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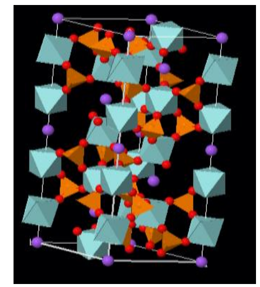

Sodium-Based Battery Development

Erik D. Spoerke, Ph.D.

Sandia National Laboratories, Albuquerque, NM

U.S. Department of Energy Office of Electricity Delivery and Energy Reliability
Energy Storage Peer Review
Washington, D.C.
September 25-28, 2016

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Teaming

- Program Sponsor
  - Dr. Imre Gyuk – Program Manger, DOE-OE
  - DOE – Office of Electricity Delivery and Energy Reliability
- Team
  - **SNL**: Erik Spoerke, Leo Small, Jill Wheeler, Paul Clem, Josh Lamb, Eric Allcorn, Ganesan Nagasubramanian, John Hewson, and David Ingersoll*
  - **Ceramatec**: Sai Bhavaraju, Alexis Eccleston, Andrew Read, Matt Robins, Tom Meaders
  - **SK Innovation**: Jeongsoo Kim

This collaboration between National Laboratory and Industry aims to utilize state of the art expertise in materials chemistry, electrochemistry, and advanced characterization to drive the development of new sodium-based batteries toward commercial application.

Sodium-Based Batteries: A Path to Safe, Reliable, Cost-Competitive Energy Storage

Objective: We aim to develop low cost, low temperature, safe, nonflammable alternatives to Na-S and Li-ion batteries.

- Low cost (reduced material costs, low CAPEX, high cycle life)
  - Unit cost ~$146/kWh, module costs ~$175/kWh, Cycle life 5,000-10,000 cycles LCOS $0.05-0.10/kWh-cycle
- Enabled by *low to intermediate temperature (<200^{o}C)* ceramic Na-ion conductor (NaSICON)
  - Robust physical barrier - *no electrode crossover*!
  - Reduced operating costs
  - Lower cost materials/seals
  - Enables new cathode chemistries
- Engineered safe
  - Fully inorganic, no volatile organic electrolytes
  - Robust ceramic separator isolates anode and cathode
  - Cross-reaction generates benign byproducts

Our approach stands to enable numerous new Na-based battery technologies:

- Sodium-air
- Sodium-ion
- Aqueous Redox Flow
- Low temperature sodium-sulfur
- Sodium-bromine: $Na + \frac{1}{2} Br_2 \leftrightarrow Na^+ + Br^-$
- Sodium-iodine: $Na + \frac{1}{2} I_2 \leftrightarrow Na^+ + I^-$
- Sodium-nickel chloride: $Na + \frac{1}{2} NiCl_2 \leftrightarrow Na^+ + Cl^- + Ni(s)$
- Sodium-copper iodide: $Na + CuI_2^- \leftrightarrow Na^+ + 2I^- + Cu(s)$

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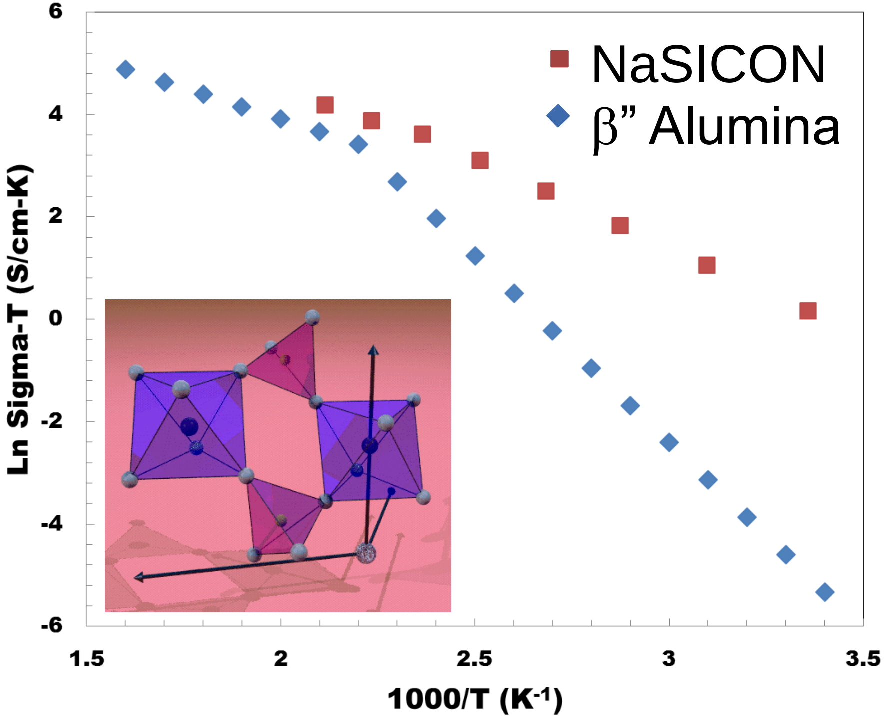
NaSICON Electrolyte Enables Multiple Na-Battery Chemistries

