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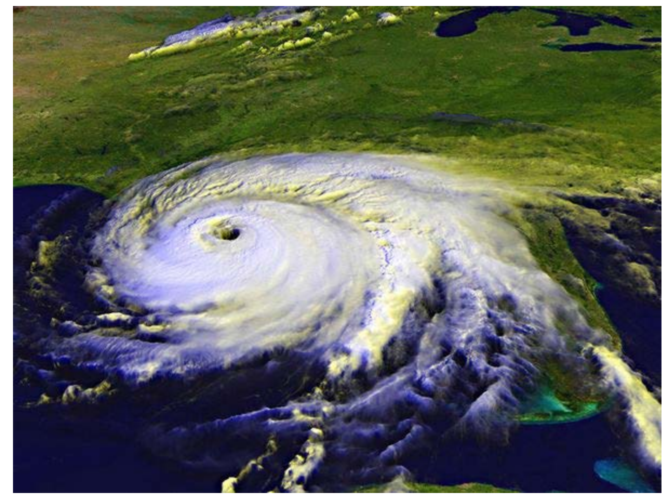

Sodium-Based Battery Development

U.S Department of Energy Office of Electricity (OE) Energy Storage Peer Review

Portland, OR,

September 21-25, 2015

D. Ingersoll

Sandia National Laboratories, Albuquerque, NM

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Program Sponsor

- *Dr. Imre Gyuk – Program Manager, DOE-OE*

DOE – Office of Electricity Delivery and Energy Reliability

Current Team Members

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Ceramatec, Inc, Salt Lake City, UT

Former Team Members (finished this year)

- *Profs. R. Kee & J. Porter, Dr. H. Zhu*

Colorado School of Mines, Golden, CO

- *Prof. E. Wachsman & A. Jolley*

University of Maryland, College Park, MD

Cost Competitive Energy Storage Sodium-based Battery Chemistries

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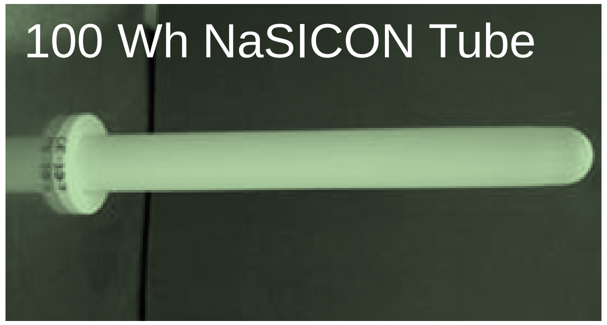
Our goal is to develop low cost (≤ \$100/kWh), low temp (≤150°C), safe, nonflammable alternatives to Na-S and Li-ion batteries. Based on sodium metal anode and sodium battery chemistries.

- High energy per unit weight and volume – Smaller devices
- Abundant domestic supply of Na reserves
- Na-ion conducting separators (NaSICON) commercially available (Ceramatec, CoorsTek) Low production cost
- Various low cost, safe cathode material couples
- - 120°C Na-I/$AlCl_3$ (fully inorganic), 25°C Na-air (aqueous)

