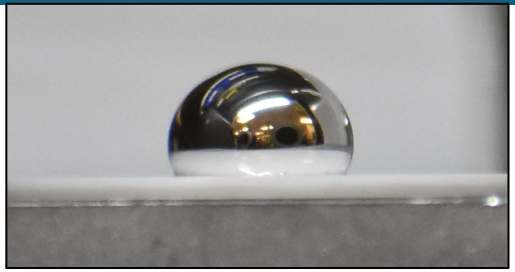
Sandia National Laboratories

Low Temperature Molten Sodium Halide Batteries



PRESENTED BY

Erik D. Spoerke

Martha Gross,
Stephen Percival,
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Thanks to: Babu Chalamala
David Sokoloff, Jaci Hernandez, Sam Roberts-Baca, Sharon Ruiz

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U.S. DEPARTMENT OF ENERGY NNSA

SAND No.: SAND2019-11482 C

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

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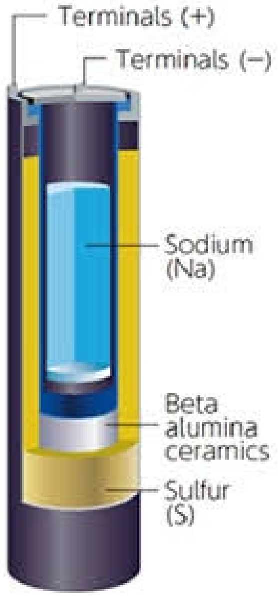
<u>Sodium-based batteries</u>

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



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

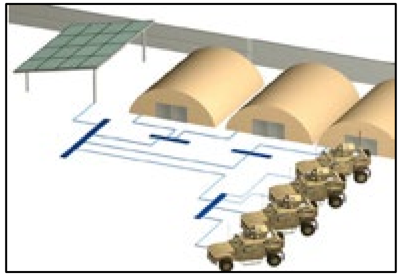
$2Na + 4S \leftrightarrow Na_2S_4$

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

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

Project Overview




Renewable/Remote Energy | Grid Reliability | National Defense | Emergency Aid

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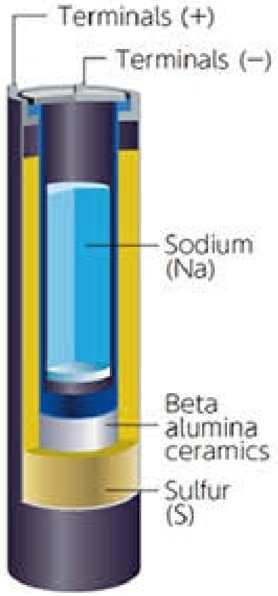


Na- ... **V)**

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

~300°C Operation!

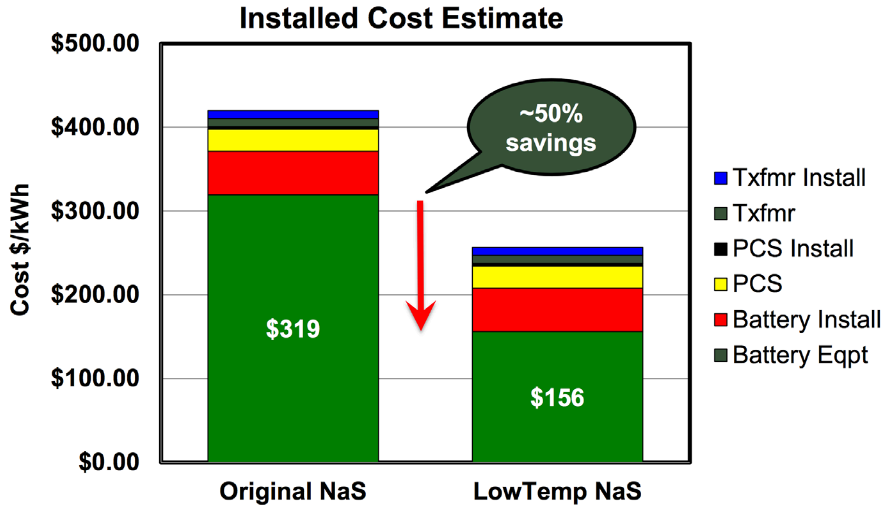
An Important Question…

What is the “big green button” we have to hit to advance Na-batteries?

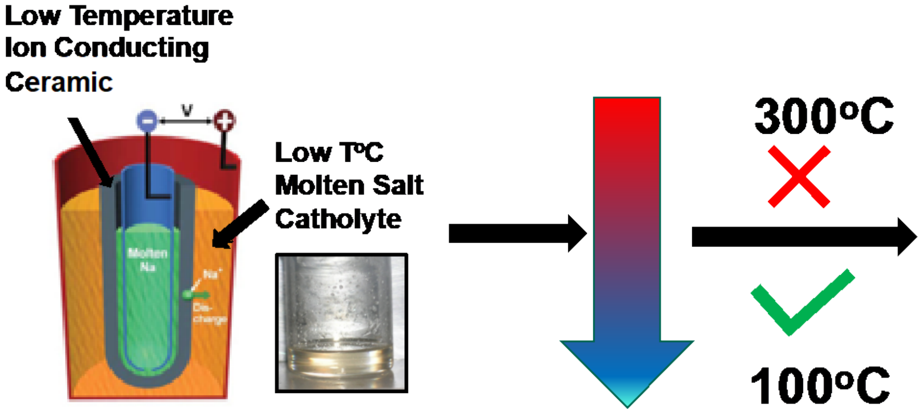
Lowering Battery Operating Temperature to Drive Down Cost

<u>Our Objective:</u> A safe, reliable, molten Na-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



Research Team

SNL Na-Battery FY19 Budget: $650k

SNL Team

- **Dr. Martha Gross (Postdoc)**
  "Interfacial Engineering in Sodium Batteries"
- **Dr. Stephen Percival (Postdoc converted to Staff)**
  "Next Generation Cell Design and Material Optimization for Sodium Batteries"
- **Amanda Peretti (Technologist)**
  "Solid State Separator Development for Sodium-Based Batteries"
- **Dr. Leo Small**
- **Dr. Josh Lamb**

External Collaborations:

- **Prof. YT Cheng (University of Kentucky)**
  - *"Understanding the Mechanical Behavior of Materials for Electrochemical Energy Storage"*
- **Prof. Youngsik Kim (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

AIChE regional Chem E-Car champions!

Low Temperature Molten Sodium (Na-NaI) Batteries

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

Ingredients for Success

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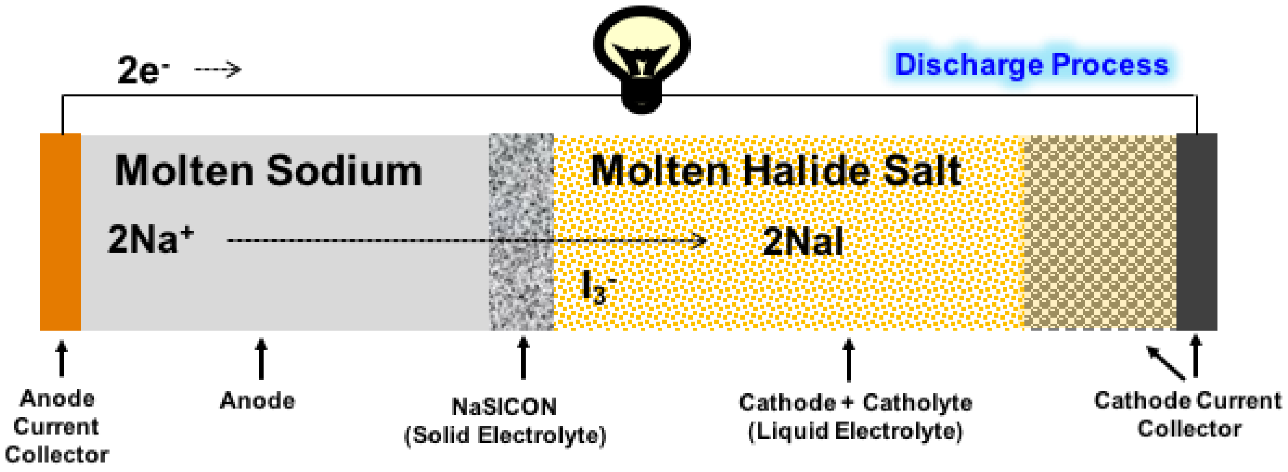
- Highly Na^+-conductive, zero-crossover separator (e.g., NaSICON
- 25 mol% NaI in AlX_3 catholyte