NaSICON (Na Super Ion CONductor): $Na_3Zr_2PSi_2O_{12}$

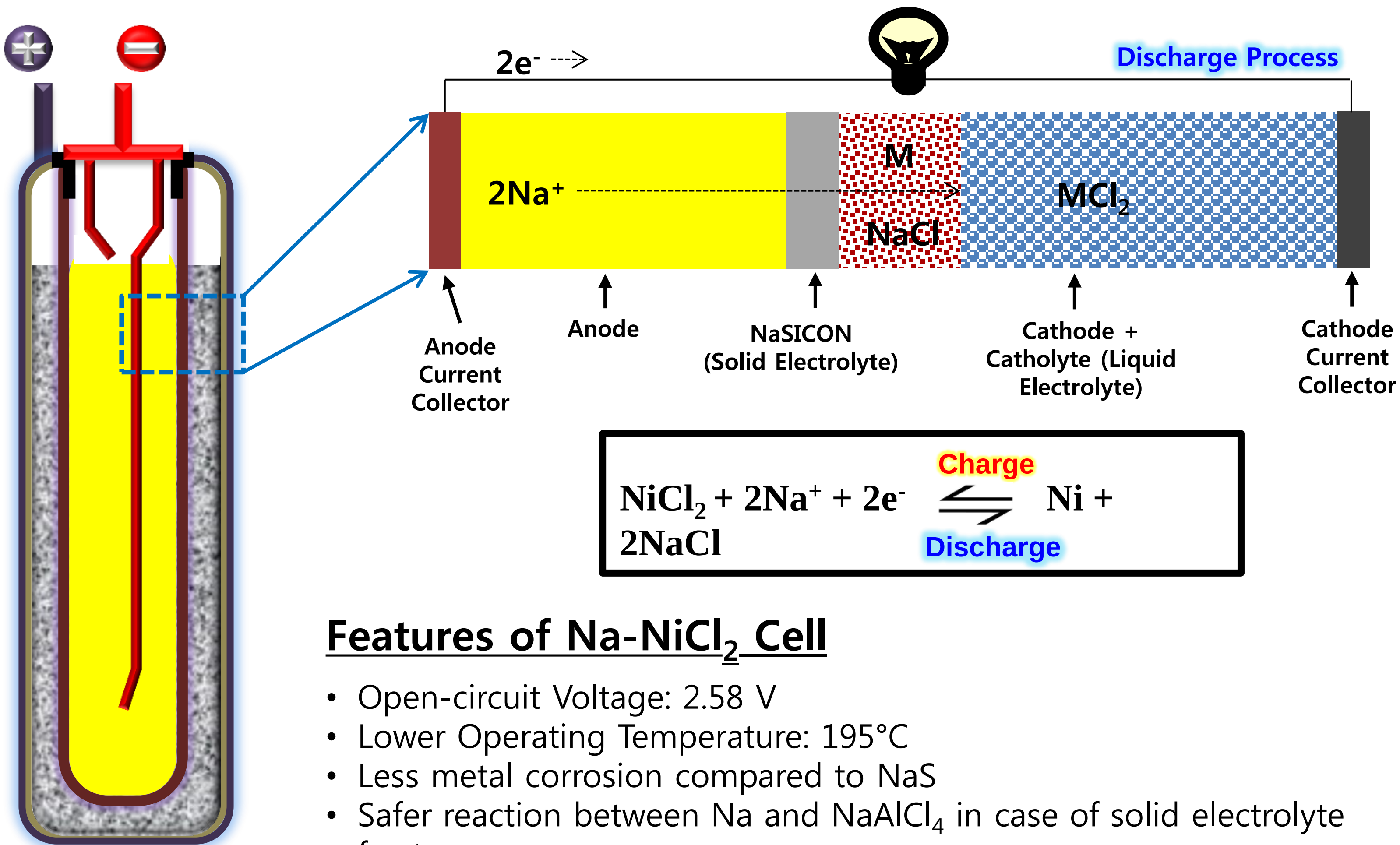


Engineered materials chemistry and advanced, scalable processing (Ceramatec, CoorsTek) make NaSICON a *chemically/mechanically stable, low temperature, high conductivity (>10^{-3} S/cm @RT)* separator technology.

CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

Poster: S. Bhavaraju

Na-$NiCl_2$ Battery Technology



$$NiCl_2 + 2Na^+ + 2e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Ni + 2NaCl$$

Features of Na-$NiCl_2$ Cell

- Open-circuit Voltage: 2.58 V
- Lower Operating Temperature: 195°C
- Less metal corrosion compared to NaS
- Safer reaction between Na and $NaAlCl_4$ in case of solid electrolyte fracture

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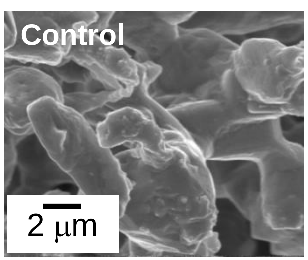
Stable Na-$NiCl_2$ Cell Performance

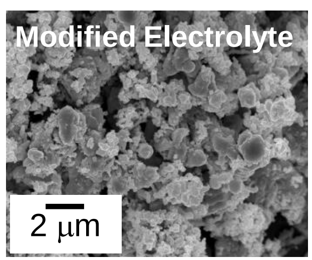
Nickel grain growth at high temperatures during cycling limits cycle life and charge-discharge kinetics for Na-$NiCl_2$ batteries.

1 micrometer Ni Particle grows by more than 10X after multiple cycles

Using a NaSICON electrolyte allows us to lower temperature below 200°C and adding Ni metal growth inhibitors.

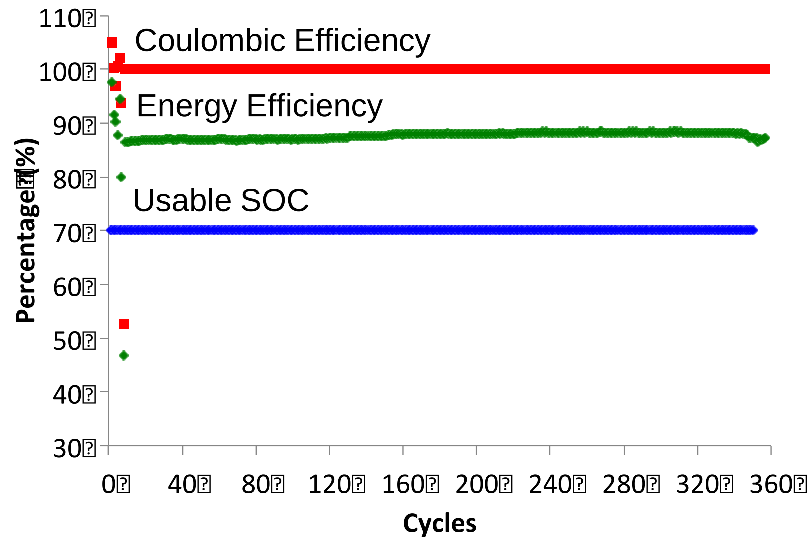
Together, these changes have allowed us to prevent Ni metal particle growth and preserve exceptional, stable battery performance over months (hundreds of cycles).