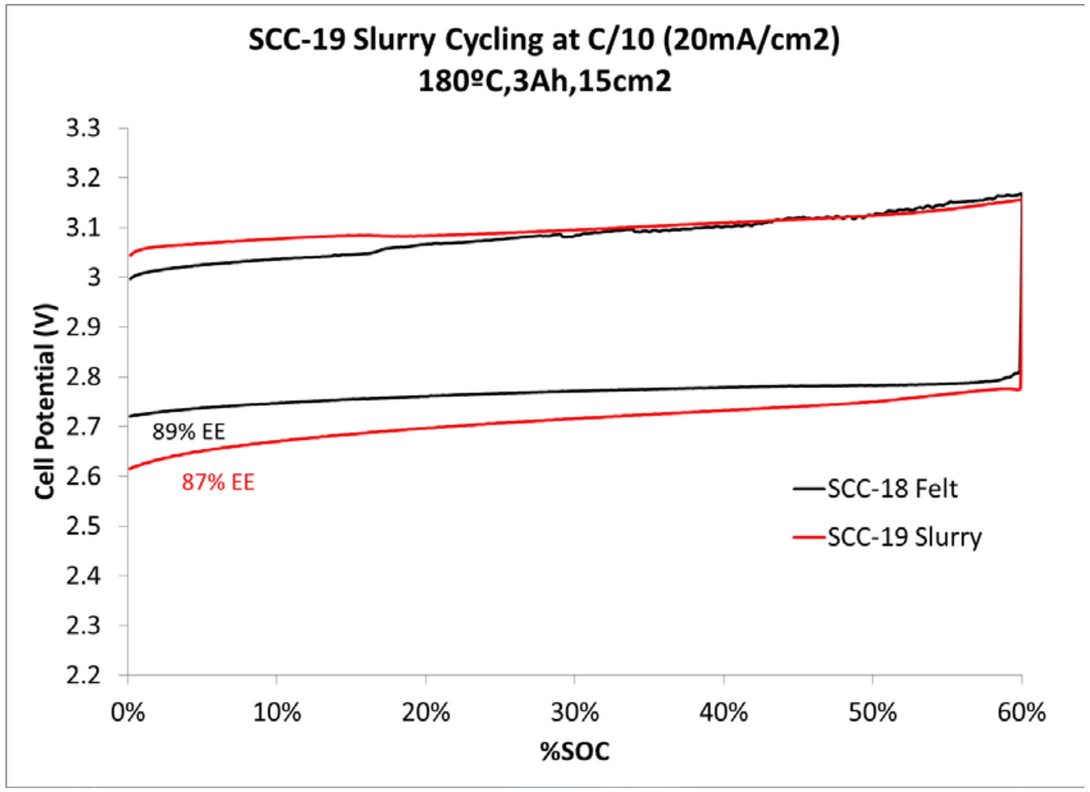
100 Wh, 120°C, NaI/$AlCl_3$ battery

Cell Chemistry and Expected Voltages	
Anodic Reaction	Voltage vs NHE
Na ⇔ $Na^+ + e^-$	-2.71 V
Cathodic Reaction	
$I_2 + 2e^-$ ⇔ $2I^-$	0.54 V
Full Balanced Cell	Est. Cell Voltage
$2Na^+ + 2I^-$ ⇔ $2Na + I_2$	3.25 V



FY15 Accomplishments:

- 100 Wh sodium-ion cell long-term cycling
- >200 cycles of large sodium-ion cell with 87.5% efficiency
- Developed cost basis analysis tool for large scale battery and performed sensitivity analysis for Na-I vs. Na-Br
- 2 papers published, 4 sodium battery patent applications, 3 invited talks
- Demonstrated bulk and thin film NaSICON separators
- ➢ Developed water-compatible NaSICON separators with improved alkaline stability (enables Na-air batteries)
- ➢ Safety protocol established for sodium batteries



Improving the behavior of the solid ceramic ion conductor

Although NaSICON (Sodium (**Na**) **S**uper **I**onic **Con**ductor) has proven an effective solid state ion conductor in organic and molten inorganic electrolytes, its' instability in acidic and alkaline (Brønsted sense) media has prevented significant use in aqueous systems.

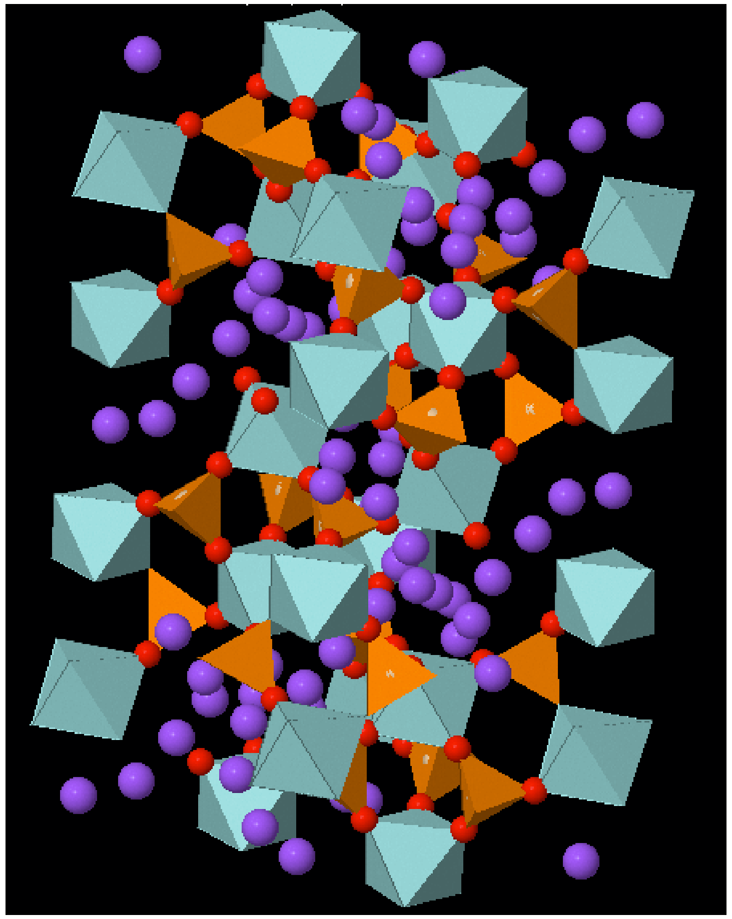
Through ionic-substitution, we modified the metal-oxygen bonds to improve its' stability to pH extremes.

