successful maturation of this technology to a deployable sensor platform could impact a variety of missions, with applications ranging from unattended ground sensing for security to biological monitoring for real-time soldier health information. With this type of sensor architecture, the designer is focusing on their application instead of wireless technologies, enabling faster deployment of time critical applications.

Refereed Communications:

C.L. Roozeboom, B.E. Hill, V.A. Hong, C.H. Ahn, E.J. Ng, Y. Yang, M.A. Hopcroft, and B.L. Pruitt, “Multifunctional Integrated Sensor Monitoring,” presented at the *Hilton Head Solid-State Sensors, Actuators and Microsystems Workshop*, Hilton Head, SC, 2014.

C.L. Roozeboom, V.A. Hong, C.H. Ahn, E.J. Ng, Y. Yang, B.E. Hill, M.A. Hopcroft, and B.L. Pruitt, “Multifunctional Integrated Sensor in a 2x2 mm Epitaxial Sealed Chip Operating in a Wireless Sensor Node,” presented at the 2014 *IEEE 27th International Conference on MEMS* (MEMS 2014), San Francisco, CA, 2014.

C.L. Roozeboom, B.E. Hill, V.A. Hong, C.H. Ahn, E.J. Ng, Y. Yang, T.W. Kenny, M.A. Hopcroft, and B.L. Pruitt, “Multifunctional Integrated Sensors for Multiparameter Monitoring Applications,” *Microelectromechanical Systems*, vol. 24, pp. 810-821, July 2015.

Optical Polarization Based Genomic Sensor

165707 | Year 3 of 3 | **Principal Investigator: R. Polsky**

Project Purpose:

Fluorescence-based detection of DNA can offer exquisite signal-to-background ratios, with high specificity. However, photobleaching, whereby fluorescent probes transition to a dark state under prolonged excitation, necessarily limits detection sensitivity. Furthermore, fluorescence detection requires relatively intense, narrow band excitation light sources, as well as expensive dichroic/band pass optical filters to isolate signal, whose alignment tolerances may preclude deployment in rugged environments. Thus, there is a clear need to explore alternative optical sensing paradigms to alleviate these restrictions. Bio-templated nanomaterial synthesis has become a powerful concept for developing new platforms for biosensing. We will explore innovative genomic sensing methodologies based on interactions between light and nanoparticle assemblies. Rod-shaped, noble metal nanoparticles (nanorods) have been shown to strongly interact with light in a resonant fashion. This interaction can be many thousand-fold larger than fluorescent dyes, and does not suffer from photobleaching. However, the full potential of this phenomenon has yet to be realized. We propose to use nucleic acid hybridization as a means to link metal nanorods end-to-end, or nanoparticles onto DNA origami structures, in order to create particle assemblies that are predicted to display unique properties for sensing specific genomic sequences. We will characterize the nanorod-DNA assemblies in complex media and explore the tunability of the optical properties of gold nanorod assemblies via dissimilar aspect ratios and widths and varying coupling geometries via DNA tertiary structures. Finally, we will synthesize nanorods exploring various surfactants to modulate binding strength of surfactant and DNA probe.

In order to take advantage of the unique optical properties of gold nanorods as fluorescent probes for DNA detection, a fundamental understanding of their optical properties needs to be achieved–specifically, with respect to how bio-templating through hybridization events can be used to produce dramatic optical enhancements. Both the characterization and ability to organize nanorods have yet to be studied.

Summary of Accomplishments:

Bio-templated nanomaterial synthesis has become a powerful concept for developing new platforms for biosensing, as the biomolecule of interest can act as part of the sensing transducer mechanism. We have shown that DNA origami can be used to immobilize gold nanoparticles in very precise localized arrangements. The placement of the gold nanoparticles in linear chains along the origami backbone was demonstrated with specific control over the number of nanoparticles in series from 1-8 nanoparticles. While a single nanoparticle immobilized showed only a transverse surface plasmon resonance (TSPR) absorption spectra, as do free nanoparticles, the 2 to 8 configurations resulted in an additional localized surface plasmon resonance (LSPR) peak. The interparticle interactions mimic nanorod absorption characteristics with each distinct nanoparticle series behaving like nanorods with differing aspect ratios. We believe that this effect has possible implications in novel DNA sensing schemes. We also explored the use of in situ transmission electron microscopy (TEM) as a novel characterization method for DNA-nanoparticle assemblies and showed that using TEM to measure interparticle distances when DNA bridging is involved must be looked at with the caveat that drying effects oftentimes produce artifacts that are confused with real results.

Significance:

Optical fluorescence-based DNA assays are commonly used for pathogen detection and consist of an optical substrate containing DNA capture molecules, binding of target RNA or DNA sequences, followed by detection of the hybridization event with a fluorescent probe. Vast opportunities exist to improve current optical-based genomic sensing approaches. For these reasons, there is a clear need to explore alternative optical sensing paradigms to alleviate these restrictions. We explored the use of DNA origami structures to immobilize gold nanoparticles in very precise localized arrangements to produce unique optical absorption properties that have implications in novel DNA sensing schemes.

Piezoelectric Nano-Optomechanical Systems

173496 | Year 2 of 3 | **Principal Investigator: M. Eichenfield**

Project Purpose:
The field of nano-optomechanical systems (NOMS) involves the properties of photon-phonon interactions confined to nanoscale volumes. Optomechanical crystals (OMCs) are man-made metamaterial NOMS that allow both light and sound vibrations to be confined within the nanoscale volume, where they strongly interact. Experiments on OMCs have been used to test quantum limits and study the quantum effects in mechanical systems due to their exquisite sensitivities to mechanical motion. However, many potentially groundbreaking applications of these systems are still outstanding.

An unexplored regime is NOMS in optically transparent piezoelectric materials, such as aluminum nitride and lithium niobate. Previous devices were fabricated using silicon and silicon nitride, which are not piezoelectric. However, Sandia has developed new capabilities in the micromachining of piezoelectric thin films, and these capabilities could and should be used to study optomechanics in piezoelectric materials.

In addition to more standard photon-phonon interactions, piezoelectric NOMS also include electromechanical-piezoelectric interactions, coupling charge distributions to light and mechanical vibrations. The dynamics of these systems are largely unexplored and offer myriad possibilities for study of fundamental properties and potential applications.

Creating piezoelectric NOMS is an extremely worthwhile goal, but it is also extremely challenging. To make these devices, one needs to precisely fabricate nanoscale systems in materials like lithium niobate and aluminum nitride, which are difficult to fabricate and still experimental compared to more standard complementary metal-oxide semiconductor (CMOS) materials. Moreover, there are theoretical, numerical, and experimental challenges to solve to design and test such devices.

This work is in collaboration with the University of New Mexico.

Programmable Piezoelectric RF Filters

165708 | Year 3 of 3 | **Principal Investigator: C. Nordquist**

Project Purpose:

The project purpose was to create a new class of programmable radio frequency (RF) filters with the high quality factor (Q) of acoustic filters and the large tuning range of electromagnetic filters. This addresses a key gap for RF front ends because miniature high Q (Q >1000) reconfigurable filters currently do not exist due to the inability to tune acoustic resonators and the large size of electromagnetic resonators. This filter technology will enable new, smaller, and more efficient RF systems that tune and adapt to changing future mission needs.

We explored using microelectromechanical system (MEMS) switches to modulate the coupling of a transducer finger to an aluminum nitride (AlN) piezoelectric film. Varying the distance between the MEMS switch finger and the substrate from nanometers to micrometers changes the electric field in the piezoelectric film, which modifies the electromechanical transduction of the signal. The finger is weakly coupled to the AlN film and inactive in the upstate, and is strongly coupled and active in the downstate. This ability to achieve high-contrast switching of these fingers enables real-time synthesis and tuning of key building blocks for piezoelectric filters: transducers, reflectors, and couplers. Changing the effective width and pitch of the fingers in these sections changes the filter center frequency and bandshape, enabling RF filters that are widely reconfigurable and adaptive.

Summary of Accomplishments:

This project achieved several significant accomplishments towards the goal of demonstrating switched RF filter technology.

We developed and demonstrated an integrated AlN resonator/MEMS capacitive switch technology. During this project, we performed several fabrication iterations of this technology, which monolithically integrates AlN contour-mode-resonators and capacitive MEMS switches using a single common release process. In addition to providing the targeted intra-resonator switching and tuning, it also provides the ability to perform integrated impedance-based tuning of resonator circuits and filters using low-loss MEMS switched capacitors instead of lossy solid state varactors or transistor switches.

We demonstrated the first MEMS-based on/off switching of a contour-mode resonator. The first devices showed 30 dB of switching with a Q of approximately 400, and later improved devices showed 35 dB of switching with a Q >2000. These first-ever demonstrations proved the concept of using a MEMS switch finger to modulate the coupling of a transducer finger to a piezoelectric and are a key advance towards reconfigurable resonators based on the technology. We analyzed and developed several switched transducer and filter designs with up to 40 separately actuated fingers. Finite-element-method and coupling-of-modes modeling were used to explore candidate designs for switched filters and MEMS switches. Fixed transducers with changing finger placement demonstrated transducer-tuning approaches and over several design iterations, we improved damping and crosstalk in the switched resonators. We explored using switchable Bragg reflectors for resonator tuning and discovered and explored thickness limits of reflectors on AlN. We identified and quantified a performance trade-off in which the reflectivity of a Bragg finger increases with metal thickness, but beyond a certain point an unbalanced acoustic medium appears to increase the reflector loss. Understanding this effect is important for future AlN contour-mode filters using Bragg reflectors but has not been predicted by modeling or discussed in prior literature.

Success required solving challenges in acoustic device modeling, microelectromechanics, and integration. We used modeling and experiments to explore the fundamental coupling mechanisms in the MEMS switches that serve as the fingers of an acoustic filter. Finite element modeling was used to simulate and optimize the piezoelectric device structures and MEMS switches, while coupling of modes modeling was used to simulate the cascaded transducer sections. Additionally, several integration and fabrication challenges were overcome to integrate the MEMS switches with the transducer fingers. The resulting technology and knowledge represents a unique capability that advances filter state of the art.

Significance:

This project provided a first-ever exploration of reconfigurable acoustic resonators and filters, which are key components for future government and commercial RF systems. This exploration provided discoveries in micromechanical devices and acoustic devices, and generated a unique capability to integrate MEMS capacitive switches with acoustic resonators. Specific knowledge advances include the understanding of transducer coupling across narrow gaps, the limitations of Bragg reflector thickness, improvements in MEMS switch design, and improvements in MEMS fabrication and release processes. The underlying design, fabrication, modeling, and characterization approaches will benefit future national security projects in RF filters and devices.

Refereed Communications:

C.D. Nordquist and R.H. Olsson, "Radio Frequency Microelectromechanical Systems," *Wiley Encyclopedia of Electrical and Electronics Engineering*, available online, December 2014.

Reduced Dimensionality Lithium Niobate Microsystems

173126 | Year 2 of 3 | **Principal Investigator: M. Eichenfield**

Project Purpose:

Next-generation optical and radio frequency (RF) communications components require unprecedented bandwidth, low power, efficiency, and small size. Because of its superior piezoelectric coupling, low acoustic/optical loss, high nonlinear optical susceptibility, and optical transparency over broad wavelengths (350 to 5200 nm), lithium niobate ($LiNbO_3$) has found widespread use in RF filters, laser frequency doublers, and acousto-optic (AO) devices. We propose a new class of acoustic, optical, and AO devices with orders of magnitude improvements in bandwidth, power consumption, efficiency, and size enabled by reducing the dimensionality of $LiNbO_3$ structures. By micromachining $LiNbO_3$ into suspended structures where the thickness and in-plane features are on the order of, or much smaller than, the acoustic/optical wavelength, the already outstanding piezoelectric and optical properties of $LiNbO_3$ can be significantly enhanced, with corresponding improvements in device performance. We propose to demonstrate these theoretical performance benefits in a novel AO modulator. Several scientific and technical problems must be solved including the realization of suspended $LiNbO_3$ structures with the desired small features, optical and acoustic properties and the modeling and co-design of AO structures in strongly anisotropic materials.

We will utilize Sandia's unique and extensive microfabrication and ion beam facilities to realize thin LiNbO3 membranes with precisely controlled nanoscale features–a significant challenge for this brittle anisotropic material. We will use our experience in finite-element, plane-wave expansion, and finite-difference time-domain modeling to explore and simultaneously optimize the acoustic and optical device properties in this highly anisotropic media, where the piezoelectric and optical coefficients and wave velocities vary considerably with the material cut and propagation direction. Using this platform we will demonstrate the co-confinement and coherent phase matching of acoustic and optical waves in an AO photonic/phononic crystal waveguide, enabling high diffraction efficiency (> 80%), low power (< 10 mW), and operation at frequencies in excess of 1 GHz–surpassing current AO devices.

Robust Operations and Algorithms for Quantum Information Systems

178675 | Year 2 of 2 | **Principal Investigator: T. S. Metodi**

Project Purpose:

Quantum information processing (QIP) is a disruptive technology promising transformative advances in information processing (including sensing, computation, and communication). Despite progress toward practical QIP, tremendous challenges exist. Chief among these is the fragility of quantum information to noise and the overhead required to actively suppress noise in quantum systems. We propose to engineer passive resilience to noise into the quantum system itself, which consists of both the gates implemented in the underlying hardware and the higher-level algorithms. Our research will proceed via two mutually supporting themes: 1) development and verification of robust physical quantum gates and 2) development of intrinsically robust quantum algorithms and topologically protected quantum operations. These themes will work together and build upon each other toward the ultimate goal of enabling reliable special-purpose QIP applications.

QIP has well-known disruptive applications in the long-term but with few near-term applications. Our proposal aims to show that innovative, specialized hardware and algorithms for few-qubit devices may solve important problems in the near term and will blaze a path for further efforts that capitalize on such opportunities.

Summary of Accomplishments:

Trapped Ions: Accurate noise characterization requires large amounts of experimental gate data. In order to achieve this characterization, we developed fully automated trapped-ion data collection utilities that can be run autonomously. We also developed an improved single-qubit Gate Set Tomography protocol and have applied it to both stand-alone broadband number 1 (BB1) control sequence-compensated microwave gates. Our results are as follows:

- We demonstrated the first high-fidelity single-qubit gate in surface traps characterized with the Glutathione S-Transferase (GST) protocol: error rate 1.3e-4
- We demonstrated state-of-the-art identity gate in surface traps characterized with the GST protocol: error rate 6e-5

Si-based Qubits and Gates: We developed a method for testing whether a charge can be moved adiabatically between the donor and dot location and numerically quantified the expected adiabatic transit times. Using this method, we accomplished the following:

- Demonstrated observation of coherent donor-dot rotations
- First demonstration of a logical qubit between a quantum dot and single donor
- Demonstrated donor-dot two-qubit operation between nuclear spin and metal-oxide-semiconductor (MOS) singlet-triplet) S/T qubit
- Demonstrated the first MOS-system S/T qubit
- Demonstrated a new latching read-out for high fidelity S/T read-out

Topological Operations and Algorithms: We developed a universal gate set for topological operations that significantly reduces the overhead of error correction. We also developed a stabilizer-based faulty-logic gate simulator for topological codes assuming generic physical noise. For algorithms, we demonstrated a simple quantum experiment relying on dissipative state engineering for state preparation. In addition, in order to study robustness, we developed tools for simulating small quantum algorithms under different noise conditions.

Significance:

This work seeks to develop and prototype functioning quantum devices and their associated algorithms that realize transformative advances in information sensing, processing, and communication.

Seebeck Enhancement via Quantum Confinement in MOSFET's: Towards Monolithic On-Chip Cooling

173128 | Year 2 of 3 | **Principal Investigator: I. F. El-Kady**

Project Purpose:

We propose to utilize quantum confinement effects in 2D electron- (2DEG) and hole- (2DHG) gases in metal-oxide-semiconductor field-effect transistor (MOSFET) structures to enhance the Seebeck coefficient (S) and subsequently the thermoelectric figure-of-merit ZT given by (S^2*sigma/k)T; where *sigma* and *k* are the electrical and thermal conductivities, respectively.

The interdependence of the three Z components makes it extremely difficult to optimize them concurrently. As such, almost all existing literature on Z employ an "Edisonian" approach where the focus is on the enhancement of only one of its three components, leaving the remaining two to chance. Furthermore, while most of the effort has been focused on either engineering k or s, given the relative ease in modifying their values, virtually no effort has focused on engineering S, despite its quadratic power in Z. The fundamental problem with such an approach is that electrical and thermal conductivities are interrelated: attempts to reduce k by incoherent phonon scattering often inadvertently also scatter electrons resulting in a reduction in sigma, thus yielding no net gain in ZT.

Our approach is based on previous theoretical research postulating that the S of a low-dimensional, high-mobility system, such as a 2DEG/2DHG, can be greatly enhanced as compared to the bulk material. Thus, we seek to demonstrate such an enhancement in Si and SiGe based depletion-mode MOSFETs operated under inversion, wherein the inversion channel functions as a high-S quantum confined system. Our models predict an S enhancement factor of 2 and 1.6 or more for these systems, respectively.

The objective of this work is to demonstrate, for the first time, the quantum confinement effects on S. This is a high-risk, high-return project with major experimental and theoretical hurdles whereby unique concurrent enhancement of all three Z components is predicted.

The Anatomy of the Minority Carrier-Atomic Cluster Interaction in Semiconductors

173127 | Year 2 of 3 | **Principal Investigator: B. L. Doyle**

Project Purpose:

The purpose of this project is to use light ion beam induced charge (IBIC) to detect damage cascades generated by a single heavy ion, and thereby reveal details of the shape of the cascade and the physics of recombination of carriers that interact with the cluster. IBIC measurements of damage cascades will improve the accuracy of theoretical models used to predict electrical degradation in devices exposed to radiation environments. In addition, light ion IBIC detection of single ion-induced damage could be used to locate single ion implantation sites in quantum computing applications.

This project uses Sandia's unique nanoImplanter (nI) technology to produce heavy ion-induced collision cascades in p-n diodes, simulating cascades made by primary knock-on atoms. The nI is also used to perform highly focused scans that generate IBIC signals. The IBIC signal produced by each light ion maps regions of lower charge collection efficiency without incurring further damage.

Vertically Injected Ultraviolet Laser Diodes

188288 | Year 1 of 3 | **Principal Investigator: M. H. Crawford**

Project Purpose:

Extension of laser diodes (LDs) throughout the ultraviolet (UV) spectral region is thus far unrealized but would be a significant technological breakthrough. Such compact, rad-hard lasers are of interest for fluorescence-based bioagent sensing, trapped-ion quantum computing, and technologies in the solar-blind region (<280 nm). To date, however, milliwatt (mW) class UV LDs are limited to pulsed operation at longer wavelengths (>335 nm) due to materials challenges of AlGaN wide-bandgap semiconductors. One major roadblock is the lack of an electrically conductive, lattice-matched substrate, yielding non-radiative defects and forcing lateral-injection designs that limit performance by current crowding and heating. A second roadblock is the deep acceptor levels that preclude thermal activation of holes needed for effective p-type doping. Finally, little is known about the dominant contributions to optical loss in these laser structures, frustrating device design optimization. To overcome these challenges, we propose to explore three primary thrusts. First, we will move beyond sapphire substrates to develop templates based on micro-patterned bulk GaN substrates. This approach will simultaneously achieve benefits of vertical-injection laser designs, crystallographically cleaved facets, and reduced threading-defect densities. We will then apply these lasers to quantify contributions of p-type doping to optical loss in UV AlGaN lasers for the first time. We will further explore the potential for magnesium-doped superlattices to enable polarization-field-based activation of holes for enhanced p-type doping. Our overall goal is to apply these advances to demonstrate lasers at < 335 nm, thereby achieving the shortest wavelength mW-class LDs to date.

This project has the potential to advance the state of the art in ultra-violet (UV) laser diode (LD) performance. The work is high risk, given the formidable materials challenges of wide-bandgap semiconductors and proposed innovative approaches that have not been previously realized for UV LDs.

Visible Quantum Nanophotonics

186113 | Year 1 of 3 | **Principal Investigator: A. J. Fischer**

Project Purpose:
Applications for ultraviolet (UV)/visible lasers are many and include free space and underwater communications, solid state lighting, biosensing, free space directed energy, quantum communication, and atomic clocks. All of these applications will benefit greatly from improvements in two key characteristics: electrical-to-optical energy-conversion efficiency, and directability. At one extreme, low-power applications need maximum useful work for minimum energy consumption; at the other extreme, high-power applications are typically heat sink limited at the source and target-localization-limited at the sink.

The key to past improvements in efficiency and directionality has been simultaneous control over electron and photon confinement (in real space) and densities of states (in reciprocal space). Though past improvements have been revolutionary, practical devices use one-dimensional structures: quantum wells for control of electrons and Fabry-Perot-like cavities for control of photons. Even more revolutionary improvements are possible when control is extended to more than one dimension.

In this project, we propose to develop a quantum nanophotonics laser architecture in the visible that enables practical control over electrons and photons in more than one dimension. We propose to control electrons by fabricating quantum dots (QDs) with precision spatial and spectral control. Photons will be controlled using photonic crystals and specifically, we propose to investigate photonic-crystal surface-emitting laser (PCSEL) architectures, again with precision spatial and spectral control. Ultimately, such quantum nanophotonic QD-PCSELs could enable unprecedented efficiency and directability and, thus, wide “forward” fan-out to the applications mentioned above; and wide “backward” fan-out to science questions associated with a new and unexplored regime of mesoscale quantum optics.

Zero-Power Wake-Up Device

173132 | Year 2 of 2 | **Principal Investigator: R. W. Brocato**

Project Purpose:

The pyroelectric demodulator is a microwave/radio frequency (RF) microelectronic component invented at Sandia and covered by Sandia-owned patent. Prior to this project, basic pyroelectric demodulator prototypes were fabricated using bulk materials, and these demonstrated the potential of this device for passive tag applications. However, in order to produce devices that are useful to potential users in the tag and radio frequency identification (RFID) community, it is essential to greatly improve device performance. Key users in the tag community at Sandia have given us a goal of -70 decibel-milliwatts (dBm) for minimum device sensitivity, versus our initial bulk device measurement of -23 dBm. To achieve this set goal, we must first develop a process for monolithic device fabrication using microelectromechanical systems (MEMS) fabrication techniques. Since the pyroelectric demodulator is a thermal device rather than a semiconductor device, it also requires fabricating devices with successively smaller physical sizes and progressively more tightly controlled thermal pathways. Then, we need to answer fundamental questions about what is ultimately achievable in fabricating these devices. We do not understand the theoretical underpinnings of noise sources that will limit optimum device performance. Our development work is necessary both to provide a framework for understanding factors that determine the voltage responsivity, and for providing a basic understanding of noise sources that will determine the noise equivalent power.

Summary of Accomplishments:

We produced pyroelectric demodulators using a succession of processing and design improvements while also advancing our understanding of the underlying science and engineering of such devices. Specifically, we met the four objectives called out in our project. First, we packaged and tested legacy devices and established a performance baseline by testing existing microwave diodes, the closest competitor to the unique pyroelectric demodulator. Second, we created a succession of improved lead zirconate titanate-based device designs and processes, leading to both improved devices and an improved understanding of the science underlying those devices. Third, we prepared lithium niobate wafers using wafer bonding and crystal-ion-slicing to obtain device-suitable material. Fourth, we created pyroelectric demodulators with good responsivity performance using lithium niobate.

The responsivity performance of the devices that we produced falls short of the numerical goals that were initially proposed. However, the performance of the devices that we fabricated was greatly improved by our proposed processing and design improvements. We outlined a series of steps that can be pursued to further improve device performance, and to likely meet the numerical goals.

Significance:

We demonstrated that the input carrier frequency bandwidth of the pyroelectric demodulator can be made to be extremely wide, without a fundamental limit. This implies that the device should be usable at millimeter and submillimeter wave frequencies. Also, we demonstrated that the pyroelectric demodulator has the unique property of a wideband and adjustable modulation bandwidth. This enables the device to be used in a two stage zero-power receiver, as explained in our patent application. This also enables the device to have a unique advantage for wireless, unpowered sensors.

These concepts are receiving strong interest from the defense community, because they could help enable communication to remote devices by reducing the logistical demands and burdens of battery usage. Batteries have been a problem in many areas for the defense community in recent years. Recent results released from the Army Research Laboratory Public Affairs Office indicate that batteries make up 20 percent of the weight soldiers carry in theater, and an infantry battalion spends more than $150,000 per year on batteries. Our goal is to reduce this problem by eliminating the need for batteries in passive RFID and sensor tags.

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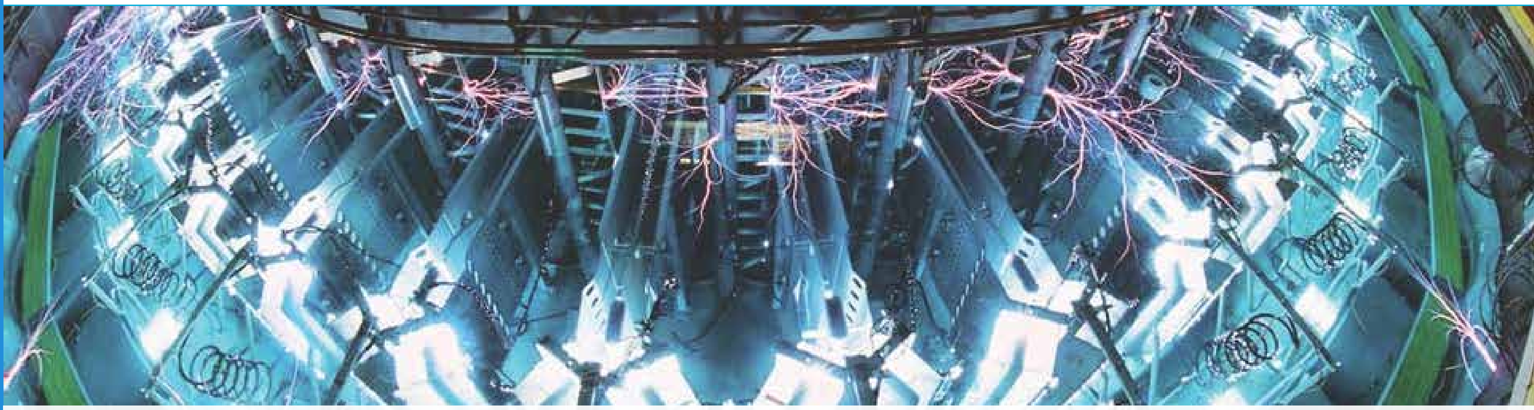

Radiation Effects & High Energy Density Sciences

The Radiation Effects and High Energy Density Science Investment Area seeks to advance science and engineering in the areas of radiation effects sciences, dynamic material properties, high energy density science, and pulsed power science. The goal of the radiation effects sciences area is to ensure that engineered systems are able to operate as intended in radiation environments they encounter, with a particular interest in developing pulsed power technologies, innovative experimental techniques, and novel diagnostics that could scale to higher energy drivers.

Projects

An ion-Neutron Electron-Gamma SIMulation System for Radiation Testing of Optical Components for Weapons Systems - NGOSIM

173192 | Year 2 of 3 | **Principal Investigator: B. L. Doyle**

Project Purpose:

The NGOSIM project is developing a capability on the Ion Beam Laboratory Tandem accelerator facility to quantify the performance degradation of optical components when exposed to hostile radiation environments. The Qualification Alternatives to the Sandia Pulsed Reactor (QASPR) program has demonstrated the utility of using high-energy ions and electrons to simulate the displacement damage and ionization in electronics caused by neutrons and gamma rays at fluxes previously only available on SPR-III and HERMES-III (much larger historical facilities, now retired). This year, the instrumentation in the QASPR-II and III endstations has been modified to enable the diagnostics of optoelectronic components. We performed ion-only exposures (MeV C, Si, Ge, and O) on laser-illuminated GaAs rad-hard photovoltaic (PV) diodes, and measured the degradation of the induced photocurrent. Plots of charge collection efficiency (CCE) vs. the 1-MeV-equivalent-neutron-fluence of the ions matched similar measurements made on the Annular Core Research Reactor. By comparing CCE measurements to analytical calculations made with the Hecht equation and to computer simulations performed with the Silvaco ATLAS drift/diffusion solver, we have discovered that CCE degrades with the square root of fluence in partially depleted photodiodes at low fluences. We are studying the relationship between CCE degradation at high fluences and the reduction of both recombination lifetime and mobility in accordance with the Messenger-Spratt equation. Also this year, we have irradiated photodiodes simultaneously with an ion beam and with an electron gun, thus simulating the displacement damage caused by neutrons and the ionization effects caused by electrons generated through Compton scattering of gamma rays. The development of a new NGSIM-O irradiation capability at Sandia will be the first of its kind to experimentally measure the response of optical devices to mixed neutron and gamma irradiations that are independently adjustable in time and magnitude. This year, we will also study optical absorption degradation in irradiated optical waveguides.

Application of Enhanced Photocurrent Models

181198 | Year 1 of 3 | **Principal Investigator: D. A. Black**

Project Purpose:
The original purpose of this work was to explore the capabilities and limitations of several analytic photocurrent models, as applied to dose rate effects in semiconductor devices and circuits. Understanding the effects of photocurrent in stockpile circuits and application specific integrated circuits is critical for characterizing weapon performance in hostile environments. Circuit simulation plays an important role in enhancing that understanding.

A thorough review of all previous compact models and correlated data revealed the current models were dubious at best. Reviewing the calibration parameters for CMOS7 and the heterojunction bipolar transistors of interest, a Phenomena Identification and Ranking Table (PIRT) was completed for CMOS7 and was started for JAZZ CMOS. The A-K model was also not implemented fully into the simulation tools; therefore, exercising of the model was unavailable for completion. Resulting from the PIRT and the extensive review of all the previous calibration efforts, documents and test/calibration circuits established that the models were done against a background of uncertainty regarding the magnitude of the parasitic effects in the test structures. It is likely that the test structures used in those calibrations had the highest parasitic effects of all the test structures now available. In addition, regarding the use of (in hindsight) questionable calibrations, the analyses appear to not explicitly include on-chip parasitics.

To conclude, because of the historically uncertain understanding of the test structure physics, and the questionable accuracy of photocurrent model calibration, the validation simulation work done in previous years is of dubious value.

We developed a dual double-exponential model that produced very good results to 90 nm CMOS data and to Sandia's CMOS7 nmos and pmos Silicon-on-Insulator (SOI) technology.

Cavity Electron Density Measurements within Pulsed Radiation Environments

177967 | Year 2 of 3 | **Principal Investigator: K. S. Bell**

Project Purpose:

The purpose of the project is to create a fiber-optic-based diagnostic that is able to measure the line-integrated electron density as a function of time and chord position within a plasma, with highly limited diagnostic access, which is driven by the Z Facility at Sandia. In order to successfully collect relevant data, the diagnostic should be malleable enough to couple to remote spaces within an experiment on the Z machine, robust enough to survive the harsh driving radiation and electromagnetic interference, have a fast time response (nanosecond), and sensitive enough to extend the measurement below 1e16 electrons per cubic centimeter. Of these, the most challenging aspect will be extending the measurement to low densities using a fiber optic system. Additional challenges exist in the interpretation of the measurement due to the possibility of several complex conditions existing within the plasma under study. These could include large currents (kiloamperes), significant electric and magnetic fields, wide electron temperature distributions (including relativistic electrons), and neutrals. The initial design incorporates existing 1550 nanometer wavelength laser and fiber optic technology, with a focus on developing novel analysis techniques to extend the diagnostic sensitivity beyond the nominal factor of 1/200 of a fringe for fiber optic based interferometry. The initial design has been built and tested in a surrogate test environment that produces less than one phase shift as a result of changes in density. The minimal changes, coupled with other mechanisms that appear in the data, such as vibration, have provided the information necessary to develop analysis tools. Planning has begun to transfer the diagnostic to Z, with concurrent modeling of the plasma conditions to correctly interpret the measurement at Z.

Compact Models for Defect Diffusivity in Semiconductor Alloys

180932 | Year 1 of 3 | **Principal Investigator: A. F. Wright**

Project Purpose:
Predicting the transient effects of short-pulse radiation in semiconductor devices is for weapons component surety missions. For instance, predicting the diffusion of radiation-induced point defects is important to Sandia's Qualification Alternative to the Sandia Pulsed Reactor (QASPR) program because defect diffusion mediates transient gain recovery in QASPR devices. Recently, the material of choice for radiation-hard semiconductor devices has begun to shift from silicon to III-V compounds such as GaAs and InAs. One benefit of this shift is that it allows engineers to optimize device designs by using alloys such as InGaAs. However, the computer codes currently used to model transient radiation effects will also need to be modified because they presume that defect properties (charge states, energy levels, and diffusivities) do not change with time. This is not the case in an alloy, since the energy and properties of a defect depend on the types of atoms near it, and hence on its location in the alloy. In particular, radiation-induced defects are initially created in nearly random locations, but as they diffuse through the alloy, the distribution of local environments–and hence the defect energies and properties–evolves with time. To incorporate these important effects into codes used to model transient radiation effects, we propose to use results from density functional theory and kinetic Monte Carlo to develop compact models that accurately describe the time dependence of defect energies and properties in alloys.

This project will advance the fundamental understanding of the complexity of defect diffusion in semiconductor alloys and synthesize the key new physics into compact models that can be then used in current device-modeling codes. Success will thereby support the expanded use of alloys in radiation-hard devices.

Creating the Foundation of Next-Generation Pulsed Power Accelerator Technology

173191 | Year 2 of 3 | **Principal Investigator: B. Stoltzfus**

Project Purpose:

This past year, we have made significant progress developing and testing the "brick," which is the foundational building block of future pulsed power machines. Using two separate linear transformer driver single brick testers, one at ASR and one at Sandia, we have conducted 100,000 full voltage brick shots this past year, which focused on Kinetech switch development. Also, using the Thor-1 test stand, we have conducted 5,000 full voltage shots to evaluate the switches, capacitors, and cables for use on larger Thor machines. Next year, we plan to expand this testing effort to include two more automated development test stands.

Sandia continues to work on nanocomposite core material, which has high susceptibility and saturation magnetization, yet exhibits a complete absence of hysteresis. A full size core built of such material could revolutionize pulsed power machines, which utilize magnetic cores. The team initially fabricated a 20 mg sample for evaluation but was able to scale this up to 10 g, which was a 500-fold increase. The goal for next year is to increase this sample size again by a factor of 50 to the half kg engineering scale.

Voss Scientific continues to develop a large-scale plasma model of the baseline Kinetech switch. Gas switches such as the Kinetech switch are arguably the most important component in our pulsed power machines and, as such, are worthy of our best efforts to better understand them. Voss' work under this project is a step in that direction, and this year they conducted the most complex simulations to date. The preliminary results were encouraging and both the switch resistance and switch inductance values obtained from simulation were reasonable. Next year, we plan to conduct simulations at even higher pressures, which will increase the gas density and frequency of interactions.

Direct Observation of Electrothermal Instability Structures in the Skin Layer of an Intensely Ohmically Heated Conductor

178661 | Year 2 of 2 | **Principal Investigator: T. J. Awe**

Project Purpose:

Magnetically driven implosions (MDIs) on the Z Facility assemble high energy density plasmas for radiation effects and inertial confinement fusion experiments. MDIs are hampered by the Magneto-Rayleigh-Taylor (MRT) instability, which can grow to large amplitude from a small seed perturbation, resulting in reduced stagnation pressures and temperatures. The liners used in Magnetized Liner Inertial Fusion (MagLIF) experiments contain astonishingly small (~10 nm RMS) initial surface roughness perturbations; nevertheless, unexpectedly large MRT amplitudes are observed experimentally.

A prevailing hypothesis suggests the electrothermal instability (ETI) provides a perturbation that exceeds the initial surface roughness. A condensed metal resistivity increases with temperature. Locations of locally higher resistivity undergo increased Ohmic heating, resulting in locally higher temperature, and thus still higher resistivity. Such unstable temperature growth produces density perturbations when the locally overheated metal changes phase. These density perturbations seed MRT growth. ETI seeding of MRT has thus far only been inferred by evaluating MRT amplitude late in the experiment. A direct observation of ETI is vital to ensure our simulation tools are accurately representing the seed of the deleterious MRT instability.

Experiments will be conducted on the Zebra pulsed power driver at the University of Nevada, Reno. We intend to directly measure the ETI structure formed on ohmically heated thick conductors using a high resolution, high sensitivity, near-IR/visible framing camera. To our knowledge, this would be a first-of-its kind measurement. Targets must be extremely smooth and metallic structure must be well characterized in order to differentiate physical mechanisms that may drive ETI.

We intend to (for the first time) directly observe the onset of ETI. Low-temperature ETI has unknown spatial scales and temperature gradients. The risk associated with measuring this not-well-understood phenomenon is mitigated by designing a high-resolution diagnostic with good near-infrared sensitivity and efficient light collection. Data will fill a gap in understanding that has persisted for many decades.

Summary of Accomplishments:

Our goal was to directly observe ETI growth from a metal pulsed with intense current. We required: 1) load hardware that would avoid the relatively high temperature nonthermal plasma production common to high voltage pulsed power drivers, so that the low intensity emission associated with low-temperature ETI phenomena could be observed, 2) development of a variety of loads with high quality (but variable) surface finishes and alloys so that various hypothesis on what drives ETI could be tested, 3) development of a high resolution gated imaging system that capable of studying ETI phenomena, and 4) executing experiments that could observe ETI strata (resistivity increasing with temperature) and ETI filaments (resistivity falling with temperature; plasma state). While analysis is ongoing, all requirements were met. Over 60 experiments were executed on the Zebra accelerator, using a load hardware platform that has been rigorously tested and has demonstrated mitigation of nonthermal plasma production. We evaluated two aluminum alloys, namely Al 6061 (with Cu/Si/Mg inclusions) and high purity 5N Al. Using both alloys, we tested (relatively rough) conventionally machined loads, diamond turned loads, and electropolished loads. The inclusions in the 6061 alloy were shown to drive overheat instabilities. If surfaces were too rough, ETI strata formed early in the experiments. These observations were made using a newly designed and constructed two-frame gated optical imager with 3 micron/2 ns spatial/temporal resolution. The instrument had sufficient sensitivity to capture emissions from sub-eV metal. While we learned that that condensed metal ETI structures were highly influenced by the alloy and surface finish under study, after plasma formed, the ETI filaments that formed were independent of such target characteristics. Finally, loads coated with 70 microns of parylene demonstrated dramatically different surface heating characteristics and developed markedly different ETI structures.

Significance:
We have made the first detailed measurements of ETI formation from an intensely ohmically heated metal carrying current in a skin layer. ETI structures were captured with 3-micron resolution; such data provides a new challenge for state-of-the-art magnetohydrodynamic (MHD) simulations, which typically ignore the ETI physics, as metals transition through the liquid and liquid/vapor states. Validating our simulation tools against this dataset will greatly advance pulsed power sciences. Once this physics is properly incorporated into our simulations, our predictive capability for magnetically driven implosions will be greatly enhanced, advancing ICF and aiding in associated national security missions.

Electrical Breakdown Physics in Photoconductive Semiconductor Switches (PCSS)

165732 | Year 3 of 3 | **Principal Investigator: A. Mar**

Project Purpose:

Advanced switching devices with long lifetime will be critical components for linear transformer drivers (LTDs) in next-generation accelerators. LTD designs employ high switch counts. With current gas switch technology at ~10e3 shot life, a potential game changer would be the development of a reliable low-impedance (<35 nH) optically triggered compact solid state switch capable of switching 200 kV and 50 kA with 10e5 shot life or better. Other applications of this technology are pulse shaping programmable systems for dynamic material studies (Z-next, Genesis, THOR), efficient pulsed power systems for biofuel feedstock, short pulse (10 ns) accelerator designs for the Defense Threat Reduction Agency, and sprytron replacements in nuclear weapons (NW) firing sets.

Optically triggered photoconductive semiconductor switch (PCSS) devices have been developed at Sandia for compact, reliable fast switching of electrical power. The shot life of a PCSS is predominately dependent on the switched charge as opposed to the switched voltage, as shown in high-power PCSS demonstrations up to 220 kV and 8 kA. Therefore, the current can be scaled with long lifetime by initiating multiple parallel filaments in multiple parallel devices.

We are pursuing exploratory PCSS designs to switch megavolt and 10 s–10 0s kA systems, supported by developing an improved model of the electrical breakdown physics in the device. This will impact filament diameter, peak current density, packing density (spacing), and optical trigger energy, which are the key parameters for scaling PCSS-based systems to the megampere regime. These higher-risk, but higher-payoff approaches have a high potential payoff potential for a range of important applications.

With a novel new vertical filament switch design, this project has demonstrated the path to develop PCSS switching modules capable of 200 kV and 5 kA current that can be stacked in parallel to achieve 100 s of kA with 10e5 shot lifetime.

Summary of Accomplishments:

- High-current density gallium arsenide (GaAs) contacts: We designed an improved metal alloy layer design of the contacts to incorporate a much thicker evaporated Au leading edge, and recalibrated the process for rapid thermal annealing to achieve better ohmic properties. We increased the lifetime of the contacts in the PCSS by an order of magnitude. In lifetime testing, there were 3.7e4 shots obtained, switching 100 A in a single filament.
- High-voltage multi-filament triggering: We also discovered the important relationship between laser rise time and beam uniformity in the production of multiple current-sharing filaments. We demonstrated two techniques for triggering multiple current-sharing filaments. This includes PCSS triggering tests using microlens arrays, and rib-etched gaps in PCSSs operating at 75 kV.
- PCSS Trigger Generator: Using PCSS, we achieved triggering of 100 kV sparkgap (Kinetech type) switches and demonstrated the potential of PCSS to impact triggering of pulsed power machines, developed for pulsed power for high power microwave (HPM).
- Novel Switch Structure–Vertical PCSS: We demonstrated a new switch design that is an alternative to in-plane (surface) geometry for multi-filament current sharing–a switch that incorporates contacts on both sides of the wafer and initiates 2D arrays filaments between the two contacts. This enables 2D scaling of filaments and total current and allows operation approaching the breakdown of the bulk GaAs while operating in air. We completed an initial design using 600 μm thick (conventional thickness) wafers. The new switches achieved: ~1e5 shots at 0.4 kA, 35 kV/cm (2.2 kV), test terminated with no detectable degradation; and 1.4e3 shots at 1 kA, 75 kV/cm (4.5 kV), limited by high-field breakdown of thin GaAs substrates. We anticipate potential game-changing, large lifetime improvements at multi-kA/kV operation with vertical switches fabricated from thicker designs.
- PCSS developments have spawned a Small Business Technology Transfer program for vertical-cavity surface-emitting laser (VCSEL) trigger laser integration, and we are also investigating other follow-on applications of the technology.

Significance:

Next-generation accelerators are an essential tool for stockpile stewardship and development of high yield fusion for DOE/NNSA. Development of PCSSs as a key enabling technology for such systems will impact these missions well into the future. PCSS technology advantages include: lower cost, fiber optic control, lower jitter, faster rise time, and lower inductance. PCSS devices are also important for NW systems and improved reliability.

This project has yielded an important novel variation of the PCSS design that is demonstrating game-changing improvements in switching efficiency, voltage capability, and lifetime. The impact could be far-reaching, including pulsed power, NW, HPM, and others.

Refereed Communications:

A. Mar, "Advanced High-Longevity GaAs Photoconductive Semiconductor Switches," presented at the *Seventeenth Annual Directed Energy Symposium*, Anaheim, CA, 2015.

Evaluation of Warm X-Ray Bremsstrahlung Diodes on Z

165738 | Year 3 of 3 | **Principal Investigator: V. Harper-Slaboszewicz**

Project Purpose:

The purpose of the project is to create a new type of warm x-ray bremsstrahlung source that could be fielded on the Z accelerator. Enhanced capability to understand and simulate nuclear weapons effects has become increasingly important as the stockpile is updated and data from previous underground tests becomes less relevant. Warm x-ray simulation sources have been developed at Defense Threat Reduction Agency facilities and on the Saturn simulator to support these studies. However, the intensity and exposure volume available with existing simulators is not sufficient to access all relevant exposure conditions. The Z facility has much greater current capability than the existing simulators and, therefore, should be able to drive higher intensities and exposure volumes than existing sources. However, the drive voltage and pulse shape on Z are incompatible with present bremsstrahlung sources. Innovative bremsstrahlung diode designs will be required to produce a usable source on Z. This project will develop the technical basis for a massively parallel bremsstrahlung diode that is scalable to Z.

Summary of Accomplishments:

We evaluated the used of graphite anode rods to delay the radiation pulse from a rod pinch diode. We characterized the impedance behavior of ultra-thin-wall hollow tantalum small aspect ratio rod pinches to enhance warm x-ray output. We showed that pulsed power penetrated to the center of an array of closely coupled small aspect ratio rod pinches. We developed and demonstrated an approach to minimizing interaction between adjacent rod pinches. We showed, first by simulation and then by experiment, that with appropriate design, losses due to magnetic nulls in the feed could be eliminated. We showed that the radiation pulse from a 51-rod-pinch array was essentially uniform across the array. We proved by example that it is feasible to design and assemble a massively parallel closely coupled small aspect ratio rod pinch array with the very tight tolerances required for warm x-ray bremsstrahlung operation. We calculated the radiation spectrum and dose characteristics of rod pinches of various material configurations, which allow design of the array configuration to achieve the desired dose profile. We evaluated the use of a central plasma-filled switch to shorten the radiation pulse from a rod pinch array.

Significance:

We established a major part of the technology base required to field a warm x-ray bremsstrahlung diode on Z, which would represent a significant enhancement to the range of radiation sources available for radiation effects sciences experiments. Such a diode would enable radiation effects sciences experiments using fluence unavailable since the end of underground testing in an important part of the radiation spectrum.

Refereed Communications:

V.J. Harper-Slaboszewicz, J. Leckbee, N. Bennett, E. Madrid, D. Rose, C. Thoma, D.R. Welch, P.W. Lake, and A.L. McCourt, "Parallel Operation of Multiple Closely Spaced Small Aspect Ratio Rod Pinches," *IEEE Transactions on Plasma Science*, vol. 43, pp. 422-432, 2015.

Exploring New Frontiers in Kinetic Physics in Inertial Confinement Fusion

165746 | Year 3 of 3 | **Principal Investigator: P. Schmit**

Project Purpose:

Progress in magnetic confinement fusion research has relied on a nuanced understanding of the kinetic features of the hot fusion fuel. Kinetic processes are those requiring detailed knowledge of the evolution of the distribution of ion and/or electron velocities in hot plasma. Inertial confinement fusion (ICF) experiments exemplify physical systems undergoing rapid evolution in time and space, where the assumption of local thermodynamic equilibrium is often dubious, and a whole host of heretofore undiagnosed and/or poorly characterized kinetic effects could play a significant role. For both historical and practical reasons, the immense complexity exhibited by ICF systems has meant most modeling efforts for designing and diagnosing experiments ignore or grossly approximate the influence of some kinetic effects, while many other effects remain unidentified.

The central objective of this Truman Fellow research is to develop theory and modeling capabilities that shed light on new and exciting kinetic physics regimes that could be exploited, or might already be present, in ICF systems. Deploying new tools to accurately resolve the physics in such regimes requires, among other things, the exceptional computational resources unique to the NNSA laboratory complex. The discovery of new physics and the development of new conceptual and design tools will both enhance Sandia's operational expertise in the execution of its own ICF program and potentially impact the broader, national ICF and stockpile stewardship mission being conducted within the NNSA laboratory complex.

This project represents an exploratory and highly technical effort in basic and applied physics research with potential payoffs for Sandia, and the broader national ICF program, that are easy to imagine but difficult to quantify precisely.

Summary of Accomplishments:

Numerous and diverse technical accomplishments were achieved during the course of this project. The primary accomplishments include:

- In collaboration with colleagues at LANL, we developed several analytical and numerical modeling capabilities describing the deleterious impacts of nuclear fusion reactivity reduction due to the "Knudsen-layer tail-ion loss" mechanism in multiple heretofore unexplored physics regimes, including magnetized fusion plasmas (of particular relevance to the Sandia-led MagLIF fusion effort) and plasmas with broken degrees of spatial symmetry (of relevance to the broader national ICF and nuclear weapons efforts)
- In collaboration with other Sandia researchers, we developed conceptual models and corresponding numerical tools to explore the relationship between secondary nuclear reactions in magnetized ICF experiments and the extreme magnetic fields present in those experiments during fusion burn. The novel techniques developed during the course of this investigation were applied to groundbreaking MagLIF experiments that took place at Sandia's Z Facility, providing the first convincing evidence that a significant fraction of the fusion products generated in the first successful experiments were indeed magnetized, the first time this has ever been accomplished in the laboratory. These techniques represent the first and only known method to diagnose extreme magnetic fields in pulsed-power-driven magnetized ICF experiments.
- In collaboration with colleagues at the Naval Research Laboratory, we developed a new analytic formalism to understand the pervasive and destructive effects of Rayleigh-Taylor hydrodynamic instabilities (RTI) prevalent in all imploding ICF experiments. This research expands on several decades of theoretical work on this broad topic and unifies a number of disparate works across multiple platforms and perspectives throughout the literature. The theoretical tools have led to and inspired investigations, which are still in progress, exploring novel experimental platforms exhibiting substantially reduced RTI that could be tested on Sandia's Z Facility in the near future.

Significance:
This work has advanced the science of cutting-edge ICF laboratory experiments across multiple technical fronts. The work on Knudsen layer phenomena represents significant contributions to a vibrant national effort exploring such effects on the National Ignition Facility and other ICF laboratories. The work on secondary nuclear reactions has proven to be a vital component of Sandia's analysis of its rapidly advancing MagLIF effort. The work on hydrodynamic instabilities advances an already mature and ubiquitous scientific field of substantial practical importance to all ICF research. Furthermore, the individual projects each represent the culmination of multiple vibrant inter- and intra-institutional collaborations.

Refereed Communications:
M.R. Gomez, S.A. Slutz, A.B. Sefkow, K.D. Hahn, S.B. Hansen, P.F. Knapp, P.F. Schmit, C.L. Ruiz, D.B. Sinars, E.C. Harding, C.A. Jennings, T.J. Awe, M. Geissel, D.C. Rovang, I.C. Smith et al., "Demonstration of Thermonuclear Conditions in Magnetized Liner Inertial Fusion Experiments," *Physics of Plasmas*, vol. 22, p. 056306, April 2015.

M.R. Gomez, S.A. Slutz, A.B. Sefkow, D.B. Sinars, K.D. Hahn, S.B. Hansen, E.C. Harding, P.F. Knapp, P.F. Schmit, C.A. Jennings, T.J. Awe, M. Geissel, D.C. Rovang et al., "Experimental Demonstration of Fusion-Relevant Conditions in Magnetized Liner Inertial Fusion," *Physical Review Letters*, vol. 113, p. 155003, October 2014.

P.F. Schmit, P.F. Knapp, S.B. Hansen et al., "Understanding Fuel Magnetization and Mix Using Secondary Nuclear Reactions in Magneto-Inertial Fusion," *Physical Review Letters*, vol. 113, p. 155004, October 2014.

M.R. Weis, P. Zhang, Y.Y. Lau, P.F. Schmit, K.J. Peterson, M. Hess, and R.M. Gilgenbach, "Coupling of Sausage, Kink, and Magneto-Rayleigh-Taylor Instabilities in a Cylindrical Liner," *Physics of Plasmas*, vol. 22, p. 032706, March 2015.

S.B. Hansen, M.R. Gomez, A.B. Sefkow, S.A. Slutz, D.B. Sinars, K.D. Hahn, E.C. Harding, P. F. Knapp, P.F. Schmit, T.J. Awe, R.D. McBride, C.A. Jennings, M. Geissel, A.J. Harvey-Thompson, K.J. Peterson, D.C. Rovang et al., "Diagnosing Magnetized Liner Inertial Fusion Experiments on Z," *Physics of Plasmas*, vol. 22, p. 056313, May 2015.

P.F. Knapp, P.F. Schmit, S.B. Hansen, M.R. Gomez, K.D. Hahn, D.B. Sinars, K.J. Peterson, S.A. Slutz, A.B. Sefkow, T.J. Awe, E. Harding, C.A. Jennings, M.P. Desjarlais et al., "Effects of Magnetization on Fusion Product Trapping and Secondary Neutron Spectra," *Physics of Plasmas*, vol. 22, p. 056312, May 2015.

Extending the Accessible Range of Strain Rates on Z using Continuously Graded-Density Flyers Fabricated using Sputter Deposition

180933 | Year 1 of 2 | **Principal Investigator: D. P. Adams**

Project Purpose:

While the research of dynamic materials properties using Sandia's Z machine has been tremendously successful over the last 15 years, there are limitations. One is the range of strain rates accessible in off-Hugoniot experiments (e.g., when measuring material strength at high pressures). Present experiments on Z are limited to strain rates ~105 s^{-1}. Experiments at laser facilities like the National Ignition Facility (NIF) operate at higher rates of ~107 to 108 s^{-1}, resulting in a strain-rate gap between Z and NIF. This strain-rate gap poses challenges for cross-platform validation of experimental results.

The purpose of the present work is to close the strain-rate gap by developing a platform for Z ramp compression at two to three orders of magnitude faster rate than currently available. The present approach to Z ramp compression is limited in strain rate by the current pulse rise time: obtaining markedly shorter rise times is not currently possible. Instead, we explore a different approach. Our team will determine whether a thin, graded-density flyer coating provides suitable generation of high loading and unloading strain rates. The leading-edge research component of the project is the reliable production of low-stress, graded-density, impactor films with uniform thicknesses of 40-60 μm, which is a length scale that lies in between the traditional range of vapor deposition (<1 μm) and thermal spray (>500 μm). A successful outcome of the proposed research would lead to a significantly extended capability on Z for materials experiments, including the first cross-platform validation of strength at extreme strain rates.

This project should increase the probability of creating a new platform for experimental/theoretical study. The proposed work is groundbreaking; it should lead to unprecedented high rates of unloading for ramp compression experiments on Z.

Fiber Optic Streak Spectroscopy of Gas Cells in Extreme Radiation Environments

170977 | Year 3 of 3 | **Principal Investigator: K. M. Williamson**

Project Purpose:

An enduring component of Sandia's core mission is to maintain our nation's technological advantages in a rapidly changing environment. An imminent challenge to this mission is the impact of system-generated electromagnetic pulse (SGEMP) on the performance and reliability of complex electronic systems. The physical mechanisms involved with coupling high-energy radiation into, and damaging, critical system components is an area of active research at Sandia.

These experiments utilize high intensity x-rays from z-pinch radiation sources on the Z machine to ionize a shielded gas-filled cell. Indirect sensing of this plasma is presently being conducted with a B-dot sensor that results in a highly averaged measurement of the changing magnetic fields. This research will be directed at the creation of a new diagnostic and analysis technique that will enable more refined characterization of this plasma that is critical for accurate modeling and simulation of the effects of SGEMP.

A major step toward understanding SGEMP is to create a spectroscopic diagnostic and analysis technique with the ability to directly measure plasma emission to characterize the temporal evolution of temperature, conductivity, and density. A shielded silica-core optical fiber will be inserted into the gas cell to capture photon emission from the plasma. The captured emission will be analyzed for blackbody inclination and spectral line transitions to determine plasma characteristics and infer current density within the cavity. Multiple gas cells will be fielded for each experiment. The location and pressure of each cell will be varied to produce a wide range of plasma characteristics.

Summary of Accomplishments:

We demonstrated the effectiveness of the streak visible spectrometer system for measuring emission from a gas cell in an extreme radiation environment. The spectral data captured was the first optical emission measured from this type of SGEMP experiment. The data were carefully analyzed to reveal a correlation between emission intensity and the current density within the cell. Spectral line transitions were observed that indicate the temporal evolution of the plasma temperature and an upper bound of ion density. The material components of these spectral features also suggest techniques for including dopants to allow for more sensitive future investigations.

Significance:

Qualification of new components in complex electrical systems in hostile radiation environments is an ongoing critical need for the NNSA. Experimentally validated results from this project will enhance capabilities to predict component behavior in electromagnetic pulse environments in support of the NNSA mission. Additionally, this project mapped the path to extend this type of investigation for future validation efforts.

High Pressure Pre-Compression Cells for Planetary and Stellar Science

165739 | Year 3 of 3 | **Principal Investigator: C. T. Seagle**

Project Purpose:

Hydrogen and helium are the most abundant elements in the universe and occur in a variety of extreme environments, both natural and man-made. Mixtures of hydrogen and helium exhibit an extraordinary degree of nonideality; the volume of the mixture is not the sum of individual components. The relative 'simplicity' of these elements would suggest theoretical calculations of the properties of the mixture would be accurate; however, major discrepancies in predicted properties exist between different calculation methodologies. Few experimental data are available on the mixture, particularly at high compression.

The difficulty associated with achieving controlled extreme states in H_2-He mixtures arises from the inability to mix homogeneous fluids of the two at ambient pressure. Initial pressures above ~200 MPa are required for a homogeneous mixture at densities relevant for shock compression. In this project, we developed a pre-compression capability to study not only H_2-He mixtures, but other super-critical fluids as well. The initial pressure of these samples is on the order of ~100s MPa; for shock experiments, this results in states at much lower temperatures compared to the principal Hugoniot and compliments Sandia's off-the-principal Hugoniot research.

Achievement of the required initial pressures on samples of reasonable size for gas-gun experiments was the largest challenge, due to the relatively large energy density of pre-compressed samples. Pre-compression cells have been successfully developed to support this initial stress. The pre-compression capability greatly expands Sandia's initial condition control for shock experiments to probe off-the-principal Hugoniot states.

The pre-compression cell was utilized in dynamic testing of super-critical fluids up to projectile velocities of 4.6 km/s. A diagnostic and optical coating scheme was developed and tested. Data return on dynamic shots was excellent. A number of off-the-principal Hugoniot points were obtained, including one 2-stage light gas gun shot on helium at an initial compression of 1.7 times the cryogenic liquid density.

Summary of Accomplishments:

A pre-compression target design was developed for use with gas guns for plate impact type Hugoniot studies. The pre-compression hardware is routinely capable of achieving 450 MPa; higher pressures are possible, but challenging. Static pressures are measured with a ruby fluorescence marker in the sample stack. Samples are large enough to avoid edge waves and maintain uniaxial compression over the course of a dynamic experiment in most cases. Gasses may be sealed in the pre-compression cell at 25,000 PSI using a gas loading system. This prevents collapse of the sample volume on compression. The gas loading system is capable of loading mixed gasses, such as hydrogen-helium mixtures, but is currently limited to nonflammable mixtures (<8.7 mol % H). Low initial sealing success rates with the system (~20%) have improved substantially with experience using the system; we acheived100% sealing success for the last six targets produced, including five helium targets and one 8 mol % hydrogen in helium target.

Several dynamic tests on an air gun were executed with pre-compressed ethanol. Tests utilizing only VISAR often provided a particle velocity, but failed to provide a clear indication of the shock velocity. A combination of velocity interferometer system for any reflector (VISAR) and photonic Doppler velocimetry (PDV) used on later tests provided all necessary information for absolute Hugoniot measurements. A small dynamic dataset on pre-compressed ethanol was obtained and is largely consistent with expectations.

One test on a two-stage light gas gun was successfully executed with an initially 1.7 times compressed (relative to cryogenic liquid) helium sample and an impactor velocity of 4.6 km/s. This shot returned excellent data on both particle and shock velocities. The configuration used for this shot provided a clear demonstration of the robustness of the hardware and diagnostic design and represents a path forward to obtaining off-Hugoniot data on hydrogen-helium mixtures at extreme conditions.

Significance:
In dynamic phenomena, such as explosions, materials are often subject to complex loading paths. Traditional dynamic experiments designed to constrain material response are often limited to particular regions of phase space, which do not always coincide with real-world material trajectories. This research led to a new capability to access regions of phase space at higher compression relative to the shock adiabat by precompressing samples prior to shock loading. This capability allows high accuracy equation-of-state data in previously inaccessible regions to be obtained, providing a mechanism to benchmark theoretical calculations and equation of state models in more relevant regimes.

Implementing and Diagnosing Magnetic Flux Compression on Z

165736 | Year 3 of 3 | **Principal Investigator: R. D. McBride**

Project Purpose:

The Z pulsed power facility offers a unique platform for producing very large magnetic fields (10s–100s MGauss) coupled to very high energy density (HED) plasmas (>>1 Mbar). These extreme states of magnetized matter offer many rich and exciting phenomena for scientific inquiry, as was highlighted by the recent NNSA Research Needs Workshop on high energy density laboratory physics. One interesting and important way to achieve very high magnetic field intensities on Z is through magnetic flux compression. An axially aligned, pre-imposed seed field, Bz0, can be trapped and compressed by a fast (100 ns) imploding liner, where the implosion is driven by the azimuthal Bθ field of the Z power pulse. Flux compression can, in principle, amplify seed fields of ~30 T to more than 10,000 T (100s of MGauss). This phenomenon is exploited by the Magnetized Liner Inertial Fusion (MagLIF) concept currently under development at Sandia. However, our ability to compress flux remains unclear due to poorly understood physics. For example, the Nernst Effect (a thermoelectromagnetic effect) can cause significant flux loss in the presence of strong temperature gradients. The Nernst Effect is included in higher order magnetohydrodynamic theory, but the physics needs to be validated experimentally. Clearly, developing diagnostics to measure these compressed fields is required to assess whether or not adequate compression is achieved.

Producing and diagnosing such intense magnetic fields on Z is nontrivial. We, therefore, propose to evaluate and eventually test on Z the most promising diagnostic methods that have been proven to work on smaller-scale facilities. These methods include Zeeman spectroscopy, miniaturized B-dot loops, Faraday rotation, etc.

Summary of Accomplishments:

We have developed an experimental platform for three independent probe-based diagnostic techniques for measuring vacuum flux compression on Z:

- Small "micro" B-dot assemblies for measuring the dynamic fringe fields above the imploding liner
- Streaked visible Zeeman spectroscopy for measuring the flux compressed magnetic fields down inside the imploding liner
- Fiber-based Faraday rotation for measuring the flux-compressed fields down inside the imploding liner

We have designed two novel micro Bz-dot concepts for measuring the flux-compressed magnetic fields down inside the imploding liner while reducing noise pickup:

- The new "Quad-pack" design uses pickup loops fabricated on printed circuit boards (these have been tested successfully at Cornell University's COBRA pulsed-power facility)
- A novel differential micro Bz-dot probe has been designed and is ready to be fabricated using new multi-material 3D printing capabilities

Liner implosion design work using GORGON and ALEGRA radiation-magnetohydrodynamics codes to ensure compatibility of diagnostics with implosion instabilities

We have developed new simple field solvers and synthetic diagnostics for simulation codes

Significance:

The diagnostics developed for this project are allowing us to test our understanding of magnetic flux compression by comparing experimental and simulated diagnostic output. Additionally, the liner implosion stability studies done for this project have already impacted our magnetized liner inertial fusion program (the stabilizing "cushion" design used by the fully integrated MagLIF program was developed to enable fringe field measurements). The understanding gained by this project is helping us to advance all of our NNSA programs that require radiation-magnetohydrodynamics simulation tools to design cylindrically imploding systems, most notably, the dynamic material properties and inertial confinement fusion programs.

Refereed Communications:

R.D. McBride, K.J. Peterson, T.J. Awe, D.B. Sinars, M.R. Gomez, S. B. Hansen, C.A. Jennings, S.A. Slutz, M.R. Martin, R.W. Lemke, D.E. Bliss, P.F. Knapp, P.F. Schmit, D.C. Rovang, and M.E. Cuneo, "Experiments on Liner Dynamics and Magnetic Flux Compression for MagLIF," presented at the *26th IEEE Symposium on Fusion Engineering*, Austin, TX, 2015.

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Investigating Laser Preheat and Applied Magnetic Fields Relevant to the MagLIF Fusion Scheme

173190 | Year 2 of 3 | **Principal Investigator: A. B. Sefkow**

Project Purpose:

Realizing controlled thermonuclear fusion (i.e., ignition) with an inertial confinement fusion (ICF) concept is important for demonstrating our understanding of atomic behavior at extreme conditions. Ignition has not been achieved yet due to challenging requirements for the traditional, thin-spherical-shell ICF concept. Magnetized Liner Inertial Fusion (MagLIF) is a new economical ICF concept, where a thick cylindrical shell, filled with fuel, is imploded with a pulsed-power driver. MagLIF has gained attention from the ICF community because its key concepts, fuel-preheat and magnetization, may relax the challenging requirements. Preheating the fuel to a few hundred electron volts reduces the compression needed to heat the fuel to ignition-relevant temperatures. Fuel-magnetization can improve ICF performance in two ways: 1) by suppressing thermal conduction to enhance the fuel heating efficiency and 2) by trapping charged particles to induce further fusion reactions.

Initial integrated Sandia Z MagLIF experiments in 2014 showed that fuel preheat and magnetization have a significant impact, but the fusion yield was lower than simulated. One hypothesis is that laser-fuel coupling was not as efficient as simulations suggest. However, to date, there have been very few experimental studies of laser heating and propagation in magnetized plasmas at conditions relevant for MagLIF testing, because the conditions are challenging to produce and diagnose. This makes studies in this parameter space of general interest to the high energy density physics community. This project aims to investigate laser preheat and fuel magnetization by performing focused experiments at major high-energy density facilities including Sandia and the Laboratory for Laser Energetics.

Measuring Plasma Formation, Field Strength, and Current Loss in Pulsed Power Diodes

180935 | Year 1 of 3 | **Principal Investigator: M. D. Johnston**

Project Purpose:
The purpose of this project is to develop and implement a novel diagnostic method to measure localized current flow in high-power diodes, and in particular, the final-feed gap on the Z machine, where presently, current losses of up to 20% occur on some loads. This research, combined with high-fidelity particle-in-cell code development using Sandia's in-house EMPHASIS code, will improve the physics understanding of high powered diodes and increase the predictive capabilities for future, high-current machines. This project plans to measure magnetic fields, as a means to diagnose current flow, in high power diodes using high-resolution visible and ultraviolet spectroscopy. Optical spectroscopy provides valuable information, such as temperature, species densities, plasma velocities, and E- and B-field orientations and strengths, all in a nonintrusive manner. Work of this type on Z is very challenging due to the limited availability of shots and the restrictive lines of sight for the diagnostic. To increase the chances of success on Z, measurements are also being taken on the self-magnetic pinch (SMP) e-beam diode on the Radiograpic Integrated Test Stand (RITS). RITS provides an easier and less costly platform for conducting spectroscopic measurements, with similarly high magnetic fields. Techniques used on RITS will then be applied to Z, which will improve efficiency and increase the likelihood of success. This past year, experiments were carried out on both RITS and Z. The RITS experiments measured magnetic fields, by Zeeman splitting, of in situ contaminant species (carbon and aluminum), while the Z experiments focused on optical hardware development and line of sight access. In addition to this, modeling of the final feed-gap on Z was completed, and the first plasma simulations looking at magnetic fields up to 200 T were performed.