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Candidate catholyte salts include $AlCl_3$, $AlBr_3$

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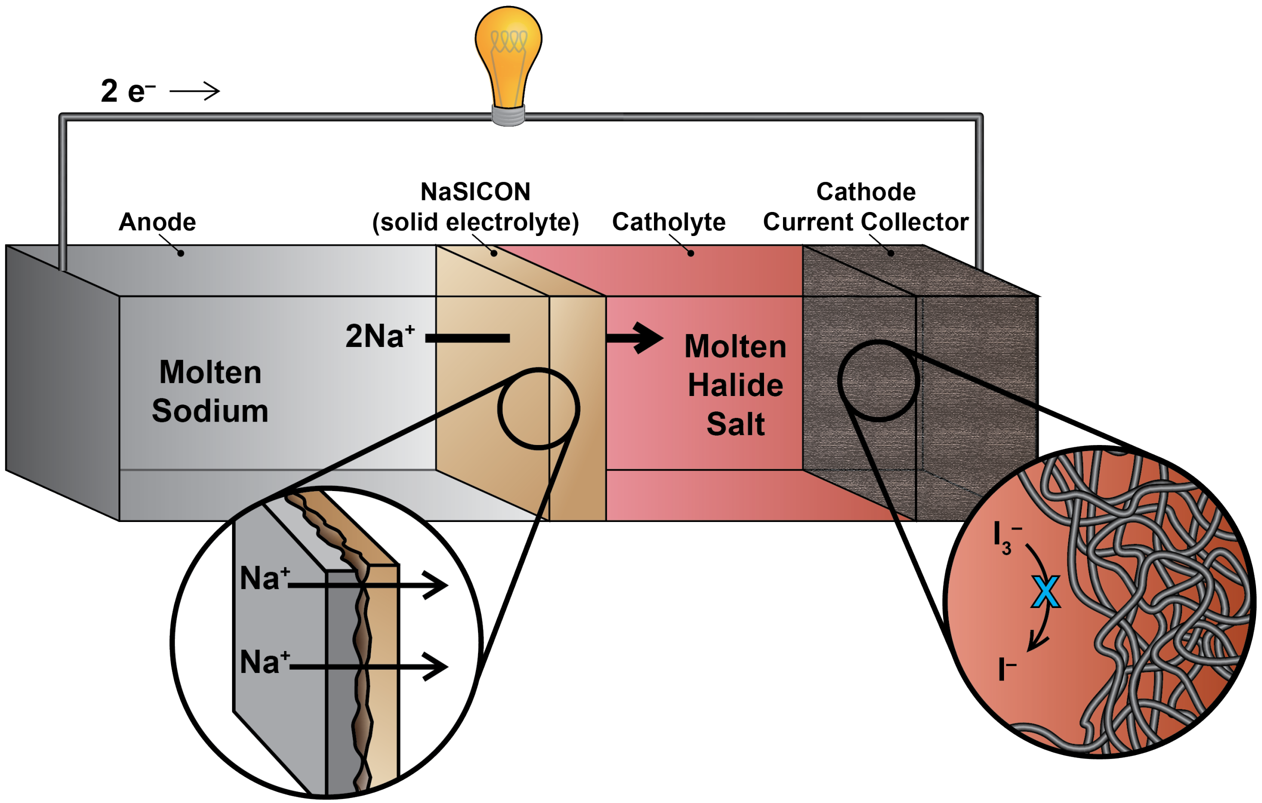

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Martha Gross

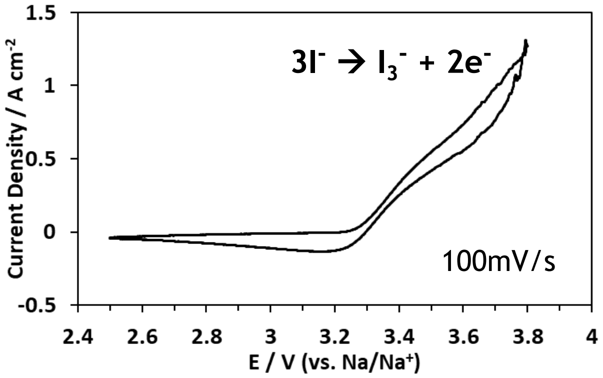
Last Year's "Really Cool" Hurrah!

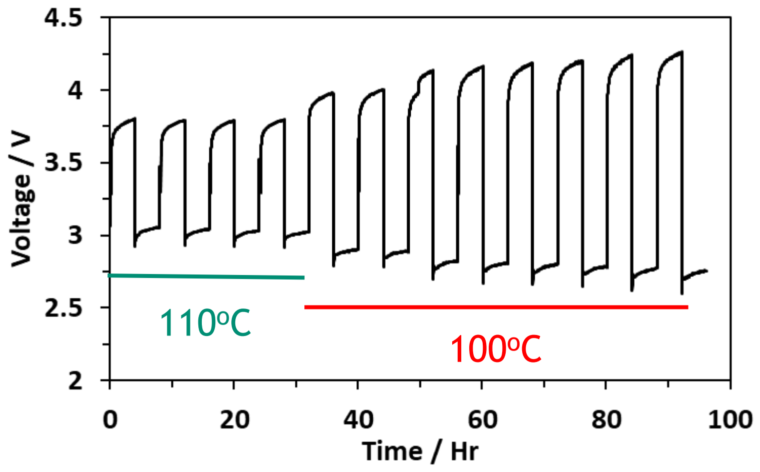
First demonstration of Molten Na-NaI battery at 100-110ºC.

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

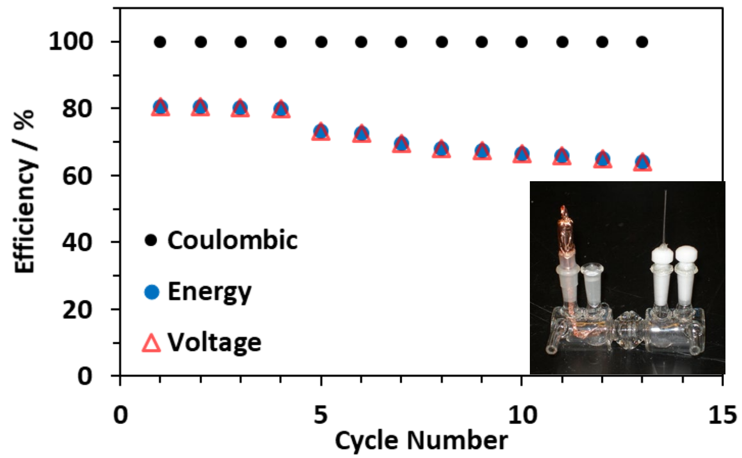
- 25:75 NaI-$AlBr_3$salt completely molten at 90 ºC
- Large fully molten capacity range (~5-25 mol% NaI)

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





Battery cycling at **100-110ºC**!