Developing an aqueous stable NaSICON formulation would open the doors to other battery systems and new application areas:

Sodium-air

Sodium-bromine Na-Br

$Na_3Zr_2PSi_2O_{12}$



Source of instability:

- Metal-oxygen bonds in the the zirconia octahedra (blue) and phosphate or silica tetrahedra (orange), however, are weak points in the NaSICON lattice.
  - Acid: Protonation of metal-bridging oxygen
  - Base: Nucleophilic attack by OH^- or deprotonation of non-bridging oxygen.

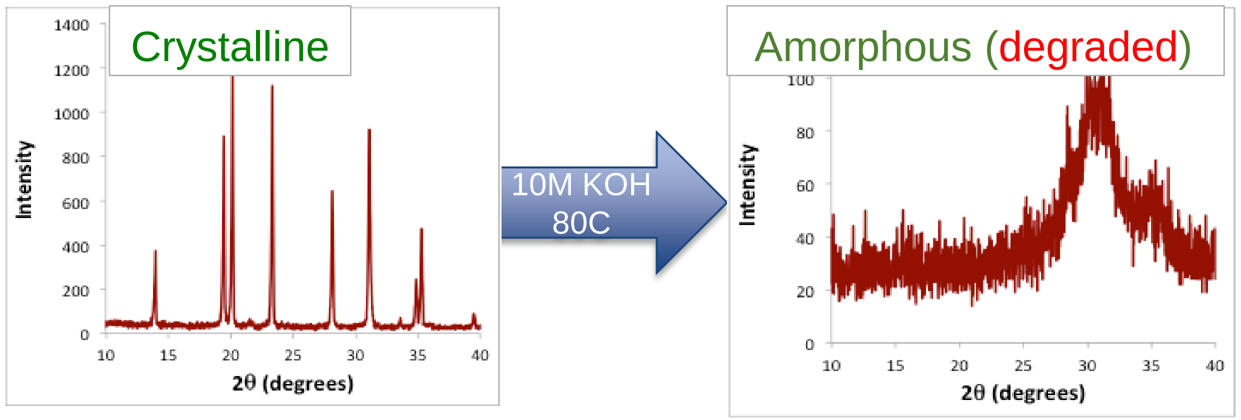
Ionic substitution shows dramatically improved stability to acidic and alkaline media

By making select science-based changes in the NaSICON composition and structure, we have dramatically improved it's stability to both high and low pH conditions