After electrochemical cycling, Ni-particle growth is suppressed using NaSICON and catholyte additives

Cycle test (Prototype cell)



13 Wh Na-$NiCl_2$ (NaX) Cell operation for 9+ months. 70% Depth of Discharge, >85% energy efficiency at 65 mA /cm² Charge/Discharge NaSICON current density

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Scalable NaSICON Enables Scalable Cell Configurations

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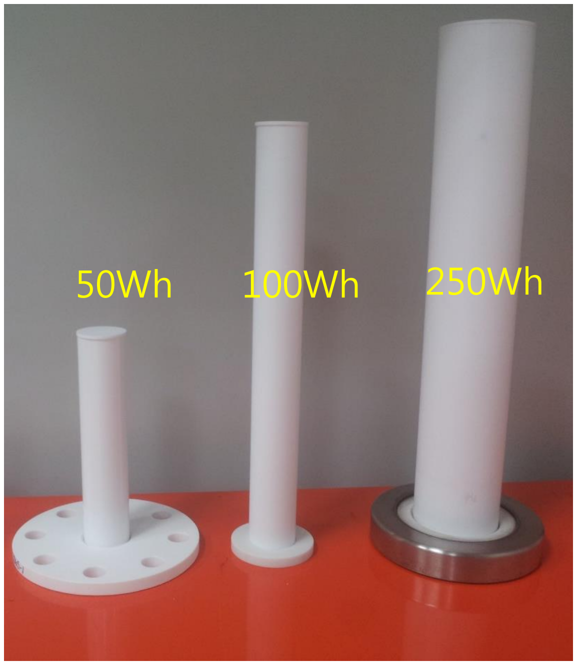
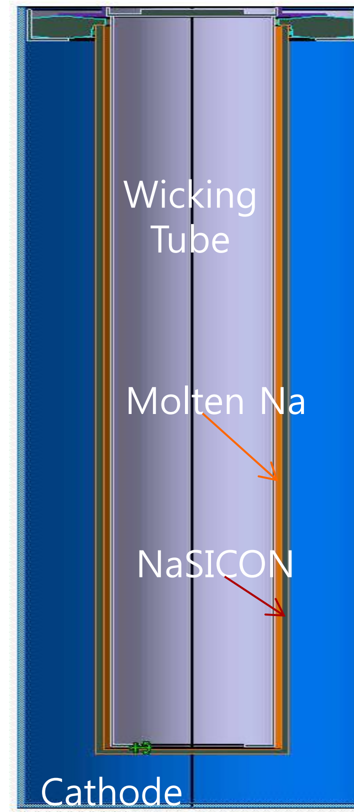
250Wh Commercial Cell Components & Design Concept



- $Na\text{-}NiCl_2$: 100-250 Wh commercial type unit cell testing/construction in progress
- NaI: 100 Wh pre-commercial prototype cell construction in progress

Assembled 250 Wh NaX Cell



Internal Structure

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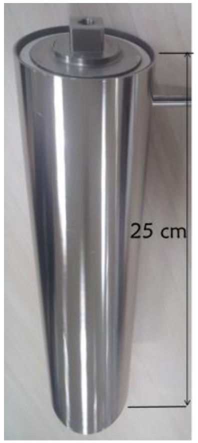
Consistent Performance Across Scales

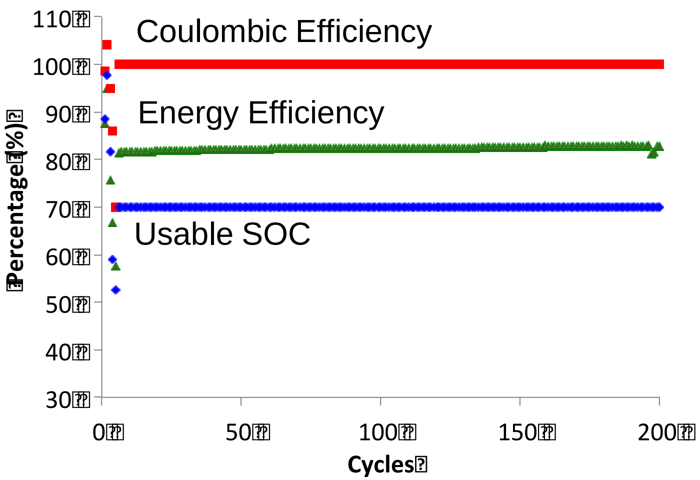
100 Wh pre-commercial Na-$NiCl_2$ unit cell:

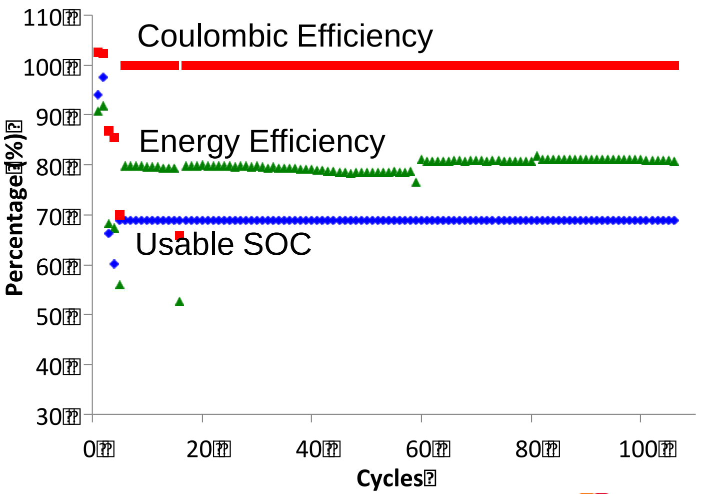
- operational for 4+ months.
- 500+ cycles (70% DOD)
- coulombic efficiency ~100%
- energy efficiency 81.5 %
- 53 mA/cm^2 & C/7 rate