Modeling of Nonlocal Electron Conduction for Inertial Confinement Fusion

173868 | Year 2 of 3 | **Principal Investigator: L. Lorence**

Project Purpose:

This research, in collaboration with the University of Wisconsin-Madison, will advance modeling of nonlocal electron conduction for direct drive inertial confinement fusion (ICF) target implosions. Current capability involves using multi-group diffusion-based theory of "diffusing" higher order moments of the electron distribution function to simulate nonlocal electron thermal conduction. In this research, a new Implicit Monte Carlo-Discrete Diffusion Monte Carlo (IMC-DDMC) numerical algorithm, developed for x-ray transport, will be used to efficiently simulate nonlocal electron conduction. The details of applying this hybrid transport-diffusion theory to electron physics, with its electromagnetic fields, are not obvious. However, the efficacy of the hybrid IMC-DDMC method for computationally efficient transport of x-ray photons appears promising. This study seeks to apply this advanced numerical method to electron physics, with a focus on more accurately including the effects of electric and magnetic fields in this theory. The result would be improved modeling of nonlocal electron conduction, an important ICF phenomenon for target implosions. The work will involve advanced modeling of nonlocal electron conduction in the multi-dimensional radiation hydrodynamics simulation code, DRACO.

Next-Generation Multiscale Plasma Codes

173193 | Year 2 of 2 | **Principal Investigator: M. Martin**

Project Purpose:
Our predictive simulation capability for the modeling of pulsed power driven targets, such as imploding solid liners for magneto-inertial fusion and wire-array z-pinches as radiation sources, is severely limited due to the exclusive use of resistive magnetohydrodynamic (RMHD) codes for the design of experiments. All of the codes (ALEGRA, HYDRA, etc.) used for the design and analysis of Sandia's experiments on the refurbished Z machine depend upon free parameters that are not a physical quantity. These parameters are tuned to experimental results and limit our predictive capability. Our proposed solution is the implementation of an implicit quasi-neutral extended MHD (XMHD) model that correctly treats the transition from collisionless to collisional plasma, maintaining the correct solution in the asymptotic RMHD limits while being computationally feasible for 3D simulation. The end result is a numerically efficient simulation capability without the "knobs" of our current codes and a large step towards a predictive simulation capability for the simulation of pulsed power experiments. It is of utmost importance to add this physics to our design codes, as our current simulation capabilities prevent us from having certainty in our predictions of the scaling of our targets to higher current machines and limit our capability to utilize our codes to better understand the physics of our current experiments.

Summary of Accomplishments:
This project was aimed at developing and verifying algorithms that could eventually lead to an extended-MHD code suitable for multi-material problems in a 3D adaptive mesh refinement setting. We focused on asymptotic preserving discretizations that preserve the numerical order of accuracy over the full range of plasma conditions (collisionless to collisional transition) that exist in practical Z-pinch computations with a vacuum interface. As part of this project, we have developed a semi-analytic verification suite for the full set of two-fluid plasma waves along with various generalized Ohm's law approximations. This verification code allows us to determine, using tabular constitutive values from SESAME (an equation state library) and Lee-More-Desjarlais (LMD), which fluid model is sufficient for the range of plasma parameters we observe in loads on Z. We have also developed an all-shock multi-material Riemann solver compatible with tabular equations of state, along with an asymptotic preserving discretization of the electromagnetic-generalized Ohm's law system that is symplectic in the AP limits of the system. These developments represent substantial progress towards a practical multi-material extended-MHD code, which can correctly model the behavior of both ideal and nonideal low-density plasmas when simulating load behavior on the Z machine.

Significance:
These results represent substantial progress towards a next-generation multiscale plasma code that will enhance the engineering capabilities for target design on the Z machine and advance the science of plasma modeling in pulsed power systems.

Predictive Modeling of Aging and Degradation of Materials in Extreme Environments

181060 | Year 1 of 3 | **Principal Investigator: R. P. Dingreville**

Project Purpose:

Although the US nuclear industry and DOE have a long-standing and well-established role in safety technologies for nuclear reactors, with the anticipated use of mixed oxide fuels and the economics-driven extension of nuclear power plant lifetimes (extension of operation licenses from forty to sixty or perhaps eighty years), materials aging issues are major concerns for long-term viability of current reactors.

Although the effects of temperature and stress on aging degradation of metals have been studied for almost a century, extensive investigations into the effects of radiation have been conducted only recently. Irradiated polycrystalline materials are typically characterized by an increase of the yield strength, a decrease of the ductility, and a decrease of work hardening rate. Such changes in the mechanical properties of an irradiated material are correlated with the material's microstructural changes, ranging from crystalline-to-amorphous transitions to the generation of large concentration of point defects. However, the quantitative relationship between such microstructural changes and macroscopic material behavior is still an open subject under intensive research. This knowledge gap is even greater when radiation is combined with temperature and mechanical loading, which often produces unexpected combined effects. To this end, we propose a suite of hierarchical computational tools, to understand and predict the long-term effects of irradiation, temperature, and stress on material microstructures and their macroscopic behavior. The work is in collaboration with Georgia Institute of Technology.

This project will for the first time: 1) develop a new multiscale capability that can predict irradiation-induced aging of microstructures and the resulting changes in macroscopic mechanical properties of structural materials that can be used to identify and quantitatively assess factors to optimize material performance and 2) elucidate how the complex interaction between irradiation-induced defects and microstructures impact materials aging.

Radiation Susceptibility of Memristive Technologies in Hostile Environments

165741 | Year 3 of 3 | **Principal Investigator: M. L. McLain**

Project Purpose:

Memristive technologies show great promise as a next-generation nonvolatile memory with high endurance (one trillion cycles), long retention (>10 years), and low power (<1 pJ switching). In order to use memristive devices (or memristors) in harsh radiation environments, it is necessary to understand the radiation susceptibility in all possible radiation environments. Currently, it is unknown how memristors will operate in a high dose rate or pulsed neutron/gamma-ray environment, and the radiation response in a total dose or heavy ion environments is not entirely understood. In this project, we will use a combined theoretical experimental effort to probe the radiation response of memristors currently being fabricated by commercial vendors and Sandia's Microsystem and Engineering Sciences Applications Facility (MESA). We will then apply this new knowledge to discover other possible radiation-resistant memristive materials that are candidates to be inserted into the memristor fabrication process at MESA. We are in a unique position to study the radiation susceptibility of potential radiation-hardened memristive technologies, due to an existing cooperative research and development agreement that has provided us with knowledge of commercial vendors' proprietary, leading-edge memristive-memory design. If successful, this work will lead to an enhanced understanding of what governs the radiation tolerance of memristive materials. This will enable the discovery of a radiation-hardened memristive technology to be used in future radiation applications.

The essence of this work is to understand the physics and material properties that lead to radiation-hardened memristors. We will use state-of-the-art radiation test facilities to investigate, for the first time in some cases, the radiation response of memristive devices. The physics of the observed response will have to be fully understood to advance the state of the art to a point at which the next generation of rad-hard circuits can be fabricated. Because there are many unknowns associated with memristors, it may be difficult identifying the primary feature contributing to the radiation hardness of the device.

Summary of Accomplishments:

Over the course of this project, there was steady progress toward the R&D goals projected in the original proposal. In particular, state-of-the-art radiation test facilities were used to explore dose rate and combined neutron/gamma-ray effects in both Sandia and commercially fabricated memristors. The focus was on tantalum oxide (TaOx), but we also studied hafnium oxide and chalcogenide devices. These were the first transient dose rate or pulsed neutron/gamma experiments on any memristive technology. In these experiments, we discovered that the memristive devices might be susceptible to high dose rate ionizing radiation; however, neutrons have a minimal impact on the electrical characteristics of the anion-based devices. In the dose rate experiments, we also discovered that higher resistant devices with high contact/series resistance might be less sensitive to high dose rate exposures. Because of this insight, we attempted to fabricate devices with increased off state and contact resistance.

Displacement damage studies were also conducted using the Ion Beam Laboratory's microbeam and nanoimplanter to target individual sections of the oxide layer. These experiments provided physical insight into the devices and identified the location of conduction channels. Moreover, we were able to produce a spatial map of radiation sensitive regions in the active layer. We also used the Colutron-transmission electron micrograph (TEM) beam line to perform in situ TEM imaging while exposing a TaOx sample to alpha/gold particles. This experiment looked at structural changes due to heavy ion bombardment. In addition to the experimental work, continuum calculations that examined the radiation-induced conductivity in a simple memristive structure were performed. These calculations revealed the internal flow of current in response to transient ionizing radiation. The results also illustrated the need for a physics model for the current flow through the electrical contacts.

Significance:

Radiation-hardened nonvolatile memories are an important technology that is needed in many nuclear weapons applications. It has become a limiting factor in the development of components, since commercially available alternatives are decreasing and/or do not meet the needs of a specific application. This project directly aligns with the DOE NNSA mission of stockpile stewardship and national security through its possible benefit to future lifetime extension programs. There is also strong potential interest from satellite hardening programs and select other DoD systems in need of a radiation-hardened nonvolatile memory.

Refereed Communications:

D.R. Hughart, J.L. Pacheco, A.J. Lohn, P.R. Mickel, E. Bielejec, G. Vizkelethy, B.L. Doyle, S.L. Wofley, P.E. Dodd, M.R. Shaneyfelt, M.L. McLain, and M.J. Marinella, "Mapping of Radiation-Induced Resistance Changes and Multiple Conduction Channels in TaOx Memristors," *IEEE Transactions on Nuclear Science*, vol. 61, pp. 2965-2971, December 2014.

M.L. McLain, H.P. Hjalmarson, T.J. Sheridan, P.R. Mickel, D.J. Hanson, J.K. McDonald, D.R. Hughart, and M.J. Marinella, "The Susceptibility of TaOx-Based Memristors to High Dose Rate Ionizing Radiation and Total Ionizing Dose," *IEEE Transactions on Nuclear Science*, vol. 61, pp. 2997-3004, December 2014.

M.L. McLain and M.J. Marinella, "Overview of the Radiation Response of Anion-Based Memristive Devices," in *Proceedings IEEE Aerospace Conference*, pp. 1-11, 2015.

M.L. McLain, M.J. Marinella, H.P. Hjalmarson, and D.R. Hughart, "Effects of Hostile Radiation Environments on TaOx-Based Memristive Technologies," presented (invited) at the Joint Working Group (JOWOG) 6 Plenary Meeting, Washington DC, May 2015.

M.L. McLain, J.L. Taggart, R. Keith, and M.J. Marinella, "Neutron/Gamma Response of TaOx-Based Memristive Bit Cells," presented at the *Hardened Electronics and Radiation Technology (HEART) Conference*, Chantilly, VA, 2015.

J L. Taggart, M L. McLain, H J. Barnaby, and M N. Kozicki, "Combined Neutron/Gamma-Ray Effects in Ag-Ge30Se70 Based Programmable Metallization Cells," presented at the *Hardened Electronics and Radiation Technology (HEART) Conference*, Chantilly, VA, 2015.

Study of Complex Power Flow Structures using Self-Consistent Particle-in-Cell (PIC) Calculations

181063 | Year 1 of 2 | **Principal Investigator: D. Reisman**

Project Purpose:

The purpose of this project is to develop an optimization procedure for isentropic compression experiments (ICE) that takes advantage of current-adder type accelerator designs. The technical challenges include:

- Developing an optimization method for the current-adder architecture
- Implementing and validating the current-adder circuit model on the ASC code ALEGRA-magnetohydrodynamic (MHD)
- Designing optimized physics loads that take advantage of the current-adder concept while mitigating 3D effects that compromise sample measurement
- Making calculations fully self-consistent with realistic drive and load conditions

Our proposed solution is to develop a gradient-based optimization technique that, given the desired pressure waveform for the experiment, can be used to determine the optimal triggering sequence. We will combine this with 3D MHD calculations that will allow us to determine specific load configurations. By doing this, we will be able to perform "virtual experiments" for a variety of dynamic material load designs. In short, our goal is to develop computational techniques, predictive capability, and high fidelity point designs for Thor, Neptune, and other next-generation current-adder pulsed power accelerators.

Accomplishments this year include:

- We have developed a fast, accurate, gradient-based optimization algorithm for delivering shaped pulsed to current-adder pulsed power machines. This is an advance over present cut-and-try methods that take weeks of circuit calculations and require actual experiments to get adequate results.
- We have developed a set of optimized, high fidelity experimental designs for the Thor accelerator. These include shockless ramp-compression, material-strength, and phase transition experiments.
- We have developed and tested a 3D ALEGRA-MHD model for the central ICE load section of Thor. This includes a self-consistent brick-based circuit model with transmission line elements.

Wavelength Conversion Arrays for Optical and X-Ray Diagnostics at Z

173189 | Year 2 of 3 | **Principal Investigator: E. J. Skogen**

Project Purpose:

Optical diagnostics play a central role in dynamic compression research. Currently, such measurements are limited by the resolution of analog streak cameras, which are employed to record temporal and spectroscopic information in single-event experiments. This project will solve the limitations that streak cameras impose on dynamic compression experiments, while reducing both cost and risk by utilizing standard high-speed digitizers that have the capability to store 100 times more data than streak cameras. The missing link is the capability to convert the set of experimental (visible/x-ray) wavelengths to the infrared wavelengths utilized by standard telecommunication fiber and components.

Although infrared-to-infrared wavelength converters exist, until now, visible-to-infrared conversion technology has not been needed. Furthermore, the characteristics required of the visible-to-infrared wavelength converter far exceed the telecom standards for wavelength conversion in terms of dynamic range, linearity, and low-frequency cut-off. Beyond the specifications, another technical challenge is the hybrid integration of differing semiconductor materials: those that respond to visible wavelengths and those capable of generating infrared wavelengths. In order to be successful, we are leveraging the expertise of Sandia's photonic integrated circuit technology and the Microsystems and Engineering Sciences and Applications infrastructure to develop a chip-scale linear array of visible-to-infrared wavelength conversion circuits: 32+ wavelength channels capable of recording over several microseconds with >1 GHz bandwidth. If successful, we will bridge the technological gaps, demonstrate the solution, and provide a clear path toward reducing cost and risk, while improving experimental capability and versatility. This project will greatly expand diagnostic capabilities in high energy density science experiments. Immediate impacts will pertain to visible optical spectroscopy (pyrometry, reflectivity, etc.) at Z; additional work could permit ultraviolet and x-ray measurements as well.

Z-Pinch X-Ray Sources for 15-60keV

165733 | Year 3 of 3 | **Principal Investigator: D. Ampleford**

Project Purpose:
The purpose of this project focused on developing higher photon energy x-ray sources than are currently available on Sandia's Z machine. By using emission lines produced by inner-shell ionization, we were able to create high photon energy x-ray sources (>15 keV) that are brighter than those that can be produced by typical thermal K-shell line emission. In experiments, we demonstrated the ability of z-pinches to produce 22 keV line emission using K-alpha radiation from a silver wire array z-pinch. We have developed methods capable of diagnosing x-ray emission on Z up to one mega-electron-volt and have been developing a Faraday cup to characterize energetic electrons in experiments on Z. Simulation tools are being developed to model energetic electrons within z-pinch plasmas, and have provided insight into the mechanisms that allow intense emission from inner-shell emission lines.

Summary of Accomplishments:
We have demonstrated the trends in thermal and nonthermal emission as a function of K shell energy continue up to at least 22.2 keV (Ag Kα) in wire arrays. Additionally, we established diagnostics for >15 keV photons on Z. Experiments have improved the x-ray pulse shape of >15 keV sources by using larger diameter arrays with higher mass. We have performed the first simulations of Kα emission in wire array z-pinches by using particle tracking in post-processed magnetohydrodynamics simulations. We have performed an initial experiment using sources at 59 keV (tungsten wire array).

Significance:
We have demonstrated the favorable scaling of nonthermal radiation sources, potentially allowing x-ray sources on the Z generator up to 59 keV. This project has significantly advanced the understanding of nonthermal K-alpha emission in z-pinches, which is necessary for any future work on >15 keV x-ray sources.

New Ideas

The New Ideas Investment Area aims to position Sandia to anticipate and respond to national security challenges (both now and in the future) by supporting high risk new ideas that have the potential to be transformational; for example, those with long time horizons, potentially high but as yet uncertain mission impacts, or nascent research in a new field that may in the future become transformational for our mission. It is intended to support leading-edge research that is outside Sandia's current research focus areas, but that may lead to breakthroughs in science and technology that could profoundly impact our national security mission.

Projects

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Can Symmetry Transitions of Complex Fields Enable 3D Control of Fluid Vorticity?

184377 | Year 1 of 1 | **Principal Investigator: J. E. Martin**

Project Purpose:

Methods of inducing vigorous noncontact fluid flow are important to technologies involving heat and mass transfer and fluid mixing, since they eliminate the need for moving parts, pipes and seals, all of which compromise system reliability. Unfortunately, noncontact flow methods are few, and have limitations of their own. Natural convection requires both gravity and a destabilizing thermal gradient. Magnetohydrodynamics requires the injection of large currents subjected to immense magnetic fields. Thermomagnetic convection in ferrofluids requires gravity, a destabilizing thermal gradient, and immense magnetic field gradients. We have discovered several methods of inducing noncontact fluid flow that do not require gravity or a thermal gradient. All that is required is a time-dependent magnetic field of extremely modest strength, ~50 Gauss. Such fields can create flow lattices, vortex lattices, and vortex fluids. We have used these flow patterns to induce controlled droplet motion, create a thermal valve, induce active wetting, and induce various biomimetic dynamics. However, at this point, the vorticity axis is confined to one the three field directions. We propose a method to achieve continuous rotation of this vector using a new concept we call Field Symmetry Transitions.

Note that the last significant advance in controlling fluid motion–magnetohydrodynamics–was awarded a Noble prize in physics 28 years after its discovery and has had broad impact.

Summary of Accomplishments:

We have succeeded in demonstrating 3D control of fluid vorticity, and the effects are much richer than anticipated. An unexpected benefit is the development of a theoretical ansatz that enables us to quantitatively predict the effects that we ended up observing. The vorticity orbits we predicted have been observed, enabling homogeneous multi-axis mixing without control.

Significance:

We have developed an extremely vigorous, stable, homogeneous, controllable method of mixing that can be effectively employed even in highly obstructed or geometrically complex volumes. We have developed methods of creating a huge variety of elaborate, periodic vorticity orbits. These orbits should greatly reduce fluid stagnation near the corners and edges of fluid volumes. An invention disclosure is being written on this work.

We expect this field to expand in the future due to the extremely modest magnetic field requirements. This investigation in controlling fluid motion without the use of moving parts could lead to significant opportunities increasingly important to high power density microsystems, such as finding solutions to difficult heat transfer problems.

Refereed Communications:

J.E. Martin and K.J. Solis, "Creating Orbiting Vorticity Vectors in Magnetic Particle Suspensions through Field Symmetry Transitions—A Route to Multi-Axis Mixing," *Soft Matter*, accepted.

J.E. Martin and K.J. Solis, "Mesmerizing Magnetic Fields," *Physics Today*, August 2015.

J.E. Martin and K.J. Solis, "Quantifying Vorticity in Magnetic Particle Suspensions Driven by Symmetric and Asymmetric Multiaxial Fields," *Soft Matter*, vol. 11, pp. 7130-7142, September 2015.

J.E. Martin and K.J. Solis, "Complex Magnetic Fields Breathe Life into Fluids," Invited presentation for the *Meeting of the APS*, San Antonio, TX, March 2015.

Closing the Nutrient Utilization Loop in Algal Production

165714 | Year 3 of 3 | **Principal Investigator: T. Lane**

Project Purpose:
Biofuel production from algae biomass is a compelling solution for domestic production of fuels but faces daunting challenges in scale-up and sustainability. For example, recent studies suggest that replacement of 10% of domestic fuel supply with algae would require a doubling of nitrogen and phosphorus fertilizer usage. Unlike ammonia, phosphate is a non-renewable resource, and a peak in worldwide production is expected as early as 2030. Thus, without significant technological progress to recycle these major nutrients, expansion of algal biofuels to commodity scale can be expected to catalyze a food versus fuel crisis.

We will close the nutrient-recycling loop by harnessing remineralization processes, the biological conversion of organic forms of nutrients to inorganic forms. We will develop a novel, cost-effective process for remineralization of phosphate and nitrogen from algal biomass and conversion capture of these nutrients in bioavailable forms. We will demonstrate that the recycled nutrients produced by our process are capable of increasing the overall nutrient use efficiency of algal production systems reducing the demand for “new” nutrients.

To facilitate separation of the remineralized nutrients from the bulk phase, we will induce the co-precipitation of ammonium and phosphate as struvite (NH_4MgPO_4). Converting nutrients to solids is a low-energy means of recovering the bulk of the phosphorous and a portion of the nitrogen with maximum transportability. The remainder of the nitrogen will be recovered as ammonium. To identify scale-up concerns, we will develop models that relate the phosphate remineralization enzyme kinetics, mixing and precipitation kinetics.

Our proposed nutrient recycling method is highly conceptual. This project is a fundamental scoping effort that will generate preliminary results and proof of principle.

Summary of Accomplishments:
We demonstrated the ability to grow micro algae on struvite (NH_4MgPO_4), a waste product from the wastewater treatment process. We have demonstrated the ability to remineralize phosphate from native osmotically shocked biomass of *Nannochloropsis salina* (a commonly used strain for algal biofuels applications) by incubation of the biomass at mild pH conditions. Such incubations resulted in the release into the soluble phase of up to 70% of the total cellular phosphate. The released phosphate included most of the nucleic acid associated phosphate (DNA and RNA) but not the phosphate from the cellular phospholipids. Addition of a low-cost commercial phospholipase, used in the petroleum industry, allowed us to access the phosphate present in the phospholipid pool. We demonstrated the growth of algal biomass on recycled phosphate and showed that phosphate could be recycled repeatedly without the accumulation of deleterious compounds. The growth rate of algae on recycled phosphate was not diminished over 10 growth and reuse cycles.

We demonstrated the production of ammonia from native and phosphate extracted biomass through a fermentation process that also resulted in the production of mixed butanols and other organics that could be used either as fuel products or commodity chemicals. This fermentation process resulted in the conversion of 57% of the total cellular nitrogen into ammonia. Finally, we integrated the phosphate and nitrogen recycle process and demonstrated the tandem recycle of both major nutrients. We demonstrated the growth of microalgae on the recycled nutrients thus reducing the demand of new nutrients for the production of microalgal biomass for biofuels or other applications.

Significance:

This project addresses a major DOE mission: to increase the energy security of the US. The development of cheap renewable alternatives to fossil fuel derived transportation fuels would reduce our dependence on imported petroleum. The economic production of microalgal biodiesel can be a significant element of this strategy. Microalgal biodiesel requires the sustained production of algal biomass, a process that requires intensive use of agricultural fertilizers such as phosphate and ammonium. The nutrient recycling technology that we have developed will lessen the need for "new" nutrients overcoming a significant roadblock to an economically viable microalgal fuel industry.

The results of this project have been communicated to the algal biomass industry in the form of presentations at national and international meetings, and in manuscripts that have been accepted for publication.

Refereed Communications:

R.W. Davis, A.J. Siccardi, N.D. Huysman, N.B Wyatt J.C. Hewson and T.W. Lane, "Growth of Mono- and Mixed Cultures of Nannochloropsis Salina and Phaeodactylum Tricornutum on Struvite as a Nutrient Source," *Bioresource Technology*, vol. 198, pp. 577-585, September 2015.

Controlling Nanoparticle Assembly to Engineer New Materials

180922 | Year 1 of 3 | **Principal Investigator: G. S. Grest**

Project Purpose:

Driving computer design integration of nanomaterials will enable transformation from a lab to fabrication within reasonable time and resources. We will develop a much-needed means to significantly expedite computational pathways to design of nanomaterials while accounting for chemical information that is critical to their controlled integration. Currently, the assembly of nanoparticles is done through a time expensive random search of a large number of parameters including the nature of the nanoparticle itself coupled with surface encoding to drive integrations. Computer-based material design has been proven to provide an effective tool to correlate a large number of parameters where in nanomanufacturing, particle size and shape, and different surface encodings are among the many variables that control direct nanoassembly.

A new effective computational method to define and access the relevant parameter space required to direct nanoparticles into well-defined arrays will be developed, establishing hierarchal coarse graining (HCG) pathways that reduce the number of objects required for computations, while retaining the essential interactions that control assembly. We will define how far coarse graining can propagate while retaining essential chemical information. HCG will be able to probe mesoscopic length scales with chemical resolution while allowing an effective computational time to guide the design of nanoparticle assembly. This research will resolve a major barrier to computer design of nanoparticle integration, controlled dispersion and organizing of nanoparticles, while retaining their unique properties. This new approach will decrease computational time leading to effective screening that will significantly enhance nanomanufacturing.

Hierarchal-coarse graining will create a differentiating new capability for materials by design, focusing on nanoparticle-based materials. Coupled with extraordinary computational expertise at Sandia, the results will drive leadership in nanomanufacturing. We will focus on the development of HCG by a novel computational approach. This innovative concept will be first validated against atomistic simulations and then validated by experiment.

Emergent Phenomena in Oxide Nanostructures

180923 | Year 1 of 3 | **Principal Investigator: W. Pan**

Project Purpose:

The purpose of this project is to discover and understand emergent phenomena in oxide nanostructures. The field of oxide electronics has seen tremendous growth over two decades and oxide materials find wide-ranging applications in information storage, fuel cells, batteries, quantum sensing, and more. In fact, the prospect of oxide electronics has been compared to what took place for III-V semiconductors ~50 years ago, with potential for broader impact. In transition metal oxides, the strongly correlated d-electrons and interactions of spin, charge, orbit, and lattice degrees of freedom determine their physical properties.

One of the most important phenomena in highly correlated oxides is the metal-insulator transition (MIT). Many novel devices utilizing MIT have been proposed, ranging from ultrafast switches for logic applications to energy dissipaters, thermal computation, quantum actuation, and more. Despite this promise and many years of research, a complete understanding of the MIT remains elusive. Recently, we observed a novel electrical current induced MIT in self-assembled, vertically aligned epitaxial $(ZnO)_{0.5}$:$(La_{0.7}Sr_{0.3}MnO_3)_{0.5}$ nanocomposite films. This current induced MIT is totally unexpected and differs significantly from that observed in monophase oxide films. In this project, we propose to conduct a systematic study of this MIT and aim to gain a solid understanding of the physics that underpins this transition. Moreover, emergent quantum phenomena due to the strong correlations and interactions among the charge, orbital, and spin degrees of freedom inherent in transition metal oxides will be explored. We will work to understand the physics that controls the MIT and emergent phenomena in these highly correlated systems. The proposed research requires expertise in the preparation of high-quality epitaxial oxide heterostructures, quantum transport measurements, and state-of-the-art, aberration-corrected scanning transmission electron microscopy characterization, rarely found together in a single place.

Exploring Revolutionary Thermoelectric Performance via Quantum Confinement

173139 | Year 2 of 2 | **Principal Investigator: M. P. Siegal**

Project Purpose:

Theory has long predicted a dramatic enhancement of thermoelectric (TE) properties through quantum confinement for nanomaterial geometries. While small performance improvements have been achieved by size reduction, improvements to date have resulted from reducing thermal conductivity via enhanced phonon scattering. The potential to improve the electronic properties via quantum confinement remains untapped due to the challenges of growing nanomaterials with the high quality needed to achieve the requisite properties. Rather than struggling to optimize the growth of TE nanomaterials to achieve the necessary dimensionalities, we propose a new approach: start with easier-to-grow high-quality films and employ a novel subtractive approach to create nanochannels of high-quality, intrinsically connected TE materials engineered to enhance TE properties via quantum confinement. Sandia is uniquely positioned to perform this research with a confluence of expertise and capabilities in TE materials growth, ion beam irradiation, structural characterizations, and thermal/electrical measurements on nanostructured materials.

We propose using heavy-ion, high-energy ion beam irradiation on highly crystalline, high-quality Bi(1-x)Sb(x) TE films to create amorphous, poor-quality, nanometer-sized channels perpendicular to the plane of the film. By properly adjusting the ion mass, energy, and fluence, the remaining high-quality TE film matrix will be connected via narrow pathways, creating the conditions for quantum confinement in the remaining undamaged high-crystalline quality matrix. This approach addresses the yet-to-be achieved challenge of increasing the Seebeck coefficient while maintaining high electrical conductivity. Ion beam parameter selection for optimal nanostructural features will be guided by modeling and characterization using Sandia's state-of-the-art transmission electron microscope facilities.

This study represents a novel approach to experimentally demonstrate a theoretical result that has yet to be proven in over 20 years. If successful, we will demonstrate a nanostructure yielding quantum confinement.

Summary of Accomplishments:

To probe quantum confinement, it is requisite to grow high-quality Bi(1-x)Sb(x) alloy films with controlled composition (20% Sb), trigonal orientation, and TE-properties comparable to bulk, none of which had ever been reported. We demonstrated within +/- 1% compositional control, resulting in very smooth as-deposited films with no preferred orientation. Trigonal orientation was achieved by annealing to 300 ˚C in forming gas. However, a major problem was identified for the first time: a continuous oxide film covers the surface that is composed of Sb-oxide. Detailed analyses found that this surface Sb-oxide depletes nearly all of the Sb from the film, leaving a nearly pure Bi layer. Since Bi is a semimetal, this explains the lack of TE property reports from Bi(1-x)Sb(x) films.

We solved this problem by hermetically sealing the Bi(1-x)Sb(x) with SiN prior to removal from the deposition system, preventing oxygen reactions. The results are smooth films with superior trigonal orientation upon annealing.

To measure the TE transport properties (resistivity and Seebeck coefficient), we developed a method to make electrical contacts to the Bi(1-x)Sb(x) film. Requirements of the contact metal are (a) to NOT form an oxide, and (b) to NOT react with Bi(1-x)Sb(x). The obvious noble metals all react with Bi. Using thermodynamic phase diagrams, we identified Nd-doped Al as appropriate: Nd-doping prevents oxide formation and neither element reacts with Bi or Sb at the required annealing temperatures. Nd-doped Al contact pads were lithographically defined on the substrate prior to Bi(1-x)Sb(x) deposition, enabling the first reliable TE-property measurements of Bi(1-x)Sb(x) films as a function of annealing temperature and correlating these properties with structure. Optimized at 285 ˚C, we report very high TE transport behavior, with properties ranging 50% higher than bulk values. Such high-quality films, both in terms of structure and TE properties, are appropriate to probe quantum confinement via ion beam nanostructuring.

Significance:

This work demonstrated the first high-quality BiSb films, a necessary first step to having a material of sufficient quality to explore thermoelectric quantum confinement for high-impact science. Such high-quality BiSb films themselves can enable new solutions for thermal management, such as low-power solid state cooling to improve the performance of critical systems for detectors (optical, microwave, RADAR, chem-bio, etc.), as well as enabling new technologies for long-lived power sources of remote operations.

Refereed Communications:

C. Rochford, D.L. Medlin, K.J. Erickson, and M.P. Siegal, “Control of Composition and Crystallinity in Bi(0.8) Sb(0.2) Thermoelectric Thin Films,” to be published in *Applied Physics Letters*.

S.J. Limmer, D.L. Medlin, M.P. Siegal, M. Hekmaty, J.L. Lensch-Falk, K. Erickson, J. Pillars, and W.G. Yelton, “Using Galvanostatic Electroforming of Bi1-xSbx Nanowires to Control Composition, Crystallinity, and Orientation,” *Journal of Materials Research*, v. 30, pp. 164-169, January 2015.

M. P. Siegal, “Toward Quantum Confinement in Bi-Based Thermoelectric Materials,” presented at the 4th *International Symposium on Energy Challenges and Mechanics: Making Things Small*, Aberdeen, United Kingdom, 2015.

M.P. Siegal, “Nanomaterial Strategies for Thermal Cooling,” presented at the Cambridge Graphene Center Colloquium, University of Cambridge, United Kingdom, 2015.

Exploring the Possibility of Exotic Ground States in Twisted Bilayer Graphene

165713 | Year 3 of 3 | **Principal Investigator: T. Ohta**

Project Purpose:

We will examine the electronic properties of twisted bilayer graphene (TBG) in a search for exotic ground states in this material. The following specific scientific question will be addressed via our leading capability in this emerging material: Can exotic ground states, or proximity-induced superconductivity, be induced in this new class of material? The ramifications of superconductivity in graphene are far reaching. As its charge carriers are readily manipulated at cryogenic temperatures using the field effect (FE), gate-tunable superconductive elements, equivalent to three-terminal switches, may be realized. Importantly, such a simple switching function is currently missing for superconductor circuitries envisioned for exascale supercomputers.

Intrinsic superconductivity in graphene has not been experimentally observed despite numerous predictions of its existence. The theoretical predictions have suggested the emergence of exotic ground states at Van Hove singularities (VHs) residing >2eV from the charge neutrality point. These energies are inaccessible using atypical FE structures. TBG, in contrast, has additional low-energy VHs, which evolve as a natural consequence of the two-graphene sheets being misaligned. Thus, TBG provides an exciting medium to explore the possibility of superconductivity in graphene. In this project, we will explore the proximity-induced superconductivity in TBG using superconductive leads.

The search for superconductivity in a low-dimensional material is a high-risk endeavor. Our proposed work is of a “discovery” nature as we investigate the unexplored low temperature properties of Twisted Bilayer Graphene, an emerging form of graphene.

Summary of Accomplishments:

In this project, we touched on three material systems seeking graphene’s exotic electronic phenomena. They include: 1) the possibility of intrinsic superconductivity in twisted bilayer graphene, 2) seeking a proximity-induced superconductivity in twisted bilayer graphene, and 3) exploring superconducting metal-graphene hybrid systems for proximity-induced superconductivity. The last direction includes tantalum coated three-dimensional graphene structure and lead-graphene sandwich structure. Our accomplishments are:

- Quantifying disorders in twisted bilayer graphene on SiC substrate
- Construction of two-terminal TBG devices and the testing of supercurrent in TBG devices at room temperature and 4 Kelvin
- Examination of tantalum decorated 3D graphene structures for its proximity-induced superconductivity
- Synthesis of the graphene-lead monolayer hybrid sandwich structure

Significance:

The project was “out-of-the-box” in each regard as it sought to demonstrate yet-to-be proven superconductivity in graphene using a new material and novel electronic structure engineering. Our work shone light into various graphene-related material systems that could display superconductivity or closely related exotic electronic phenomena. To this end, the fundamental materials properties and insights gained from this project may enable multiple national-security and energy-security technologies, such as superconductor-based supercomputers.

Refereed Communications:

C.S.F. Cobaleda, X. Xiao, D. B. Burckel, R. Polsky, D. Huang, E. Diez, and W. Pan, “Superconducting Properties in Tantalum Decorated Three-Dimensional Graphene and Carbon Structures,” *Applied Physics Letters*, vol. 105, p. 053508, 2014.

T. E. Beechem, T. Ohta, B. Diaconescu, and J.T. Robinson, “Rotational Disorder in Twisted Bilayer Graphene,” *ACS Nano*, vol. 8, pp. 1655-1663, January 2014.

Low Afterglow Scintillators for High-Rate Radiation Detection

180925 | Year 1 of 1 | **Principal Investigator: P. L. Feng**

Project Purpose:

The purpose of this project is to develop high-speed and high light-yield scintillating materials, as relevant to several diverse applications such as nuclear nonproliferation and inertial confinement fusion (ICF) studies. In the former, the NNSA seeks new technologies to enhance the detection of special nuclear materials (SNM) at border crossings and ports of entry. An invaluable technique to this end is active interrogation, wherein a radiation pulse induces fission events from difficult to detect SNM such as highly enriched uranium. Present detectors for this application are inadequate due to insufficient timing response characteristics that limit the measurement fidelity under typical acquisition conditions.

A similar problem exists when attempting to measure the neutron spectrum in ICF studies at the National Ignition Facility (NIF), Z machine, or Omega laser facility. These extremely important measurements can supply information on the source characteristics such as the fuel and linear areal densities. Unfortunately, significant background radiation is produced in these experiments, which precedes the neutron signals of interest and limits the ability to measure the neutron spectra. The response time of existing materials is too slow to resolve these events, which leads to overlapping signals and insufficient measurement resolution. This work will address the count-rate limitations of existing materials by applying an innovative optical filtering approach in conjunction with a new class of scintillators developed at Sandia.

We propose the use of Sandia-developed triplet-harvesting plastic scintillators (THPS) to address the count-rate limitations of existing materials. THPS materials were originally produced for neutron discrimination, although the proposed work takes advantage of their novel two-color response to achieve faster kinetics. This innovative approach is not possible in any other known material, and circumvents the problems associated with existing alternatives.

Summary of Accomplishments:

In this project, we tested two types of metal-loaded plastic scintillators as potential replacements for existing materials used in high count-rate radiation detection. The strategy followed in this work involved the addition of an organometallic iridium or an organometallic tin compound to reduce the extent of deleterious delayed luminescence following exposure to ionizing radiation. Key results include a seven times greater light yield compared to existing high-rate scintillators (i.e., BC-422Q plastic, stilbene-doped benzyl crystal), while achieving comparable or even faster decay characteristics than these benchmark materials. The implications of this finding are significant towards the applications stated above, namely, high-rate radiation detection where pulse pile-up leads to a reduction in the fidelity of collected scintillation data. Pulse pile-up is simply defined as the observance of overlapping pulses that are not able to decay fully within the time scale of recurring radiation events.

Attributes characteristic to the materials developed in this study include low cost, non-liquid, non-gaseous, and non-hazardous materials that are temperature insensitive and robust.

Significance:

Based on the technical results described above, the scintillators developed in this project are well positioned to make an impact to nuclear nonproliferation radiation detection applications (among others).

Refereed Communications:

P.L. Feng, "Molecular Origins of Scintillation in Plastic Scintillators," presented (invited) at the *13th International Conference on Inorganic Scintillators and their Applications* (SCINT 2015), Berkeley, CA, 2015.

P.L. Feng, W. Mengesha, M.R. Anstey, and J.G. Cordaro, "Distance Dependent Quenching and Gamma-Ray Spectroscopy in Tin-Loaded Polystyrene Scintillators," to be published in *IEEE Transactions of Nuclear Science*.

Probing Small-Molecule Degradation to Counter Enzyme Promiscuity

173142 | Year 2 of 3 | **Principal Investigator: S. Rempe**

Project Purpose:

Enzymes that degrade specific small molecules could save lives by neutralizing threats from chemical agents in the blood or environment, but promiscuous interactions with other molecules typically limit their effectiveness by blocking the enzyme active site. An obvious solution is to reengineer the enzyme to enhance catalytic fidelity, but lack of understanding about how enzymes discriminate between molecules remains a formidable challenge to this approach. Our recent work in collaboration with University of Texas (UT) suggests a new approach and a model system for understanding enzyme specificity. Asparaginase enzymes catalyze degradation of asparagine, which forms the basis of a medical treatment. Competition by other abundant molecules interferes with asparagine decomposition, thus hindering enzyme efficacy. Asparaginase is advantageous as a model degradation enzyme because variants that demonstrate different binding affinities and catalytic rates can be compared. Current work suggests that the mechanism of molecular specificity in asparaginase depends on a different set of chemical interactions than previously speculated. To overcome current barriers to progress, we will leverage Sandia's strengths in state-of-the-art quantum/classical molecular simulation and UT experimental expertise in asparaginase modification and functional assays to understand enzyme degradation of small molecules. Our simulations will probe how local properties of the asparaginase active site determine molecular binding affinities and free energy barriers to degradation, and predict mutations (tested experimentally) to tune catalysis to favor a specific molecule.

Sandia's high performance computing, extensive expertise in classical/quantum simulation, and established collaboration for testing theory-generated hypotheses on modified enzymes holds potential for gaining new insights previously unattainable. The result will be proof of principle for a broadly applicable, yet innovative strategy for reengineering enzymes to favor degradation of specific molecules important for national security (e.g., chemical warfare agents).

Sandia's RVCC Technology: A Pathway to Ultrahigh Efficiency Building Air Conditioning, Heating, and Refrigeration

180924 | Year 1 of 3 | **Principal Investigator: J. P. Koplow**

Project Purpose:

A large fraction of US energy consumption is due to space heating and cooling in the residential and commercial sectors. Currently, vapor compression cycles (VCCs) are used widely for heating and cooling due to their robustness and ability to heat or cool greater than the energy supplied (coefficient of performance >1). However, real world VCCs deviate substantially from the Carnot efficiency due to loss mechanisms such as parasitic thermal resistance, excessive vapor superheating, and chaotic refrigerant two-phase flow behavior. Prominent thermal parasitics in VCCs include the thermal resistance between the heat exchanger fins and ambient air and the added thermal resistance associated with evaporator frost formation. Furthermore, the widespread use of vapor superheating to prevent liquid from entering the compressor generates additional entropy. Undesirable phase-change flow patterns in high aspect ratio channels prevent effective vapor (liquid) escape in evaporators (condensers), impairing heat transfer and increasing pressure drop in the flow. The rotary vapor compression cycle (RVCC) embodies a radical rethinking of conventional VCCs, wherein the condenser, throttle valve, evaporator, and compressor rotate at high speed on a common axis to counteract the above sources of inefficiencies. Rotation of the evaporator and condenser results in enhanced airside heat transfer, as pioneered in an LDRD-funded grand challenge. Rotation of the refrigerant is expected to separate the liquid and vapor phases through centrifugal and Coriolis forces, and this separation is predicted to improve heat transfer in the refrigerant flow and prevent liquid from entering the compressor. Through this project, we will experimentally study the uninvestigated regime of two-phase flow in the rotating frame. The new understanding will make it possible to explore and optimize proof-of-concept designs for RVCC.

Synthetic DNA for Highly Secure Information Storage and Transmission

173140 | Year 2 of 3 | **Principal Investigator: G. Bachand**

Project Purpose:

Protection of information is one of the greatest challenges to our nation's security and will continue to be for the foreseeable future. In particular, digital storage and transmission has proven increasingly susceptible to compromise, necessitating the development of disruptive technologies to secure highly sensitive information. The use of synthesized DNA to store digital information with high capacity and low maintenance was first reported in 2013, and offers a novel paradigm for information storage, particularly as DNA can be stably stored for >10,000 years. Moreover, synthetic DNA may also be used to transmit information in a highly secure biomolecule, rather than an encrypted digital format. We propose to apply the general premise of information storage in DNA, but focus on developing a fundamentally novel approach for transmitting encrypted data within DNA constructs. We will borrow from nature's means of translating genomic information into functional units to encrypt data. As in living organisms, we propose to use a "triplet codon" (i.e., three adjoining DNA nucleotides) to develop more than 1,089 (i.e., 64 factorial) individual 64-character libraries that can be used for data encryption. The design will involve synthetic DNA constructs consisting of: 1) a "lock" securing the DNA from being "read" by anyone lacking authorization, 2) a "translation key" sequences that specify the language for decoding the encrypted data, and 3) the encrypted data itself. In addition, this approach will allow us to use "nonsense" code sequences, mimicking the intron/exon structure found in genomic DNA.

This project directly aligns with LDRD's objective of enhancing Sandia's ability to address future national security needs by developing a potentially disruptive technology for the safe and secure storage of national security information using synthetic DNA. Work on this project will provide the foundational R&D necessary to demonstrate the proof of principle.

NEW IDEAS

National Nuclear Security Administration

Defense Systems & Assessments

The Defense Systems and Assessments Investment Area (IA) delivers advanced science and technology solutions to deter, detect, track, defeat, and defend against threats to our national security. The work includes the development of innovative systems, sensors, and technologies for the nation's defense communities. This IA seeks to draw upon Sandia's state-of-the-art ST&E capabilities through focused investments in three strategic program areas: Space Mission and Remote Sensing (SMRS), Information and Intelligence Technologies (ITT), and Precision Engagement (PE). SMRS is focused on next-generation satellite flight and ground systems and future challenges facing the space community. The work supports the development of enabling technologies for revolutionary remote sensing and collection systems. IIT addresses the asymmetric threats arising from our nation's dependence on information networks and on anticipating disruptive capability and technology developments that threaten national security. PE identifies enabling technologies that support precision knowledge, precision decisions, and precision response for the national security community.

Projects

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Adaptive Waveform and Signal Processing Techniques that Mitigate Adversarial Anti-Access/Area Denial (A2AD) Technology

173066 | Year 2 of 3 | **Principal Investigator: C. Musgrove**

Project Purpose:

Recent research and development efforts and proliferation of electronic warfare (EW) technologies have strengthened adversarial anti-access/area denial (A2/AD) capabilities. These threats pose a significant risk to our national security missions that rely on Intelligence, Surveillance and Reconnaissance (ISR) systems. The objective of this project is to develop techniques that can mitigate select adversarial A2/AD technologies and maintain mission performance (e.g., image quality and image production rate). Mitigation efforts will focus on developing waveforms and signal processing techniques for electronic counter-countermeasures (ECCM). Challenges associated with operating in an A2/AD environment include understanding advanced jamming methods, false target generation, and employing techniques to decrease the interference-to-signal ratio. We will work to develop techniques for employing adaptive waveforms, interference rejection, false target discrimination, statistical signal, and image processing and reducing computational loads associated with adaptive signal processing.

Advanced Beamsplitter Fabrication Techniques for Enabling a Novel Compact Multispectral Diffraction-Limited Imaging System

173058 | Year 2 of 2 | **Principal Investigator: T. D. Henson**

Project Purpose:

The purpose of the project is to prove the capability of designing, fabricating, and mounting a thin, all-dielectric beam splitter that transmits visible light while reflecting short-wave and mid-wave infrared light in order to enable a new class of multi-spectral optical sensor systems. Current technology for transmitting visible wavelengths and reflecting infrared wavelengths utilizes hybrid metallic/dielectric coatings where the metal layers reduce the visible transmittance significantly, negatively impacting the radiometric sensitivity of the system. An all-dielectric coating design will improve the visible transmittance dramatically but will require a very large number of coating layers to produce high reflectivity in the infrared, thereby making fabrication difficult. Furthermore, the beam splitters must be very thin to control aberrations in the optical system and the very thick beam splitter coating will create significant bowing of the beam splitter substrate. To combat the bowing effect, an extremely complex anti-reflection (AR) coating design is required on the second surface of the beam splitter to stress balance the beam splitter coating. While coating vendors have produced thick coatings for other applications, they had never faced the challenge of maintaining a tight surface flatness requirement on a thin optic while applying a coating that is over 600 layers thick. Our approach was to advance the state of the art in beam splitter coatings through the use of precise material thickness control and complex stress balancing with the AR coating design. The high aspect ratio of the beam splitter substrate also makes the beam splitter susceptible to deformation due to mount stresses and thermal induced mount stresses. Our approach was to design a lightweight flexure mount that would impart minimal stress into the beam splitter. A beam splitter will be fabricated, mounted, and exposed to thermal vacuum cycling to prove the ability to meet optical system requirements with this novel beam splitter concept.

Summary of Accomplishments:

We proved the ability to deposit an all-dielectric coating exceeding 600 layers with sufficient thickness control to achieve the desired transmittance and reflectance. We also proved the ability to properly balance the coating stress to achieve the required surface flatness on a 20:1 aspect ratio glass substrate. We learned that the transition region where the coating is tapering off from full thickness to zero thickness has a larger impact on the surface figure near the transition region than we originally anticipated. As a result, we edged down the size of one of the beam splitters after coating and proved that the coating integrity is maintained, while the surface power and irregularity were greatly reduced. For future applications, one can consider coating an oversized substrate; if a smaller final size is required, simply edge down the beam splitter to final size after coating, thus removing the impact of the coating transition region. The coating integrity was tested using the 24-hour humidity test, cheesecloth abrasion test, and the standard tape pull test. The beam splitters were thermally cycled for 10 cycles between -40 °C and +60 °C to demonstrate coating performance and integrity is maintained after exposure to a wide range of temperatures. We also proved that the beam splitter coating can withstand space radiation doses up to 14.4 mega-rads with no change in spectral transmission. We designed and built a mount for the beam splitter and demonstrated that the mount could hold the delicate beam splitter without imparting significant mount induced stresses. We did not observe any permanent thermal mount induced deformation following thermal cycling of the beam splitter from -40 °C to +60 °C. Analysis also indicated the beam splitter can withstand typical space launch loads.

Significance:

The results of this project enable a whole new class of multi-spectral optical system design concepts. Through utilization of a short-wave pass beam splitter, novel systems have been demonstrated allowing for improved system performance and a significant reduction in size and weight. This can revolutionize the achievable performance for national security and intelligence missions. The risks of this new technology have been significantly reduced and the technology readiness level elevated, building confidence in our ability to utilize this technology in operational systems in the near future.

Advanced Detection and Focusing of “Peak Through” SAR Imagery in Foliage

180853 | Year 1 of 2 | **Principal Investigator: D. L. Bickel**

Project Purpose:

The purpose of this project is to investigate using higher frequency (e.g., x-band) radar systems for detection and imaging objects under foliage. The challenge for these frequencies is that limited penetration of the radar waves means that we need to rely on “peak through” in foliage, which leads to sparse information. The reliance on “peak through” elevates the technical risk of this project.

The approach taken in this project is to investigate the use a combination of different degrees of freedom at our disposal to separate unwanted returns from desired returns. These degrees include such things as polarization diversity, waveforms, and judicious choice of radar flight geometries. Once we have filtered out the undesired signals, we are left with a sparse desired signal space. This will require combining this residual information sparse imaging techniques, such as compressive-sensing-like techniques.

An advantage Sandia has is the ability to collect high quality x-band full-polarization radar data under controlled geometries. This allows us to investigate real data and apply our algorithms directly to these data sets.

Assessing the Security Impact of Moving Target Defense (MTD) Approaches

173071 | Year 2 of 3 | **Principal Investigator: B. P. Van Leeuwen**

Project Purpose:

While moving target defense (MTD) approaches promise to increase complexity and cost for attackers by continually changing the operating cyber environments, their security impact to the overall network is largely unexamined. Dynamic reconfiguration of computing elements and their connectivity must take into consideration the stability and security impact to the overall networked-system. While an attacker may encounter unpredictability in a MTD environment, system and network administrators must also assure the stability and overall security of such a continuing and changing environment. Current MTD techniques assume that the effect of change is contained, localized, and does not have any adverse impact to system-wide operation and security.

Recently, MTD approaches extend to Internet Protocol version 6 (IPv6) networks and use software-defined-networking (SDN) to dynamically change the underlying network along with end-point configurations. A major challenge is how to determine the effectiveness and security impact of MTDs since techniques are rarely tested in any operational environment. Limited analysis is performed on the effectiveness of a MTD technique and, thus, understanding the effectiveness of the approach to specific classes of threats is also limited. Additionally, limited analysis and experimentation capability exists for understanding and measuring the effectiveness of MTD techniques to confuse or obscure the target from an adversary.

Currently, no capability exists to assess MTD approaches at large scale and employing IPv6 and SDN technologies. Researchers focus on developing the MTD rather than the challenges of evaluation of the approach and use simplified models to estimate the MTD approach at scale, which produces unreliable results. Our research will result in an unbiased analysis platform to assess effectiveness of MTDs.

Automated Blind Signal Characterization

173047 | Year 2 of 2 | **Principal Investigator: J. R. Templin**

Project Purpose:

Blind signal characterization (BSC) is the practice of detecting, classifying, and identifying radio frequency (RF) transmissions. This technique is valuable to various efforts at Sandia. For field-deployable systems, there is a need to make the process more efficient and real-time such that BSC can be accomplished with greatly reduced computing resources. Doing so requires a great deal of optimization and improvement to the current state of the art in BSC, which is intended to be done on workstation-class computers and as a post-processing step.

This research seeks to explore the feasibility of developing embedded, autonomous BSC solutions. This involves the process of performing computation complexity analysis of existing algorithms, optimization of algorithms for embedded and real-time execution, and the development and demonstration of a prototype embedded BSC system. For the algorithms whose computational complexity is beyond the capability of real-time, embedded systems, alternatives will be explored and created.

Summary of Accomplishments:

We analyzed metrics for performance and computational complexity. We invented metrics of our own that included the use of deep machine learning. We developed a classifier capable of performing blind signal characterization in the computational power available on embedded system classes of devices. We verified select metrics' performance on a candidate battery-powered software-defined radio. We investigated and demonstrated the feasibility of constructing a universal demodulator by composing a linear modulation demodulator of modulation-agnostic processing elements. We verified the feasibility of performing blind signal characterization in real-time and on embedded devices.

Significance:

Our research has performed an important verification needed to advance national security missions across many government agencies. Additionally, we have opened up new areas of research, including the applicability of machine learning to this problem space as well as the exploration of alternative compositions for demodulators, which will likely provide fertile ground for future research.

Biologically Enabled Remote Sensing for Real-Time Detection and Threat Response

180842 | Year 1 of 3 | **Principal Investigator: A. Ruffing**

Project Purpose:
Remote monitoring technologies are vital tools for maintaining national security. These technologies provide valuable information to help guide policymakers' decisions regarding nuclear, chemical, and biological incidents. With the consequences of these decisions, accurate and reliable data is necessary to enable our government to rapidly assess and respond to potential national security threats or acts of terrorism. While optical remote sensors have advanced in terms of spatial resolution and sensitivity, the molecular signatures of nuclear, chemical, and biological weapons are difficult to optically detect with the necessary specificity. Biological systems have evolved unparalleled mechanisms of detection, with extraordinary sensitivities and specificities. Natural sensing mechanisms have been engineered to monitor manmade chemicals, such as trinitrotoluene (TNT) and pinacolyl-methyl-phosphonic acid (PMPA, hydrolytic product of the nerve agent soman), by linking the biological sensing element to an optical reporter signal. While these laboratory-based biosensors illustrate the potential of this technology, there are numerous obstacles to developing a sustainable, field-based biosensor for remote sensing applications. Many questions remain regarding the dynamic regulation of the biologically produced optical signals, particularly under natural environmental conditions. We propose to develop well-characterized synthetic biology tools for optical signal production and dynamic control, to characterize the response to stimuli under various environmental conditions, and to demonstrate and assess remote monitoring of a chemical stimulus under realistic environmental conditions. If successful, this research would provide a foundation for the development of biosensors capable of high-specificity chemical identification that can be persistently and passively monitored.

Broadband Digital AESA Radar Prototype for Multi-Mission ISR Applications

173060 | Year 2 of 3 | **Principal Investigator: H. Loui**

Project Purpose:

The purpose of the project is to develop a broadband active-electronic-scanned-array (AESA) radar prototype for broad mission intelligence, surveillance, and reconnaissance (ISR) applications to counter anti-access/area-denial (A2/AD) strategies that may actively jam, spoof, or interfere with our frontline electromagnetic sensors. Currently, the lack of practical, compact, low-loss, broadband, high-resolution, analog phase shifters (APSs) and true-time-delay (TTD) devices at radio frequencies (RF) limits bandwidth, reduces efficiency, and constrains electronic beam steering of existing electromagnetic sensors. These difficulties ultimately result in complex mission-specific radars that require significant time and exorbitant costs to develop, build, maintain, and upgrade.

Our approach to broadband AESA-based radar avoids the aforementioned difficulties by not utilizing any analog RF APS and TTD devices for beam steering. An initial proof-of-principle experiment at Sandia has demonstrated multi-GHz of instantaneous electronically steerable bandwidth. Though impressive, this feat was produced using expensive, heavy, and bulky general-purpose bench-top equipment. Hence, a miniaturized prototype must be created to demonstrate feasibility in practical applications, a task carrying tremendous risk. If successful, mission-agile radars using broadband AESAs will enable rapid mode reconfiguration and in-the-field enhancements. Multichannel, multiple phase-center, and multibeam capabilities would allow adaptive nulling of jammers, multiple-target tracking while scanning, rapid target identification, and broadband secure communications.

Carrier Lifetime Mapping for Infrared Detectors

173050 | Year 2 of 2 | **Principal Investigator: G. Soehnel**

Project Purpose:

Material defects are a common problem among infrared detectors. These defects create high rates of carrier recombination, which in turn produces pixels in focal plane arrays (FPAs) with high dark currents and other undesirable characteristics. Defects can range from individual pixels to clusters hundreds of pixels or more in size. One method of characterizing a detector or material sample is to perform carrier lifetime mapping. Locations with a decreased lifetime indicate material defects. This capability exists in very few places, particularly for infrared materials. We propose to modify an existing detector spot scanning station to perform a photo-luminescent decay measurement. A pulsed laser will excite the sample, and the decay of photons in time created by radiative carrier recombination will be recorded. The ability to perform this measurement would give us an important tool that can characterize detectors and material samples with a passive noncontact measurement.

Time resolving the physics of defect-dependent carrier recombination requires the use of impulse excitation and sufficient signal-to-noise to resolve when the recombination rate becomes linear with carrier density. This happens at low carrier densities so collecting and sensing enough emitted photons leaving the sample will be challenging. We intend to improve on the current state of the art in two key areas: working distance and spatial resolution.

Summary of Accomplishments:

We were successful in designing and assembling an experiment capable of measuring the time-resolved photoluminescent (PL) decay with good signal to noise. A carrier recombination simulation was also written in MATLAB that was able to aid in the analysis of measurement data. All three recombination mechanisms (radiative, auger, Shockley-Read-Hall [SRH]) were simulated to fully model carrier density and decay in response to an impulse. The simulation itself was used in an optimization routine to fit to measured data with the SRH lifetime as a variable. In the end, four fully operational mercury cadmium telluride (MCT) FPAs, along with several InAsSb wafers and devices, were measured. Dark current and relative response maps for the operational FPAs matched very well with the lifetime maps produced. It was demonstrated that the lifetime mapping measurement is able to identify defects that affect performance of an FPA, and also that lifetime features can be measured on bare wafer samples. Sweeps over temperature were also performed that matched reasonably well with the recombination simulation (equations were used that model recombination coefficients as a function of temperature).

In addition, we demonstrated a measurement technique using a different approach that we have called “PL vision.” This measurement involves broadly illuminating a sample under test and imaging the PL return with an infrared camera. Quantitative lifetimes cannot be extracted from the data like they can with the time resolved method, but the measurement has higher spatial resolution and takes much less time to perform. The same features and defects can be qualitatively observed in the contrast images produced from PL vision. The measurement was demonstrated to work fairly well with the sample at room temperature.

Significance:

This work developed a very unique measurement and analysis capability. Yielding high quality infrared FPAs with high pixel operability is still a challenge in industry, and infrared FPAs are a key part of our remote-sensing missions. This measurement, particularly the PL vision approach, has the potential to improve the fabrication process when implemented as a screening technique. It also has the potential to continue to aid our own materials and FPA research at Sandia.

Refereed Communications:

G. Soehnel, “Time Resolved Photo-Luminescent Decay Characterization of Mercury Cadmium Telluride Focal Plane Arrays,” *Optics Express*, vol. 23, pp. 1256-1264, January 2015.

Co-Design of Sensors and Analysis Methods for Optical Remote Sensing of Spectral-Temporal Signals

173056 | Year 2 of 3 | **Principal Investigator: M. W. Smith**

Project Purpose:

We propose to create a new process for co-designing remote sensing instruments and the accompanying data analysis methods for application to spectral-temporal signals. Events, or signal sources, are, in fact, generally the items of primary interest. Our philosophy is that sensors and analysis methods should be designed together from the beginning to produce a system that efficiently delivers high-value information. The co-design process should incorporate field measurements and phenomenology models to identify important features in the signals. This project will develop a new co-design process by targeting events that produce transient spectral-temporal optical signals, specifically lightning and munition detonations. Lightning is an ubiquitous background signal in optical remote sensing, and there is wide application for measuring munition optical signatures. Our team will apply a combination of phenomenology models, sensor models, observations, and data visualization and analysis to: 1) predict key spectral-temporal features of the optical signals produce by explosions and lightning, 2) measure real signals, 3) analyze the signals in the spectral-temporal domain, 4) identify key features, and 5) create a conceptual design for a sensor that is optimized to observe small explosions and discriminate them from other sources such as lightning.

Computer Network Deception

165547 | Year 3 of 3 | **Principal Investigator: V. Urias**

Project Purpose:

The modern approach to computer network defense has led to an assumption that our networks will likely be compromised. This assertion stems from the idea that the existing defense tools are challenged in defending against today's threats. Enterprises are consistently compromised by multiple classes of adversaries despite significant amounts of money and effort. As these threats become more aggressive, there emerges a need for different, proactive strategies beyond existing plug-and-play and commercial solutions that exist to date. Research needs to focus on revolutionary and not evolutionary defenses that will affect a broader class of threats and threat vectors.

This project's purpose is to develop, implement, and test a novel computer network operations architecture that enables proactive defense by managing and monitoring the enterprises resource allocations and network flows. The architecture will leverage three emerging concepts: software-defined networks, cloud computing, and deception. It will enable the detection and identification of anomalous access and intrusions to adjust to the dynamic nature of the adversary and to provide a mechanism to discover and react to the adversary's attacks in a methodical and proactive manner. Additionally, new technologies will be developed that allow network defenders to gather information on the adversary's tools, tactics and procedures. This information will provide insight into what, why, and how they are conducting their operations.

Summary of Accomplishments:

The last year of this project was focused on integration, analytics, and testing of ideas. We discovered several new methods for creating a highly efficient transparent monitoring tool to collect a variety of data from the guests. We also developed a series of zero agent tools to traffic generation and service provisioning within the environment. Finally, we developed some new algorithms and tools to do parallel network and host cloning.

Significance:

This research effort has been received exceedingly well from several NNSA partners interested in physical security and cyber defense.

Confidence in Cyber Modeling and Simulation

180830 | Year 1 of 3 | **Principal Investigator: S. T. Jones**

Project Purpose:

The purpose of this project is to create a methodology for establishing the credibility of emulation-based models of distributed systems. Today, we don't understand how well such models capture the behavior of the real world systems they represent. Lack of understanding compels us to build bigger and higher fidelity computational models, which is expensive and may be unnecessary. To effectively use the powerful tools that emulation-based modeling and simulation provide we must understand:

- Which components of real world systems to include in a model
- If model components are implemented correctly
- How faithfully the modeled components and their relationships must be emulated to get meaningful results
- How much to trust a model to predict the behavior of real systems

Progress toward answering these questions would revolutionize our ability to confidently develop and use models based on emulation technology to understand cyber systems. In this project, we will build on Sandia's experience in validating computational physics models and will adapt those techniques to the domain of emulation-based models of distributed cyber systems. The resulting methodology will contribute to the scientific maturity of cyber security modeling and simulation.

Deployable, Ground-Based, Discrete Zoom Telescope

173059 | Year 2 of 3 | **Principal Investigator: E. G. Winrow**

Project Purpose:
Many optical system missions require both a wide field and high resolution views for both scanning and characterization activities. The high cost of large-aperture optics and high- performance detectors often requires a system to be either one or the other. We plan to create a hybrid zoom system capable of both mission areas, utilizing a single large aperture optic and a single detector, with reconfigurable smaller optics in the train. A ground-based system is planned to prove out concept, manufacturability, and cost. Technologies and methods devised will be instrumental in enabling future air and space optical systems. Major challenging technical objectives will be to devise an achievable optical design with few moving components and a stable, lightweight, robust structure that holds the optics in multiple precise locations without excessive complexity or cost. Our team of engineers will bring a practical approach to the problem through truly integrated optical, optomechanical and structural design. The envisioned system will achieve zoom capability over a wide field of view in the visible wavelength bands through a combination of high-precision movements of the components and novel optical design forms. The optical design will be tailored to reduce the number and magnitude of moving parts. Phase diversity techniques will enable precise imaging with affordable optical fabrication and alignment/motion tolerances. Advancements in optical alignment techniques, tooling, and adhesive bonding will enable precise optical alignments without the need for ultra-precise and expensive hardware. Additively manufactured structural components will greatly increase the speed of fabrication. Relying on each of these advancements holds risk, and bringing all together into an elegant, unified system is both high-risk and high-reward.

Developing a System for Testing Computational Social Models using Amazon Mechanical Turk

173062 | Year 2 of 2 | **Principal Investigator: K. Lakkaraju**

Project Purpose:

The US faces persistent, distributed threats from malevolent individuals, groups and organizations around the world. Computational Social Models (CSMs) help anticipate the dynamics and behaviors of these actors by modeling the behavior and interactions of individuals, groups, and organizations. The Behavioral Influence Assessment tool being developed at Sandia is one example of a CSM. Understanding the dynamics of the model will enhance confidence in the model.

One major problem is designing an appropriate controlled test of the model, similar to the testing of physical models. Lab experiments can do this, but are limited to small numbers of subjects, with low subject diversity and are often in a contrived environment. Natural studies attempt to test models by gathering large-scale observational data (e.g., social media); however, this loses the controlled aspect.

We propose a new approach to run large-scale, controlled online experiments on diverse populations. Using Amazon Mechanical Turk (AMT), a crowdsourcing tool, we will draw large populations into controlled experiments in a manner that was not possible just a few years ago. If successful, the methods developed here will revolutionize our ability to test social theories by allowing large scale, temporally extended, controlled experiments of diverse populations.

There is high risk as we are utilizing an online platform to do large-scale experiments and we do not yet know how to design, execute and interpret the results of these new types of experiments.

This project is cutting edge in developing a new means of systematically and rigorously testing and validating CSMs. Experiments of this scale and complexity have not taken place using Amazon Mechanical Turk yet, thus this work requires basic research and development.

Summary of Accomplishments:

We have designed an experimental platform to conduct controlled, large, online social experiments (the Controlled, Large Online Social Experimentation [CLOSE] Platform). This platform allows for experiments in which we can study the influence of communication on information diffusion.

We have implemented the experimental platform using the GRAILS web application framework. Our platform allows for a wide range of experiments to be developed in a rapid manner.

We have conducted studies to assess the viability of drawing subject pools from AMT. We find that subjects drawn from AMT are willing to participate in longitudinal experiments (we observe that 30% of subjects returned to participate in our three-wave survey study), and that responses of participants were stable over time.

Significance:

CSMs help anticipate the dynamics and behaviors of malevolent actors by modeling the behavior and interactions of individuals, groups, and organizations. The CLOSE platform provides a new, novel method for gathering data about social influence. This data can be used to validate models of social influence, leading to a better understanding, and increased predictive ability, of behavior change.

Refereed Communications:

K. Lakkaraju, "A Study of Daily Sample Composition on Amazon Mechanical Turk," in *Social Computing, Behavioral-Cultural Modeling, and Prediction, number 9021 in Lecture Notes in Computer Science*, Springer International Publishing, pp. 333–338, 2015.

K. Lakkaraju, B. Medina, A.N. Rogers, D.M. Trumbo, A. Speed, and J.T. McClain, "The Controlled, Large Online Social Experimentation Platform (CLOSE)," in *Social Computing, Behavioral-Cultural Modeling, and Prediction, number 9021 in Lecture Notes in Computer Science*, Springer International Publishing, pp. 339–344, 2015.

Development of an In Situ Sensing Technique for Characterizing Fissionable and Fissile Materials in the Presence of Fission Debris

170798 | Year 3 of 3 | **Principal Investigator: S. Mitra**

Project Purpose:

Rapid in situ techniques are desirable for the isotopic analyses of fission and fissionable material. Methods that use destructive analysis are time consuming and require sample dissolution. For nondestructive analysis, proof-of-principle studies are performed to demonstrate the utility of employing low energy neutrons from a portable pulsed neutron generator for rapid isotopic analysis of nuclear material. The key challenge is isolating the signature gamma rays from the prompt fission and beta-delayed gamma rays that are also produced during the neutron interrogation. To address the challenge, a commercial digital multi-channel analyzer has been specially customized to enable time-resolved gamma ray spectral data to be acquired in multiple user-defined time bins within each of the ON/OFF gate periods of the neutron generator. In particular, time-sequenced data acquisition—operating synchronously with the pulsing of a neutron generator—partitions the characteristic elemental prompt gamma rays according to the type of the reaction—inelastic neutron scattering reactions during the ON state and thermal neutron capture reactions during the OFF state of the generator. Preliminary results on new signatures from depleted uranium, as well as modeling and benchmarking of the concept, have been obtained.