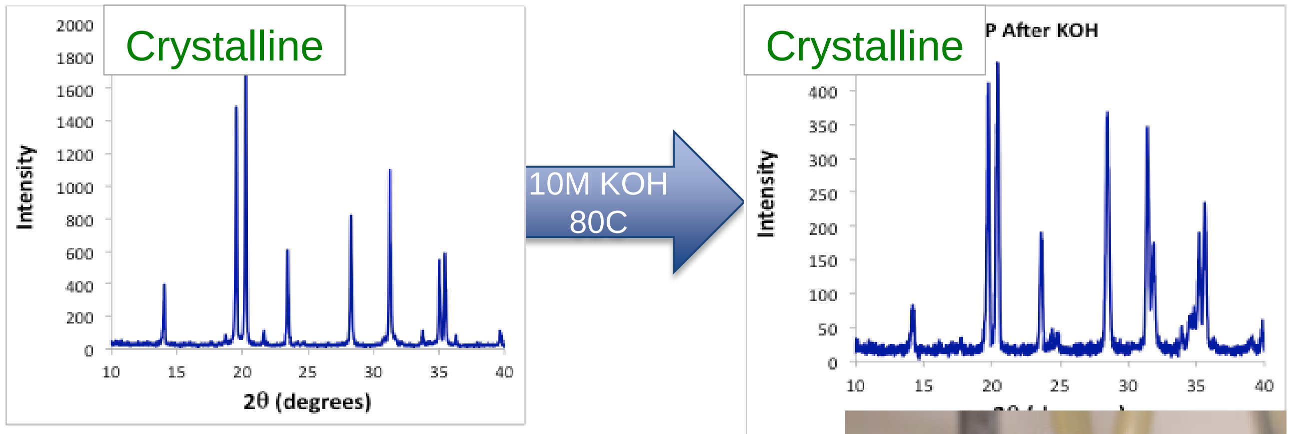
- High pH: 10M KOH at 80 °C
  - baseline material fully degraded, and only an amorphous phase with minor ZrO_2 secondary phase is present (forms a sludge)
  - The new material retains its structure throughout
- Low pH
  - baseline material fully degraded, and only an amorphous phase with minor ZrO_2 secondary phase is present
  - The new material retains its structure throughtout

Baseline NaSICON fully degraded after exposure to 10 M KOH at 80 C.

Baseline material NZP ($NaZr_2P_3O_{12}$)



Ionically substituted NaSICONm-NZP



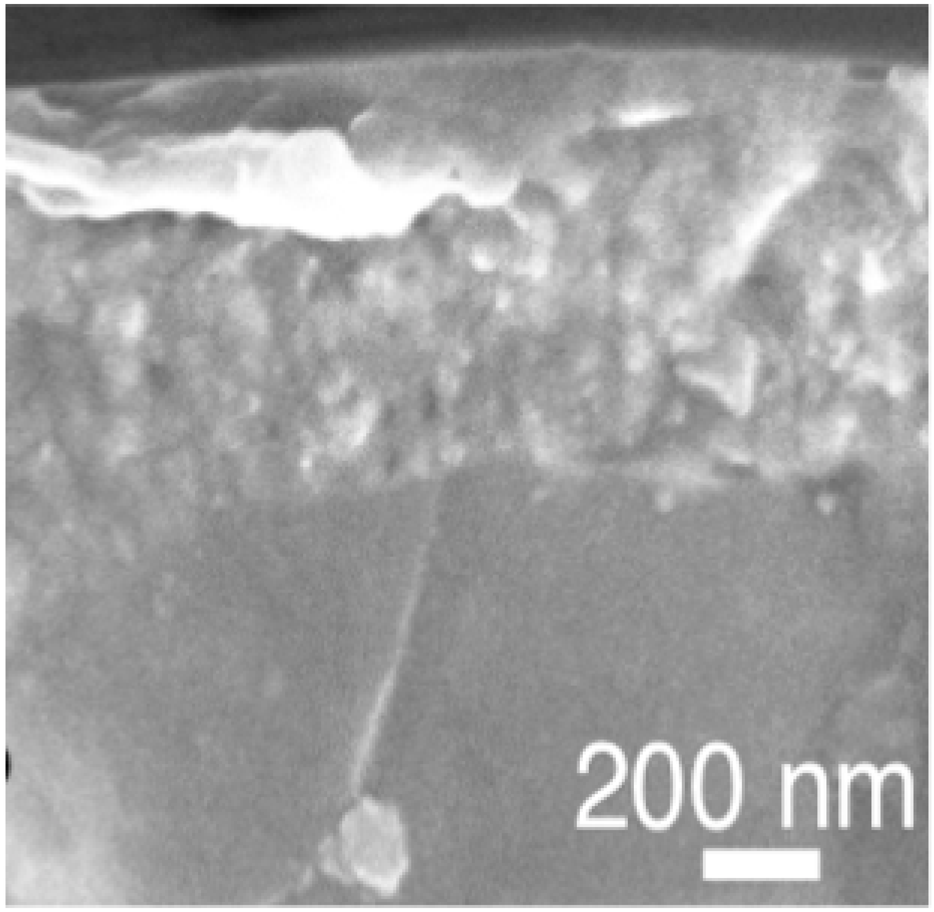
Toward a Relevant Configuration

The new material does have inferior conductivity, so we have engineered around that shortcoming by developing a method for growing a thin film on top of the unmodified material.