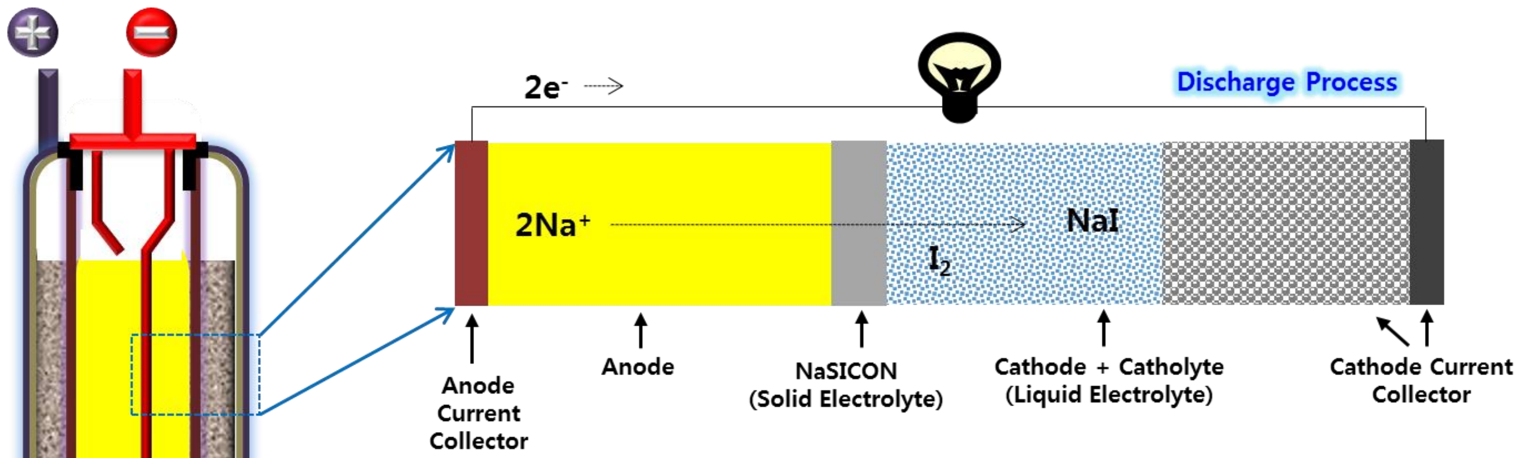
250 Wh pre-commercial Na-$NiCl_2$ unit cell:

- operational for 3+ months
- 110 cycles (70% DOD)
- coulombic efficiency ~100%
- energy efficiency 80 %
- 53 mA/cm^2 & C/7 rate





Na-I_2 Battery Technology



$$I_2 + 2Na^+ + 2e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} 2NaI$$

Consider Na-I_2 Batteries:

- Increased cell voltage (3.25V)
- Lower temperature (120-180ºC)
  - ➢ Lower cost materials/seals
  - ➢ Lower operational costs
  - ➢ New cathode chemistries
- Liquid cathode increases feasible cycle life

Na-I$_2$ Prototype Performance

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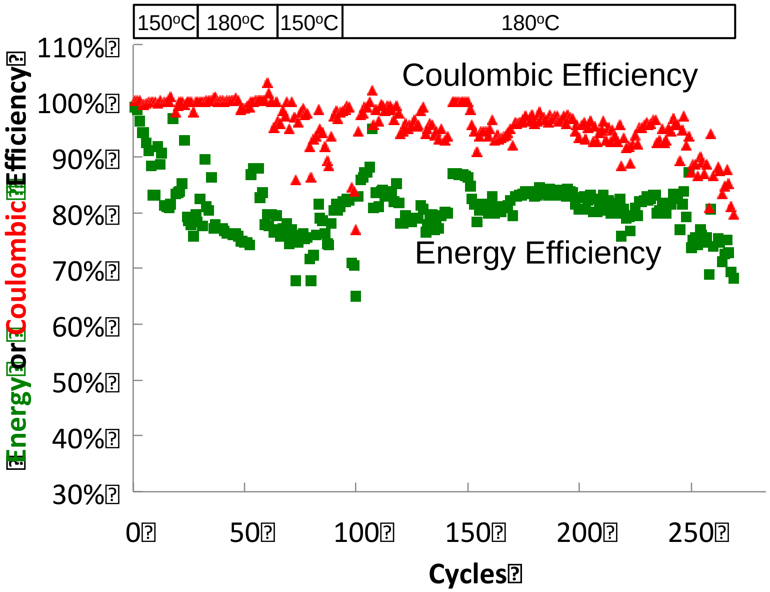
Lab Scale Test Conditions

- 8.7 Wh lab-scale cell
- Graphite felt + tungsten wire current collectors
- NaI-AlCl$_3$ based molten salt catholyte
- 1" NaSICON tube (15 cm^2) glass sealed to α-alumina
- T = 150-180˚C

✓ Demonstrated long term performance

- More than 269 cycles @ 60% DOD Discharged 483Ah
- C/7 rate
- High energy efficiency of ~ 80%
- 28.5 mA/cm^2 current density



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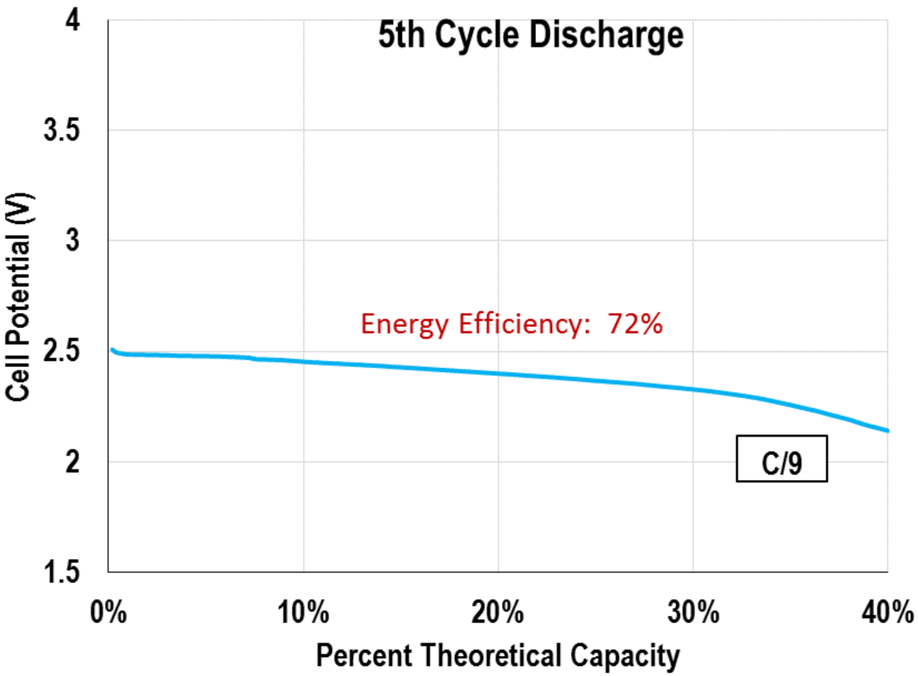
Preliminary Operation of 100 Wh $Na\text{-}I_2$ Battery



- The 100 Wh cell was built using Carbon felt/Tungsten mesh, infiltered with NaI.
- The majority of the cycling was done at 150 ºC, until the last 9 cycles where the temperature was raised to 165 C.
- The cell operated 360 hours (29 cycles) before failure.

