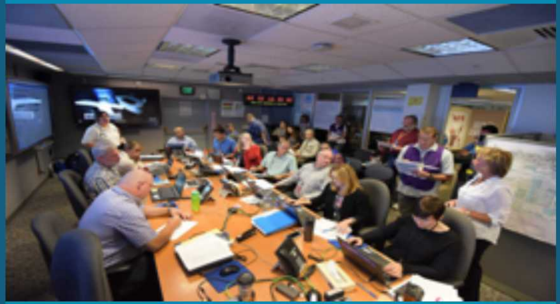
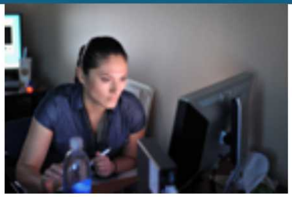
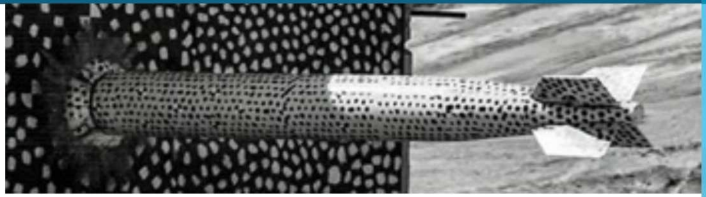
Sandia National Laboratories

SAND2019-11482C

Low Temperature Molten Sodium Halide Batteries







PRESENTED BY

Erik D. Spoerke

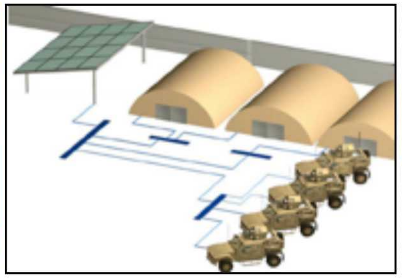
Martha Gross,
Stephen Percival,
Leo Small,
Amanda Peretti,
Josh Lamb, and
Babu Chalamala

This work at Sandia National Laboratories is supported by Dr. Imre Gyuk through the U.S. Department of Energy Office of Electricity.

Project Overview


Renewable/Remote Energy

Grid Reliability



National Defense

Emergency Aid

As part of the DOE Office of Electricity efforts to create a modern, resilient, reliable, and agile grid system, we are developing new battery technology characterized by:

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalability

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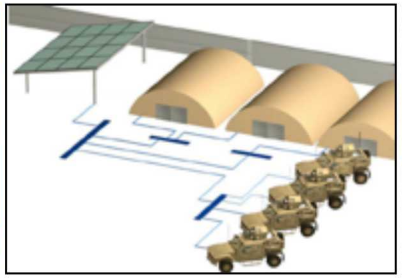


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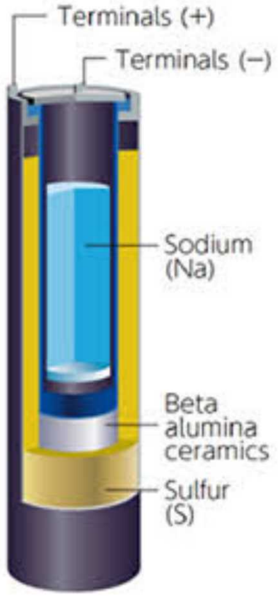
Sodium-based batteries

- 6th most abundant element on earth.
- 5X the annual production of aluminum.
- Proven technology base with NGK Sodium/Sulfur (NaS) and FzSoNick ZEBRA (Na-$NiCl_2$) systems.
- Utilize zero-crossover solid state separators.
- Favorable battery voltages (>2V).



Na-S (*E_{cell} ~ 2V*)

$2Na + 4S \leftrightarrow Na_2S_4$

Na-$NiCl_2$ (*E_{cell} ~ 2.6V*)

$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$

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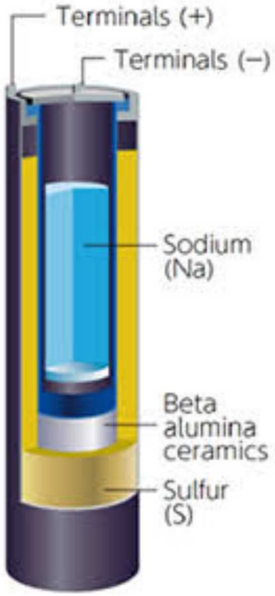


Na- ... **5V)**

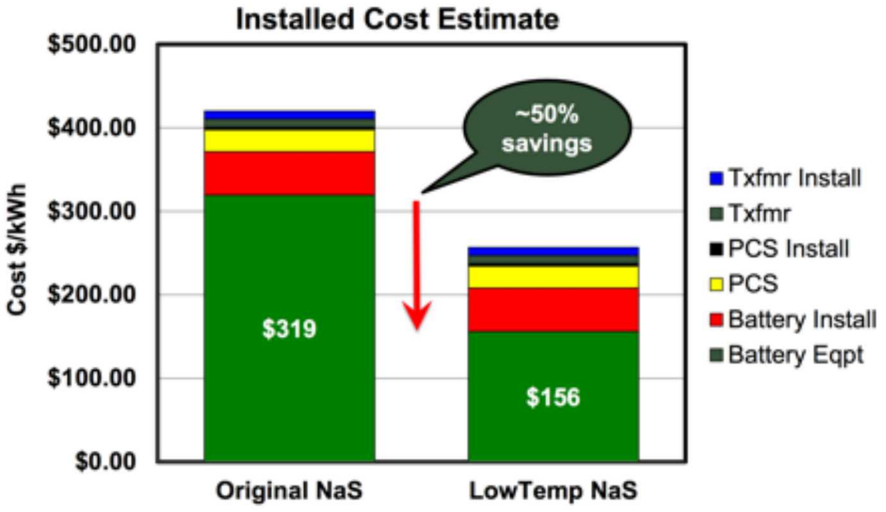
~300°C Operation!