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

FY19 Focus

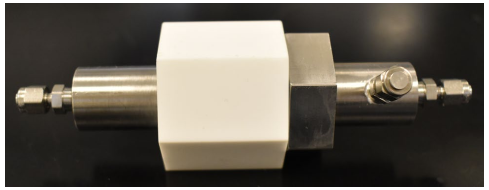
FY19 Priority: Applying new materials innovations, demonstrate improved cycling performance of Na-NaI battery operating near 100^{o}C.

Identifying a Viable Na-Battery Test Platform

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

Re-Engineered Cell Variants

A functional cell design is critical to prototype development and testing.

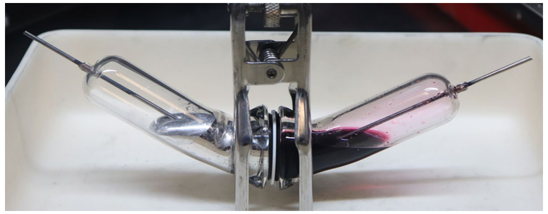


Many new cell designs and geometries built and tested (7 different types!)

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

New Cell Designs

Enable easy assembly, high throughput and functional geometry



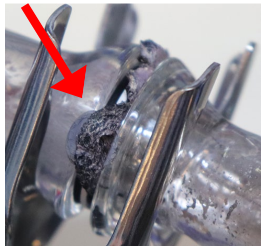
Includes 3 designs that are fully interchangeable and reusable

Importance of Seals

Testing failures in many prototypes was due to compromised seals.

Sodium Compatible Seal Material

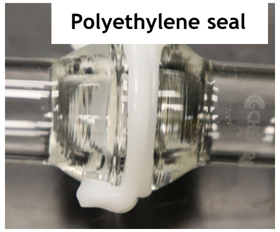
Sodium reacting with the Kalrez o-ring



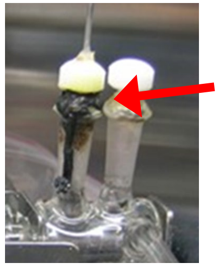
Polyethylene seals from molten polyethylene to seal the sodium side

Not re-useable and hard to apply properly

Identified new EPDM o-rings that do not react with molten Na

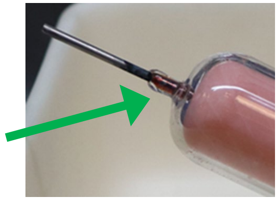


Molten Salt Compatible Seal Material



Vapors from molten salt aggressively attacking the epoxy seals

Glass to metal seals eliminate unwanted side reactions from salt vapors



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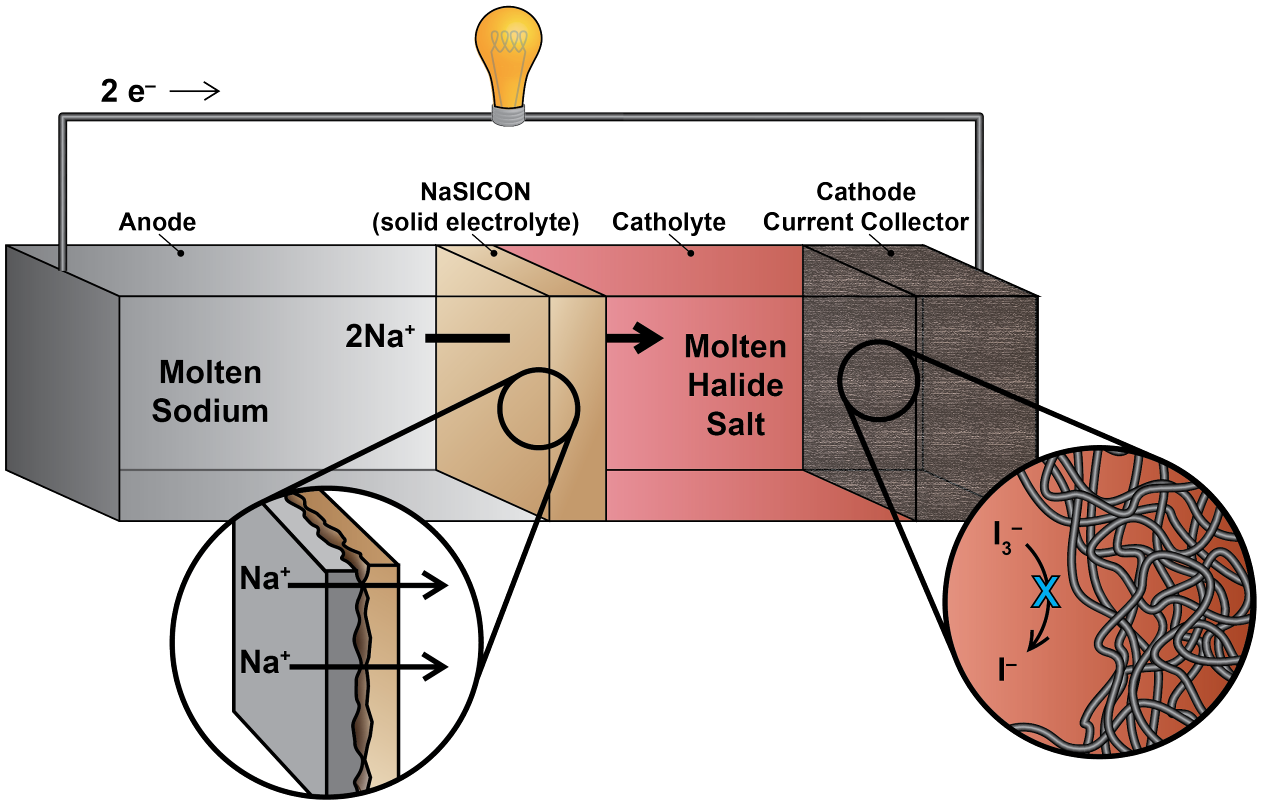
- 25 mol% NaI in AlX_3 catholyte



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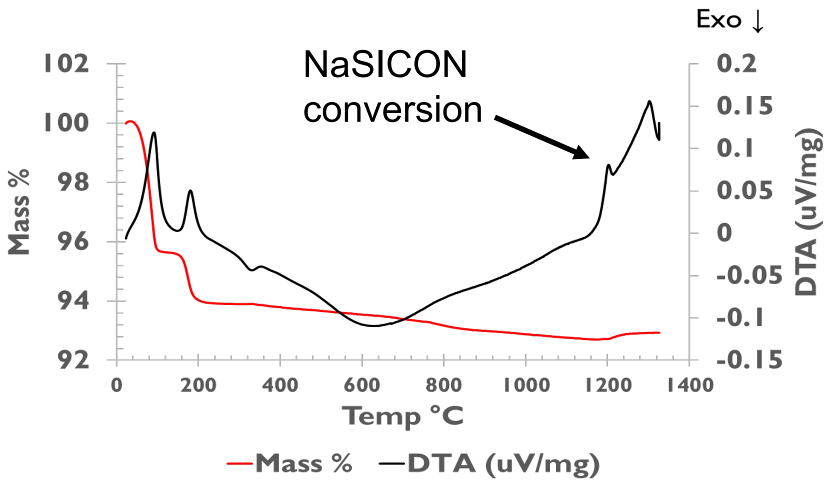
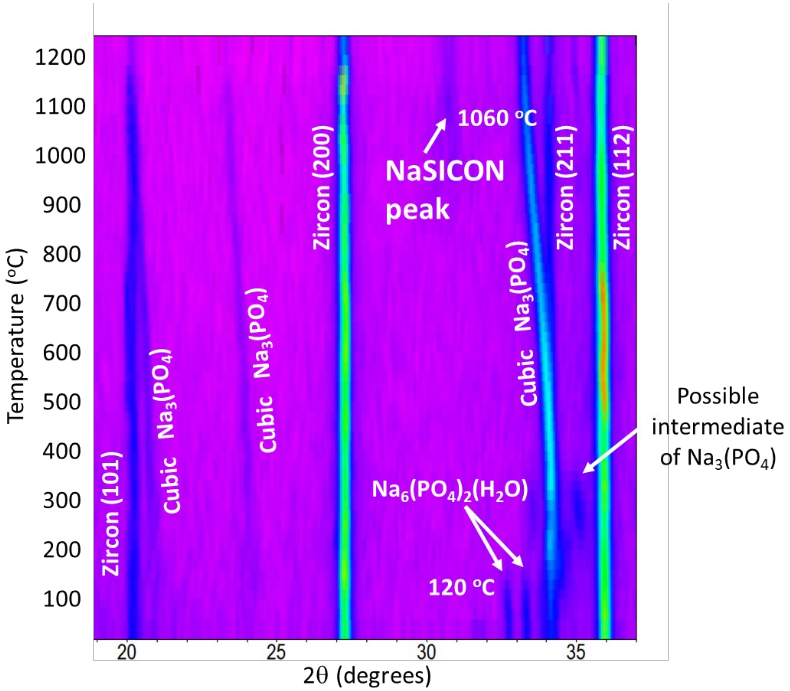
NaSICON Synthesis