Promising Progress!

Improving Cathode Structure

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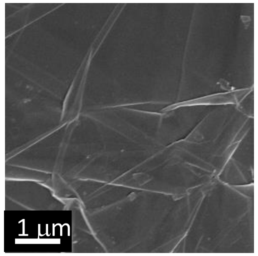
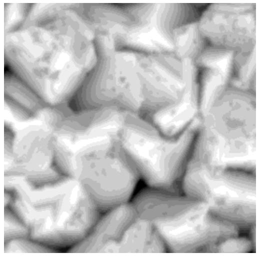
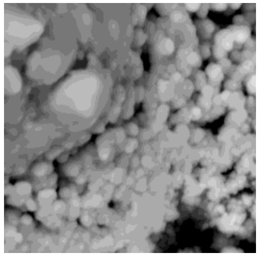
Electrolessly Coated Tungsten/Carbon Electrodes



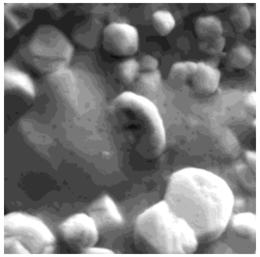
Carbon electrode
(graphite, powder, foam)



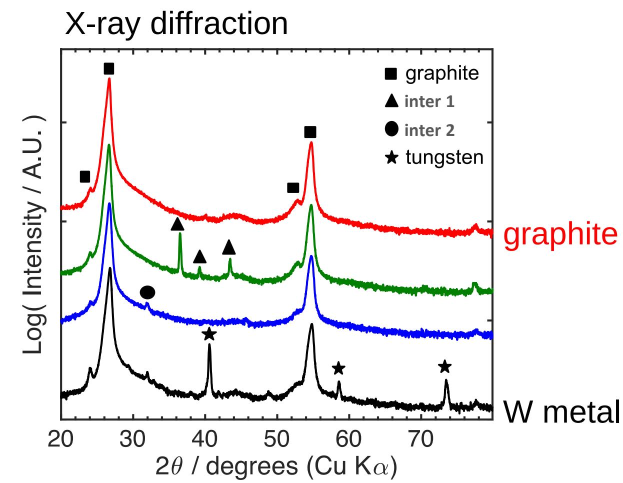
Intermediate coating

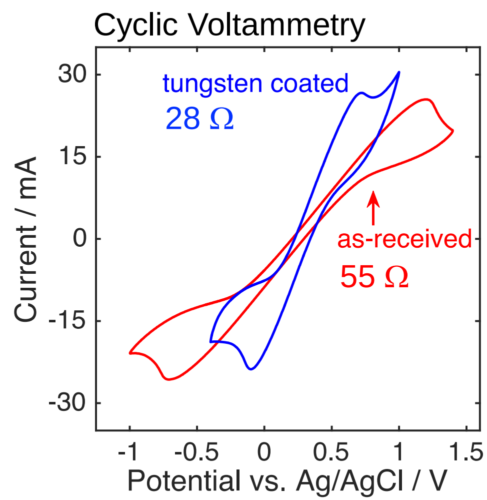


Convert to W-precursor



Reductive anneal creates
Crystalline, metallic tungsten.





carbon foam
10 mM $K_3Fe(CN)_6$
500 mM NaCl
100 mV/s

2X Reduction in electrode resistance will reduce ASR and enable superior electrochemical performance.

Poster: L. Small

Na-Batteries: Engineering Safety

Galaxy Note 7

Laptop Computer

Tesla EV Battery

Battery Recycling Plant

Thermal runaway and flammable organic electrolytes remain serious hazards for Li-ion batteries!

Li-Ion batteries are inherently intolerant of harsh conditions…

In contrast, Na-batteries are engineered safe:

- All inorganic construction eliminates explosive organic solvents
- Robust ceramic separator isolates anolyte and catholyte
- Cross-reaction generates benign byproducts (Al metal and NaCl)

$$3Na + AlCl_3 \rightarrow 3NaCl + Al(s)$$

Accelerating Rate Calorimetry (ARC)