2Na ... Na$^+$ + 2Cl$^-$ + Ni(s)

Lowering Battery Operating Temperature to Drive Down Cost

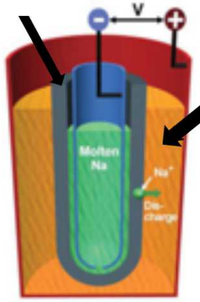
<u>Our Vision:</u> A safe, reliable, molten sodium-based battery that operates at drastically reduced temperatures (near 100°C).

- Improved Lifetime
  - Reduced material degradation
  - Decreased reagent volatility
  - Fewer side reactions
- Lower material cost and processing
  - Seals
  - Separators
  - Cell body
  - Polymer components?
- Reduced operating costs
- Simplified heat management costs
  - Operation
  - Freeze-Thaw

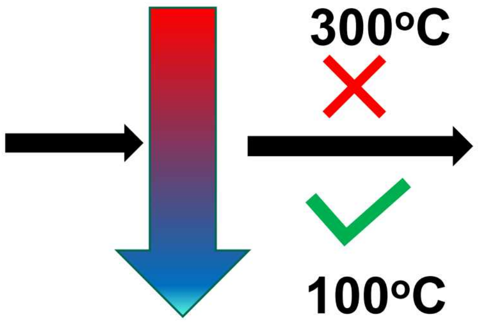


Gao Liu, et al. "A Storage Revolution." 12-Feb-2015 (online): https://ei.haas.berkeley.edu/education/c2m/docs/Sulfur%20and%20Sodium%20Metal%20Battery.pdf

Low Temperature Ion Conducting Ceramic



Low T°C Molten Salt Catholyte



Research Team

SNL Na-Battery FY19 Budget: $650k

SNL Team

- Dr. Martha Gross (Postdoc)
- Dr. Stephen Percival (Postdoc converted to Staff)
- Amanda Peretti (Technologist)
- Dr. Leo Small
- Dr. Josh Lamb

External Collaborations:

- Professor YT Cheng (University of Kentucky)
    - Mechanical characterization of electrochemical materials
- Youngsik Kim (UNIST (Ulsan National Institute of Science and Technology)
    - Secondary NaSICON development and supply

Students

Current and Former Stars

Ryan Hill
Sara Russo

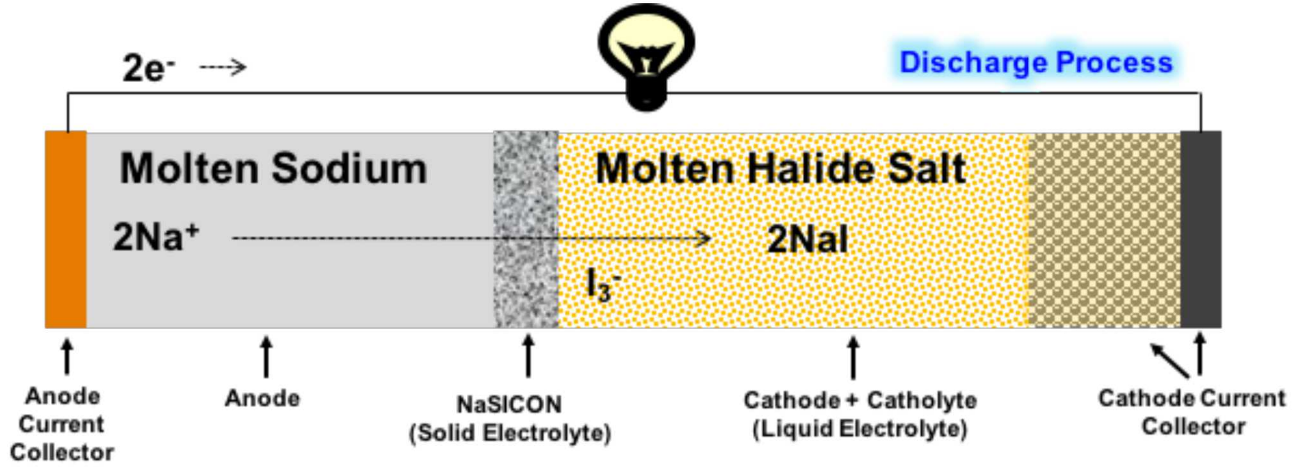
Future Star:
Rose Lee

Low Temperature Molten Sodium (Na-NaI) Batteries

Realizing a new, low temperature molten Na battery requires new battery materials and chemistries.

<u>Ingredients for Success</u>

- Molten Na anode
- Highly Na^+-conductive, zero-crossover separator (e.g., NaSICON
- 25 mol% NaI in AlX_3 catholyte