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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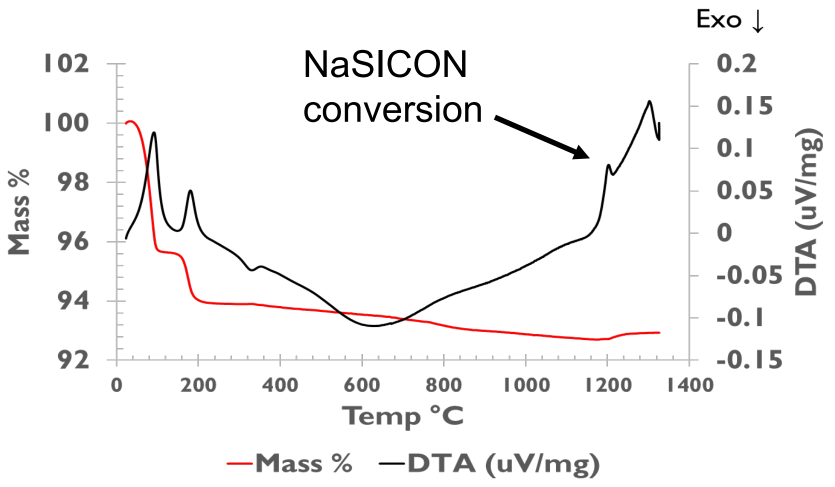

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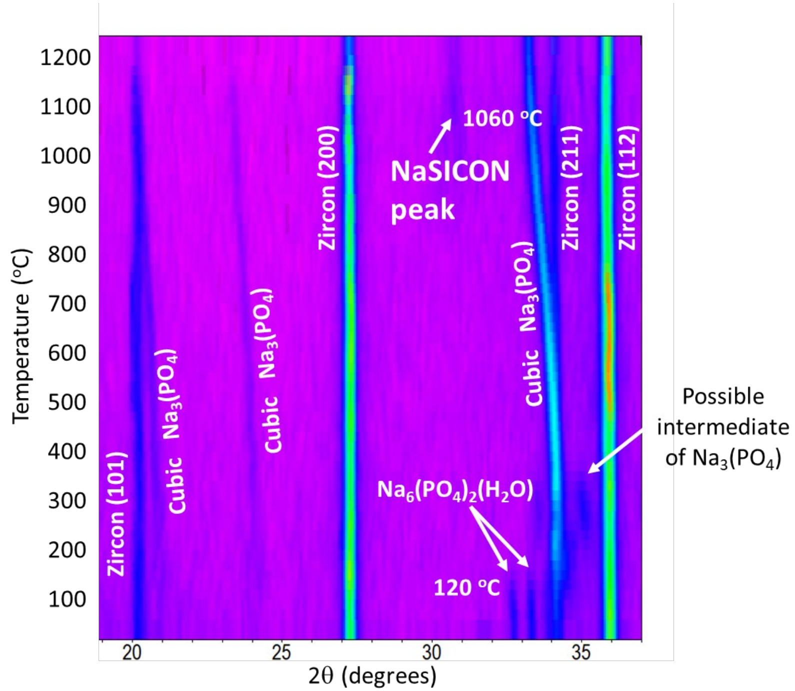

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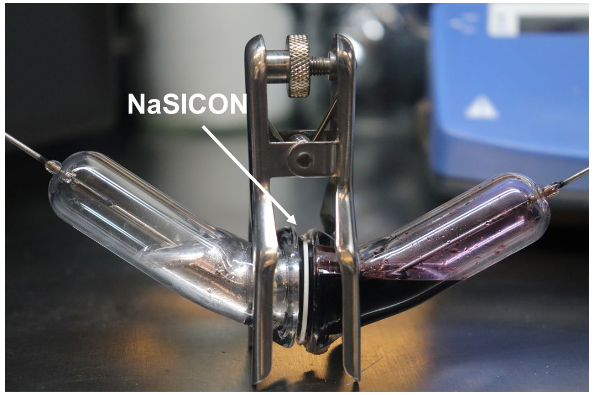

Molten Na Battery Cell Set-Up

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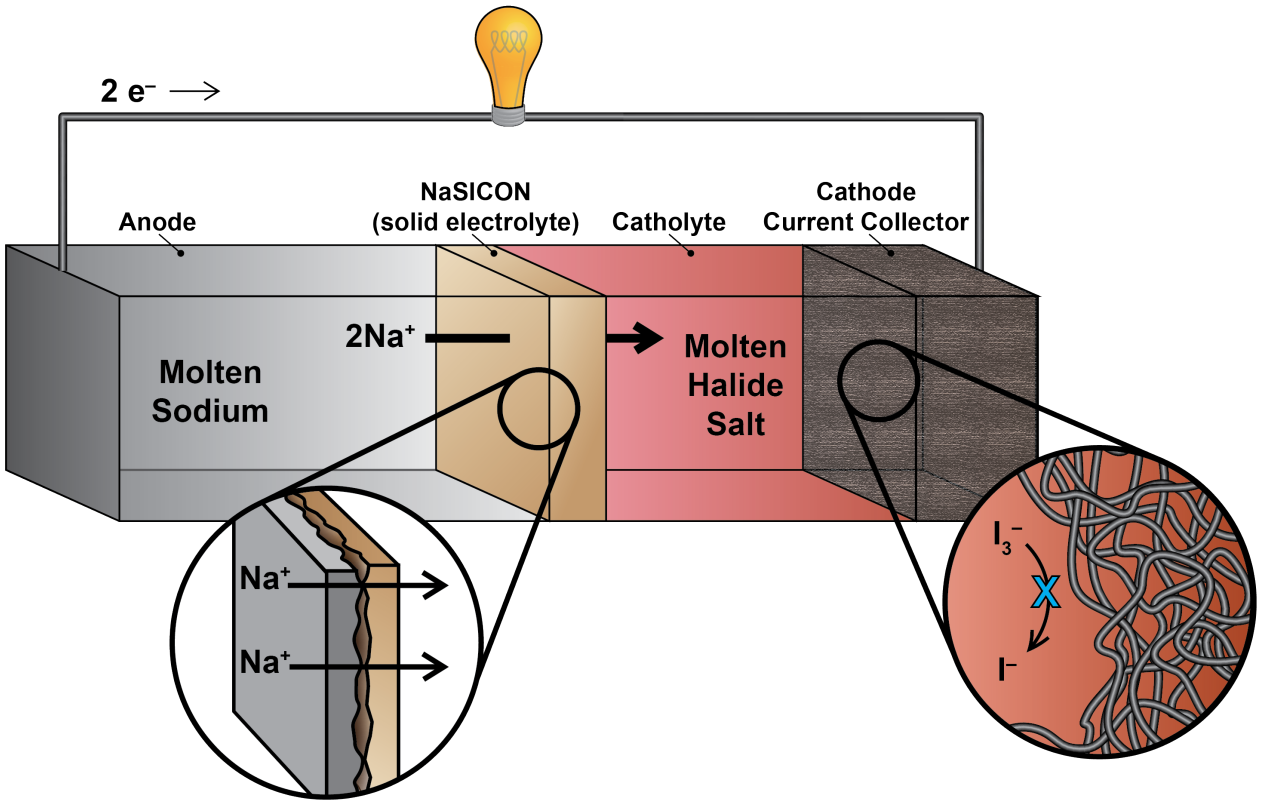