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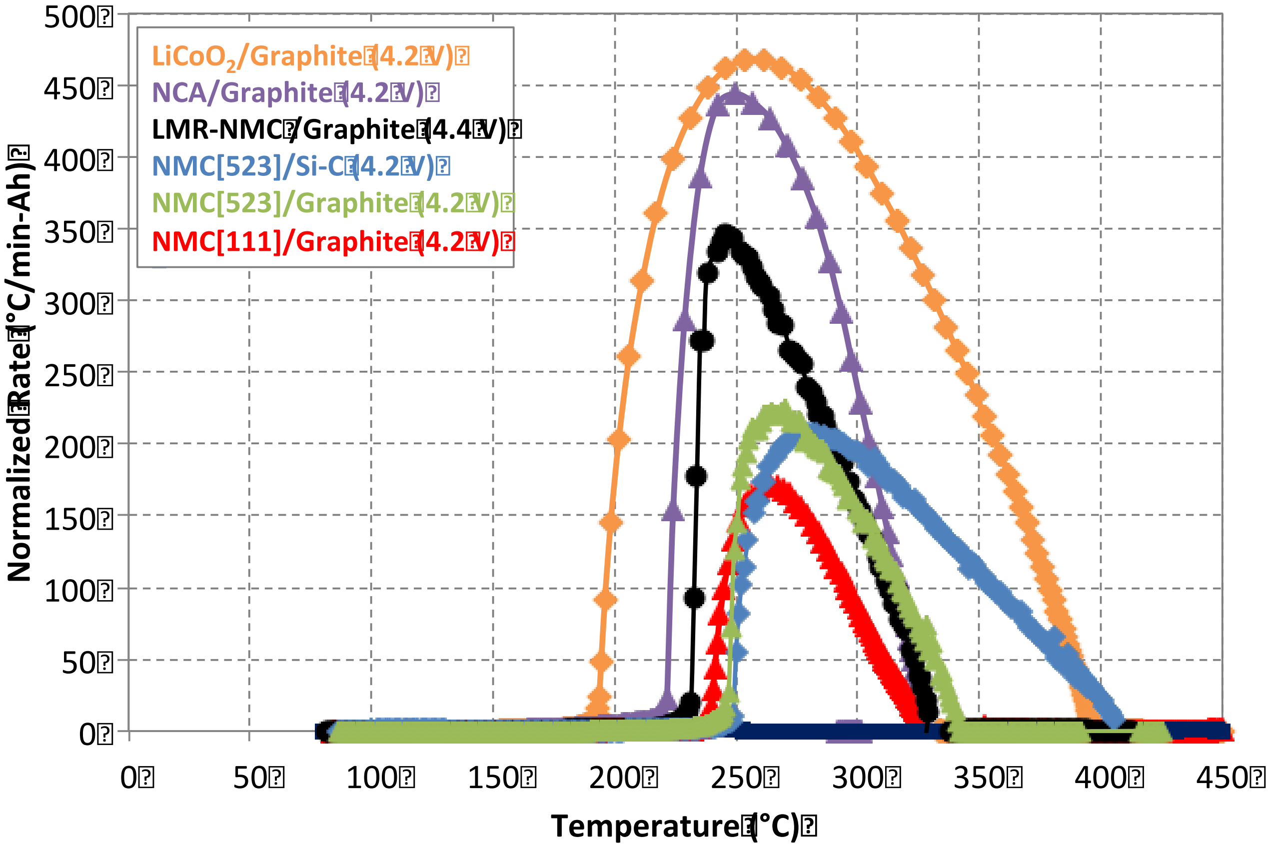
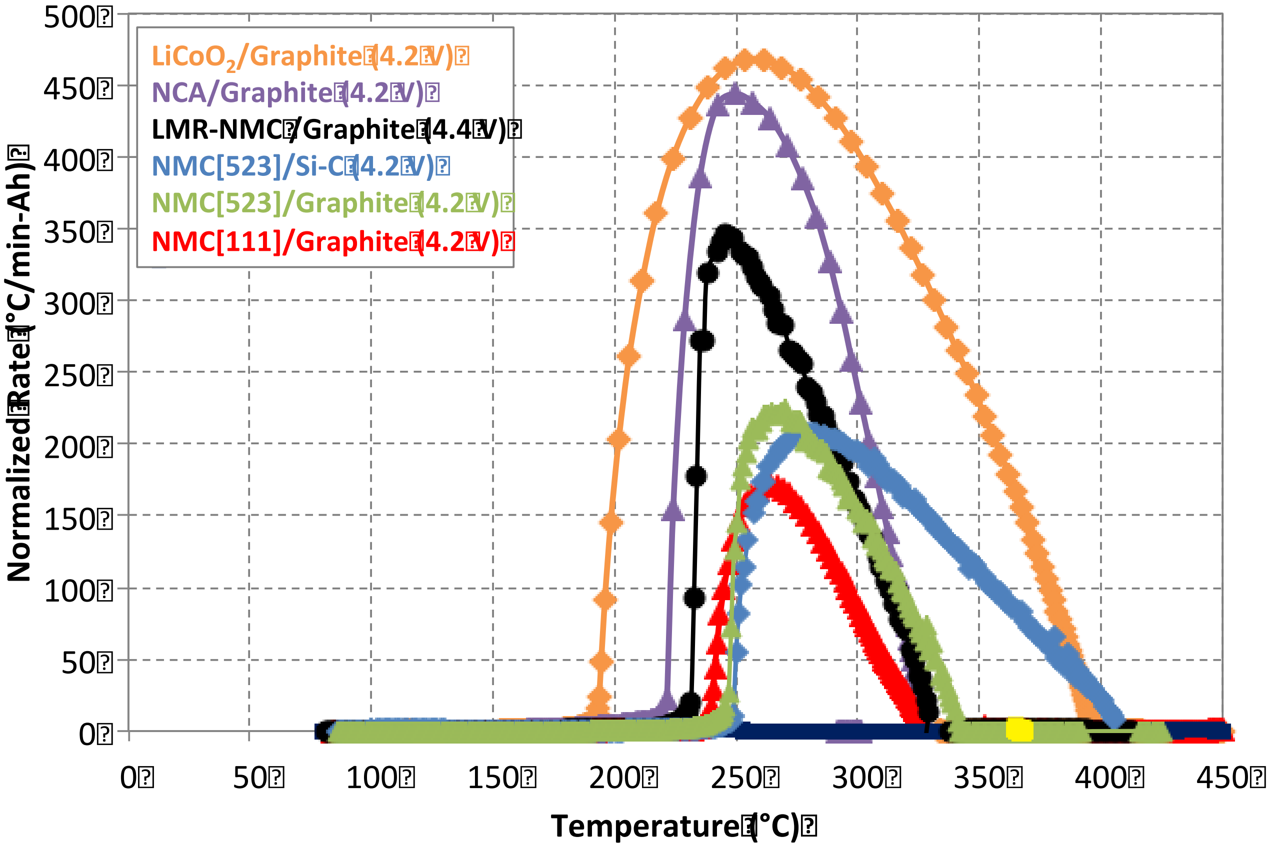
- ARC testing is used to determine the time, temperature, and pressure relationships for exothermic reactions.



Josh Lamb

Accelerating Rate Calorimetry (ARC)

When complete separator failure is simulated by mixing Na metal and $NaI/AlCl_3$ salt, ARC testing reveals essentially no self-heating.