Summary of Accomplishments:

A commercial digital multi-channel analyzer was specially customized to enable time-resolved gamma ray spectral data to be acquired in multiple user-defined time bins within each of the ON/OFF gate periods of a pulsed neutron generator. Experiments and modeling were performed to demonstrate the feasibility of the rapid response sensor for detecting fissile material. Proof-of-principle experiments with depleted uranium samples produced characteristic prompt gamma rays from inelastic neutron scattering reactions during the ON state of a D-D neutron generator. There was minimal interference to the inelastic lines from beta-delayed fission product gamma rays or from slow neutron capture prompt gamma ray lines. The multi-channel analyzer was also optimized to work with a fast neutron detector. This has added the capability to investigate the differential die-away technique, which detects fast neutrons from fissioning nuclei. During modeling, it was realized that the particle transport simulation tool like Monte Carlo N-Particle (MCNP) does not have the evaluated nuclear data file (ENDF) cross-section data files of actinides to allow simulation of active interrogation. This capability will need to be developed and, in conjunction with a burn-up code like CINDER or ORIGEN, the full simulation of the temporal characteristics will be possible.

Significance:

This project has advanced the state of the art for active detection and rapid characterization of nuclear material in complex environments. The work developed unique custom firmware and software for an all-digital data acquisition of neutron induced gamma ray signals. Two approaches investigated were: 1) pulsed activation and 2) associated particle technique. The pulsed interrogation is fully functional and a gamma ray and a neutron detector can concurrently acquire signals in real time. The work will benefit R&D funding agencies who are seeking potential technologies to rapidly determine nuclear or radiochemical composition and quantitative isotopics of fissionable and fissile material samples in the presence of fission product debris.

Refereed Communications:

S.S. Mitra, O. Doron, A.X. Chen, and A.J. Antolak, “Rapid Response Sensor for Analyzing Special Nuclear Material,” *Physics Procedia*, vol. 66, pp. 226-231, 2015.

Dim Target Tracking using an Adaptively Tuned Velocity Matched Filter on High Performance Computing using A Priori Information for Real-Time Tracking

180839 | Year 1 of 2 | **Principal Investigator: D. K. Melgaard**

Project Purpose:

The purpose of this project is to extend our detection capabilities for real-time detection of moving target signatures fulfilling the increasing demands in space and remote sensing missions. Current methods are designed for point targets and consequently do not take advantage of the moving signature of the targets. We are creating, improving, and evaluating several track before detect (TBP) approaches for that purpose. These algorithms include velocity-matched filters (VMF), steerable filters, phase congruency and a new dynamic programming algorithm, recursive estimation of velocities, energies and locations (REVEAL). VMF has demonstrated significant improvements in improving the signal-to-nose ratio (SNR) but exhaustive searches of the hypothesis space can be intractable. The steerable filters employ specialized basis filters to reduce the computational load for determining orientation. Phase congruency uses wavelets to find and display the common phase inherent in moving targets to reveal the location and direction of the target. REVEAL–developed at Sandia–selects a maximum of repeated motion models to improve the detection. Each algorithm has a unique computational complexity that will impact real-time performance. We will utilize Sandia-developed algorithms operating on high performance-computing (HPC) architectures to enable near real-time track determination. By creating and utilizing parallelized algorithms, we will be able to achieve the detection and tracking of low SNR moving targets in real time with adequate responsiveness for tracking maneuvering targets. When cues are available, we also propose using them to reduce the VMF hypothesis search space and restrict the search area to a region of interest. Our goal is to determine the target detection enhancement capabilities of each method and to evaluate how their computational complexity impacts their use for real-time application in order to make recommendations for their utilization.

DISeG: Data Inferencing on Semantic Graphs

180834 | Year 1 of 2 | **Principal Investigator: J. D. Wendt**

Project Purpose:
Standard node/edge graphs are often insufficient for representing complex real-world data. Semantic graphs can be used to more accurately represent reality by adding attributes and relationship types to nodes and edges. However, solving complex equations (e.g., global function minimization) on such graphs and subsequently understanding the interactions between various elements in the graph are open research. To solve such problems, two general solution techniques are typically employed: 1) either ignore the semantic information and solve using standard graph techniques or 2) solve using a standard graph technique for each semantic "layer" (for all nodes and edges of a specific type) and merge the results. Both solutions are incomplete as the first ignores all semantic information stored in the graph and the latter ignores cross-type information flows.

We propose that existing data inferencing techniques (e.g., Belief Propagation) be mapped to semantic graph problems. Furthermore, we will analyze the inferencing results using information-theoretic metrics to understand how influential nodes and subgraphs affect the rest of the graph. Critical national security problems benefited by inferencing on semantic graphs include –but are not limited to–computer network analysis and social media analytics.

Dynamic Analytical Capability to Better Understand and Anticipate Extremist Shifts within Populations under Authoritarian Regimes

173067 | Year 2 of 3 | **Principal Investigator: M. L. Bernard**

Project Purpose:

The US' inability to adequately assess geopolitical and sociocultural dynamics of extremist groups has led to failures in understanding, anticipating, and effectively responding to shifts in their movements and allegiances. Recent attacks within the US highlight the need to more precisely understand and anticipate changes in societal attitudes and behaviors due to radicalization. This is particularly important, as new terrorist cells have begun in Southeast Asia and Africa. A significant concern is their stated intent and effort to plan and conduct terrorist attacks against the US.

The purpose of this work is to create a generalizable data- and theory-supported capability to better understand and anticipate (with quantifiable uncertainty): 1) how the dynamics of allegiance formations between various groups and society are impacted by active conflict and by third-party interventions and 2) how/why extremist allegiances co-evolve over time due to changing geopolitical, sociocultural, and military conditions.

We seek to develop a standalone computational assessment tool for evaluating dynamic military, geopolitical, and socioeconomic interaction effects of extremist groups. Using engineering and social science validation techniques, this effort will produce a capability to quantifiably assess current events and choice options ("what-if" queries) concerning geopolitical intergroup/regional dynamics within a distribution of likely rest-of-the-world reactions to investigate underlying attitudinal and behavioral (extremist) shifts across time. The resulting structure will be designed to be broadly applicable across different ethnic, political, and social groups and will focus on specific extremist group behaviors in response to military, social, economic, and political intercessions.

Dynamic Multi-Sensor Multi-Mission Optimal Planning Tool

180833 | Year 1 of 2 | **Principal Investigator: C. G. Valicka**

Project Purpose:
Cooperating, high-fidelity sensing systems and growing mission applications have exponentially increased the number of potential sensor schedules. A definitive lack of advanced tools places an increased burden on operators, as planning and scheduling remain largely manual tasks. The purpose of the project is to develop new techniques for scheduling remote sensors under the constraints of concurrent missions and uncertainty. A mixed-integer linear program (MILP) model has been formulated to explore the stochastic nature of ad hoc tasks inserted within various time scenarios. MILPs have also been formulated to explore alternative solutions to the computational geometry problem of arranging sensor footprints in time while guaranteeing mission coverage, using few footprints, and satisfying constraints.

Operator experience will guide solver selection within the speed versus optimality domains and assess the capabilities of these new techniques. A working software library is being developed iteratively with the goal of accurately modeling the essential metrics of a variety of sensing missions. Sandia expertise in physics-based simulation of sensing phenomenology and sensor performance will be applied to the scheduling models to aid in scheduling decisions. A framework built upon these techniques aims to aid time-critical scheduling by increasing planning efficiency, clarifying the utility of alternative schedules and model parameters, and quickly presenting organized scheduling information to operators. A scheduling tool derived from this framework will help operators fully utilize sensing systems, a high interest objective within the current national community.

Automated scheduling through identification and comparison of alternative schedules remains a challenging problem applicable across all remote sensing systems. Geometric coverage and real-time scheduling problems representative of newly identified missions remain to be formulated and solved. Existing scheduling algorithms under-perform operators and do not accurately represent the decision space sensor operators face. Exploration of these problem spaces fundamentally advances the state of research in these fields and positions Sandia as a center of expertise for the national community.

Enabling Nanoink Materials for Direct Write and Additive Manufacturing

173045 | Year 2 of 2 | **Principal Investigator: A. Cook**

Project Purpose:

Advancements in electronics printing and integration techniques are changing how engineers use additive manufacturing for the deployment of conductive circuitry. Materials development can further the operational design space afforded by additive manufacturing. Commercially available feedstocks for electronics printing notably lag behind the process improvements of the deposition tools. Tailored nanoparticle ink formulations that can accommodate numerous metals with select deposition arrangements will advance the printed electronics and additive manufacturing state of the art. To affect this, a fundamental understanding of nanoparticle ink dispersions and the processing conditions is required. The main challenge of this project is to create enabling materials compatible with direct write and additive manufacturing technologies. Variations in elemental density, thermodynamic energies, and atomistic variance will be explored to determine governing forces associated with nanoparticle sintering process.

Summary of Accomplishments:

High purity metal and ceramic nanoparticles were synthesized and subsequently used to formulate previously undocumented nanoparticle ink systems. Following an aerosol deposition printing process, selective sintering was used to test and evaluate novel post-process techniques to establish an electrically conductive state in thin metal films. Imaging was performed to reveal evidence of complex film morphology. Phase field computational modeling was employed to simulate nanoparticle ink sintering processes, which helped explain the role free surface energy plays during sintering process.

Significance:

The fundamental research and engineering conducted under this activity enabled the development of functional materials with tunable electrical responses. The materials synthesized were used with additive manufacturing processes and are expected to have utility for national security missions. Furthermore, the development of a phase field computational model that accurately predicts the formation of heterogeneous microstructures was a significant outcome that will guide future research and applications of printed electronics.

Engineering Efficient Human-System Interaction in Defense Systems-of-Systems

180856 | Year 1 of 3 | **Principal Investigator: M. J. Hoffman**

Project Purpose:
The purpose of the project is to develop a unique modeling capability for quantification of human-technology interactions within system-of-systems engineering. Engineering complex systems-of-systems typically does not include initial consideration of how humans will interact with the system-of-systems' heterogeneous constituent technologies/systems. But these interactions have vital effects on overall system-of-systems functionality; quantitative understanding of these effects and their propagation through the system over time can provide significant cost and performance improvements, and possibly save lives.

In general, human-technology interactions are handled through training, after design engineering is complete and systems are fielded. *Prior* to system fielding, understanding where technology might benefit human performance in a system-of-systems (e.g., where automation and task augmentation is beneficial) is very limited. Similarly, ranges of potential operators' knowledge, skills, and abilities are not always adequately considered in understanding system performance at the design stage. When assessing effectiveness metrics like troop-to-task ratio (critical in military system-of-systems engineering), quantifying such effects is essential.

Sandia has significant capability in quantitative system-of-systems modeling–this capability enables understanding technology/system and system-of-systems effectiveness when engineering complex system-of-systems. However, this capability does not include (with adequate fidelity) human entities, which are necessary to understand effects of human-technology interaction within the system-of-systems context. We intend to expand Sandia's system-of-systems modeling capabilities to include human-system interactions modeling at sufficient fidelity—leveraging Sandia's expertise in quantifying and modeling human behavior and behavioral effects on interactions with technology. We have developed, and are refining, a small representative use case in the context of a military forward operating base (FOB) for researching the quantification of human-technology interaction effectiveness.

Quantifying the impacts of technology on human performance (and vice-versa) as part of evaluating system-of-systems effectiveness is a novel area of research with very few existing capabilities. Developing and demonstrating credible fundamental/prototype capability would be a prerequisite for maturation into an operational capability.

Exploitation of Optical Polarimetry for Remote Sensing

180840 | Year 1 of 3 | **Principal Investigator: J. C. Jones**

Project Purpose:

Investments have been made by multiple customers to produce optical remote sensing systems with polarimetric measurement architectures. However, due to limited effort and rigor in characterization and validation, a comprehensive understanding of the capabilities of many of these systems is lacking. Furthermore, the utility of polarization data products for remote sensing missions remains relatively unclear. A frequently cited application is improved contrast for detection of inherently polarized manmade objects against weakly polarized natural scenes. However, the effectiveness of even this regularly cited example has not been well-quantified, and the general utility of a given polarimeter in situations that an operational system will encounter such as low light, long standoff distances, bad weather, etc., remains unknown. Furthermore, whether polarization signatures can provide some exceptional utility that more established sensing modalities cannot cover has not been established.

By leveraging our well-established and multidisciplinary remote sensing expertise, Sandia is uniquely suited to address the uncertainties related to the utility of optical imaging polarimetry for remote sensing. Through a multi-faceted research approach, this project will investigate both instrument characterization and validation (through simulations and experimental data), as well as data exploitation and analysis. This work will also assess novel polarimetric data acquisition and processing technologies to provide a path towards the next generation sensor architecture. The outcomes of this project will directly impact Sandia's future national security missions in nuclear nonproliferation and other mission areas, and could provide the foundational research that establishes Sandia as a premier research center for optical polarimetric remote sensing.

Exploring 2D Materials for Remote Sensing Applications

180836 | Year 1 of 2 | **Principal Investigator: J. A. Bartz**

Project Purpose:

The purpose of the project it to create 2D heterostructure devices, specifically sensing devices, with properties not realized through the use of bulk materials, in order to improve remote sensing capabilities.

In order to produce and characterize novel 2D material heterostructures, this research will pursue three parallel approaches: modeling, flake-based heterostructure assembly, and chemical vapor deposition. With density functional theory, materials will be modeled, providing insight and guidance. Next, this research aims to create, characterize and compare these 2D material heterostructures to the modeled results. Initially, this will involve experimental verification of methods used to produce monolayers through mechanical exfoliation, including Raman spectroscopy, photoluminescence measurements, and atomic-force microscopy. Following reliable production of micron-sized monolayers, heterostructures will be assembled and metal contacts will be formed for electrical probing and characterization. The third approach pursues large area production of monolayers through chemical vapor deposition. As this research focuses on sensing applications, large area production of materials of interest is essential.

The challenge of optical absorption in atomically thin materials may be overcome with nanoantennas. This active area of research and development at Sandia can potentially increase a material's effective absorption by a factor of 20. Development of a 2D material-based infrared detector, combined with nanoantennas, may provide high quantum efficiency with extremely low dark current. Such a device has been theorized but not realized. The realization of the suggested device will require the development and refinement of techniques by which heterostructures can be assembled yielding high quality devices with good properties.

Flux: Toward a General Model of Moving Target Defense Efficacy

180831 | Year 1 of 2 | **Principal Investigator: C. Lamb**

Project Purpose:

The goal of this project is to establish a validated foundational model describing why moving target defense (MTD) controls succeed or fail.

The primary deliverable is a validated predictive model that can identify promising MTD controls, leading to effective MTD control development and deployment. The deliverable ties directly to the primary purpose of the work–the establishment of a more rigorous theoretical foundation for MTD development. Essentially, we propose the development of a general model we hypothesize will identify current known problems with MTD solutions at a variety of levels, ranging from application-level controls to host controls to network controls. Challenges in developing this model primarily impact the use of the model with regard to developing and deploying real MTD controls. The research community has proposed many different MTD approaches to date, but has yet to establish a common foundational systems theory that addresses common failures and successes experienced with individual controls.

Though the project team has worked through the concept and rudimentarily validated the approach, the concept is not currently represented in MTD research literature. This project is high-risk and proposes a revolutionary, not evolutionary, approach to MTD in a field characterized by ad hoc vertically integrated efforts.

Ground Moving Target Extraction, Tracking, and Image Fusion

165555 | Year 3 of 3 | **Principal Investigator: T. J. Ma**

Project Purpose:

The purpose of this project was to investigate a new concept of applying image fusion prior to detection and tracking to solve the multi-sensor fusion problem. Traditionally, multi-sensor data fusion often occurs by fusing the output of detections generated by individual sensors. However, if images were fused prior to detection processing, it is possible that the fused image can provide more complete information about the scene and the target, which can potentially enhance detection performance. A fused image has more complete information than any single sensor alone because it combines complementary information from other sensors. For example, some sensors may be better detecting a target in certain situation than others. Another important benefit of a fused image is that it reduces redundant information. Rather than reviewing individual images from multiple sensors, the user can review the unique fused image. Additionally, a fused image improves reliability of information. For example, the same object may be seen by multiple sensors. Our proposed solution to the multi-sensor fusion problem contains three main steps: registration, fusion, and detection. We investigated two approaches to image registration: sensor-to-sensor registration and sensor-to-scene registration. Additionally, we explored various types of multi-sensor image fusion techniques such as principle components analysis and wavelet-based approaches. Finally, we processed the fused image into our existing detection framework so that performance can be assessed.

Summary of Accomplishments:

Image registration is a prerequisite to image fusion. We investigated two approaches to image registration: sensor-to-sensor registration and sensor-to-scene registration. Sensor-to-sensor registration involves the use of images from a single sensor as the source reference images and registering all other sensors into this reference. Registration results were found to be inconsistent, as sometimes bad images from one sensor can cause degraded performance in registration. On the other hand, we discovered that registration results using sensor-to-scene registration approach provides a more consistent registration result. Sensor-to-scene registration involves registration of sensor images using pre-determined sets of scene data as a reference. We also investigated an image fusion algorithm based on a dual-tree complex wavelet transform. We have the fusion algorithm implemented in MATLAB and tested with real data. Additionally, we tested our initial hypothesis by processing fused images through our detection and tracking framework. Our resulting fused tracks are demonstrated to have a higher signal-to-noise ratio than a single sensor's tracks. Also, our fused tracks were compared with a traditional fused-after-detect approach and found to be more reliable and accurate.

Significance:

The general field of remote sensing plays an important role in Sandia's national security mission in the design of novel sensor systems, manufacture and testing of components and hardware, and development of algorithms and software for sensor command and control, data collection, and data analysis. Multi-sensor fusions are priorities with the remote sensing community as a whole. Results from this project will have a broad impact on how future data processing will be conducted in the remote sensing communities.

High Fidelity ARM Virtualization for Large-Scale Mobile Emulytics

180832 | Year 1 of 2 | **Principal Investigator: D. J. Fritz**

Project Purpose:

We propose a three-part project designed to add Advanced RISC Machine (ARM) architecture based, representative mobile device emulytics to Sandia's existing emulytics platforms.

With the rapid growth and availability of smart phones coupled with modern society's dependence on them, smartphones have become a prime target for cyber criminals and nation states. Smartphones are embedded in almost every facet of life, ranging from communication (calls, email, texting, and social-networking) to online banking, GPS navigation, and medical records. Government and industry both heavily rely on smartphones in the workforce.

This project aims to add a representative and large-scale ARM architecture capability, as well as emulated sensors and radios for mobile devices, to Sandia's existing emulytics framework. ARM is the dominant processor architecture for smartphone and tablet devices, and is making headway into the laptop market. Existing platforms, both public and private currently only provide x86_64 virtualization. While these platforms certainly provide performance and scale for desktop operating systems, they fail to provide an effective and realistic platform for mobile devices.

Holistic Portfolio Optimization using Directed Mutations

173063 | Year 2 of 2 | **Principal Investigator: M. A. Smith**

Project Purpose:

The purpose of this project is to develop much better algorithms for helping military decision makers design optimal portfolios of systems over time where both the system technologies and the counts of systems are decision variables. Important examples of such portfolios are: 1) fleets of vehicles, aircraft, or ships, 2) grids of electric power source technologies, and 3) networks of information processing and communications devices. The problem is particularly hard due to the nonconvexity of the decision space, which is defined by binary technology choices and integer system counts.

Current approaches to this problem involve separate optimization steps: first optimizing individual system technology choices over multiple objectives and then optimizing the integer number of these systems in the portfolio over time. This two-step approach simplifies the problem at the risk of ignoring important decision variable interactions. Solving the problem in one step has proven computationally intractable because of the large scale combined with having a nonlinear multi-objective trade space.

Our proposed, holistic solution to the problem is to search the design space more rapidly by using large yet coordinated steps. In particular, coordinated steps in system counts will be generated using gradient information from the performance measures. These steps will be included as mutations in an iterative genetic algorithm (GA) to evolve a Pareto optimal trade space of portfolios to help inform military decision makers.

Directed mutations based on gradients have been used in GAs for single-objective continuous optimization, but their use in multi-objective integer optimization is new. To make this approach work, we have to devise, run, and analyze new algorithms for using gradient information to suggest intelligent portfolio design changes. Success in this effort would open up new approaches to the field of operations research more generally.

Summary of Accomplishments:

We demonstrated how directed mutations can have substantial benefits in improving the performance of GAs for portfolio optimization. Specifically, when the objective function (or functions) to be optimized is an analytic function of the system counts, then the information contained in the gradients of the function can be leveraged to direct mutations that work much better than the purely random mutations and crossovers of a basic GA.

Using a basic GA as a baseline for comparison, we achieved spectacular speedups as measured by clock time. Depending on the problem and exactly how the speedups are measured, we conservatively attained at least a factor of 1000x in performance. Speedups of this magnitude make more than a quantitative difference: they also make a qualitative difference in the types of problems that are in the realm of tractability and in the ability to do multiple what-if optimizations instead of just a few.

Various types of gradient-directed mutations can be used in conjunction with basic mutation and crossover to generate multiple trial solutions. In the case of a single objective, we discovered synergistic effects in that multiple types of mutations work much better together than individually. Moreover, we found that as the optimization algorithm proceeds, different types of mutations are more effective early or late during the evolution.

We extended the above results to multi-objective optimization wherein a Pareto-efficient trade-space of good design options are generated. In this case, we discovered that not only is the optimization much faster, the quality of the solutions better approximates the full depth and breadth of the true Pareto frontier.

Finally, we incorporated a custom mutation injection capability into Sandia's GA-based Technology Management Optimization (TMO) software. This new feature of TMO will facilitate further research, development, and application of directed mutations.

Significance:

Designing portfolios of systems over time is a ubiquitous problem for both military and energy applications. This project combines mathematical science and computing technology to further our ability to analyze and optimize such portfolios. As such, it is directly related to DOE's mission of ensuring security and prosperity through transformative science and technology solutions. Furthermore, it is linked to the national security and energy missions of Sandia thorough its strategic partnering projects with the DoD. Finally, this type of work continues to help nurture Sandia's optimization staff and grow its internal operations research capabilities.

Hypersonic Autopilot Adaptive Control for Aerodynamic Uncertainty Mitigation

180826 | Year 1 of 2 | **Principal Investigator: D. M. Kozlowski**

Project Purpose:

The purpose of the project is to develop reliable adaptive control strategies for agile hypersonic flight vehicles subject to large uncertainties and time-varying system parameters. Intelligent control development for hypersonic flight applications remains a difficult, outstanding research problem. Uncertainties associated with large operational flight envelopes at extreme speeds make control design a particularly complex problem. Controllers can be tailored to specific, well-defined trajectories, but these methods are unrealistic for operational systems. The main drivers of system instability are aerodynamic uncertainties to which the vehicle is subjected to throughout flight. Complicated aerodynamic phenomena are difficult to predict through ground testing or computational simulations. Imprecise high altitude atmospheric models are additional uncertainty contributors. Flight test data provides discrete validation points for models, but the full continuum of the flight envelope is not well modeled and changes with mission objectives.

Adaptive control strategies have emerged in the aerospace community as potential solutions for handling these types of parametric uncertainties. In this work, we propose two adaptation strategies for parallel implementation. First, a software adaptive control solution will be developed to supplement existing nonlinear control strategies for a representative hypersonic vehicle. Second, a mechanical adaptive control solution will be designed to provide a physical, real-time method for manipulating stability in the presence of large aerodynamic uncertainties. Together, this stability supplementation system will deliver new, forward-looking control solutions for operational hypersonic vehicles.

Hyperspectral Hypertemporal Database Reference Search Project

180845 | Year 1 of 3 | **Principal Investigator: J. D. Zollweg**

Project Purpose:

Sandia has invested in explosives testing for decades. A goal of this testing is to better understand high explosive (HE) phenomena, in order to inform improved discrimination algorithms. To date, this wealth of data has not been integrated into a common format and processing framework spanning the range of possible HE materials, masses, case configurations, and other parameters affecting observed optical signatures. As such, there has been no standardized working environment to develop classification tools applying to the entire breadth of HE test data already owned by Sandia. Similarly, there has been no method to scientifically and statistically state the broad-ranging detection and discrimination capabilities of proposed mission sensors.

The initial challenges of creating a hyperspectral hypertemporal database (HHD) are compiling massive amounts of data from disparate sources then developing a powerful format to standardize to, and creating tools to manipulate, visualize, and process the data. The true technical challenge of this project is to utilize the comprehensive database to study various types of detonations and identify new discrimination parameters for improved classification. Phenomenologically tuned, frequentist-based classification algorithms will be developed as a result of improved HE understanding. Additionally, predictive sensor performance models will be established to confidently estimate new sensor capability and intelligently guide future designs. This will be accomplished by degrading the “pristine” database signals to proposed sensor configurations and testing detection/classification performance at those resolutions.

This project is high-risk because it will inform still-developing HE optical emission science. Presently, detonations are partially understood, making simulation and classification difficult. Varied device configurations leave telltale signatures in shock and afterburning regimes. Knowing which device parameters caused these is challenging with current diagnostic methods. Predictive sensor performance will represent a powerful Sandia-exclusive capability, but is a technical leap.

Imaging LIDAR and Raman Imaging LIDAR through Fog and Dust for Maritime Surveillance

173064 | Year 2 of 3 | **Principal Investigator: S. A. Kemme**

Project Purpose:

This project supports Airborne Intelligence, Surveillance, and Reconnaissance for tactical situational awareness in challenging environments with modified imaging LIDAR (light detection and ranging). LIDAR produces an irradiance-based scene with high, 3D, spatial resolution; differentiating reflecting surfaces and surface textures not just for target detection, but also target recognition.

LIDAR is generally prevented from working through all weather—as the traditional source wavelengths are scattered and/or absorbed by fog, clouds, and dust. However, we at Sandia and other researchers have identified and quantified improved optical propagating wavelength regimes, taking advantage of the Christiansen effect, and polarization strategies that should open this otherwise opaque operating window for LIDAR.

We will demonstrate modified imaging LIDAR's utility and ability to produce images in environments that have been challenging for traditional LIDAR (fog, dust) systems as well as environments that are challenging for RADAR/SAR (target identification, water interfaces, foliage penetration) systems.

Imaging Mass Spectrometry for Biometric and Forensic Detection

173069 | Year 2 of 3 | **Principal Investigator: J. M. Hochrein**

Project Purpose:

There is significant need to unambiguously determine a person's identity and locations where he/she has been. Traditional biometric approaches such as fingerprinting, hair analysis, DNA, and retina/ iris scanning, typically target one characteristic and often require previous knowledge of the individual. We propose using imaging mass spectrometry to identify new biometric signatures addressing several characteristics simultaneously and generating a fingerprint map. High-resolution mass spectrometry combined with imaging is a highly versatile tool applicable to many analytes including small molecules, semi-volatile, and non-volatile species including biomolecules. This technique has been demonstrated on explosive residues, drugs of abuse, inks, and many other organics. In most cases, complex matrices have not been investigated. Specific markers that would be of interest to identify not only a specific person or group of people but also provide information on their activities or working environment remain to be characterized. This research will focus on the discovery of new chemical markers from fingerprints and other biological targets including hair, nails, skin, ear wax, and saliva that will be used to identify biological and environmental signatures unique to an individual or group of people of interest. Significant advances have been made to enable the positive identification of people based on biometric signatures but many of these techniques require considerable knowledge of the person prior to identification. Additionally, some of the biometric signatures can be manipulated rendering them ineffective or ambiguous. The focus of this work will be to identify several new key signatures while at the same time generating a high-resolution image making identifications much higher fidelity.

Improving Radiation Spectra Identification for Radioactive Materials with Uncertain Configurations

180846 | Year 1 of 2 | **Principal Investigator: M. L. Koudelka**

Project Purpose:

The goal of the project is to advance the state of the art in the identification of radioactive materials using low fidelity gamma radiation spectra, where the configuration of the radioactive object is unknown. Due to the varied environments in which sensors may operate, data may be of poor statistical quality. In some scenarios, radioactive sources may be shielded and distant, leading to smooth and nearly featureless spectroscopic signatures. Current signature identification techniques involve fitting computed spectral signature exemplars to measured data of interest to determine the radiation source. These methods generally require high fidelity or experienced spectroscopists to guide the analysis by intelligently selecting and computing exemplars to match against measured radiation spectra. Improved methods are needed to further the state of the art for the rapid assessment of gamma-ray signatures with uncertain configurations. We propose the development of algorithms and techniques that can capture the variability in radiation spectra across an array of possible configurations with a limited set of template-based representations. To do this, we will leverage target identification algorithms developed at Sandia and currently employed for radar signature identification. While these algorithms have been extremely successful in identifying radar targets, they will need to be extended to capture different types of variation, including the nonlinear effects caused by shielding of radioactive materials. This work will enable significant improvement in spectroscopic identification capabilities, and will provide much-needed automation in the analyst's ability to identify sources in uncertain configurations.

Integration of a Neutron Sensor with Commercial CMOS

170803 | Year 2 of 2 | **Principal Investigator: W. C. Rice**

Project Purpose:

The purpose of the project is to produce a radiation sensor using commercial complementary metal-oxide semiconductor (CMOS). The sensor will make use of the existing technology platform to provide a viable detection option. The device will achieve this purpose by leveraging existing technologies and overcome the challenges that prevented implementation in prior designs.

Summary of Accomplishments:

The project successfully demonstrated radiation detection was possible in a commercial off-the-shelf (COTS) device. It met target detection thresholds. The processed devices demonstrated the expected phenomenology and we quantified performance. Improvements and modifications to prior unsuccessful designs led to greater sensitivity and capability.

Significance:

The device represents a suitable option for radiation detection to meet mission area priorities. It can be used wherever circuits are exposed to incident radiation (i.e., in space environments). Additional power savings can be achieved for remote sensing applications. The work led to a collaborative effort with partners working on a similar design.

Intelligent Control for Autonomous Penetration (ICAP)

180825 | Year 1 of 2 | **Principal Investigator: S. Buerger**

Project Purpose:

The purpose of the project is to research the application of advanced feedback control to improve the performance and autonomy of select non-kinetic penetration technologies. The present state of the art requires expert human operators to manually operate most relevant non-kinetic penetration systems, exploring system settings, and working to optimize performance via a combination of learned expertise and trial and error. The operator makes adjustments at arbitrary intervals to maximize performance (e.g., rate of penetration and energy efficiency) and to manage disturbances such as variations and transitions in material properties. Recent advances in sensors, control systems technology, and penetration capabilities make it possible to develop novel intelligent penetration systems that adapt in real-time to reject disturbances and optimize performance without operator intervention. This project will develop and demonstrate intelligent penetration systems. Work will include a combination of modeling, control system analysis and design, and experimentation. Models of penetration processes will be developed and parameterized through experiments conducted at existing specialized Sandia test facilities, which will be outfitted with additional instrumentation. Controllers will be designed in simulation and tested experimentally. The project will culminate in "one-touch" demonstrations, in which a prototype system autonomously penetrates a multi-layer sample with a single operator command. Performance will be shown to significantly exceed that capable with any single, open-loop system setting.

Internal Structure Mapping with X-Ray Phase Contrast Imaging

180838 | Year 1 of 2 | **Principal Investigator: A. L. Dagel**

Project Purpose:
The purpose of this project is to develop a lab-based x-ray phase contrast imaging (XPCI) system to study XPCI as an alternative approach to existing destructive imaging and test modalities.

Authenticity and verification of commercial components used in trusted electronics is a complex process of procurements and inspections. It is critical that inspection methods effectively identify material, process, or mechanical variations between procurements. Current effective methods are destructive in nature and employ “slice and dice” inspection of randomly selected samples. Less effective non-destructive methods are limited in imaging depth, require complicated sample preparation, and are limited in materials that can be inspected. X-ray absorption imaging is currently used for non-destructive imaging; however, it has poor sensitivity to low absorbing (low-Z) materials that compose the oxides and nitrides prevalent in integrated circuits (ICs).

XPCI is an approach for non-destructive mapping of internal microstructure. In all materials, the phase coefficient is larger than the absorption coefficient, resulting in much higher contrast in phase-based imaging than traditional x-ray absorption imaging. For low-Z materials, the difference between coefficients is three orders of magnitude. The increase in contrast sensitivity can be employed for the internal mapping of multi-material stacks where neighboring materials have small changes in density. Differences between ICs in the form of intentional or unintentional addition or deletion of materials can be identified. One of the keys to making XPCI successful is large area, high aspect ratio x-ray gratings with high uniformity. The gratings enable the transition of this imaging modality from synchrotron beam lines to the lab environment and Sandia has demonstrated the unique ability to fabricate these devices with unparalleled precision.

Liquid Metal Embrittled Structures for Fragmenting Warheads

170806 | Year 3 of 3 | **Principal Investigator: J. J. Rudolphi**

Project Purpose:

The purpose of this project is to investigate novel materials to assess their application in fragmenting structures. Specifically, the goal of the project is to quantify the behavior of these novel materials when exposed to rapid material failure during explosive fragmentation and assess the technology's viability to be incorporated into fragmenting devices. Typically, fragmenting devices are macroscopically weakened to create fragments of a specified shape and size. Furthermore, the ductility of the fragmenting material must be considered to determine the statistical distribution of fragment sizes. This project considers a quasi-metallurgical technique that creates weakened regions of variable ductility through the incorporation of special agents into the fragmenting materials' microstructure. This specific method has not been used before to control fragment size and size distribution. By creating a practical method of material modification that allows a wider and more controllable range of particle sizes to be accessed, fragmenting devices could be engineered that create a wider and more variable range of effects.

Summary of Accomplishments:

Several technical accomplishments were made during the course of this project. We quantified a preparation procedure and material verification process for the test materials. This process was created by trial and error and allowed materials to be accurately duplicated for multiple tests. We tested modified materials to determine shock Hugoniot and static properties. The shock Hugoniot properties were the first reported tests of these materials and showed significant changes from base materials with only a small addition of modifying material. Finally, we showed the utility of these materials in explosively fragmenting geometries. Tests were conducted using naturally fragmenting cylindrical charges to compare the fragmentation properties of base and modified materials. Tests were conducted at full and reduced shock loadings, which were modified by inserting a polycarbonate buffer between the explosives and fragmenting materials. These tests showed a dramatic difference in particle sizes and shapes between unmodified and modified cylinder materials. Specifically, it was shown that a much smaller fragment size with narrow distribution was attainable using modified materials, but not possible using unmodified materials. Furthermore, depending on the base material, there are energetic enhancements that are realized due to the smaller particle size.

Significance:

The results of this project may allow for smaller and more tailored fragmenting munitions to be engineered. Furthermore, energetic applications may be created due to the much smaller particle size that can be attained using this method. This method of material preparation could advance both fragmenting munitions and energetic munitions capabilities.

Macro Supply Chain Decision Analytics

180859 | Year 1 of 2 | **Principal Investigator: G. K. Kao**

Project Purpose:

Today's global supply chains are intrinsically complex systems that make security and integrity risk difficult to manage. The US Government Accountability Office (GAO) reports that many US Government agencies lack sufficient capabilities to address global supply chain security risks. No analytic tools exist that assist decision makers in capturing, visualizing, and assessing the state of health of a supply chain holistically at a policy level. A NIST Special Report explicitly calls out the importance of holistic supply-chain metrics: visibility and traceability. Complex corporate structures and distribution networks *reduce supply chain visibilities and traceability,* making it extremely difficult to secure the supply chain of an end product. Furthermore, the ownership of corporate structures can change overnight; hence understanding a supply chain is an evolving and continuous process. As a result of these factors, it is difficult to understand supply chain risk and decide where to gather more information or apply mitigations.

We propose developing analytic methods to construct a bird's-eye view of a production process and its associated supply chains, and to identify and assess macro-level indicators to help policy and decision makers make better decisions. This is analogous to measuring vital signs (blood pressure, pulse, respiration, temperature) before administering a diagnoses or prescribing more extensive tests. These methods will help policy and decision makers address the following questions. Who and what are involved in a supply chain? How do changes in policy affect the supply chain security? When is a more in-depth analysis of a specific aspect of a supply chain needed?

Meta-Meta-Optimization for Integrated Requirements Development

180855 | Year 1 of 2 | **Principal Investigator: A. Dessanti**

Project Purpose:

The purpose of this project is to develop a novel approach that fuses optimization and data exploration techniques in order to address a fundamental flaw in government acquisition processes that often results in program cancellation, billions of dollars wasted, and warfighter capability stagnation (see Future Combat Systems and Ground Combat Vehicle programs). Requirements have traditionally been developed with limited consideration of their interactive effects, often resulting in unattainable, unaffordable, mutually incompatible requirements that doom a program from the start. Simply stated, a complex military system cannot be built from a foundation of broken requirements documents.

This research will dramatically improve defense acquisition processes by injecting a “feedback loop” into the early requirements definition process. This enables a deep understanding of the interactions and potential conflicts between system requirements during their inception and suggests defensible, mutually compatible goals that satisfy multiple stakeholders. Traditional multi-objective optimization (meta-optimization) approaches explore candidate solutions under fixed “goal posts” (requirements). In contrast, this meta-meta-optimization will simultaneously explore system designs (“finding the best players”) *and* system requirements (“designing a winnable game”)—driving programs toward feasible, consistent goals from the onset (avoiding the need for damage control when requirements conflicts eventually arise).

This concept is novel within the optimization literature and would likely lead to new industry standards for optimization under indeterminate value measures. It will put Sandia on the cutting-edge of robust analytics for acquisition programs, with applications across the US government.

This project will produce novel advances in genetic algorithms and data exploration—significantly impacting acquisition processes and the Operations Research community. Unlike current Sandia system design exploration capabilities, this work will apply earlier in the acquisition process and therefore provide a new, distinct capability.

Micro Scale, Low Power RF Power Detector using IC-Based Calorimeters

173048 | Year 2 of 2 | **Principal Investigator: K. Wojciechowski**

Project Purpose:
Current state of the art radio frequency (RF) power spectrum sensing is limited by sensor size, power, and integrated circuitry bandwidth. This project investigated a technology that has the potential of reducing size and power while providing expanded and selective bandwidth monitoring from DC to 10 GHz.

Summary of Accomplishments:
We have successfully demonstrated an enhanced RF detector capable of detecting very low RF power levels. Since power detection is performed passively, ultra-low power consumption can be achieved. The novel RF power detector technology developed leverages our capability to create microscale devices with high thermal isolation. Integrated RF filters enable selective RF power detection at multiple frequencies. A prototype has been demonstrated which can detect low power at multiple RF frequencies on a single integrated circuit (IC).

Significance:
This work represents the state of the art with respect to minimum detectable signal (RF power) for a microelectromechanical systems (MEMS)-based device. The developed technology enables a new capability to perform low power, high resolution, RF environmental sensing over a wide range of narrow band frequencies in a single chip with low power operation. These sensors can be integrated into smart/adapting RF systems, aligning well with homeland security, DOE, and NNSA missions.

Finally, these novel sensors could potentially be incorporated into new (commercial non-government) adaptable communication systems that would help make the US a world leader in these technologies.

Model Reduction for Quantum Technologies

170973 | Year 3 of 3 | **Principal Investigator: M. Sarovar**

Project Purpose:

Precisely controlled, engineered quantum systems will be critical to next-generation measurement, computing, and communication technologies. However, as we attempt to design and construct larger and more complex quantum devices, we quickly approach a difficult impasse. Namely, the task of modeling and simulating such large-to-medium scale quantum mechanical devices becomes computationally challenging since the size of modeling state-space increases exponentially with the number of degrees of freedom. This difficulty severely limits our ability to perform predictive simulation of quantum technology devices.

In this project, we will take a systems-level approach to this problem and develop techniques for reducing the modeling complexity of a broad class of potential quantum devices. The primary thrust of the research will be to extend rigorous model reduction techniques from mathematical engineering (*e.g.*, proper orthogonal decomposition, unsupervised manifold learning) to the quantum realm. Properties such as noncommutative structure preservation will be incorporated into these classical model reduction techniques in order to make them suitable for quantum systems. The successful formulation of such quantum model reduction methods will enable rigorous performance analysis of quantum devices, including application of methods for uncertainty quantification (UQ) and verification and validation (V&V). This, in turn, will enable more rapid development of near-term quantum technologies for tasks such as precision measurement and secure communication. In addition, the research has the potential to have broad impact on the quantum information sciences by generating new insights into the modeling and simulation of quantum mechanical systems.

The proposed research is highly interdisciplinary and develops methods that bridge mathematics, engineering, physics, and computer science.

Summary of Accomplishments:

Our accomplishments are as follows:

We developed new techniques for estimating parameters in closed and open quantum systems from measurement time traces. This technique utilizes minimal model realization theory and allows one to incorporate prior information about the Hamiltonian, if available. Also, the technique is applicable even when a limited number of observables are measurable in the system.

We developed new methods for Hamiltonian model reduction that operate by certifying and generating invariant subspaces for parameterized Hamiltonians. These methods allow one to identify when error-free model reduction is possible for the dynamics generated by a Hamiltonian, and also, to construct the resulting reduced order model. These powerful methods can be seen as constructively identifying and exploiting symmetries of a dynamical system.

We established collaborations with teams at two major universities (University of California, Santa Barbara and Shanghai Jiao Tong University) to investigate model reduction and model realization in the quantum domain.

We began development of a general technique to assess the robustness of quantum simulation models. This stemmed out of work on model reduction but has wider impact into the burgeoning field of quantum simulation.

Significance:

In the coming decades, quantum information sciences and associated quantum technologies are expected to have significant impact on many fields. Some of these are particularly relevant to the national security missions of DoD and DOE, including cybersecurity and information processing, precision measurement, nanoscale manufacturing, and secure communications. The techniques we developed over the course of the project allow for more effective modeling, simulation, and probing of key quantum technologies. These methods will further our understanding of such technologies and significantly aid in their development by enabling efficient simulation and verification.

Refereed Communications:

J. Zhang and M. Sarovar, "Identification of Open Quantum Systems from Observable Time Traces," *Physical Review A*, vol. 91, p. 052121, May 2015.

A. Kumar and M. Sarovar, "On Model Reduction for Quantum Dynamics: Symmetries and Invariant Subspaces," *Journal of Physics A: Mathematical and Theoretical*, vol. 48, p. 015301, December 2014.

J. Zhang and M. Sarovar, "Quantum Hamiltonian Identification from Measurement Time Traces, *Physical Review Letters*, vol. 113, p. 080401, August 2014.

Modeling and Experimental Validation of Jet Vane Forces for a New Type of Missile Defense Kill Vehicle Steering System

173065 | Year 2 of 2 | **Principal Investigator: L. A. Jones**

Project Purpose:

Many guided rockets control pitch and yaw by moving their rocket exhaust nozzle. Control actuators point the nozzle, which changes the thrust direction of the rocket, and hence the name thrust-vector control for this type of pitch and yaw control. A downside of thrust-vector control is that roll must be controlled with a separate system using additional actuators. In smaller rockets, control-system actuators often do not scale down in size and mass as much as desired, and it is therefore beneficial to reduce the number of actuators required for pitch, yaw, and roll control. In these small systems, jet vanes in a fixed exhaust nozzle can be used for pitch, yaw, and roll control using fewer actuators.

In some applications, control is needed over long periods of time—many tens of seconds—where the survivability of the jet vanes comes into question. The rocket propellant must be carefully chosen in these applications and the jet vanes and actuators must be carefully designed.

The purpose of this project was to model and experimentally test the pitch, yaw, and roll forces that can be generated by jet vanes operating in the exhaust flow of small solid rocket motors. Vane heating and erosion was also investigated. The primary goal was to obtain data to validate the design process for small jet vane systems that might be used in a variety of applications.

Summary of Accomplishments:

This project identified multiple low-cost materials that will survive long-duration rocket motor burns with minimal degradation. Confirmation that these materials will survive was obtained through live rocket motor burns where representative material coupons were subjected to the environment.

To investigate the lift curves generated by deflected jet vanes, a shock-free, high-specific-impulse nozzle was designed. Because a low-temperature propellant was used to help the jet vanes survive, it was important to highly over-expand the flow in a vacuum to obtain a high specific impulse. The desired specific impulse was achieved during vacuum chamber burn experiments and there was no evidence of shocks interacting with the jet vanes. Later burn experiments used movable jet vanes to measure their lift curve. A simple jet vane thrust vector control (JV-TVC) system was developed to rotate the jet vanes in the nozzle 25 degrees in either direction.

The forces created by the rocket motor thrust and the jet vanes were measured using a custom-build, 6 degrees of freedom measurement stand in the vacuum chamber. This test stand can be reused in future efforts.

Thrust, pitch, yaw, and roll forces generated by the rocket motor and the jet vanes were collected using the measurement stand in a vacuum chamber. Five burns were performed using various jet vane configurations and various jet vane movements.

Analysis of the experimental data revealed that the analytical jet vane lift predictions matched the experimental data within 1% over multiple operating conditions.

Significance:

The feasibility of jet vanes for turning and rotating rocket motor thrust and generating significant lateral and roll forces was demonstrated. Jet vanes can be used to control the pitch, yaw, and roll of a rocket motor.

The experiments conducted in this project dismissed concerns about jet vane survivability in long-duration, high-enthalpy rocket exhaust flows. The experiments also provided aerodynamic force measurements of steering effectiveness and measurements of the accuracy of the jet vane models.

Possibly most important is the excellent agreement obtained between the analytical models and the experimental data. This result has created confidence that custom jet vanes can be designed for future interceptor steering systems.

Motion Estimation and Compensation for Focusing Maritime Targets

173061 | Year 2 of 2 | **Principal Investigator: D. W. Harmony**

Project Purpose:

The purpose of this project is to develop algorithms for estimating the dynamics of moving ships from radar measurements. The approach is based on comparing a sequence of synthetic aperture images enhanced by CLEAN and RELAX processing assuming the ship behaves as a rigid body. A goal of the project was to extract rolling and pitching motion of the ship as functions of time.

Summary of Accomplishments:

Analysis was performed using simulations and data collected by Sandia radar systems on actual ships. The collected data included measurements from a dual-axis monopulse system that enabled 3D motion estimation. We developed algorithms for extracting the rolling and pitching motion of moving ships from radar measurements and collected radar data on actual ships for assessing the performance of the algorithms.

Significance:

This effort is an essential step in the ability to create high-resolution synthetic aperture radar (SAR) images of moving surface vessels for ship identification. Marine environments with clouds, fog, and rain often limit the ability of electrooptical/infrared sensors to identify objects of interest. While radars are largely unaffected by these environments, they have historically been unable to create high-resolution images because of the unknown dynamics of the moving ship. Measuring the dynamics and correcting for ship motion enables the creation of high-resolution SAR images for ship identification.

Multi-Resolution Image Fusion

178851 | Year 2 of 2 | **Principal Investigator: E. A. Shields**

Project Purpose:
Ground sample distance and field-of-view are competing metrics for remote sensing systems. At higher altitudes, remote sensing systems are typically less resolved but more persistent because of an increase in field-of-view. At lower altitudes, remote sensing systems are more resolved but less persistent because of a decrease in field-of-view. Persistent systems can more easily track targets; however, detecting and identifying them is more difficult. What may be readily identifiable by a low-altitude system may appear as a point object to the high-altitude system. For these reasons, a single imaging system cannot both effectively identify and track a moving target for an extended period of time.

This project studied methods for combining information from remote sensing systems that collect data in a variety of different ways, including those based on completely unrelated physics. Fundamental differences in underlying physics complicate data fusion and require development of new/novel techniques. The premise is that, if successfully fused, data from two or more systems with different resolutions and/or phenomenologies can provide new information to the end user that is timelier, more accurate, or otherwise unobtainable. In the limit, the resultant information products could help enable *virtual* persistence at large scale.

Summary of Accomplishments:
Numerous techniques were advanced to address this problem. Studies were performed to analyze the current state of the art and upcoming systems from both commercial and government suppliers. A base understanding of what systems are available and their underlying physics was obtained to support utilizing them in new ways.

New methods of simply fusing imagery were studied. Multi-modal image registration techniques (i.e., techniques for registering images from different systems) were analyzed to determine how to best combine the imagery. Super-resolution techniques were employed to improve the resolution of more persistent systems in order to improve the image quality as well.

A variety of techniques were studied to determine how information from systems with different resolutions and underlying physics can be combined to provide new information and support new missions. For example, measurements from a low-resolution system were used to seed algorithms for a high-resolution system of a different sensing modality to obtain better, faster performance. These results could then be fed back to the low-resolution system in a timely fashion to improve critical metrics. Using information from both systems in this fashion established that they could be used jointly to improve the performance of each.

New ways of characterizing targets from both high-resolution and low-resolution systems were also studied. Low-resolution imaging systems are generally poor at characterization due to their limited resolution. New ways of characterizing targets were found to aid in tracking them and correlating their information with other systems. We also studied how deep learning techniques could be used to aid in reducing false alarm rates for high-resolution systems. These new techniques were shown to potentially provide a tremendous advantage over the current state of the art. By reducing the number of false alarms more accurate results can be obtained and new missions enabled.

Significance:
This project developed and demonstrated a variety of techniques to improve ways in which information is obtained from a wide array of remote sensing systems. By making better use of available data through fusion, more and better information can be obtained, thus improving the performance of our nation's assets and our national security. Furthermore, utilizing the information from multiple systems can enable new missions and can increase their cost effectiveness more intelligently.

Nonlinear Response Materials for Radiation Detection

165701 | Year 3 of 3 | **Principal Investigator: D. R. Wheeler**

Project Purpose:

The specific detection of nuclear weapons is vital in a variety of national security scenarios. Nuclear weapons have a distinct radiation signature. The special nuclear materials emit neutrons and gamma rays. Indication of the proximity of a nuclear weapon could be achieved with two independent sensors, provided that the sensors do not have cross sensitivity and have either very nonlinear response or a threshold-based response. Typical neutron and gamma sensors rely on data processing to address background radiation. Additionally, many 'autonomous' materials are really just dosimeters severely limiting their use due to accumulated integration of background radiation. We will attempt to create autonomous materials with intrinsic behaviors to give nonlinear responses to radiation. Autonomous sensing routes have not been closely examined, because only recently have the benefits of this approach been identified. We are striving to develop new materials that are especially sensitive to neutrons and/or gamma rays to serve in novel sensor architectures. The payoff for new autonomous materials that function to discriminate background from targets is immense. Despite the payoff, the risk of failing to develop materials and methods to utilize them has driven the sensor community to lower risk approaches and the reliance on data processing to address materials shortcomings.

Summary of Accomplishments:

We have developed novel methods to engineer the band structure of aluminum gallium nitride so as to more closely match that of gadolinium oxide. This novel diode structure has the potential to improve electron capture efficiency during neutron irradiation. The gadolinium oxide converts the thermal neutrons into conversion electrons that can then be captured. Engineering the band structure helps ensure that more of the conversion electrons can be 'swept' out of the gadolinium to the electrometer to be measured.

We developed Monte Carlo methods to understand the fate of the conversion electrons. This modeling helped inform the design of test structures to test our ideas about sensing.

We synthesized a number of new materials and, while many of them did not generate improved sensor materials, they did generate new scientific understandings. For instance, we now know more about gadolinium containing perovskites, which had previously been almost unknown in the literature.

Significance:

New materials and structures designed for the detection of special nuclear materials enables improvements to the detection and management of special nuclear materials. Our development of new materials and electronic structures keeps the technical work fully engaged and at the forefront of research. This ensures both that we have the best technologies going and can also fully evaluate the technologies emerging in other places.

Refereed Communications:

J.F. Ihlefeld, M. Brumbach, A.A. Allerman, D.R. Wheeler, and S. Atcitty, "AlGaN Composition Dependence of the Band Offsets for Epitaxial $Gd_2O_3/Al^xGa_{1-x}N$ ($0 \le x \le 0.67$) Heterostructures," *Applied Physics Letters*, vol. 105, pp. 012102/1-4, 2014.

DEFENSE SYSTEMS & ASSESSMENTS

Novel Materials and Devices for Solid State Neutron Detection

176117 | Year 2 of 3 | **Principal Investigator: R. P. Manginell**

Project Purpose:

There is a need in many fields, such as nuclear medicine, nonproliferation, energy exploration, national security, homeland security, nuclear energy, etc., for miniature, thermal neutron detectors. Until recently, thermal neutron detection has required physically large devices to provide sufficient neutron interaction and transduction signal. Miniaturization would allow broader use in the fields just mentioned and potentially open up other applications. Recent research shows promise in creating smaller neutron detectors through the combination of high-neutron-cross-section converter materials and solid state devices. Yet, it remains difficult to measure low neutron fluxes by solid state means given the need for optimized converter materials (purity, chemical composition, and thickness) and a lack of designs capable of efficient transduction of the neutron conversion products (x-rays, electrons, and gamma rays). Gadolinium-based semiconductor heterojunctions have detected electrons produced by Gd-neutron reactions but only at high neutron fluxes. One of the main limitations to this type of approach is the inability to capture all the conversion electrons due to device thickness limitations, the broad energy range of the electrons and geometric configuration. In this project, we have optimized the converter material thickness and chemical composition to improve capture of conversion electrons and have detected thermal neutrons with high fidelity at low flux. We are also examining different semiconductor materials to attempt to capture a greater percentage of the conversion electrons, both low and higher energy varieties. We have studied detector size and bias scaling and hope to explore the effect of band bending in heterojunction devices in improving response. We also intend to explore novel geometrical implementations of the converter to increase sensitivity. The advancement of sensitive, miniature neutron detectors will have benefits in energy production, nonproliferation, and medicine.

Optical Detection of Ultratrace Molecules

173073 | Year 2 of 2 | **Principal Investigator: C. F. Lacasse, IV**

Project Purpose:

The intent of this project is to create a new optical remote sensing technique for measuring ultra-trace concentrations of gas phase particles of interest. Potential applications include nuclear nonproliferation, treaty monitoring, environmental monitoring, and detection of chemical agents. Various techniques for remote sensing of gas phase species already exist. However, with existing techniques, the length of the optical absorption path is generally limited to a single pass from an illumination source out to a scattering agent (either a solid surface or atmospheric aerosols) and then to a receiver. The finite length of the absorption path is one parameter that constrains the minimum detectable quantity of a given absorbing species. The goal of this project is to create a new active remote sensing technique that will use a multi-pass effect to dramatically increase the effective length of the absorption path and reduce the minimum detectable quantity of various gas phase particles of interest.

This work is inspired by a technique known as intra-cavity laser absorption spectroscopy (ICLAS), which is a method for measuring extremely faint optical absorptions by placing a sample of gas inside of a laser resonator cavity. While extremely sensitive, ICLAS as currently practiced is strictly an in situ measurement technique. The creative approach proposed here consists of employing the basic mechanisms of spectrally selective extinction, light amplification, and optical feedback, but replacing the traditional laser resonator cavity with a different gain and feedback loop to allow open path measurements. The technique is innovative since, while the ICLAS was originally developed in the 1970s, after 40 years no analogous remote sensing technique has been attempted. We call the new approach extended cavity laser absorption spectroscopy (ECLAS). The approach proposed here is new and unproven, but it has the potential to establish a new remote sensing modality with unprecedented sensitivity to ultra-trace concentrations of gas phase particles of interest.

Summary of Accomplishments:

This project did not result in the intended product of developing a new optical remote sensing technique. However, necessary advancements along the path were made that will inform future related projects.

We developed a model and graphical user interface for intra-cavity laser absorption spectroscopy. The model has been validated against published literature results and can be used to model in house-developed lasers. This model is a forward model that predicts the output of a laser spectrum as a function of time, given a distribution of absorbers (trace molecules) inside of the laser cavity. Using this forward model, it is theorized that we can solve the inverse problem (given a laser spectrum as a function of time, what molecules were present in the cavity), by performing an optimization problem on molecule distribution and comparing the measured output of the model to the calculated output. This is a necessary step towards the goal of developing a remote sensing technique for ultra trace gasses because it enables processing the data taken by the proposed laser based technique.

We have designed and integrated a benchtop demonstration of the proposed optical remote sensing technique that consists of the following apparatus: a Ti:Sapphire laser with a gas cell in the beam path, fiber coupled to a 2m McPherson spectrometer, and the output of the spectrometer fed to a high temporal resolution streak camera. Performing experiments with the lab based set up uncovered technical challenges such as pulse-to-pulse variations in the laser output that did not behave according to theory in the very early time of the pulse and difficulty acquiring high temporal resolution data with the streak camera technology. Future proposals on related topics should consider plans to overcome the various technical challenges uncovered in this work. The test setup can be leveraged in the future to perform a number of high-resolution sophisticated measurements, such as intra-cavity absorption spectroscopy, cavity ring down spectroscopy, and intra-cavity florescence experiments.

Significance:

The integrated instrument produced under this effort advances the capability of Sandia workforce to perform various ultra-trace gas analyses. Many experiments can be performed with the instrument that was integrated for this experiment, including high speed, high spectral analysis methods such as intra cavity absorption spectroscopy, or cavity ring-down spectroscopy. The laser used has a broadband gain and is tunable to specific molecules of interest. These experiments hold potential value for treaty monitoring communities as well as others.

Patterns of Life via High Performance Computing

180828 | Year 1 of 1 | **Principal Investigator: S. J. Bussell**

Project Purpose:

The purpose of the project is to demonstrate that semantic graphs have utility in identifying complex patterns of life within a network. We also want to demonstrate the use of feature selection algorithms to identify areas of interest that might become nodes to be analyzed as part of a network.

Summary of Accomplishments:

We demonstrated the ability of a semantic graph code base to create a static graph structure by ingesting the locations (and other meta data) of specified sites of interest. Associate spatiotemporal data with these static sites represent time-variant activity at the sites.

Significance:

Our results were significant in two primary ways:

- We demonstrated a first-time use of the GeoGraphy semantic graph code base to merge spatially static points with temporally variable activity point data
- Our research sets the foundation for further development/extension of the GeoGraphy code base in order to provide more robust analytical capabilities, such as activity level trending over wide areas and activity correlation detection among nodes within a network

Persistent Space Situational Awareness

173055 | Year 2 of 2 | **Principal Investigator: D. D. Cox**

Project Purpose:

The purpose of this project is to provide a modeling and simulation environment for Sandia to evaluate sensor capabilities and spectral modalities that will address the national need for solutions to rapidly evolving threats to US space systems. Three key space situational awareness (SSA) functional needs are chain of custody, space object characterization, and indications and warnings. Persistent SSA of geosynchronous resident space objects can be accomplished with the right combination of sensors and sensor placement addressing the gaps of the current SSA system. This project adapted existing astrodynamics libraries, reflectance models, and sensor models to assess, with a low to medium level of fidelity, the utility of multispectral collections in detecting and identifying space objects, anchored by surrogate sensor collections.

Summary of Accomplishments:

Using existing tool suites, we designed and demonstrated a new rapid processing pipeline needed to model the spectral signatures of realistic targets in various poses viewed from real or proposed SSA sensor systems over a range of viewing conditions.

Significance:

This project resulted in a new capability to model/assess SSA needs at Sandia and will ultimately benefit future DOE- or WFO-funded efforts. This tool suite enables performance assessment of actual and proposed sensor systems against the critical national need for enhanced space situational awareness. This assessment capability can be used to inform the mission engineers of the utility of potential design choices to enhance chain of custody, space object characterization, and indications and warnings.

Pinned Photodiode Pixel Development Enabling High Performance Visible FPAs

180841 | Year 1 of 3 | **Principal Investigator: R. R. Kay**

Project Purpose:

Commercial technology has advanced the state of the art in visible focal plane arrays to reduce pixel size to about 1 square micron. A key enabling technology is the pinned photodiode, which substantially reduces dark current and temporal noise by drastically reducing the contribution from surface states when compared with traditional photodiodes. However, no consideration has been given to other attributes important to national security remote sensing missions; namely, ultra-wide dynamic range, large area, and on-shore availability.

This project will develop pinned photodiode intellectual property (IP) for an on-shore foundry, nominally Sandia's CMOS7 silicon-on-insulator (SOI) process, and fabricate and test small focal plane arrays to demonstrate pixel performance and applicability to national security remote sensing missions. This investment will provide sufficient risk buy-down towards the ultimate development of a large format focal plane array utilizing the technology.

Pixels that incorporate nondestructive read will be developed. Nondestructive read can be used to extend the dynamic range of the sensor in real time, as compared to commercial techniques that rely on low sample rate and loss of temporal information. This capability can be used to develop very high dynamic range focal plane arrays that are optimized for national security missions. Incorporation of nondestructive read capability in a pinned photodiode pixel is a first-of-its-kind activity. Requirements for commercial imaging have not yet driven pixel design along this direction. Initial research is required to establish a foundation on which to base further development.

Plasmonic Pixel-Level-Tunable Detector

180847 | Year 1 of 2 | **Principal Investigator: D. W. Peters**

Project Purpose:
Nearly all infrared sensing and imaging currently use discrete or arrays of photodetectors with broad spectral response. However, most infrared systems also employ spectral filters to achieve their function, incurring size, weight, and power penalty, as well as performance limitations. Thus, many mission areas could benefit greatly from a radically new adaptive detector architecture where the spectral response of individual photodetector pixels can be rapidly tuned with a voltage bias.

Such an integrated tunable detector with individually addressed pixels could revolutionize infrared imaging and sensing. For example, it could enable absolute temperature measurements in parts of an image, small arrays could be used as dynamical "spectrometers on a chip" for gas sensing and chemical fingerprinting, and new imaging/sensing modalities using spectral dithering and demodulation could be done using single detectors and cameras to enable super-sensitive spectral or thermal imaging, essentially recovering data from noise.

Recently, we demonstrated a proof of concept for a voltage tunable infrared filter in the thermal band (8-12µm) based entirely on III-V semiconductors and a top patterned nanoantenna. This filter can be tuned **in wavelength** by ~1µm with the application of a bias voltage <5V. We propose here the integration of this filter with Sandia's nBn infrared detectors, since both can be grown epitaxially in on a common wafer, thus increasing likelihood of success.

Plasmonic-Based Optical Modulators and Switches

173490 | Year 2 of 3 | **Principal Investigator: W. F. Seng**

Project Purpose:

Traditional interconnect wiring at the chip level is too slow and not able to carry the massive amounts of information required by "Big Data." Optical fibers and photonic circuits can handle the data, but their components are currently too large to be integrated at the chip level to merge with electronics. Surface plasmon-based circuitry is the key way to integrate electronics with photonics at the nanoscale for chip level application, achieving a circuit that can carry both electrical current and optical signals.

Exploring nanoscale device structures offering the possibility to achieve sub-wavelength mode volumes will result in previously unattainable light-matter interactions. Therefore, such efforts offer truly unique opportunities for switching/modulation and wave mixing applications, and devices operating based on this approach are anticipated to greatly surpass the performance of the current state-of-the-art in speed, size, loss, and efficiency. These devices have direct application in optical networking and in creation of chemical and biological sensors that will fuel future growth in health and energy industries.

The work is in collaboration with UCLA.

Current photonic sensors, switches, and mixers are constrained in frequency response and overall SWaP requirements. A new approach is needed offering the possibility to achieve sub-wavelength mode volumes resulting in previously unattainable light-matter interactions. The project utilizes a necessary cross-pollinating combination of groundbreaking materials science with semiconductor fabrication uniting electrical and optical device characterization work.

Recent progress in this research has led to development of MiBo (modulation index boosting) as a key component to increase both low and high frequency sensitivity while reducing electrooptical modulator drive voltage V-pi by a factor of 50, especially useful for multi-channel wide bandwidth high energy pulse diagnostics.

Precision Laser Annealing of Focal Plane Arrays

165545 | Year 3 of 3 | **Principal Investigator: D. A. Bender**

Project Purpose:

Optical detectors in the visible or infrared often undergo thermal annealing in manufacturing to allow dopant activation, thermal oxidation, metal reflow, and chemical vapor deposition. Thermal annealing is typically done with equipment that heats the entire semiconductor wafer by using a flash lamp, hot plate, or furnace. Lasers are also employed with a cylindrical lens focusing a beam into a thin line that is swept across the wafer, homogenizing the surface. These techniques, however, are performed over the entire sensor and do not discriminate between adequately manufactured and defective regions. Ideally, processing techniques would precisely target only pixels or pixel clusters that are noisy, while leaving functional pixels and surrounding electronics untouched.

Our idea is to perform laser annealing on detectors after they have been hybridized with readout electronics (ROIC). Targeted laser annealing on packaged focal plane arrays (FPAs) prior to mission use represents an enhancement to the state-of-the-art thermal annealing and laser procedures currently done during the manufacturing process. Laser annealing can be performed at any point after manufacturing and before mission commencement. For example, if an FPA resides in flight storage for extended durations after manufacturing, laser annealing could potentially be used to restore individual pixels or clusters that may have degraded with time or were substandard initially.

Summary of Accomplishments:

The precision laser annealing of focal plane project achieved three major milestones. The first was quantification of the optical damage threshold for HgCdTe photodiodes for the short wave infrared. It was found that there are, in fact, two damage thresholds for such devices; one for the electrical damage as measured by an increase in dark current and the second being morphological damage. The second major accomplishment of the project was a demonstration of a technique to image photoluminescence (PL) emitted from direct bandgap semiconductor sensor layers. The photoluminescence mapping shows the presence/absence of defects in a sensor layer and does so at video refresh rates. The project showed that defects found in the PL map have excellent spatial correspondence regions of high dark current on the sensor. Because this technique is rapid in its implementation, it can be used for screening of sensor material in the infrared (IR) where detectors are often plagues with excessive dark current and noise. The third major accomplishment centered on the demonstration of longitudinal phase tuning in Si waveguides. By laser annealing along the waveguide axis, subtle index of refraction changes can be created resulting in a slight phase shift (approximately 14 mRad/pulse).

We submitted two invention disclosures.

Significance:

The significance of this work has resulted in a technique for rapid screening of direct bandgap semiconductor material for use in remote sensing systems (space-based or terrestrial). Creating high performance infrared sensors is often difficult and time consuming because of reduced yield issues arising from bad pixels. With the advent of a rapid screening technique, defects can be identified and resolved earlier in the manufacturing process thereby reducing the impact to cost and schedule.

Refereed Communications:

N.K. Grady et al., “Rapid PL Imaging for Defect Identification in Semiconductor Sensors,” in *Proceedings of the Military Sensing Symposium (MSS) – Detectors and Materials*, 2015.

Pulsed Ultraviolet Light-Assisted Chemical Etching for Failure Analysis of Advanced CMOS Circuitry

180844 | Year 1 of 2 | **Principal Investigator: D. P. Adams**

Project Purpose:
The purpose of this project is to investigate pulsed ultraviolet (UV) light etching of silicon and to develop methods for controlled, large area etching. Our approach involves chlorine gas-based, laser light stimulated etching. A scanned laser approach is implemented in order to attain uniform, low roughness feature surfaces. Experiments will determine thresholds for laser induced melting, effects on re-solidified microstructure and defect structure, and retained chlorine concentrations for different pulsed laser characteristics. We expect to investigate both pyrolytic and photolytic methods. The novel methods developed could benefit the failure analysis of different integrated circuits and other compound semiconductor substrates.