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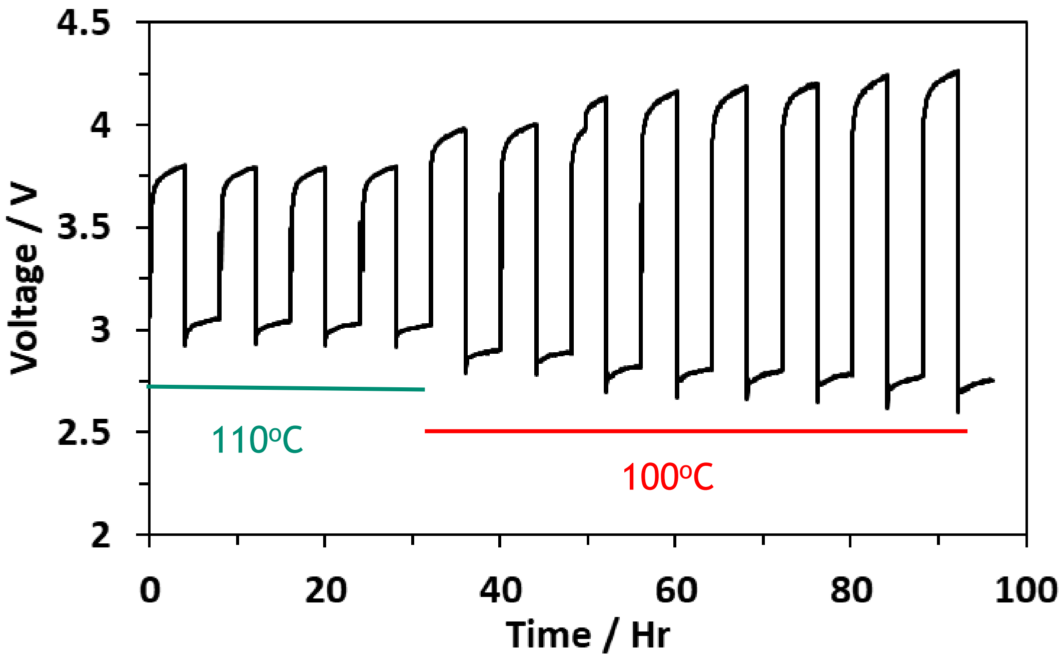
Follow the Bouncing…Sodium!

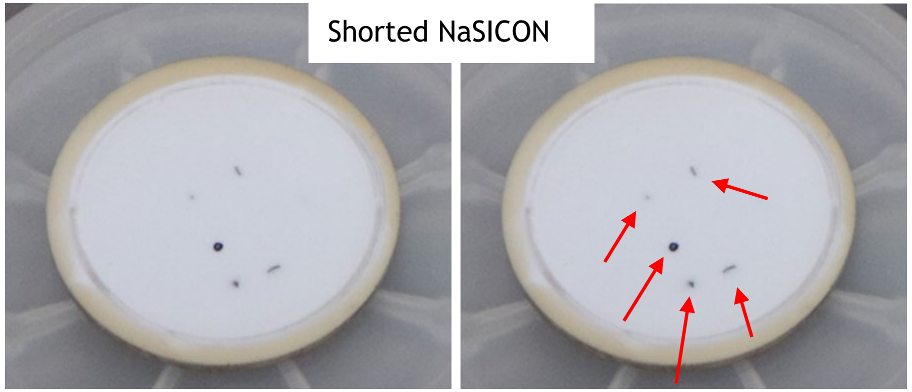
Poor sodium wetting on NaSICON is a problem.



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.



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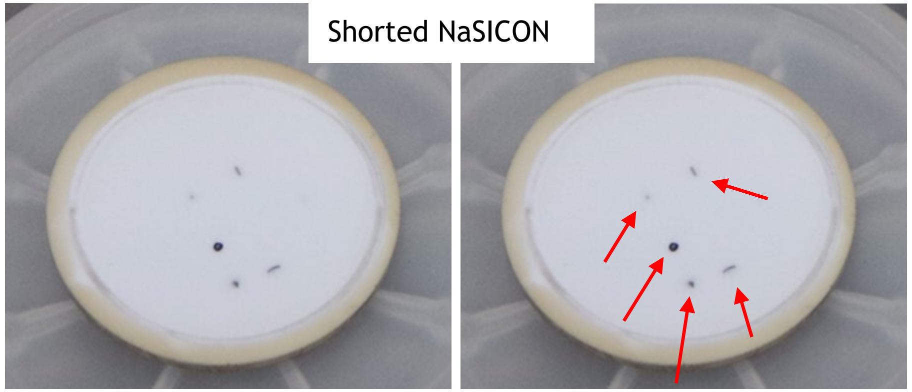


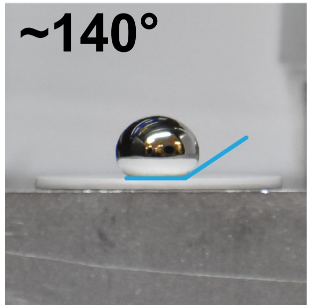
NaSICON Coated with Sn-Based Coating Shows Drastically Improved Adhesion!

An Improved Na Interface

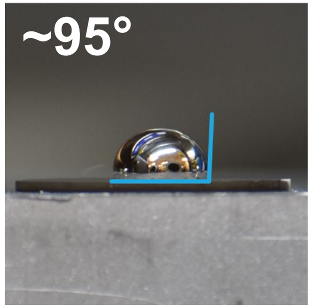
Symmetric cell cycling (Na on both sides) shows that the Sn-based coating improves wetting on NaSICON and drastically reduces overpotentials on cycling!