Accelerating Rate Calorimetry (ARC)

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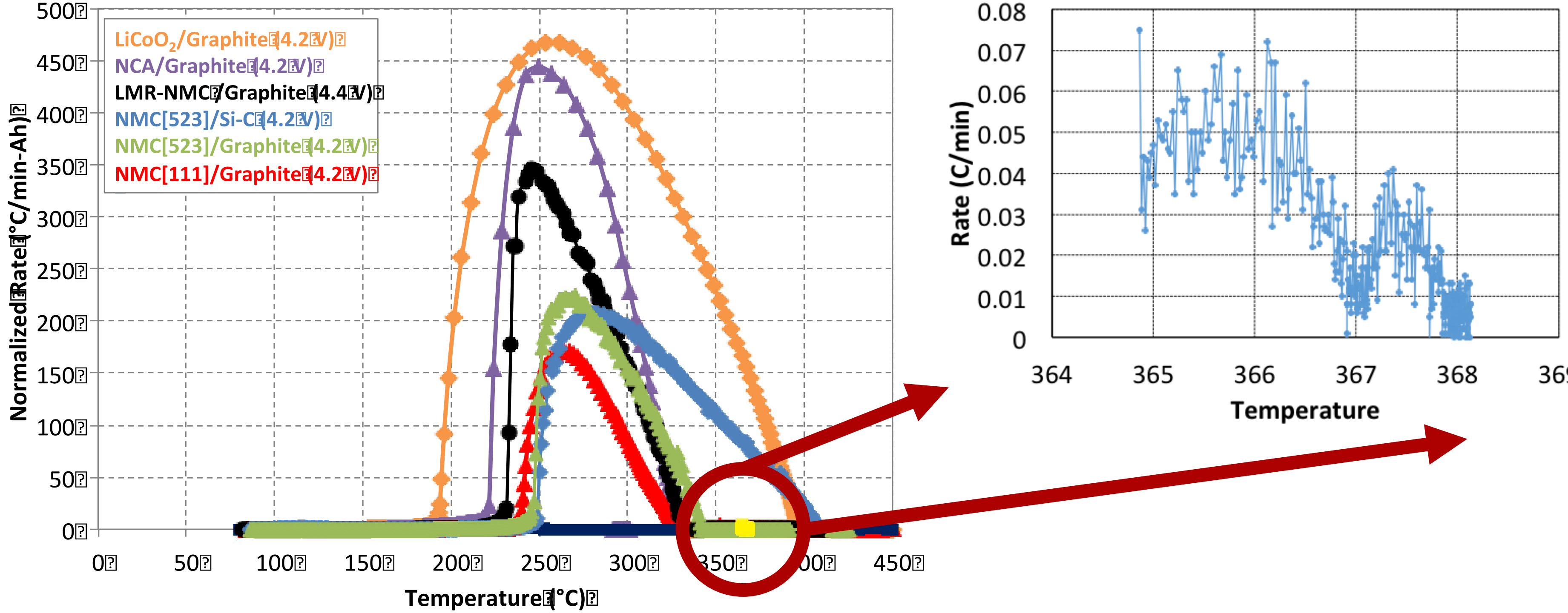
When complete separator failure is simulated by mixing Na metal and $NaI/AlCl_3$ salt, ARC testing reveals essentially no self-heating.

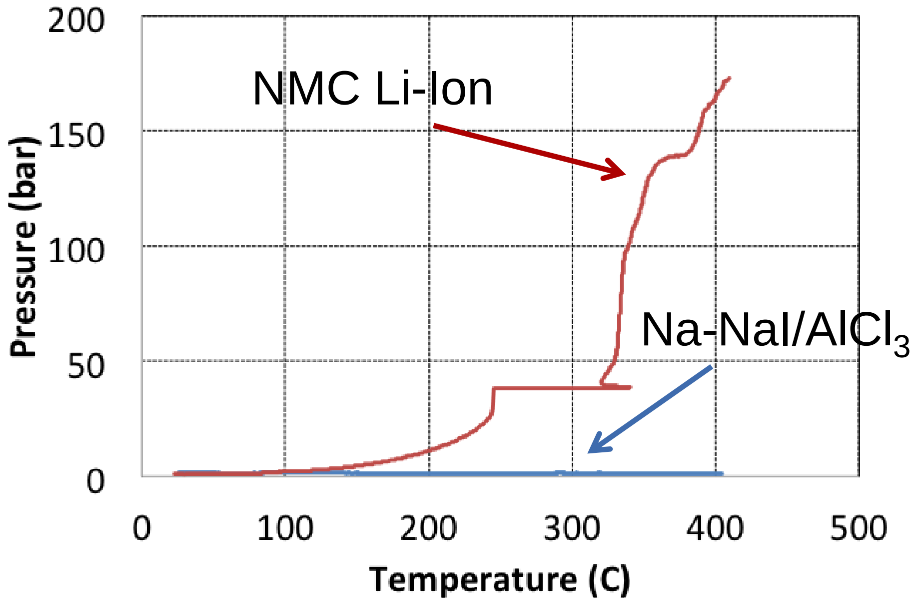
Minor exotherm from Na-$NaI/AlCl_3$



Na-System Shows Minimal System Pressurization

Measuring pressure generated during ARC testing shows no significant gas generation/pressurization from the Na-NaI/$AlCl_3$ mixture.

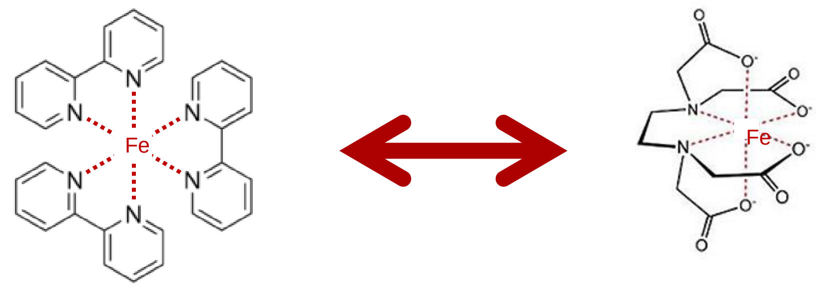
In contrast volatile components of an NMC Li-Ion produce a dramatic pressure spike at elevated temperatures.