<u>Na-NaI battery:</u>

$Na \rightarrow Na^+ + e^-$ $E^0_o = 0V$

$I_3^- + 2e^- \rightarrow 3I^-$ $E^0_o = 3.24$

$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0_{cell} = 3.24V$

Candidate catholyte salts include $AlCl_3$, $AlBr_3$

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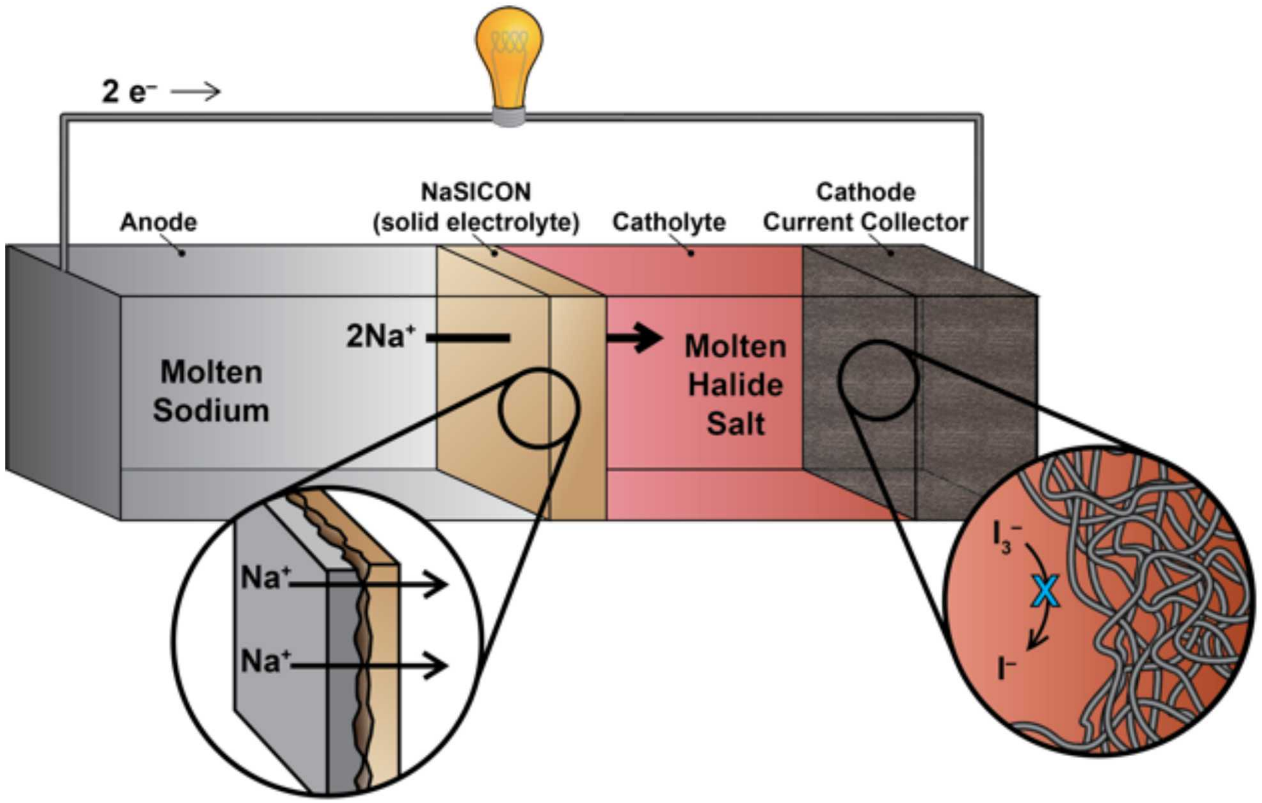

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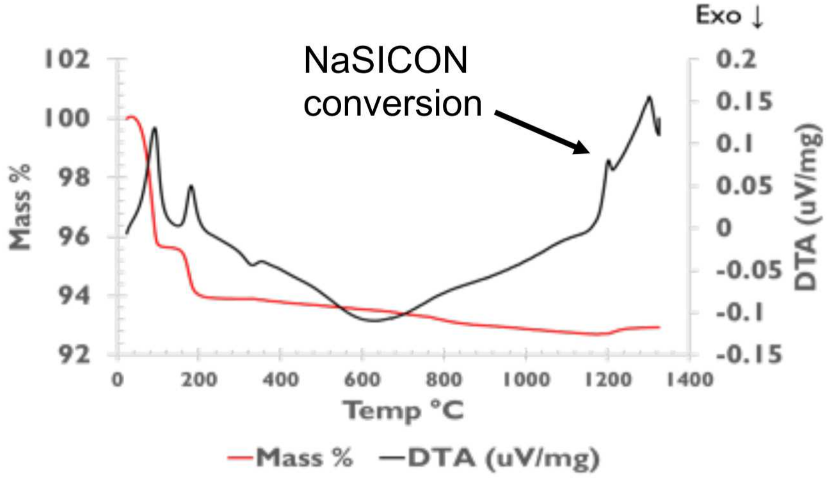
Martha Gross

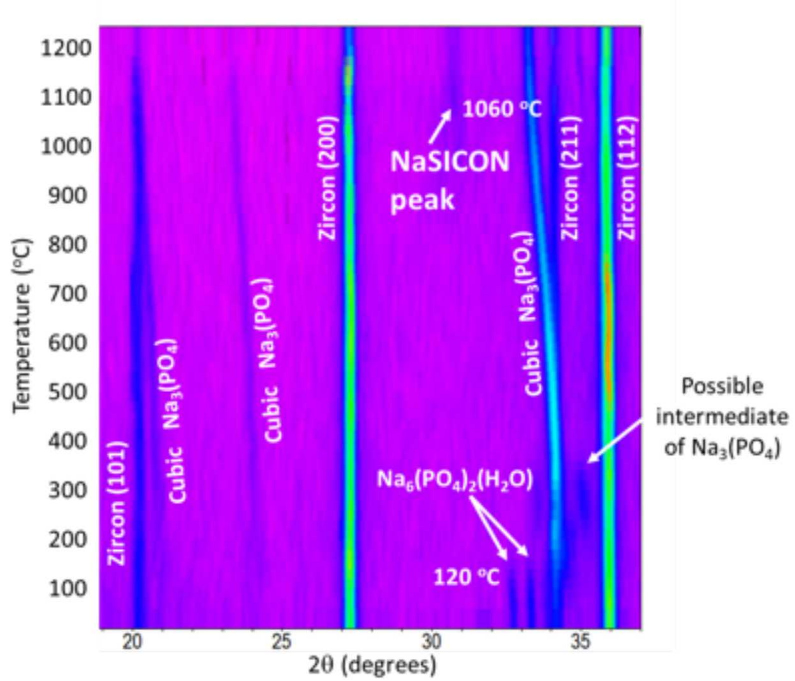
NaSICON Synthesis

Thermal analyses reveal pathway to functional NaSICON synthesis!



NaSICON calcined to remove hydrates, sintered at 1230°C, yields >94% density and >0.4 mS/cm at 25°C.

These ceramics are suitable for lab-scale testing of molten sodium batteries.



- DTA/TGA show water removed from precursor powder by ~250°C.
- NaSICON conversion reaction evident between 1150-1230 °C.
- Sintering above 1230°C → poor ceramic integrity (melting?)

- VTXRD shows conversion of Zircon and cubic $Na_3(PO_4)$ to NaSICON starting near 1100°C
- Hydrate form of $Na_3(PO_4)$ up to 120°C, converts to cubic $Na_3(PO_4)$ at ~300°C.