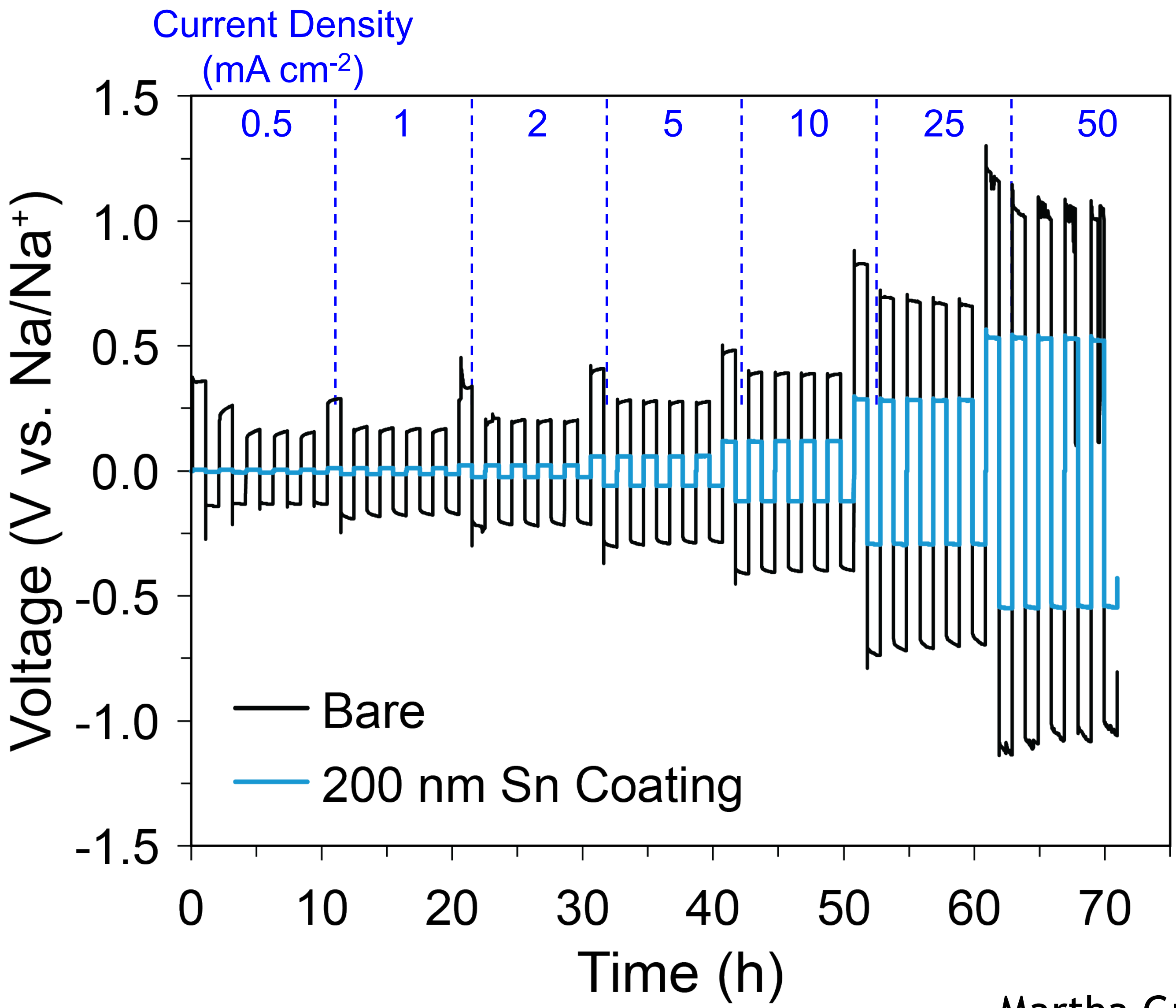
This improved interface is critical to realizing effective battery performance.

Untreated NaSICON



With Sn-Based Coating





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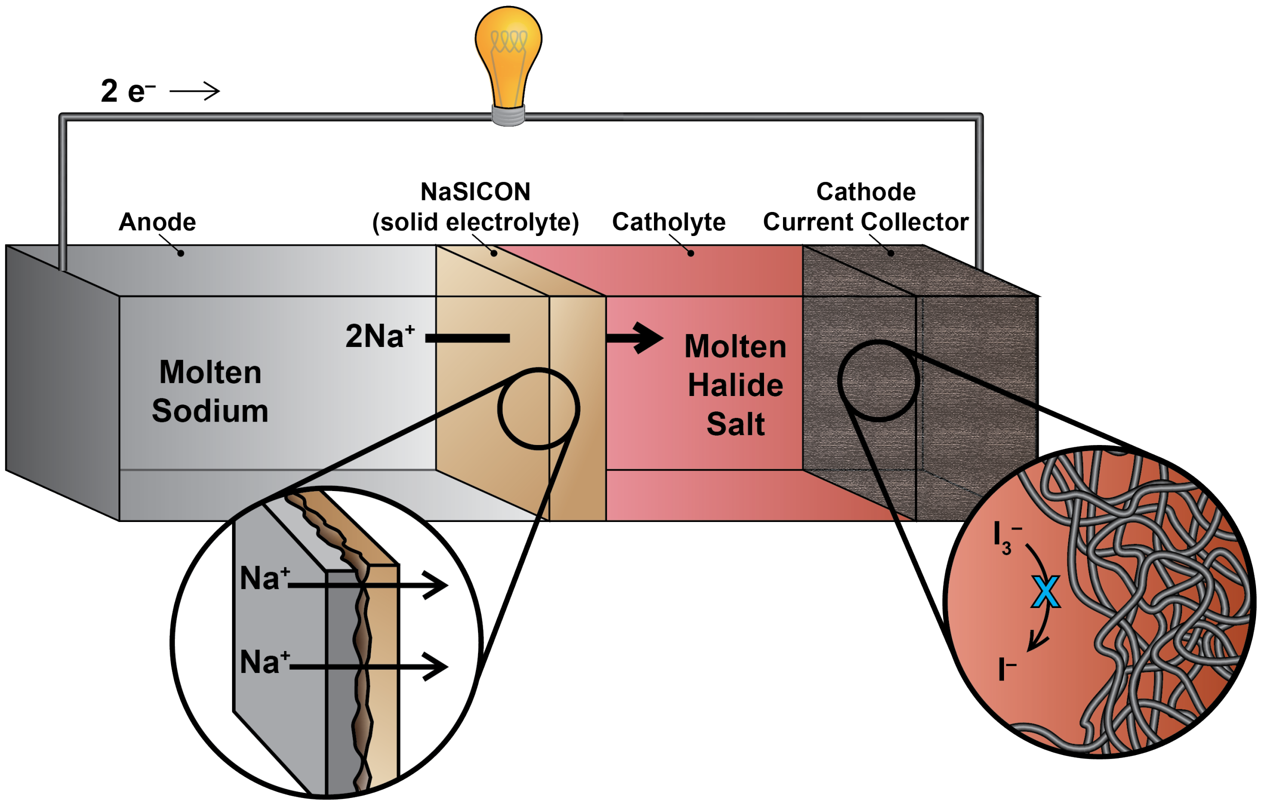