- In this configuration, the new, thin layer material protects the unmodified material from hydrolytic attack *without* degrading it mass transport characteristics

thin film of new material which acts as a protective coating

baseline material as a substrate



We have applied for a patent on the material composition and process, and are currently in negotiations for transfer of this technology to industry

Establishing the Safety Basis Is Important for Commercialization of Large-Scale Systems

Consequences of an abnormal event must be considered, and they:

1) scale with energy: increasing energy ➔➔➔ increasing consequences

2) depend on location: proximity to casuals ➔➔➔ increasing consequences

This 10 kWh battery pack depicted on the side of a building likely has 5 liters of liquid electrolyte (rough estimate based on 18650 size cells, the number of cells in the pack, and 5 ml electrolyte in each cell)

* http://www.greencarcongress.com/2009/12/panasonic-20091225.html

Battery Safety Basis: Predictive Modeling of High Consequence Low Probability Events

We have modified the chemistry to enhance safety

- Non-flammable solvent, reformulated electrolyte, final products are benign – engineered safe.

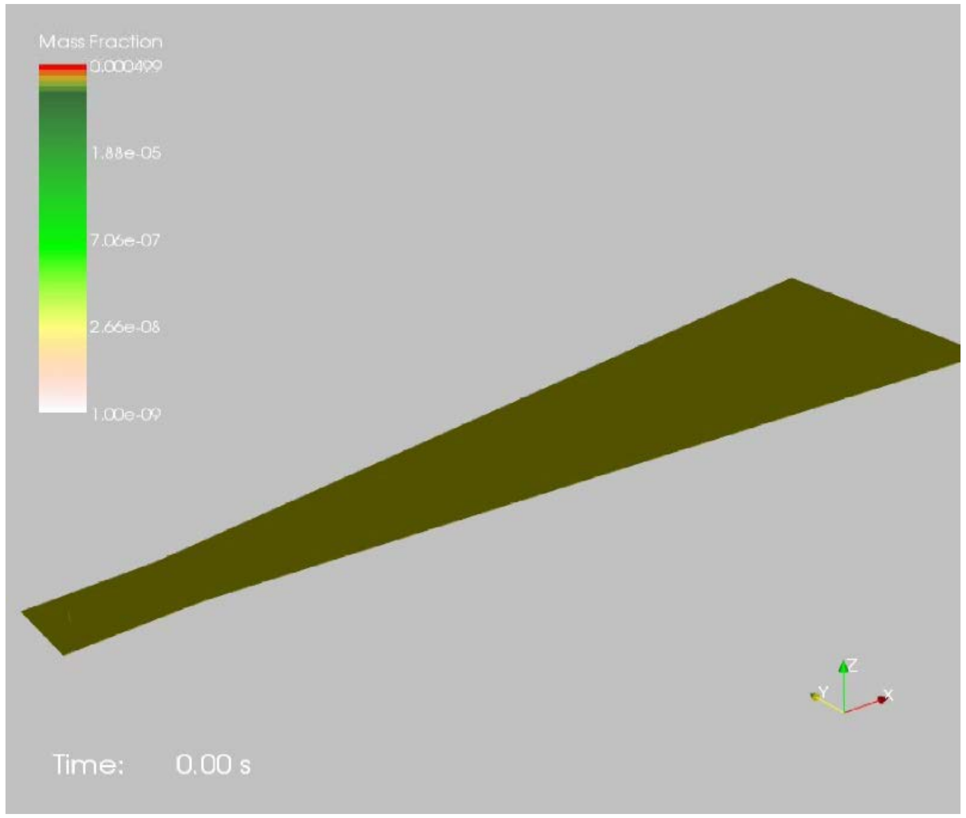
We have developed modeling & simulation tools that ***predict*** thermal environments and the response of an object to that environment. (Advanced Scientific Computing (ASC) Program)

- We can predict: Turbulent fluid mechanics (buoyant plumes); Participating Media Radiation (PMR); Reacting flow (hydrocarbon, particles, solids); Conjugate Heat Transfer (CHT)

We have adapted the ASC modeling framework to our battery system to establish its' safety basis

- We have demonstrated proof of concept
- We are in discussions for spinning this off (Work for Others)
- This will be spun off as a stand alone activity

Image Source: WindPower Monthly
http://www.windpowermonthly.com/article/1284038/analysis-first-wind-project-avoids-storage-30m-fire



Predictive Simulation of Smoke Plume from Abnormal Event. The colors correspond to concentration of chemical species

Future Plans

FY16-17 Plans:

- Demonstration of 10 kWh sodium battery (with Ceramatec: 180 Wh/l, $150/kWh, 2.8V, 40 cells)
- Scale-up of cell size to 250 Wh sodium-ion cells
- Demonstrated low cost $100-200/kWh
- Head to head safety basis analysis (Li vs. Na etc.)
- Quantified safety advantage of all-inorganic sodium chemistry relative to Li ion

Questions?