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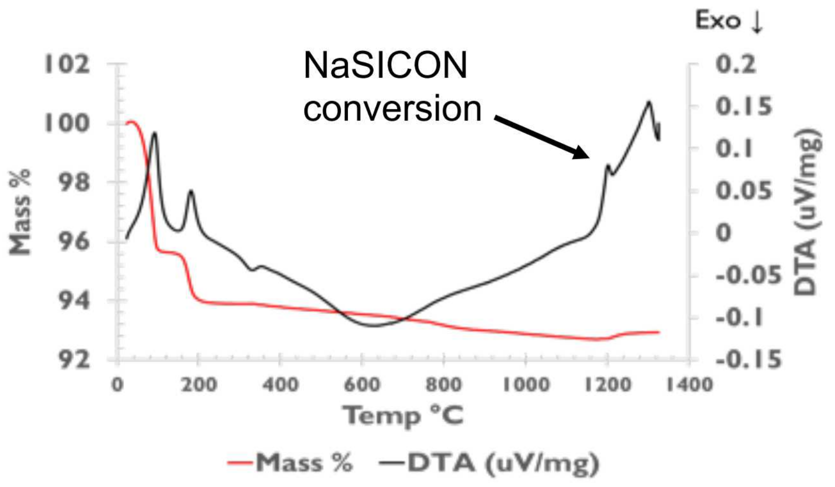

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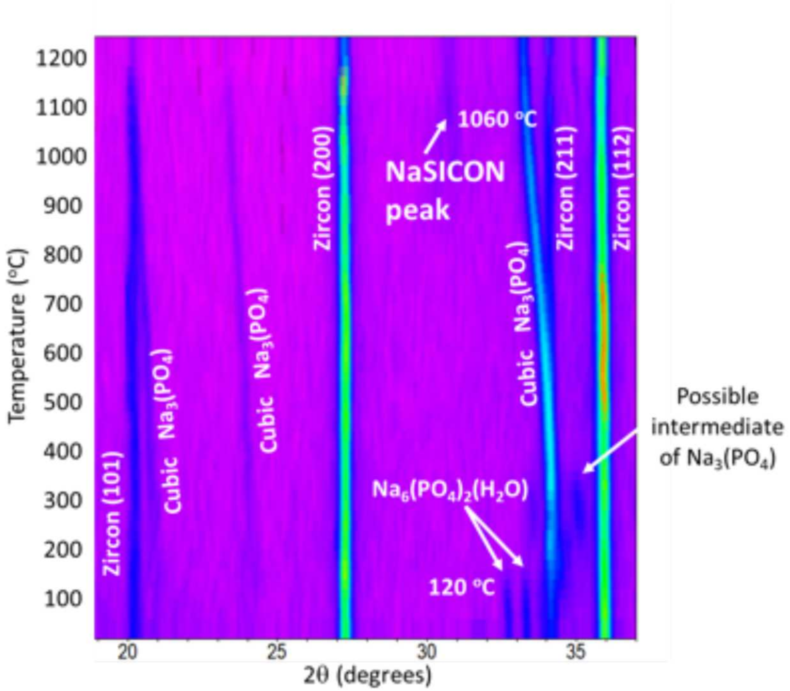

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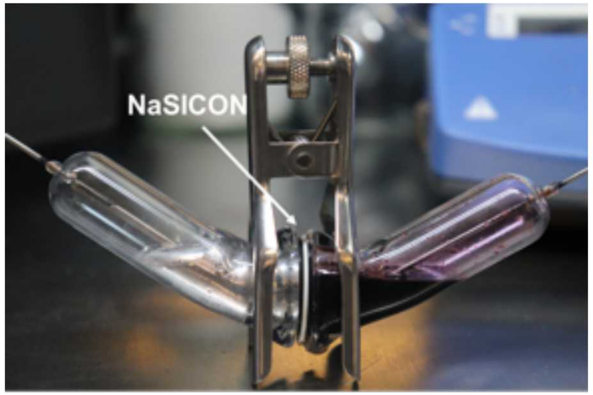

Molten Na Battery Cell Set-Up

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Identifying a Viable Na-Battery Test Platform

Cell geometry, interfacial interactions, and materials compatibility were identified as key design elements

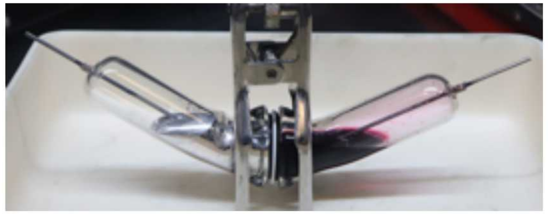
Re-Engineered Cell Variants

Many new cell designs and geometries built and tested (7 different types!)

Some designs were time consuming, laborious and could be **used only once!**

New Cell Designs

Enable easy assembly, high throughput and functional geometry



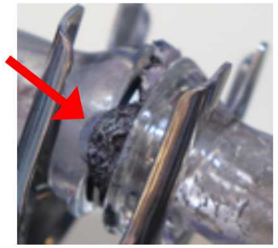
Includes 3 designs that are fully interchangeable and reusable

Importance of Seals

Many times failure was due to materials incompatibilities of the seals and the constituents.

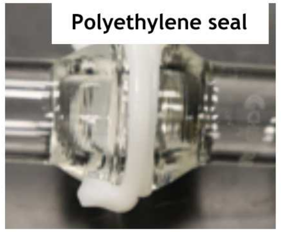
Sodium Compatible Seal Material

Sodium reacting with the Kalrez o-ring



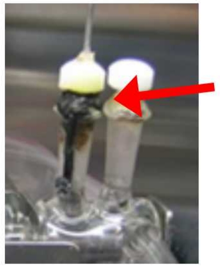
Polyethylene seals from molten polyethylene to seal the sodium side

Not re-useable and hard to apply properly



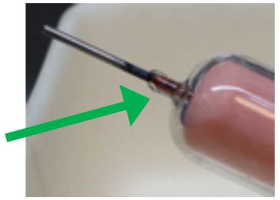
Identified new EPDM o-rings that will not react with sodium metal

Molten Salt Compatible Seal Material



Vapors from molten salt aggressively attacking the epoxy seals

Glass to metal seals eliminate unwanted side reactions from salt vapors



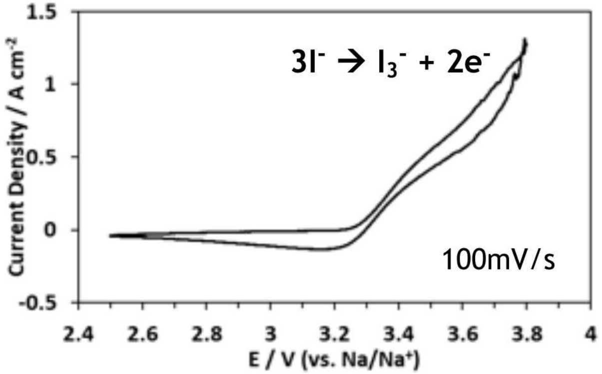
Last Year's "Really Cool" Hurrah!