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Martha Gross

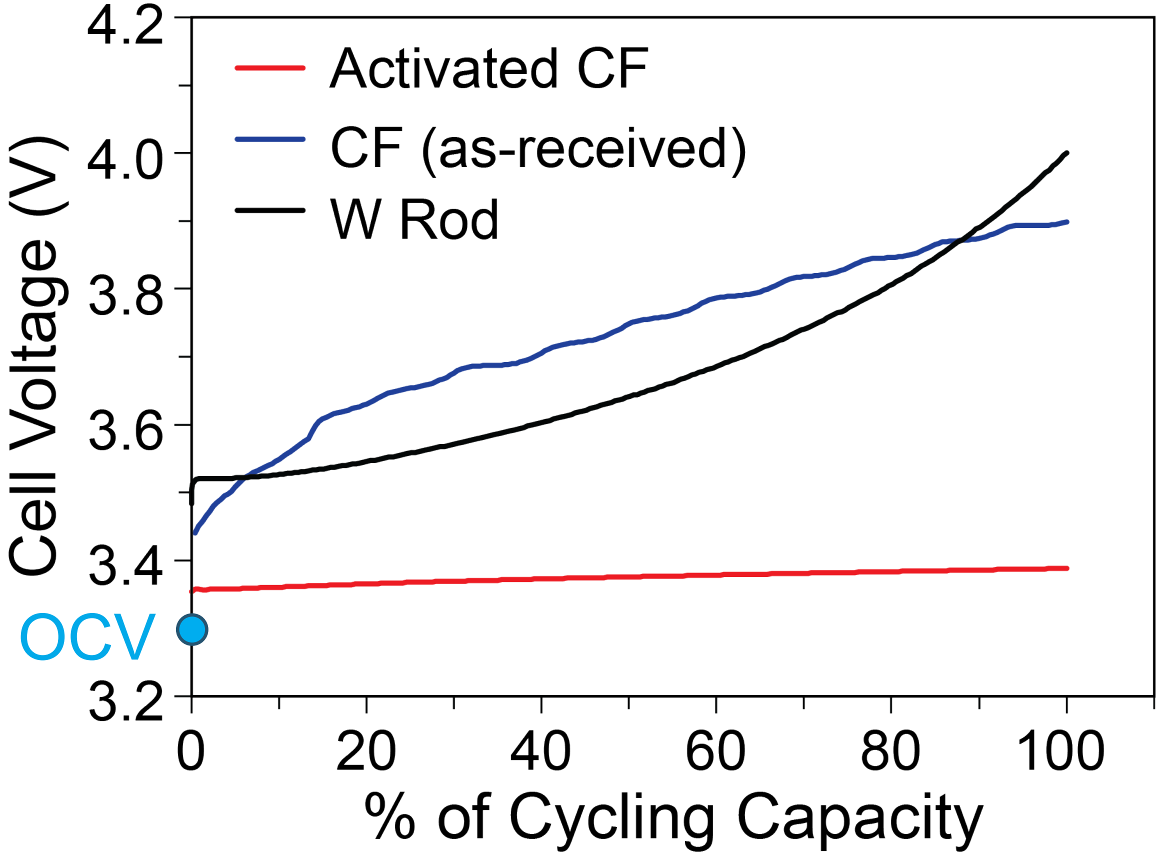
Improving Cathodic Current Collector

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



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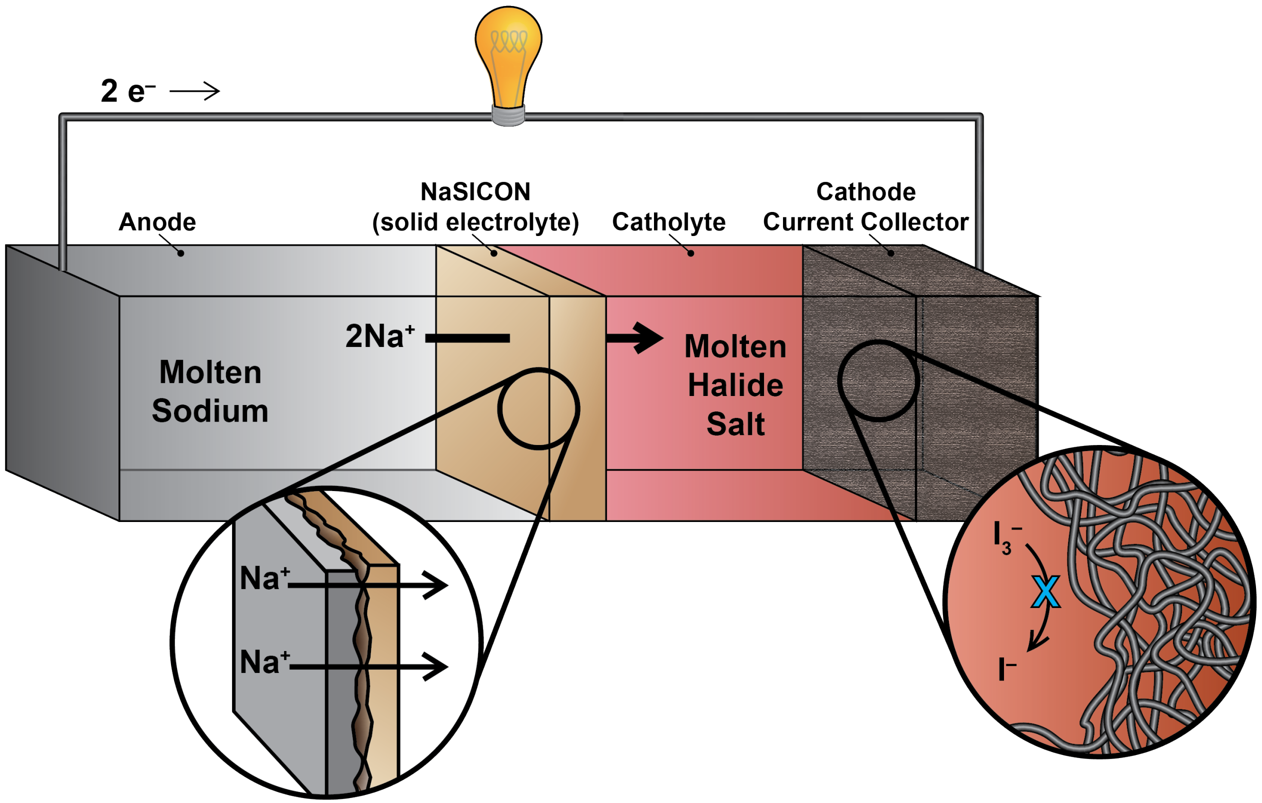

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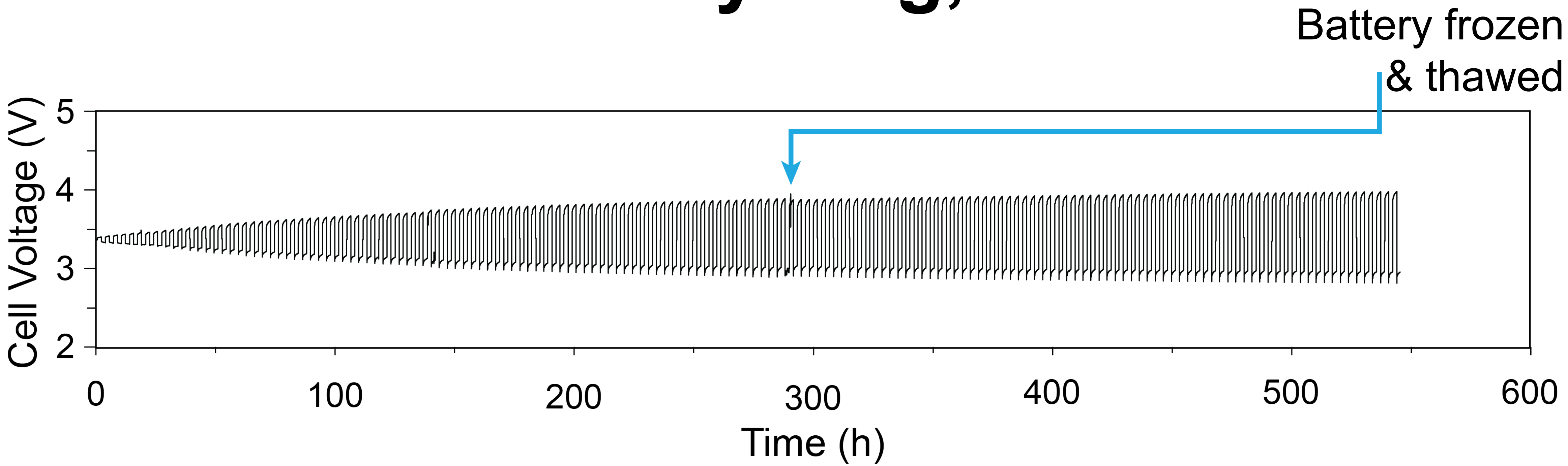
This Year's "Really Cool" Hurrah!