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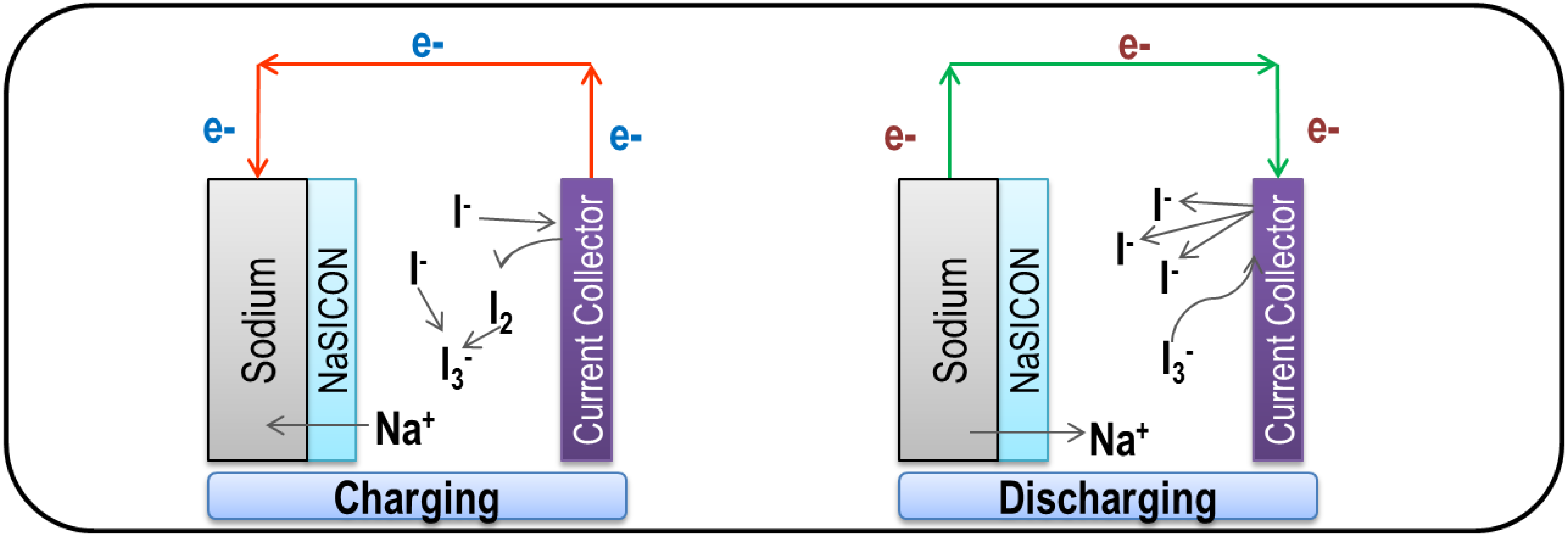
Backup