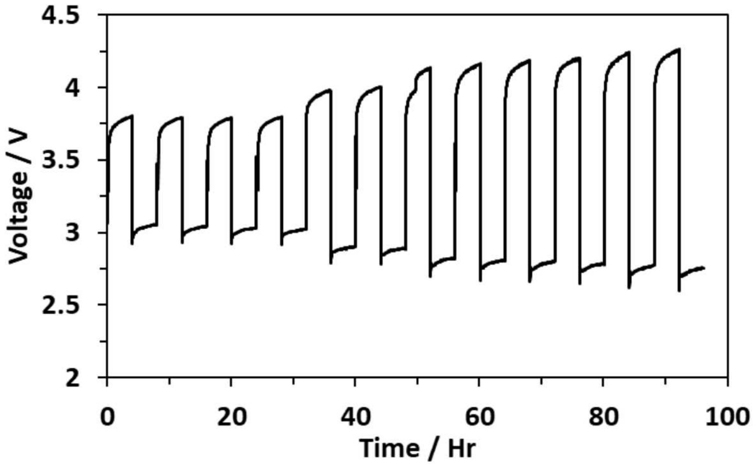
Novel demonstration of Molten Na-NaI battery at 100-110°C

The NaI-$AlBr_3$ catholyte system is molten and exhibits excellent electrochemical behavior at reduced operating temperatures.

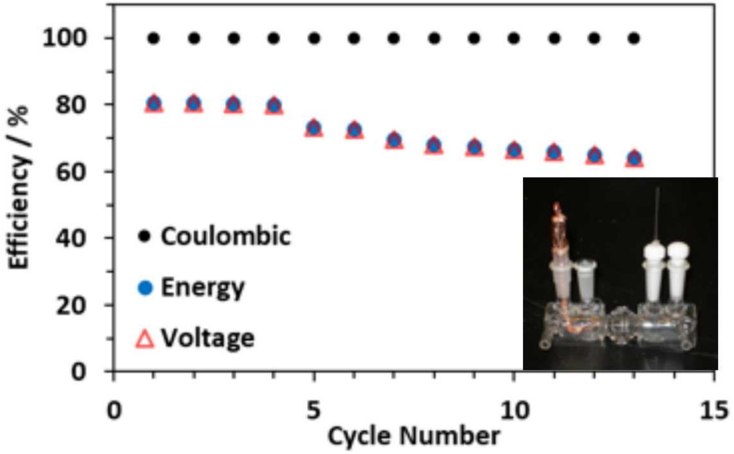
- 25:75 NaI-$AlBr_3$salt <u>completely molten </u>at 90 °C
- Large fully molten capacity range (~5-25 mol% NaI)

Iodide is electrochemically active in 25 mol% NaI-$AlBr_3$ at 90°C





Battery cycling at **<u>100-110°C</u>**!



25 mol% NaI-$AlBr_3$ with NaSICON separator.

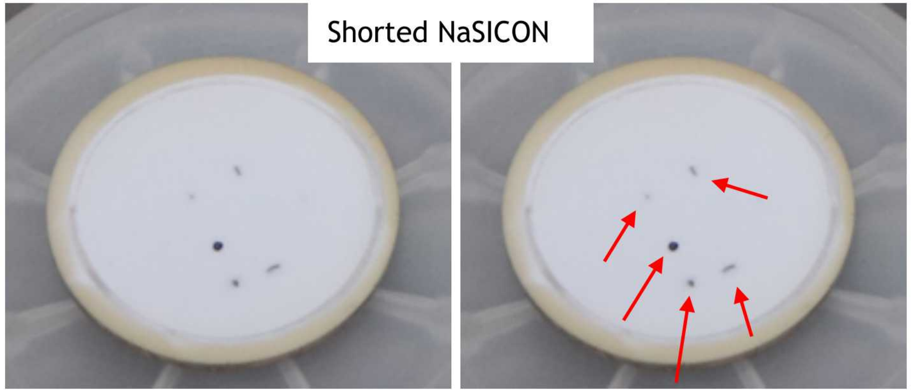
Follow the Bouncing...Sodium!

Poor sodium wetting on NaSICON is a problem.

Improper Na-wetting of NaSICON.

Red arrows pointing to shorts

Improper wetting leads to current constriction through small active areas of NaSICON eventually forming shorts.



NaSICON Coated with Sn-Based Coating Shows Drastically Improved Adhesion!