Quantifying the Uncertainty of Risk Assessment for High Consequence Flight Tests

173070 | Year 2 of 3 | **Principal Investigator: T. M. Jordan-Culler**

Project Purpose:

High consequence flight tests for nuclear weapons applications require review and approval of the risks associated with any flight program involving Sandia personnel or assets. The Range Commanders Council 321-10 Standard has provided guidelines for uncertainty quantification (UQ) in probabilistic risk assessments. DoD continues to fly increasingly more complex flight tests, which will be better designed when informed about uncertainties.

Risk analysis is dependent upon mathematical models with many parameters used to simulate the consequences of vehicle failures. The models are approximations at various levels of sophistication and the model parameters are frequently difficult to quantify accurately. We will focus on reducing uncertainty and lessening the conservatism of designated hazard areas.

We will investigate novel techniques of incorporating uncertainty into the current Sandia range safety probabilistic assessment tool, Predict, without significantly increasing computer run time. Analysts who run probabilistic risk assessments for national ranges do not have the expertise to develop uncertainty quantification; as a national security laboratory, Sandia has such expertise.

Risk assessment software must include the ability to reevaluate the risk based on the latest launch information related to wind, atmosphere, and demographics in a near real-time mode such that high consequence launch decisions can be made quickly. We will incorporate uncertainty determination into the risk assessment methodology, such that the near real-time requirement is achieved. Novel techniques will be employed and evaluated for efficiency, such as concurrent parallel sampling and unique importance sampling schemes to estimate epistemic uncertainty.

Of the probabilistic risk assessment tools existing at the national ranges for flight safety analyses, none currently contain uncertainty quantification or confidence bounds on the predictive risk calculations. Sandia's high consequence flight tests for national security applications require review and approval of risks associated with flight. Support of these reviews must deliver quantified risk uncertainties to decision makers.

Quantum Graph Analysis: Engineering and Experiment

165577 | Year 3 of 3 | **Principal Investigator: P. L. Maunz**

Project Purpose:

In recent years, advanced network analytics have become increasingly important to national security with applications ranging from cybersecurity to detection/disruption of terrorist networks. While classical computing solutions have received considerable investment, the development of quantum algorithms to address problems, such as data mining of attributed relational graphs, is a largely unexplored space. Recent theoretical work has shown that quantum algorithms for graph analysis can be more efficient than their classical counterparts. Specifically, an adiabatic quantum version of Google's PageRank algorithm (QPR) was proposed that offers polynomial speedup in the time required to identify the most important nodes on a graph. We propose a combined theoretical/experimental effort to implement QPR in a system of trapped-ion quantum bits (qubits). In addition, we will identify classical web-graph analysis methods most relevant to national security and seek to develop more computationally efficient quantum alternatives. Implementing a quantum computer is extremely difficult because qubits must be precisely controlled and well shielded from their environment to avoid decoherence. Academic groups with quantum algorithm capability are few in number and typically focus on demonstrating elements of universal quantum computing or simulating physical systems. In contrast, Sandia is the perfect setting to develop quantum capabilities that target concerns of national security, such as quantum graph analysis (QGA).

Summary of Accomplishments:

To realize quantum algorithms, we have established the infrastructure necessary to initialize, control, and detect an ytterbium hyperfine qubit. First demonstrations were done in the Sandia Thunderbird trap. For final experiments, we used the most advanced Sandia High Optical Access trap (HOA-2). We achieved initialization and detection fidelity of more than 99% and measured the qubit coherence time at more than 2x. We have achieved radial trapping frequencies for ytterbium of up to 3MHz and were able to hold a single ion in the trap for more than 96h while collecting data.

Single qubit gates were realized using microwave radiation–a simple technique limited to global single qubit gates, and Raman interactions, allowing for individual addressing of ions for single qubit gates and the realization of multi qubit gates. We characterized the microwave gate operation using gate set tomography (GST) and achieved a worst-case infidelity of less than 6×10^{5}. In addition, we were able to show that the infidelity in half the diamond norm is less than $8\pm1\times10^{5}$. Because fault tolerance analysis is done using the diamond norm, this is the first demonstration of single qubit gates below the fault tolerance threshold. We have characterized and eliminated non-Markovian noise by significantly improving the stability of the setup and classical control infrastructure. For the Raman transitions, we are using an industrial 355 nm picosecond pulsed laser and have established the necessary beatnote locking electronics to compensate for drifting repetition rates. Using GST, we have characterized motion insensitive single qubit gates to have an infidelity $<1.3\times10^{-4}$ and motionally sensitive gates to have an infidelity $<6\times10^{-4}$.

Significance:

We have realized a two-qubit gate with fidelity >97.7%, the best fidelity demonstrated to date in any scalable ion trap. While microfabricated ion traps are essential to scale trapped ion quantum information processing to the system sizes needed to make quantum information processing useful, microfabricated ion traps were not applied in the leading edge quantum information processing demonstrations. The work of the project established Sandia microfabricated surface ion traps as serious and scalable contenders for leading edge experiments in trapped ion quantum information processing.

Real-Time Case-Based Reasoning using Large High-Dimensional Data

170800 | Year 3 of 3 | **Principal Investigator: J. Woodbridge**

Project Purpose:

Case-based reasoning (CBR) systems aid in decision processes by comparing current cases to past well-known cases. Current CBR systems often focus on low-dimensional data or small archives of historical data. However, richer high-dimensional datasets are essential in understanding many measured phenomena. Large archives of historical cases are necessary to account for variations in how a phenomenon is revealed. For example, a seismogram can be used as conclusive evidence that the source of activity was a potential nuclear test and not an earthquake, but only after properly accounting for other important factors, such as the source to receiver path through Earth. It is necessary to analyze large archives of both types of events recorded for a variety of paths to conclusively make the distinction. Unfortunately, large high-dimensional archives are not currently feasible for CBR systems due to the complexities of search in high-dimensional spaces.

Our technique, a new paradigm in high-dimensional search, learns the structure of a dataset in high-dimensional space to construct an inverted index for the high-dimensional space. The index is applicable to any measure of similarity with any configuration across multiple domains. This project spans many domains, giving new capabilities in machine-guided decision making. The results of this project might potentially be applied to a specific domain for the implementation of a specialized CBR system. Example projects include nuclear explosion monitoring, cybersecurity, and satellite monitoring.

Summary of Accomplishments:

In this project, we developed a kernalized dimensional locality sensitive hashing (KD-LSH) algorithm, a high-dimensional indexing technique that outperforms the current state of the algorithms. This technique perturbs the distribution of a dataset in high-dimensional space to construct an inverted index. The technique is compatible with kernelized locality sensitive hashing (KLSH) (Kulis & Grauman, 2009) and, therefore, can be applied to any generic measure of similarity and spans many domains, giving new capabilities in machine-guided decision making.

The indexing system is unsupervised and classifications are never learned by the system. The system intends to only return the most relevant past cases to the current case. The user can then use this information to make guided decisions. In the seismic domain, seismologists can use such a system to not only classify an event, but to calculate its origin, magnitude, and potential damage. In the cybersecurity domain, network administrators can extract the current state of a network and compare to past security threats to determine if and what type of security threat is currently faced by the system.

The algorithm is simple to implement, runs with a small computational complexity, and returns highly accurate results. The efficacy of this technique is demonstrated using several open datasets including SIFT, GIST, MNIST (hand writing recognition) and uniform random data. The results in terms of runtime and recall consistently match or beat the current state of the art. The speed offered by the algorithm will enable real-time analysis of extremely large databases.

Significance:

Applications of the developed KD-LSH technique include those requiring analysis of high-dimensional data (such as time series, images, and feature vectors). Example projects include nuclear explosion monitoring, cybersecurity (such as network behavior analysis), and satellite monitoring.

Reconfigurable Structure Coupler for Antenna Mode Excitation

180861 | Year 1 of 3 | **Principal Investigator: N. J. Smith**

Project Purpose:

Robust antenna solutions are critical for modern sensing, tagging, tracking, and locating (TTL), RADAR, and other wireless systems. Antenna miniaturization has been a recent research topic as communication systems continue to become more mobile. While good progress has been achieved, antennas remain large and bulky especially at low frequencies where they are naturally tens of feet or larger. For field applications, it is not feasible to erect an antenna of such size.

Current antenna miniaturization techniques sacrifice efficiency and gain to reduce physical size. System link margins drive antenna gain specifications setting the antenna's size. To mitigate this problem along with the issue of portability for large antennas, we propose a solution that will turn an existing metallic object into a radiating antenna. This is accomplished by developing an antenna mode excitation coupler (AMEC) that would attach to an existing metal object (fence, file cabinet, electrical wiring, etc.) to create the required current distribution facilitating radio frequency (RF) radiation. In many cases, a mobile antenna is no longer required; rather, existing metal structures are excited with a portable AMEC system.

Research will include defining the required conditions to make a continuous metallic structure radiate, bounding the impedance matching range, properly coupling the AMEC to the structure, and development of reconfigurable phase shifters and matching networks accommodating different sized structures and operating frequencies. This work will be highly synergistic with reconfigurable antennas and array R&D at Sandia. If feasible, the AMEC concept will revolutionize a wide range of wireless applications.

Reversible Electrical Interconnect

173052 | Year 2 of 2 | **Principal Investigator: S. S. Mani**

Project Purpose:
Nondestructive characterization techniques do not exist for large area detector arrays. Current detector tests leave defects that render the detector ineffective for further assembly. Electrooptic assemblies (e.g., readout integrated circuits - ROICs) in systems are well characterized before detector integration; therefore, better detector characterization could greatly improve yield and shorten development time. For large area electronics such as Focal Plane Arrays (FPAs), most detector pixels undergo limited to no testing prior to ROIC attachment. The performance of a few detector pixels is extrapolated to the larger array. Device performance and assembly yield would increase with a detector chosen based on performance rather than ad hoc selection. We propose exploring anisotropic conductive films (ACFs), and conductive polymers to develop a reversible electrical test, which would allow the large area detectors to be characterized prior to being committed to the highly valued, read out electronics. Reversible detector interconnects were explored using a third party's ACFs, Sandia's polyaniline conductive polymers and silver inks. ACFs use continuous fibers instead of particles to eliminate interface resistances, which create films with unprecedented Z-axis electrical conductivity with a ten-micron pitch. This company has used films for automotive companies, production IC (integrated circuit) testers and the NREL (National Renewable Energy Laboratory) vehicle programs to streamline microfabrication. Like ACFs, polyaniline is attractive due to its high electrical conductivity, and simple preparation. Polyaniline's crystallinity can be modulated via synthesis to tune conductivity. Then, polyaniline can be made chemically, electrochemically or dissolved in solvents, to ease microfabrication and reduce the pitch below ACFs. Silver inks using aerosol jet approaches are viable alternatives that demonstrated the most promise of all the possibilities.

Summary of Accomplishments:
This project provided the resources to establish a process to pattern conductive polymers which were identified along with limitations to the process. Further, the team established a process to work with anisotropic conductive films and identified process boundaries. The most promising candidate for the reduced feature size and pitch are associated with printing process involving conductive inks. The members from the project submitted multiple invention disclosures.

Significance:
This option created and developed in the project allow for a pathway to fully test FPA combination along with other complex 3D electronics structures. There is external interest in pursuing this work with CRADA or similar platforms. Any products involving 3D heterogeneous microelectronics where yield is an area to address would benefit from this approach.

Refereed Communications:

D. Keicher, S. Mani, M. Essien, A. Cook, J. Lavin, C. Sanchez, S. Homeijer, and J. Chen, "Improvement and Application of Aerosol-Based Printing Technology for Electronic Applications," presented at the *26th Annual International Solid Freeform Fabrication Symposium, An Additive Manufacturing Conference*, Austin, TX, 2015.

D. Keicher, S. Mani, M. Essien, A. Cook, J. Lavin, C. Sanchez, and S. Homeijer, "Advancing 3D Printing of Metals and Electronics using Computational Fluid Dynamics", presented at the *26th Annual International Solid Freeform Fabrication Symposium, An Additive Manufacturing Conference*, Austin, TX, 2015.

J. Chen, "3D reversible Interconnect," presented at the *AVS New Mexico Symposium*, Albuquerque, NM, 2015.

J. Lavin, S. Mani, M. Essien, D. Keicher, and A. Cook, "Additive Manufacturing-Based Printing Technology for Electronic Applications," presented at the *27th Annual Rio Grande Symposium on Advanced Materials*, Albuquerque, NM, 2015.

Rocket Engine Test System for Development of Novel Propulsion Technologies

176311 | Year 2 of 3 | **Principal Investigator: W. Saul**

Project Purpose:

A novel small-scale rocket engine testing capability is needed for development of new propulsion systems–specifically "green" propellants that eliminate toxicity of current systems. By leveraging Sandia's unique background in propulsion systems engineering with cutting edge instrumentation and imaging techniques being developed at New Mexico Tech (NMT), the result will be a testbed for propulsion initiatives developed at both institutions. The initial goal (completed in FY 2015) is to develop an instrumented rocket engine test stand for liquid propellant engines. At minimum, the new capability will enable hot- and cold-flow testing of rocket engines with a thrust range of 10-200 pounds. This level of thrust will allow sufficient, but manageable, propellant flow rates and enthalpies for Sandia and NMT research interests. This testbed will utilize a blow-down fuel and oxidizer system with high-pressure nitrogen push gas, eliminating the need for expensive pumps. The test stand will have the capability to measure thrust produced and allow for significant optical access of the exhaust plume and nozzle exit. This will provide both a unique test capability for NMT and Sandia and as well as important research results in alternative "green" propulsion technologies, necessary for the development and advancement of safer and more economical propulsion systems. Hot flow tests and fuel exploratory studies were also completed.

The combination of a rocket test stand with cutting edge optical diagnostics presents a unique core capability for the laboratory. The capability presents an opportunity to address fundamental R&D activities, which eventually may be leveraged across many areas of the laboratory and in the propulsion industry.

Simulation of Optical Phenomena in the Upper Atmosphere

173491 | Year 2 of 3 | **Principal Investigator: W. C. Sailor**

Project Purpose:

The purpose of this project is to discover the appropriate theory to the simulation of optical phenomena (aurora) in the upper atmosphere and identify the governing equation. This requires understanding quantum theory, transport theory, atmospheric physics, integro-differential equation theory, complex variable theory, and numerical theory. The work is in collaboration with Rensselaer Polytechnic Institute.

Speech Detection with MEMS Zero Power Acoustic Sensor

173043 | Year 2 of 2 | **Principal Investigator: B. Griffin**

Project Purpose:

We propose a microelectromechanical systems (MEMS) zero power acoustic sensor capable of waking up a device upon the detection of acoustic signatures. Eliminating standby power is critical to extending the lifetime and reducing the size of these devices. Ideally, such a device would remain in standby consuming zero power until an event triggers power up of the entire device for data logging, processing or transmission. In reality, processing the wakeup event often requires significant power consumption, particularly for complex event signatures, which limits device lifetime and size.

The challenges of creating a wake-up sensor are generating a large enough signal, consuming minimal power, having sensitivity in the audio band (20 Hz–20 kHz) while in a small form factor, and rejecting undesired acoustic signatures. MEMS represent an opportunity for small form factor sensors; however, conventional MEMS microphones found in cellphones are electrostatic and require a constant bias voltage. Also, the operational range of a conventional microphone is well below resonance. We propose to address the challenge of passive audio speech detection using resonant, piezoelectric MEMS technology.

The proposed sensor operates based on piezoelectric transduction of mechanical strain due to pressure waves. The pressure perturbation of an acoustic wave causes deflection of a membrane creating strain in the piezoelectric material. Under strain, the piezoelectric film generates an electrical signal. This eliminates the need for a constant voltage supply. Since the sensor structure can be engineered to respond to frequencies of specific acoustic signatures, complex profiles can be programmed into the sensor and processed passively in the mechanical domain.

Summary of Accomplishments:

In this project, we demonstrated piezoelectric resonant microphones for near zero power wakeup. Device resonant frequencies from 1-10 kHz were demonstrated. The microphones were manufactured simultaneously using batch fabrication such that all of the designs were contained in a single wafer. Microphone designs with quality factors in excess of 3000 were achieved, which was a 20x increase over the initial predictions in the proposal. The devices were studied in both air and vacuum to understand air effects on performance. Experiments varying the back cavity volume were used to boost the quality factor of the devices by nearly 10x from their nominal state. A parameterized finite element model was developed to predict the resonant modes and response of the devices. A method was developed to process actual audio recordings with the device model to predict the wakeup signal. This method can be used to tailor device designs for response to different acoustic signals.

Significance:

The microphones as well as a resonant accelerometer were part of a demonstration of high interest to the DoD community. This work was used in a successfully funded proposal to the DARPA NZERO program, where we will be designing resonant microphones and accelerometers to perform near zero power wakeup for operationally relevant circumstances.

Staghorn: An Automated Large-Scale Distributed System Analysis Platform

180824 | Year 1 of 2 | **Principal Investigator: K. G. Gabert**

Project Purpose:
Sandia has developed large-scale emulation-based cyber analysis platforms (e.g., Firewheel). This project builds on the significant investment Sandia has made in Firewheel by creating a new analysis platform for large-scale distributed systems: Staghorn. This platform is based on a novel primitive: the ability to take a snapshot of the entire distributed system that includes both its network and input/output state. This primitive opens up the possibility for many avenues of analysis, ranging from "single stepping" through a massive system's execution, to forking execution at a given point in time, in order to vary system inputs and find optimal configurations.

There are numerous technical challenges in constructing such a system, including significant modifications to key Linux virtualization and networking components and development of an algorithm to perform distributed snapshots that include network state. Each challenge has been shown possible through our own experience in developing Firewheel and recent academic publications. Staghorn's contribution is to tie each challenge together to form the first large-scale emulation based distributed system analysis platform.

Technology Improvements for the Design and Analysis of Hypersonic Scramjets for Prompt Strike Applications

173074 | Year 2 of 2 | **Principal Investigator: J. Fulton**

Project Purpose:

The purpose of this project was to develop an understanding of airbreathing hypersonic engines (ABHEs) at Sandia, and then to discover how these devices could be used for prompt-strike missions in a way that would complement boost-glide (B/G) technology. One of the main challenges in this effort was that ABHE technology is still at a very low level of development. Design and analysis techniques are not well established and data availability is very sparse. In addition, Sandia had little experience with airbreathing propulsion, so analysis methods and tools had to be established as part of this effort before any real analysis could be done. The physics governing the operation of B/G and ABHE systems are very different and there was no established way of comparing the two. New methodologies had to be developed as part of this effort. This approach was, however, the first of its kind. Development work done by aerospace groups up to this point tended to focus on only one or the other option and how it could be optimized for a particular mission. In contrast, this effort compared both options side-by-side, explored the tradeoffs between them, and identified which one was the best choice for a certain mission on the warfighter-relevant system level.

Summary of Accomplishments:

A robust, agile ABHE simulation toolset that will allow Sandia to analyze ABHE engine performance on multiple levels of detail was implemented. This toolset uses methods that are well validated and at or above the state-of-the-art level. Collaboration with some of the best experts in the ABHE field was made and data and advice in the design and analysis of ABHEs was acquired. A novel comparison methodology between ABHE and B/G systems was devised with help from other Sandians. Experience was gained in the operational characteristics of ABHE systems and how this translates into system-level strengths and weaknesses. Some key system parameters that are common between B/G and ABHE systems were identified, which are useful for system comparisons. Furthermore, trends were discovered and optimal areas in the prompt-strike mission envelope were identified for ABHE or B/G systems to be used.

Significance:

In the short term, the results of this project can be immediately used to inform the designer and warfighter of their best options when faced with a certain prompt-strike mission scenario. In the long term, the project's results represent a giant step toward closing a significant capability gap in airbreathing propulsion that has existed at Sandia since its founding. Combined with our background in B/G, this new capability will give Sandia a great edge over other groups when addressing design and analysis problems in the prompt-strike field.

Refereed Communications:

J.R. Edwards and J.A. Fulton, "Development of a RANS and LES/RANS Flow Solver for High-Speed Engine Flow-path Simulations," presented at the *20th AIAA International Space Planes and Hypersonic Systems and Technologies Conference*, Glasgow, Scotland, 2015.

Towards Global Persistent Surveillance

177966 | Year 2 of 2 | Principal Investigator: M. E. Buckman

Project Purpose:

Global persistent surveillance, particularly for denied areas, is viewed to be a critical enabler for US National Security. Some existing sensor systems achieve global persistence in one or more sensing modalities (seismic, low-resolution optical, etc.) but trade away other performance attributes, such as sensitivity, resolution or accuracy, for their large area coverage. In contrast, some persistent sensor systems provide exquisite performance over relatively small areas, and thus depend on multiple sensors and appropriate tasking to gain access to high priority areas. Recent advances in focal plane array technologies suggest that large-scale persistent space-based electrooptical sensors may be realizable within the next decade, possibly at significantly lower cost. However, other system considerations, such as communications, processing, command/control, and satellite bus/launch costs must be addressed to develop viable global persistent sensing systems.

FY 2014 efforts focused on creating numerical models to quantify the interdependencies between design parameters: focal plane arrays (FPAs,) optics, bandwidth, and processing, and their relationships to orbit regime, space/weight/power, and constellation size. FY 2015 focuses on completing performance analysis of the postulated persistent sensing architectures. The most promising sensor architectures will be analyzed for relevance to national security needs, and a first-order estimate of cost drivers and areas for potential savings will be developed.

Summary of Accomplishments:

Through this project, two analytical models were created and enhanced.

The first model is an orbital access model. This can calculate access of different satellite constellations to any target. The model includes constraints such as solar exclusion, eclipse considerations, and elevation angle. With these constraints, the model can accurately predict the access to a target for a given constellation. This is important because there are national security needs that require a certain amount of access to different regions of the world. Therefore, the model identifies the constellations that will meet national security needs. The model differs from existing tools in that it is made to easily run batch analyses and create custom results for entire constellations with little effort by the user.

The project has also expanded and improved the TOMCAT modeling tool. This tool assesses different architectures (optical designs, FPAs, and range) for performance against certain targets. It models performance parameters (resolution, sensitivity, etc.) for each architecture, which can then be rated against national security needs. This project enhanced the tool by adding modeling capabilities for optical designs and properties, custom focal plane array characteristics, and better scene definition. With these updates, the model yields more realistic results. Four million architectural designs were run through model, and the results created bounding box on the trade space that gives significant insights into what constitutes an optimal design. This tool was also optimized for analytical performance, running the four million scenarios in only 48 hours.

Significance:

This project brought together a diverse group of engineers across Sandia. With that team, we were able to apply multidisciplinary expertise to the problem: optical design, sensor/FPA modeling, and orbital mechanics. This broadened the knowledge of all team members and thus enhanced the technical workforce.

The results from the project could be applicable to address national security needs. The final orbit and sensor designs were correlated to specific national needs to ensure future intelligence gaps could be filled by these results. The tools from this project have also advanced the labs ability for rapid quantitative analysis for modeling potential architectural designs.

Trusted Materials using Orthogonal Testing

180857 | Year 1 of 3 | **Principal Investigator: M. Van Benthem**

Project Purpose:

The purpose of this project is to prove (or disprove) that a reasonable number of simple tests can be used to provide a unique data signature for materials, changes in which could serve as an indication of material deviation, prompting further evaluations. The routine tests are mutually orthogonal to any currently required materials specification tests.

Materials represent the building blocks for all physical products. Unanticipated materials changes can result in undesirable and costly consequences in product reliability and performance. These changes may result from a vendor's process improvements driven by technological advances and/or economic considerations. Of greater concern is the manufacturer's, and in turn the consumer's, vulnerability to potential nefarious actions. The functional impact of integrating dubious materials into the manufacturing process spans the range from processing and fabrication through reliability assessment activities, as anomalies may manifest early or be aging-related.

One method of addressing the materials assurance process is to use an array of material specifications. Functionally, these specifications may range from weak (manufacturer part number) to robust (a comprehensive series of physical or chemical tests). However, the potential for detrimental material changes going undetected while using the existing specifications dictates that we develop a new testing paradigm to verify that materials are precisely those that are required for their intended purpose.

We have proposed a new approach for assuring materials, complementing the current specifications process. The orthogonal testing (OT) approach could be a complete paradigm shift for how we accept incoming materials and fabricated parts. In this new paradigm, we would only use OT during refurbishment to determine that the material is, or is not, from the same family that was qualified.

Using Graphene to Enable Trusted Microelectronics

180850 | Year 1 of 2 | **Principal Investigator: B. L. Draper**

Project Purpose:
Containing up to a billion transistors and literally miles of wiring in an area of about 2 square cm, modern microelectronic integrated circuits (ICs) are amazingly complex. Despite that, they can be reverse engineered by some fairly straightforward techniques. This poses a great risk to systems architects who would prefer that the intent and functionality of their circuitry remain unknown to those who might attempt to subvert, corrupt, or copy the technology.

A key element in the reverse engineering process is the mapping of electrical interconnections among the individual devices and circuit modules. In fact, it is the interconnections in the first few layers of wiring that provide the biggest clues to the circuits' intended functions (modern ICs have up to a dozen layers of metal wiring stacked on top of each other and separated by thin layers of insulators). The reverse engineering and mapping of these layers is done through a combination of optical, x-ray, and scanning electron microscopy (SEM) techniques. However, if some of the wiring were to be replaced by graphene, which is conductive enough to provide adequate connectivity but is only one atom thick and, therefore, virtually undetectable, it would be extremely difficult for an adversary to discern the function of the circuit.

Processes need to be developed that are compatible with the complementary metal oxide semiconductor (CMOS) materials and processes used in Sandia's Microsystems and Engineering Sciences and Applications (MESA) Facility. Graphene will be grown on copper, nickel, or silicon carbide substrates, and then transferred to silicon wafers containing ICs pre-processed through metal-1, metal-2, or metal-3 but lacking some of the key wiring. The graphene layers will then be patterned using standard photolithography and plasma etch techniques, completing interconnections that were intentionally omitted in the normal metal wiring. After graphene processing, ICs will be finished through the addition of the final few standard wiring levels.

Using Linkographies of Cyber Attack Patterns to Inform Honeytoken Placement

173035 | Year 2 of 3 | **Principal Investigator: J. C. Jarocki**

Project Purpose:

Several research and development projects have deployed honeypots, honeynets, and honeytokens to confuse, slow, and detect cyber adversaries. However, the placement of these resources is typically agnostic of the behavior patterns and goals of the adversaries. The purpose of this project is to learn adversary behavioral patterns during cyber attacks so that the placement of false flags (honeycues) can be chosen to minimize attacker goals while maximizing defensive objectives. By acquiring data on cyber attack steps from real incidents, we can construct similar representations for normal patterns of adversarial understanding, behavior, and activity through a target network. Armed with this information, defenders can reduce the intelligibility of the target network and maximize the effort an adversary must apply to complete the mission.

This project explores new methods to gain insight into cyber attacker behavior and response to stimuli, seeding future research with data and methods for modeling attacker interactions. This work involves arraying defenses and decoys in real time on a live network using experimental models, a technology area that is presently underdeveloped.

Using Machine Learning in Adversarial Environments

173037 | Year 2 of 3 | **Principal Investigator: W. L. Davis, IV**

Project Purpose:

Intrusion/anomaly detection systems are among the first lines of cyber defense. Commonly, they either use signatures or machine learning (ML) to identify threats, but fail to account for sophisticated attackers trying to circumvent them. We propose to embed machine learning within a game theoretic framework that performs adversarial modeling, develops methods for optimizing operational response based on ML, and integrates the resulting optimization codebase into the existing ML infrastructure developed previously. Our approach addresses three key shortcomings of ML in adversarial settings: 1) resulting classifiers are typically deterministic and, therefore, easy to reverse engineer, 2) ML approaches only address the prediction problem, but do not prescribe how one should operationalize predictions, nor account for operational costs and constraints, and 3) ML approaches do not model attackers' response and can be circumvented by sophisticated adversaries. The principle novelty of our approach is to construct an optimization framework that blends ML, operational considerations, and a model predicting attackers reaction, with the goal of computing optimal moving target defense. One important challenge is to construct a realistic model of an adversary that is tractable, yet realistic. We aim to advance the science of attacker modeling by considering game-theoretic methods, and by engaging experimental subjects with red teaming experience in trying to actively circumvent an intrusion detection system, and learning a predictive model of such circumvention activities. In addition, we will generate metrics to test that a particular model of an adversary is consistent with available data.

Little research has been conducted to date on providing a mathematical framework for rigorously analyzing the impact of defensive postures (e.g., network configurations) on the interactions between cyber defenders and adversaries. This work is novel and risky, yet, if successful, could serve as the catalyst for extending theoretical understanding of interactions towards practical decisions that will improve computer security.

Using Trusted Execution Environments to Provide Monitoring and Protection of Mobile Operating Systems

173034 | Year 2 of 2 | **Principal Investigator: T. G. Fine**

Project Purpose:

This project is investigating the feasibility of using TrustZone to support security functionality in mobile devices.

Most mobile devices are currently based on the Advanced RISC Machine (ARM) CPU and associated peripherals. TrustZone is a technology embedded in the ARM CPU and peripherals that logically partitions the hardware into a "Secure World" and a "Normal World." Implementing security functionality in the Secure World (the Trusted Execution Environment, or TEE) and a commodity operating system such as Linux or Android in the Normal World (the Rich Execution Environment, or REE) provides some hope of protecting the security functionality in spite of flaws in the commodity operating system.

While this technology has been implemented in ARM hardware for years, it is just starting to be commonly used. Many of the reported uses are proprietary with little openly available information. While some examples are open source they are typically very tightly tied to a specific hardware platform or example security feature. Given an arbitrary ARM processor and a desired security feature, little is generally known about how to use TrustZone to help support that feature. Subtle interactions between the various security configuration options complicate this problem.

This effort is focused on examining worked examples of TEEs providing desirable security features and analysis of the impact of the various security configuration options on the end security. Some mobile devices might be locked down so tightly as to prevent adding new security features. Others might not implement enough TrustZone functionality to add security features.

We aim to leverage TrustZone's Secure World in implementing features relevant to national security, but are challenged by vendors claiming Secure World for their use. We will investigate forward-thinking approaches to add our features to Secure World without breaking existing vendor mechanisms. While doing so, we will also consider ways to address security flaws that plague existing TrustZone-based solutions.

Summary of Accomplishments:

We studied different TEE implementations and found that most mobile device vendors have locked devices down to the point where it would be difficult for us to add a new security feature based on TrustZone.

When a device is not locked down, the device boots into Secure World and never uses Normal World. In theory, we should be able to move the operating system and applications to Normal World and then load security critical processing into Secure World. However, we found that modern operating systems often implicitly assume they are running in Secure World. This can lead to a system crash when processing is moved from Secure World to Normal World. This means that even when a device is not locked down, we often cannot use Secure World unless we are able to patch the operating system to support running in Normal World.

We found that vendors treat many details of TrustZone hardware and software as proprietary. This is essentially "security through obscurity" since a significant reverse engineering effort is required to determine details necessary to meaningfully analyze a system.

One of the challenges in analyzing TrustZone software is that typical debugging tools have no visibility into Secure World data and processing. While static analysis is an option, we found that Secure World software in modern devices is complicated enough to make this tedious and error-prone. We experimented with using symbolic execution to simplify analysis and found it to be a promising approach.

DEFENSE SYSTEMS & ASSESSMENTS

Significance:
While our work suggests it would be difficult to add TrustZone-based solutions to existing mobile devices, using TrustZone in custom systems appears feasible and of value. By working with others tasked to develop ARM-based systems in support of national security missions, we could apply the lessons learned on this effort to improving the security of those systems. For missions dependent on the use of existing mobile devices, our experience using symbolic execution could help analyze those systems for fitness of use.

Wound Ballistics Modeling for Blast Loading, Blunt Force Impact, and Projectile Penetration

165554 | Year 3 of 3 | **Principal Investigator: P. A. Taylor**

Project Purpose:

Light body armor development for the warfighter is based on trial-and-error testing of prototype designs against ballistic projectiles. Torso armor testing against blast is nonexistent but necessary to protect the heart and lungs. In tests against ballistic projectiles, protective apparel is placed over ballistic clay and the projectiles are fired into the armor/clay target. The clay represents the human torso and its behind-armor; permanent deflection is the principal metric used to assess armor protection. Although this approach provides relative merit assessment of protection, it does not examine the behind-armor blunt trauma to crucial torso organs. The purpose of the project was to perform R&D to inform prototype development of a modeling and simulation (M&S) capability for wound injury scenarios to the head, neck, and torso of the warfighter. The toolset could be used to investigate the consequences of, and mitigation against, blast exposure, blunt force impact, and ballistic projectile penetration leading to damage of critical organs comprising the central nervous, cardiovascular, and respiratory systems. The project leverages Sandia codes and our M&S expertise on traumatic brain injury to develop virtual anatomical models of the head, neck, and torso and the simulation methodology to capture the physics of wound mechanics. Specifically, we will investigate virtual wound injuries to the head, neck, and torso without and with protective armor to demonstrate the advantages of performing injury simulations for the development of body armor. The toolset is anticipated to constitute a significant advance over current methods by providing a virtual simulation capability to investigate wound injury and optimize armor design without the need for extensive field testing.

Summary of Accomplishments:

We developed high-fidelity virtual models for the stand-alone human torso, as well as a combined head-neck-torso structure, in order to investigate wound injury and assess personal protective armor for the warfighter. These models exist in formats that permit their import into shock wave physics codes for simulation of blast loading and ballistic projectile impact leading to behind-armor blunt trauma. To demonstrate personal protective armor assessment, we developed prototype chest armor for the human torso model comprised of a fiber-reinforced composite hard shell with polymer foam padding to offset the hard shell from the torso.

We implemented advanced constitutive models to represent the nonlinear elastic and viscoelastic nature of the biological tissues comprising the human head, neck, and torso. Specifically, we created model representations for the brain, heart, lungs, liver, kidneys, spleen, and musculature. We fostered development and employed an equation-of-state (EOS) model to capture the volumetric response of human fluids such as blood and cerebrospinal fluid. This EOS captures the liquid-vapor phase transformation associated with impulse-induced fluid cavitation that can occur in these fluids. For the protective armor, we created a transverse-isotropic constitutive model representation for the hard shell to simulate a glass fiber-reinforced composite laminate.

We constructed a simulation methodology that allowed us to investigate injury scenarios to our human models without and with protective armor. Specifically, we simulated blast loading and ballistic projectile impact to our human models, demonstrating the details of wound injury and the ability to perform relative merit assessments of personal protective armor.

Significance:

The completion of this project allows us to expand our injury scenario simulation capabilities to address the challenges of protecting our warfighters and civilian protective forces. Our newly developed modeling and simulation capability allows us to investigate injury scenarios and conduct protective armor assessments without the need for extensive and/or expensive field testing.

Refereed Communications:

P.A. Taylor, C.F. Cooper, R. Terpsma, and D. Dederman, "Computer Simulation of Blast Injury, Behind Armor Blunt Trauma, and their Mitigation," in *Proceedings of Personal Armour Systems Symposium (PASS)*, 2014.

C.F. Cooper and P.A. Taylor, "Virtual Simulation of Blast, Behind-Armor Blunt Trauma, and Projectile Penetration leading to Injury of Life-Critical Organs in the Human Torso," in *Proceedings of ASME International Mechanical Engineering Congress and Expo (IMECE)*, 2015.

C.F. Cooper and P.A. Taylor, "Human Torso Model Development for Computer Simulation of Blunt Trauma, Blast Injury Projectile Penetration, and their Mitigation," presented at the *26th Rio Grande Symposium Advanced Materials*, Albuquerque, NM, 2014.

Energy & Climate

The Energy and Climate (EC) Investment Area is focused on research and development that advances the state of knowledge and overcomes barriers to deployment of energy technologies for both supply and demand. The IA encourages research and development, building directly on the results of fundamental research, to provide real solutions to the most pressing mission challenges. The EC LDRDs are investments to develop and create products and capabilities to incubate solutions for future program needs. The challenges include reducing our dependence on foreign oil through R&D focused on renewable energy alternatives; increasing the use of low carbon power generation; advancing credible carbon management strategies; assuring water safety, security, and sustainability; increasing security and resiliency of the electrical grid and energy infrastructure; and, providing the scientific foundation for understanding global climate.

Projects

Active Suppression of Drilling System Vibrations for Deep Drilling

165620 | Year 3 of 3 | **Principal Investigator: D. W. Raymond**

Project Purpose:

Advanced R&D is needed to develop an autonomous, adaptive and high-reliability drilling system for the range of conditions encountered during drilling, reaching depths of 5 km in continental crystalline basement rock, for example. A reference design has been developed that demonstrates viability of the engineered system that can be realized with currently available drilling technology. Drill string vibrations are one potential cause of trouble relative to deep-hole drilling as they increase the technical risks and final costs of well construction. They are a constant issue in all drilling operations and cause increases in drilling trouble and damaged components, and decreases in the rate of penetration, and bit and tool life.

While the drilling industry routinely attempts to deal with these dysfunctions using fixed-rate damping tools, the consequences are exacerbated when drilling deep wells due to increased drillstring flexibility and greater times to replace worn or damaged components. Additionally, the mechanism of self-excitation depends upon the rock formation being drilled, which changes continually in heterogeneous rock. Vibrations are particularly problematic in high strength rock where the risk of tool failure increases dramatically. External controls are imperative for improved reliability and drilling performance. Current science and technology has not solved these problems due to: 1) telemetry limitations during drilling operations making field observation of the problem challenging, 2) difficulty with laboratory simulation of the problem due to geometric limitations in the laboratory, and 3) the challenge of developing controls/tools with autonomous features.

Our project will focus on an autonomous and adaptive solution for the range of conditions encountered. This research and development is cutting edge, as conventional systems do not use this technique; it is nontrivial, as drillstring property variations must be adjusted remotely. It possesses high potential for applicability to make deep drilling more efficient and less costly.

Summary of Accomplishments:

We developed drillstring computational models with sufficient fidelity to accommodate evaluation of active vibration suppression concepts. Dynamic substructure modeling methods were applied to drillstrings to enable rapid simulation of alternatives without repeated derivation of dynamics equations. Impedance and admittance-based port functions were used in substructured drillstrings to address actuator alternatives to enable modular modeling. A model for rock-bit interaction was integrated with a dynamic model of a drillstring and a dynamic model of bottom-hole geometry to enable real-time simulation of drilling instability. A passive equivalent of a drillstring model was developed in a drilling dynamics simulator and used to simulate instability with and without a variable rate spring. Candidate technologies were evaluated for use as down-hole variable rate springs to modify the physical response of deep drillstrings. A prototype concept for a solid-state spring drilling assembly was developed that achieves the form, fit, and function necessary to be considered a valid design concept for a down-hole variable rate spring. Laboratory hardware simulations were conducted demonstrating benefits available from deployment of variable rate springs in deep drillstrings.

A laboratory-based deep drilling applicability experiment was completed that demonstrated the prevalence of drilling vibrations, its dependence upon bit design, and the performance improvements available from a variable rate spring element in the bottom hole assembly. A unique Shape Memory Alloy (SMA) system was developed for high force, low power actuator applications including a unique application of Teflon insulation on the actuator. An additional concept for vibration mitigation using a down-hole inertial exciter was conceived and simulated using an enabling hardware simulation. An invention disclosure was submitted for use of smart materials, advanced sensing, processing, and control techniques for development in a down-hole tool for mitigation of drilling vibrations.

Significance:

The technology developed is applicable to the entire drilling sector, especially deep, high value wells. These improvements in drilling technology are significant to our national security objectives of maintaining energy independence.

Advanced Fuel-Injection System for Rapid Control of High-Efficiency Low-Temperature Combustion Engines using Gasoline and other Gasoline-Like Fuels, Including Biofuels

180862 | Year 1 of 3 | **Principal Investigator: J. E. Dec**

Project Purpose:
Establishing a secure energy future and mitigating carbon dioxide emissions requires significant improvements to the fuel efficiency of the nation's vehicle fleet. By far, the largest gains can be made by raising the efficiency of gasoline engines, which consume the majority of fuel and have much lower thermal efficiencies than diesel engines. Engines using low-temperature gasoline combustion (LTGC) can provide efficiencies above those of diesels, improving fuel economy by 30 to 40% over current gasoline engines. A key impediment to the commercialization of LTGC is that current techniques for controlling ignition timing over the load-speed map are complex, insufficiently robust, and have difficulty with rapid transients. This project would develop and demonstrate an advanced fuel-injection system to provide the required robust, rapid control. Despite the risks, this project is based on sound fundamentals, and this technology could be a "game changer" for the commercialization of LTGC engines, with benefits for energy security and the environment.

Advanced SMRs using S-CO2 Power Conversion with Dry Cooling

165619 | Year 3 of 3 | **Principal Investigator: B. Middleton**

Project Purpose:

Small modular reactors (SMRs) continue to be proposed around the world to meet ever-increasing electrical energy needs, particularly in areas where large-scale transmission is not feasible. The DOE has recently announced a program of $1 billion aimed at licensing of light-water SMRs, demonstrating a high priority for this technology.

Light-water SMRs are promising in the near term, however, they require a large nearby water source for evaporative cooling, and ultimately suffer from the same waste issues and shutdown heat removal concerns as their larger predecessors. This project identifies two ways in which supercritical-CO_2 (S-CO_2) is uniquely capable of addressing these problems.

First, recent studies have shown that the S-CO_2 power cycle is strongly compatible with dry-air cooling. Because the cycle is optimized to reject heat around 88 °F, its efficiency does not degrade sharply with relatively high ambient temperatures, unlike steam plants. Turbomachinery size and capital cost both overwhelmingly favor S-CO_2 over steam. Therefore, the dry-cooled S-CO_2 cycle is advantageous even when coupled to light-water SMRs.

Furthermore, next-generation SMRs will undoubtedly be fast reactors cooled by high-temperature gas or sodium, capable of operating 20 years or more without refueling. Their used-fuel value would be high, advancing reprocessing and reducing waste volume. S-CO_2 itself can be used effectively as the primary reactor coolant for a direct-cycle turbine. CO_2 fluid properties near the critical point promote large natural circulation flowrates, allowing for passive decay heat removal for safe shutdown during accident scenarios.

This study will be aimed at experimentally investigating these two thermal-fluid phenomena. We are developing models and correlations of CO_2 fluid properties in the highly compressible region near the critical point. Air-cooled natural circulation of supercritical fluids has not been experimentally investigated.

Summary of Accomplishments:

We designed, built, and operated an air-cooled natural circulation loop with supercritical carbon dioxide (S-CO_2) as the working fluid. In 2014, we accomplished the first known controlled air-cooled natural circulation of S-CO_2. We have since modified the loop to cool it with water. We have modeled the loop in Relap5 and in FUEGO (computational fluid dynamics codes). From these models, we have calculated heat transfer coefficients, Nusselt number, and Grashof numbers, and developed correlations for these dimensionless parameters.

We have demonstrated the potential of S-CO_2 as a working fluid in an air-cooled natural circulating decay-heat-removal loop for nuclear power. Calculations are ongoing to scale our results to that needed for realistic power operations. These calculations will be detailed in the final report for this project.

Significance:

This project has demonstrated that control of S-CO_2 is feasible and has the potential to place energy production in arid regions. For the US, the importance of this is most obvious in the southwestern portion of the country. However, water for power production is becoming scarcer and the water that is available is becoming more expensive. At some point, the cost of water will become prohibitive and the air-cooling capabilities demonstrated in this project will be a means of producing power without the need for water as a source of cooling.

Aggregating Distributed Energy Resources as Secure Virtual Power Plants

180867 | Year 1 of 3 | **Principal Investigator: J. Johnson**

Project Purpose:

This project will create optimization and control tools to increase the quantity of variable, non-dispatchable renewable energy on electric distribution systems by providing electric utilities with a greater capacity to perform voltage/frequency regulation and respond to grid disturbances. This capability is established through virtual power plants (VPP) consisting of a cyber-resilient real-time power flow optimization system connected to various distributed energy resources (DERs). The VPP optimizes the behavior of distributed power electronics-based converters to provide services traditionally reserved for larger power plants (e.g., spinning reserve, inertial damping, and voltage/frequency regulation). Specifically, the individual DERs are programmed with VPP-optimized configurations for autonomous and commanded advanced grid functions (AGFs) to provide ancillary services via real and reactive power flows to the grid. However, the VPP construct necessitates control communications to distribution-level devices at residential and commercial facilities over wired and wireless Internet channels. The inherent unsecure nature of these communications increases the risk of an adversary potentially leveraging a VPP to control large quantities of grid-connected generators, ignore or spoof supervisory control and data acquisition (SCADA) signals, manipulate bids on energy exchanges, or instigate grid instabilities. Therefore, this project will establish a broadly applicable VPP control architecture that includes: 1) stochastic optimization of renewable energy resources that could meet potential power plant commitments, 2) a secure interoperability command dispatch system, and 3) dynamic reallocation of DER operations based on communication failures and natural/adversarial attacks. The cyber-secure communications and resilient controls will be demonstrated at the Distributed Energy Technologies Laboratory (DETL) by aggregating renewable and traditional energy DERs. This R&D effort has far-reaching implications in electric grid distribution level controls, forecasting, and cybersecurity.

An Advanced Decision Framework for Power Grid Resiliency

173090 | Year 2 of 3 | **Principal Investigator: J. Watson**

Project Purpose:

The national power grid is the foundational infrastructure upon which our economy, national defense, health care, emergency response, and standard of living rely. Grid resiliency is, therefore, imperative: grid control systems must prepare for and adapt to changing conditions and withstand and recover rapidly from disruptions, whether caused by deliberate attacks, accidents, or naturally occurring threats. Two key factors drive our need to boost grid resilience: 1) the increasing frequency and magnitude of natural disasters and 2) tighter linkages with other infrastructures (e.g., cyber) driven by grid modernization efforts.

Current performance metrics for power systems address reliability, but they neither quantify resiliency nor consider delivery failure consequences. Without guidance from rigorous metrics, grid operators are ill prepared to anticipate and operate through large-scale cascading failures and blackouts, and lack analytical capabilities to support restoration. We propose to develop foundational grid resiliency metrics and leverage state-of-the-art simulation and decision analysis tools to devise a novel control system to support operate-through and restoration.

We propose to implement an advanced anticipatory decision architecture that will guide the system in order to maximize expected future resiliency. System inputs include a description of the grid control elements and the range of their feasible values in each of many projected scenario trajectories. We will employ stochastic and robust optimization paradigms as the core decision formalism in our proposed framework. Sandia's Pyomo optimization system will be leveraged and extended to express and solve the resulting nonlinear anticipatory decision problems.

The proposed research is high-risk, developing core metrics and technologies required for resilient grid infrastructures. Resiliency metric development is a complex, iterative process involving multiple stakeholders, with disparate interests. Metric acceptance is key, and requires social, institutional, and technical analyses. The proposed grid control system requires integration of state-of-the-art analytic techniques, including uncertainty quantification, predictive simulation, optimization, and high performance computing.

C2R2: Compact Compound Recirculator/Recuperator for Renewable Energy and Energy Efficient Thermochemical Processing

170805 | Year 3 of 3 | **Principal Investigator: I. Ermanoski**

Project Purpose:

While fluid-fluid and bulk fluid heat exchangers are ubiquitous in today's world (from microelectronics to massive power plants), the challenging, yet promising field of heat exchange between packed particle beds remains almost entirely unexplored and undeveloped. Existing applications in need of this kind of heat exchange, such as cement manufacture, employ workarounds involving fluids to achieve satisfactory results. The need, however, has been steadily increasing in emerging technologies, such as solar coal and natural gas upgrade, solar thermochemical energy storage, water and CO_2 capture, or solar thermochemical fuel production, where workarounds would be difficult, if possible at all. These technologies will benefit significantly or depend critically on the development of heat exchangers for packed particle beds.

This critical need is especially well documented in the field of solar fuels. Having recently invented, and analyzed in detail the performance of a novel type of thermochemical reactor for the specific application of solar fuel production, two key issues have been identified that must be resolved before heat exchangers for packed particle beds can be deployed in real world applications: 1) effectiveness and 2) scaling. These two are intimately connected; the larger the exchanger, the more effective it is. But increasing its capacity also requires an increase in size and cost, and the key question is how to maximize capacity at the smallest size and cost—to the point of practical feasibility. This project will experimentally demonstrate solid-solid heat exchange, in the compact compound recirculator/recuperator (C2R2), a scalable package.

Despite the promising numerical models and preliminary measurements, this research remains high risk because it rests on sound but invalidated assumptions, based on a limited understanding of the underlying processes.

Summary of Accomplishments:

This project consisted of four main technical phases:

- Designing an auger with minimal heat transfer lengths which, nonetheless, is capable of efficient particle conveying
- Demonstrating conveying using zero-profile inlets, compatible with nesting of multiple elements into a compact device
- Design for nesting multiple elevators
- Heat transfer over distances beyond the limitations of static particle beds

In the first phase, the conveying rate of four multi-flight auger prototypes designed with different number of flights and single flight pitch were measured. Two of the best performing designs, both double-helix augers, were selected.

Second, the conveying effectiveness of a zero-profile cutter (ZPC) was evaluated. Among other advantages, the ZPC is compatible with a tightly nested auger elevator, which is needed for the scalability of the particle elevator. The conveying efficiency of the ZPC was good, but affected by the auger design, and the better performing of the two remaining augers was selected for the remainder of the project.

Third, the feasibility of a functional nested auger system was demonstrated. The nested auger elevator was fully functional and conveyed 100% more particles at half the casing angular velocity than the most efficient single auger elevator evaluated.

Finally, the heat recovery between particle flows was evaluated. A maximum heat recovery effectiveness of ~50% was achieved, surpassing project goals. In light of the high heat losses and modest scope of evaluated auger geometries, a heat recovery effectiveness >80% seems feasible in a well insulated device and with auger geometry optimizations.

This work demonstrated a first-of-a-kind, mechanically simple solid-solid heat exchanger with a potential for high effectiveness, overcoming the limitations imposed by the low thermal conductivity of particle beds.

Significance:

The results of this project advance the energy security mission by demonstrating, for the first time, a compact, scalable, and efficient heat exchanger for packed particle beds. More specifically, this invention is of special interest in solar-thermochemical fuels and concentrated solar power, where no liquid heat transfer fluid is available for the highest process temperatures. The discovery that heat exchange substantially surpasses that possible with static beds, indicates a significant quasi-convective addition to the thermal conductivity, unobserved before, and warrants substantial further inquiry into the matter.

Calibration, Validation, and Uncertainty Quantification for Turbulence Simulations of Gas Turbine Engines

165635 | Year 3 of 3 | **Principal Investigator: J. A. Templeton**

Project Purpose:

Large eddy simulation (LES) has the potential to reduce pollutant emissions and increase the fuel efficiency of gas turbine engines through model-based investigations of engine design space. High-fidelity LES simulations have greatly enhanced our understanding of turbulent combustion. Engineering calculations, by contrast, use low-order numerical methods necessitated by the coarse, unstructured grids needed in complex geometries. High-fidelity LES often produces excellent agreement with experiments while engineering LES of the same case does not yield sufficiently accurate data for engine design. Such results lead to key questions regarding the applicability of LES models to the engineering process: in what situations will they work and why? Is the true solution even within the space spanned by existing models? How will uncertainties in model parameters impact the results? This work will answer these questions using validation and uncertainty quantification (UQ) to connect science-quality LES with desktop calculations design engineers can use to improve gas turbine engine performance.

Our solution builds on the Advanced Strategic Computing (ASC) program's validation and UQ expertise while developing innovations to handle challenging chaotic flows from engine simulations. Novel UQ approaches will be created to account for the fluctuating turbulent structures. These UQ strategies will enable the calibration and validation problems to be posed in a statistical sense relative to high-fidelity solutions leveraged from existing and on-going scientific calculations. This will determine if existing LES models are capable of the necessary fidelity at acceptable costs, and if so, how to realize this predictive power.

The engineering community has mostly decided against using Reynolds-Averaged Navier-Stokes (RANS) models for turbulent combustion processes, and development of accurate engineering LES models has eluded the research community for several decades. We are testing the hypothesis that recent uncertainty quantification techniques can enable such models.

Summary of Accomplishments:

The primary accomplishment of this project was to bring calibration of models for LES up to the same capability as lower fidelity RANS models. RANS models have the advantage of being low cost, so calibration studies can easily use several thousand simulations. While our work considered engineering LES, which is typically on coarse meshes with lower order numerical methods relative to scientific LES, each simulation requires several weeks of compute time on O(100) processors. Our research identified several pathways, which can produce high-quality calibration results with relatively few simulations (< 100). We achieved this by using physical analysis to eliminate redundant parameters, pioneering "first-principles" calibration of models from high-fidelity LES or direct numerical simulation (DNS) data, being the first to use an embedded-error model form to better capture physical variability, and by designing surrogates which could tolerate sparse, nonsmooth data.

In addition to calibration, we also critically assessed what factors limit the domain of applicability of a calibrated model. First, this project demonstrated solution verification for LES to help estimate the effect of numerical methods. We identified certain sets of numerical parameters, which strongly influence the flow and showed what values they should have to limit their impact on the solution. We also were able to separate physical variability from mesh variability in some cases so each could be measured. This set of results demonstrated that mesh and numerical methods uncertainty are dominant in many flows, and that formal numerical parameters studies can be used to bound the latter.

Finally, we considered the model form error in turbulence models. A key conclusion is that model constants can vary by over two orders of magnitude when assessed from highly resolved simulation results. In addition, dissipative models can never fully recover the physics due to unmodeled energy backscatter processes.

Significance:

This project advanced engineering capabilities by developing and demonstrating calibration strategies for engineering LES that bring it to the state-of-the-art level relative to other engineering simulation approaches. It also advanced science by quantifying what is missing in turbulence models, which limits their predictive power. Our results will enable new analyses to be performed in two national security mission areas: nuclear weapons and energy security. These new methods provide the capability to quantify uncertainty in turbulent flows impacting normal and abnormal environments. They also will enable industry partnerships to use simulation to reduce engine emissions and increase efficiency.

Classifier-Guided Sampling for Complex Energy System Optimization

173494 | Year 2 of 2 | **Principal Investigator: P. Backlund**

Project Purpose:

The purpose of this project was to develop a novel optimization technique known as classifier-guided sampling (CGS) in order to solve large, computationally expensive, discrete variable, single- and multi-objective optimization problems. CGS reduces objective function evaluations by using an inexpensive Bayesian network (BN) classifier to leverage knowledge gained from all prior evaluations and to predict the qualitative performance of candidate solutions. The effectiveness of CGS was demonstrated by comparing performance to a standard genetic algorithm on a set of single- and multi-objective test problems. As a domain-specific case study, CGS was used to design a microgrid for use in islanded mode during an extended bulk power grid outage.

Prior to the start of this project, CGS was a new technology with significant shortcomings that rendered it incapable of handling large-scale, single- and multi-objective optimization problems. First, in its initial form, CGS was only suitable for small design spaces because it required enumeration and processing of every solution in the discrete design space. To address this issue, the probability distributions on which the BN classifier is based can be sampled directly to guide the search towards the most promising designs in the solution space. Second, accounting for interactions between variables is critical to the performance of CGS. Prior to this effort, these dependencies had to be programmed into the algorithm manually. While doing so is feasible for small problems that are well understood, identifying and assigning these dependencies for a large problem is a nearly impossible task. This issue can be addressed by incorporating an algorithm that automatically builds the BN based on a set of training data. Lastly, the ability to perform multi-objective optimization with CGS had not previously been developed and was, therefore, the third major task of this project.

Summary of Accomplishments:

We designed and implemented a new version of CGS that specifically addresses three shortcomings. First, CGS was made to be scalable to large problems by directly sampling the distributions that comprise the classifier to generate new exploratory designs. Second, we enabled CGS to automatically learn variable interactions by implementing an automatic BN learning algorithm that learns these interactions on the fly and updates the classifier accordingly. Lastly, CGS was extended to multi-objective optimization by using the classifier to generate and classify designs when multiple performance criteria are present.

Having designed and implemented the updated version of CGS, we analyzed its effectiveness by testing it on a set of representative single- and multi-objective optimization problems. The rate at which the algorithm converges towards optimal designs is recorded, and the performance is compared to a standard genetic algorithm. As a domain-specific case study, CGS is used to design a microgrid for use in islanded mode during an extended bulk power grid outage. The microgrid design problem has a single- and multi-objective problem formulation. In the single-objective case, the average load not served (LNS) during the outage is minimized, subject to a constraint on installation cost. In the multi-objective case, a set of Pareto optimal designs is sought that efficiently trade minimization of installation cost and LNS.

In six of six single-objective benchmark experiments, CGS identified higher quality results than genetic algorithms (GAs) with fewer objective function evaluations. On the microgrid design problem, CGS identified results of similar quality with roughly 2,000 fewer function evaluations. In the multi-objective optimization tests, CGS also outperformed GAs on some (but not all) of the problems considered. Further study and experimentation is required to gain an understanding of the types of problems for which CGS outperforms GAs.

Significance:

This project demonstrated that CGS has the potential to significantly reduce the time required to solve large, discrete variable, black-box optimization problems. In a customer-analysis scenario, this would enable us to perform a higher quantity of optimization runs in a given time frame. As a foundational capability, CGS benefits a variety of national security projects that utilize simulation-based design optimization. Projects may leverage this R&D via a stand-alone CGS solver or by integrating the CGS optimization library into existing optimization software tools. Furthermore, the Bayesian classifier piece of the software can be used for general machine learning and classification purposes.

Climate Induced Spillover and Implications for US Security

165630 | Year 3 of 3 | **Principal Investigator: V. C. Tidwell**

Project Purpose:

Developing nations incur a greater risk to climate change than the developed world due to poorly managed human/natural resources, unreliable infrastructure, and brittle governing/economic institutions. These vulnerabilities often give rise to a climate induced "domino effect" of reduced natural resource production leading to economic hardship, social unrest, and humanitarian crises. Integral to this cascading set of events is increased human migration, leading to the "spillover" of impacts to adjoining areas with even broader impact on global markets and security. Given the complexity of factors influencing human migration and the resultant spillover effect, quantitative tools are needed to aid policy analysis.

Summary of Accomplishments:

A dynamic model of international human emigration was developed. The model was structured according to the Theory of Planned Behavior. This national-level model integrated dynamics of human security, adaptive capacity, and social interaction that inform the migration decision. The model was established through regression analysis utilizing historical migration data for 166 countries. Specifically, dependent variable time series data, 1960-2010, were extracted from the bilateral migrant stock data published by the World Bank, while associated independent variable time series data were largely taken from the World Bank's World Development Indicators database. Results for the all nations emigration model yielded a surprisingly strong fit to historical data (R2 on the order of 0.8). Coefficients for Lagged Migration, Gross Domestic Product, Telephone Lines, Adjusted Savings, Infant Mortality, and Cereal Production were significant at the 1-5% level. This emigration model was designed to operate within the broader context of integrated assessment modeling of global climate change.

A system dynamics-based model that couples migration behavior with the interacting dynamics of economy, labor, population, violence, governance, water, and food was also developed. The model provides a quantitative framework for assessing migration/spillover risk and adaptive pathways to better prepare vulnerable populations. While this framework was specifically demonstrated for the West African nation of Mali, the tool can easily be transferred to other regions of interest. Results of the case study show a relatively robust pattern of migration of the Malian population in response to climate change. As temperatures increase, economic factors make migration from Mali to other locations more attractive. The population tends to move out of both urban and rural areas of Mali, and toward neighboring countries, the United States, and the rest of the world. The case study also evaluated the efficacy of a variety of competing adaptive measures.

Significance:

Climate and environmental factors have been recognized as threat multipliers in much of the unrest, conflict, and migration plaguing the Middle East and North Africa. Affected governments and the international community at-large have shown little ability to proactively cope with these issues, which are likely to intensify with a changing climate. The tools developed by this project are a positive step toward understanding the complex dynamics governing human migration and the related spillover effect. These tools may also provide a framework for evaluating and prioritizing policy response.

Coating Strategies for High Energy Lithium-Ion

165637 | Year 3 of 3 | **Principal Investigator: C. Orendorff**

Project Purpose:

The performance and safety of lithium-ion batteries are dependent on interfacial phenomena at the positive and negative electrodes. For example, the solid electrolyte interphase (SEI) layer that forms on the graphite anode is known to affect the kinetics and capacity of lithium-ion batteries. Interfacial reactions between the electrolyte and the cathode are also known to initiate electrolyte combustion during thermal runaway events that compromise battery safety.

Interfacial phenomena can be sensitively influenced by ultrathin coatings on the electrodes. These ultrathin coatings can profoundly alter the interfacial interactions between the electrode and the electrolyte. This project is focused on developing atomic layer deposition (ALD) and molecular layer deposition (MLD) coatings for electrode surfaces. These ALD and MLD coatings can dramatically improve lithium-ion cell performance and safety.

ALD and MLD are thin film deposition techniques based on sequential, self-limiting surface reactions. ALD and MLD can deposit ultrathin and conformal films on high aspect ratio and porous substrates such as composite particulate electrodes in lithium-ion batteries. Previous results have revealed that ultrathin coatings of Al_2O_3 ALD have a dramatic effect on the capacity stability of electrodes for lithium ion batteries such as graphite anodes and $LiCoO_2$ cathodes. The potential of these ALD coatings has been widely acknowledged and additional ALD materials need to be tested to determine their effectiveness. This project will explore new ALD and MLD based coatings such as AlF_3 and metal oxide-carbon composites. The work is in collaboration with University of Colorado-Boulder.

Summary of Accomplishments:

This project primarily focused on studying the effects of Al_2O_3 ALD coatings on the performance and thermal abuse tolerance of graphite based anodes and $Li(Ni_xMn_yCo_z)O_2$ (NMC) based cathodes. It was found that five cycles of Al_2O_3 ALD on the graphite anode increased the onset temperature of thermal runaway by approximately 20 °C and significantly reduced the anode contribution to the overall amount of heat released during thermal runaway (measured by accelerating rate calorimetry [ARC]). Although Al_2O_3 ALD improves the cycling stability of NMC based cathodes, the thermal runaway response on NMC electrodes was not greatly improved. This is likely due to the fact that ALD coatings are too thin to support inhibition of the interfacial combustion reactions that contribute to thermal runaway. We also found that attempts to grow thicker Al_2O_3 ALD coatings had a negative impact on cell electrochemical performance.

As a strategy to grow thicker electrically conductive ALD films to improve cathode electrode thermal runaway response, we developed a process for molecular layer deposition (MLD) of composite films. A series of conductive aluminum oxide/carbon composites were created and characterized as potential thicker protective coatings for use on NMC based cathode materials. We found that the pyrolysis conditions of alucone MLD films can be optimized to give films with a sheet resistance as high as 5 x 10^{-5} Ω/cm^2.

As an alternative for composite films that improve thermal runaway reactivity at the cathode electrodes, we also studied the idea of oxygen scavenging-based ALD coatings. These are chemically active components designed to react liberated oxygen from cathode electrodes before electrolyte combustion can occur. We developed a process for coating manganese monoxide ALD films that could be used in the oxygen scavenging strategy.

Significance:

This work advances our understanding of interfacial chemistry that governs thermal runaway reactivity in lithium-ion batteries. Improving the safety and reliability of transportation energy storage systems and enabling the emergence of hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs), directly supports core missions of the NNSA laboratories of national security and energy security. The interest in safe and reliable transportation energy storage is of growing interest to DOE and other agencies including the National Highway Traffic and Safety Administration (NHTSA), Department of Transportation (DOT), and the Federal Aviation Administration (FAA).

Refereed Communications:

C. J. Orendorff et al., "Battery Safety R&D and Sandia National Laboratories," presented at the *FAA Fire Systems Working Group Meeting*, Atlantic City, NJ, 2014.

C. J. Orendorff et al. "Comprehensive Understanding of Battery Safety," presented at the *International Battery Association Meeting*, Waikaloa, HI, 2015.

C. J. Orendorff et al., "Quantifying Thermal Runaway and Improvements through Materials Development," presented at the *Next-Generation Batteries*, San Diego, CA, 2015.

Developing Next-Generation Graphene-Based Catalysts

165636 | Year 3 of 3 | **Principal Investigator: T. N. Lambert**

Project Purpose:

This project aimed to develop next-generation catalysts based on nanoscale 3D networks of graphene, ceramics, and graphene-ceramic hybrids in order to establish a leading role for Sandia in nanoscale-based catalysis. High electrocatalytic (EC) activity, selectivity, and stability for the oxygen reduction reaction/oxygen evolution reaction (ORR/OER) is critical for successful transition of next-generation fuel cells and rechargeable metal/air batteries into today's renewable energy technologies. The high cost and overall rarity of platinum (Pt) preclude it from use in larger-scale widespread commercial applications. Pt-based catalysts in fuel cells also suffer from crossover and fuel poisoning issues, which severely lowers the EC activity and performance. Replacing Pt with less costly ceramics, graphene, and/or graphene-ceramic materials is in support of the critical materials supply issues. Electrocatalysts based on nanoscale 3D networks of EC carbon represent a promising approach to developing cost-effective electrocatalysts that operate at higher current densities and cell voltages, with significantly greater EC stability in metal-air batteries and fuel cells. Practical EC applications of graphene are still severely limited by the lack of fundamental understanding on the origin of its EC properties and its 2D morphology, as the fabrication of practical 3D electrodes for ORR/OER is currently not established. A way to assemble these graphene-based materials into larger macroscopic 3D EC form factors is also needed. We aim to demonstrate that such 3D structures can be prepared in a meaningful way and that they can be utilized to improve electrochemical devices. Additionally, we have discovered that 3D porous ceramics can have exceptional activity for bifunctional oxygen electrochemistry and that these catalysts can be prepared without binder materials, thereby improving their activity and overall utility.

Summary of Accomplishments:

This project resulted in the development and testing of several new materials systems. Some of the highlighted work includes the development of graphene/ceramic hybrid materials as catalysts for the ORR. This included a fundamental study with the University of New Mexico to understand how copper- or nickel-ion metal ion doping improved the catalysis of manganese oxide nanowires. We had previously shown in collaboration with Rice University that, when blended with a graphene-like carbon, these manganese oxide nanowires performed as well as the Pt/C commercial benchmark. This collaboration also examined silver-graphene nanoribbon (Ag-GNR) composites as ORR electrocatalysts. The Ag-GNR outperformed the commercial Ag/carbon catalysts and also showed better electrocatalytic selectivity for ORR versus methanol oxidation than the commercial platinum/carbon catalysts. We received an invitation to publish this work in a Special Graphene Issue of Electroanalysis. We then switched our focus to the development of bi-functional electrocatalysts: that is, electrocatalysts than can effectively perform both the ORR and the OER. With this in mind, we demonstrated that electrodeposited 3D nickel doped cobalt oxide films were highly effective bifunctional catalysts. Their activity was attributed to the intimate contact between the catalyst and the conductive substrate, their high surface area, mesoporous structure, and improved conductivity upon doping the spinel cobalt oxide with nickel ions.

Significance:

This project developed several cost effective, highly active electrocatalysts for the oxygen reduction and oxygen evolution reactions. These efforts are relevant to the DOE's Energy Security and Scientific Discovery and Innovation strategic themes as well as the DOE Critical Material Supply concerns regarding precious metal catalysts materials. This project grew Sandia's graphene knowledge base and capabilities in electrocatalysis, which could be leveraged in other energy-generating methods (e.g., battery, fuel cells, photocatalytic fuels, water-splitting), materials (e.g., strong composites), and security (sensing, radiation detection) applications as well.