R&D of 120 ˚C Na-I_2 Secondary Battery



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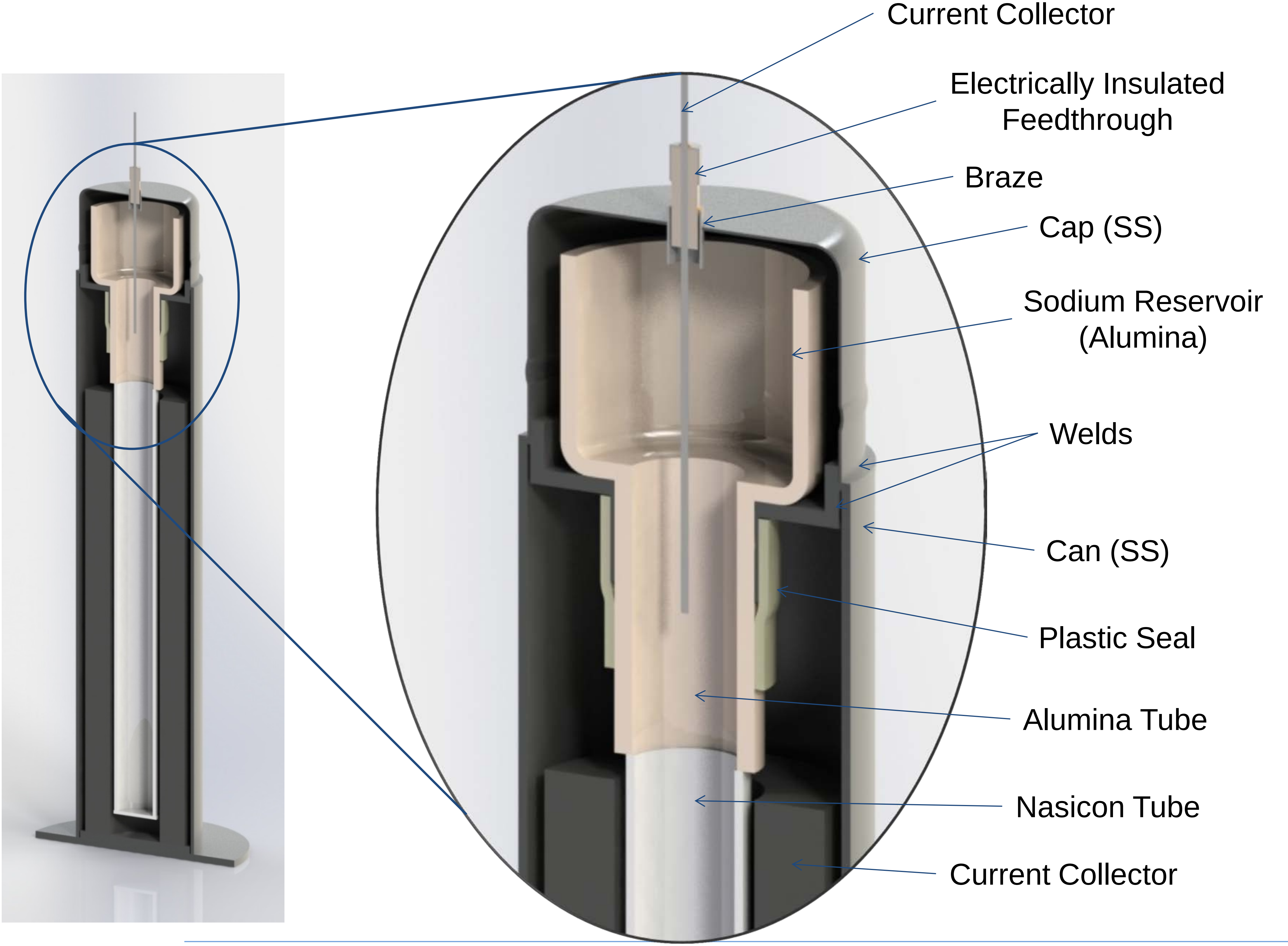
Full Balanced Cell	Est. Cell Voltage
$2Na^+ + 2I^- \Leftrightarrow 2Na + I_2$	3.25 V

Metric	Na-S	Na-I_2
Increased Cell Voltage	2 V	2.8 to 3.4 V ✓ 1/3rd fewer cells compared to Na-S
Increased Energy Density	~ 180 Wh/kg	~ 200 Wh/kg ✓ Comparable energy density to Na-S
Lower Operating Temperature	> 300 ˚C	120 ˚C ✓ Moderate temperature while retaining high power ✓ Plastic components used in Battery construction
Module Production cost	300 $/kWh	< 200 $/kWh
Safety	Low safety	Safe due to formation of non-combustible salts