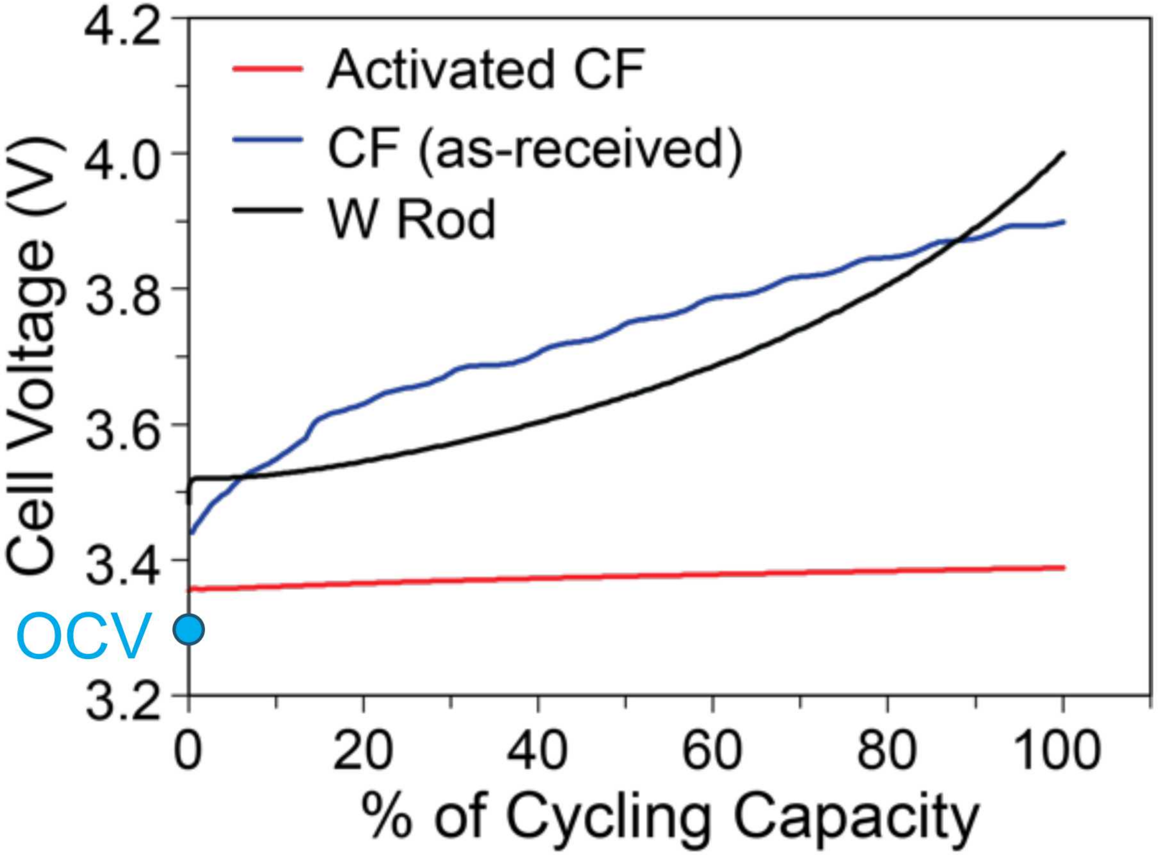
Improving Cathodic Current Collector

Important Properties of the Current Collector

- Fast Charge Transfer
- High Surface Area
- Chemically & Electrochemically Inert

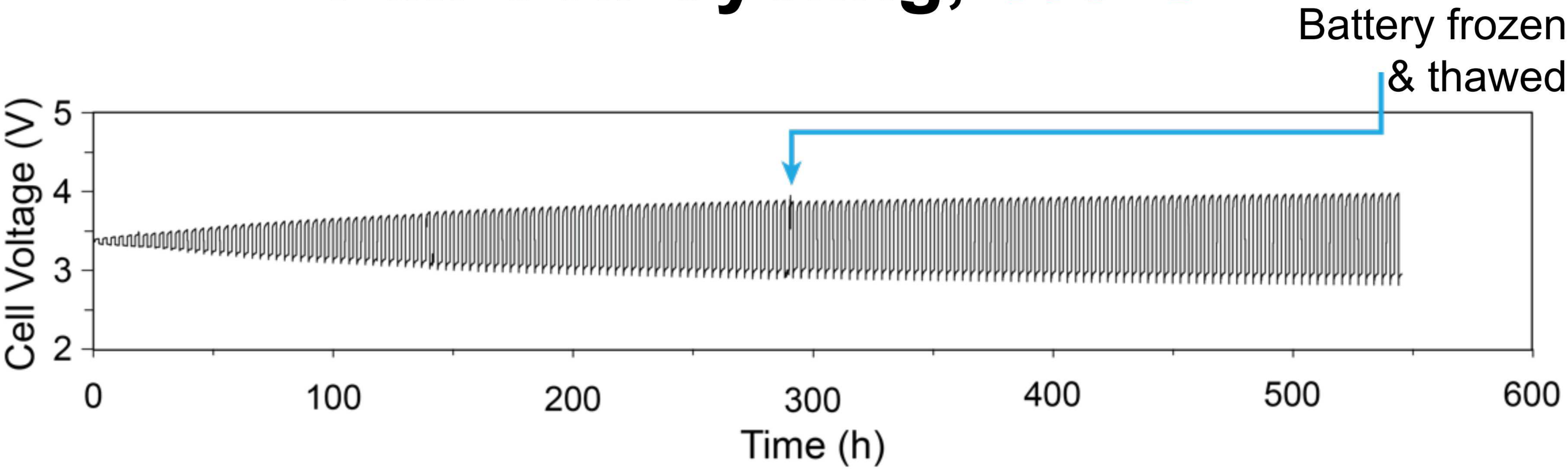
- Tungsten (W) rod: high stability, low surface area
- Carbon Felt (CF) – 1000x surface area of W rod, but no improvement in overpotential
  - – poor charge transfer
- Activation of CF: thermal treatment by heating 400°C in air, or acid treatment by cleaning with 0.1M HCl
- **Activated CF dramatically lowers overpotential**

Full Cell, Single Charge: 110°C



This Year's "Cool Hurrah"

Full Cell Cycling, 110°C



- Integration of Sn-based coating and activated CF enables long-term battery cycling: **Battery achieved 200 cycles!**
- Even after freeze/thaw, interfaces remain intact with uninterrupted cycling!