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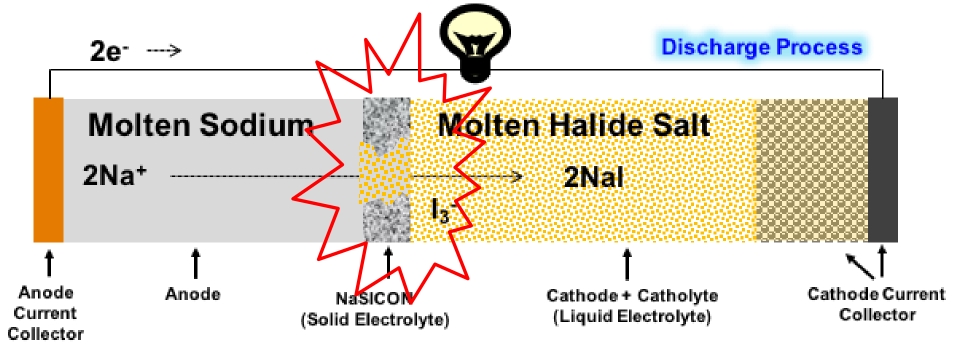
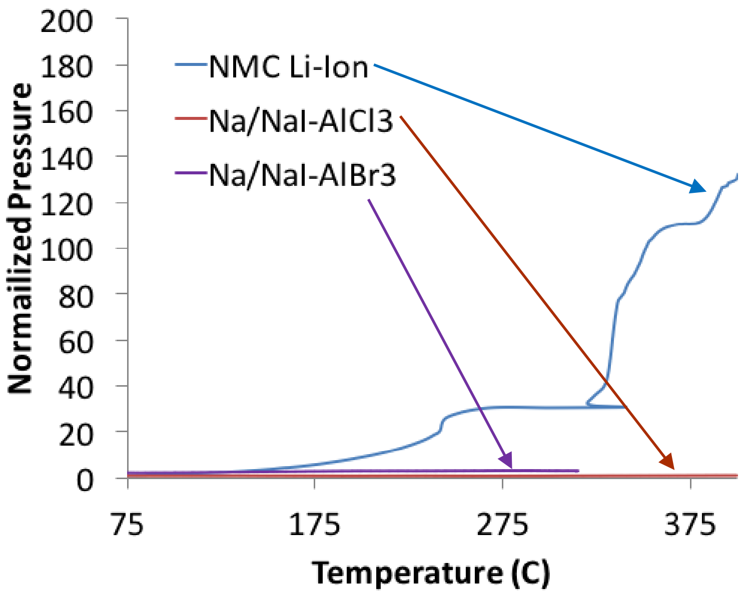


Simulating separator failure, metallic Na and NaI/AlX_3 were combined and heated.

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



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

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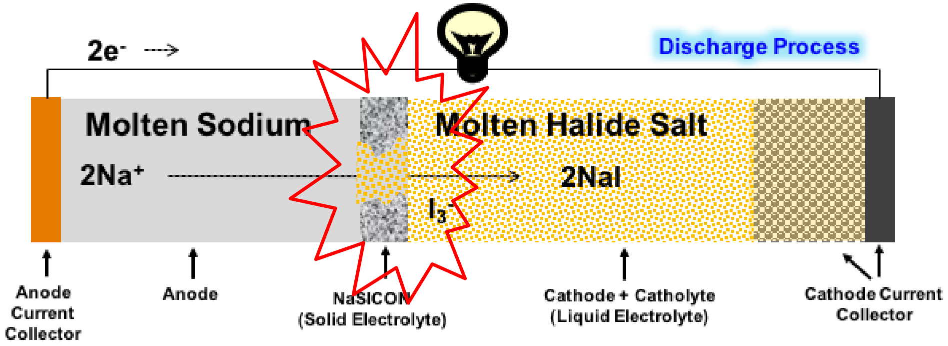

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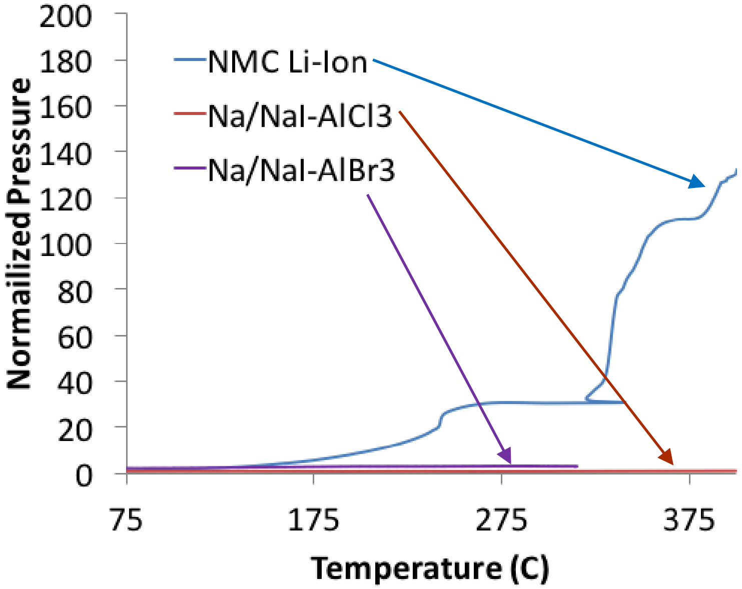

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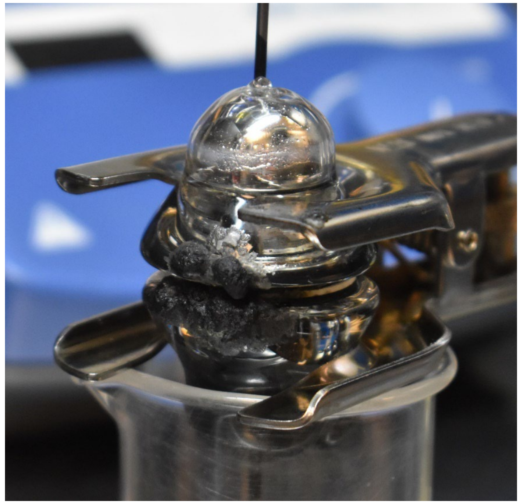

Failed separator led to termination of battery, but no significant hazardous conditions.

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.

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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)**

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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*)

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Technical Community 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

Program Objective: A safe, reliable, molten Na-based battery that operates at drastically reduced temperatures (near 100°C).

FY19 Priority: Applying new materials innovations, demonstrate improved cycling performance of Na-NaI battery operating near 100°C.

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

- ✓ Redesigned Na battery testing platform, accounting for cell materials compatibility, sealing, and interfacial chemistry.
- ✓ Improved production of functional NaSICON for use in low temperature prototype test cells.
- ✓ Discovered Sn-based coating will improve critical Na-wetting of NaSICON at 100°C.
- ✓ Revealed that activating interfaces on "high" surface area carbon felt leads to significant reduction of cell overpotentials.
- ✓ 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°C.

Summary and Path Forward

Future work will focus on:

1) Innovating new cost-effective, mechanically robust, high conductivity solid state separators.

2) Optimizing materials chemistry to enable higher current density (correlates with depth of discharge) while retaining strong cyclability.

3) Build on developing understanding of battery chemistry to further reduce temperature.

4) Continue to advance collaborations and disseminate research.

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…

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Acknowledgments and Thanks

THANK YOU!

Babu Chalamala

David Sokoloff, Jaci Hernandez, Sam Roberts-Baca, Sharon Ruiz

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Questions?

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