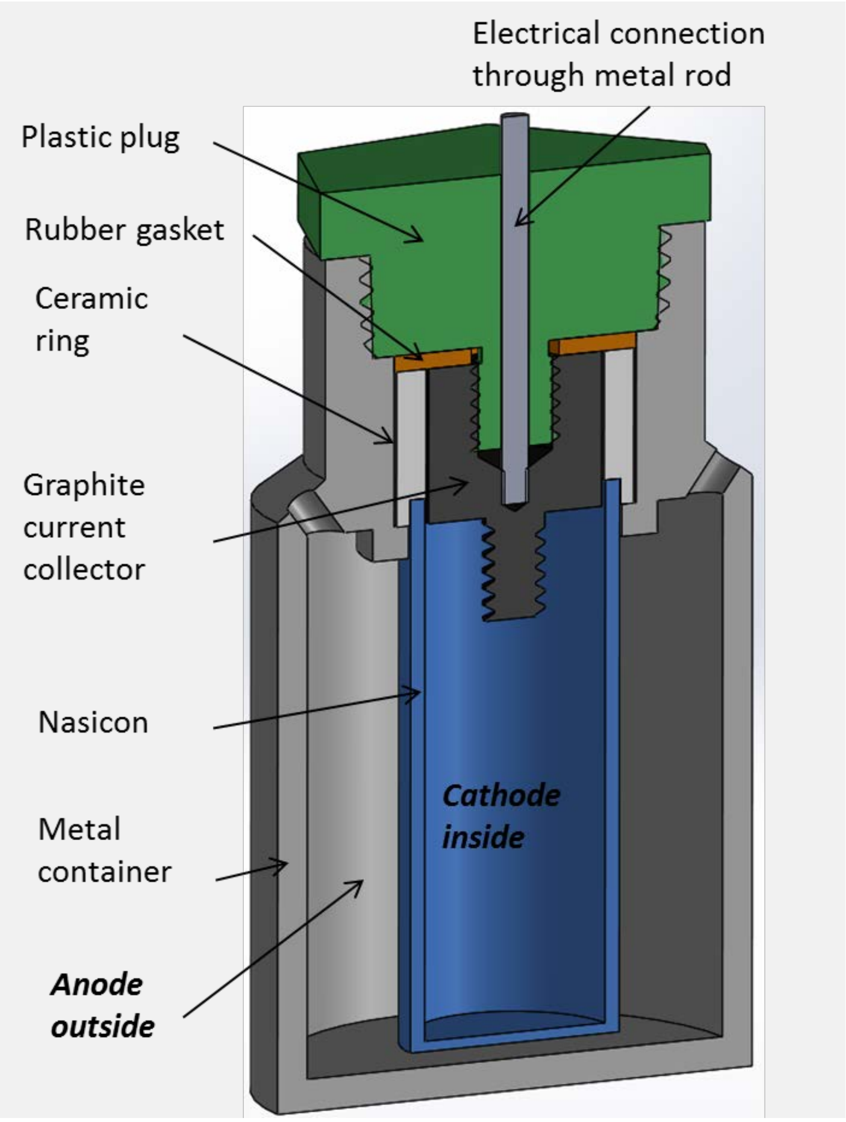
Scale-up in cell size to 100 Wh Welded Can Design



Sodium battery design

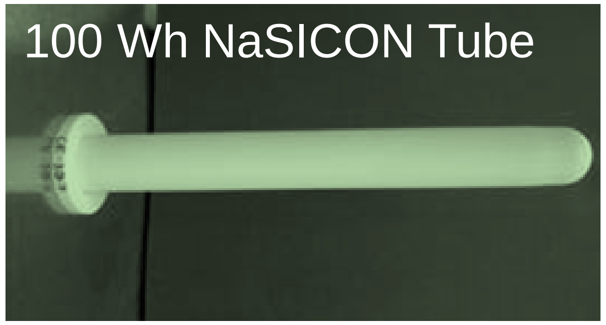
Sodium-Iodine Battery Chemistry

Anode	$2Na$	$= 2Na^{+} + 2e^{-}$	$E_0 = 2.71V$
Cathode	$I_2 + 2e^{-}$	$= 2I^{-}$	$E_0 = 0.54V$
Overall	$\mathbf{2Na + I_2}$	$\mathbf{= 2Na^{+} + 2I^{-}}$	$E_0 = \mathbf{3.25V}$



Sodium-conductive ceramic separator

- Physical barrier between anode and cathode improves efficiency and eliminates crossover
- High sodium-ion conductivity for fast charge/discharge
- Proprietary sodium (Na) superionic conductor (Nasicon) which is stable against molten sodium
- Scaling from 100 Watt-hour to 250 Watt-hour modules



250 Watt-hour

Focus on safety and low cost

- Inherently safe chemistry – nonflammable
- Projected cost: \$35-100 / kWh, 3-10X below lithium