0.15 Ah cell
0.5 mA cm^{-2}
25% SOC assembly

Evaluating Potential Hazards of "Failed" Na-NaI Batteries

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
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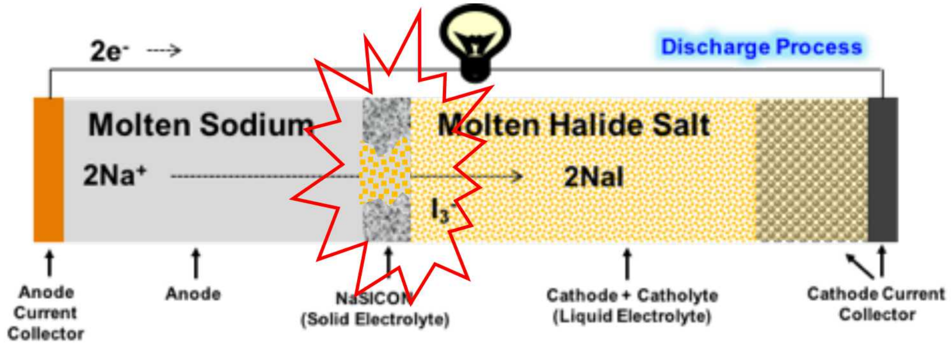
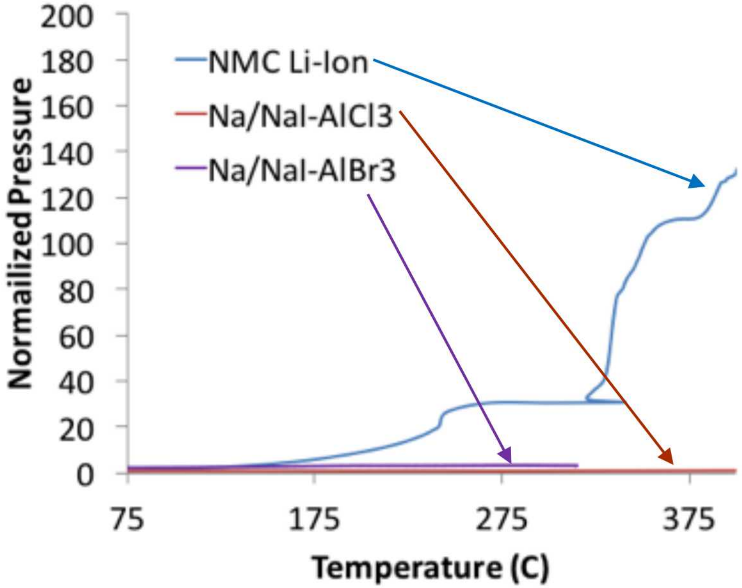


Simulating separator failure, metallic Na and NaI/AlX_3 were combined and heated.

Byproducts of reaction are aluminum metal and harmless sodium halide salts.



Accelerating rate calorimetry reveals that Na-NaI/AlX_3 mixtures exhibit:

1) *no significant exothermic behavior*
2) *no significant gas generation of pressurization*

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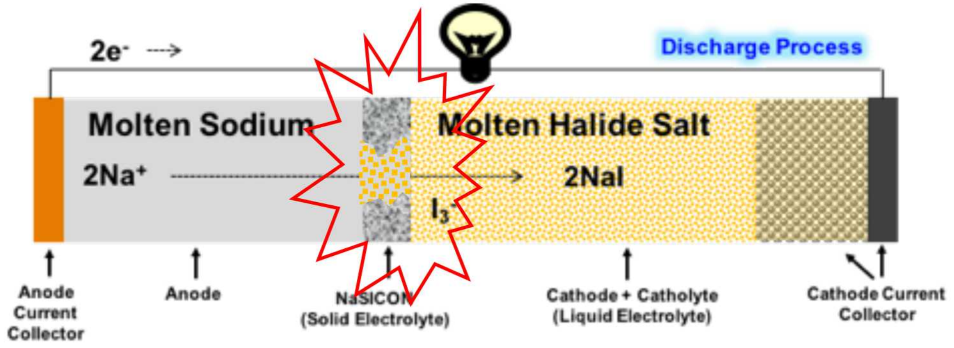

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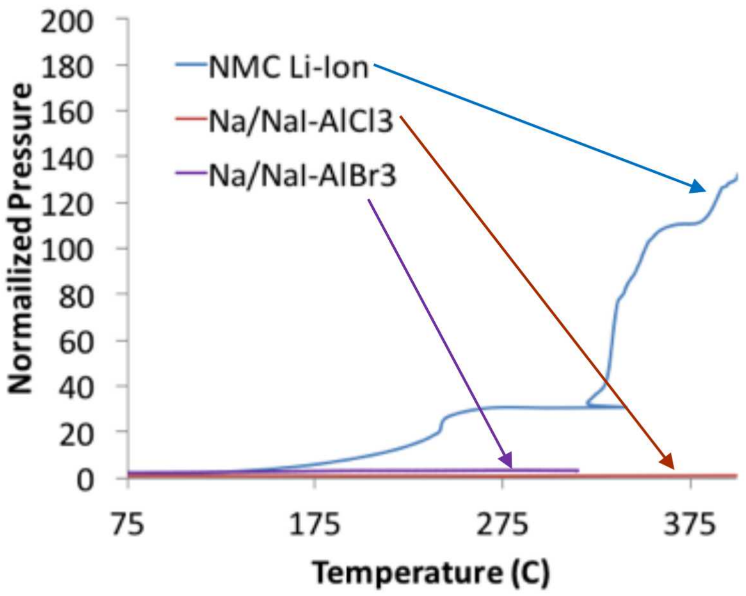

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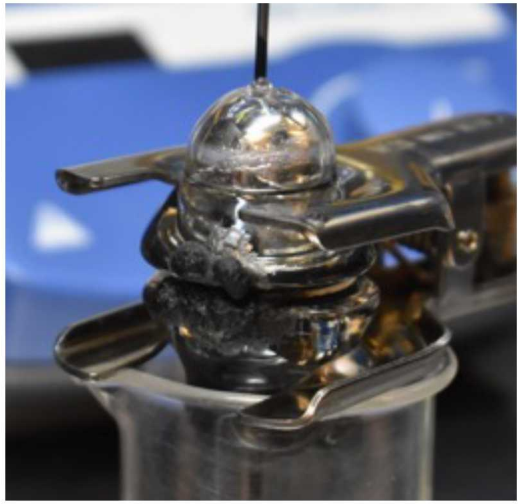

Failed separator led to termination of battery, but no significant hazardous conditions.