Refereed Communications:

T.N. Lambert, J.A. Vigil, S. White, D. J. Davis, S.J. Limmer, P.D. Burton, E.N. Coker, T.E. Beechem and M.T. Brumbach,"Electrodeposited NiXCO3-XO4 Nanostructured Films as Bifunctional Oxygen Electrocatalysts," *Chemical Communications*, vol. 51, pp. 9511-9514, May 2015.

T.N. Lambert, D.A. Miller, C.M. Washburn, N.S. Bell, T.J. Boyle, and B.A. Hernandez-Sanchez, "Graphene Nanocomposites," presented (invited) at the *2014 MRS Fall Meeting*, Boston, MA, 2014.

D.J. Davis, T.N. Lambert, J.A. Vigil, M.T. Brumbach, M. Rodriguez, E. Coker, and S.J. Limmer, "Role of Cu-Ion Doping in Cu-alpha-MnO2 Nanowire Electrocatalysts for the Oxygen Reduction Reaction," *The Journal of Physical Chemistry C*, vol. 118, pp. 17432-17350, 2014.

Development of High-Fidelity Models for Liquid Fuel Spray Atomization and Mixing Processes in Transportation and Energy Systems

170975 | Year 3 of 3 | **Principal Investigator: R. N. Dahms**

Project Purpose:

Significant inadequacies of current models for multiphase flows are a major barrier to rapid development of advanced high-efficiency low-emissions combustion devices. While substantial improvements in the design of such devices are possible, they require a high level of precision that can only be reached through development of advanced simulation capabilities. The present empirical understanding of sprays must be replaced by a first-principles approach, and this need will only become more critical as requirements become more stringent. The objective of this research is to develop a first-principles approach in the context of high-fidelity large eddy simulation (LES). We will systematically develop a coupled system of advanced subgrid-scale models for LES aimed at treating liquid spray phenomena.

Predicting multiphase flow phenomena in modern liquid fueled combustion devices is widely recognized as a critical area of research for the design of advanced systems. These needs have been consistently highlighted over many years in a variety of industry, government, and academic forums, including recent DOE workshops such as the "Workshop to Identify Research Needs and Impacts in Predictive Simulations for Internal Combustion Engines" (PreSICE), and the "Workshop on Clean and Efficient Combustion of 21st Century Transportation Fuels." Needs and priority research directions emphasize the importance of establishing a basic science foundation for the development of advanced predictive models in this area. Developing such models requires a highly specialized effort that combines detailed theory, advanced simulation capabilities, and high performance massively parallel computing. While Sandia has already developed substantial capabilities in simulating turbulent reactive gas flows, such capabilities do not yet exist in the area of multiphase flows. The development of the foundational science to understand and predict spray atomization, evaporation, and multicomponent mixing processes in the context of high-fidelity large-eddy simulation techniques requires a highly specialized effort over a period of time.

Summary of Accomplishments:

The current work has introduced a fundamentally consistent framework suitable for large eddy simulations to understand and quantify the effects of drop oscillations, internal flow dynamics, and breakup processes on mass, momentum, and energy exchange functions. This framework is based on the Taylor-Analogy-Breakup (TAB) model, which naturally quantifies local drop deformation dynamics. It was also established that TAB model is valid over the full range of drop conditions typically encountered. Real-fluid thermodynamic property modeling and Gradient Theory facilitated accurate calculations of molecular two-phase interface exchange functions, surface tensions forces, drop oscillations, and breakup processes. Statistical analysis from local drop flow and thermodynamic states established the drop Reynolds number as the most important parameter to describe the coupling of drop dynamics and interface exchange functions. This is a nontrivial conclusion since drop dynamics are determined by the temporal evolution of the drop distortion. Drop deformations, however, are mainly determined by the Weber number as the main parameter of widely accepted regime diagrams for drop deformation and breakup. However, the analysis revealed a strong correlation between the local drop Weber number and the local drop Reynolds number. Both parameters are mainly determined by the local slip velocity. As a consequence to the nonlinear effect of fluid dynamics around the drop, quantified by the Reynolds number, local drop oscillations are determined by the Weber number while the resulting coupling dynamics to the turbulent flow are determined by the Reynolds number.

Significance:

Development of advanced models to treat turbulent multiphase combustion processes and the Large Eddy Simulation technique will advance predictive simulation capabilities in mission-critical areas, such as energy surety. With turbulent reacting flow as our target application, the models could have relevance in a wide range of multi-scale flow problems relevant in the defense, energy, and climate areas. The product of this research will also strengthen Sandia's position in the area of high-fidelity simulations.

Development of Quality Assessment Techniques for Large Eddy Simulation of Propulsion and Power Systems in Complex Geometries

170976 | Year 3 of 3 | **Principal Investigator: G. Lacaze**

Project Purpose:

Large eddy simulation (LES) is quickly becoming a method of choice for studying complex thermo-physics in a wide range of propulsion and power systems. It provides a means to study coupled turbulent combustion and flow processes in parameter spaces that are unattainable using direct numerical simulation (DNS), with a degree of fidelity that can be far more accurate than conventional engineering methods such as the Reynolds-Averaged Navier-Stokes (RANS) approximation. However, development of predictive LES is complicated by the complex interdependence of different type of errors coming from numerical methods, algorithms, models, and boundary conditions. On the other hand, control of accuracy has become a critical aspect in the development of predictive LES for design.

The objective of this project is to create a comprehensive framework of metrics aimed at quantifying the quality and accuracy of state-of-the-art LES in a manner that addresses the myriad of competing interdependencies. In a typical simulation cycle, only 20% of the computational time is actually usable. The rest is spent in case preparation, assessment, and validation, because of the lack of guidelines. The approach proposed here will facilitate control of the tradeoffs between cost, accuracy, and uncertainties as a function of fidelity, models, and numerical methods employed. This goes well beyond the scope of isolated model development efforts and requires an integrated crosscutting approach. Development of these metrics will have broad impact on research supported by the DOE and significantly contribute to strengthening the role of high-fidelity simulations in the community.

Control of errors in a complex solver is an issue common to all numerical studies. An enormous amount of time and money is wasted because of the absence of a clear and quantitative method to perform simulations. This research will provide quantitative guidelines that improve the usage of available resources while maximizing solution accuracy.

Summary of Accomplishments:

This project was aimed at quantifying the quality and accuracy of state-of-the-art LES in a manner that addresses the complex interdependencies between errors. Three different metrics were identified: 1) statistically converged flow field quantities, 2) relevant turbulence scales, and 3) power density spectra of resolved turbulent energy. Those three metrics have been tested in various configurations. Results showed their own advantages and drawbacks. Converged statistics can be directly compared to experimental measurements and then can be used for both validation and convergence analysis. Turbulence scales estimation allows a deeper description of turbulence mechanisms as well as a priori guidelines on how to design LES grids. Energy spectra reveal accurately grid convergence and give access to a verification of model assumptions by looking at the spectra shape and the location of the LES cutoff. Those metrics are currently used in the LES group and have been very well received in the community at large.

This project also initiated the creation of a library of benchmark simulations with well-controlled boundary conditions. Those benchmarks are recognized to be useful for code validation and data mining for model development, and are already in use within Sandia to perform RANS model optimization and uncertainty quantification.

Significance:

The project has marked the beginning of a shift in the way simulations are performed at the Combustion Research Facility. This shift is characterized by the inclusion of model uncertainties and quality assessment within computational efforts and makes our predictions much more accurate. This helps strengthen the capabilities available to the DOE to solve urgent issues related to emissions and the understanding of new physics needed for the development of future transportation technologies. The project also created a new funding opportunity in the domain of uncertainty evaluation in very complex propulsion systems. This new project (DARPA-EQUiPS) has been initiated in FY 2016 for a period of three years. It focuses on estimation of multi-physics uncertainties and device optimization in the context of hypersonic SCRAMJET propulsion.

Refereed Communications:

A.M. Ruiz, G. Lacaze, and J.C. Oefelein, “Flow Topologies and Turbulence Scales in a Jet-In-Cross-Flow,” *Physics of Fluids*, vol. 27, p. 045101, 2015.

A.M. Ruiz, G. Lacaze, J.C. Oefelein, R. Mari, B. Cuenot, L. Selle, and T. Poinsot, “A Numerical Benchmark for Validation of High-Reynolds Number Supercritical Flows with Large Density Gradients,” *AIAA Journal*, doi: 10.2514/1.J053931, 2015.

M. Khalil, G. Lacaze, J.C. Oefelein, and H. N. Najm, “Uncertainty Quantification in LES of a Turbulent Bluff-Body Stabilized Flame,” *Proceedings of the Combustion Institute*, vol. 35, pp. 1147-1156, 2015.

L. Hakim, G. Lacaze, M. Khalil, H. Najm, and J.C. Oefelein, “Modeling Auto-Ignition Transients in Reacting Diesel Jets,” *ASME Journal*, 2015.

Electrostatic Coating with Naked Copper Nanoparticles

173495 | Year 2 of 3 | **Principal Investigator: T. J. Boyle**

Project Purpose:
In collaboration with the University of Arizona (UA), low-cost nanoinks for interconnect applications will be developed, focusing on nanocopper inks. An alternative coating method that allows for conductive film formation on a variety of substrates is desirable, both as an alternative to conventional conductive thin-film processing as well as the emerging field of flexible electronic and photovoltaic devices. In conventional approaches, a metal catalyst is used that can be both expensive and increases the resistance of interconnect lines. An alternative approach to the formation of copper thin films is electroless deposition (ELD). The ELD process applies the use of colloid suspensions of metallic nanoparticles (NP) attracted to a substrate surface and allows for a number of bottom-up tailoring options to conductive pathway formation. A rudimentary coating of metal NPs is hypothesized to require substrates maintain a partial-positive electrical surface charge. NPs offer feature resolution that is dependent on controllable physical properties, and their electrochemistry may be tailored to eliminate grain growth catalysts. The use of NPs over a bulk phase allows for the bottom-up creation of electric paths that conform to the local shifts in position of the underlying layer and are formed at moderate (<673K) temperature. ELD films may conduct current in low-thermal budget applications, where the substrate undergoes macroscopic flexing. The proposed research may lead to applications in flexible electronics, bottom-up device creation, and environmentally sustainable/benign electronic device manufacture.

Fractal-Like Materials Design with Optimized Radiative Properties for High-Efficiency Solar Energy Conversion

173092 | Year 2 of 3 | **Principal Investigator: C. K. Ho**

Project Purpose:

High-temperature solar receivers and radiative heat-collection components are used in renewable energy systems, space and satellite applications, and military operations. The purpose of these components is to collect heat by maximizing solar absorption while minimizing thermal losses. However, at high temperatures (receivers can reach 600 °C and higher), the radiative losses are significant. While previous studies have tried to improve the efficiency of these receivers at high temperatures by increasing solar absorptivity and reducing thermal emissivity of surface coatings, very little research has investigated the optimization of features and radiative properties of receivers and other components at multiple length scales.

Our proposed work will develop fractal-like structures and designs at multiple scales (millimeters to meters) that will maximize solar absorption while minimizing heat loss. Through our background research on radiative properties of surfaces, we have identified that self-similar features of fractal structures over a large topological dimensional range will provide an effective trapping mechanism for solar irradiation. In addition, synthesis and design of fractal-like structures will be tailored to reduce reflective losses, local view factors, and thermal emittance at multiple scales. Novel radial and star-like patterns at the macroscale have been shown to reduce radiative view factors by up to 70% and total heat loss by 50%. Incorporation of these hierarchical features and designs at multiple scales is expected to significantly increase thermal efficiencies of solar energy receivers and a broad range of thermal collection devices for sustainable, lower-cost, and high-efficiency energy conversion.

The proposed work aims to develop novel designs for high-temperature solar thermal receivers with increased efficiencies that address DOE's mission to develop sustainable energy technologies. The work requires complex modeling, as well as testing available only at Sandia's National Solar Thermal Test Facility, that will answer fundamental radiative transfer questions to improve the performance of solar thermal receivers.

Holographic Spectrum Splitting Demonstration System for Duel Photovoltaic and Biofuel Operation

180870 | Year 1 of 3 | **Principal Investigator: W. C. Sweatt**

Project Purpose:

The purpose of this work is to demonstrate spectrum splitting optical components that enable increased solar energy conversion and reliability. Solar collectors such as photovoltaic semiconductors and biofuel systems have a limited spectral response range. Optical components can be incorporated to redistribute wavelengths onto appropriate collectors for maximum conversion efficiency. Hybrid photovoltaic (PV)/biofuel systems are of particular interest because the storage capacity of biofuel can supplement the intermittent power output from a PV cell. There is also interest in incorporating spectrum-splitting optics with micro-concentrators developed at Sandia.

The optic explored in this work is an algorithmically designed surface relief diffractive optical element (DOE) for spectrum splitting. A broadband expansion of the Gerchberg-Saxton algorithm has been developed. Several designs were generated and verified in simulation to achieve >87% optical efficiency and 37.7% conversion efficiency in a two-bandgap (CdSe/Si) system. One technical challenge with a microlens/DOE system is the detrimental effect of lens aberrations on spectrum splitting capability. A simple diffraction grating placed over a lens will encounter off-axis aberrations, which broaden the focal line of dispersed light. A holographic grating recorded in a conjugate geometry using this lens has been shown to counteract this aberration. In a similar approach, the next step of this work is to incorporate a specific lens prescription into the algorithm, which will allow the DOE to compensate for expected aberrations in the converging beam. Another challenge of applying diffractive optics to solar energy is scalability in manufacturing. A path towards solving this is to create a lithographically fabricated master and use an embossing process to mass-produce the DOE.

The final stage of this work, in collaboration with the University of Arizona, is to design and fabricate a DOE for a particular microconcentrator array, construct a proof-of-concept micro spectrum splitting system, and test its performance under a solar simulator.

Lithium Oxysilicate Compounds as Stable Analogs for Understanding Li-P-S High Rate Li-Ion Separators: Moving Solid Electrolytes into High Rate Applications

181205 | Year 1 of 3 | **Principal Investigator: C. A. Apblett**

Project Purpose:

We propose to study an alternative to current solid state lithium ion (Li+) conducting solid electrolytes to improve the safety and reliability of lithium battery systems. Lithium ion batteries require an electrolyte to support transport of Li+ between electrodes, which is often a liquid to enhance conductivity. These liquid electrolytes suffer from being highly volatile, pose health risks, and are highly flammable, making them a concern for implementation into larger scale systems. Solid phase electrolytes exist, but they are typically several orders of magnitude lower in ionic mobility than their liquid counterparts, limiting the utility of these systems to niche applications. Understanding the ionic transport of Li+ through a solid phase electrolyte would assist in the design of solid state batteries that would be safer, easier to manufacture, and perhaps cheaper than existing vehicle and grid solutions.

A new class of highly conductive Li+ solid phase conductors is being investigated based on Lithium Oxide-Silicon Oxide compounds, which have been little studied in the literature, but have an analog in the lithium oxynitride systems that have reasonable solid state mobilities. We propose to collaborate with University of Colorado-Boulder to support research into physical vapor deposition (PVD) of these materials, map the stoichiometry space, and understand the effects on the transport performance and long term stability of the resultant materials. By fully developing these ternary compounds, we expect to develop a fundamental understanding of Li ion transport in complex oxide systems chemistry that would provide insight into improved solid state electrolytes for transportation and stationary power.

Measurements and Modeling of Black Carbon Aerosols in the Arctic for Climate Change Mitigation

173094 | Year 2 of 3 | **Principal Investigator: H. A. Michelsen**

Project Purpose:

Growing evidence suggests that black carbon (BC) particles contribute significantly to global climate change and are largely responsible for the enhanced warming of the Arctic (~twice that of the global rate). Because of the relatively short atmospheric lifetimes of particulates compared to CO_2 and the large radiative forcing of BC aerosols (~65% that of CO_2), BC reductions are being considered as a viable near-term climate change mitigation approach. Assessing the effectiveness of such a strategy, however, will require better estimates of BC climate forcing, which are hampered by large uncertainties associated with a paucity of atmospheric observational constraints, particularly in the Arctic, and poorly represented BC physical and optical properties in climate models. This project aims to reduce the uncertainties of Arctic climate forcing of BC by combining Arctic field observations, laboratory experiments, and modeling.

This project embodies a unique combination of: 1) Arctic field instrument deployment, which leverages Sandia's expertise in Arctic measurements, 2) controlled laboratory experiments, which exploit Sandia's unique capabilities in BC particle diagnostics, and 3) detailed process modeling to investigate BC radiative properties and improve its parameterizations in the state-of-the-art Community Earth System Model (CESM), which includes the new Spectral Element Community Atmospheric Model (CAM-SE) developed at Sandia. Risks include uncertainties in the performance of BC field instrumentation, deployment of instruments in extreme environments, and addressing the complexity of BC properties and implementing parameterizations in CESM. If successful, the benefit will be an improved capability to resolve large discrepancies between modeled and measured atmospheric BC, leading to a new understanding of BC in the global and Arctic atmosphere.

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Multi-Objective Optimization of Solar-Driven, Hollow-Fiber Membrane Distillation Systems

180872 | Year 1 of 3 | **Principal Investigator: T. M. Nenoff**

Project Purpose:

Securing additional water sources remains a primary concern for arid regions in both the developed and developing world. Climate change is causing fluctuations in the frequency and duration of precipitation, which can be can be seen as prolonged droughts in some arid areas. Droughts decrease the reliability of surface water supplies, which forces communities to find alternate primary water sources. In many cases, ground water can supplement the use of surface supplies during periods of drought, reducing the need for above-ground storage without sacrificing reliability objectives. Unfortunately, accessible ground waters are often brackish, requiring desalination prior to use, and underdeveloped infrastructure and inconsistent electrical grid access can create obstacles to groundwater desalination in developing regions. The objectives of the project are to: 1) mathematically simulate the operation of hollow fiber membrane distillation systems and 2) optimize system design for off-grid treatment of brackish water. It is anticipated that methods developed here can be used to supply potable water at many off-grid locations in semi-arid regions including parts of the Navajo Reservation. This research is a collaborative project between Sandia and the University of Arizona.

This algorithm research and computer code development, utilizing Sandia unique hardware, has broad applications and mission relevance to critical issues of energy security.

Multiscale Multiphysics for Subsurface Science and Engineering of Shale

180869 | Year 1 of 3 | **Principal Investigator: H. Yoon**

Project Purpose:

Shale is becoming an increasingly important rock type with emerging climate and energy security problems including shale gas extraction, sealing for geologic carbon storage, and suitable repositories for domestic nuclear waste. However, there is no consensus as to fundamental mechanisms underlying observed rapid decline in gas production and the fate of fracking fluids in shale gas fields. Movement of CO_2 plumes in the subsurface through shale caprocks has not followed model prediction. Furthermore, nanoscale pore size, surface chemistry, and complex connectivity in shales result in unique flow properties in contrast to those in other rock types. Consequently, the response of anisotropic heterogeneous shale geomaterials to engineered 3D thermal, fluid flow, and stress perturbations are not currently quantifiable to a degree where prediction is viable.

The purpose of the project is to discover a fundamental mechanism of poromechanical and flow responses of shales with broad compositional range and physical and chemical heterogeneity in order to enhance our capabilities in multiscale multiphysics-based characterization of heterogeneous porous materials for resource extraction and energy storage. Detailed nanometer-to-core scale characterization and mechanical and transport properties of shale rocks are achieved by integrating multiscale imaging, experimentation, state-of-the-art modeling schemes, and high performance computing. Multiscale imaging techniques and geomechanical testing allow us to demonstrate the nanoscale variability of structures of pores, clay aggregates, organics, mineral grains and cements in a few common shale variants, including response to perturbations in stress, pore pressure, temperature, and time. Detailed pore-scale modeling integrated with multiscale imaging, allows for direct correlation of flow properties scaled up to correspondingly increased chemical reactivity and poromechanical properties. Overall, this project leads us to develop a quantitative workflow for understanding petrophysical and geomechanical behavior of shale lithologies in the subsurface.

Nanocomposite Barrier Films for Enhanced Thin Film Photovoltaic Stability

180865 | Year 1 of 3 | **Principal Investigator: E. D. Spoerke**

Project Purpose:

Long term reliability, functional device lifetime, and consumer safety are central concerns for the cost-effective integration of photovoltaic (PV) systems in the rapidly evolving global stationary energy scheme. Failure or degradation of encapsulant coatings protecting sensitive PV materials and electronics from environmental moisture and oxygen is arguably the leading cause of PV degradation and failure. These failures affect reliable utility and introduce unacceptable maintenance and replacement costs. We propose to develop and evaluate a robust, low-cost, optically transparent, highly impermeable polymer-clay nanocomposite (PCN) thin film barrier/encapsulant alternative. Currently, used glass barriers suffer from cracking or poor sealing, while polymer encapsulants (e.g., ethylene vinyl acetate) are temperature sensitive, discolor, and can degrade to form damaging acidic byproducts. Our alternative composite thin film barrier, comprising delaminated clay platelets, dispersed and oriented within a polyelectrolyte polymer matrix, is deposited using scalable layer-by-layer (LBL) processes. These composite thin films are transparent, flexible, conform to irregular shapes, and exhibit excellent oxygen/moisture exclusion. Moreover, known fire retardant properties of these oxygen barriers introduce unprecedented protection against fires caused by device arc faults.

Novel PCN thin film PV encapsulants offer potentially high rewards, promising improvements in PV reliability, stability, and safety, critical issues plaguing the integration of PV into the national electrical energy infrastructure. We will explore the feasibility of this approach, employing scientific study to inform system optimization and address risks associated with using these untested materials. Mating Sandia's strengths in materials development and PV reliability also promises expanded leadership opportunities within the photovoltaic community, while the barrier technology itself may impact additional national security mission space applications concerned with air and moisture-sensitive optics or electronics (e.g., satellites, and nuclear weapons).

Natural Gas Value Chain and Network Assessments

165631 | Year 3 of 3 | **Principal Investigator: P. H. Kobos**

Project Purpose:
The DOE Energy Information Administration maintains a traditional network equilibrium model used for natural gas (NG) price, supply, and demand forecasting that does not yet account for nonequilibrium and infrastructure feedback behaviors. The NG system has undergone an abrupt change due to increases in supply driven by hydraulic fracturing technology, adding substantial supplies. This created a system where little historic data exists to represent the possible system evolution. The purpose of the project is to model the nonequilibrium factors affecting natural gas prices, supplies, and demand in the US due to recent shale gas supply developments. This project will develop two methods that include nonequilibrium and infrastructure feedback behaviors. We conceptualize this problem as supply shock propagation that pushes the NG system and the economy away from its current state of infrastructure development and level of natural gas use. The goal of the modeling effort is to understand future states of the NG system and effects of possible regulatory actions.

Summary of Accomplishments:
First, the team developed a dynamic agent-based modeling (ABM) approach based on existing pipeline network size, flow, and price data, which addresses shock propagation throughout the existing natural gas distribution system. The ABM illustrates several stylized scenarios including large liquefied natural gas (LNG) exports from the US. The ABM preliminary results demonstrate that the price of natural gas in the US may rise by about 50% when the LNG exports represent 15% of the system-wide demand. The main findings of the system dynamics (SD) model indicate that future proven reserves for coalbed methane, conventional gas, and now shale gas can be adequately modeled as well as a CO_2 tax scenario's effects on proven reserves based on geologic, economic, and technology-based variables. These approaches represent a new capability for Sandia and others to analyze the nonequilibrium effects across networks. The ABM study develops an operational model as well as implements four different scenarios including a stylized network shock caused by an addition of significant LNG exporting capacity, high and low NG availability, and their comparisons with the base case. We believe the agent-based modeling is a viable tool to understand the future possible evolution of the NG system and received favorable feedback from Stanford University's Energy Modeling Forum.

The second approach uses a System Dynamics-based model to illustrate the feedback mechanisms related to finding new supplies of natural gas–notably shale gas–and how those mechanisms affect exploration investments in the natural gas market with respect to proven reserves. The system dynamics (SD) model successfully develops NG proven reserves and price endogenously based on technological change, and the buildup over time of a desired reserve to production ratio with feedback from the demand and exploration for new sources of NG. With the base case, environmental CO_2 tax and increased demand scenario, these policy scenarios affect proven reserves of natural gas in the years to come. Modeling the complex relationship between the geoscience, economic, and engineering aspects of the natural gas industry in a SD framework offers several advantages. First, temporal nonlinearities affecting relationships including technological change, demand, and supply elasticities are easily replicated using the SD framework. Second, the evolving, feedback-rich nature of these complex interactions can be easily represented in the SD model while identifying how to calibrate against historic data with uncertainty in future natural gas markets.

Significance:
The nonequilibrium-focused approach of the agent-based and system dynamics models is widely applicable to not only natural gas energy and infrastructure system changes, but to many other networks and technologies. The key insights highlight how the interactions and feedback in the infrastructure and markets greatly affect the impact of acute and chronic events that affect the performance and cost across the system's operations. This research could ultimately benefit DOE's objective to support the environmentally responsible development, delivery and use of domestic natural gas.

Refereed Communications:

P.H. Kobos, "Shale Gas: Modeling the Economic Factors and Quantifying Uncertainty," presented (invited) at the *Shale Gas Symposium*, Korea Gas Technology Corporation, Seoul, Korea, 2015.

P.H. Kobos, "Shale Gas: Modeling the Economic Factors and Quantifying Uncertainty", Invited Presentation at Seoul National University, Seoul, Korea, March 19, 2015.

Next-Generation Global Atmosphere Model

173079 | Year 2 of 3 | **Principal Investigator: W. Spotz**

Project Purpose:

To assess the national security implications of climate change, the US will need climate models that run efficiently on a multitude of emerging computing architectures, as well as models capable of quantifying uncertainty. No existing climate model possesses either of these capabilities, and modifying existing models to attain them is daunting enough to warrant the development of new models that incorporate these capabilities from the start. This project will develop a new global atmosphere model that addresses these needs by using Sandia technologies Trilinos, Dakota, and Albany.

Emerging computing platforms are taking many different forms and developing algorithms that exploit each form to maximum effect is a cutting-edge design goal called performance portability. Sandia has developed a strategy to achieve this goal, one supported by enabling code in the Trilinos suite of scientific software packages.

Uncertainty quantification is an emerging field of study within the computational sciences, closely related to optimization, and Sandia has developed the Dakota package to enable these capabilities. Dakota can treat existing science applications as black boxes, but more advanced algorithms required embedded logic within the application.

Albany is an application development code base, built on top of Dakota and the many packages within Trilinos, to provide rapid development of finite element scientific applications with access to cutting-edge computational capabilities. We are using Albany to develop a state of the art global atmosphere model that is performance portable and can quantify uncertainty.

This project will address regional refinement and uncertainty quantification (UQ) processes and tools in a new atmospheric dynamical core. If successful, we will demonstrate what is possible in a modern Earth system model, and provide the groundwork for using such a system model in a DOE policy and decision support role for enabling the mitigation of, or adaptation to, climate change impacts.

Novel Metal-Organic Frameworks for Efficient Stationary Energy Sources via Oxyfuel Combustion

165632 | Year 3 of 3 | **Principal Investigator: T. M. Nenoff**

Project Purpose:

Oxy-fuel combustion is a well-known approach to improve the heat transfer associated with stationary energy processes. However, its overall penetration into industrial and power markets is constrained by the high cost of existing air separation technologies for generating oxygen. Cryogenic air separation is the most widely used technology for generating large flows of oxygen but is a complex and expensive technology. Pressure swing adsorption (PSA) is a competing technology that uses separations materials such as activated carbon, zeolites, and polymer membranes. Current PSA technology is expensive and limited to moderate purity O_2 applications because of limitations of existing separations materials. Metal-organic frameworks (MOFs) are cutting edge materials for gas separations at ambient pressure and room temperature, potentially revolutionizing the PSA process and providing dramatic process efficiency improvements through oxy-fuel combustion. This project will produce fundamental knowledge on novel MOFs for gas separations that will be leveraged to applied studies and/or commercialization of new oxy-fuel processes. Our energy analysis of MOF air separation processes coupled to oxy-fuel combustion will demonstrate greater than 5% efficiency improvement, with decreased overall carbon emissions. Our project is both an innovative approach for developing novel high selectivity MOFs for O_2 purification and is cutting edge for: 1) optimized MOF synthesis, 2) testing of preferred O_2 sorption from multicomponent streams, 3) combined molecular dynamics simulations and crystallography of gas siting in pores for structure-property relationship studies, 4) combustions testing, and 5) systems analysis to aid in real-world implementation.

This project is basic research focused on the predictive design and tuning of MOFs for oxygen separation from air at higher temperatures than cryogenic processes, plus the design and building of advanced burners. Synthesis and testing of new MOFs in lab scale separations may potentially provide valuable information relevant to the DOE's energy security mission.

Summary of Accomplishments:

We accomplished all of our FY 2015 milestones. We focused on a number of simultaneous and related research fronts. We successfully accomplished discrete Fourier transform (DFT) calculations (VASP code) of MOFs with coordinative unsaturated metal sites; consequently, we calculated the O_2 and N_2 binding energies at MOF metal sites. Calculations have been completed for HKUST-1 and M-MOF-74 and results indicate that early transition metals, such as vanadium, will result in the strongest binding to O_2 over N_2. We then successfully synthesized a number of MOFs with those early transition metals and showed preferred O_2 binding over N_2 at temperatures above room temperature.

The newly designed and built burner was successfully tested with a variety of oxygen enrichment levels. Systems analysis models were built to analyze costs and efficiency savings; incorporation of adsorption isotherms from gas sorption tests allowed for predictive modeling of the operation costs for different materials in pressure swing adsorption (PSA) processes.

Significance:

The work is directed at the production of materials that will directly reduce the amount of energy required to produce pure oxygen for use in burners. The project positively affected our energy security mission. Furthermore, it produced advanced science in the fields of materials science (new nonporous materials) and combustion research (new burner designs and flame studies).

Refereed Communications:

T.M. Nenoff, "Hydrogen Purification, MOF Membranes Put to the Test," *Nature Chemistry*, vol. 7, pp. 377-378, 2015.

M.V. Parkes, D.F. Sava Gallis, J.A. Greathouse, and T.M. Nenoff, "The Effect of Metal in M3(btc)2 and M2(dobdc) MOFs for O2/N2 Separations: A Combined Density Functional Theory and Experimental Study," *The Journal of Physical Chemistry C*, vol. 119, pp. 6556-6567, March 2015.

J.B. Michael, P. Venkateswaran, C.R. Shaddix, and T.R. Meyer, "Effects of Repetitive Pulsing on Multi-kHz Planar Laser-Induced Incandescence Imaging in Laminar and Turbulent Flames," *Applied Optics*, vol. 11, pp. 3331-3344, April 2015.

D.F. Sava Gallis, M.V. Parkes, J.A. Greathouse, X. Zhang, and T.M. Nenoff, "Enhanced O2 Selectivity versus N2 by Partial Metal Substitution in Cu-BTC," *Chemistry of Materials*, vol. 27, pp. 2018-2025, March 2015.

T.M. Nenoff, D.F. Sava Gallis, M.V. Parkes, J.A. Greathouse, M.A. Rodriguez and K.W. Chapman, "Light Gas Separations and Storage with MOFs via Modeling, Synthesis and Pressurized Induced Structural Changes," presented (invited) at the *6th Microporous and Mesoporous Materials Symposium*, Black Sea, Bulgaria, 2015.

Optimizing Microgrid Energy Delivery under High Uncertainty

181202 | Year 1 of 3 | **Principal Investigator: A. Ellis**

Project Purpose:

The purpose of the project, in collaboration with New Mexico State University, is to explore fundamental mathematical and engineering concepts in order to achieve the establishment of a new power system "energy delivery" paradigm, which would replace the current power delivery paradigm of just-in-time generation. The current paradigm requires substantial excess generation capacity, and continuing with this model would require that current generation capacity be doubled over the next thirty years in order to meet future demand. This growth in generation capacity is neither environmentally or economically sustainable. Therefore, a new paradigm is required, and it is believed that the "energy delivery" paradigm is a viable alternative. The new model would fundamentally change the structure of the power grid, by making bulk generation providers into energy providers supplying electricity at negotiated amounts and prices. Instantaneous power balancing would be shifted to the consumers, since it is the consumer who ultimately controls net power demand.

The first step in establishment of the "energy delivery" paradigm requires reformation of the existing power operations optimization methods in order to account for the inherent uncertainty associated with loads, generation, and the evolving grid. To address this, a research focus has been placed on stochastic optimization and the inclusion of risk in the objective function of the optimization problem. Stochastic optimization will provide a solution to the new model, but may require a substantial amount of time to solve due to the infinitely possible number of scenarios created by the uncertainty discussed above.

Predictive Engineering Tools for Novel Fuels

173664 | Year 2 of 3 | **Principal Investigator: C. A. Taatjes**

Project Purpose:
This project aims to use the best combustion engineering tools available to explore methods for increasing efficiency and reducing the climate effects of energy utilization. For example, successful biofuel implementation may involve cooperative evolution of fuel discovery and engine innovation, which requires rapid but reliable means to assess the performance characteristics of novel fuels based simply on their molecular structure. This project is in collaboration with University of California Berkeley and will develop and expand predictive engineering models, employing artificial neural networks and predictive data analysis tools to infer quantitative structure-performance relationships. These relationships will serve as a first sorting tool for more detailed and fundamental structure activity investigations.

Other investigations will focus on novel ways of efficiently utilizing noncarbon energy carriers such as hydrogen, developing new engine cycles that will dramatically improve efficiency. For example, using a noble gas as the working fluid in a closed-loop internal combustion engine cycle could potentially offer substantial improvements in efficiency, by 30% or more, potentially bringing large-bore engines into competition with fuel cells for grid hydrogen energy storage. Such an engine could also be used in a carbon capture and sequestration scheme (using either pre-combustion or post-combustion capture); this engine would have the advantage of excellent part-load and ramp-rate characteristics—key features for future electrical grids that will have more and more renewable (variable) generation.

Sandia's Twistact Technology: The Key to Proliferation of Wind Power

165633 | Year 3 of 3 | **Principal Investigator: J. P. Koplow**

Project Purpose:

DOE's report,"20% Wind Energy by 2030," estimates that wind power could supply 20% of all US electricity without requiring development of grid energy storage technologies. But wind power only becomes competitive with coal-generated electricity when scaled up to multi-megawatt (multi-MW) turbines. Unfortunately, the traditional gear-box-plus-induction-generator wind turbine architecture does not scale up well. The extremely high shaft torque of slowly rotating multi-MW wind turbines results in frequent gearbox failure. Direct-drive generators are, therefore, required—specifically high-pole-count synchronous generator technology. The choice must then be made between a permanent magnet or electrically excited rotor. The problem with electrically excited synchronous generator technology is the requirement for high-current slip rings (also known as "brushes"), which have a short operating lifetime. Materials costs have always been the main stumbling block for permanent magnet synchronous generator (PMSG) technology. And recently, worldwide demand for rare earth magnet materials overtook production, resulting in a 500% to 1000% price increase in 2011. This has created a crisis in the wind power industry. Sandia's Twistact technology is a fundamentally new architecture for high current slip rings that eliminates the sliding contact and electrical arcing inherent to existing slip-ring technology, and thus eliminates the maintenance problem. The promise of Twistact technology is that it would completely solve the rare earth magnet crisis and provide the wind power industry with a simple path forward.

We expect research from our final year to prove that the Twistact rotary electrical contact topology is technically viable, and can lead to disruptive technologies in motor/generator architectures, eliminate dependence on foreign reserves of rare earths, and improve reliability of MW solar photovoltaic (PV) systems, wind power farms, and grid scale energy transmission.

Summary of Accomplishments:

This project has met all of its original milestones. We achieved our goals of 1000 amps current carrying capacity with a series resistance of ≤ 1 milliohm and an endurance of 50 million rotation cycles. Further, we confirmed our initial hypotheses regarding how to design Twistact belts for high fatigue resistance. Through a combination of coupon and in situ testing, we also determined the best working fluid from the standpoint of resisting catalytic degradation on nascent copper (exposed by wear). Such catalytic decomposition results in the formation of highly adherent electrically insulating films that interfere with current transmission. In the course of this project, we also observed noticeably increased wear at the belt/sheave interface at sufficiently high current. We hypothesize that this is a current threshold effect that affects the balance between two competing kinetic processes–work hardening and grain refinement at belt/sheave interface vs. adhesive wear and resultant grain coarsening associated with resistive heating at asperity contacts.

During the course of this work, we have also conducted outreach activities with the DOE Wind Office, National Renewable Energy Laboratory (NREL's) wind power group, and leading wind turbine manufacturers such as Vestas, Siemens, and GE. Not surprisingly, the prospect of eliminating rare earth magnets in favor of copper and steel is viewed as extremely desirable. But the central question that has emerged concerns how we can prove the longevity of Twistact technology to the very conservative wind turbine industry via accelerated lifetime testing. Proving the equivalence of accelerated lifetime testing requires a detailed mechanistic understanding of the hierarchy of chemical and physical processes occurring at the belt sheave interface, and the functional dependence of such processes on variables such as current density, contact pressure, rolling contact speed, temperature, and the chemical composition of the liquid-phase coolant/lubricant and additives.

Significance:
The development of scalable, cost-effective renewable energy technology is fundamentally important to national security, economic security, and sustainability. Wind power is among the few renewable energy resources that has the potential for massive scalability and cost-competitiveness. Twistact technology is being developed to make wind power more cost competitive and to eliminate the problem of rare-earth magnet usage in direct drive wind turbines. In particular, neodymium and dysprosium are strategic materials because the vast majority of these elements are mined from high-value, rare earth deposits in China, and because such rare earth materials are vitally important to other energy applications and defense applications.

Refereed Communications:
N. Argibay, J.P. Koplow, M.T. Dugger, B.L. Boyce, W.L. Staats, B.L. Nation, B. Salzbrenner, and T.F. Babuska, "Materials Challenges for a Novel Wind Turbine Rotary Electrical Contact Technology," presented (invited) at *144th Annual TMS Meeting*, Orlando, FL, 2015.

The Effect of Proppant Placement on Closure of Fractured Shale Gas Wells

173076 | Year 2 of 3 | **Principal Investigator: M. D. Ingraham**

Project Purpose:

This project was undertaken to further our understanding of the interaction of proppant used in hydraulic fracturing processes with fractured host rock. Production declines in hydraulically fractured shale gas wells are far higher than conventional wisdom predicts and gas yields are low. By better understanding the placement of proppant in fractures and the interaction of the proppant with the formation, it may be possible to develop more efficient proppant placement methodologies and reduce production declines from fractured wells. For the security of the US energy economy, it is critical that all energy resources are exploited to their fullest; therefore, it is necessary to improve production from wells that are at best accessing 15% of the estimated gas in place.

To achieve this goal a science-based approach to understanding proppant flow and proppant-formation interactions has been undertaken. Unique laboratory-scale fracture and proppant injection experiments have been conducted (and continue to be performed) to determine the location of and necessary injection parameters for proppant. Flow visualizations experiments in millifluidic-idealized fractures have been undertaken to elucidate proppant flow and placement, and to provide validation data for the numerical models. Rheological characterization has been undertaken for the guar-based proppants in terms of shear-thinning, elasticity, and particle concentration.

The millifluidic experiments inform and validate a series of state-of-the-art multiphysics computational models capable of simulating multiphase flow. Once validated in this simplified, transparent geometry, they will be applied to modeling flow in the laboratory-scale fracture experiments. By parameterizing the model with experimental data, it should then be possible to optimize the proppant injection process and particle type/size to ensure maintenance of fracture permeability over longer durations. Knowledge gleaned from this approach will advance the potential to design effective, low-water-use, fracking techniques with environmentally friendly materials, thereby enhancing gas production and yield.

The Role of Real-Time Decision Making in Grid Resilience

173078 | Year 2 of 3 | **Principal Investigator: L. Burnham**

Project Purpose:
The rapid transformation of the distribution grid from a centralized to decentralized architecture, with bidirectional power and data flows, is made possible by a surge in network intelligence and grid automation. While these changes are lowering operational costs, speeding restoration times and enabling the integration of renewable resources, they are changing the way human operators view and run the grid, resulting in vulnerabilities that are not well understood. Particularly concerning is the lack of domain-specific data to show how automation impacts decision making during high stress, unplanned events.

The purpose of this project, improving grid resilience through informed decision making, or (IGRID), is to explore the impact of grid automation on operator performance and to measure that impact in terms of outage metrics. Working with distribution utilities in Vermont (Green Mountain Power, Vermont Electric Cooperative and Burlington Electric Department), the IGRID team has developed a prototype risk-based model that reflects the dynamic interplay between automation and operator expertise under different scenarios, including routine operations and disturbances. Inputs to the model include both objective measurements of automation and operator expertise, the latter ascertained through a combination of observational and simulator studies.

The result of this research will be a cause-effect performance model that could enable utilities to visualize and evaluate the interactions between operators and machines, both in real time and historically, allowing planners to better understand when automation will improve system performance versus when the human operator is mentally overloaded, and at risk for poor performance. The utilities can then take steps to reduce risk. Overall, the intended outcome is to help utilities balance the roll out of new technologies with the need to maintain critical thinking skills. This understanding could potentially inform the hiring, training and scheduling of operators and also the introduction of new “smart” technologies that are considered key contributors to a self-healing, resilient grid.

Understanding Photo-Induced Oxidation Mechanisms of Volatile Organic Compounds

176312 | Year 2 of 3 | **Principal Investigator: D. L. Osborn**

Project Purpose:

Understanding of the oxidation mechanisms of volatile organic compounds (VOCs) in the troposphere is crucial to human health. Atmospheric modeling relies on well-known oxidation mechanisms to interpret the changing global environment and assess the health risks associated with climate change. Oxidation of VOCs leads to the formation of photochemical smog, yet insufficient data exists on the initial oxidation steps that occur in polluted and pristine environments, especially at temperatures relevant to the atmosphere. We recently developed a low-temperature flow reactor that is used in conjunction with the Multiplexed Photoionization Mass Spectrometer to directly probe chemical reactions as they occur at atmospherically relevant temperatures. Initial tests were successful in using the cooled reactor to study a prototypical system down to temperatures as low as 220 K; however, the temperature stability was only ±5 K. Improvements are under way to reduce the stability to better than ±1 K using an active feedback element. The larger temperature range now available will be directly applicable to tropospheric chemistry, and provide a more rigorous test of radical-radical associations important in combustion chemistry.

The Criegee Intermediate (CI) forms during hydrocarbon oxidation in the atmosphere; until recently, its reactivity with other atmospheric species was largely unknown. The reaction of CI with ozone has been theorized to be fast; however, the rate has not been measured experimentally due to the complex nature of this chemical system. Using the Sandia Broadband Cavity Enhanced Absorption Spectrometer, we are directly measuring the CI + ozone rate of reaction. Preliminary results suggest that this reaction is indeed fast.

This project investigates fundamental chemistry relevant to atmospheric sciences through a partnership with the California Institute of Technology. This research seeks to quantitatively measure oxidation reaction rates at relevant temperatures. If successful, this innovation would place models of smog formation on a more sound scientific footing and increase fidelity of model predictions.

Use of Slurries for Salt Caverns Abandonment

171525 | Year 3 of 3 | **Principal Investigator: G. Bettin**

Project Purpose:

Abandoned underground storage caverns create significant safety and environmental risks. Such abandoned openings are prone to collapse and, thus, contamination of near-surface groundwater aquifers and structural damage to surface facilities. For example, currently a cavern collapse in Louisiana has required the excavation of the Bayou Corne community for nine months due to natural gas venting. Current approaches to risk are limited to watchful monitoring and installation of alarm systems.

Conceptually, an approach would be to refill the underground caverns or mines with buttressing material. Especially for caverns, backfilling is currently not technically feasible. But conceptually, if the technology existed to emplace backfill as large-scale slurries through cavern wells, then we can finally mitigate the collapse of abandoned caverns and mines. The largest scale slurries to date were used to move coal from the Hopi Reservation to a coal power station near Lake Mead. But for a cavern, we need a process to move 500 million gallons of suspended particulate through two 20-inch diameter wells.

State government natural resource departments and environmental departments are responsible for the long-term stewardship of abandoned caverns and mines. But states have limited resources to develop new technology. Similarly, the underground storage industry is small. The DOE Strategic Petroleum Reserve's budget is focused on operation of the oil caverns, not on research. If we can create the scientific and technical basis for large-scale slurry emplacement, then we can work with states, industry, and DOE to develop a medium-scale field test of the new technology.

Summary of Accomplishments:

This study constitutes a first step to understand the behavior of highly loaded slurries and their ultimate application to cavern backfilling. We evaluated a currently available computational tool, Barracuda, to simulate such processes as slurry flow at high Reynolds number with high particle loading. Using Barracuda software, a parametric sequence of simulations evaluated slurry flow at Reynolds number up to 15,000 and loading up to 25%. Limitations come into the long time required to run these simulations due in particular to the mesh size requirement at the jet nozzle. This study has found that slurry-jet width and centerline velocities are functions of Reynolds number and volume fraction. The solid phase was found to spread less than the water-phase with a spreading rate smaller than 1, dependent on the volume fraction. Particle size distribution does seem to have a large influence on the jet flow development.

Significance:

The conclusions of the study have not only furthered the understanding of the behavior of highly loaded slurries, but also demonstrated and brought new capability to Sandia in two-phase fluid flow modeling. The results of this project represent the first stepping-stone in a safe, environmentally friendly, underground cavern abandonment procedure. Additionally, the work has vast applications in geosciences and beyond which include deposition of reactive barriers for hazardous or nuclear waste, flow of sand in shorelines or estuaries, and sand screen flow modeling.

Validating Hydrogen Concentration Fields at Crack Tips

186839 | Year 1 of 3 | **Principal Investigator: J. A. Ronevich**

Project Purpose:

The purpose of the project is to measure and validate the magnitude of hydrogen concentrations that develop ahead of cracks in structural materials through use of advanced analytical techniques. Crack tip stress fields generate elevated hydrogen concentrations as a result of hydrostatic stresses and local hydrogen traps. Predictive models currently rely on adjustable parameters to account for uncertainty in the crack tip stress field and its associated hydrogen concentration field. To date, hydrogen concentration predictions have not been validated through experimental measurements. The goal of this work is to measure hydrogen concentration fields at crack tips to validate the magnitude of the hydrogen field and concurrently infer the form of the stress field. Additionally, uncertainty surrounds the hydrogen fugacity at the crack tip compared to the bulk material in electrochemical environments, and measuring hydrogen concentrations can help quantify fugacity values, which control hydrogen uptake. The approach is to introduce hydrogen into notched or cracked specimens through gaseous and electrochemical charging, apply a static load, and then perform high resolution hydrogen measurements in the crack tip region using advanced analytical techniques such as nuclear reaction analysis. Development of an innovative fixture is required to apply static load to the specimen while hydrogen measurement is performed. This work is unique in that hydrogen depth profiles will be measured in the direction parallel to the stress gradient (e.g., below the crack tip), thus these experiments will have the highest resolution capable by the analytical equipment. Initial testing will be performed on notched specimens to demonstrate feasibility of technique. This work is directed at measuring hydrogen concentration fields at crack tips with high fidelity for the first time. Quantifying the magnitude of the hydrogen concentration field and concurrently inferring the form of the stress field will inform and enhance the development of predictive hydrogen-assisted cracking models applied to materials and components in energy technologies.

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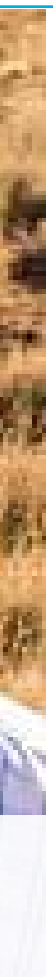
International, Homeland, & Nuclear Security

A vital US national security concern is that various adversaries who want to acquire power, support, and legitimacy are attracted to weapons based on nuclear, radiological, chemical, biological, cyber and explosives threats, or some combination of these threats. As the threat becomes more sophisticated and creative, we must identify effective solutions that mitigate current and future risks. We are seeking research that enables creative solutions in international and domestic risk reduction against these threats.

Projects



3D Imaging with Structured Illumination for Advanced Security Applications

173492 | Year 2 of 2 | **Principal Investigator: G. C. Birch**

Project Purpose:

Three-dimensional (3D) information in a physical security system is a highly useful discriminator. The 2D data from an imaging systems fails to provide target distance and 3D motion vector, which can be used to reduce nuisance alarms and increase system effectiveness. However, 3D imaging devices designed primarily for use in physical security systems is uncommon. The purpose of this project is to develop a 3D imaging system with features, such as real time 3D imaging, needed in a physical security system.

A snapshot 3D imaging method using active pattern projection was investigated and demonstrated with custom developed hardware. Illumination design evaluated spectral irradiance data and determined maximum performance windows in which to operate, all while using low cost sensors. Software was developed and demonstrated complexity reduction when fixing certain physical constraints of the active 3D imaging hardware. Finally, the mathematics of actively illuminating a complex scene with an arbitrary pattern was explored and a robust model for rectification was created.

Summary of Accomplishments:

A method of snapshot 3D imaging was evaluated called pseudo random binary array (PRBA) 3D imaging. This method projects a unique binary matrix onto the scene of interest. This method was chosen because a single image of the pattern projected onto the scene contains all information necessary for 3D reconstruction. Thus, PRBA-based systems can operate in a real-time 3D imaging configuration given satisfactory illumination. A custom diffractive optical element was created to enable projection of the PRBA and tested in a laboratory and outdoor setting.

Illumination design evaluated spectral irradiance data collected at Albuquerque, New Mexico, and analyzed system trade-offs given different illumination wavelengths, sensors, and pattern sizes. The use of narrow band illumination and imaging was demonstrated outdoors using a low power source.

Software was developed that utilizes the unique nature of the PRBA to build confidence based on the number of known pattern elements extracted from the scene. Unique testing was designed to generate simulated imagery in software and evaluate complex edge cases.

An exploration of the fundamental mathematics of projecting patterns onto arbitrary complex scenes is included. A general framework for rectifying any pattern incident upon complex geometry was developed.

Significance:

This project showed the feasibility of active 3D imaging systems for use in physical security systems. By balancing the complexity of the system across both the hardware and software, a different approach for physical security 3D imaging was proposed that utilized no moving parts and could be optimized for use in outdoor real time imaging.

Refereed Communications:

C. Smith, A.L. Young, and G.C. Birch, “Rectification of Projected Images using Piecewise Homographies,” *Imaging and Applied Optics 2015*, OSA Technical Digest (online) (Optical Society of America, paper CM4E.2, 2015.

A Complex Systems Approach to more Resilient Multi-Layered Security Systems

173114 | Year 2 of 3 | **Principal Investigator: N. J. Brown**

Project Purpose:

In July 2012, protestors cut through security fences and reached the exterior of the Highly Enriched Uranium Materials Facility (HEUMF) at the Y-12 National Security Complex. This identified an issue with what was believed to be a highly reliable, layered security system. The configuration of layered security measures is at the center of efforts to protect a range of systems from high-value facilities to large-scale infrastructures.

Historically, analyses of security systems have been performed using directed graph and path analysis tools like Adversary Sequence Diagrams (ASD). However, there are many dimensions in the design space of a security system, including selection of technologies, alternative locations/configurations, different threats, and competing cost limitations. The dimensionality of this problem makes it effectively impossible to evaluate all permutations of potential system architectures using traditional methods. The experience of the individuals configuring the system drives the careful examination of a small subset of architectures.

The key goal of this proposal is the creation of a consistent, robust mathematical framework using complex systems analysis algorithms and techniques to better understand the emergent behavior, vulnerabilities, and resiliency of layered security systems subject to budget constraints and competing security priorities. Because there are several dimensions to security system performance and a range of attacks that might occur, the framework must be multi-objective for a performance frontier to be estimated. Since security measures can fail for a range of reasons, this research will also explicitly include resiliency as a dimension of system performance.

To extend beyond traditional methods, innovative modeling of multi-layered security systems requires a complex system approach, which integrates multiple dynamic and stochastic algorithms, including an optimization model for selecting security architectures. This project develops a rigorous computational framework, flexible enough to apply to a range of layered security system design instances, including complex system behaviors like emergence and resiliency.

Advanced Imaging Algorithms for Radiation Imaging Systems

173669 | Year 2 of 3 | **Principal Investigator: P. Marleau**

Project Purpose:

Radiation-imaging devices are important to the nuclear security and safeguards communities due to their ability to detect and localize radioactive sources. Due to a low natural background, difficulty to shield, and unique association with special nuclear materials (SNM), fast-neutron imaging provides a promising means for the detection of SNM. To make these R&D systems useful for end-user applications, robust reconstruction and analysis algorithms must be developed that provide detailed information on the location, energy spectrum, and intervening material. To date, deconvolution, match filtering, and maximum likelihood expectation maximization (MLEM) have been demonstrated. However, the information provided is limited to an approximate location of the source.

The intent of the proposed work, in collaboration with University of Michigan, is to develop the algorithms that will bring the analysis from qualitative images to quantitative attributes of objects containing SNM. The first step to achieving this is to develop an in-depth understanding of the intrinsic errors associated with the deconvolution and MLEM algorithms. A significant new effort will be undertaken to relate the image data to a posited 3D model of geometric primitives that can be adjusted to get the best fit. In this way, parameters of the model such as sizes, shapes, and masses can be extracted for both radioactive and non-radioactive materials. This model-based algorithm will need the integrated response of a hypothesized configuration of material to be calculated many times. As such, both the MLEM and the model-based algorithm require significant increases in calculation speed in order to converge to solutions in practical amounts of time.

We will improve simple backprojection and MLEM reconstruction techniques that will make imaging systems more robust to these various detection scenarios. Such improvements include the development of algorithms to more accurately model a specific measurement scenario. These advanced image reconstruction algorithms can be applied to existing imaging systems and used as a basis for designing and optimizing novel imaging techniques.

Building the Scientific Basis for Cyber Resilience of Critical Infrastructure

179224 | Year 2 of 3 | **Principal Investigator: M. J. Hutchins**

Project Purpose:
Through the proposed research, we will develop new mathematically rigorous algorithms and models for quantifying, measuring, and increasing the cyber resilience of critical infrastructure. The number of vulnerabilities is large and increasing, the attack surface is changing over time, and the problem combines technical and non-technical factors. Given this complex and dynamic landscape, mitigating risk is an important strategy, but it is also necessary to ensure that critical infrastructure is resilient, that is, able to effectively reduce the magnitude and duration of a deviation from targeted performance levels.

Scientifically rigorous approaches to address cyber resilience are in the nascent stages; further research is required to develop algorithms that accurately represent the full complexity of real-world systems and threats. The goal of this project is to further the science of cyber resilience through design and modeling of ICS as they relate to the critical infrastructure (CI) they support. This work will extend existing efforts through the research and development of mathematical models and algorithms that facilitate the design of resilience-enhancing countermeasures for specific CI (i.e., energy delivery systems). We will identify the operation and design factors that affect cyber resilience of CI and create systems models that represent the dynamic interplay between these factors and the cyber threats that CI face.

Combinatorial, Microscale Fuel/Oxidizer Formulations for the Systematic Determination of HME Properties

173105 | Year 2 of 2 | **Principal Investigator: C. L. Beppler**

Project Purpose:

The global threat of improvised explosive devices (IEDs) that contain homemade explosives (HME) continues to increase. Due to the inherent nature of HMEs, there are countless combinations of precursor chemicals and materials, especially fuel/oxidizer mixtures that could be used, making it difficult with conventional formulation techniques to adequately study the properties of the materials that govern their ability to be detected and/or identified. Current research on HMEs has focused on the explosive properties of the material to understand their effects and safety in handling, both of which require large amounts of material (grams to kilograms). As such, the idea of formulation strictly for chemical and physical property determination has yet to be developed, though it is these properties that govern a material's signatures that are available for detection and identification.

We propose to implement a combinatorial, microscale (<10 mg per sample, 96 physically samples per well plate) approach to studying dual-component, fuel/oxidizer-based HMEs that increases speed and safety and reduces cost in their formulation and determination of properties. The use of an existing research grade inkjet printer will allow for high throughput, reproducible and systematic formulation of materials. The formulated materials will then be analyzed with commercial, lab-based analysis techniques. The applications of the proposed capability extend beyond counter-IED applications; this approach to rapid microscale energetic materials deposition would be highly beneficial in nuclear weapons development and stockpile surveillance activities by allowing for more efficient study of materials' aging and compatibility.

Summary of Accomplishments:

We produced several key accomplishments including a novel method to accurately and precisely inkjet print binary mixtures of FOX-based HMEs. We also better understand how to inkjet print into various sample holders including ceramic crucibles, Teflon well plates, and borosilicate glass vials. We tailored the inkjet printing process to print >10 mg of HMEs, a necessary step needed to safely handle these materials.

We also developed an analytical workflow framework that was applied to streamline sample analysis. The analytical workflow framework went through several iterations before being finalized. These iterations helped determine weak points in our original workflow and ultimately helped to streamline and speed up the analyses. This type of process knowledge will then feed into any future analyses using emerging HME threats. We have also begun to develop a data analysis method to rapidly pre-process the different types of data. These various data 'streams' will be combined to produce value-added information not found by analyzing individual data sets.

The development of this capability has also paved the way for using this technique to more rapidly obtain approval to work with new HME materials.

Significance:

This project created a new capability to rapidly, safely, and inexpensively create and characterize existing and new explosive threats to aid in their detection and attribution. We also advanced the state of the art in inkjet printing of explosive mixtures and advanced the field, which studies the chemical and physical properties of HMEs. Additional benefits include a new way to rapidly age and analyze the trace signatures of stockpile relevant and FOX-based HMEs. This capability could also allow rapid development of analyses for emerging HME threats based on this previous work.

Refereed Communications:

C.L. Beppler, P.J. Hotchkiss, and A.S. Tappan, "Combinatorial, Microscale Fuel/Oxidizer Formulations for the Systematic Determination of Homemade Explosives Properties," presented at the *7th Annual Trace Explosives Detection Workshop*, Pittsburgh, PA, 2015.

Decontamination of Radiological-Contaminated Materials using Magnetotactic Bacteria

173106 | Year 2 of 3 | **Principal Investigator: M. D. Tucker**

Project Purpose:

Decontamination of radiological-contaminated materials is a difficult task. Unlike toxic chemicals or biological organisms, which can be neutralized or killed, radiological contaminants must be physically extracted from a material. The objective of this project is to develop a novel approach for decontaminating materials that have been contaminated with radionuclides using magnetotatic bacteria (MTBs)–bacteria that contain small magnetic structures. MTBs have the capability to bind to and/or adsorb radionuclides. After deployment of MTBs onto a material, the bound radionuclide can then be extracted from contaminated materials using separation techniques that utilize the magnetic properties of the bacteria. In order to develop a system for radionuclide decontamination utilizing MTBs, four objectives must be demonstrated:

1) Identify, select, and culture an MTB strain with magnetic properties
2) Demonstrate that the selected MTB strain is radiation-tolerant
3) Demonstrate that the magnetic properties are maintained in the selected MTB strain and can be used to extract the bacteria from a material
4) Demonstrate that the selected MTB strain will uptake and/or sorb radionuclide contaminants

We have successfully achieved the first three objectives. Work is currently focused on demonstrating uptake/sorption of a radionuclide (i.e., the fourth objective above). Successful completion of this project will reduce the need for removal and disposal of contaminated material surfaces, which would enhance our nation's resilience to disruptive radiological contamination events.

Denial of Use of Bulk Chemical Agents and their Precursors

173115 | Year 2 of 3 | **Principal Investigator: M. K. Kinnan**

Project Purpose:
Rapid bulk neutralization and/or the ability to rapidly render at-risk stockpiles unusable and/or safe for transport elsewhere are high-priority, high-visibility needs. Past and present research projects have focused their efforts on the surface decontamination of chemicals of interest (COIs), leaving a gap when it comes to bulk neutralization. Current technologies for bulk neutralization of COIs require heavy equipment and/or significant quantities of materials, resulting in major logistical burdens. This includes incineration, the explosive destruction system, and the field deployable hydrolysis system. The purpose of this research is to develop bulk neutralization technologies that are irreversible, rapidly deployable, broad spectrum, and solidify a variety of COIs.

This project is demonstrating effective neutralization/solidification of bulk COIs without the use of high quantities of materials. For example, batch reactor-based neutralization can require up to a 100:1 dilution ratio of solvent (e.g., water with bleach) to COI. That introduces logistical burdens due to the high quantity of neutralizing materials required that will inevitably generate a significant amount of waste. The chemical pathways used in this research have utilized small quantities of materials and no solvents. In this work, the neat (undiluted) COI solution is consumed during the neutralization, which inherently changes the properties of the solution that can alter the reaction performance. Other technical challenges include performing the reactions at room temperature with no mixing.

Development and Field-Testing of a Diagnostics Platform for Global Syndromic Disease Surveillance

165676 | Year 3 of 3 | **Principal Investigator: M. Finley**

Project Purpose:

Infectious disease epidemics continue to threaten the homeland and international security landscape. Global biosurveillance programs are critical for detecting and mitigating outbreak scenarios due to natural, emerging, or engineered biological threats. However, many agencies lack the infrastructure and resources to implement effective disease surveillance, particularly in low-resource settings. Public health and veterinary professionals lack the necessary skills to provide an accurate clinical diagnosis; therefore, many incidents of infection with high consequence agents go undetected, and thus, unreported. New tools are urgently needed to meet the stringent operational and economic requirements for biosurveillance, including cost, speed, ease of use, field portability, and reliability. Furthermore, disease surveillance activities may be streamlined by shifting from traditional diagnosis to syndromic-based testing, in which the diagnostic tool screens for a panel of high-priority pathogens and diseases based on clinical symptoms.

We plan to meet these needs with the development of novel syndromic-based assays and an accompanying device based on Sandia's proprietary SpinDx diagnostic platform for global disease surveillance. The inherent advantages of our approach (low cost, ultra-sensitivity, easy to use, no sample preparation, broad assay menu, and a novel syndromic approach) differentiate us from other conventional biosurveillance methods. Another key advantage of our approach is that, rather than focus on particular pathogens, we will develop a syndrome-based screening allowing access to useful, actionable information faster. Field-portable assays for most of the diseases that we plan to target do not exist; hence, the first task will be to develop assays to diagnose a panel of high-priority zoonotic diseases. Disease of focus will be sudden death and hemorrhagic syndrome in cattle or gastro-respiratory in small ruminants. The assays will be developed in collaboration with the Veterinary Diagnostic Laboratory (VDL) and Biosecurity Research Institute (BRI) at Kansas State University. This work merges Sandia's expertise in point-of-care diagnostics and biosecurity in low-resource settings to uniquely address this need.

Summary of Accomplishments:

We adapted SpinDx to function easily to use screening panels to detect livestock infections associated with pathogens that are on the US Department of Agriculture's and the US Department of Health and Human Services' list of select agents, as well as those that negatively impact trade and animal production. Screening panels are dependent on clinical symptoms rather than a single diagnosis. If commercialized the tool could standardize the collection of surveillance data globally.

We developed two panels, one targeting pathogens that cause oral erosions in livestock and one targeting pneumoenteritis in sheep and goats. The established assays will enable laboratories to screen for select agents such as foot and mouth disease virus, sheep and goat pox, bluetongue virus, and contagious caprine pleuropneumonia, as well as diseases that adversely affect animal production. During FY 2015, we tested for cross-reactivity to determine selectivity and specificity. Individual assays have been validated against gold-standard targets. Antigen and antibody based assays are working consistently.

We developed molecular-based tests for agents that were difficult to detect using immunodetection, including mycoplasma mycoides, Mannheimia hemolytica, and sheep and goat pox virus. Integration of molecular-based assays has the potential to enhance the breadth of data collected in similar screening panels.

The panels have been validated with positive serum samples and antigen, and the assays have been tested against near neighbors. All assays have been shown to be sensitive and specific in the presence of similar agents. The successful demonstration of the panel with validated positive samples is a key milestone for the project. By testing near neighbors and other potential sources of false positives, the assays can produce higher quality results with greater diagnostic and clinical value for the end user.

Significance:

This work will deliver an innovative and flexible tool designed for rapid detection of high-priority infectious agents in low-resource areas. This work directly addresses objectives of the DHS Strategic Plan by greatly enhancing our national and international biodefense capabilities to prepare for, monitor, and promptly respond to intentional or accidental outbreaks of emerging infectious disease. The requirements for such capabilities are further highlighted by Objectives of the National Security Council's "National Strategy for Countering Biological Threats" and are a priority of Cooperative Threat Reduction programs within the Departments of State and Defense.

Development of a Novel Nanoparticle Delivery Vehicle for Pre-Treatment with Nerve Agent Countermeasures

173110 | Year 2 of 3 | **Principal Investigator: C. E. Ashley**

Project Purpose:

Nanotechnology promises to revolutionize the prevention and treatment of organophosphorus (OP) nerve agent poisoning through encapsulation of nerve agent countermeasures in nanoparticles that improve their in vivo effectiveness. The two primary classes of nerve agent countermeasures are OP scavengers–proteins that directly bind or hydrolyze nerve agents–and acetylcholinesterase (AChE) reactivators–small molecule drugs that reverse the effects of nerve agent poisoning in the central nervous system (CNS). Chemical strategies for enhancing the efficacy of these countermeasures in rodent models have thus far failed. However, many existing nanoparticle delivery vehicles, including liposomes and polymerosomes, suffer from limited capacities, uncontrollable release profiles, and complex, specialized synthesis procedures that must be re-adapted for each new cargo molecule, leading to drug- and disease-specific 'one-off' approaches. To address these limitations, we propose to develop mesoporous silica nanoparticle-supported lipid bilayers ('protocells') for encapsulation and controllable delivery of OP scavengers and AChE reactivators. We will demonstrate that protocells can be loaded with high concentrations of OP scavengers and AChE reactivators, administered to rodents via Sandia-developed polymer microneedles, and achieve either broad, systemic distribution or targeted accumulation within the CNS in order to prevent or reverse effects of poisoning by G- and V-series nerve agents. Importantly, we will also demonstrate that protocells protect rodents from lethal challenge with G and V agents when administered prophylactically (i.e., in advance of nerve agent exposure).

Protocells are potentially a 'game-changing' technology because their porous silica core and lipid shell can be modulated independently, which allows us to solve limitations of other nanoparticle delivery vehicles. We plan to prove that protocells dramatically enhance the effectiveness of nerve agent countermeasures in vitro and in vivo.

Distinguishing Bioengineering from Natural Emergence in Biothreat Genomes

165683 | Year 3 of 3 | **Principal Investigator: K. P. Williams**

Project Purpose:

To understand biothreat severity, it is crucial to test microbial strains for novel and dangerous gene combinations. It is also important to determine whether these gene combinations were acquired naturally (through horizontal gene transfer into an emerging pathogen) or through bioengineering. High throughput sequencing enables rapid detection of threat genes or organisms from clinical or environmental samples, and yields nearly complete genomes from laboratory isolates. We developed software for detecting unusual gene combinations in such data. The software was first applied to existing microbial genomic data to illuminate the range of gene combinations that arise naturally through horizontal transfer. This background knowledge allows assignment of a probability that any novel gene combination arose unnaturally.

Our full bioinformatic pipeline detects and characterizes exogenous DNA in microbial genomes, by: 1) assembling high-throughput DNA sequencing reads, 2) identifying threat genes, by comparing assembly against a curated database of antibiotic resistance genes, pathogenicity islands, virulence factors, etc., 3) detecting unusual combinations of threat genes, assigning probability that the combination is unnatural, and 4) explicit search for typical traces of bioengineering (vector and selectable marker sequences), in case these have not been intentionally deleted. This work will provide decision makers with statistical evaluations of whether (1) a suspect organism or sample has a dangerous novel genome and (2) the organism emerged naturally or through bioengineering.