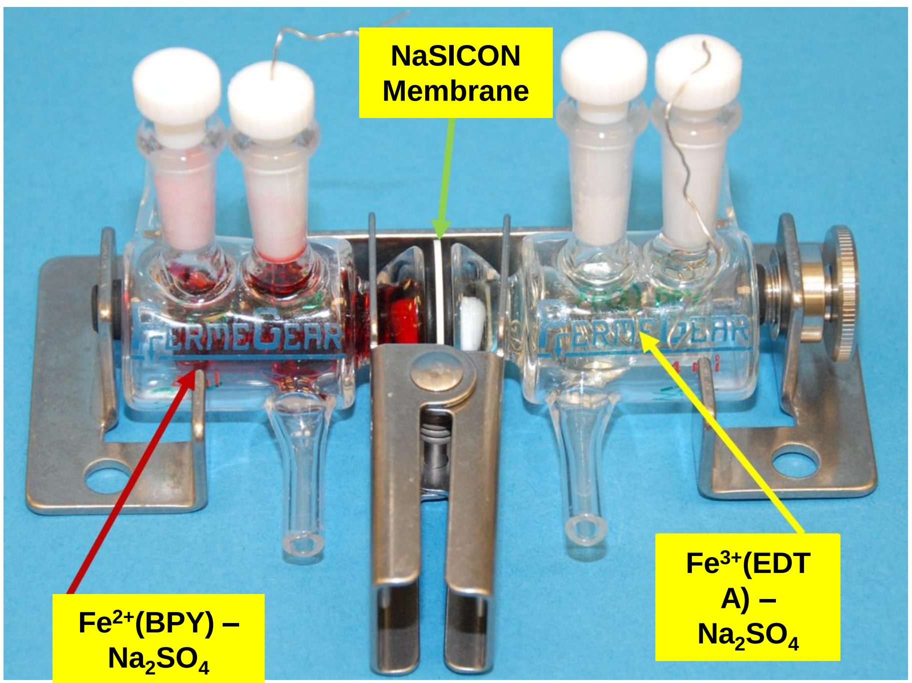
This minimal pressurization represents a dramatic safety benefit of Na-batteries.

Alternative Na-based Battery Chemistries

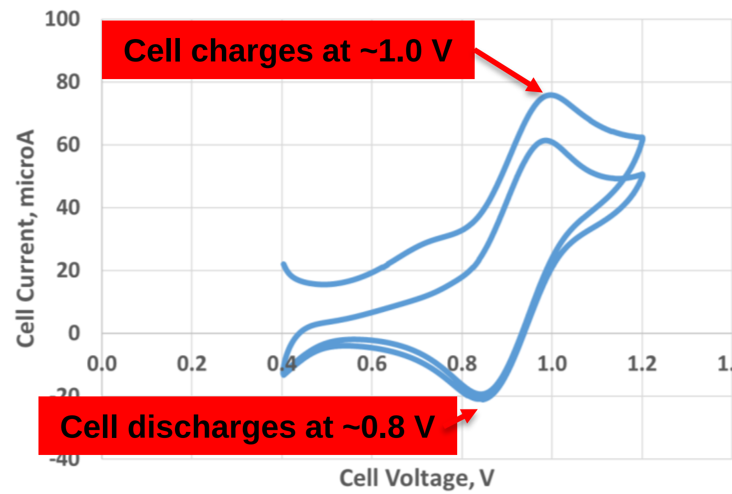
NaSICON separators offer the high conductivity, chemical and mechanical stability, and ion-selectivity needed to enable Na-based, aqueous redox flow batteries.



$Fe(bpy)^{2+/3+}$ (0.9V) **$Fe(EDTA)^{2-/3-}$ (0V)**



Full Cell CV @ 5 mV/sec
Fe^{3+}(EDTA) // NaSICON // Fe^{2+}(BPY)
0.4M Na_2SO_4



Poster: E. Allcorn

FY16 Programmatic Accomplishments

- Papers
  - H. Zhu and R.J. Kee. "Computational modeling of Na-I_2 secondary batteries." *Electrochemica Acta, 2016. In Press.*
  - L.J. Small, M.T. Brumbach, P.G. Clem, and E.D. Spoerke. "Deposition of Tungsten Metal by an Electroless Process." *ACS Appl. Mater. Interfaces*. 2016 (*in final preparation*)
  - L.J. Small, S. Bhavaraju, A. Eccleston, A.C. Read, P.G. Clem, and E.D. Spoerke. "NaSICON-Enabled Next Generation Sodium-Iodide Batteries." *Adv. Energy Mater.* 2016 (*in preparation*).
  - L. J. Small, J.S. Wheeler, J. Ihlefeld, P.G. Clem, and E.D. Spoerke. "Alkaline-Resistant NaSICON." *Adv. Funct. Mater*. 2016. (*in preparation*.)

- Intellectual Property
  - Bhavaraju, et al. "Sodium-Halogen Secondary Cell." US. Patent No.: US 9,413,036 B2.
  - E.D. Spoerke, *et al*. "Cation-enhanced chemical stability of ion-conducting zirconium-based ceramics." US Prov. Appln. No.: 62/311,523.
  - D. Ingersoll, *et al*. "Solid Membrane Flow Battery" US Prov. Appln No.: 62/397,664
  - L.J. Small, *et al.* "Electroless Process for Depositing Tungsten Metal." (SNL SD 14064)

Path Forward (FY17-18)

NaSICON-enabled batteries offer a promising pathway to cost-effective, commercially scalable, safe energy storage.

- Target 10 kWh sodium demonstration
  - 40 250Wh Cells
- Improve performance (cycle life, energy efficiency) of larger-scale (100Wh and 250Wh) cells for Na-I_2 chemistry
  - Improved cathode structure/chemistry
  - Optimized cell design

Thanks

This work was generously supported by Dr. Imre Gyuk through the Department of Energy Office of Electricity Delivery and Energy Reliability.

Work on Na-$NiCl_2$ batteries was performed through collaboration between Ceramatec and SK Innovation.

Follow on posters:

- Dr. Sai Bhavaraju: “Low-cost Sodium Battery for Grid Scale Energy Storage”
- Dr. Leo Small: “Electroless Process for Depositing Tungsten Metal for Sodium Battery Electrodes”
- Dr. Eric Allcorn: “Aqueous Na-ion Redox Flow Battery with Ceramic NaSICON Membrane”