Project Metrics

Publications

- S.J. Percival, L.J. Small, and E.D. Spoerke. “Electrochemistry of the NaI-AlCl3 Molten Salt System for Use as a Catholyte in Sodium Metal Batteries.” (2018) *J. Electrochem. Soc.* **165** (14). A3531-A3536.
- E.D. Spoerke, M.M. Gross, S.J. Percival, and L.J. Small. Molten Sodium Batteries. In Review for Publication with Springer, Inc. 2019.
- M.M. Gross, A.S. Peretti, S.J. Percival, L.J. Small, and E.D. Spoerke. “Interfacial Modifications of NaSICON for Low Temperature Molten Sodium Electrochemistry.” In preparation.
- A.S. Peretti, E. Coker, M. Rodriguez, and E.D. Spoerke. “Impact of Humidity on Solid State Synthesis and Performance of NaSICON Ceramic Ion Conductors.” In preparation.

Project Metrics

Presentations (Invited)

- E. D. Spoerke. S.J. Percival, L.J. Small, A.Peretti, J. Lamb, B.Chalamala. “Materials Advances to Enable Low Temperature Molten Sodium Batteries for Grid-Scale Energy Storage.” *2019 World Materials Research Institutes Forum*. Budapest, Hungary. June 16-20, 2019. **(Invited)**
- E.D Spoerke, S.J. Percival, L.J. Small, A. Peretti, and J. Lamb. “Molten Sodium Batteries: Promise for Advancing Grid-Scale Battery Utility.” *NAATBatt 2019 Annual Meeting and Conference*. Litchfield Park, AZ, USA. March 11-14, 2019. **(Invited)**
- E.D. Spoerke, S.J. Percival, L.J. Small, A. Peretti, J. Lamb and B. Chalamala. “Advancing ‘Low’ Temperature Molten Sodium Batteries.” *2019 International Coalition for Energy Storage and Innovation and Pacific Power Source Symposium Joint Meeting (ICESI - PPSS 2019)*, Waikoloa Village, HI. January, 2019. **(Plenary)**
- E.D. Spoerke, “Advancing Grid-Scale Electrical Energy Storage.” *2nd NELHA Conference on Energy Storage Trends and Opportunities*. Kailua-Kona HI. December, 2018. **(Invited)**
- E.D. Spoerke, M. Gross, S. Percival, L. Small, A. Peretti, J. Lamb, and B. Chalamala. “Materials Chemistry to Advance Na-Batteries.” *DOE Na-Battery Workshop,* Richland, WA. Sept., 2019. **(Invited)**
- E.D. Spoerke, M. Gross, S.J. Percival, L.J. Small, A. Peretti, J. Lamb, B. Chalamala. “Really Cool Molten Sodium Batteries.” 31st Rio Grande Symposium on Advanced Materials. Albuquerque, NM. September, 2019. **(Invited)**

Project Metrics

Presentations (Contributed - 2 poster awards)

- E.D. Spoerke, S.J. Percival, L. J. Small, A. Peretti, J. Lamb, and B. Chalamala. "Low Temperature Molten Sodium-Based Batteries for Large Scale Electrical Energy Storage." *235th Electrochemical Society Meeting*. Dallas, TX, USA. May 26-30, 2019.
- E.D. Spoerke, A. Peretti, S. Percival, J. Bock, H. Brown-Shaklee, L.J. Small, and B. Chalamala. "Adapting Processing and Structure Toward Improved NaSICON-Based Sodium Ion Conductors." *Materials Research Society Spring 2019 Meeting*. Phoenix, AZ. April 22-26, 2019.
- E.D. Spoerke, A. Peretti, S.J. Percival, J. Bock, H. Brown-Shaklee, L.J. Small, and B. Chalamala. "Rethinking Solid State Sodium Ion Conductors for Low Temperature Molten Sodium Batteries." *Electronic Materials and Applications 2019*, Orlando, FL. January, 2019.
- E.D. Spoerke, S.J. Percival, L.J. Small, A. Peretti, and J. Lamb. "Tailoring Molten Sodium-Halide Battery Chemistry for Safe, Low Temperature, Rechargeable Batteries." *2018 Fall Materials Research Society Meeting*, Boston, MA. November, 2018.
- S.J. Percival, L.J. Small, E. Alcorn, and E.D. Spoerke. "Molten Salt Catholyte Development for Low Temperature Na-Halide Batteries." *SPD's 12th Annual Postdoctoral Technical Showcase*. Santa Fe, NM. November, 2018. (*Best Poster Runner Up*)
- A. Peretti, S. Percival, L. Small, B. Chalamala, and E.D. Spoerke. "Sodium Ion Conducting Separator Development." *30th Rio Grande Symposium on Advanced Materials*. Albuquerque, NM. October, 2018. (poster).
- A. Peretti, E. Coker, M Rodriguez, M. Gross, and E.D. Spoerke. "Ceramic Sodium Ion-Conducting Separator Processing." 31st Rio Grande Symposium on Advanced Materials. Albuquerque, NM. September, 2019. (*Best Poster Runner Up)*

Project Metrics

Technical Engagement

- E. Spoerke. Conference chair and organizer for Composites at Lake Louise, 2019. (Alberta Canada, November 2019).
- E. Spoerke. Organized Symposium on "Ion-Conducting Ceramics" at the Electronic Materials and Applications 2019 Meeting in Orlando, FL (Jan, 2019).
- Ph.D. Committee Member (E. Spoerke), University of North Texas (Sanket Bhoyate).

Summary and Path Forward

Building on FY18 progress identifying a low temperature, functional NaI-based molten catholyte and demonstrating initial battery cycling at 100^{o}C, in FY19, we

1) Identified need to improve Na battery cell materials compatibility, sealing, and interfacial chemistry.
2) Improved production of functional NaSICON for use in low temperature prototype test cells.
3) Discovered Sn-based coating will improve critical Na-wetting of NaSICON at 100^{o}C.
4) Revealed that activation of carbon felt leads to significant reduction of cell overpotentials.
5) Comprehensive integration of new cell design with new cell materials, demonstrated first ever long-term cycling (200 cycles!) of molten Na-NaI battery at 110^{o}C.

Future work will focus on:

1) Innovating new cost-effective, mechanically robust, high conductivity solid state separators.
2) Improving battery materials to enable higher current density (correlates with depth of discharge).
3) Build on developing understanding to further reduce temperature.

PROJECT CONTACTS

THANK YOU!

This work at Sandia National Laboratories is supported through the Energy Storage Program, managed by Dr. Imre Gyuk in the U.S. Department of Energy Office of Electricity.

Questions?

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