This project will provide a valuable national security software platform. It promises to greatly advance understanding of emerging pathogens and bacterial evolution in general. Rather than only detecting toolmarks, which clever bioengineers can now avoid, we probe deeply into natural pathogens' composition to assess the statistical significance of suspicious deviations from naturalness.

Summary of Accomplishments:

We developed toolmark identification software that analyzes a genome sequence to detect sequences arising from cloning efforts.

We developed virulence gene detection software that analyzes the threat level an organism presents due to disease-causing genes.

We also developed a suite of algorithms that may be useful for differentiation between natural vs. engineered pathogens based on factors including phylogenetic relationship and genomic island detection.

We sequenced and analyzed the genome of an extremely antibiotic-resistant emerging pathogen (Klebsiella pneumoniae BAA2146), explaining all its resistance and revealing how this new combination of resistances emerged.

We developed a new method for examining DNA mobility in bacteria (the basis for pathogen emergence) using high-throughput sequencing technology that we argue should be a routine component of bacterial genome sequencing projects.

We developed an approach to expand genomic island detection beyond the tRNA gene sites we traditionally cover, to protein-coding gene targets.

We have initiated a Sandia bioinformatics website that presents our software and data (on tmRNA and genomic islands) that have been approved for public release

Significance:

We have advanced national and Sandia capabilities to detect bioengineering in the genome of a biothreat organism. This will provide decision makers with an important tool for deciding whether a biothreat arose naturally or if instead there may be a need to search for a perpetrator. We have built, strengthened, and supported a bioinformatics team, and built a repository of software tools that will be useful in future projects. We have advanced science by presenting our bioinformatic databases and software online and in publications, and by developing a new experimental method for discovering mobile DNAs.

Refereed Communications:

A.I. Petrov et al., "RNAcentral: An International Database of ncRNA Sequences," *Nucleic Acids Research*, vol. 43, pp. D123-129, October 2014.

C.M. Hudson and K.P. Williams, "The tmRNA Website," *Nucleic Acids Research*, vol. 43, pp. D138-140, January 2015.

C.M. Hudson, B.Y. Lau, and K.P. Williams, "Islander: A Database of Precisely Mapped Genomic Islands in tRNA and tmRNA Genes," *Nucleic Acids Research*, vol. 43, pp. D48-53, January 2015.

Distributed Session Types for Trusted Systems and Communications

180921 | Year 1 of 2 | **Principal Investigator: G. C. Hulette**

Project Purpose:

Distributed systems connecting groups of servers and weakly trusted clients, while intermixing varying information sensitivities, are becoming increasingly important. These systems provide a good opportunity for engineering-out of dangerous behavior, the design-in of levels of assurance, and dynamically detecting malicious changes. The proposed research, in collaboration with the University of Illinois at Urbana-Champaign, will develop a dynamic model that will be both more flexible and also guaranteed correct by construction, leveraging recent results in type theory for distributed systems based on linear logic to achieve soundness.

This last year has seen progress on evaluating the suitability of session subtyping for authorization. After initial theoretical work, we determined that a dependent session typing system might be more suitable for expressing these concerns and initiated an ongoing effort to implement our session typing system in Idris, a practical dependently typed programming language.

In addition to this work, we have investigated logically motivated language extensions: integrating multiple modalities (e.g., linear, affine, and unrestricted types) into our language; studied polarization, enabling a uniform treatment of synchronous and asynchronous channels; focusing, which permits type-level expression of message fusion; asynchronous rule non-determinism, which enables safe programming of an important class of racy programs; and programs that asynchronously read, resolving an annoying asymmetry in our program semantics.

Both the Idris implementation and the more full featured OCaml based interpreter have a glaring weakness, they are nearly useless to general programmers. To remedy this, we have implemented the language as a prototype Haskell library, based on a phantom session typing environment, which should enable much wider and easier adoption of our type system features, if not necessarily the most advanced ones.

Dual-Particle Imaging System with Neutron Spectroscopy for Safeguard Applications

180897 | Year 1 of 3 | **Principal Investigator: T. M. Weber**

Project Purpose:

This project, in collaboration with the University of Michigan, involves research using a spectroscopic radiation imaging system that is sensitive to both neutrons and gamma rays for safeguard applications. Such a system will enable more accurate and robust verification of declared materials and activities. In the past year, progress had been made on the dual-particle imager (DPI) in three main areas: development of the stochastic origin ensembles (SOE) imaging method as an alternative method to maximum-likelihood (ML) imaging, advanced analysis of measured energy spectra, and the successful measurement of special nuclear material (SNM).

SOE was used to successfully image a point source, multiple point sources, and a line source. We found that algorithm offered comparable quality in terms of signal-to-noise ratio and image resolution to an ML solution without the need of a large system response matrix. The algorithm has been improved in terms of speed and memory usage. Current efforts to parallelize the algorithm to take advantage of the fast performance offered by graphics processing units are under way. Parameters of image reconstruction are being studied to optimize the use of the algorithm.

An ML algorithm has also been implemented to unfold the resolution effects present in the measured neutron energy spectrum. This method provides a result that is more characteristic of the energy spectrum emitted by the source as opposed to the measured neutron spectrum that has been convoluted with system response. These methods were used to successfully distinguish between a PuBe and Cf-252 source measured simultaneously.

The DPI was sent the Nevada National Security Site for benchmark measurements with weapons grade plutonium (WGPu) and highly enriched uranium (HEU). Both WGPu samples were about 4 kg and the HEU was about 13 kg. Measurements were also taken with the individual SNM samples and a Cf-252 and/or AmBe source simultaneously. These measurements provided valuable information concerning DPI performance in a high gamma-ray field.

Emulation for Cyber-Enabled Physical Attack Scenarios

180891 | Year 1 of 2 | **Principal Investigator: J. Clem**

Project Purpose:

The nuclear security community relies on physical protection systems (PPS) under the presumption they are isolated, operating as expected, and not themselves targets. The National Academies criticized DOE for failing to account for attack scenarios with imaginative elements and adversaries have compromised cyber-based components in similar systems. Unfortunately, current tools do not provide enough fidelity to answer PPS cyber misuse cases. To date, decision makers lack knowledge and quantitative evidence of potential cyber threat impacts on PPS performance and are, therefore, not making strategic investments to address such emerging threats.

Our research consists of two principal parts:

1) Development of tools and methodology to create high-fidelity models of PPSs in an emulation environment. R&D challenges include: emulation of PPS components at sufficient fidelity to support experimentation reasonably representative of the original physical hardware; emulations must interface with hardware-in-the-loop and simulated components; and emulations should be scalable to eventually represent entire PPS infrastructures.
2) Identify and experimentally execute credible cyber exploits/attacks against emulated elements of a PPS, compare outcomes to those same attacks against physical testbed systems and then refine the emulytics to ensure realistic interactions and simulation results.

Our research will develop a capability for testing and evaluating cyber-enabled components of PPS in a cost-effective fashion. Results will enable Sandia to demonstrate the problem to decision makers with a repeatable methodology and develop critical design principles for more effective physical protection.

The cyber-physical security dynamics of PPSs have not been characterized and an emulytics capability to computationally extend analysis has not been developed. This research will enable analysis and support decisions based on experimental data describing cyber-physical dynamics within components of PPSs.

Enabling Explosives and Contraband Detection with Neutron Resonant Attenuation

186363 | Year 1 of 3 | **Principal Investigator: M. Sweany**

Project Purpose:

Material identification by resonant attenuation is a technique that measures the energy-dependent attenuation of 1-10 MeV neutrons as they pass through a sample. Elemental information is determined from the neutron absorption resonances unique to each element. With sufficient energy resolution, these resonances can be used to categorize a wide range of materials, serving as a powerful discrimination technique between explosives, contraband, and other materials. Our proposed system is unique in that it simultaneously down-scatters and time tags neutrons in scintillator detectors oriented between a d-T generator and sample. This allows not only for energy measurements without pulsed neutron beams, but for sample interrogation over a large range of relevant energies, vastly improving scan times. Our system's core advantage is a potential breakthrough ability to provide detection discrimination of threat materials by their elemental composition (e.g., water vs. hydrogen peroxide) without opening the container. However, several technical and computational challenges associated with this technique have yet to be addressed. There are several open questions: what is the sensitivity to different materials, what scan times are necessary, what are the sources of background, how do each of these scale as the detector system is made larger, and how can the system be integrated into existing scanning technology to close current detection gaps? In order to prove the applicability of this technology, we will develop a validated model to optimize the design and characterize the uncertainties in the measurement, and then test the system in a real-world scenario.

This project seeks to perform R&D and laboratory tests that demonstrate proof of concept to establishing an integrated system and evaluating its performance through both laboratory tests and a validated detector model. The validated model will allow us to explore our technology's benefits to explosive detection in various applications.

Exploring Growth Conditions to Identify, Quantify, and Reduce the Risk of False Negatives

188289 | Year 1 of 1 | **Principal Investigator: M. Finley**

Project Purpose:

Bacillus anthracis causes anthrax, a disease of livestock that affects humans by means of accidental exposure through infected livestock products, contaminated soil, or by laboratory exposure. Moreover, B. anthracis has long been considered a potential biological warfare agent.

It is critical that specific diagnostics are available to positively identify infections. The most reliable and widely used diagnostic is isolation and propagation of the agent, which leaves pure cultures vulnerable to theft and places laboratory staff at risk. Thus, it is critical to develop a highly specific assay for detection, and concurrently, minimize production of biological materials. An earlier Sandia LDRD project team designed an assay that incorporates the gold standard onto a self-contained and self-decontaminating platform to minimize access to the pathogen.

The device, BaDx (Bacillus anthracis diagnostic), is under development, and requires studies to evaluate the potential for false negative results. False negatives are extremely detrimental to the functionality of the assay, and can trigger accidental exposures, and possibly result in human deaths. Characterization and reduction of false negatives will require analysis of bacterial contaminants from clinical samples that grow in the device's micro-culture chamber that is designed to select for B.anthracis. Because contaminants can impact the test results, studies must be completed to quantify, characterize, and determine the impact on B. anthracis growth. Selection of B. anthracis and reduced growth of environmental bacteria will eliminate false negatives. The described micro-culture chamber is fundamental to the success of the device, and is the first of its kind.

Summary of Accomplishments:

We conducted several critical control experiments to identify the source of the 20 percent false negative rate using BaDx. We analyzed the functionality of several components of the device and compared the results to the gold standard of conventional isolation, culture, and testing with a commercialized lateral flow assay. We tested: 1) the growth conditions in the device, 2) the functionality of the commercialized Tetracore® lateral flow strips in the device, and 3) the efficiency of the microfluidics. All BaDx assays were compared with controls.

We found that the flow onto the strip was inconsistent and, therefore, created a mechanism to resolve this issue.

The data collected from these experiments are a critical step in improving the specificity of the device. It is essential to minimize false negative results to ensure the accurate determination of B. anthracis in animal populations, possible incidences of bioterrorism, and from the environment.

Significance:

Senator Lugar's trip to Africa underscores the importance of biological threat reduction initiatives. Lugar stated, "Deadly diseases like Ebola, Marburg, and Anthrax are prevalent in Africa. These pathogens can be made into horrible weapons aimed at our troops, our friends and allies, and even the American public. This is a threat we cannot ignore." The Department of State's Office of Cooperative Threat Reduction and DoD's Defense Threat Reduction Agency's primary mission is to mitigate the biological threat worldwide; these agencies target facilities with B. anthracis. Success of the proposed diagnostic assay could substantially advance their missions.

High Fidelity Forward Model Development for Nuclear Reactor Spent Fuel Technical Nuclear Forensics

170995 | Year 3 of 3 **| Principal Investigator: M. R. Sternat**

Project Purpose:

Spent nuclear fuel (SNF) is an attractive material to an adversary with potential uses in an Improvised Nuclear Device or Radiation Dispersal Device. Nuclear forensics is a major pillar of nuclear security efforts to reduce the risks from this threat. A key requirement of a credible nuclear forensics capability is accurate and timely characterization of material that is interdicted outside of regulatory control. Nuclear forensics typically compares signatures from interdicted materials with information from libraries to determine the source of the materials. However, in most cases adequate libraries do not exist, or not available due to restrictions on sharing information between countries.

In past work, ORIGEN is utilized in a SNF forensics system to reconstruct reactor information from spent fuel characteristics. This basic forward model does not use any geometric or non-fuel material characteristics that may be recoverable from an interdicted item and relies on predefined cross-section libraries to predict SNF characteristics. These libraries only exist for well-known power reactors and cannot accurately predict SNF characteristics in research or other reactor types. Another problem is that current database information is not always reliable since most are optimized for criticality and other purposes.

Nuclear forensics in its current state is primarily a comparative science. Unreliable database information or lack of availability causes comparative methods to be ineffective. In addition, establishment of a complete database is not practical.

This work is innovative and unique as it expands the boundaries of nuclear forensics science and establishes a predictive technique for SNF forensics. Creativity will be required to develop a practical predictive system, including the implementation of higher fidelity forward models that work with limited amount of information recoverable from an interdicted SNF sample.

Summary of Accomplishments:

The fidelity of the forward model within a spent fuel forensic analysis system was improved by using two unique methodologies. The first consisted of developing a system to create accurate one-group neutron cross-section libraries for any user specified reactor system. In such, a detailed model is developed using the depletion code MONTEBURNS. During MONTEBURNS execution, cross-section libraries are generated at every user specified burnup step in time. These libraries could be developed for many reactor systems, then housed in a database and used for analyzing unknown fuel samples. The forensic analysis system for spent fuel resulted in higher accuracy at predicting the initial uranium isotopic compositions and burnup from spent fuel samples. Using this method, the error in results was reduced from the order of 1-6% down to less than 1% when recovering a fuel sample's burnup and initial uranium isotopic composition.

The second method consisted of implementing 2D/3D reactor depletion codes as the forward model within the system's framework. This method would allow the usage of potentially recoverable geometric information from an unknown sample. No predetermined cross-section library is required for the system using this method, therefore, potentially reducing model error associated with the neutron flux spectrum. The accuracy of the recovered initial uranium isotopic compositions and burnup from spent fuel samples were also improved using this method, even more so than the first. For MTR reactors, the error using this method was significantly reduced and was driven to below 0.5%. However, additional research may be required to determine the ideal fission yield and recoverable energy per fission for cases where significant amounts of 239Pu are bred and burned throughout the life of the fuel.

Significance:

The results from this work enhanced technical capabilities and skill sets, and lead to potential follow on funding for efforts supporting multiple national security missions.

Identification of Nucleic Acid Biomarkers of Infection in Blood

165767 | Year 3 of 3 | **Principal Investigator: S. Branda**

Project Purpose:

Infectious disease surveillance and outbreak mitigation require rapid, accurate, and reliable distinguishing of infected versus healthy individuals, for rational use of countermeasures (diagnostics, therapies, and quarantine). Screening populations to directly detect the pathogen is problematic, because accessible samples like blood contain little or no pathogen, particularly at pre-symptomatic stages of disease. However, host response to pathogens is rapid, robust, and evident at early stages. Screening for host response biomarkers is attractive, especially nucleic acid (NA) biomarkers that can be recovered from tiny samples and detected sensitively and specifically via PCR. Proof-of-concept studies have not been definitive, as sub-optimal sample preparation and detection has undermined sensitivity, specificity, and throughput.

Sandia has developed new methods and technologies for: 1) isolating NA that are unique to, or shared between, samples and 2) preparing NA for highly efficient second generation sequencing (SGS). Our sample preparation pipeline is used for high-throughput screening for NA biomarkers of infection. Samples from in vitro infections, as well as blood draws from human burn patients who become septic, were fractionated (DNA versus RNA), and each NA pool converted into an SGS-compatible library. Molecular suppression of libraries preceding SGS enabled identification of rare NA that segregate with infection state. Biological and statistical interactions between candidate biomarkers were identified through pattern recognition and network/pathway analyses. A predictive framework based on pathway activation signatures was generated via supervised classification methods. Through this systematic and comprehensive approach, we identified predictive panels of candidate NA biomarkers of infection. In this project we used newly developed methods to screen for candidate biomarkers of infection.

Summary of Accomplishments:

We developed new sample preparation pipelines for isolating and sequencing both abundant and rare RNA species in white blood cells and plasma isolated from human blood specimens. We have begun applying these methods to blood specimens drawn from mice infected with the bacterial pathogen Burkholderia thailandensis, in order to identify NA biomarkers of B. thailandensis infection in vivo. Additionally, we have a carried out a comprehensive transcriptomics analysis of human primary cells (monocyte-derived macrophages and small airway epithelial cells) infected with either B. thailandensis or B. pseudomallei (a select agent bacterial pathogen), in order to identify NA biomarkers of these infection types in vitro. Through these analyses we have identified genes, transcription factors, and biological pathways that are activated/repressed during Burkholderia infection, thereby greatly improving our understanding of pathogenesis and revealing a diverse set of targets for development of new diagnostics and therapeutics to combat this problematic group of bacterial pathogens.

Significance:

Our new techniques for identifying NA biomarkers can be applied to a wide variety of sample sets (clinical specimens, animal study specimens, in vitro samples), and used to address a wide variety of national security problems (e.g., infection with select agent pathogens, exposure to chemical weapons, human performance under high stress). Additionally, the results generated over the course of this project greatly improve our understanding of host-pathogen interactions, and reveal a diverse set of targets for development of new diagnostics and therapeutics to combat pathogens of biodefense concern.

Refereed Communications:

Z.W. Bent, K. Poorey, D.M. Brazel, A.E. LaBauve, A. Sinha, D.J. Curtis, S.E. House, K.E. Tew, R.Y. Hamblin, K.P. Williams, S.S. Branda, G.M. Young, and R.J. Meagher, "A Transcriptomic Analysis of Yersinia Enterocolitica Biovar 1B Infecting Murine Macrophages Reveals New Mechanisms of Intracellular Survival," *Infection and Immunity*, vol. 83, pp. 2672-2685, July 2015.

Improved Pulse Shape Discrimination in a Multicomponent Water/Organic System

165687 | Year 3 of 3 | **Principal Investigator: J. G. Cordaro**

Project Purpose:

Active interrogation for sensitive nuclear materials (i.e., 235U) and reactor monitoring for treaty verification are critical for the security of our nation. The development of organic-based scintillators, motivated by their intrinsic sensitivity to neutrons and particle shape discrimination (PSD) has proceeded rapidly based on this need. PSD using liquid scintillators finds widespread application for direct detection of fast neutrons, although these organic materials perform poorly in high radiation fields due to the pile-up of long-lifetime pulse tails. Development of new materials is needed for efficient PSD on short timescales.

We propose a water-based organic-inorganic scintillator for the improved discrimination of fast neutrons. Enhanced PSD will be achieved by selectively quenching the rate-limiting 'background' emission (>1μs) from the organic scintillator, and by comparing the ratio of fast organic (<10 ns) to delayed inorganic (<60 ns) luminosity. This combination will not only increase the maximum practical count rate for the material, but will significantly improve PSD due to differences in the particle-specific luminescence response (α:β ratio) that are significantly larger than in current PSD materials. Based on known α:β values, an organic scintillator and CeCl3 combination is expected to show a 76% difference in the prompt versus delayed components; more than three times greater than what is observed for traditional organic scintillators alone.

If successful, this new system will show enhanced performance compared to current PSD organic scintillators. Organic and inorganic scintillators in an amphiphilic polymer matrix or hydrogel provide a low-cost and large-scale solid-state scintillator system that exhibits superior fast neutron discrimination capabilities.

Summary of Accomplishments:

We demonstrated that adding water to an organic-based liquid scintillator decreases the light yield. We attribute the decrease in performance to two main causes: 1) loss of aromatic content and 2) quenching by water radiolysis products. The correlation between water content and dimensioning light yield came from a series of experiments. Interestingly, the decrease was not linear and an uptick in light yield was observed at 50/50 vol% water/organic. First, we exhaustively measured optophysical properties of scintillating cocktails as function of water content. These mixtures did not phase separate because of additive salts and surfactants. Second, we also measured phase properties of these mixtures using light scattering and found that at certain concentration, evidence for a bicontinuous microphase was obtained. This phase change occurred at the same concentration as the increase in light yield.

In other work, we developed a synthetic route to make water-soluble immidizolium salts. These salts were intended to coordinate with cerium (III) upon deprotonation forming carbene complexes. Cerium (III) carbene compounds were initially intended to function as our second emitter in the originally proposed two-state scintillation system. However, we learned that making water-soluble cerium complexes was problematic due to hydrolysis reactions at anything but near neutral pH levels. This requirement inhibited the formation of isoluble cerium (III) carbenes.

Significance:

Our synthetic method for making carbene precursors following a two-step procedure will be published and useful for other researchers seeking to make water-soluble carbene complexes. Our systematic investigation into the mixing of water with organic liquid scintillators should serve as a reference point for others seeking to make large-scale water based scintillators. Water improves the optical transparency of the system but inhibits energy transfer and quenches emission from organic dyes compared to pure organic systems. The trade-offs between improved optical path length and decreased light yield should be weighed evenly when proposing new scintillation cocktail mixtures.

Refereed Communications:

P.L. Feng, "Molecular Origins of Scintillation in Organic Scintillators," presented at the *13th International Conference on Inorganic Scintillators and their Applications (SCINT 2015)*, Berkeley, CA, 2015.

Jam-Proof Wireless Communications

165685 | Year 3 of 3 | **Principal Investigator: D. A. Perea**

Project Purpose:

The costs associated with installing wired intrusion detection systems at current DOE nuclear material protection sites are becoming prohibitively expensive. Wireless solutions that can mitigate the vulnerabilities associated with a wireless threat create an opportunity to introduce very significant cost savings to DOE. This R&D is a significant step toward creating the technologies required for such a policy change.

The mission impact of the accomplishment has clearly demonstrated Sandia as solving a real problem that no one else is working on in the same way. In addition to demonstrating the R&D hardware/software in a fielded scenario, a provisional patent has been granted to the "Ultra High Reliable Wireless" concept. Additionally, a three-year, $4M effort has been funded by NNSA to pilot the inclusion of this wireless technology at a nuclear site by FY 2018.

This concept represents a new philosophy in security that addresses issues in Threat Level I, Protection Level I – Nuclear and Non-Nuclear Security. The NNSA follow-on effort to this project demonstrates the imminent need for this work and is a critical step in proving the wireless concept can meet, and in some cases, exceed a wired network security while reducing costs.

Summary of Accomplishments:

This project performed fundamental R&D for a robust and secure distributed wireless networking technology. The project realized a solution through the combination of advanced physical layers, detection, and cognitive networking to produce a new form of "jam-proof" wireless communications that meets high security needs.

The technologies required to create a cognitive robust and secure networking topology that is scalable to many nodes and sensors required research and development of cognitive network controllers that can act intelligently and autonomously since the wireless threat environment is dynamic and unpredictable. The networked system required advanced approaches in hardware/software actor based frameworks to realize the many complex tasks of managing incoming intrusion detection data, and ensuring reliable communications of networked resources. It incorporated attack detection and triangulation as an active component of the cognitive network, providing real-time data and geolocation of possible threats and allowing specific action to be taken by the end user.

Significance:

This concept represents a new philosophy in security that addresses issues in Threat Level I, Protection Level I – Nuclear and Non-Nuclear Security, which is not owned by any single customer and crosses US agency boundaries and authorities. By researching, developing, and demonstrating a new and unique paradigm for robust cognitive communication and attack detection, this project will position Sandia to work with customers in the future to address "wireless threats." It demonstrates how the inclusion of our wireless technology can address new wireless policies securely and robustly, while radically reducing costs in tightening budgetary environments.

Magnetic Smart Tags (MaST) for Arms Control and Treaty Verification

180893 | Year 1 of 2 | **Principal Investigator: E. Langlois**

Project Purpose:

The ability to track nuclear material is a challenge for resiliency of complex systems (e.g., harsh environments). RF tags are frequently used in national security applications, but sometimes cannot be used for technological, operational, or safety reasons. Magnetoelastic tags are an alternative technology and are a familiar security measure used in stores to prevent theft. Current magnetoelastic tags are large, single frequency devices, cut from strips of an amorphous magnetic material. They only convey information that a tag is magnetically activated (e.g., when passing through a portal) limiting their utility. A more useful tag would be small, cheap, and respond with a unique combination of multiple resonant frequencies. These tags could also detect environmental parameters of interest such as variations in temperature, pressure, and pH. Recently, giant magnetostriction has been observed in CoFe thin films fabricated by sputter deposition, a technique often used in microfabrication. Unfortunately, sputter deposited materials suffer from a high degree of intrinsic stress, slow deposition rates, and lack compatible anisotropic patterning etch processes.

Our proposed solution is to create magnetoelastic smart tags (MaSTs) by electrochemical deposition, a cost-effective, batch-manufacturing process. MaSTs are multi-frequency tags capable of providing millions of possible codes for tag identification. They may be safely interrogated near high explosives and through barriers where RF tags cannot be used. They would be especially suitable for national security missions where radiation hardness, tamper resistance, immunity to long-range interrogation by adversaries, zero power (passive), and code complexity are important.

This is the first-of-its-kind magnetostrictive CoFe electrodeposition process to determine if giant magnetostriction (λ_s = 260 ppm) or greater can be achieved. We will elucidate the microstructural mechanism leading to giant magnetostriction. Furthermore, we will determine the deposition conditions and post processing necessary to produce thick films (≥ 10 µm).

Measuring Human Performance within Computer Security Incident Response Teams

173036 | Year 2 of 2 | **Principal Investigator: J. T. McClain**

Project Purpose:

Human performance has become a pertinent issue within cybersecurity. However, this research has been stymied by the limited availability of expert cybersecurity professionals. This is partly attributable to the ongoing workload faced by cybersecurity professionals, which is compounded by the limited number of qualified personnel and turnover of personnel across organizations. Additionally, it is difficult to conduct research, and particularly, openly published research, due to the sensitivity inherent to cyber operations at most organizations. As an alternative, the current research has focused on data collection during cyber security training exercises. The Tracer FIRE (Forensic Incident Response Exercise) consists of a multi-day event that combined classroom instruction in the use of cybersecurity software tools, forensic analysis techniques, and adversary tactics and techniques with a team competition exercise. These events draw individuals with a range of knowledge and experience extending from seasoned professionals to recent college graduates to college students. The current research involved data collection at two separate cybersecurity exercises. This data collection involved multiple measures, which included behavioral performance based on human-machine transactions and questionnaire-based assessments of cybersecurity experience.

Summary of Accomplishments:

Subjects consisted of Tracer FIRE participants from two separate training exercises. Measures collected included human-machine transactions and self-reported cybersecurity experience. Additional questionnaire-based measures were collected which included the Big Five Personality Inventory, the Need for Cognition Scale, and the General Decision-Making Style Inventory. Additionally, EEG and eye-tracking data collection occurred for a subset of participants as they performed tasks outside the context of the Tracer FIRE training exercise. The purpose of these measures is to determine not only what tools are being used in the cyber context, but how cyber defenders utilize various cognitive attributes to approach cyber-based problems.

The study found that the more successful participants combined the use of specialized software with general-purpose software tools (e.g., Notepad, Microsoft Excel, and Cygwin). Similarly, participants with more professional cybersecurity experience made greater use of certain general-purpose software tools. These included the Windows command line, Windows Task Manager, vmware, and the Firefox and Chrome Internet browsers.

Our research showed that novices and experts behaved comparably with regard to the overall structure of their activities. There was no apparent difference in the duration of blocks of activity, or the number of actions, the number of software tools used, the number of transitions between software tools and the number of returns to a previously used software tool within blocks of activity. Instead, experts differed in their use of general-purpose software tools and their integration of the use of general purpose and specialized cybersecurity software tools. While the current analysis describes behavior at a fairly high level (e.g., instances using a specific software tool), the next step must be to consider the specific content accessed and actions taken. With this level of detail, opportunities may be created to understand both conceptually and procedurally how expert and novice performance differs.

Significance:

Highly skilled cyber security incident responders are paramount to DOE, NNSA, and national security missions. This project has allowed us to acquire a deeper understanding of the characteristics of high performing individuals in cybersecurity, as well as their impact on incident outcomes. Such understanding could lead to a broad range of capabilities, such as the ability to identify individuals with a high aptitude for cybersecurity tasks in order to enhance training and inform recruiting. The ability to build a better cybersecurity workforce will directly contribute to the crucial task of protecting our nation's information, infrastructure, and citizens.

Refereed Communications:

J.T. McClain, A. Silva, B. Anderson, K. Nauer, R. Abbott, and J.C. Forsythe, “Performance Factors in Competitive Cyber Security Exercises,” in *Proceedings of the 6th International Conference on Applied Human Factors and Ergonomics* (AHFE2015), 2015.

A. Silva, G. Emmanuel, J.T. McClain, J.C. Forsythe, and L.E. Matzen, “Measuring Expert and Novice Performance within Computer Security Incident Response Teams,” in *Proceedings of HCI International 2015* (HCII2015), 2015.

Online Mapping and Forecasting of Epidemics using Open-Source Indicators

173112 | Year 2 of 3 | **Principal Investigator: J. Ray**

Project Purpose:

Fast, dependable forecasting of disease activity can revolutionize medical planning and response and is important to threat reduction missions of agencies such as DHS, DTRA, and DoD. Collection of public health (PH) data, traditionally used for this purpose, is slow, has incomplete spatial coverage and is not useful for effective response. Thus, real-time mapping and forecasting of epidemiological activity is still not feasible.

Online, open-source indicators (OSI) of disease activity (e.g., disease-related searches, media reports, etc., and meteorology) can serve as strong covariates and leading indicators of outbreaks. They are readily available, timely, and have superior spatiotemporal resolution compared to PH data. Currently, there are no data assimilation methods that can fuse disparate datastreams to compensate for delayed/unavailable PH data, nor meteorology-driven disease models for accurate forecasting. We propose to develop the methods and models and integrate them into a data assimilation system (DAS).

Within the DAS, a spatial model based on co-kriging will interpolate sparse disease data. OSI are noisy datastreams, and the spatial model will allow noise suppression by pooling of information across monitored sites. It, along with a meteorology-driven disease model, will allow OSI-calibrated forecasts in regions outside OSI coverage. Scalable ensemble Kalman filters will provide the mathematical underpinnings of data fusion.

The game-changing potential of data assimilation has not yet been applied to disease forecasting. OSI, and our DAS, would be a novel development with impact in data-poor regions. We will demonstrate this by tracking the evolution of the annual influenza outbreak in California and dengue outbreak in India using data from Google Flu and Dengue Trends and HealthMap (HM).

Some of the hypotheses (e.g., the information content of various epidemiological OSI) on which the data assimilation framework rests have only been partially verified in literature. There are also no guidelines on how to perform the data assimilation robustly and accurately.

Portable Reagent-Free, Label-Free, Early Infectious Disease Signature Detection System

180890 | Year 1 of 2 | **Principal Investigator: M. Wu**

Project Purpose:

In the early stages of infection, patients develop non-specific symptoms or no symptoms at all. While waiting for identification of the infectious agent, a precious window of opportunity for early intervention is lost. Standard diagnostic methods require affinity reagents such as antibodies or polymerase chain reaction probes, and also require sufficient pathogen titers to reach the limit of detection. In the event of a disease outbreak, triaging the at-risk population rapidly and reliably for quarantine and medical intervention is more important than waiting for the identification of the pathogen by name. We aim to develop novel technologies and systems that provide warning and inform rapid and effective response, should chemical or biological agents be used against US military forces or civilian populations. To achieve this goal, we will utilize advancements in Raman spectrometry to analyze dendritic cell subsets in whole blood. Plasmacytoid dendritic cells only respond to a virus within hours of initial infection, and myeloid dendritic cells respond specifically to bacterial pathogens in the same timescale. Examining the activity of these two dendritic cell subtypes will rapidly distinguish infected from non-infected, and bacterial from viral infection, for the purpose of triage during an emergency outbreak. The purpose of this project is to: 1) determine whether Raman spectroscopy can provide label-free detection of early disease signatures and 2) define a miniaturized Raman detection system that meets requirements for low-resource settings.

Summary of Accomplishments:

We performed label-free Raman bulk analysis of macrophage cell line and fresh whole blood exposed to bacterial and viral simulants, as well as heat-killed bacteria and live virus. We also explored the feasibility of using gold nanoshells to enhance the cellular Raman signals. We determined and utilized data acquisition parameters to collect data from over 150 samples. We performed PCA data analysis and built a machine-learning model to predict the type of immune stimulation based on Raman signatures of immune cells. We were able to distinguish infected vs. uninfected blood cells and readily distinguish virus-infected macrophages from all other treatments.

With the bacterial and viral stimulation of cell lines, we determined that Raman signatures of immune cell subsets can characterize type of pathogen. We also determined the feasibility of miniaturization of a portable Raman detector device by performing our data acquisition on a portable Raman spectroscope. Results from our project pave the way for development of a portable, label-free disease diagnostic device that can be deployed with troops in low-resource settings where diagnosis of viral vs. bacterial infection is unattainable with affinity based tests. A technical advance was filed in June for the proposed portable Raman disease diagnostic system.

Significance:

The results from this project addresses threat detection missions from multiple agencies (e.g., DHS, DoD, DTRA) to develop novel technologies and systems that provide warning and inform rapid and effective response should chemical or biological agents be used against US military forces or civilian populations. Label-free pathogen detection will access previously untapped windows of opportunity for passive monitoring of at-risk populations as well as provide triage in the event of a bioterror attack.

Processing Radiation Images behind an Information Barrier for Automatic Warhead Authentication

165679 | Year 3 of 3 | **Principal Investigator: C. W. Wilson**

Project Purpose:

The purpose of this project is to develop enabling technologies and options that could facilitate future arms control treaty negotiations. Future arms control treaties may not be possible without the ability to utilize nuclear measurements to count warheads on delivery systems and/or measure weapon signatures to verify nuclear weapon type or status. A consensus within the arms control verification community agrees that sophisticated radiation imaging, never before used in this environment, offers the ability to measure new types of signatures of treaty-limited nuclear weapon systems or components. However, to protect sensitive information, information barriers (IB) must be used with any imaging systems. Analysis of the images behind an IB is a complex task that must be performed reliably, without human assistance. The most advanced IB systems developed to date, both developed at Sandia, perform gamma spectroscopy analysis behind an IB and have been demonstrated in several realistic exercises. The image-processing problem is far more complex, and to date, no one has demonstrated a functional system for reliable image verification behind an IB.

New radiation imaging techniques are just becoming available. The quality, characteristics, and measurable features available in the images they produce are still uncertain. While other techniques such as radiography imaging are mature, exploration of the image features available from any of these techniques is at a very early stage. Many new and advanced feature extraction algorithms have been developed but have not yet been applied to radiation images of nuclear weapons. The risks are high since it is unclear whether such techniques can uniquely identify nuclear weapon features in the highly reliable and robust fashion needed for automated processing behind an IB; however, the potential result is a game-changing advance in the way that arms control treaties are verified.

Summary of Accomplishments:

The crowning accomplishment of this project was the development of an algorithm for matching a probe image to a set of reference images that allows all images to be reduced to a set of features, which cannot be used to recreate the original images. In a treaty verification environment, this would allow highly sensitive radiological images to be captured and reduced to non-sensitive features in a relatively simple IB system. We called our approach "Feature Soup." The non-sensitive feature sets could be stored and processed in the open. We developed and tested this algorithm primarily on x-ray imagery, which is most effective at revealing details of the non-nuclear (less dense) parts of a warhead. This aspect of a warhead has not previously been used in treaty verification but could contribute greatly to verifying the type and status of a warhead. We demonstrated that this algorithm could identify the nearest image from a reference set of images and that if the probe did not belong to the reference set subject it would not match. We also demonstrated that real x-ray images could be matched to a reference set generated from simulated imagery.

Along the way, we improved and extended the SimXray add-in to Sandia's XTK x-ray tool kit. We developed a software tool to convert CAD drawings to the MCNP (Monte Carlo N-Particle) input deck format used for neutron emission and imaging simulation. We developed an initial requirements document for an information barrier to protect imaging and image processing systems.

Significance:

The mission impact of these accomplishments is that we have developed a new tool that offers technological options for automated warhead verification to negotiators of future arms limitation treaties. This addresses NNSA's nonproliferation mission. Emergency Response colleagues have expressed interest in the Feature Soup and MCNP deck generation capabilities. NNSA has found our work sufficiently promising to support an additional two years of development.

Radar Detection of Personnel Obscured by Foliage

170996 | Year 3 of 3 | **Principal Investigator: K. J. Pascoe**

Project Purpose:

The purpose of the project was to develop and demonstrate a ground-based radar system to solve the problem of detecting intruders outside a facility, including in foliage, before intrusion occurs. Some government sites require heightened security due to the consequences of successful enemy incursion. Detecting intruders beyond the perimeter of the protected facility assists in a timely response. A variety of sensors can detect intruders. Frequently, human eyes and video cameras are used. Foliage and inclement weather can obscure intruders, making detection difficult and potentially providing them a sanctuary. To ensure detection of intruders in foliage and weather, non-visual sensors such as radar must be combined with visual sensors in a way that exploits the best features of each sensor.

Two concerns with detection systems are false alarms that do not correspond to detection of real objects, and nuisance alarms that correspond to real objects but not to intruders. Any security detection system needs a low false alarm rate (FAR) and nuisance alarm rate (NAR). This research uses frequency-modulated, continuous-wave (FMCW) radar to penetrate foliage and provide precise range information. Multiple radars operating as a virtual-array radar, similar to phased-array radar, allow precise azimuth information over a wide range of azimuths. Another part of the research is data fusion to reduce NAR and FAR, and enable display of a common operational picture combining radar, camera, and other data in a way that reduces the nuisance alarm rate.

This project is the first known use of foliage-penetration FMCW radar for ground-to-ground detection for perimeter security. The ground-to-ground environment poses many challenges for radar. Reducing NAR with data fusion will be a significant advance opening up new ways to use sensors.

Summary of Accomplishments:

We designed, constructed, and tested a radar system intended to detect personnel in the presence of, or obscured by, foliage. The system was intended to detect and track personnel automatically, and report detection and tracking information to security personnel. The chosen frequency band was intended to balance penetration of foliage and detection of personnel, within limits of available frequency spectrum. Hardware development was very successful and culminated in field experiments with a human target. The user interface software was very successful. The data processing and detection algorithms need more development to determine if success can be achieved. Initial target characterization work involving swept frequency measurement, transformation into the time domain, and background subtraction, showed some promising initial results. The final system used a frequency-modulated, continuous wave technique. Results at the end of the project were inconclusive. More research is needed to further explore the capability of the existing hardware and improved algorithms.

Significance:

Results were intended to improve security around selected sites by extending intrusion detection beyond the perimeter. Further research in this area may provide a viable capability that improves the information available to a facility response force about intruders near the facility.

Radiography Signature Science of Homemade Explosives

165682 | Year 3 of 3 | **Principal Investigator: J. E. Parmeter**

Project Purpose:

The purpose of this project was to determine representative x-ray radiographic properties for credible threat formulations of key families of homemade explosives (HME). This is a critical national security issue based on the need to use x-ray radiography to detect explosives in aviation security applications. Credible threat formulations are those that are detonable and can be readily prepared by an adversary. In this project, characteristic x-ray attenuation parameters of key types of HME, including hydrogen peroxide (HP)/fuel formulations, potassium chlorate (KC)/sugar formulations, and pentaerythritol tetranitrate (PETN) and erythritol tetranitrate (ETN) in powder form have been determined. These attenuation parameters have been compared to those of various benign materials in order to gauge the ease of discrimination using x-ray radiography, and hence, the likely impact of nuisance alarms in various real-world applications. The work performed included a combination of experimental measurements and computational studies. Detailed characterization of x-ray source output and detector response has served as an important prerequisite to the experimental investigations of HME x-ray attenuation parameters and constituted an important part of the project. Development and documentation of safety procedures for working with small quantities of HME was also critical and required substantial effort. The theoretical work provides a better understanding of the experimental results, and agreement between theory and experiment was good to excellent. Theoretical work involved not only the application of existing codes to compute x-ray attenuation parameters, but also the development of new algorithmic approaches for improved extraction of these parameters from experimental data sets.

Summary of Accomplishments:

The work performed as part of this project led to several key accomplishments.

1) In the first year of the project, significant work was performed on the characterization of the x-ray source output and detector response of a research-grade radiography system at Sandia. This work allowed representative x-ray attenuation parameters for different HME to be determined in subsequent work, and laid a foundation for additional x-ray radiography studies of explosives.
2) Representative x-ray attenuation parameters were derived for HP/fuel formulations made with three different fuels, KC/sugar formulations, and PETN and ETN in powder form. Data are most extensive for the liquid HP/fuel formulations, and comparative x-ray attenuation data have been obtained for a number of benign liquids, including some that contain low concentrations of HP. The data thus provide useful information on the distinction of threat and non-threat materials using x-ray radiography. Among the potential uses of this information is the optimization of detection algorithms used by radiography equipment vendors to detect these materials.
3) Calculations were also used to estimate the x-ray attenuation parameters of the HME investigated. In the case of HP/fuel formulations, and to a lesser extent in the case of KC/sugar formulations, agreement between the calculated and experimentally derived values is excellent. This is extremely useful information because it suggests that the computational methods are accurate enough that the attenuation parameters of many closely related HME formulations can be calculated with a high degree of confidence rather than measured. This will potentially allow for great savings in time and funding in future work, since experimental determination of these parameters is costly and time consuming.
4) Novel new approaches to algorithm development for analysis of raw radiography data have been investigated, with promising results.

Significance:

The work performed in this project establishes representative x-ray attenuation parameters for several types of HME. This relates directly to checkpoint screening in airports, where radiography is used to detect explosives. Knowledge of these parameters will aid government agencies in understanding how readily such threats can be detected, and equipment vendors in optimizing detection algorithms. Data were presented to the Transportation Security Administration in January 2015, and this work helped to establish Sandia's expertise in this area, and thus, to secure funding for a major new TSA program, the Open Threat Assessment Platform (OTAP) project.

Refereed Communications:

E.S. Jimenez and K.R. Thompson, "Exploring the Existence of Null Spaces in Mediated-Reality Supplemented Methods to X-Ray Attenuation Estimation," in *Proceedings of the ASNT 24th Research Symposium*, 2015.

E.S. Jimenez, L.J. Orr, M.L. Morgan, and K.R. Thompson, "Object Composition Identification via Mediated-Reality Supplemented Radiographs," in *Proceedings of the IEEE Nuclear Science Symposium and Medical Imaging Conference*, 2014.

E.S. Jimenez, L.J. Orr, M.L. Morgan, and K.R. Thompson, "Exploring Mediated Reality to Approximate X-Ray Attenuation Coefficients from Radiographs," in *Proceedings of the Penetrating Radiation Systems and Applications XV Conference at the SPIE International Symposium on SPIE Optical Engineering + Applications*, 2014.

I. Perez, E.S. Jimenez, and K.R. Thompson, "A High-Performance GPU-Based Forward Projection Model for Computed Tomography Applications," in *Proceedings of the Medical Applications for Radiation Detectors XV Conference at the SPIE International Symposium on SPIE Optical Engineering + Applications*, 2014.

K R. Thompson, E.S. Jimenez, and L.J. Orr, "Comparison of Computed Tomography Values from Industrial CT Systems to Measured X-Ray Attenuation Values," in *Proceedings of the ASNT 23rd Research Symposium*, 2014.

Real-Time, Autonomous Field Surveillance for Vector-Borne Pathogens

173111 | Year 2 of 3 | **Principal Investigator: R. Meagher**

Project Purpose:

Vector-borne pathogens—including arboviruses, such as Dengue Virus and Rift Valley Fever Virus, as well as parasites such as Plasmodium—are among the most significant emerging (and re-emerging) pathogens worldwide. The recent spread of West Nile Virus to the western hemisphere provides a striking example of how quickly a vector-borne disease can spread across borders and oceans, and become endemic across entire continents within a few years. Vector-borne diseases represent an acute threat to personnel stationed overseas. Conventional vector surveillance is a low-throughput process dependent upon skilled labor and detailed laboratory analysis. Novel approaches are required to improve the spatial and temporal resolution of vector-borne disease surveillance to better combat the spread of vector-borne viral diseases.

We propose to develop and deploy a new generation of rugged yet inexpensive "smart traps" to perform autonomous field surveillance of vector-borne pathogens, with daily assays and wireless data reporting. Our approach represents a revolutionary advance in vector surveillance, which presently relies upon skilled labor and minimal technology for data collection. Long-term, our smart traps will reduce costs by reducing the labor bottleneck in vector surveillance, but to encourage adoption in the short term, the smart traps must be simple, reliable, accurate, and inexpensive to deploy. Creating a reliable, accurate device within these constraints requires creative new approaches to engineering autonomous systems, emphasizing simplicity of design in place of costly, complex components.

This project aims to develop fundamentally new technology for vector-borne disease surveillance, requiring basic research and engineering to achieve proof of concept. We will build upon novel detection and multiplexed assay, recently invented at Sandia.

Sampling-Based Algorithms for Estimating Structure in Big Data

186366 | Year 1 of 3 | **Principal Investigator: K. M. Matulef**

Project Purpose:
The purpose of this project is to develop sampling-based algorithms to discover hidden structure in massive data sets. Inferring structure in large data sets has become an increasingly common task in many critical national security applications (e.g., cybersecurity, remote sensing). These data sets come from many places: network traffic, sensor data, and data generated by large-scale simulations, to name a few. Identifying hidden structure in this data is crucial to exploiting it effectively, but the data is often so large that traditional data-mining algorithms become time consuming and sometimes infeasible. Even simple computations, such as computing an average of a list of values, become excruciatingly slow when the number of values reaches into the billions. Traditional algorithms often obsess over computing quantities like averages exactly, even when those same quantities can be estimated with high fidelity in much less time using sampling. Our goal is to identify a variety of useful quantities and methods for sketching or estimating them in a mathematically justified way. We plan to do this by leveraging new theoretical tools that come from the field of "distribution testing." Recently, there has been a flurry of work from the theoretical computer science community on testing and learning properties of probability distributions over large, discrete domains. These new methods have the potential to infer important properties of big data with much less computational overhead. So far, these methods have mainly been theoretical, but we plan to gain a deeper understanding of the methods and evaluate their efficacy on real world data. Successful application could lead, for instance, to an increased ability to predict normal behavior and detect anomalous behavior in computer networks.

Single-Volume Neutron Scatter Camera for High-Efficiency Neutron Imaging and Source Characterization

173113 | Year 2 of 3 | **Principal Investigator: E. Brubaker**

Project Purpose:

The neutron scatter camera (NSC), an imaging spectrometer for fission energy neutrons, is an established and proven detector for nuclear security applications such as weak source detection of special nuclear material (SNM), arms control treaty verification, and emergency response. Relative to competing technologies–such as coded aperture imaging, time-encoded imaging, neutron time projection chamber, and various thermal neutron imagers–the NSC provides excellent event-by-event directional information for signal/background discrimination, reasonable imaging resolution, and good energy resolution. Its primary drawback is very low detection efficiency due to the requirement for neutron elastic scatters in two detector cells. We will develop a single-volume double-scatter neutron imager, in which both neutron scatters can occur in the same large active volume. If successful, the efficiency will be dramatically increased over the current NSC cell-based geometry. If the detection efficiency approaches that of coded aperture imaging, the other inherent advantages of double-scatter imaging would make it the most attractive fast neutron detector for a wide range of security applications.

There are significant technical challenges to implementing this concept, especially when resolving nearby scatter events, which we contend can be resolved using recent advances in photodetection technology and associated electronics. If we are successful, a calculation of the achievable improvement in effective area is at least an order of magnitude. The detector footprint will also be greatly reduced.

Tamper Indicating Materials using Microvascular Networks

173107 | Year 2 of 2 | **Principal Investigator: H. A. Smartt**

Project Purpose:
Sandia is researching materials that provide an inspection agent the ability to readily recognize visually that penetration into a material was attempted, without providing adversaries the ability to repair damage without detection. Such a material can significantly enhance the current capability for tamper-indicating technologies, used to support treaty verification regimes by maintaining continuity of knowledge regarding information or materials of concern. Many tamper-indicating technologies attempt to secure entry points of enclosures, and some attempts have been made at designing approaches for securing whole volumes; however, some challenges include: 1) enclosures are non-standard in size and shape, 2) enclosures are both host and facility owned, 3) it may be cost-prohibitive to secure an entire enclosure, 4) tamper attempts must be detectable, 5) solutions must be robust and stable, and 6) a technology may be found that can indicate penetration, but it may be difficult to prevent adversaries from repairing that penetration. Several types of dispersed microencapsulated liquid dyes have been investigated that exhibit a 'turn-on' fluorescence response upon fracture of the encapsulated material. These approaches are intended to address the stated challenges by allowing flexibility in application, creating materials that are low-cost, and providing a secure technology by working iteratively with Sandia's vulnerability review team.

Summary of Accomplishments:
This research demonstrates the feasibility of tamper-indicating materials based upon a turn-on fluorescence mechanism. Key results include the preparation of fluorophore compounds in liquid organic matrices that have been encapsulated in copolymer microspheres. The different components of the sensor system have been investigated in isolation and in combination.

The ideal turn-on fluorophore is one that undergoes a change from fully non-fluorescent to highly fluorescent following exposure to the analyte, or microcapsule breakage in this case. Three such compounds were prepared and investigated in this work, although all were found to be unstable over a time period of several months. Following those results, the investigation turned to an exciplex turn-on fluorescence mechanism that provides very high environmental stability but reduced sensitivity than the aforementioned true turn-on fluorophore compounds. This was due to lower quantum efficiency of the exciplex emission. Future work would comprise the design and synthesis of higher quantum yield exciplex compounds or turn-on fluorophores that exhibit greater stability over time.

A second component of the research is the organic material that serves as a matrix for the fluorescent sensor compound. Different polymerizable 'self-healing' materials and aliphatic oils were investigated in this work. While the most promising results were obtained for the organic oils due to favorable flow and mass-transport characteristics, there is still a compelling case for self-healing monomers due to the permanence of their response following polymerization.

The third component for this system involves optimization of the tamper-indicating device architecture. The present state of development involves 3D printing using dispersed microcapsules in an ultraviolet-curable resin. While this has been successful as a proof of concept, there are considerations related to long-term compatibility of the microcapsule/resin mixture, as well as the mechanical characteristics/detection sensitivity of the corresponding tamper-indicating device design.

Significance:
The results of this research demonstrate that it is feasible to develop materials that provide an inspector the ability to readily recognize using simple visual observation that penetration into the material has been attempted without providing adversaries the ability to repair damage. Such material can significantly enhance the current capability for tamper-indicating technologies, used to support treaty verification regimes by maintaining continuity of knowledge regarding information or materials of concern. Many current tamper-indicating technologies attempt to secure entry points of enclosures only, or employ complex methods that make inspection difficult, costly, or are limited in application.

Towards Representativeness in Emulytics

180889 | Year 1 of 2 | **Principal Investigator: D. J. Fritz**

Project Purpose:

Our nation's critical infrastructures depend on distributed information systems, which must be resilient against malicious attempts to disrupt their operation. Security mechanisms must be deployed and continuously assessed in order to prevent adversaries from disrupting critical infrastructure. These information systems employ a broad range of technologies including fixed Ethernet, point-to-point wireless, and cellular communications. Additionally, these systems employ enterprise architectures, cloud-based data centers, and emergency response wireless architectures. With the extensive reliance of critical infrastructure on secure information systems, techniques and mechanisms to assess security must be created.

Efforts to extend state-of-the-art security modeling via emulation capability are hindered by our current ability to model meaningful emulations of real-world networks. To date, emulation research has focused on the means and mechanisms of emulation with little emphasis on fidelity or representative behavior of experiments. We propose creating a method to conduct information system discovery and develop tools to enable the creation of high-fidelity emulation models that can be used to enable assessment of our infrastructure information system security posture and potential system impacts that could result from cyber threats. Furthermore, this work will help gauge the fidelity of the constructed emulation model, which is critical in providing confidence in research questions answered on this platform.

Providing confidence and fidelity in emulation experiments is fundamental to addressing current and future US cybersecurity missions. This research will directly impact the landscape of research in large-scale emulation, and enable addressing critical research areas that can only be answered using a high-fidelity emulation platform.

Understanding Chemical Threat Agent Interaction with Concrete: Critical Step Toward CI Restoration

180896 | Year 1 of 2 | **Principal Investigator: C. M. Tenney**

Project Purpose:

The purpose of this project is to develop simulation tools to investigate and understand mechanisms that inhibit or enhance the decontamination of concrete exposed to hazardous chemical agents. The long-term goal of this work is to improve our ability to respond to, and recover from, the release of such chemical agents in a subway station, airport, military base, etc. In addition to guiding the development of decontamination strategies and materials, an understanding of agent fate and transport better enables officials to confidently certify infrastructure as safe for reoccupation.

Restoration of critical civilian or military infrastructure after attack with a "persistent" chemical agent is not guaranteed. Contamination of infrastructure by chemicals characterized by low vapor pressure, high chemical stability, and high toxicity could cause social, economic, and mission disruption through long-term access denial. A lack of understanding of the transport and fate of persistent chemical agents hinders the development of safe and cost-effective remediation and recovery strategies. Of particular concern is the transport and fate of persistent agent in concrete, a ubiquitous infrastructure building material that cannot be simply removed and replaced.

Starting at the molecular scale, this project uses predictive simulation to identify mechanisms that significantly influence agent fate and transport in concrete. Prior research on persistence has mostly involved empirical measurement of agent (or simulant) interactions with bulk materials. Due to the chemical and physical complexity of materials such as concrete, the primary mechanisms controlling persistence remain unknown. Molecular and mesoscale simulation is ideal for predicting fundamental interactions between chemical agent molecules, decontamination materials, and the interior surfaces of porous materials. Once validated, these model-based tools will be well positioned to evaluate new or emerging threats.

Using Electroencephalography (EEG) and other Methods to Understand Domain-Specific Visual Search

165686 | Year 3 of 3 | **Principal Investigator: A. Speed**

Project Purpose:

Often, national security problems demand rapid decision making in uncertain, risky situations. In such circumstances, consequences of false positives and misses can both be significant, yet high-consequence decisions are often made using "instinct," or implicit processes, as much as explicit facts. Furthermore, how an expert analyst processes incoming information is as much a stimulus-driven process (i.e., bottom-up) as it is driven from past experience (top-down). In the first two years of this project, we attempted to identify experts making errors using EEG. However, due to large variability in accuracy between individuals, there was significant noise in the EEG data. Thus, it became clear that we needed to first understand the nature of this variability.

As there exist multiple populations of experts making similar decisions (e.g., Transportation Security Officers (TSOs), imagery analysts, and cyber analysts), understanding common characteristics across domains and understanding the blend between top-down and bottom-up processes influencing these risky, uncertain decisions provides significant advantage in selection and training of these experts. Numerous measures (e.g., eye tracking and reaction time) offer mechanisms for characterizing implicit processes (e.g., number of eye fixations can predict likelihood of error). We will test the hypotheses that experts across multiple similar domains share some common features and that factors influencing their decision making are regularly patterned. We will continue to work with TSOs and will collaborate with other projects to test these hypotheses.

If successful, we could significantly improve risky, ambiguous decision quality in numerous domains including transportation security, imagery analysis, and materials characterization. This project is poised to contribute to significant scientific understanding of the factors that influence rapid, uncertain decisions in several national security domains–something that would be very publishable in peer-reviewed literature as well as impactful at Sandia and other national security agencies.

Summary of Accomplishments:

We did not analyze other datasets in any formal way, although through the Visual Search Working Group we helped to establish, we did make informal comparisons between TSOs and other expert visual searchers (e.g., SAR analysts, neutron generator analysts, and novices). Generally, our accomplishments include:

- Development of software for:
  - Fusing multimodal human subjects data (keystrokes, eye tracking data, and behavioral performance)
  - Automatically determining quality of eye tracking data
- Identification of various types of errors TSOs make when searching bags using eye tracking
- Determination that EEG, in its current state, is not appropriate for data collection on visual search in operationally complex environments
- Collection and analysis of an extensive dataset on expert visual searchers performing domain-general cognitive tasks
- Started a Visual Cognition interest group at Sandia

Significance:

The peer-reviewed literature involves using undergraduate novices. Some researchers have used radiologists, but radiology is a fairly well-defined task, with anatomy and biology acting as constraints. TSOs (and other experts) deal with a more difficult problem: having no ground truth, and in searching for threats that are actively hidden by an adversary. Understanding how expertise impacts performance on domain-general tasks, and how expert visual search behavior/performance differs from novices can inform: 1) design of image processing algorithms/interfaces, 2) selection and training of individuals in job/careers with a visual search component, and 3) design of open studies that more closely mimic expert situations.

Refereed Communications:

M.C. Trumbo, L.E. Matzen, A. Silva, M.J. Haass, K. Divis, and A. Speed, "Through a Scanner Quickly: Elicitation of Event-Related Potentials in Transportation Security Officers Following Rapid Image Presentation and Categorization," in *Proceedings 9th International Conference*, AC 2015, held as part of HCI International, pp. 348-360, 2015.

D.J. Stracuzzi, A. Speed, A. Silva, M.J. Haass, and M.C. Trumbo, "Exploratory Analysis of Visual Search Data," *Foundations of Augmented Cognition*, vol. 9183, pp. 537-547, 2015.

A. Speed, "Visual Search in Operational Environments – Balancing Operational Constraints with Experimental Control," *Foundations of Augmented Cognition*, vol. 9183, pp. 528-536, July 2015.

VMD Fused Radar (VFR) - The First Volumetric Ultra-Low NAR Sensor for Exterior Environments

173108 | Year 2 of 3 | **Principal Investigator: J. L. Russell**

Project Purpose:

The objective of this video motion detection fused radar (VFR) project was to create an exterior volumetric sensor system with an ultra-low nuisance alarm rate (NAR), capable of differentiating weather-generated alarms from alarms caused by an intruder. Specifically, the sensor should be capable of detecting intruders while greatly outperforming the NAR requirements set by DOE.

The VFR team developed a two-layer algorithm capable of machine learning (layer 1) and applied expert knowledge using a Dynamic Bayes Network (layer 2) to deduce adversary deliberate motion. All data collected to date shows the deliberate motion algorithm is capable of differentiating weather-caused alarms from intruder motion. The two-layer algorithm is not totally dependent on machine learning, and as a result, is not subject to many of the known weaknesses associated with machine learning. The two-layer algorithm strives to balance the desired strengths of machine learning and expert knowledge to differentiate alarms caused by weather or an intruder.

To validate the performance of the two-layer algorithm, data was recorded and processed from radar and video motion detection (VMD) data sets collected during the harshest weather conditions in FY 2014 at Sandia's Sensor Technology Evaluation Center, including very heavy rain, hail, high winds, and light snow. The radar and VMD generated in excess of 100,000 nuisance alarms from weather during these periods. After processing the alarm data from the radar and VMD, which combines spatial and temporal information, only one nuisance alarm was declared by the deliberate motion algorithm. In addition to the NAR performance, all simulated physical intrusion tests were successfully detected, indicating the VFR sensor can detect intruders, as required by DOE and with a much lower NAR than is required. Reduction of NAR from wildlife was not a primary objective, although results to date have proved promising, with no documented nuisance alarms from wildlife, including insects on the camera lens, large birds, and rabbits.

Summary of Accomplishments:

This is the first physical security sensor system that effectively integrates the complementary phenomenologies of radar and VMD, including different nuisance alarm sources, overlapping detection envelopes, and different defeat modes. In addition to the complementary nature of the two sensors, a two-layer algorithm is used to fuse alarm data from both sensors, and differentiate intruder-induced alarms from alarms caused by weather and wildlife. The algorithm relies on advances in multi-hypothesis tracking (MHT), accomplished by this research, to create a deliberate motion multi-hypothesis tracking (DMMHT) algorithm, which is a variant of the MHT that has been designed to focus on the identification of deliberate motion characteristics as a signal of the presence of a human intruder. It is implemented by applying a range of heuristic functions to assess indicators of deliberate motion in target tracks and produces a figure of merit (FOM) associated with each track. The DMMHT allows the creation of an intruder feature vector that reflects a number of attributes that are designed to differentiate an intruder from weather related alarms, such as intruder motion towards the secure side of a perimeter.

A Dynamic Bayes Net (DBN) is implemented in layer two of the algorithm, and processes the alarm states from the DMMHT and the intruder feature vector. The DBN calculates the probability of the presence of a human intruder, given its general probability model and the current evidence. The DBN takes as input the aggregate feature vector propagated forward by DMMHT and determines whether an alarm should be raised.

Significance:

This new generation of sensor technologies establishes deliberate intruder motion prior to declaring an alarm, which significantly reduces nuisance alarm rates from weather and wildlife. Deployment of this technology will reduce the workload on Central Alarm Station officers at high security sites and improve their efficacy. This is a significant departure from any sensor system deployed at DOE or DoD high security sites. It represents a disruptive technology that will enable future security concepts not considered prior to this work.

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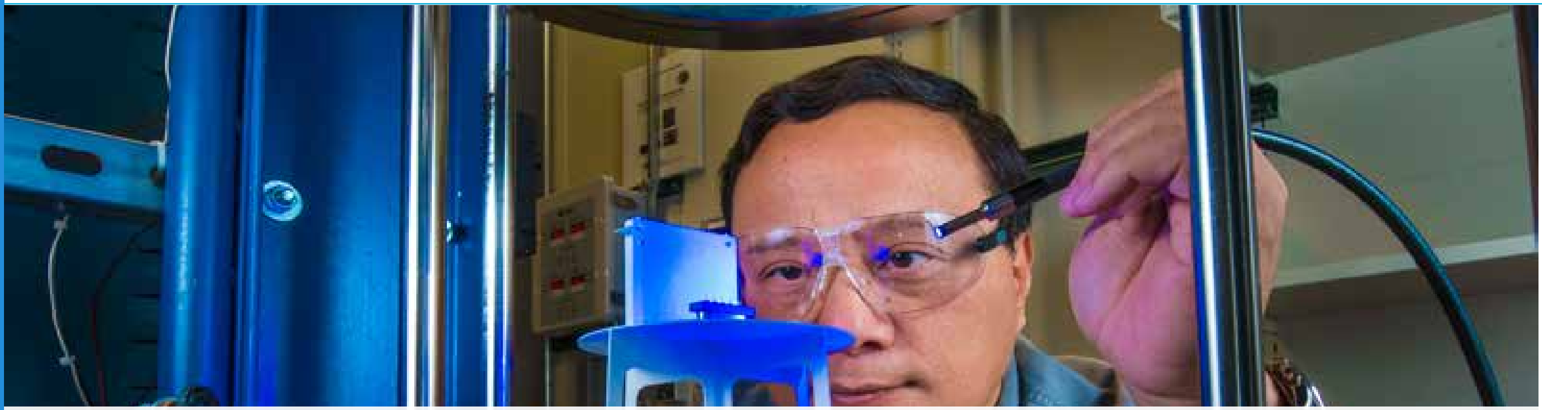
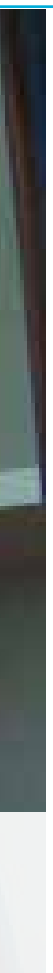


Nuclear Weapons

The primary goal of the Nuclear Weapons (NW) Investment Area is to support Sandia's strategic objective of excellence in our NW mission through investments in leading-edge science and the incubation of new technologies and capabilities. These investments are intended to promote exceptional innovation in our core products to meet future mission needs, to develop new tools and technologies for design, qualification and surveillance, and to nurture the seamless integration of science and engineering in all we do.

Projects



Additive Manufacturing of Metallic Components by Laser Powder Forming

181204 | Year 1 of 3 | **Principal Investigator: C. W. San Marchi**

Project Purpose:

Additive manufacturing (AM) technologies offer a new platform for innovation of advanced components. Reasonably complex geometrical features can be manufactured by laser powder forming, which has demonstrated the potential to enable innovative designs, reduce costs, lower manufacturing energy consumption, and improve customer response. The engineering community, however, lacks confidence in the structural integrity and reproducibility of additively manufactured metals, in particular the distribution of defects (e.g., interfaces and porosity) and presence of residual stresses. The lack of a robust understanding of the physical and mechanical metallurgy of AM materials and the lack of predictive manufacturing simulation tools are two important limitations of broad acceptance of AM by the design community. In order to demonstrate the structural integrity of AM processes, fundamental understanding of the physical and mechanical metallurgy is critical.

In collaboration with the University of California at Davis, we propose a metallurgical investigation to provide a framework for understanding microstructure, fracture properties, and residual stress in AM structures. We propose: 1) to benchmark the microstructure and structural properties against known properties of nominally equivalent stainless steels, 2) to assess the defects intrinsic in AM and the sensitivity of the AM microstructures to process variability, and 3) to optimize the AM process for combination of strength and fracture resistance (defect tolerant design metric), including control of residual stress. This experimental study will interface with complementary modeling efforts. The outcome will be a significant advance that provides a basis for defect tolerant design of AM components as an alternative to conventional materials and manufacturing.

Additive Manufacturing of Porous Materials

180929 | Year 1 of 3 | **Principal Investigator: D. Robinson**

Project Purpose:

Additive manufacturing is heralded by mechanical engineers as a new path to load-bearing structures that use material very efficiently. The emerging field also has promise in chemical engineering, where there is ubiquitous reliance on randomly packed powders in chemical reactors, electrodes and separator membranes for batteries and fuel cells, separation columns, filters, and other devices that manipulate fluid flow and ion transport. In cases where randomly arranged materials have been replaced by deterministically fabricated devices with optimized geometries, major performance and efficiency improvements have been achieved. Notable examples can be found in gas chromatography, microfluidic medical devices, and recently emerging "3D battery" structures. However, such improvements are not widespread because the appropriate fabrication techniques are not available in most situations.

The key technology gaps are:

1) Limited access of additive manufacturing techniques to the 1-100 μm length scale, especially for inorganic materials. This length scale is often needed for efficient fluid-solid contact.

2) Lack of parallelism in existing fabrication methods, which typically involve a rastered laser or extruder.

The goal of this project is to develop efficient, scalable manufacturing methods for porous chemical engineering devices, relying on several key Sandia technologies:

1) Nanoporous powders of well-defined particle and pore size that can be sintered through mild chemical or thermal treatments

2) Photochemical and electrochemical methods that permit deposition a plane at a time, without relying on rastering

3) Small-scale platforms for high-throughput characterization of filters and separation columns

4) State-of-the-art powder-based 3D printers for inorganic materials

We will focus on delivering, as a proof of principle, a sub-millimole scale separation column that achieves much more sharply defined separations at a much lower pressure drop than a similarly sized packed-powder column.

Carbon Composite MEMS Accelerometer

165725 | Year 3 of 3 | **Principal Investigator: C. Dyck**

Project Purpose:

Pyrolyzed carbon as a mechanical material is promising for applications in harsh and high radiation dose environments. Although pyrolyzed carbon microelectromechanical systems (MEMS) have been reported in the literature, little is understood at a fundamental level about these materials, and the processes that have been reported are not adequate for many practical applications. During FY 2015, we continued to focus on developing an understanding of the materials required to develop MEMS structures with known and stable properties. We also focused on creating novel fabrication processes that met our MEMS design needs.

We showed that the time-dependent increase in the material resistivity is due to ambient exposure and that the effects are reversible by vacuum pumping/heating in an inert ambient. Hermetic packaging in a nitrogen ambient stabilizes the materials' resistivity. We demonstrated that the material is unchanged in either the resistance or microstructural properties at high total dose levels of gamma radiation. Two novel processes were developed on 6" wafers consisting of a conductor layer and a mechanical layer. This demonstrates both the scalability of the process to a production level and the ability to drive and sense MEMS sensors and actuators.

Summary of Accomplishments:

Irradiation experiments were completed and showed that pyrolyzed carbon is robust to both gamma and neutron total dose irradiation. During gamma irradiation, the material displayed no visible changes in either its resistance or microstructure. The experiment was controlled to separate out previously observed ambient-related changes from irradiation-induced changes. Cantilevers and thin film resistors were irradiated with neutrons. The material displayed no visible changes in either its resistance or first resonant mode due to the exposure.

Based on calculations and high preparation temperatures, we surmise that pyrolyzed carbon thermal actuators should be more efficient than their polysilicon counterparts, as long as they are operated in a non-oxidizing ambient, achieving greater displacement and reliability. Thin film resistors were hermetically packaged in N2. Heating the devices during packaging dropped the resistance significantly from their prepackaged levels, and hermetically sealing them stabilized the resistance. The resistance remains unchanged after one year.

Two novel processes were developed on 6" wafers. In the first process, carbon MEMS structures were post-processed over Poly0 and the first sacrificial oxide layer. Structures were successfully demonstrated in this process. Because the pyrolysis process is thermally compatible with the SUMMiTV (Sandia ultraplanar multilevel MEMS technology V) process, we expect that carbon structures could be integrated with the complete SUMMiTV process. The second process consisted of carbon for the routing layer and carbon for the mechanical layer. The routing layer was deposited, pyrolyzed, and patterned. The mechanical layer was then deposited over a polysilicon sacrificial layer, pyrolyzed, and patterned. Released structures were demonstrated using this process.

Significance:

The results of this project demonstrate the feasibility and the potential for scaled production of pyrolyzed carbon MEMS structures for harsh environment applications relevant to Sandia's mission.

Cognitive Data Science for Neutron Generator Predictive Pattern Analysis

173153 | Year 2 of 3 | **Principal Investigator: R. A. Roach**

Project Purpose:
Recent neutron generator problems with internal/external high voltage breakdowns, loss-of-bias, and active braze processing have highlighted the need to increase understanding of neutron tube (NT) and neutron generator (NG) performance. Over 25 years of data from neutron generator testing are available for analysis and there is an acute need to discover methods to extract information. These data are an underutilized resource that offers undiscovered information on behaviors, trends, and relationships. As we gain sophistication in collecting and modeling this information, it is critical that we support the development of leading-edge technologies to provide predictive assurance of product performance.

To address this challenge, our project focuses on the performance aspect of NTs and NGs where waveforms of data are collected for each tube and generator as performance assessments relative to requirements. Each of these waveforms contains thousands of data points. Human visual pattern recognition and interpretation are the primary methods to assess the waveforms. Trained, experienced personnel perform this “eyes-on” analysis. One primary research challenge will be to assess whether expert visual pattern recognition on tester waveform images can be captured and integrated into automated models of product performance patterns (failure/success); and, together with models of the underlying data, provide leading indicators for future product performance. Although this project focuses on NG and NT data, developing cognitively informed models of waveforms is a novel approach in product engineering analysis. This work will provide novel technologies to address design and performance issues proactively, significantly enhancing the quality of current and future designs.

Composing Formally Verified Modules to Analyze Security and Reliability Properties of Large-Scale High-Consequence Systems

165537 | Year 3 of 3 | **Principal Investigator: G. C. Hulette**

Project Purpose:

Modern high-consequence systems, including weapons, transportation control systems, and communication networks, incorporate digital components. Yet the complexity of digital logic design implies that any such component will almost certainly include numerous unintended flaws. Such flaws may lead to unexpected failures and, even more worrisome, they expose an attack surface that sophisticated adversaries can exploit. Traditional testing and simulation techniques, while important, can prove the absence of flaws in only a tiny fraction of the behavioral spaces for even moderately sized system. It is in DOE and Sandia's interest to develop more robust methods for verifying our digital designs—especially for high-consequence control systems related to nuclear weapons, the power grid, and nuclear power generation.

Formal methods prove specific security or reliability requirements in digital designs and serve to locate flaws compromising these requirements. These techniques offer a total guarantee of correctness with respect to specified safety/security requirements. Unfortunately, this approach does not map well to the digital design process: formal analysis can only be done on the entire finished system and has no divide-and-conquer strategy that is de rigeur in digital design currently. Today, practitioners of formal methods verify smaller subsystems independently—Intel's Core i7 processor, for example, was verified in this way—but flaws may lurk in the interactions between subsystems. Our research addresses this limitation using a novel idea of refinement over state machines, enabling components to be formally verified independently, and then composed into larger machines while preserving formal properties.

Formal methods allow strong guarantees of correctness for high-consequence digital logic designs. The impact of wider use would be both broad and deep: applicable across many national security missions and applications, and transformative with respect to guaranteed quality. However, formal verification is currently not practically scalable to large systems. Our research addresses these fundamental scalability challenges.

Summary of Accomplishments:

This work has established a foundation for formally informed digital ASIC (application specific integrated circuit) design for nuclear weapon (NW) systems, which is both scalable and robust. The approach combines temporal logic with descriptions of state machines and their safety properties, and extends it with compositional refinement.

Refinement is a process by which an abstract specification is gradually elaborated in a formally verified way. This allows the designer to provably preserve safety, security, and reliability properties in the detailed implementation that were originally present in the specification. In principle, designs can be refined from initial requirements down to hardware. Our work enables composition of formally verified components into a formally verified whole. NW ASIC development will benefit from increased scalability and applicability of formal analysis throughout the design process. We developed a novel technique based on refinement for proving out-of-nominal requirements (e.g., that the digital system should "fail safe" in some particular way). Out-of-nominal properties are treated as abstractions of the system's nominal specification, and proven via refinement.

For scalability, we developed methods of refining subcomponents independently, and implemented them in our own prototype language and proof system for temporal logic specifications. This implementation extends existing open source tools used within industry. Our implementation takes a novel approach based on type theory. .

Significance:

This project has led to important advances in understanding of refinement-based formal methods, and the role they might play for Sandia's NW mission. The work has already had an impact on NW digital design, and we expect it shall continue to do so. Our work on refinement represents a novel and scalable strategy for the formal verification of safety, reliability, and security properties, applicable to NW digital designs and including crucial out of nominal requirements. The ability to verify these properties is crucial to Sandia's strategy in digital design for NW.

Refereed Communications:

J. Mayo, R. Armstrong, and G. Hulette, "Leveraging Abstraction to Establish Out-of-Nominal Safety Properties," presented at the *Fourth International Workshop on Formal Techniques for Safety-Critical Systems*, Paris, France, 2015.

Compressed Sensing to Support Reduced Flight Testing

173180 | Year 2 of 3 | **Principal Investigator: J. Helms**

Project Purpose:

In telemetry, there is a drive to quantify margins and uncertainties. This drive requires an increase in sensor data by an order of magnitude, yet there is no corresponding increase in the bandwidth. Furthermore, the reduced number of flight tests makes it imperative to maximize the amount of data collected per flight test. Traditional compression methods prove inadequate, as they require an increase in onboard complexity, resulting in greater power consumption, and volume. Complex onboard processing introduces latency, limiting the capability for end-event measurements. Using the same compression algorithm for various types of telemetry signals may not be possible. The cost and complexity of having multiple algorithms based on traditional compression schemes make this approach unfeasible.

Compressed sensing (CS) is a new, fast growing field that fundamentally changes data acquisition by allowing sampling at sub-Nyquist rates. Our research will investigate how to implement concepts of CS in telemetry systems. We will show that CS has comparable compression performance with traditional compression techniques, while offering significant decrease in cost, power, on-board processing and complexity.

Our research has focused on two areas: the compression algorithm and the decompression/reconstruction algorithm. We are currently developing two compression algorithms that are showing significant promise. One compression algorithm is based on random filtering and down sampling. The second algorithm is based on a two-stage approach where the first stage removes large time-series spikes and the second stage performs linear predictive coding. The spike removal can be efficiently compressed using CS techniques. In order to achieve maximum compression, cutting edge reconstruction algorithms are required. We have implemented and tested the latest and best performing reconstruction algorithms from the literature on our compression algorithms and have observed improved performance. The greatest technical challenge in applying these algorithms to telemetry data is optimizing the trade-off between rate and distortion.

Defect Characterization for Material Assurance in Metal Additive Manufacturing

180928 | Year 1 of 3 | **Principal Investigator: B. H. Jared**

Project Purpose:

Additive manufacturing (AM) offers unprecedented opportunities to design complex geometries and topologically optimized designs for performance gains inaccessible under conventional manufacturing constraints. AM also introduces the ability to generate engineered materials with microstructures and properties that are impossible via traditional synthesis techniques. However, to facilitate adoption in high consequence applications, fundamental questions regarding the intrinsic reliability and repeatable performance of additive metals must be answered. Distinct from traditional subtractive processes, component geometry and material are formed concurrently in additive processes and preclude an a priori knowledge of material performance from feedstock properties. Of particular interest are powder bed fusion processes where a laser or electron beam scans across successive layers of metal powder to fuse material and generate the desired part geometry. Characterizing, predicting, and controlling material properties are currently difficult for powder bed processes since they involve complex melting and solidification interactions, and are implemented on equipment lacking process feedback. Consequently, material performance is currently unquantified and introduces unacceptable uncertainties. This work will reduce these uncertainties by exploring the additive formation of a precipitation-strengthened stainless steel. Characterization will identify the nature of critical defects and quantify how additive-induced defects impact material properties and performance. To reduce or eliminate critical defects in the additive process, we will rely on a combination of mechanism-based process modeling and experimental optimization. We will explore three optimization pathways: metallurgical modification of the feedstock powder, adjustment of the additive process parameters, and modification of post-forming aging heat treatment.

Direct Mechanical Ignition of Reactive Materials for Improved Safety and Performance

180926 | Year 1 of 3 | **Principal Investigator: C. Yarrington**

Project Purpose:

Direct ignition of nonexplosive, reactive materials through shock or shear loading could improve performance and safety for nuclear weapons (NW) components. A working knowledge of mechanical ignition would allow for simpler component designs that reduce hazardous handling and manufacturing steps, as well as the associated costs. For example, directly initiating a percussive battery's heat source would simplify future design and manufacturing efforts by eliminating an explosive device and increase performance through reduced turn-on time. Safety components—like failsafes/weaklinks—or component improvements—like fusible contacts to mitigate chatter—could also be realized. Unfortunately, the knowledge to accurately describe the response of reactive materials to high-rate, mechanical loads is unavailable. Difficulties in separating material property effects and the complexity of the process have limited our current understanding.

The purpose of the project is to discover the mechanisms leading to ignition in reactive nanolaminates during dynamic mechanical loading. Sputter-deposited nanolaminates allow for precise control of material properties, so effects of material property changes can be studied individually. Ignition limits will be probed by varying stress wave strength, orientation, microstructure, and material properties. Testing will uniquely isolate relevant loading conditions including planar impact, mixed compression/shear, and high shear. The physicochemical alterations leading to ignition will be characterized experimentally and described with numerical models to aid future material selection and material design. It will be possible through these experimental and numerical studies, to engineer reactive materials with tailored mechanical ignition characteristics, allowing component-level integration of mechanically ignited reactive materials and realization of safety/performance improvements.

Distributed Sensing

186869 | Year 1 of 1 | **Principal Investigator: P. L. Feng**

Project Purpose:

The purpose of this project is to provide a prototype distributed and low-power detection system that is simultaneously sensitive to x-rays and optical photons. In typical photon detection systems, sensitivity and power consumption are inversely related, leading to significant compromises to meet performance or power consumption targets.

In response to these limitations, we propose a distributed light and x-ray sensing network based upon scintillating fiber detection media and silicon photomultiplier (Si-PM) photodetectors. This approach combines the high sensitivity of a distributed detection network with the unrivaled photon detection sensitivity and low power operation of Si-PMs. Si-PMs are a relatively recent breakthrough in optical detectors that allows high detector gain, yet low power consumption in a rugged, solid state device. Different fiber materials and configurations will be coupled to the Si-PMs, ranging from intrinsically scintillating plastic fibers to sections of inorganic scintillating fibers spliced with index-matched light pipes. Optical and radiation transport simulations will be employed to guide materials selection and the distributed detector configuration, while experimental approaches will be used to validate the model and provide feedback for system refinements. If successful, we anticipate this work will provide a generalized sensor design that possesses the highest performance-to-power consumption ratio for x-ray detection. The distributed nature of the detection media will also enable facile expansion of the monitored volume.

The project seeks a potentially transformative sensing platform for the detection of optical and x-ray photons. While commercial detector systems are available, no existing sensor system combines high sensitivity, low-power, and distributed sensing capabilities. The present work employs recent breakthroughs in electronic detectors and radiation detection materials that have yet to be applied to this problem.

Summary of Accomplishments:

In this project, we developed distributed x-ray detectors based upon different types of plastic scintillating fibers used in conjunction with low-power Si-PM photodetectors. The detectors were tested using a continuous x-ray generator in the energy range of 10-150 keV and beam current range of 0.1-5 mA. The detection performance was compared to a reference design based upon a silicon photodiode operational amplifier detector developed for a similar purpose. Noteworthy results for the fiber/Si-PM system include a twelve-fold improvement in the signal-to-noise at 150 keV/0.1 mA, and a fifty-fold improvement in the signal-to-noise at 60 keV/0.1 mA relative to the fiber/photodiode system. Additionally, the power consumption of the commercial, off-the-shelf Si-PM was determined to be 50 microwatts, which compares favorably to the 35 microwatts consumed by the amplified photodiode reference detector. Similar improvements in the visible light detection sensitivity were observed for the fiber/Si-PM system when configured with mixtures of scintillating fiber types. The purpose of this configuration was to increase the sensitivity to different parts of the visible light spectrum, which was achieved by combining violet/blue absorbing, blue/green absorbing, and orange/red absorbing fibers. In this way, we successfully demonstrated the feasibility of a low-power, distributed x-ray and light sensor.

Significance:

There are several national security missions that could benefit from this x-ray and light detector, principally comprising applications that require low-power and distributed sensor coverage. Potential applications include several remote sensing and monitoring scenarios. The results of this project demonstrate significantly improved detection sensitivity relative to a reference x-ray/light detector design while exhibiting comparable power consumption values.

Electro-Syntheses of Intermetallic Couples as Thin-Film Heat Sources for Advanced Thin-Film Thermal Batteries

173184 | Year 2 of 3 | **Principal Investigator: C. A. Apblett**

Project Purpose:

We seek to develop low-cost, high-energy electroplated heat sources based on nickel-aluminum intermetallic formation that can be rapidly formed into shape for use in advanced thermal batteries and for fast brazing, joining, and energetic components. Current heat sources of this type use alternating nanostructured layers of reactive metals made by sputtering, a process requiring thousands of iterations, high capital investment, and expensive shaping to fabricate the heat sources. We propose electroforming the couples as an alternative. Using pulse electrodeposition, we will create an equivalent structure on a preformed substrate, eliminating both slow sputtering and expensive shaping. This will result in a smaller, faster, and cheaper heat source for both current and future thermal battery systems.

We will develop a process for electrodepositing compositionally modulated metal multilayers (CMMMs) using aprotic solvent/electrolytes. Tailoring the concentration and deposition mode of the noble material allows tuning thickness and resolution of the CMMMs. We will investigate continuous dispersion electroplating processes—electrochemical deposition while simultaneously electrophoretically codepositing a colloidal solid, which is then intimately bound to the substrate with the metal. Rather than layer formation, inclusions of one reactant will be embedded into a matrix of the other reactant, which allows for oxide exchange reactions to be developed. The use of aprotic solvent/electrolytes to deposit these reactive chemistries is in its infancy, and while there have been reports of several candidate elements deposited from aprotic solvent/electrolytes, no one has yet synthesized a discrete laminar or dispersion matrix of constituents to make a reactive heat source.

NUCLEAR WEAPONS

Engineered Composite Materials Science and Technology for Next-Generation Glass to Metal Seals

173186 | Year 2 of 3 | **Principal Investigator: K. G. Ewsuk**

Project Purpose:

Steadily increasing demands on nonnuclear components in nuclear weapons (NW) have pushed critical properties like the strength of traditional glasses in glass-to-metal (GtM) seals to their limits, eliminating margins critical to predictable performance and reliability. Glass ceramics (GCs) in GtM seals have improved tolerance to cracking/chipping, but at the expense of robust manufacturability, and with unresolved hermeticity issues attributable to poor interface bonding. Novel, interface-engineered, advanced composites comprised of two or more chemically compatible materials can take advantage of the desirable attributes of the constituent materials while circumventing their deficiencies.

Particle-filled glass composites (FGCs) will be developed as new sealing materials to make improved performance and reliability GtM seals. Although introducing new materials into NW components always presents significant risk, the need and potential for better performance and reliability warrants the investment. FGCs offer enhanced manufacturability, performance, and reliability by combining the processing robustness and thermodynamic stability of a glass, with the physical stability, design flexibility, and enhanced performance of a crystalline solid. FGCs also afford more robust processing and greater control of microstructure and properties compared to GCs. FGC seal materials will be developed, employing: 1) experimentally validated molecular modeling to develop glasses with controlled chemistry and structure to improve interface bonding and seal reliability, 2) property and process modeling to optimize FGC design, manufacturability, and performance, and 3) interface engineering to produce metal surfaces/interfaces that are thermodynamically more stable. Coupled modeling and experiment will be employed to optimize GtM interface bonding through understanding and control of critical glass chemistry-structure relationships.

The development and implementation of new seal materials for NW components presents significant technical challenges and risk. Additional research is needed to enhance and further contribute to the fundamental understanding and control of critical glass interface chemistry-structure-property relations.

Organic Semiconducting Materials for Thin-Film Optoelectronic Devices

173183 | Year 2 of 3 | **Principal Investigator: J. G. Cordaro**

Project Purpose:

The purpose of the project is to develop the next generation of tunable photonic and electronic devices.

Specifically, materials with optoelectronic properties in the 900–2,600 nm spectral region are attractive for a variety of applications ranging from photodiodes to photovoltaic devices, to detectors. Conventional systems rely on solid state inorganic materials, which operate at low temperature, can have high costs, and poor mechanical properties. Alternatively, the photoinduced electron transfer from semiconducting polymers to fullerenes, which is well established in the visible region of the spectrum, forms the basis for a variety of applications including polymer photodetectors, which exhibit fast temporal response and high sensitivity. The possibility of using semiconducting conjugated polymers as an alternative to inorganic materials is, thus, a real possibility. The benefits include tunability, ease of manufacturing, and flexibility to be incorporated into a variety of architectures. The main goal of this project is to determine whether or not semiconducting polymers can replace solid state inorganic materials in devices operating at wavelengths longer than 900 nm. The challenges we will address include overcoming synthetic challenges, device fabrication optimization, and engineering a system that can meet the requirements for applications of interest. If successful, this research will give us insight into fundamental processes that govern charge transfer in organic materials. Success will also lead to tunable, conformal, and low cost organic electronic devices suitable for a wide range of applications

Organosilicon-Based Electrolytes for Long-Life Li Primary Batteries

165726 | Year 3 of 3 | **Principal Investigator: K. R. Fenton**

Project Purpose:
We aim to develop new lithium primary power sources designed to have wider operating temperatures using inherently safe materials to increase the performance and safety of power sources used in nuclear weapons (NW) testing applications. The primary concerns with organic electrolytes used in lithium primary and secondary batteries are instability at elevated temperatures and the chemicals released during a thermal runaway event. In order to eliminate flammability concerns at elevated temperatures, we propose to develop a new class of 'organosilicon' electrolyte materials with high temperature stability and high ionic conductivity that are nonflammable, nontoxic, and have low viscosities. Informed by new discrete Fourier transform (DFT) models, these compounds will offer high temperature (>75 °C) and low temperature (-40 °C) performance in a nontoxic, nonflammable electrolyte solvent. We will fabricate CFx (carbon monofluoride)-based lithium primary cells with these optimized electrolytes, employing advanced packaging concepts, and focusing on NW needs for safe, high energy density primary batteries for ground controller applications.

Organosilicon electrolytes exhibit several important properties for use in lithium cells that include: 1) high conductivity/low viscosity and 2) thermal/electrochemical stability. By directly incorporating anion-binding agents (ABAs) to the silicon backbone, both safety and electrochemical performance can be controlled. Additionally, direct attachment of binding agents allow for increased LiF dissolution, which will lead to increased performance from the lithium carbon monofluoride battery chemistry. The knowledge developed in this project is expected to have an immediate impact on battery technology for NW, but in addition will be more broadly valuable to other Sandia missions.

The safety consideration for many current power sources excludes them from use in applications within both Sandia and the DoD. Development of a direct replacement for current power source that increases safety has value across the complex. These solutions require high-risk reinvention of current electrochemical systems, including new classes of electrolytes.

Summary of Accomplishments:
Synthesis work focused on protocols for incorporating viable anion binding agents to the organosilicon backbone structures. Several synthesis schemes were developed to successfully link anion binding agents to the organosilicon backbone. While the development and demonstration of this new type of battery electrolyte was achieved, further development is required to increase both purity and yield. Additionally, a secondary material was developed as an intermediate step in the joined material synthesis that was found to be nonflammable and a potential cosolvent for lithium primary and secondary batteries.

Test data was systematically collected on all synthesized compounds for this project. Several of the materials show good conductivity and electrochemical stability. Additionally, several potential cosolvents were identified to allow for additional adjustment of electrolyte viscosity or conductivity. Electrolytes were tested for both electrochemical performance and safety response. Aggressive flammability testing was conducted and excellent nonflammable behavior was observed for cosolvents containing dissolved binding agents. The OPLS-AA (optimized potentials for liquid simulations–all atom) OPLS-AA force field parameters for ethylene carbonate (EC) and propylene carbonate (PC) provide reasonable agreement with the available experimental data on pure solvent dielectric properties, both for the static dielectric constant and the dielectric relaxation times. This study provides a benchmark for force field parameters for pure EC and PC solutions and can be extended to study the electrical properties of mixed electrolyte solutions. This study is applicable to many electrolyte systems widely used in many common battery systems today.

Development of new materials with potential new mechanisms and properties will be key to the expansion of battery performance. Without a large increase in battery performance through materials discoveries or new electrochemical systems, it is likely that technology may vastly outpace the ability for the electrochemical power sources to provide reliable and safe power.

Significance:

The development of a reliable, safe, nonflammable, and long shelf life lithium battery is becoming an increasingly important objective for many federal agencies. While we envision applications such as flight tests or use control, this project aims to develop man safe power sources with potential applications throughout DOE/DoD/NNSA. By bringing together key team members and resources for battery design, modeling, synthesis, and characterization, we will attempt and mitigate the key concerns involving primary battery safety, performance, and size. The push towards reliability and safety for users is well aligned with other federally funded power source goals.

Refereed Communications:

K. Leung, K. Fenton, and G. Nagasubramanian, “Density Functional Theory and Conductivity Studies of Boron-Based Anion Receptors,” *Journal of the Electrochemical Society*, vol. 162, pp. A1927-A1934, 2015.

Predictive Assessment of State of Health and Lifetime of Components

180864 | Year 1 of 1 | **Principal Investigator: P. Tangyunyong**

Project Purpose:

Power spectrum analysis (PSA) is a technique developed at Sandia to detect electrical differences in devices. The purpose of this project is to determine whether PSA can detect aging effects when devices are subjected to accelerated life tests at elevated temperatures and voltages. The devices selected for this study were COTS (commercially off the shelf) discrete devices, diodes and capacitors. The samples were aged by subjecting them to accelerated life testing at elevated temperatures and voltages. After each accelerated life testing cycle, PSA measurements and electrical testing were performed on the test devices. Physical analyses were also performed on a few samples of aged and unaged devices. Correlations were then made between the PSA data and data from conventional electrical testing and physical analyses.

Summary of Accomplishments:

We found that PSA showed good sensitivity in detecting aging effects. In some cases, the aging effects detected by PSA were not detected by conventional electrical testing. We also found that there were strong correlations between changes in PSA data and physical changes in the test devices.

Significance:

PSA can potentially be used to study the aging effects as a standalone technique or as a complementary technique to existing electrical testing methods.

Process-Structure-Properties Relationship of Electrodeposited Au Thin Films used in Thermoelectric Power Generation Device

173666 | Year 2 of 2 | **Principal Investigator: D. Banga**

Project Purpose:

The purpose of this project is to develop a knowledge base of gold electrodeposition for thermal mitigation and contact of the next generation high performance thermoelectric power source device by fundamentally understanding the mechanisms whereby microstructure, grain size, and crystallographic texture influence mechanical and optoelectronic properties in gold electrodeposits. We will combine quantitative electrochemical measurements, x-ray diffraction, and surface and bulk microscopies to understand how grain structure affects properties and performances of Au electrodeposits, and then use such understanding to develop electrodeposition conditions favorable for the growth of films with controlled and stable microstructure which are critical to the performance and reliability of many technologies of interest to Sandia. This work will culminate with the production of low emissivity and electrically conductive Au films containing twin boundaries. Because of their electron scattering coefficient that is one order of magnitude lower than that of other high angle conventional grain boundaries, twin boundaries are effective in increasing strength without negatively affecting conductivity. We will introduce nanosized twin boundaries in electrodeposits by controlling deposition conditions including reduction rates of the precursors by the use of pulsed electrodeposition. Technical challenges to the success of this project include: 1) the difficulty of capturing the actual nucleation and growth processes using electrochemical techniques due to side reactions and 2) the effects of bath chemistry and additives. To solve 1), in addition to the electrochemical current transient technique for instantaneous and progressive nucleation model, we developed an in situ electrochemical scanning probe microscopy (EC-SPM) technique for dynamic observations of evolving surface morphology and structure. To address 2), we chose a cyanide bath with no added additive and limited ourselves to one primary bath chemistry, placing our primary experimental emphasis on deposition parameters influencing the rates of mass and energetics incorporation.

Summary of Accomplishments:

We successfully demonstrated an electrodeposition process capable of producing smooth, porous free, highly crystalline, strongly textured, low emissivity, reduced contact resistance, enhanced electrical conductivity, and mechanically strong Au electrodeposits using an additive-free stable Au plating bath chemistry. We discovered that the introduction of atomically sharp nanoscale twins was responsible for enhanced mechanical and electrical properties of Au electrodeposits. To accomplish this, we initially studied the nucleation and growth mechanism of Au electrodeposition from our bath. We found that both instantaneous and progressive nucleation modes could be achieved during Au electrodeposition. Instantaneous nucleation was observed at low overpotentials (≥ -0.75 V) while progressive nucleation occurred at large overpotentials (< -0.75 V). We then studied Au electrodeposition using two electrodeposition methods consisting of galvanostatic and potentiostatic electrodeposition. In each method, we compared direct current (DC) with pulse current (PC) electrodeposition modes and their effects on mechanical and electronic properties of the electrodeposits. The following conclusions were drawn from this study:

1) The use of a low current density (-0.5 mA/cm2) in galvanostatic electrodeposition and large overpotentials (≤ -0.9 V) in potentiostatic electrodeposition was discovered to produce films with the most enhanced properties
2) Pulsed films had improved physical and electronic properties with emissivity as low as 0.006, contact resistance five times less than DC films, and hardness and electrical conductivity twice the values in DC films
3) Long pulse on-times (≥ 2 ms) and small duty cycle (10%) were needed to obtain enhanced properties in both galvanostatic and potentiostatic electrodeposition of pulsed Au films
4) Films generated potentiostatically possessed far superior mechanical and electronic properties than those electrodeposited galvanostatically

5) The introduction of highly crystalline atomic structure in the interior of each grain of Au electrodeposits and perfectly coherent and atomically sharp nanoscale growth twin boundaries was achieved and demonstrated in potentiostatically pulsed Au films

Significance:

The successful growth of dense and porous-free Au coatings with enhanced mechanical and electronic properties is of interest to the development of thermoelectric power sources for the nuclear stockpile where Au coatings are used for contact and thermal mitigation. Understanding the effects of Au electrodeposition processing conditions on the film microstructure also makes possible the production of reliable and low friction hard Au coatings.

Radiation Hardness of MEMS Capacitive and Electromagnetic Accelerometers

173154 | Year 2 of 3 | **Principal Investigator: B. D. Homeijer**

Project Purpose:

Fuzing options based on path length traveled are central to the performance of the ballistic legs of the nuclear deterrent. The approach of this project has been driven by the lack of available sensors that can meet the radiation hardness requirements. While evaluations of radiation effects on some commercial microelectromechanical systems (MEMS) accelerometers have been published, the fundamental understanding of why such devices fail in radiation environments is incomplete, and techniques for designing inherently hardened sensors based on this understanding have not been developed. Acquiring this knowledge is a necessary step to enable the development of an intrinsically radiation-hardened, large dynamic range accelerometer. We propose to investigate the fundamental effects of radiation on MEMS materials, including the physical mechanisms of radiation-induced dielectric charging and stiffness changes due to displacement damage. We will then develop a modeling capability to quantify and predict changes in performance of MEMS-based electrostatic or electromagnetic sensors and actuators due to these radiation effects. This combined knowledge will allow us to develop designs and processes that enable intrinsically radiation-hardened MEMS accelerometers. The commercial MEMS accelerometer market has not addressed this problem because the market size for radiation-hardened accelerometers is miniscule relative to consumer grade devices.

There is a risk that the added radiation hardness achieved through this work will still be insufficient to meet some of the more demanding nuclear weapons environments. However, should it be successful this project has the potential to significantly improve sensing capabilities in nuclear weapons and space-based applications by providing a radiation-hardened MEMS accelerometer technology that is currently unavailable.

Reconfigurable Matching Networks for High-Efficiency GaN Power Amplifiers

173187 | Year 2 of 3 | **Principal Investigator: M. M. Elsbury**

Project Purpose:

Modern radar transmitters under development are based on single-chip gallium arsenide power amplifiers (PAs) capable of producing unprecedented levels of radio frequency (RF) power and integration. Unfortunately, because these PAs are designed to cover wide bandwidths, they operate with low power-added-efficiency (PAE), resulting in tremendous waste heat. The thermal management problem created by this high power dissipation is a daunting technical challenge.

Gallium nitride is a new RF semiconductor technology capable of operating at much higher voltages and temperatures than conventional GaAs. Recently, researchers have exploited the high-voltage capability of GaN to design highly efficient, switching-mode RF PAs. Unfortunately, the maximum practical bandwidth of these switching mode PAs is too low for many applications. This project has created a first prototype 60W PA design utilizing narrow-band 50%-efficiency matching networks reconfigurable to operate in any one of multiple sub-bands.

This project will create a suite of reconfigurable 60W output-matching networks to enable high-efficiency PA operation across a larger bandwidth; this will significantly reduce the thermal design complexity while maintaining the required application bandwidth. For example, in a 100W amplifier, increasing PAE from 30% to 50% cuts the dissipated power from 230W to 100W, thus significantly relaxing the requirements and manufacturing complexity of the thermal design. Such improvements require an increase in electrical design complexity with a corresponding large initial investment of research and development time and resources. These band-reconfigurable PAs will not only be an enabling technology for future fuzing radars, but will yield technology broadly applicable to multi-band commercial communications, software-defined radios, and other defense-related applications.

The final phase of the project will create thermal package solutions appropriate for tightly integrated high-reliability systems utilizing high-power band-reconfigurable GaN power amplifiers. These advanced packaging solutions will demonstrate improved performance by utilizing newly developed high-thermal-conductivity materials while leveraging commercially available printed-circuit-board processing technologies.

Recycling Scandium and Erbium from Nuclear Weapon Manufacturing Operations

173156 | Year 2 of 3 | **Principal Investigator: R. F. Hess**

Project Purpose:

The main goal of this project is to establish a scientific basis for the dissolution and deposition of lanthanides using ionic liquids (ILs). Initial efforts will focus on isolating scandium metal from process generated coated tungsten (Sc-W) crucibles as a benchmark. The separation of Sc3+ from other metal ions using solvent extraction techniques has been demonstrated but relies heavily on the use of concentrated acid and organic solvents similar to the PUREX process for actinides. In contrast, the IL dissolution of lanthanides has been relatively unexplored. ILs have low vapor pressures and larger electrochemical windows that will allow for the reduction of Sc3+/Er3+. We will develop tailored IL materials to selectively electrochemically dissolve scandium metal from the crucible and determine the conditions necessary to electroplate scandium metal. This novel IL solution route will also enable the more delicate instrumentation to be 'washed.' After the scandium is solubilized, select electrochemical deposition of Sc(0) will be necessarily developed from the IL. Little information is available to direct these fundamental electrochemical studies but literature reports support this as a reasonable approach. In addition, we will study the separation and recovery of Ln3+ from process solutions containing large amounts of cerium, which itself will be recovered for further use. Technical risks that may be encountered include potential difficulties in crystallizing IL-metal complexes, which make structural characterization problematic, and challenges in achieving high product purity after electrodepositing the scandium and erbium metals.

The study of the dissolution and electro-winning to produce pure lanthanide metals has not been explored in depth. The development of a benign separations process will yield the fundamental scientific information necessary to produce a long-term cost savings and enable the recycling of other lanthanides from products (e.g., fluorescent lights and magnets).

Trust of Third-Party Digital Design Tools using Formal Methods

180931 | Year 1 of 3 | **Principal Investigator: T. Mannos**

Project Purpose:

The use of commercial, uncontrolled development tools to support trusted ASIC (application-specific integrated circuit) design presents a potential avenue for system manipulation. The purpose of this project is to develop the trust verification platform (TVP), an approach for the independent verification of register transfer level (RTL) to graphics data systems II (GDSII) equivalence that minimizes common modes of attack, and to provide recommendations for the secure integration of untrusted software tools into trusted digital ASIC flows.

Understanding H Isotope Adsorption and Absorption of Al-Alloys using Modeling and Experiments

165724 | Year 3 of 3 | **Principal Investigator: D. Ward**

Project Purpose:

The aging performance of austenitic stainless steel reservoirs for hydrogen (H) isotopes can be limited by time-dependent H-metal interactions (e.g., embrittlement). Aluminum (Al) alloys, alternatively, have very low solubilities for H-isotopes and no evidence of embrittlement in dry H environments, suggesting improved resistance towards aging vulnerabilities. Unfortunately, the long time scales associated with effects of H-isotopes make solely experimental investigations impractical. Therefore, robust simulation tools need to be developed to strengthen our understanding of Al/H-isotope interactions and guide accelerated testing. A continuum level model capable of capturing aging of the material does not exist. Such a model requires a fundamental understanding, at the atomistic level, of H-isotope interactions with Al-metal/oxide surfaces and crystalline defects (e.g., dislocations, precipitates). This work focuses on H interacting with binary Al-Cu containing a surface oxide. Copper is a common alloying element in Al-alloys and is the primary source of strengthening in candidate alloys such as Al2219. First, we are developing the first-ever chemical-reaction-simulation-enabling high fidelity ternary bond-order-potential (BOP). The fidelity of the BOP is achieved by extensively benchmarking with high quality density function theory calculations and then validating with experiments. The BOP is then used in molecular dynamics and Monte Carlo simulations to study atom trapping energies and absorption mechanisms. Second, we are developing a defect dynamics model, informed from atomistics and experiments, to study effects of hydrogen and precipitates on the motion of dislocations within the binary system. In addition, the corresponding experiments to explore H on alloy surfaces and trapping in Al-Cu will both be firsts in the field.

Summary of Accomplishments:

This work has resulted in a new high-fidelity bond-order potential for Al-Cu-H. This potential is the only available potential to correctly capture the Al-rich portion of the phase diagram. Additionally, this potential correctly captures the complex nature of the chemistry involved with molecular and atomic hydrogen. New advances were made in the modeling of line defects (dislocations), responsible for plastic behavior, and precipitates, responsible for material hardening. These advances were made for the discrete dislocation code ParaDiS. The advances include new geometries to more realistically represent Cu precipitates and new algorithms to detect the collision of a dislocation and a precipitate. Simulations were performed incorporating information from three different length and time scales (density functional theory, molecular dynamics, and dislocation dynamics) to understand the mechanical response of a realistic alloy material, demonstrating the power of a hierarchical multiscale-modeling framework. Additional advances were made through low energy ion scattering (LEIS) experiments to explore H adsorption on alloy surfaces. These studies revealed that the low energy adatom location is the hollow site on a (100) Al surface. Also, these studies showed modest increases of adsorption on alloy surfaces. This work has established a path for looking at additional surface conditions such as oxides. Trapping of H in bulk materials was also explored using thermal desorption spectroscopy. This study showed that the presence of Cu introduces an additional trap location for H. This additional trap results in an increase in potential H concentrations within the material.

Significance:

This work has advanced modeling capabilities for Sandia. This BOP is now readily available through the public release of LAMMPS (molecular dynamics software). This study has advanced the tools for studying the interactions of H with Al-alloys (AA2219) and is expected to answer many questions relevant to long time exposure of oxidized alloys. Additionally, this work has potential impact in the energy and transportation fields and could answer questions about corrosion for Al structural materials.

Refereed Communications:

X.W. Zhou, D.K. Ward, M. Foster, and J.A. Zimmerman, "An Analytical Bond-Order Potential for the Copper-Hydrogen Binary System," *Journal of Material Science*, vol. 50, pp. 2859-2875, April 2015.

Welding of Advanced Shape Memory Alloys

173188 | Year 2 of 2 | **Principal Investigator: J. Rodelas**

Project Purpose:

Shape memory alloys (SMAs) represent a group of metallic materials with the ability to be deformed and then returned to original shape after heating above a specific temperature. Conventional SMAs such as Nitinol used in arterial stents, eyeglass frames, orthodontic wire, etc., change shape at relatively low temperatures (e.g., <100 °C). Applications in which materials operate at temperatures >100 °C require the use of more complex high temperature shape memory alloys (HTSMAs) including Ni-Ti-Hf/Pt/Pd alloys currently under development at Sandia.

Eventual SMA/HTSMA application in nuclear weapons (NW) safety and surety components, as well as for aerospace, energy, or other applications, requires joining. However, a fundamental understanding of SMA/HTSMA weld microstructural evolution is lacking despite promising avenues for application. Nonequilibrium melting and solidification associated with welding destroys the highly engineered starting microstructure and can result in diminished or elimination of shape memory effect, loss of mechanical properties, and/or formation of cracks. This project will develop a fundamental, science-based understanding of the solidification behavior and solid state microstructural evolution in simple binary systems to enable successful SMA/HTSMA joining.

The research represents a first-of-kind study of the weld solidification behavior and weld microstructural evolution of binary SMAs and ternary HTSMAs that will serve as the scientific foundation for development of kinetic (i.e., process) and compositional techniques for weld microstructural control. This research aims to characterize weld microstructure/property relationships using highly dynamic thermomechanical simulation and advanced electron microscopic techniques. Ultimately, the science-based tools developed for the weld microstructure control will be of use not only for joining, but also for other SMA/HTSMA melt process fabrication techniques.

This project will develop a fundamental, scientific understanding of SMA/HTSMA weld metallurgy including solute redistribution, solidification path and solid state reactions. Understanding these metallurgical factors is the foundation of robust weld technique development. Very few studies exist on welding metallurgy of these alloys so it represents fertile ground for LDRD. Ultimately, tools developed can be applied to other difficult-to-join alloy systems.

Summary of Accomplishments:

In this project, we gained insight into the fundamental metallurgical reactions that control the weldability of shape memory and high-temperature shape memory alloys (SMA, HTSMA). With university partners, we utilized a novel casting technique that simulated the complex thermomechanical conditions experienced during weld solidification. This testing produced a first-ever ranking assessment of weld solidification cracking susceptibility for HTSMAs, as well as conventional binary Ni-Ti SMAs. It was found that most HTSMA compositions based on the Ni-Ti-Hf and Ni-Ti-Pd system were highly solidification crack susceptible relative to binary Ni-Ti and other primary austenite solidifying alloys tested. Moreover, it was found that Ni-rich HTSMA and binary SMA compositions were more resistant to solidification cracks compared to Ti-rich compositions. Computational thermodynamic analysis combined with microstructural analysis of cast samples and autogenous laser welds suggests Ni-rich HTSMA/SMA compositions possess increased crack resistance due to decreased solidification temperature range (i.e., decreased brittle temperature range). Thermomechanical physical simulation was also used to assess heat affected zone (HAZ) crack susceptibility using a simplified model binary Ni-Ti SMA system. For a range of compositions about equiatomic NiTi, the hot ductility response was measured both on heating and cooling to make an assessment of crack susceptible regions in weld HAZs. Both fractographic and microstructural analyses were used to understand fracture-controlling features in HAZ test samples above the effective solidus temperature. This work resulted in the successful identification of temperature-dependent 'ductility-dip' behavior for Ni-Ti SMAs. Similar behavior is expected for substituted NiTiX ternary HTSMAs. This insight for both the weld metal and HAZ will help designers of components using welded HTSMA/SMAs select weld process conditions and base metal alloy compositions with more robust weld solidification behavior and HAZ thermomechanical characteristics.

Significance:

Advanced shape memory alloys represent a class of difficult-to-join, ordered intermetallic alloys that are of particular interest to Sandia. Welding of these materials has not been explored until this work. This work developed the tools and technical expertise to examine the weldability of alloys unavailable in conventional product forms through the use of specially developed casting techniques and physical simulation of simplified binary alloy model systems. These tools build upon fundamental welding research capabilities at Sandia and can be applied to other difficult-to-join alloys used in Sandia-relevant systems.

Refereed Communications:

J. Rodelas, "Weldability of High-Temperature Shape Memory Alloys," presented at the Joining of Advanced and Specialty Materials (JASM XVI), *Materials Science & Technology 2014*, Pittsburgh, PA, 2014.

J. Rodelas and B. Alexandrov, "An Assessment of High-Temperature Shape Memory Alloy Weldability," presented at the Special Symposium on Advances in *Weldability and Welding Metallurgy Honoring Prof. John Lippold, FABTECH: American Welding Society Professional Program 2015*, Chicago, IL, 2015.

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Grand Challenges

Grand Challenges are bold, game-changing ideas with the potential for enormous impact to the security of the nation through significant advances in science and engineering. Grand Challenge projects are expected to drive the future of Sandia by providing new directions, capabilities, and solutions and to provide long-term impact to multiple programs. These projects result in a long-term ST&E legacy for Sandia from breakthrough scientific discoveries through development of unique and differentiating technical capabilities. These projects are multimillion dollars in size and utilize multidisciplinary teams, often including external collaborators.

Projects

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Hardware Acceleration of Adaptive Neural Algorithms for Dynamic and Intelligent Threat Detection

180885 | Year 1 of 3 | **Principal Investigator: C. D. James**

Project Purpose:

Modern threats to national security are increasingly difficult to detect. They emerge rapidly, and once active, they engage in evasive behavior to avoid detection. These types of time dynamics are very difficult to detect given that human analysts cannot handle large volumes of data and automated techniques require time and power-consuming training to be effective. These factors make the current detection technologies slow to adapt to new threats and threats that evolve over time. We will develop a data analysis platform that uses neural-inspired algorithms and hardware to rapidly identify, learn, and track the evolution of threats—Hardware Acceleration of Adaptive Neural Algorithms (HAANA). Neural-inspired algorithms are well suited for unsupervised feature extraction from training data (no prior labeling of threats signatures by an expert), thus we will use these algorithms to detect threat signatures in the highly dynamic cybersecurity and physical target tracking (video analysis) arenas. We will also use a neural-inspired streaming architecture to speed up data processing, and we will use a crossbar array to speed up learning. Modeling/emulation will be conducted to evaluate the performance of HAANA, and we will benchmark the performance using objective metrics including classification accuracy and time-to-detect. After performing simulation work, HAANA will be implemented into hardware using field programmable gate array (FPGA) technology for the stream processing component and a nanoionic resistive memory (NRM)-based crossbar array for the learning component. This technology will provide a fast, low-power, small-footprint module for embedded system applications in cybersecurity and physical target tracking.

New Capabilities for Hostile Environments

173104 | Year 2 of 3 **| Principal Investigator: P. J. Griffin**

Project Purpose:

The purpose of this project is to develop new physical simulation capabilities in order to support the qualification of nonnuclear weapon components in hostile radiation environments. The project contributes directly to the goals of maintaining a safe, secure, and effective US nuclear stockpile, maintaining strategic deterrence at lower nuclear force levels, extending the life of the nuclear deterrent capability, and to be ready for technological surprise.

We will develop fast neutron and warm x-ray sources and provide radiation effects testing environments on the Z Pulsed Power Facility that will fill gaps in presently available experimental capabilities at fluences and spectra of interest and over object sizes of interest to stockpile qualification. These new capabilities will enable the stockpile modernization program to take advantage of risk-informed tradeoffs between margin, cost, schedule, and hardness for the design and qualification of advanced technologies.

Our planned technical path leverages the advances made in our understanding of the physics and performance of classified z-pinch targets over the last six years. Development of the sources requires the use of innovative ways to increase the delivery of current to z-pinches, further advances in the target design of warm x-ray and neutron sources, and development of an innovative scientific and engineering basis to safely use tritium on the Z Facility. Equally important, we must develop warm x-ray and fast neutron science platforms on Z that allow the fielding and diagnosis of powered and actively probed circuits during Z operation.

This project utilizes a dual-pronged approach to develop experimental platforms and innovative neutron and x-ray sources that will bridge present and forecasted gaps in nuclear weapons mission space. We will significantly enhance our capability through iterative development cycles of theory, simulation and design coupled with experiments on Z to validate innovative source designs, and development and fabrication coupled with experiments on Z to validate experimental configurations and advanced diagnostics.

Pattern ANalytics to Support High-Performance Exploitation and Reasoning (PANTHER)

165535 | Year 3 of 3 | **Principal Investigator: K. R. Czuchlewski**

Project Purpose:

Sandia has approached the analysis of big datasets with an integrated methodology that uses computer science, image processing, and human factors to exploit critical patterns and relationships in large datasets despite the variety and rapidity of information. The work is part of a three-year Grand Challenge called PANTHER (Pattern ANalytics To support High-Performance Exploitation and Reasoning). To maximize data analysis capability, Sandia pursued scientific advances across three key technical domains: 1) geospatial-temporal feature extraction via image segmentation and classification, 2) geospatial-temporal analysis capabilities tailored to identify and process new signatures more efficiently, and 3) domain-relevant models of human perception and cognition informing the design of analytic systems.

Our integrated results include advances in geographical information systems (GIS) in which we discover activity patterns in noisy, spatial-temporal datasets using geospatial-temporal semantic graphs. We employed computational geometry and machine learning to allow us to extract and predict spatial-temporal patterns and outliers from large aircraft and maritime trajectory datasets. We automatically extracted static and ephemeral features from real, noisy synthetic aperture radar imagery for ingestion into a geospatial-temporal semantic graph. We worked with analysts and investigated analytic workflows to: 1) determine how experiential knowledge evolves and is deployed in high-demand, high-throughput visual search workflows and 2) better understand visual search performance and attention.

Through PANTHER, Sandia's fundamental rethinking of key aspects of geospatial data analysis permits the extraction of much richer information from large amounts of data. The project results enable analysts to examine mountains of historical and current data that would otherwise go untouched, while also gaining meaningful, measurable, and defensible insights into overlooked relationships and patterns. The capability is directly relevant to the nation's nonproliferation remote-sensing activities and has broad national security applications for military and intelligence-gathering organizations.

Summary of Accomplishments:

PANTHER developed new methods for spatial-temporal data analysis and focused on geospatial data because a large proportion of national security data includes geospatial and temporal attributes. Research focused on two themes: 1) rethinking traditional GIS and 2) analyzing trajectories. A distinguishing aspect of this work is elevating the ability of national security analysts to discover and disambiguate threat patterns in large spatial-temporally tagged datasets. We made significant advances in several enabling capabilities:

- sensor exploitation of synthetic aperture radar data
- conveying search confidence with noisy or uncertain data
- understanding visual search workflows

The key insight on GIS was to leverage geospatial-temporal semantic graphs to provide a compact, flexible representation that supported advanced search. This research demonstrated the ability to populate geospatial-temporal semantic graphs with image-derived, geo- and time-tagged features from multiple data sources (including synthetic aperture radar [SAR]-derived products); developed search techniques that can find novel relationships in geospatial data; and accurately captured the structure in different types of geospatial data.

Trajectory analysis supports the analysis of patterns in motion in a very flexible manner and demonstrated a novel geometric and temporal representation for trajectories that enabled the fastest known trajectory comparison algorithms, the discovery of spatial-temporal relationships in trajectory data sets, and performed a one-to-many comparison on large-scale data sets (gigabytes of tracks).

Sensor exploitation, visual search, and uncertainty analysis are enabling capabilities that require and support spatial-temporal data analysis. Research:

- validated efficient algorithms that extract static and ephemeral features from SAR imagery for activity analysis
- elicited analytic knowledge through work domain and task studies for national security and high consequence decision workflows
- developed experimental studies of visual search and visual attention that provided new insights into visual processing for national security data sets
- adapted trajectory analytics to provide novel capabilities for analyzing eye tracking data

Significance:
PANTHER's technical accomplishments have led to new avenues of inquiry, new internally and externally funded research and development efforts, and funding to transition PANTHER technology to operational systems. The technical scope of the work has grown as the reach of PANTHER technology has extended beyond defense and intelligence stakeholders.

PANTHER fostered an emerging internal data science community and academic partnerships with SUNY Stony Brook, Colorado State University, Utah State University, University of Illinois at Urbana-Champaign, and University of Vermont. Further, we deepened our collaborations with other DOE Laboratories: LANL, LLNL, and NETL via ongoing nuclear nonproliferation work and through proposed R&D.

Refereed Communications:
R. Brost, W. McLendon, O. Parekh, M.D. Rintoul, D. Strip, and D. Woodbridge, "A Computational Framework for Ontologically Storing and Analyzing Very Large Overhead Image Sets," presented at the 3rd *ACM SIGSPATIAL International Workshop on Analytics for Big Geospatial Data (BigSpatial)*, Dallas, TX, 2014.

M.J. Haass, L.E. Matzen, T. Bauer, and L. McNamara, "Assessing User Interactions with Information: Applying the Normalized Compression Distance Metric to Log File Analysis," presented at the 17th *International Conference on Human-Computer Interaction*, Los Angeles, CA, 2015.

M.J. Haass, L.E. Matzen, L.A. McNamara, and K.R. Czuchlewski, "Top-Sown Saliency Estimation for Advanced Imaging Scenes using Pixel Statistics," presented at the *European Conference on Eye Movements (ECEM15)*, Vienna, Austria, 2015.

L.E. Matzen, "Effects of Professional Visual Search Experience on Domain-General and Domain-Specific Cognition," presented at the 17th *International Conference on Human-Computer Interaction*, Los Angeles, CA, 2015.

L. E. Matzen et al., "Effects of Professional Visual Search Experience on Domain-General Visual Search Tasks," presented at the *European Conference on Eye Movements* (ECEM15), Vienna, Austria, 2015.

L.A. McNamara, K.S. Cole, S.M. Stevens-Adams, et al., "Ethnographic Methods for Experimental Design: Case Studies in Visual Search," presented at the 17th *International Conference on Human-Computer Interaction*, Los Angeles, CA, 2015.

L.A. McNamara, D.J. Stracuzzi, and K.R. Czuchlewski, "Challenges in Eye Tracking Data Analysis: From the Laboratory to the Wild World of Information," presented at the *European Conference on Eye Movements* (ECEM'15), Vienna, Austria, 2015.

R.M. Steinbach, M.W. Koch, M.M. Moya, and J. Goold, "Building Detection in SAR Imagery," presented at the *SPIE Defense, Security, and Sensing Conference*, Baltimore, MD, 2015.

D.J. Stracuzzi, R.C. Brost, C.A. Phillips, D.G. Robinson, A.G. Wilson, and D. Woodbridge, "Computing Quality Scores and Uncertainty for Approximate Pattern Matching," *Statistical Analysis and Data Mining*, vol. 8, pp. 340-352, September 2015.

D.J. Stracuzzi, A. Speed, A.R. Silva, M.J. Haass, and D. Trumbo, "Exploratory Analysis of Visual Search Data," presented at the *17th International Conference on Human-Computer Interaction*, Los Angeles, CA, 2015.

Revolutionary SWaP Capability from Ultra-Wide-Bandgap Power Electronics

180884 | Year 1 of 3 | **Principal Investigator: R. Kaplar**

Project Purpose:

The purpose of this project is to create and demonstrate new approaches to improve the Size, Weight, and Power (SWaP) characteristics of power conversion systems, and to demonstrate their robustness in harsh environments. This is a critical need broadly crosscutting federal mission areas in both the civilian and defense sectors. To this end, this project is developing the next generation of materials and power switching devices based on ultra-wide-bandgap (UWBG) semiconductors, leapfrogging current power electronics technology. In so doing, it will enable orders-of-magnitude SWaP advances in power conversion systems across multiple Sandia mission areas for decades to come. The project consists of four complimentary and integrated thrusts: 1) UWBG materials development, focused primarily on epitaxial growth; 2) novel design and fabrication methods for high-power UWBG devices; 3) understanding and eliminating defects that degrade performance and reliability; and 4) characterizing device performance in power conversion environments, and prototyping novel demonstrations for exemplar application needs. The four thrusts are integrated through the common vision of developing two specific categories of power devices, vertical and lateral, both of which will exceed today's state of the art in terms of specific quantitative metrics such as breakdown voltage, on-resistance, and switching time. The development of each type of device requires coordinated expertise from each of the four thrust areas. Our approach is science-based, whereby fundamental physical understanding rooted in experiments, theory, and simulation is leveraged to provide a long-term foundation for high performance and high reliability power semiconductor devices. Sandia's enduring world-class expertise in wide-bandgap materials excellently positions us to overcome the challenges in developing this next generation of power semiconductors. Ongoing collaborations with select government, industry, and university partners are extending our capabilities and providing potential follow-on opportunities. We are revolutionizing the state of the art in power electronics, establishing Sandia as the undisputed technology leader in this area of increasing national importance.

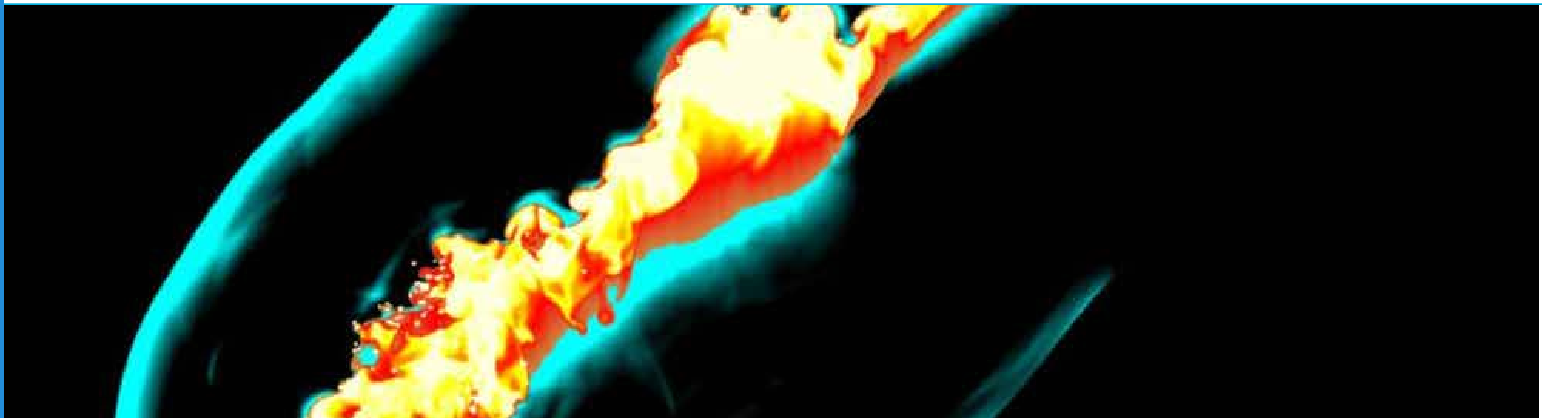
Sandia Enabled Communications and Authentication Network using Quantum Key Distribution (SECANT QKD)

173103 | Year 2 of 3 | **Principal Investigator: R. Camacho**

Project Purpose:
This project addresses the challenge of securing communication networks against increasingly sophisticated cyber attacks via a microsystems-enabled communications environment with theoretic unconditional information security using a radically new approach to quantum key distribution (QKD). This technology, if successful, could dramatically change the landscape of cybersecurity and mitigate technology surprise. Currently, communications security relies on widely accepted (though never proven) beliefs in the difficulty of solving certain mathematical problems and requires authentication by trusted third parties. In contrast, the SECANT project uses the laws of quantum mechanics to enable a network of authorized parties to authenticate users directly and establish secret cryptographic keys. All current QKD systems rely on bulky tabletop apparatus and require central trusted nodes for network operation. Through this project, we will address major scientific challenges in chip-scale quantum optics to integrate a full QKD system on a chip.

Addressing these challenges requires leveraging leading-edge capabilities across Sandia. For example, developing multiplexed chip-scale single-photon detectors (one of many QKD components) requires several innovations, substantial microfabrication equipment, and years of expertise in materials, semiconductor, and quantum science. The entire effort will also require state-of-the-art expertise in integrated silicon photonics, fiber lasers, quantum sources, optical communications, and cryptography.

Chip-scale quantum transceivers will displace current QKD systems and potentially transform secure communications. If successful, this project will establish a critical intellectual property portfolio for Sandia with major commercial and national security importance, and serve as a national resource for secure communications research.



Exploratory Express

The Exploratory Express Investment Area provides a mechanism for maturation and testing of a novel idea that has potential to become very important for one of Sandia's strategic missions. This Investment Area was initiated to provide a vehicle to explore novel ideas that are generated by researchers spontaneously through the year rather than in response to a specific proposal call. Proposals may be submitted throughout the year with the selection of funded projects occurring approximately monthly. A small amount of funding (≤ $50K) is provided to Exploratory Express projects over a period of no more than a few months to address one critical question as the basis for determining whether the idea is desirable for Sandia to pursue more thoroughly to mature its strategic importance for Sandia's national security missions.

Projects

10x Power Capture Increase from Multi-Frequency Nonlinear Dynamic Sources

188720 | Year 1 of 1 | **Principal Investigator: D. G. Wilson**

Project Purpose:

Existing energy capture technology for waves is inadequate for self-powering of desired remote sensing and increased energized payloads for military applications. Our goal is to increase the power/energy capture from multi-frequency nonlinear dynamic sources by a factor of 10 or greater. Our focus will be a wave energy converter (WEC) and will be achieved by: 1) capitalizing on the resonance of the system over a broad range of frequency spectrum and 2) by leveraging the nonlinear hydro coupling in the control design between multiple degrees of freedom (DOF). This will be a disruptive advancement of existing state of the art (SOA), which currently works at a single frequency chosen specifically for a given wave site and resistive control that is proportional to velocity feedback. Current SOA for the industrial community has been to isolate the heave DOF for energy/power capture while de-emphasizing the coupling with surge and pitch with notch filtering. This has resulted in WEC device failures. Our approach will be to design a controller for this model that resonates in the heave DOF and through parametric excitation in stiffness, coupled with the surge and pitch DOFs to more effectively capture the wave energy. The control design for the remaining DOFs will determine the optimum parametric stiffness and parametric frequency, obtained by using Den Hartog's optimality, to increase the resonating frequency capture bandwidth and, thus, to maximize the peak power.

Summary of Accomplishments:

This research has demonstrated a greater than 10x performance increase in wave energy capture technology for self-powering of desired remote sensing and increased energized payloads for military and commercial applications. By shaping the geometry and reducing the size of the device, the off-resonance energy/power capture of the longer waves produce larger increases in performance. During this research, we: 1) achieved improved models that captured detailed nonlinear coupling terms between the device and the hydrodynamics, 2) developed a multi-DOF controller methodology that has the potential to capture additional energy/power from the nonlinear wave coupling inputs, and 3) demonstrated through analysis/numerical simulations with only a single DOF heave nonlinear controller and various geometry designs, additional power capture ranging from 10x to 35x as a function of wave period (5-10 seconds). These increases in power capture are with respect to the SOA linear resistive controls for the given wave energy spectrum. Both symmetric (sphere, fishing bobber) and asymmetric (cone, golf tee) devices were investigated, which led to different nonlinear coupling terms that became significant and contributed as power multiplying factors. In addition, detailed power electronics models calibrated with experimental data and motor/generator models were developed that captured the efficiency in the power train. The power train efficiency was approximately 75% and will not impact the increases in power capture with the new controller designs.

Significance:

Sandia is a recognized leader in the design of control architectures for renewable energy applications. Through the development of advanced control architectures, our research has enabled high performance energy/power capture for remote sensing applications with increased power density. The focus of this work has expanded our capabilities in remote sensing performance mission space within the DoD. This research has developed new control methodologies that will significantly impact increases in renewable energy penetration and reduce use of carbon-based energy to help evolve the future US power grid and renewable energy portfolio, which are all major DoD/DOE missions.

A High-Voltage Cathode for Thermal Batteries

185271 | Year 1 of 1 | **Principal Investigator: W. A. Averill**

Project Purpose:

Current thermal battery cells use lithium-silicon (Li-Si) alloy anodes and iron disulfide cathodes (FeS_2) with a cell voltage of 1.9. Since the anode is fixed by the thermal battery-operating envelope, the only option for increasing cell voltage lies with the cathode chemistry. Several attempts to use cathode materials that have higher voltage potentials and have been demonstrated in room temperature (20-25 °Celsius) systems have all failed due to chemical instability at the higher operating temperatures of thermal batteries (350-500 °Celsius). Vanadium pentoxide is stable at these higher temperatures, but it is an electrical insulator and requires a conductive binder to be practical in a thermal battery system. Several attempts to develop such a binder have failed due to binder-cathode incompatibilities. This project depends upon a conductive binder that is impervious to vanadium pentoxide reaction, and has been used for applications (other than batteries) at elevated temperatures. Furthermore, thermochemical modeling predicts that this binder is stable with respect to vanadium pentoxide and the molten salts used in the thermal battery separators at these elevated temperatures. Should this project develop to a successful conclusion, there would be a 40% reduction in the volume of thermal batteries in current application along with 40% fewer components, interfaces, and parasitic impedances.

Summary of Accomplishments:

A high voltage cathode material for thermal batteries was developed using a new electrochemical system. This chemistry is capable of producing cell voltage of 3.1 or higher depending upon operating temperature. The data indicated that an open-circuit voltage of 3.7 volts is generated experimentally but has a short life at a 100mA load current. We demonstrated that the open circuit voltage was stable for six hours at temperature—indicating that there are no significant side reactions in this system. The recovery of voltage to the former level of 3.7 indicates that the short life is not related to capacity, but rather to high cathode impedance. This may be addressed with increased concentrations of binder.

Significance:

This electrochemical system for thermal batteries will enable a 45% reduction in thermal batteries with the same application parameters as that currently deployed. In addition, using alternative separator chemistries, a 30% reduction in external operating temperature of the battery will increase the flexibility of application for this battery in weapon systems.

Bulk Consolidation of Thermodynamically Stable Nanocrystalline Metal Alloys via Cold Spray

180934 | Year 1 of 1 | **Principal Investigator: A. C. Hall**

Project Purpose:

Nanocrystalline metals (NCMs) exhibit exceptional properties making them attractive engineering materials. The obstacle preventing their use is inherent thermodynamic instability of nanoscale structures. In 2012, researchers at MIT discovered a new class of binary metals exhibiting intrinsic thermodynamic stability. High temperature (>1000 °C) stability of these NCMs was demonstrated using unconsolidated powders. We propose to produce the first bulk thermodynamically stable NCMs through solid-state consolidation using cold spray.

The key scientific question we will answer is: Does the grain boundary decoration, thought to be responsible for thermodynamic stability in NCMs, remain after solid-state consolidation? Confirming grain boundary decoration in particle-particle bond regions will provide evidence of a thermodynamically stable nanostructure after particle-particle bonding. This evidence is critical to relating the properties of bulk NCMs to the measured properties of NCM powders. High temperature exposures will be used to confirm the microstructural findings.

The primary technical challenge is preparing a free flowing, thermodynamically stable, NCM powder. Cryogenic ball milling, a proven technique, will be used. Powder consolidation using cold spray is high risk. Other NCMs (not thermodynamically stable) have been consolidated using cold spray. Preparing a bulk thermodynamically stable NCM sample using cold spray is significant because cold spray can be extended for 3D printing. Thus, this work would not only enable study of bulk thermodynamically stable NCMs but would also prove a pathway to manufacturing components from these extraordinary materials.

Consolidation of a thermodynamically stable NCM has never been attempted using cold spray. It is a fundamental step necessary to study NCM properties and prove feasibility of NCM manufacturing.

Summary of Accomplishments:

Nanocrystalline copper-tantalum powders were prepared by cryomilling and were consolidated successfully using cold spray deposition. Consolidation using cold spray did preserve the nanocrystalline structure present in the cryomilled copper-tantalum powders. This experiment was motivated by recent reports that nanocrystalline copper-tantalum powders prepared by cryomilling are thermodynamically stable. Importantly, thermodynamically stable copper-tantalum powders, prepared elsewhere by cryomilling, contained a dispersion of tantalum atomic clusters in a nanocrystalline copper structure. This dispersion is thought to be key to thermodynamic stability of nanocrystalline copper-tantalum. Microstructural analysis of copper-tantalum cryomilled powders and cold spray deposits showed that this dispersion was not achieved. However, despite the lack of atomic tantalum dispersion in copper, these initial experiments clearly demonstrated that solid-state consolidation of nanocrystalline copper-tantalum mixtures is possible without compromising the mixture's nanostructure using cold spray.

Significance:

The data generated through this project demonstrates a likely pathway to solid-state consolidation of thermodynamically stable nanocrystalline metals. To date, no successful consolidation process for these interesting new materials has been reported. Thus, these experiments, while not fully solving the problem, demonstrate that it is likely solvable. Furthermore, they point to a method for additive manufacturing using nanostructured metals.

Can Asteroid Airbursts Cause Dangerous Tsunami?

184520 | Year 1 of 1 | **Principal Investigator: M. B. Boslough**

Project Purpose:

One of the most widely reported conclusions from our previous airburst modeling (see Nature, 2013) was that previous risk assessments might have significantly underestimated airbursts. In 2014, NNSA identified asteroids as a national security issue. There are two reasons for upgrading the risk: 1) most airbursts deliver more energy to the ground than a nuclear explosion of the same yield and 2) there is a higher flux of small but dangerous asteroids than previously thought. A third reason has never been tested: under some conditions, airbursts can couple energy directly into ocean tsunami much more efficiently than surface impacts can. This project would, for the first time, couple the output of an airburst simulation to the input of a tsunami model to address that question.

The primary goal is to perform proof-of-principle simulations to determine whether or not the downward momentum from an inclined airburst can couple energy into a dangerous tsunami in deep water. Specifically, we will use CTH to generate source functions for various airburst scenarios. CTH is a multi-material, large deformation, strong shock wave, solid mechanics code developed at Sandia. There are at least five different shallow-water models that can be used to simulate the resulting tsunami, either at Sandia or with external collaborators.

Up until the last year, all our well-documented measurements of large (kiloton to megaton-scale) airbursts were cold-war-era atmospheric tests. Our risk assessments for asteroid airbursts have always been based on the effects of nuclear weapons, which have no upward-directed plume and, therefore, no downward reaction force that can couple to a tsunami. We now know, based on Sandia's models of Shoemaker-Levy 9, Tunguska, and now Chelyabinsk, that asteroid airbursts are fundamentally different. We will improve the risk assessment by including the airburst/tsunami component, which has never before been considered.

Summary of Accomplishments:

A series of high-resolution hydrocode simulations were performed to generate "source functions" for tsunami simulations as part of a proof-of-principle effort to determine whether or not the downward momentum from an asteroid airburst can couple energy into a dangerous tsunami in deep water. New CTH simulations show enhanced momentum multiplication relative to a nuclear explosion of the same yield. Extensive sensitivity and convergence analyses demonstrate that results are robust and repeatable for simulations with sufficiently high resolution using adaptive mesh refinement. Surface overpressure and wind velocity fields were provided to tsunami modelers to use as time-dependent boundary conditions and to test the hypothesis that this mechanism can enhance the strength of the resulting shallow-water wave. The enhanced momentum result suggests that coupling from an over-water plume-forming airburst could be a more efficient tsunami source mechanism than a collapsing impact cavity or direct air blast alone, but not necessarily due to the originally-proposed mechanism. This result has significant implications for asteroid impact risk assessment and airburst-generated tsunami. Analysis of the simulations performed for this project support a modified version of the original hypothesis, that asteroid airbursts can generate tsunami waves without an actual surface impact.

Significance:

NNSA is now treating asteroids as a serious national security issue and this work represents a direct contribution to risk assessment that forms the basis for cost-benefit analysis, which informs policy decisions. NNSA's primary interest is the potential need for nuclear deflection of an asteroid as a means of threat mitigation. The decisions on whether or not to maintain weapons in the stockpile for this potential use comes from the risk analysis based on the work of this and related projects.

Creating Physically Based Three-Dimensional Microstructures: Bridging Phase Field and Crystal Plasticity Models

185053 | Year 1 of 1 | **Principal Investigator: C. C. Battaile**

Project Purpose:

Before the completion of this project, our capabilities to perform large-scale continuum simulations with microstructure fidelity were hindered by a lack of technology to model realistic 3D microstructures using finite elements. Most finite element based polycrystalline models use idealized grain shapes or Voronoi tessellations, 3D microstructures digitized from experiments that conform to a uniform grid. This project will address the need for a technique to create physically based 3D microstructures in order to enable realistic, large-scale, 3D simulations of microstructure mechanics.

The development of this new capability for creating finite element meshes of complex, interconnected topologies has been an ongoing area of research, and collaboration with materials science subject matter experts has historically been underexploited. As such, this project involved research in order to create a new capability to enable future technology for simulating mesoscale mechanical deformation.

Summary of Accomplishments:

This project successfully addressed the need for a technique to create physically based 3D microstructures in order to enable realistic, large-scale, 3D simulations of microstructure mechanics. This project successfully developed the technology required to interface SCUPLT, a grid-based approach to creating a volumetric mesh to various types of materials microstructure models and to produce conformal finite element meshes from those input topologies. The work delivered a practical computational capability based on materials science needs and enabled more realistic engineering-scale simulations of polycrystalline metals for a variety of mission-critical applications.

Significance:

Current trends in a wide variety of technologies are pushing component miniaturization and increased realism in predictive simulations. In addition, the recent surge of interest in research for additive manufacturing has emphasized the need to model very complex microstructures. In order to better incorporate microstructures in continuum scale models, our new meshing technique delivered a practical computational capability based on materials science needs enabled by production meshing software and will enable more realistic engineering-scale simulations of polycrystalline metals for a variety of applications. Further extension of this work will anticipate fundamental materials design and synthesis of application-optimized microstructures.

Development of 3D Nanoscale H2 Evolution Catalysts

185268 | Year 1 of 1 | **Principal Investigator: T. N. Lambert**

Project Purpose:

This effort aimed to develop next-generation hydrogen (H2) evolution reaction (HER) electrocatalysts (ECs) based on nanoscale 3D networks of metal phosphides. Hydrogen is the most ubiquitous element in the universe and has the highest energy density per mass, yet it is not widely being used as a fuel source or for energy storage. High electro-catalytic activity and stability of ECs for the HER is critical for successful generation of H2 from water splitting reactions. The leading EC, platinum (Pt), has prohibitive high cost and overall rarity that precludes it from use in larger-scale widespread commercial applications. Replacing Pt with less costly ceramic materials is in support of the Critical Materials Supply concerns outlined by DOE. Current non-Pt approaches based on nanoparticle ceramics are encouraging; however, these materials require the use of binder and often-conductive carbon supports leading to poorly defined random structures with inhibited catalytic surfaces and poorer electron transport. ECs based on nanoscale 3D ceramic networks represent a promising approach to developing cost effective ECs that can operate at higher current densities with lower over potentials (i.e., higher efficiencies), while potentially avoiding the issues confronted within the use of nanoparticle based catalysts. We aimed to demonstrate that such 3D structures can be prepared facilely and that they can exhibit useful and improved activities for the HER reaction. Recently, we have developed similar 3D structures for other electrocatalytic applications; these have outperformed the commercial benchmarks, due to their unique structure, high surface area, and tunable electronic structure.

Summary of Accomplishments:

We prepared 3D nanostructured high surface area cobalt phosphide (CoP) films and tested them for their ability to act as bifunctional water splitting ECs: that is, as ECs for both the HER and the oxygen evolution reaction (OER). The CoP films compare favorably to literature HER-OER bifunctional electrocatalysts and to the commercial benchmark. Water electrolysis with CoP electrocatalysts at both the anode and cathode was demonstrated. This versatile approach has provided a simple way of preparing a new HER-OER bifunctional catalyst with high activity and an added insight of substrate selection for this class of materials.

Additionally, we also performed density functional theory (DFT) modeling in order to evaluate the surface energies of the CoP surface.

Significance:

The development of non-precious metal ECs is in support of the Critical Materials Supply concerns outlined by DOE. The new 3D ECs developed here are among the most effective bifunctional electrocatalysts prepared to date and a manuscript has been submitted detailing this scientific achievement. Replacing the benchmark precious metal group catalysts for water electrolysis with non-precious materials will allow for cost effective water electrolysis to be performed, providing H2 for various clean energy applications.

Enhanced Near-Field Radiative Heat Transfer to a Nanoantenna Coupled Direct Infrared Detector

184516 | Year 1 of 1 **| Principal Investigator: P. Davids**

Project Purpose:

We propose to measure and analyze enhanced near-field radiative heat transfer and direct conversion of infrared radiation between an AFM (atomic force microscopy) micro-heated sphere and an integrated infrared nanoantenna coupled tunnel diode detector. The enhancement of radiative heat transfer is due to near-field surface coupling of evanescent cavity modes, and we intend to demonstrate direct conversion of these coupled modes into electrical power. The experiment is performed using a thermally heated AFM sphere placed precisely above a planar nanostructured infrared detector. This represents a new development in waste heat to electrical conversion by direct rectification of radiated waste heat in the form of infrared radiation. In going to the near field, we expect large enhancement in the conversion due to evanescent coupling in addition to radiated modes.

The result of this research will be the first demonstration of active detection of enhanced near-field radiative heat transfer. This will be an unambiguous demonstration of direct infrared rectification and energy conversion and will lead to a preliminary examination of enhanced near-field radiative cooling.

Summary of Accomplishments:

We have completed the build out of a new and unique radiometric test capability: the ability to measure near- and far-field radiative heat transfer using our new vacuum microradiometry setup. This new apparatus enables us to carefully control source and receiver temperature, source emissivity, and precise distance control for exact determination of radiative heat transfer. In addition, we are currently using this capability to measure heat to electrical conversion in a novel infrared rectenna device. This experiment allows for the determination of absolute power conversion efficiency and will be instrumental in designing new thermoelectric conversion devices. We anticipate this new highly adaptable capability to be widely used to characterize new thermoelectric conversion devices and to lead to advances in fundamental understanding of heat transfer at the microscale.

Significance:

We are exploring the application of radiative energy harvesting and cooling for nuclear weapons (NW) and satellite applications. For NW, we want to examine radiative heat conversion as a potential power source. For satellite applications, we would like to use the new rectenna in cooling mode to cool electronics and recover energy in the process.

Refereed Communications:

P.S. Davids, R.L. Jarecki, A. Starbuck, D.B. Burckel, E.A. Kadlec, T. Ribaudo, E.A. Shaner, and D.W. Peters, "Infrared Rectification in a Nanoantenna-Coupled Metal-Oxide-Semiconductor Tunnel Diode," *Nature Nanotechnology*, doi:10.1038/nnano.2015.216, September 2015.

Enhancing Target Delivery and Uptake of Molecular Cargos via Viral Membrane-Fusion Proteins

180892 | Year 1 of 1 | **Principal Investigator: D. Ye**

Project Purpose:

One of the major bottlenecks in developing countermeasures of biological and chemical threats is target delivery and uptake of therapeutics to infected cells. An effect method is needed not only to lead the therapeutics to the target, but also facilitate their penetration into the infected cells. Lipid-coated nanoparticles (e.g., protocells) could be promising delivery systems if problems of target delivery and cellular uptake could be overcome. Viruses efficiently deliver their cargo via specific viral entry proteins that bind cellular receptors. Enhanced delivery and uptake of cargos can be achieved by coating protocells with functional viral membrane-fusion proteins. However, using viral entry pathways to enable protocell targeting is hindered due to complexity in producing soluble functional viral fusion proteins using conventional cell-based expression system.

Summary of Accomplishments:

A method of using cell-free protein synthesis system to generate hard-to-express viral proteins was developed. Bioinformatic analysis was used to identify full-length and truncated versions of Niaph G and F proteins. Sequences of Nipah full length G, soluble G, and full-length F were selected and cloned into suitable vector for cell-free expression. Human epithelial cells and insect cell-free systems were used to express Nipah G and F proteins. Different combinations of transcription/translation conditions were screened and optimized. Cell-free conditions were determined to generate functional Nipah G and F proteins.

Significance:

Nipah virus is a National Institute of Allergy and Infectious Disease priority pathogen. This project developed a new platform of cell-free protein production of hard-to-express Nipah viral proteins, and demonstrated the proof-of-principle that cell-free protein synthesis is capable of generating viral proteins with post-translational modifications. The successful production of functional Nipah G and F protein complex creates a technology of cell-free protein synthesis of difficult-to-express proteins from BSL-3 or BSL-4 organisms under a BSL-2 environment. Successful expression of Nipah fusion protein complex will advance the understanding of Nipah entry pathway and, therefore, the capability of adapting viral entry pathway to facilitate therapeutics cargo delivery. The success could also enhance the capability in design of antiviral strategies. The proof of principle demonstrated in this project could be applied to generate a broad spectrum of viral proteins of interest, which could generate invaluable new reagents for developing biological and chemical countermeasures.

This project aligns with DOE's scientific discovery and innovation mission and will have potential benefit to the biodefense mission of DHS and DoD.

Exchange Coupled Fe/Co/FePt Nanoparticle Magnets

185270 | Year 1 of 1 | **Principal Investigator: J. D. Watt**

Project Purpose:

Currently, the strongest permanent magnets contain rare earth elements (REE) (e.g., neodymium-iron-boride). However, due to supply concerns, there is a need to develop rare earth-free permanent magnets with superior magnetic properties.

Exchange spring magnets hold great promise for high performance permanent magnets. These materials couple a high magnetization, soft magnetic phase with a hard magnetic phase on the nanoscale, yielding a thermally stable magnet with large saturation magnetization. An exciting candidate is iron/iron-platinum (Fe/FePt) core-shell nanoparticles. When exchange coupled, Fe/FePt has been theoretically predicted to possess an energy product 150% that of REE magnets.

Despite many synthetic efforts, no Fe/FePt nanoparticles have been reported. We believe this is due to the large lattice mismatch between Fe and Pt of ~36%. FePt synthesis begins with the formation of Pt, which catalyzes the decomposition of iron precursors to form FePt. Therefore, the growth of FePt on Fe requires the initial deposition of Pt, which is unfavorable. To address this, we will use a cobalt (Co) interlayer which will act as a 'crystallographic mediator' to yield Fe/Co core-shell nanoparticles. These can then be used to grow FePt through a redox reaction to yield Fe/Co/FePt nanoparticles. By controlling the thickness of the FePt shell, we will tune the magnetic properties to achieve effective exchange coupling and approach the maximum theoretical energy product.

Our mechanistic insight described above is unique, and our proposed solution is a potentially groundbreaking advance. If achieved, this would be the first major leap in the strength of permanent magnets since the mid-1980s.

We propose a novel solution to the formation of Fe/FePt exchange coupled magnets using a metallic interlayer in the nanoparticle synthesis. We have a very good knowledge of what is known in the field. We believe that our mechanistic insight is unique, and our proposed solution a potentially groundbreaking advance, both scientifically and technologically.

Summary of Accomplishments:

This study identified new, non-volatile, iron precursors for the synthesis of zero valent iron, Fe(0) and bimetallic iron nanoparticles. Common solution phase approaches for the synthesis of Fe(0) and bimetallic iron nanoparticles include the reduction of iron salts and the thermal decomposition of iron complexes. Perhaps the most widely used approach in the literature is the thermal decomposition of iron pentacarbonyl, $Fe(CO)_5$. Iron pentacarbonyl is cheap and readily available, which makes it a popular choice for nanoparticle synthesis. However, it is highly toxic and volatile which introduces safety concerns as well as uncertainty in reaction stoichiometry. Furthermore, the formation of insoluble decomposition products under storage introduces the need for a purification step.

We developed the synthesis of well-defined Fe(0), $Fe_{1-x}Co_x$, and $Fe_{1-x}Pt_x$ nanoparticles from the nonvolatile, solid and commercially available iron precursors, triiron dodecacarbonyl ($Fe_3(CO)_{12}$) and diiron nonacarbonyl ($Fe2(CO)_9$). These compounds are stable at ambient conditions, enabling ease of handling, and are up to two thousand times less toxic than $Fe(CO)_5$. Furthermore, they can be used directly from the supplier, removing the need for purification. These precursors are most commonly employed as catalysts in organic transformations. However, they are insoluble in high boiling point organic solvents and have seen limited use as precursors for nanoparticle synthesis, despite the obvious benefits over $Fe(CO)_5$.

Here, we solved the solubility issues by using the long chain surfactant dodecylamine (DDA) to form an iron-amine complex, $Fe(CO)_x[DDA]_y$, which is fully soluble in a common high boiling point solvent (octadecene). The complex is formed by simple mixing in an inert atmosphere, removing the multiple synthetic steps that can be required for other complex nanoparticle precursors. This new complex precursor is then used in thermal decomposition reactions to form Fe(0), $Fe_{1-x}Co_x$, and $Fe_{1-x}Pt_x$ nanoparticles with the liberated DDA acting a dual role as stabilizing agent.

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Significance:

Compared to more commonly used techniques (i.e., decomposition of $Fe(CO)_5$), the use of these nonvolatile and easily handled iron precursors will allow for improved synthetic control for the formation of iron and bimetallic nanoparticles. The precursor can be applied to any synthetic method, which requires the use of a zero valent iron precursor. Furthermore, due to the increased stability the versatility of the precursor is expanded. Our new chemistry also provides safer and much less toxic methods for the synthesis of Fe and bimetallic iron nanoparticles, a significant advantage to the working chemist.

Exploring Rapid Nuclear Material Assay with a Pulsed Associated Particle Neutron Generator

180800 | Year 1 of 1 | **Principal Investigator: S. Mitra**

Project Purpose:

Sandia has recently demonstrated a pulsed associated particle type neutron generator (NG), which offers the unique opportunity to concurrently measure pre-fission inelastic gamma rays and delayed fission products for rapid assay of nuclear materials. This was hitherto not possible because commercial NGs of the associated particle type operate in the continuous mode and, to be able to measure delayed fission product signatures, the NG would need to be switched off and a separate run conducted. A digital multi-channel analyzer was customized to operate synchronously with the pulsing of the NG. The approach is based on measuring the characteristic tagged neutron-induced pre-fission inelastic gamma ray signatures during the ON state of the NG, and delayed gamma rays from fission products and other related materials of interest during the OFF state. An external gate signal is imported from the NG for recognizing its ON and OFF states. During the ON state, coincident events occurring between the alpha particle detector integrated in the neutron generator and external gamma ray detectors are captured and corresponding tagged neutron-induced gamma ray spectra are recorded. Within each OFF state, delayed gamma ray events are tagged within user-defined sub-periods and the results recorded for pulse height computation and analysis. This project enables a new capability for rapidly performing non-intrusive material assays with vastly improved signal/noise (S/N) ratios compared to conventional neutron interrogation techniques.

Summary of Accomplishments:

The customized data acquisition (DAQ) system demonstrated the benefits of employing an electronically collimated beam of tagged neutrons for active interrogation of materials. The signal/background ratios of gamma rays produced due to inelastic scattering reactions of neutrons with the material of interest are vastly improved when nanosecond wide time windows operate within the burst gate of the neutron generator. Since a continuous source of neutrons was used from a commercial associated particle type NG, the burst gate was simulated using a pulse. Experiments verified that the improvements in the S/N are related to the DAQ correctly measuring neutron time-of-flight of 14 MeV neutrons to the material being assayed. The basic firmware is now developed so that temporal gamma ray signatures that are induced by using pulsed neutron interrogation can be recorded. The custom DAQ used a 100 MHz processor allowing sampled times of 10 nanoseconds. This sampling time is inadequate for processing sub nanosecond fast rise time signals of the neutron generator's alpha particle detector. The timing lead to considerable jitter in the time pick-off of the arrival of pulses at the detector and the time resolutions are, therefore, not optimum. It is envisioned to use 250-500 MHz processors in the future.

Significance:

The active neutron interrogation technique explored in this project enables a new capability for rapidly performing non-intrusive material assays in various applications. Fast neutrons are highly penetrating and can induce characteristic prompt and delayed gamma ray signatures in shielded material. The technology explored in this work provides concurrent recording of the temporal gamma ray signatures with superior S/N compared to conventional neutron interrogation techniques.

Feasibility of Observing and Characterizing Single Ion Strikes in Microelectronic Components

184518 | Year 1 of 1 | **Principal Investigator: R. P. Dingreville**

Project Purpose:

The research objective of this project is to demonstrate the feasibility of observing and quantifying the evolution of single ion strikes in a prototypical semiconductor material, such as silicon (Si). This proposed exploratory work consist of both an experimental and modeling component. The experimental component consists of in situ transmission electron microscopy (TEM) characterization under ion irradiation conditions of a Si thin film sample during real time nanoscale observation. The modeling component consists of simulating the experimental conditions on a scale that can be directly compared to the in situ TEM experiments by using a 3D spatially resolved stochastic cluster dynamics.

The coupling between the computational modeling with microscopy observations will demonstrate the potential for predictive and interpretation capabilities beyond currently existing capabilities.

Summary of Accomplishments:

Study of defect formation in silicon after irradiation with heavy ions—we conducted in situ ion irradiation TEM experiments to characterize defect formation in silicon after irradiation with heavy ions. TEM samples were irradiated in Sandia's In Situ Ion Irradiation TEM (I3TEM) facility. Imaging during experiments was performed at higher magnifications in order to better resolve the irradiation-induced defect clusters. For different beam energies (46 keV Au1- and 1.8 MeV Au3+), defect clusters caused by single ion events were successfully resolved in the video collected in situ over long period of times (seconds to minutes), demonstrating the feasibility of observed in real-time radiation damage in prototypical semiconductors. Preliminary atomistic simulations to help with the interpretation of the experimental observations complemented this effort.

Significance:

This capability will enable Sandia and key programs in this field to gain an insight into the fundamental ion strike induced mechanisms influencing the performance degradation of electronic circuits. Research findings will provide advancement in the quantitative correlation of irradiation induced defects with microstructure in semiconductors and interconnects used within national security mission areas.

General, Physics-Based Predictive Model of Friction and Wear of Metallic Contacts

188025 | Year 1 of 1 | **Principal Investigator: N. Argibay**

Project Purpose:

The prediction of macroscale friction and wear behavior based on first principles and material properties has remained an elusive but highly desirable target for tribologists and material scientists alike. Stochastic processes (e.g., wear), statistically described parameters (e.g., surface topography), and their evolution tend to defeat attempts to establish practical general correlations between fundamental nanoscale processes and macroscale behaviors.

There is a large body of literature that describes the existence of behavioral regimes for metal contacts, characterized by differing dominant mechanisms, though the tipping points between them are highly phenomenological, remaining not well understood or predictable. We proposed to experimentally and analytically investigate the validity of a framework that correlates the various well-understood physics that describe these regimes of wear and friction, utilizing the concepts of energy transfer rates and thermo-mechanical-kinetic stability bounds to lay the foundation for a fundamentally different and novel approach of describing tribological behavior in a predictive and quantitative way.

The proposed effort will correlate a host of molecular dynamics simulations, experimental results, and analytical modeling carried out at Sandia and by the community (nearly 80 years of research) to identify the primary mechanical and thermal stability parameters that may be used to predict these transitions in behavior. This work touches on recent and ongoing cutting-edge fundamental and applied research at Sandia and by external collaborators, many published in high-impact journals including Science, to lay the groundwork for a much larger effort to develop a general model of friction and wear behavior for metals, alloys and composites.

Summary of Accomplishments:

The purpose of this project was to advance the state of the art one step closer to the highly ambitious goal of developing and demonstrating a predictive model for the friction behavior of metal contacts. We developed and validated a general model that predicts the friction behavior regimes of metal contacts, founded exclusively on materials properties and thermokinetic models of grain evolution.

The model was born out of molecular dynamics (MD) simulations, and verified using experiments and microstructural characterization. Simulations provided invaluable insight about the atomistic mechanisms for well-documented experimentally observed transitions between low and high friction as a function of stress and temperature. A new, unconventional experimental procedure was developed to investigate apparent crossovers in friction behavior predicted via atomistic simulations to occur as a response to the transition between grain boundary and dislocation mediated plasticity. Experiments successfully validated the predicted behavior for two pure metals, gold and copper.

Significance:

These findings will likely pave the way for a fundamentally new approach to the prediction of friction and wear, where nanoscale processes are directly and predictably connected to macroscale behavior. This work ties together recently published models for stress-driven grain growth with classical contact mechanics and thermodynamics models of grain growth. This work also added another facet to the literature in the form of both a predictive equation for and qualitative interpretation of the transient behavior underlying a regime of quasi-stability that has been reported for many metals in varying contact conditions.

The research performed as part of this project provided invaluable, cutting-edge insight about the fundamental performance limits of materials typically used in moving electrical components from microelectromechanical systems (MEMS) and devices to wind turbines. This work bridges the gap between basic science and engineering application as well, providing a predictive framework of friction behavior that is both useful as a design tool for engineers and a guide toward the development of superior-performing materials for researchers.

Improved Performance of NW Solenoid Alloys by Novel Processing Methods

180927 | Year 1 of 1 | **Principal Investigator: D. F. Susan**

Project Purpose:

Recent brittle failures in development tests have highlighted the previously unavoidable tradeoff between magnetic performance and mechanical properties of soft magnetic solenoid alloys such as Hiperco 50A. Forged bar material is weak (<40 ksi yield strength) and brittle (<5% elongation), and the properties are inhomogeneous across the bar diameter. A previous project explored Hiperco 50A microstructural refinement via unique cyclic heat treatment. This technique produced some microstructural refinement. Studies suggest microstructural refinement alone may not be the key to obtaining high strength (>50 ksi yield strength) with appreciable ductility (>10%). Data suggest high strength and ductility are realized because of both microstructural refinement and a unique distribution of ordered (brittle) and disordered (ductile) phases produced by plastic deformation via sheet rolling. We propose to produce the unique microstructure of sheet material in bar form using novel severe plastic deformation (SPD) equal channel angular extrusion (ECAE) to produce deformation without net shape change. ECAE represents a long-sought-after application for this process, with the age-old promise of improving both strength and ductility simultaneously, while maintaining magnetic performance as well. ECAE involves extruding a bar of material “around a corner,” thereby producing significant deformation strain without reducing the cross sectional area of the bar. Because the cross-section remains the same, a work piece can be extruded multiple times with each pass introducing additional plastic deformation.

ECAE has never before been attempted on relatively brittle magnetic alloys suitable for solenoid applications. The prospect of inducing high amounts of shear deformation in a brittle alloy presents significant research challenges. This research will determine if ECAE processing can produce improvements in alloy mechanical properties, which could open up new opportunities for solenoid designs.

Summary of Accomplishments:

The soft magnetic alloy Hiperco 50A was subjected to ECAE, a superplastic forming process, at Texas A&M University. The ECAE parameters such as temperature, extrusion route, and extrusion speed were adjusted to minimize surface cracking and optimize the mechanical properties of the material. Microstructural characterization showed that the ECAE process dramatically refined the grain size (1-3 micron range) compared to conventional Hiperco bar (>25 microns). Such microstructural refinement has previously only been possible for the alloy in sheet form. The mechanical properties of ECAE Hiperco are far superior to conventional bar. Yield strengths of 650-700 MPa (94-102 ksi) and ultimate tensile strengths of 900-1400 MPa (130-200 ksi) were achieved, which represents a two to three-fold increase in strength compared to conventional bar. And importantly, the ductility of Hiperco was also vastly improved by ECAE, with % elongation values between 15-20% for optimized ECAE samples compared to 5-7% elongation for conventional bar material. The microstructure and property improvements discovered in this work show that ECAE is a very promising technique for processing of Hiperco soft magnetic alloy for enhanced performance applications.

Significance:

The results of this work show that ECAE processing is a very promising technique for improving soft magnetic alloys used in Sandia applications. Further development of the process will open up design opportunities for our component designers in critical Sandia mission areas. In addition, several scientific questions have arisen as a result of this project. First among these is the question of enhanced ductility in FeCo-based magnetic alloys. The exact mechanism for the observed improvement in tensile ductility is unknown. Understanding this ductility enhancement mechanism would be a significant breakthrough in the metallurgy of ordered alloys. We hope to explore these questions in future efforts.

Lipid Membrane Coated Alginate Particles: Development of the Surrogate Cell

184581 | Year 1 of 1 | **Principal Investigator: D. Y. Sasaki**

Project Purpose:

A need exists for biocompatible particles that can be readily engineered to manufacture and express biomolecules on demand for applications in biofuels, in situ medicine, and pathogen mitigation. Silica-based protocells have demonstrated remarkable versatility and effectiveness as drug delivery vehicles, with other possible applications on the horizon. However, the process of forming mesoporous silica is inherently incompatible with biological activity. We propose to develop a new composite architecture that will enable entrapment of cell extracts, nanoparticles, and even whole cells, in nano-to-attoliter volume particles. Particles will be composed of alginate droplets hardened by the addition of calcium and coated with a tethered lipid bilayer. Entrapment of molecular cargo will be demonstrated with fluorescent dyes and proteins. If successful, this technology offers a readily configurable platform that can be integrated into and potentially transform a range of technologies ongoing at Sandia, including biofuels, biological warfare/chemical warfare (BW/CW) detection and decontamination, and pathogen mitigation.

We will evaluate the feasibility of the new composite surrogate cell architecture effort, establish the basic protocols and strategies for preparing the bilayer-coated materials, and gain some knowledge, experience, and credibility in this area.

Summary of Accomplishments:

The results of our work showed the successful development of a biocompatible process to form bilayer-coated calcium-alginate gel beads. These results have advanced the field in several areas: 1) biocompatible conditions towards micron-sized beads using a water-in-oil emulsion process, 2) localized functionalization of the calcium-alginate particle corona using interfacial coupling on hydrogel surfaces, and 3) bilayer coated hydrogel particles as a first step towards artificial cell constructs. One of the most questionable procedures proposed was the use of an interfacial approach to confine the tethering of lipids to the calcium-alginate's corona. Our results showed that the approach was viable and achieved under mild and facile conditions. The bilayer-coated beads we prepared were found to have a uniform coating of a single lipid bilayer. We are currently advancing our efforts to study the entrapment of proteins and evaluate the leakage rates of the bilayer-coated hydrogels. We will further develop protocols to generate nanoscale particles as delivery vehicles for proteins and biomolecular machinery for therapeutics and cell mimetic systems.

Significance:

The results of our work will be used to extend efforts in the NanoCRISPR Grand Challenge project. The bilayer-coated alginate beads will be used as a delivery vehicle for the CRISPR package to pathogen infected cells. The biocompatible process developed in the project will be used to entrap proteins and DNA and cloak the assembly in a lipid bilayer envelope. This body of work will further Sandia's effort in the Bioscience and Biodefense arena as we will continue research in these areas.

Low Temperature Exhaust Remediation Based on Metal Organic Framework Nanoparticle Hybrid Catalysts

188028 | Year 1 of 1 | **Principal Investigator: M. D. Allendorf**

Project Purpose:

Current light-duty vehicle fuel-economy regulations require >100% increase in US fleet average mpg by 2025 in mpg versus the 2008 baseline. Simultaneously, the EPA requires >70% reduction in NOx and >85% reduction in hydrocarbon emissions. These aggressive new standards are creating a strong pull for the development of new engine designs. Low-temperature combustion (LTC) is particularly promising, because both fuel efficiency and NOx emissions can be improved. Unfortunately, carbon monoxide (CO) and hydrocarbon emissions are higher for LTC, but because exhaust temperatures are also lower, existing three-way exhaust catalysts are not effective. Catalysts that operate at 150°C are needed, but achieving these is a major scientific challenge. Novel catalysts, such as metal-oxide nanoparticles (MNP), are effective at LTC exhaust temperatures, but sintering, poisoning by fuel impurities, and poor understanding of catalyst morphology impede implementation, in spite of decades of research. Consequently, an urgent need exists for novel LTC after-treatment catalysts that can enable these new fuel-economy and emission standards to be met.

The objective of this project is to obtain proof-of-concept data showing that nanoporous metal-organic frameworks (MOFs) can catalyze CO and hydrocarbon oxidation at low temperatures. MOFs are hybrid inorganic/organic materials that have multiple advantages for low-T after-treatment: unsaturated metal ions in the framework provide reactive sites that activate CO and hydrocarbon bonds, accelerate oxidation, and deactivate fuel poisons; record-high surface areas promote uptake of pollutant gases, and high thermal stability should enable operation under variable exhaust conditions.

Summary of Accomplishments:

A flow reactor was set up for testing metal-organic framework (MOF) catalysts. Selected catalysts were loaded into a quartz tube, which was then inserted into the furnace of the flow reactor. Mixtures of CO, O_2, and N_2 were delivered to the catalyst bed and gases exiting the reactor were monitored and quantified using a gas analyzer connected to the downstream end of the reaction tube. Experiments were performed in which temperature, flow rate, and oxygen concentrations were varied. We tested several MOFs already reported in the literature and the results were reproduced for two MOFs, but using a broader range of reaction conditions. The results indicate CO conversion starting at temperatures as low as 30 °C, with complete conversion occurring at 40-50 °C. Experiments using novel MOF-based catalysts were also performed; the results indicate some conversion of CO to CO_2 occurred, but higher temperatures were required than for the two previously reported catalysts. Problems were encountered concerning the distribution of MOF powder within the reaction tube. Fine powders tended to pack toward the end of the tube, which in some cases caused a pressure drop. Alternative experimental configurations were identified that should solve this problem.

Significance:

With 9 to16 million light-duty vehicles produced annually, effective catalysts for LTC engine designs could transform vehicle technology. Unfortunately, current three-way catalysts are not effective at the relatively low temperatures of the exhaust produced by LTC engines. Additional problems include the loss of catalyst activity as a result of sintering. The synthetic flexibility and wide range of known structures of novel low-temperature catalysts based on MOFs could address these issues; their potential for this application has not been explored. Our experiments suggest that additional research to explore the capabilities of these materials is warranted.

Nanoscale-Enabled Piezoelectrically Tunable Optomechanical Photonic Devices

188024 | Year 1 of 1 | **Principal Investigator: M. Eichenfield**

Project Purpose:

Aluminum nitride (AlN) is an incredibly unique material: it is one of the few piezoelectric materials that can be vapor deposited as a thin film while keeping its piezoelectric properties and it is also completely compatible with the stringent requirements of silicon semiconductor electronics microfabrication. These two properties make AlN unique in the world of microfabrication, which is why it has become an indispensable part of modern electronic components like radio frequency cellular phone filters.

We have recently demonstrated that AlN deposited on silicon can be used to make ultra-high quality factor optical resonators in films of nanoscale thickness. In particular, we demonstrated telecommunications-band whispering gallery microdisk resonators with AlN thicknesses of 200 nm and quality factors greater than 150,000, corresponding to a 1 GHz bandwidth at 195 THz center frequency. This demonstration of such narrow-band filters in a piezoelectric material opens up a novel class of piezoelectrically tunable nanophotonic devices with unique capabilities.

As a first demonstration of AlN's potential as a piezoelectrically tunable optical material, we propose to demonstrate a stacked pair of AlN microdisks with a nanoscale gap between them, sandwiched between a pair of electrodes. Split-disk optical resonators have been demonstrated in silicon dioxide and are powerful platforms for photonic routing, optomechanics, and even the study of quantum phenomena. Building this system in a piezoelectrically tunable platform adds a powerful new degree of freedom to the system, allowing both optomechanical and electrical forces to manipulate the optical properties of the system.

Summary of Accomplishments:

We demonstrated several key results through finite element method (FEM) modeling. First, we demonstrated with an optical-mechanical multiphysics model that with a 100 nm gap between the stacked disks, optomechanical tuning rates can be as large as df/ds=90 GHz/V. Second, we demonstrated with a piezoelectric-mechanical model that with a 100 nm gap, we can achieve a piezoelectric separation of the disks at a rate of ds/dV=0.35 nm/V. The product of these two gives a piezo-optic tuning rate of df/dV=df/ds*ds/dV=32 GHz/V. Given our experimental demonstration of single aluminum nitride microdisks with linewidths of 1 GHz (quality factor of 150,000), this corresponds to 32 linewidths/V. Thus, we have demonstrated the feasibility of making a telecom-band switch that can change its transmission by 30 dB with the application of just 30 mV. In addition, FEM simulations show it should be possible to achieve this performance with 100 MHz resonant frequencies, allowing 10 ns switching times. This would represent a revolutionary advancement in performance of telecom-band optical switches.

We demonstrated a novel microfabrication process for planarization of patterned electrodes with silicon dioxide. This is a crucial step for fabricating prototype devices for this project. Though we are only about 50% through the fabrication process of the complete prototype, this was the first and most significant hurdle; so we have significantly reduced the risk associated with completion of the prototypes.

Significance:

The progress on this project gives confidence that we can make telecom-band switches with 30 mV on/off voltages and 10 ns switching times. This will be a revolutionary increase in performance that decreases the time and power required to switch between data packets in optical telecommunications networks, which is to say that all data transmitted over the Internet could be impacted by this technology. This work has also added general capability in the area of aluminum nitride electromechanics since we have demonstrated the ability to make patterned bottom electrodes that are planarized with a surrounding dielectric.

PDE Constrained Digital Image Correlation

188029 | Year 1 of 1 | **Principal Investigator: D. Z. Turner**

Project Purpose:

This project proposes to address many of the common pitfalls in digital image correlation (DIC) that lead to inaccurate strain measurement. We propose to do so using partial differential equation (PDE) constrained optimization to build more information into the correlation process. The S&T problem we intend to address is calculating smooth and accurate strains given inherently noisy images.

The technical challenges to achieving this are related to solving the PDE constrained optimization system. This includes selecting an appropriate regularization term, working out the details of the discretization for the PDE constraint, solving the coupled system that includes the objective function and the constraint equations, and establishing the right boundary conditions so that the problem is well posed.

Rather than simply correlate between images based on the image intensity profile, we propose to determine the solution that best correlates the images, but also satisfies a conservation law. For example, the PDE constrained approach to DIC will give a solution that not only minimizes the correlation criteria, but also fits within the behavior of the material being imaged. This endeavor is high-risk in that there are many moving parts in the overall formulation, many of which have their own challenging complexities. There is high potential for major leaps forward in DIC based on being able to include much more information into the optimization process.

Summary of Accomplishments:

This research made considerable strides forward for DIC technology including the following accomplishments:

- Identified a robust and sensitive functional for the PDE constrained optimization approach to DIC. This is an important step required to ensure that the inverse problem has a unique solution. We conducted several numerical experiments to demonstrate this.
- Proposed a novel initialization step for the inversion process. This was a critical missing piece in prior work in this area.
- Demonstrated that the DIC problem is, in general, ill posed and proposed a regularization model that fixes the problems associated with being ill posed
- Compared the proposed formulation with existing DIC approaches via numerical examples
- The proposed regularized solution has the added benefit that it is based on well-understood technology and can be efficiently implemented

Significance:

Since DIC was invented in the 1970s, we were the first to provide a systematic mathematical analysis of why the DIC problem is ill posed and propose a solution. This will greatly improve the robustness and accuracy of the DIC work that is done at Sandia. We have established a new way of doing DIC that will become the internationally recognized standard practice.

Refereed Communications:

D.Z. Turner, “Towards DIC Methods Robust Enough to Characterize Degradation of Materials,” presented at the *US National Congress on Computational Mechanics*, San Diego, CA, 2015.

Photoelectrochemical Etching of GaN Quantum Wires

185054 | Year 1 of 1 | **Principal Investigator: A. J. Fischer**

Project Purpose:

We propose to use photoelectrochemical etching to demonstrate GaN quantum wires with a diameter of less than 10 nm. Although GaN nanowires with much larger sizes (200 nm – 2 microns) have been demonstrated by a number of techniques, quantum wires are much more difficult to realize due to the very small dimensions (<10 nm) required to enter the quantum size regime. Previous demonstrations of semiconductor quantum wires have relied on colloidal methods resulting in large size distributions or complicated regrowth on the edge of a cleaved wafer. We propose to use photoelectrochemical etching to realize GaN quantum wires. Previously, we have been able to show that this technique can be used to make InGaN quantum dots and we propose to use similar methods to realize GaN quantum wires. To our knowledge, GaN quantum wires have never been demonstrated due to growth and fabrication difficulties. Photoelectrochemical etching has also never been used to demonstrate quantum wires in any material system. If our quantum wire fabrication method is successful, it will open up a new research area centered on GaN quantum wires and related applications. Quantum wires can be used as an efficient nanoscale conduit for the transport of charge and energy and will find applications in nanoelectronics, energy harvesting (solar), nanoscale light emitters, and chem/bio sensors. This project will generate proof-of-concept demonstrations.

Summary of Accomplishments:

We have investigated photoelectrochemical (PEC) etching of GaN nanowires with the goal of demonstrating GaN quantum wires with a diameter of less than 10 nm, which would be an indication that our nanostructures have entered the quantum size regime. To date, we have demonstrated GaN nanowires with a diameter of about 30 nm, which is already an interesting and useful accomplishment. This gives us a simple method of reproducibly fabricating nanowires with very small dimensions. For these initial studies, the GaN nanowire diameter was about 30 nm when etching at both 370 nm and 355 nm. We would have expected wires with a smaller diameter when etching using a shorter PEC etch wavelength. Since the quantum size control process works for InGaN quantum dots, it is likely that we have not found the correct experimental parameters to realize PEC etched quantum wires. Specifically, we think that the PEC etching is limited by transport through a narrow diameter GaN nanowire. The PEC etch dynamics and electron transport will likely change at higher bias voltages and we think this is a particularly promising area for further investigation. With further work, we believe we will be able to show that quantum size controlled PEC etching is a viable method for fabricating quantum wires.

Significance:

Our goal is to demonstrate GaN quantum wires with a diameter of less than 10 nm. To date, we have demonstrated nanowires with diameters of about 30 nm, which is very difficult and already a significant accomplishment. We have demonstrated that photoelectrochemical etching is a viable method for making nanowires with very small diameters, which will be useful for future nanowire studies. We have also learned that etch damage can impede the PEC etch process. Further development work will almost certainly yield GaN quantum wires, as the process of quantum size control likely will extend beyond zero dimensional quantum dots.

Predictive Modeling of Selective Laser Melting Additive Manufacturing

188721 | Year 1 of 1 | **Principal Investigator: F. B. van Swol**

Project Purpose:

The quality, performance, reproducibility, and reliability of metal components created via selective laser melting (powder bed) additive manufacturing processes are complex functions of the detailed history of the underlying physical processes. In a nutshell, this constitutes an inherently multiphysics problem involving placement of the metal powder, laser heating and melting of particles, (reactive) wetting coupling interfacial chemistry with capillary flow of the melt pool and cooling and re-solidification of the new metal mixture. The final part displays compositional heterogeneity and its resulting microstructure determines the success or failure of the entire part.

We propose to provide the essential deep physics that supports mesoscale computational tools by providing the molecular level description of the nonequilibrium composition and interfacial tensions that determine the melt pool flow, thermal history, and eventual nonuniform solidification. At present, such constitutive models for additive manufacturing do not exist, and the engineering scale, mesoscale computational tools are only in development.

We will focus on the role of spatial composition on the interfacial tension and how it affects the process of dynamic wetting. The interfacial tension is a strong function of composition, as can be measured in equilibrium experiments. The challenge is to determine the nonequilibrium tension under conditions encountered in laser melting processes used in additive manufacturing, where the composition changes at the interface (about 1 to 10 nm wide).

We will develop an approach that allows one to exclusively use equilibrium data for diffusion and the interfacial tension, to predict the nonequilibrium interfacial tension. The proposed work seeks to provide the missing constitutive relationships to enable effective modeling of the additive manufacturing process. The focus is centered on the nonequilibrium nature of that which the melt pool interface shares with its surroundings.

Summary of Accomplishments:

We used equilibrium molecular dynamics simulations of a binary ideal solution mixture to calculate the wall-fluid surface free energy ("surface tension"). We used statistical mechanics of inhomogeneous fluids to formulate an ansatz about the distribution of species throughout the nanoscale interfacial region, applicable to time-dependent interfacial regions. In turn, this ansatz allowed us to define an effective bulk composition that, ultimately, facilitated the assignment of an interfacial tension.

The predictive method was developed and partially verified with the help of molecular dynamics simulation. We have provided a brief description of how one could use the continuum reaction-diffusion equation to conveniently generate predicted interfacial tensions from equilibrium thermodynamic data and bulk diffusion coefficients.

Significance:

A high-fidelity simulation capability for powder bed fusion (PBF) represents a significant advance in the ability to predict defects of parts built by additive manufacturing processes as pertained to DOE missions, including porous media flow and brazing. With a continuum level tool, one could readily impact PBF (and metal joining processes) by computationally exploring the effects of materials and processing variables such as powder size, building direction, laser scan rate, and scanning patterns. It should greatly reduce processing and manufacturing cost, and provide a scientific tool for assessing and controlling product quality.

Resolving and Measuring Diffusion in Complex Interfaces: Exploring New Capabilities

188719 | Year 1 of 1 | **Principal Investigator: T. M. Alam**

Project Purpose:

This project targeted the development of new high-resolution spectroscopic diffusion capabilities at Sandia to resolve transport processes at interfaces in heterogeneous polymer materials. In particular, the combination of high resolution magic angle spinning (HRMAS) nuclear magnetic resonance (NMR) spectroscopy with pulsed field gradient (PFG) diffusion experiments were used to directly explore interface diffusion within heterogeneous polymer composites, including measuring diffusion for individual chemical species in multi-component mixtures. Several different types of heterogeneous polymer systems were studied using these HRMAS NMR diffusion capabilities to probe the resolution limitations, determine the spatial length scales involved, and explore the general applicability to specific heterogeneous systems. The investigations pursued include: 1) the direct measurement of the diffusion for poly(dimethyl siloxane) polymer (PDMS) on nano-porous materials, 2) measurement of penetrant diffusion in additive manufactured (3D printed) processed PDMS composites, and 3) the measurement of diffusion in swollen polymers/penetrant mixtures within nanoconfined aluminum oxide membranes.

Summary of Accomplishments:

The initial results obtained under this project clearly demonstrate that the improved resolution obtained using this new HRMAS NMR spectroscopy capability does indeed allow for the measurement of diffusion of different chemical species in heterogeneous environments and surfaces. The greatest impact will be for heterogeneous polymer systems where the diffusion of multiple chemical species needs to be individually measured at the same time. These types of diffusion experimental measurements can be used to directly access and test proposed models to describe transport in complex system. As an example, the role of confinement on diffusion is not explained by simple free-volume theory, and instead must incorporate a hydrodynamic argument to correctly predict the experimental results obtained using this technique.

There were limitations to the HRMAS NMR diffusion capabilities identified during this study. The current hardware places a lower limit on the magnitude of diffusion rates that can be measured, with the current study concentrating on penetrants and low molecular weight PDMS at surfaces, which have relatively rapid diffusion rates. Diffusion experiments of rigid (highly cross-linked) polymer materials would not be possible until probes with higher gradient strengths could be manufactured. For materials that produced enhanced chemical resolution due to the material properties (i.e., nanoporous carbon), it was possible to resolve distribution of pores/surfaces on the order of hundreds on nm. On the other hand, for the silica-filled PDMS composites studies this type of chemical spectral resolution was not realized, such that the measured diffusion was a weighted average of all the local polymer environments and, thus, unable to resolve heterogeneities smaller that a μm.

In conclusion, this new characterization capability does provide the ability to measure diffusion in a wide range of heterogeneous materials and gives a novel tool to look at diffusion/transport properties in complex multi-component systems.

Significance:

The HRMAS NMR diffusion results obtained were encouraging and allowed for an improved understanding of diffusion and transport processes at the molecular level, while at the same time demonstrating that the spatial heterogeneity that can be resolved using HRMAS NMR PFG diffusion experiment must be larger than ~μm length scales, expect for polymer transport within nanoporous carbons, where additional chemical resolution improves the resolvable heterogeneous length scale to hundreds of nm.

This work demonstrated the novel HRMAS NMR PFG characterization technique to measure interface diffusion in mixed component systems. This developed capability will directly impact the characterization of both existing and future materials including polymers, composites, metal-organic frameworks, and biologically inspired materials. The demonstration also impacts national security by providing an improved understanding the role interfaces play in transport and the impact on aging or improved performance predictions in energy related materials (battery/fuel cell membranes, high strength composites), materials such as coatings and encapsulants, as well as an improved understanding chemical transport and mitigation objectives.

Sphere-by-Sphere Manufacturing of 3D Microscale Granular Materials

188023 | Year 1 of 1 | **Principal Investigator: M. R. Brake**

Project Purpose:

The purpose of this project is to develop a novel additive manufacturing (AM) technique based on particle-by-particle deposition to fabricate highly ordered granular microstructures. The resulting 3D structures are expected to provide highly tunable control of shock waves (e.g., funneling or mitigation) depending on the pattern of assembled particles. To develop robust AM techniques for such structures requires fundamental scientific understanding of the manufacturing processes. This is achieved through combined experimental and computational research. This will enable extension of the technique to capabilities for various particle types/sizes, process design, and granular geometry optimization for specific applications.

Previously, macroscale granular structures have demonstrated high effectiveness for shock and ballistic impact protection and for shock localization for energetic components; however, macroscale granular structures are infeasible for many applications at Sandia, which have strict size and weight limitations. By developing a new AM technique based on the assembly of micron-sized particles into 3D structures, a new class of solutions for many problems faced at Sandia will become available.

This technique will have direct application to many challenges faced at Sandia, including shock energy dissipation to protect sensitive internal components and shock localization for energetic materials to tailor energy needed for detonations. Another consequence is the development of an ideal platform for fundamental studies of granular matter, including validating current granular modeling capabilities. This project focuses on developing the new AM technique and understanding the physical phenomena occurring during fabrication so it can eventually be applied to these and other problems.

Summary of Accomplishments:

We developed a proof of concept for the additive manufacturing of granular materials using a sphere-by-sphere assembly method. Due to the size scale requirements of the intended applications, this research has focused on developing this new additive manufacturing method for use with micro-sized spheres. A successful demonstration of a pyramid constructed out of 100-micron spheres has been achieved. Multiple manufacturing techniques have been assessed in order to determine the best option for realization of this new additive manufacturing technique. More work, however, is needed to refine the technique and to minimize the errors in particle placement.

To help facilitate the refinement of the process to eventually operate with particles as small as 1 micron in diameter, a numerical framework has been developed to simulate the response of the particles. This framework is the first step in the eventual modeling of the manufacturing process, which will enable a better understanding of the force interactions at the microscale and will be necessary to address the challenges of scaling down. Ongoing work is focused on assessing the adhesion models that are most appropriate for modeling this system, and validating the results of the numerical simulations with experiments on the manufactured assemblies.

Significance:

This research is the first step in developing a new additive manufacturing technique that could be used to design novel methods of energy dissipation and shock localization that have application to multiple DOE/DoD mission areas (weapons, satellites, etc.). The control of grain structure and the corresponding material performance inherent in this new technique is important to multiple US government agencies.

Super-Sensitive and Robust Biosensors from Supported Polymer Bilayers

185269 | Year 1 of 1 | **Principal Investigator: W. F. Paxton**

Project Purpose:

Biological organisms are potentially the most sensitive and selective biological detection systems known, yet we are currently severely limited in our ability to exploit biological interactions in sensory devices, due in part to the limited stability of biological systems and derived materials. This project addresses an important aspect of integrating biological sensory materials in a solid state device. If successful, such technology could enable entirely new classes of robust biosensors that could be miniaturized and deployed in the field. The critical aims of the work were: 1) the calibration of a more versatile approach to measuring pH, 2) the use of this method to monitor pH changes caused by the light-induced pumping of protons across vesicles with bacteriorhodopsin (bR) integrated into the membranes (either polymer or lipid), 3) the preparation of bilayer assemblies on platinum surfaces, and 4) the enhanced detection of light-induced pH changes driven by bR-loaded supported bilayers.

Summary of Accomplishments:

With the resources available, three of the four objectives were accomplished, which are critically important to moving forward with this approach. Unfortunately, the imperfection of the supported bilayers that were formed prevented the integration of bR into supported bilayers in a way that provided any meaningful determination about its feasibility.

We developed a methodology that may enable enhanced detection of light-induced pH changes at interfaces and developed a methodology to characterize the functionality of bilayer membranes with reconstituted membrane proteins. The integrity of the supported bilayer films however must be optimized prior to the full realization of the work envisioned in the original proposal.

Significance:

This work greatly supported the efforts of developing sensors that detect chemical and biological threats based on their biological function rather than their chemical form. This area of impact is highly relevant to developing sensors that are more robust, and more sensitive than existing sensors. The work to create supported hybrid polymer/lipid bilayer systems with reconstituted functional biomolecules, even though unsuccessful, expanded our understanding of the principles that enable biomolecules to function in non-native matrices.

Refereed Communications:

I.M. Henderson, H.A. Quintana, J.A. Martinez, W.F. Paxton, “Capable Crosslinks: Polymersomes Reinforced with Catalytically Active Metal-Ligand Bonds,” *Chem. Matter 27*, pp. 4808-4813, 2015. (SAND2015-2925 J)

Tightly Coupled GPS/INS Flight Test Demonstration

176605 | Year 2 of 2 | **Principal Investigator: J. D. Madsen**

Project Purpose:

The purpose of this project is to demonstrate in a real world environment the application of a tightly coupled Global Positioning System/Inertial Navigation System (GPS/INS) aiding algorithm. The algorithm was designed to allow a GPS receiver to track the required signals for a position solution during periods of extreme dynamics. Typical receiver algorithms cannot track under these conditions. The induced Doppler Shift experienced during the proposed dynamics is well outside the bandwidth of the phase lock loops used by commercial off-the-shelf GPS receivers. Sandia developed an aiding algorithm that utilizes acceleration information from an inertial measurement unit (IMU) to augment the phase lock loops and allow them to track through much higher Doppler Shifts. These algorithms were demonstrated to work in high fidelity radio frequency simulations of high dynamic rocket launches. The next step in the development of the approach is to demonstrate the same ability in a real world environment. Tracking under the proposed dynamics has never been demonstrated on a real vehicle previous to this attempt.

This objective will be accomplished by taking advantage of a ride of opportunity on a single stage Orion test rocket to be launched out of White Sands Missile Range (WSMR) in New Mexico.

Summary of Accomplishments:

We designed, assembled, and tested a flight worthy set of hardware and software for use on the test flight. This included modifying the previously developed algorithms to function on a lab flight computer. We further designed and had fabricated the necessary flight cables to connect the lab flight computer to a lab asset IMU. Sequencing and telemetry (TM) flight code was developed to interface with the Orion vehicle components to ensure the algorithms were in the proper state prior to launch and that all required data would be retrieved from the experiment. We took the completed set of flight hardware and software to WSMR and successfully integrated it into the vehicle and support all pre-launch testing activities.

On the day of launch the flight computer successfully placed the algorithms, flight computer, and IMU into the correct modes. The aiding algorithms were initiated and GPS signals were tracked and position solutions generated prior to launch. The vehicle launched and flew a successful mission and we were able to collect all the data on the performance of the algorithms that we desired to collect. The rocket executed a soft landing via parachute and all flight hardware was recovered in working order and returned to our lab.

Preliminary data review shows that the dynamics of flight were extreme, even beyond those predicted. The aiding algorithm appears to have allowed several signals to be tracked, but others were not. A detailed review of the data, in combination with additional simulations anchored on the actual dynamics, is required to validate the approach. Future missions and efforts in the realm of high dynamic tracking can significantly reduce risk by utilizing this data.

Significance:

This project established a future capability for high dynamic GPS tracking by providing the data necessary to verify simulation results. Additionally, it allowed for the development of new TM techniques, which may be utilized on future flights.

Tunable Graphitic Carbon Nano-Onions Development in Carbon Nanofibers for Multivalent Energy Storage

184519 | Year 1 of 1 | **Principal Investigator: H. L. Schwarz**

Project Purpose:

Rapidly expanding energy demands need high-performance rechargeable batteries, a key enabler for electric vehicles and smart grids. The initiative to develop multivalent-ion (MV-I) batteries (Mg, Ca, Al) requires higher volumetric energy density, resulting from a greater number of electrons transferred per metal cation. Using metals or alloys as anodes via deposition-dissolution theoretically yields higher energy density, however, such anodes suffer inhibited cation transmission due to surface passivation, or poor lifetime due to volume expansion. To date, no reversible, efficient, extended life cycle MV-I battery has been achieved. An intercalation anode eliminates the above concerns and enjoys precision, reliability, and enhanced safety, as demonstrated in the highly successful lithium ion battery. Nevertheless, graphite is unsuitable for MV-I intercalation because the limited interlayer spacing poses hurdles for intercalation due to the multivalent nature of the cations (i.e., a high charge/radius ratio).

No published work presently exists on a reversible and functional intercalation carbon anode. We propose to develop novel ultraporous graphitic carbon nanofibers with internal fullerenic nanostructures and tune the graphitic interlayer spacing. We will introduce transition metal salts into the carbon precursors, form nanofibers via electrospinning, followed by in situ catalytic graphitization. Within individual carbon nanofibers are nanometer-sized graphitic nano-onions consisting of concentrically layered graphene shells resembling fullerene structure. The distance between adjacent graphene layers will be further tuned through selective oxidation and reduction. The goal is to develop electrically conductive novel carbons as anode materials allowing reversible MV-I intercalation, with high surface areas and open accessible porosities that minimizes the diffusional resistance.

No published work presently exists on a reversible and functional intercalation carbon material for multivalent batteries. The fundamental aspects and developing ultraporous carbon-nanofiber materials with tunable graphitic interlayer spacing are critically important in order to have broad impact for specific applications.

Summary of Accomplishments:

The overarching goal of this project is to create graphitic carbon nanofibers containing internal fullerenic nanostructures and subsequently enlarge their graphitic interlayer spacing so that such electrically conductive graphitic carbons can be used as anode materials allowing reversible MV-ion intercalation.

Significance:

Successful MV-I battery technologies will lead to higher energy density, lower cost, and better safety and reliability to meet power demands for vehicle electrification and smart grids.

Vertical GaN PIN Diodes with 5 kV Avalanche Breakdown

188026 | Year 1 of 1 | **Principal Investigator: A. A. Allerman**

Project Purpose:

This project aims to determine the true critical electric field (Ec) of gallium nitride, (GaN), and demonstrate a GaN power diode with a record avalanche breakdown voltage of 5 kV. The Ec of GaN is not well known, and pinpointing the true Ec allows for properly designing various elements within the diode such as layer thicknesses, doping, and edge termination in order to achieve high breakdown voltages. Up until now, the Ec of GaN has been determined either by unproven simulations or with experimentation on defective GaN material. Now with the availability of GaN substrates, we can create low defect GaN power diodes and achieve higher breakdown voltages and determine Ec. This project will use complementary efforts in both Technology Computer-Aided Design (TCAD) simulations and experimentation on GaN power diodes grown on GaN substrates with various edge termination schemes, allowing us to meet the project goal. The experimental results of the diodes will be used in the simulations to determine the Ec. Conversely, the simulations will guide the design of the GaN power diodes to achieve record breakdown voltages.

The project aims to find the true value of the critical electric field of GaN (a fundamental parameter) and push the state of the art of GaN power diodes by achieving record breakdown voltages.

Summary of Accomplishments:

High-voltage diodes are desired for many high-power switching applications. GaN pin diodes have the potential to replace conventional silicon diodes for applications requiring very low size and weight and high power. GaN diodes have several advantages including the ability to operate at high temperatures and a higher tolerance to radiation damage. We have developed a simple method of edge termination for GaN pin diodes. This method does not require complicated ring structures in order to demonstrate a high breakdown voltage. A combination of TCAD modeling and experimental measurements were used to validate our hypothesis that a very thin layer of p-type material with a lower-hole concentration is critical to the edge termination in our devices. This work positions us well to demonstrate GaN pin diodes with reserve bias breakdown voltages of 5 kV or greater.

Significance:

We now have a simple method of edge terminations for GaN pins, which we understand based on comparison between experimental results and TCAD simulations. This will enable us to maximize the high-voltage breakdown in our devices and to achieve much better device performance for a given intrinsic layer thickness and carrier concentration. Based on these results, we expect to be able to demonstrate GaN pin diodes which can be operated at 5 kV or greater which will be useful for many future high power solid state switching applications. If successful, these high voltage GaN pin diodes will revolutionize power conversion technology and enable novel systems with extremely low size and weight and high power. This will, in turn, enable many new applications where improvements in size, weight, and power are particularly important and will help usher in a new era where highly efficient power conversion can be obtained in extremely small packages.

Refereed Communications:

M.P. King, J.R. Dickerson, G. Vizkelethy, R. Fleming, J. Campbell, W.R. Wampler, I.C. Kiziyalli, D.P. Bour, O. Aktas, H. Nie, D. Disney, J.J. Wierer, and A.A. Allerman, “Performance and Breakdown Characteristics of Irradiated Vertical Power GaN P-i-N Diodes,” *IEEE Transactions on Nuclear Science*, 10.1109/TNS.2015.2480071, October 2015.

J.R. Dickerson, A.A. Allerman, B.N. Bryant, A.J. Fischer, M.P. King, M.W. Moseley, A.M. Armstrong, R.J. Kaplar, I.C. Kizilyalli, O. Aktas, and J.J. Wierer, “Vertical GaN Power Diodes with a Bilayer Edge Termination,” *IEEE Transactions on Electron Devices*, vol. 62, February 2015.

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Unpublished Summaries

For information on the following FY 2015 LDRD Projects, please contact the LDRD Office:

Laboratory Directed Research and Development
Sandia National Laboratories
Albuquerque, NM 87185-0359

Project #	Title
173039	Novel, Semi-Destructive FA Technique for Stacked Die
173044	New Methods for Characterizing Hardware Protocols
173046	Novel Technology Development
173049	Advanced Target Phenomenology for Emergent Threat Detection
173051	High Speed Remote Sensing of Optical Signatures
176115	Advanced Deprocessing Techniques to Investigate White Light LVP and other Imaging
173182	Non-Linear Transmission Line Based Technology
178917	Unconventional Approaches to Neutron Generators
180827	Additive Manufacturing of Integrated Functional Materials
180829	Mitigating Information Disclosure Vulnerabilities
180848	Electromagnetic Propagation and Prediction
180851	Optical Distortion in the Hypersonic Environment
180852	An Ultra-low SWaP Multi-Mission Bi-Static Sensor
180854	Alumina Materials Chemistry
180930	Microenergetic Logic for Safety Applications
185586	Pulsed Laser Effects on Integrated Circuits

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Awards & Recognition

Black Engineering Award, Most Promising Engineer: Jon Madison
Project 150683, "Studies in High Rate Solidification"

Asian American Engineer of the Year, Outstanding Asian American Professionals in STEM: Somuri Prasad
Project 158856, "Synthesis of Wear-Resistant Electrical Contact Materials by Physical Vapor Deposition," and others

Chinese Institute of Engineers, Most Promising Engineer of the Year Award: Patrick Feng
Project 180925, "Low Afterglow Scintillators for High-Rate Radiation Detection," and others

HENAAC Award, Great Minds in STEM: Abraham Ellis
Project 181202, "Fault Survivability of Lightweight Operating Systems for Exascale"

Innovation Fellow Award, University of New Mexico: Jeff Brinker
Project 165609, "The Engineering and Understanding of Nanoparticle/Cellular Interactions," and others

New Mexico Women of Influence Award, Albuquerque Business First: Susan Rempe
Project 173142, "Probing Small-Molecule Degradation to Counter Enzyme Promiscuity," and others

Distinguished Lecture in Nanoscience, Materials Research Society Spring Meeting: Hongyou Fan
Project 165700, "Tunable Quantum Dot Solids: Impact of Interparticle Interactions on Bulk Properties," and others

Department of Energy's Ernest Lawrence Award, Pioneering Theoretical and Practical Methods for Partial Differential Equations: Pavel Bochev
Project 173025," Coupling Computational Models: from Art to Science," and others

Erwin Marx Award, IEEE Pulsed Power Conference and Symposium on Fusion Engineering: Bill Stygar
Project 173191, "Creating the Foundation of Next-Generation Pulsed-Power-Accelerator Technology"

DOE Office of Science Early Career Award: Chris Kliewer
Project 151338, "Theoretical and Experimental Studies of Electrified Interfaces Relevant to Energy Storage"

Early Career Award, IEEE Technical Committee on Scalable Computing: Kurt Ferreira
Project 158852, "Fault Survivability of Lightweight Operating Systems for Exascale," and others

Future Leader Award, American Rock Mechanics Association: Matthew Ingraham
Project 173076, "The Effect of Proppant Placement on Closure of Fractured Shale Gas Wells"

Outstanding Young Engineer Award, SME: Margot Hutchins
Project 179224, "Building the Scientific Basis for Cyber Resilience of Critical Infrastructure"

Morris Cohen Award, Electrochemical Society for Graduate Research: Eric Schindelholz
Project 180865, "Nanocomposite Barrier Films for Enhanced Thin Film Photovoltaic Stability"

Popular Science's 100 Greatest Innovations of 2015: for BadX technology: Melissa Finley, et al.
Project 158813, "Development of a Sustainable Anthrax Diagnostic Test for Countering the Biological Threat"

National Innovation Award, TechConnect National Innovation Summit Award for BadX: Melissa Finley, et al.
Project 158813, "Development of a Sustainable Anthrax Diagnostic Test for Countering the Biological Threat"

National Innovation Award, TechConnect National Innovation Summit award for Flexpower: mPower Inc. (spun off from a Sandia LDRD project)
Project 159257, "Science-Enabled Next Generation Photovoltaics for Disruptive Advances in Solar Power and Global Energy Safety and Security"

Federal Laboratory Consortium, Award for Excellence in Technology Transfer for BadX: Melissa Finley, et al.
Project 158813, "Development of a Sustainable Anthrax Diagnostic Test for Countering the Biological Threat"

Federal Laboratory Consortium, Outstanding Technology Development Award for Twistact Technology: Jeff Koplow
Project 165633, "Sandia's Twistact Technology: The Key to Proliferation of Wind Power"

Federal Laboratory Consortium, Award for Decontamination Technology for Chemical and Biological Agents: Mark Tucker
Project 67015, "Massively Parallel Scalable Atmosphere Model"

Fellow of the American Physical Society: Steve Slutz
Project 171061 "First to High Yield Fusion," and others

Fellow of the American Physical Society: Dan Sinars
Project 141537, "Stability of Fusion Target Concepts on Z," and others **Fellow of the Society for Industrial and Applied Mathematics: Tamara Kolda**

Project 181052, "A Domain-Specific Language for Distributed Tensor Computations," and others

Best Paper Award, IEEE Aerospace Conference: Mark Boslough
Project 184520, "Can Asteroid Airbursts Cause Dangerous Tsunami?"

Best Paper Award, Symposium on the Application of Geophysics to Engineering and Environmental Problems: Nedra Bonal
Project 173101, "Imaging the Subsurface with Upgoing Muons"

Best Paper Award, IEEE International Parallel and Distributed Processing Symposium: Jonathan Berry, et al.
Project 159258, "Extreme Scale Computing Grand Challenge"

Best Paper Award, 3rd ACM SIGSPATIAL International Workshop on Analytics for Big Geospatial Data: Randy Brost, et al.
Project 165535, "Pattern ANalytics to Support High-performance Exploitation and Reasoning (PANTHER)"

Best Paper Award, Tanasawa Award: Marco Arienti and Mark Sussman
Project 173096, "Modeling Primary Atomization of Liquid Fuels Using a Multiphase DNS/LES Approach"

Best Paper Award, Nuclear and Space Radiation Effects Conference: Nathaniel Dodds
Project 173134, "A Space-Like Low-Energy Proton Test Environment to Rapidly Qualify Advanced Microelectronics for Flight Readiness"

Best Student Paper, 42nd Annual ICOPS Conference: Sonal Patel
Project 180935, "Measuring Plasma Formation, Field Strength, and Current Loss in Pulsed Power Diodes"

Best Poster Award, Materials Research Society Spring Meeting 2015: Jon Ihlefeld
Project 173117, "Phonon Scattering at Mobile Ferroelastic Domain Walls: Toward Voltage Tunable Thermal Conductivity"

Best Poster Award, Atom Probe Tomography and Microscopy Conference: Stephen Foiles and Chris O'Brien
Project 165825, "The Role of Grain Boundary Energy on Grain Boundary Complexion Transitions," and others

Best Speaker Award: Robert Johnston
Project 173339, "Chemical Vapor into Liquid (CViL) Encapsulation of Microorganisms for Hazardous Agent Detection"

RPI's Founder's Award: Mark Durniak
Project 168763, "Creating a Novel Silicon Substrate for the MOCVD Growth of Low Defect GaN"

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Abstract

This report summarizes progress from the Laboratory Directed Research and Development (LDRD) program during fiscal year 2015. In addition to the programmatic overview, the report includes progress reports from 380 individual R&D projects in 14 categories. Information for 182 projects in their final year is presented in a more comprehensive format, while for those 198 in their pre-final years, only an abstract is presented herein.

LDRD Annual Report Staff

Marie Arrowsmith, Rita Betty, Donna Chavez, Greg Frye-Mason, Sheri Martinez, Yolanda Moreno, Donna Mullaney, David Trimmer

SAND 2016-XXXX X March 2016

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration