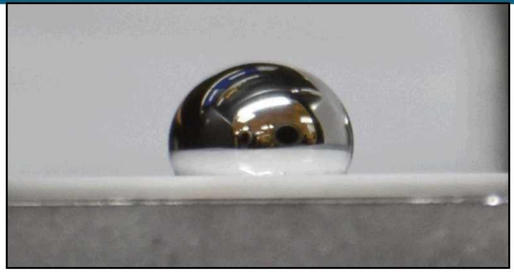
SAND2019-12415C

Tailoring Materials Chemistry to Advance Low Temperature Molten Sodium Batteries



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

PRESENTED BY

Erik D. Spoerke

236th Electrochemical Society Meeting
October 13-17, 2019 | Atlanta, GA USA

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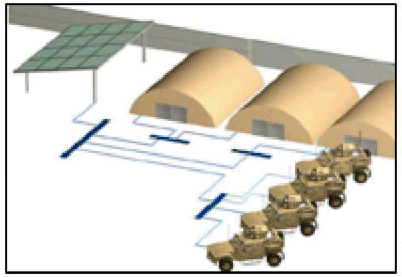
SAND No.: SAND

Our Motivation

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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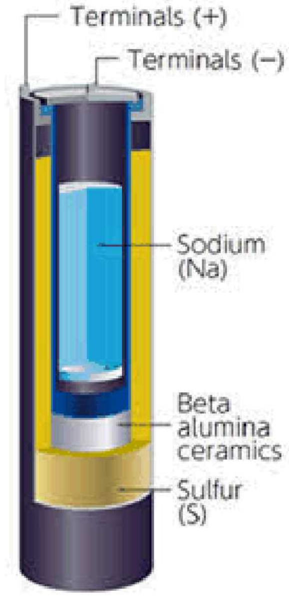
Sodium-based batteries

- 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)

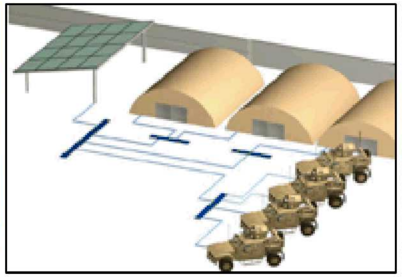
$2Na + 4S \leftrightarrow Na_2S_4$

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

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

Our Motivation

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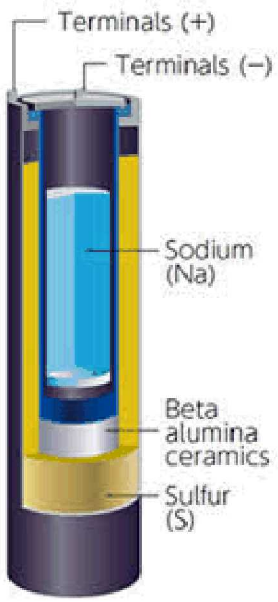
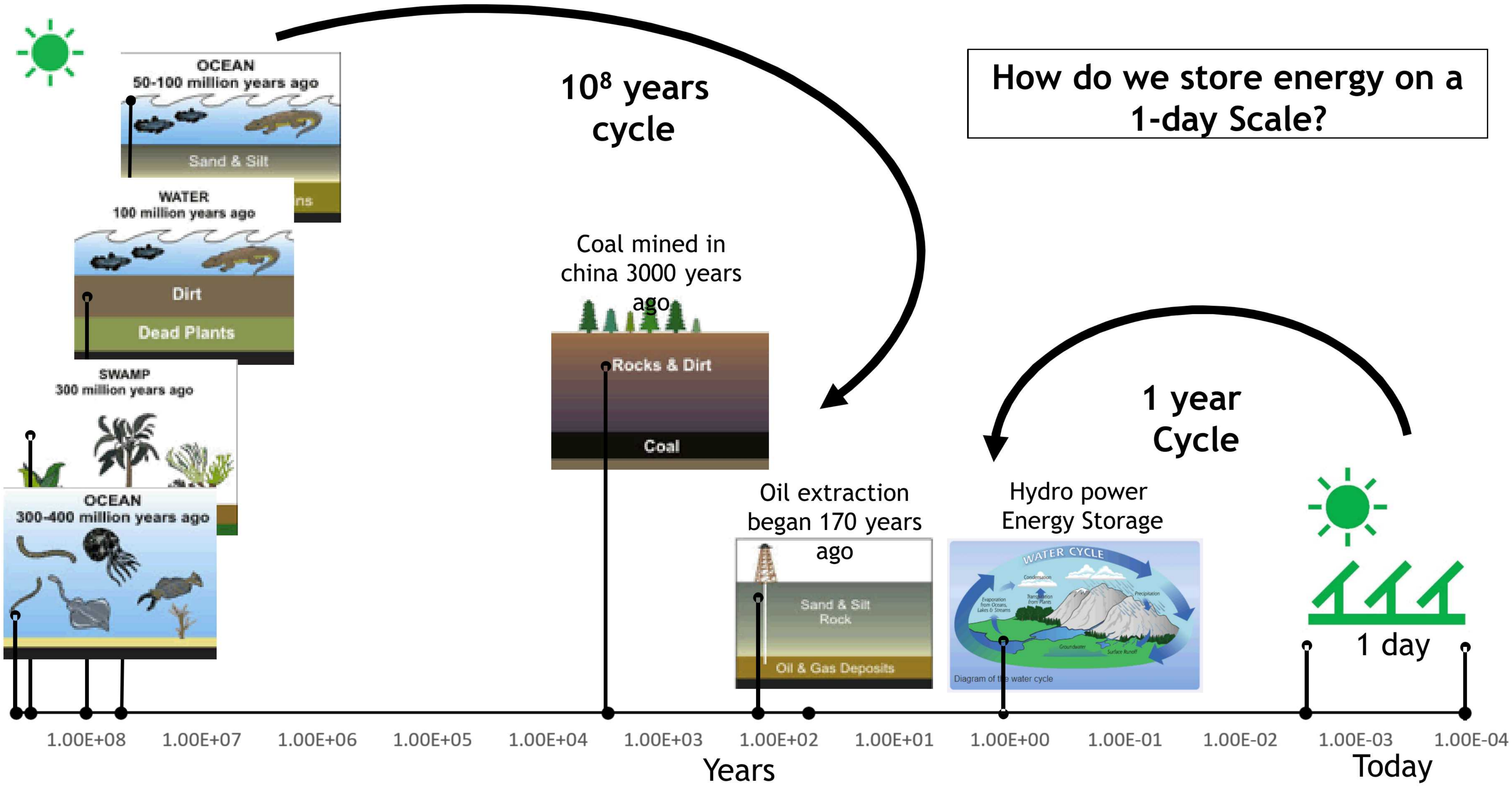


Na- ... **6V)**

2Na ... Na^{+} + 2Cl^{-} + Ni(s)

~300^{o}C Operation!

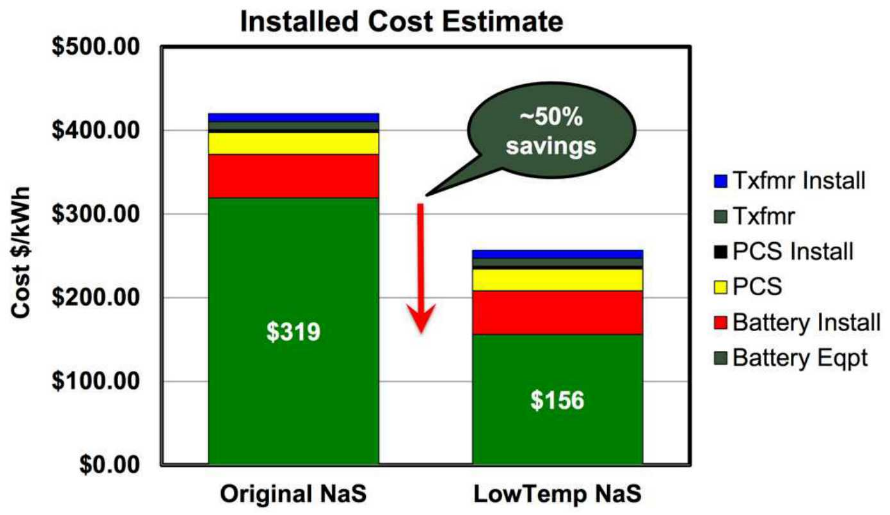
Where Does Our Energy Come From?



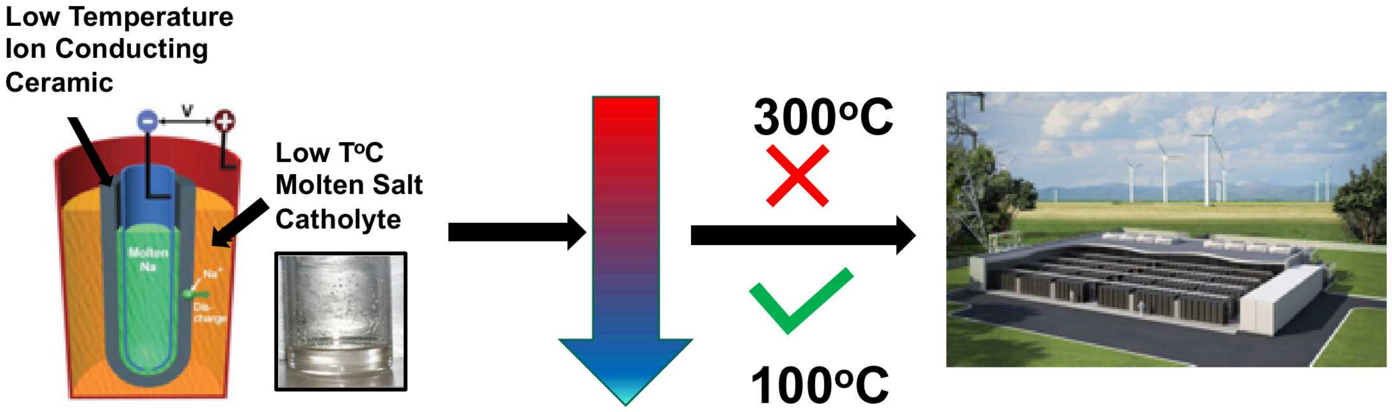
Lowering Battery Operating Temperature to Drive Down Cost

<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



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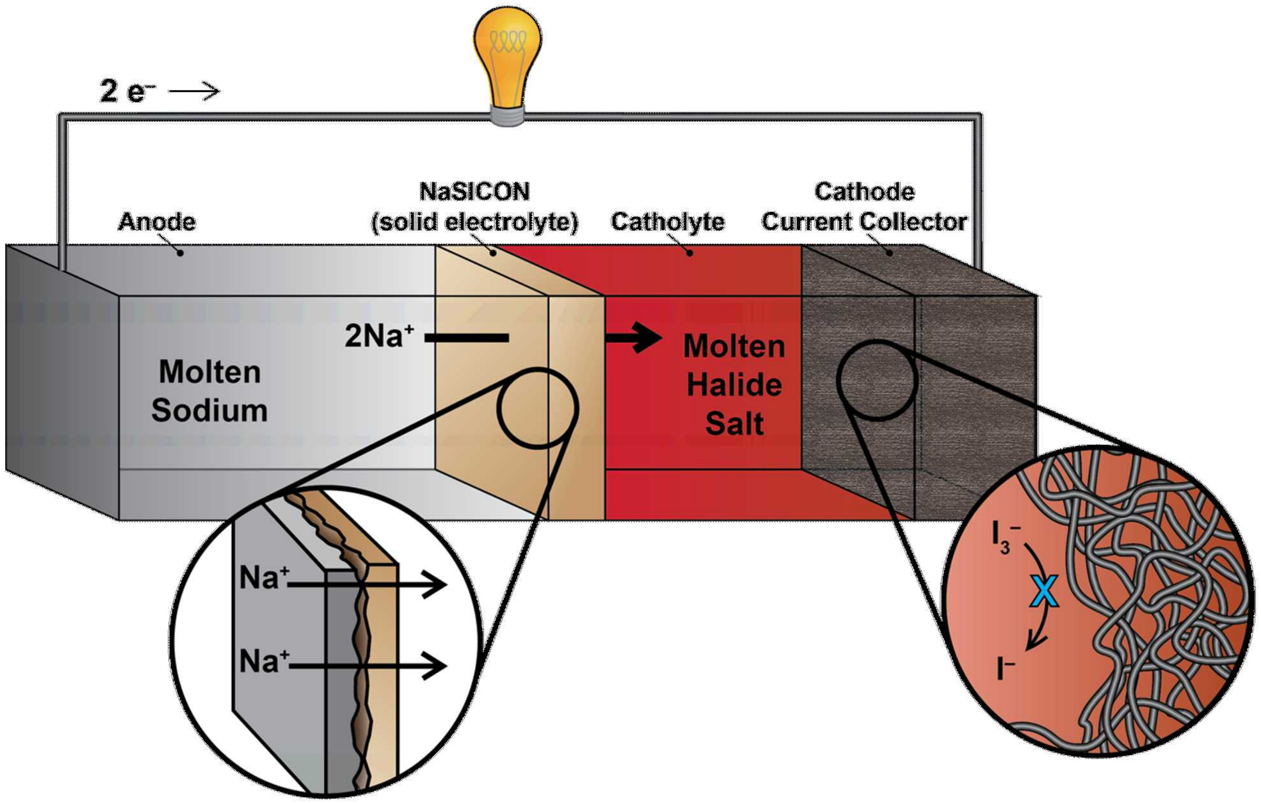

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$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

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Martha Gross

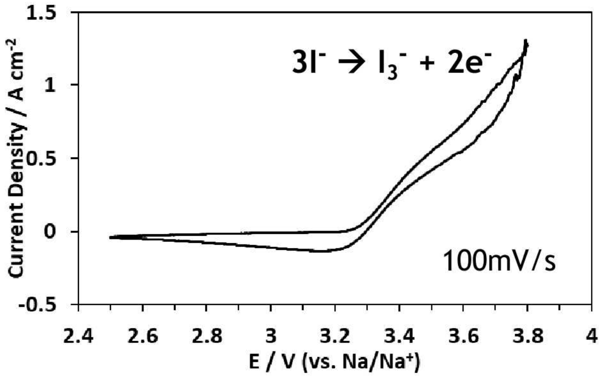
Early Low Temperature Na-Battery Performance

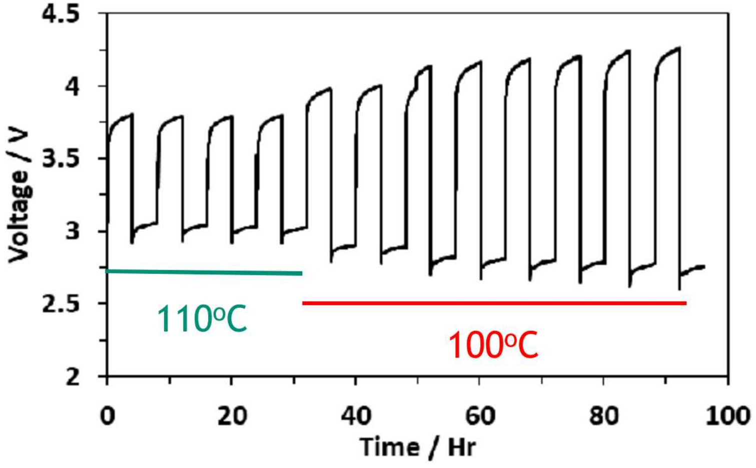
First demonstration of molten Na-NaI battery at 100-110°C.

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

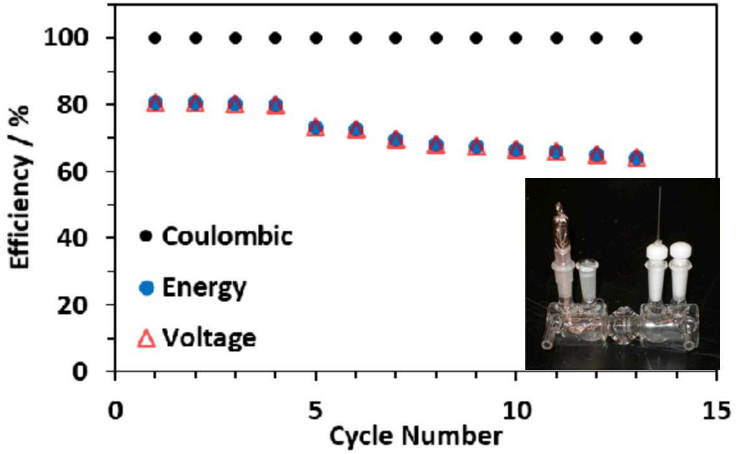
- 25:75 NaI-$AlBr_3$salt completely molten at 90 °C
- Large fully molten capacity range (~5-25 mol% NaI)

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





Battery cycling at **100-110°C**!



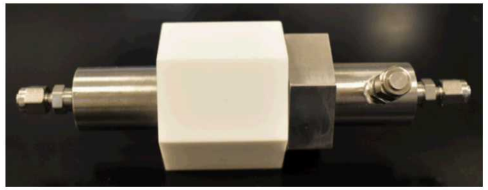
25 mol% NaI-$AlBr_3$ with NaSICON separator.

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.

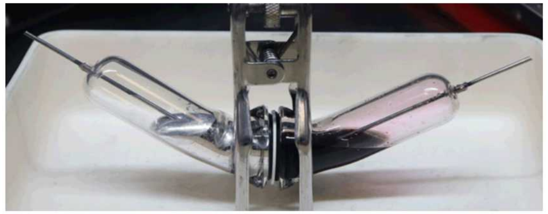


Many new cell designs and geometries built and tested (7 different types!)

Some designs were time consuming, laborious and could be **<u>used only once!</u>**

New Cell Designs

Enable easy assembly, high throughput and functional geometry



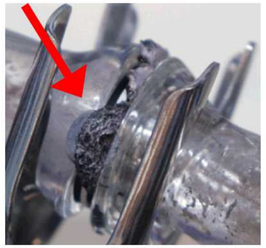
Includes 3 designs that are fully interchangeable and reusable

Importance of Seals

Testing failures in many prototypes was due to compromised seals.

<u>Sodium Compatible Seal Material</u>

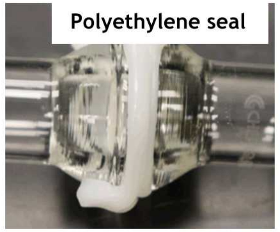
Sodium reacting with the Kalrez o-ring



Polyethylene seals from molten polyethylene to seal the sodium side

Not re-useable and hard to apply properly

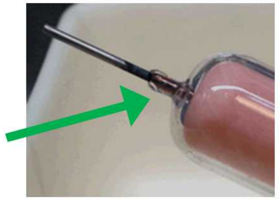
Identified new EPDM o-rings that do not react with molten Na



<u>Molten Salt Compatible Seal Material</u>

Vapors from molten salt aggressively attacking the epoxy seals

Glass to metal seals eliminate unwanted side reactions from salt vapors



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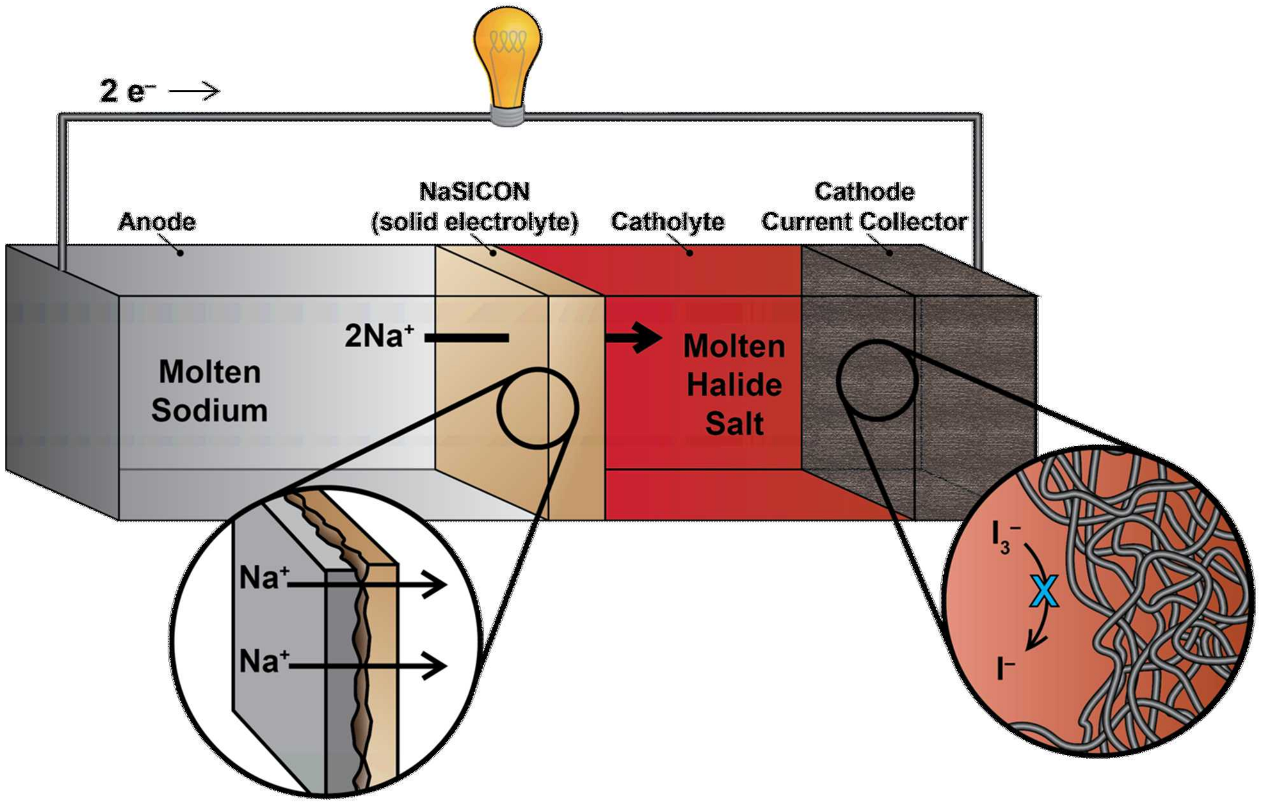

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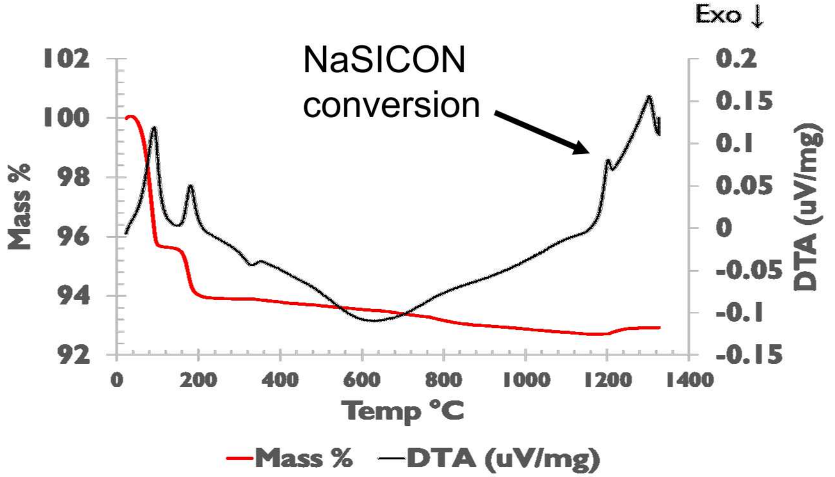
Martha Gross

NaSICON Synthesis

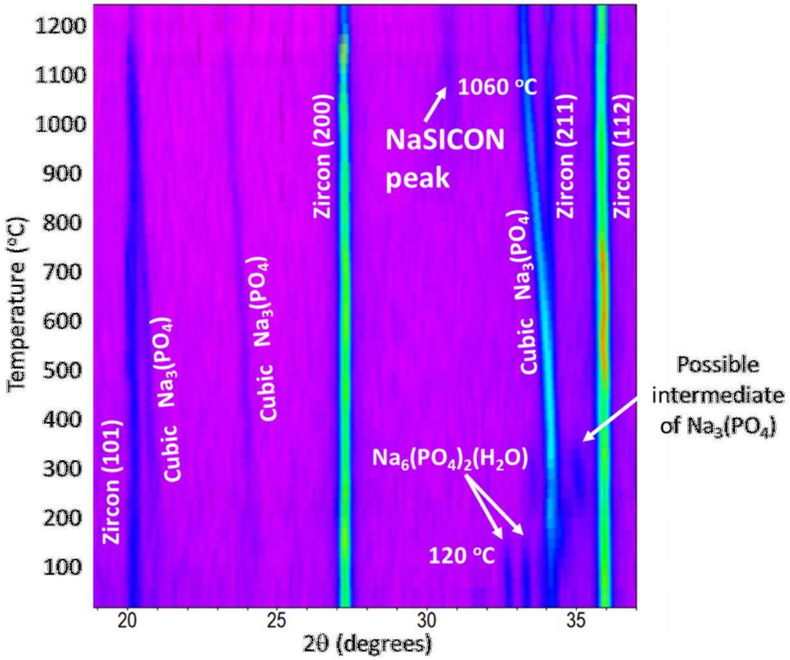
Thermal analyses reveal pathway to functional NaSICON synthesis!



- 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?)

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.



- 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^{o}C, converts to cubic $Na_3(PO_4)$ at ~300^{o}C.

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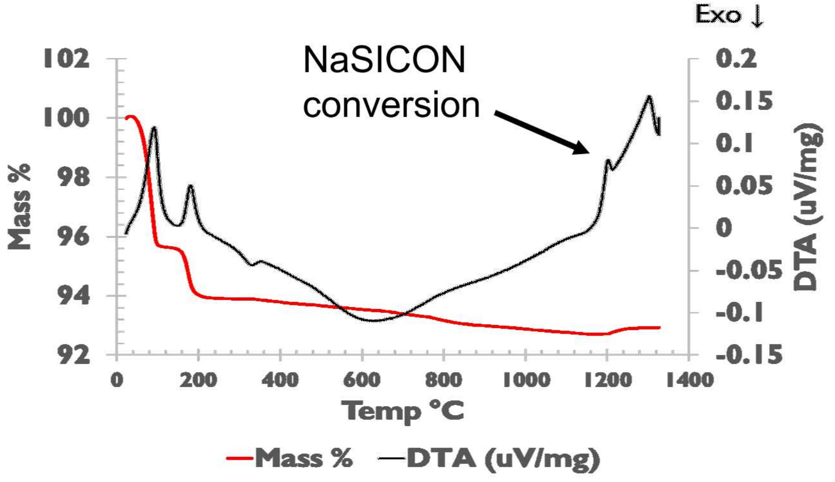

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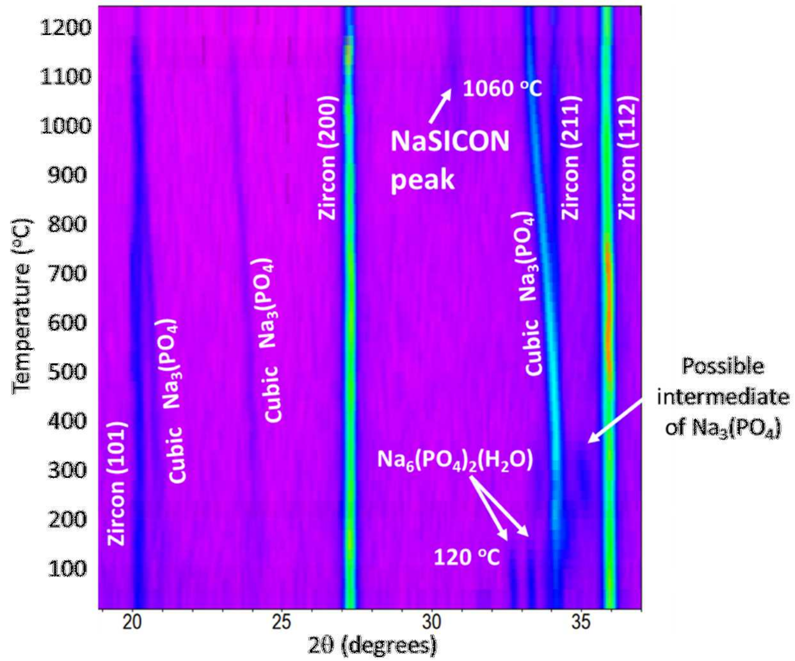

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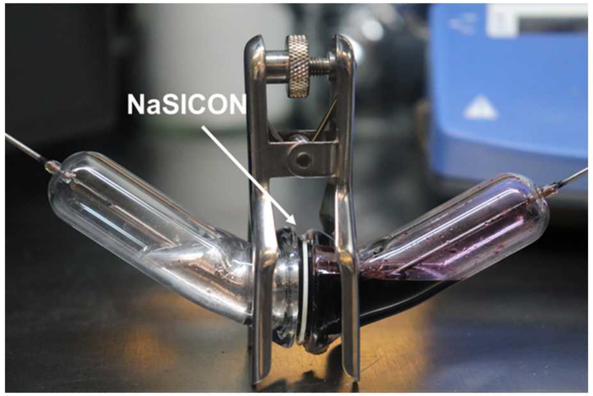

Molten Na Battery Cell Set-Up

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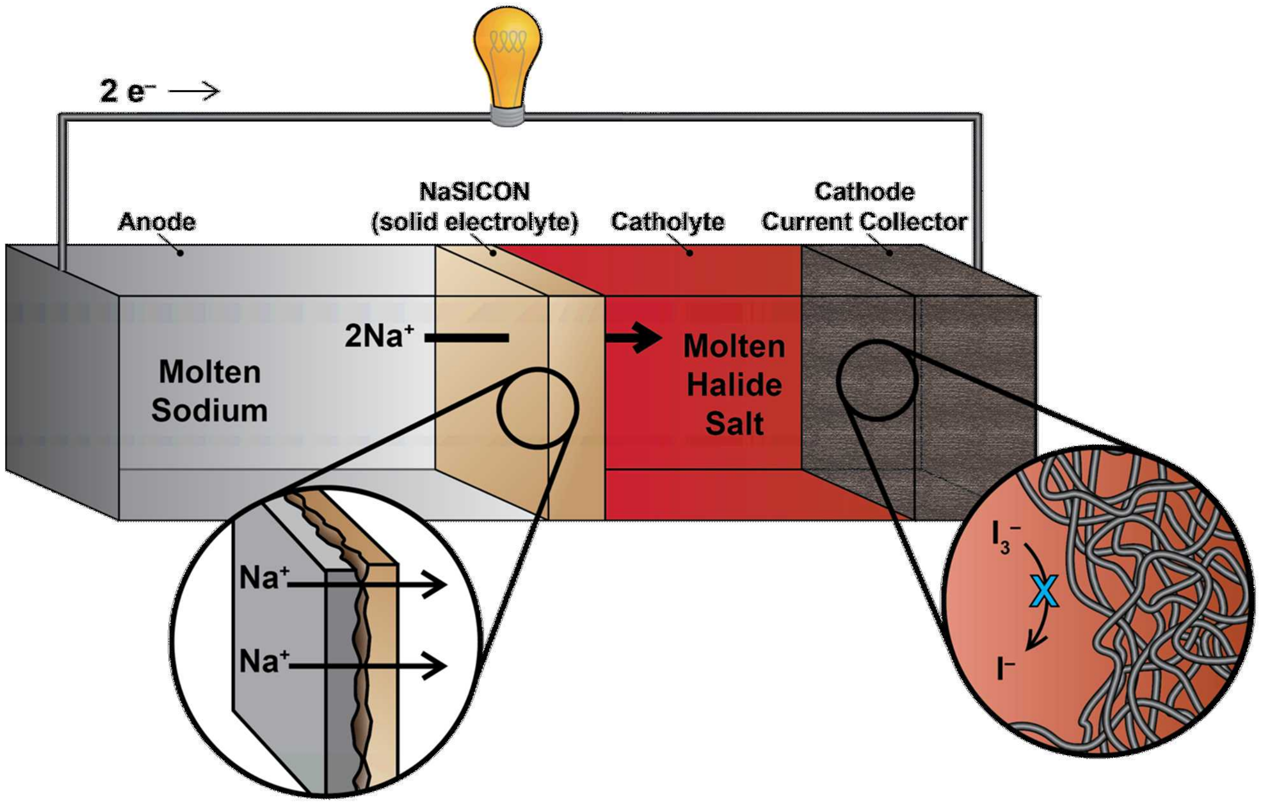

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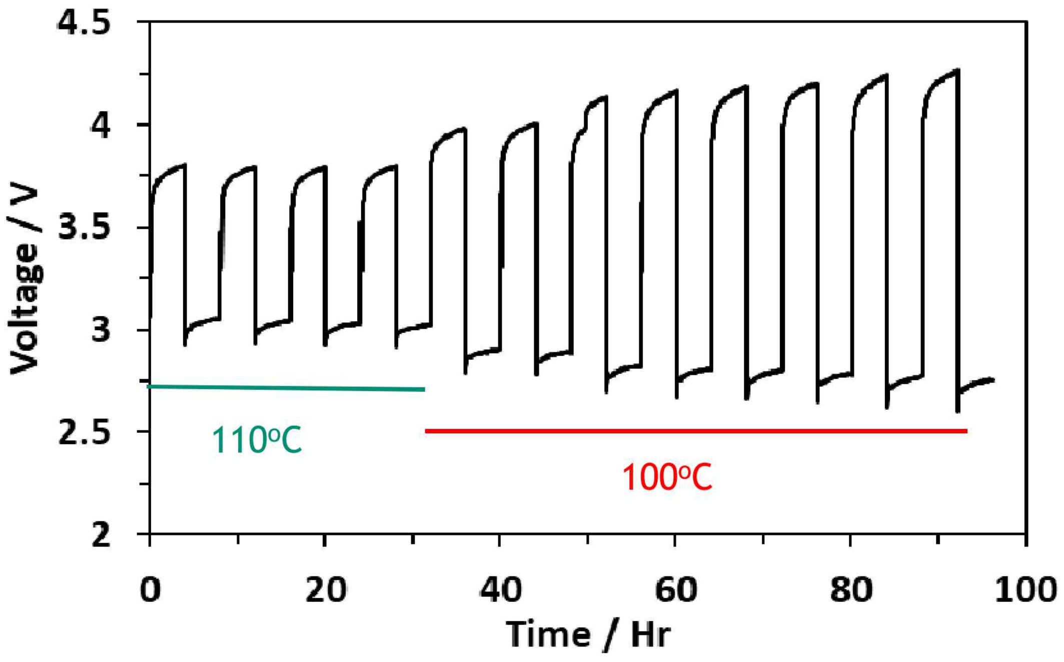
Follow the Bouncing…Sodium!

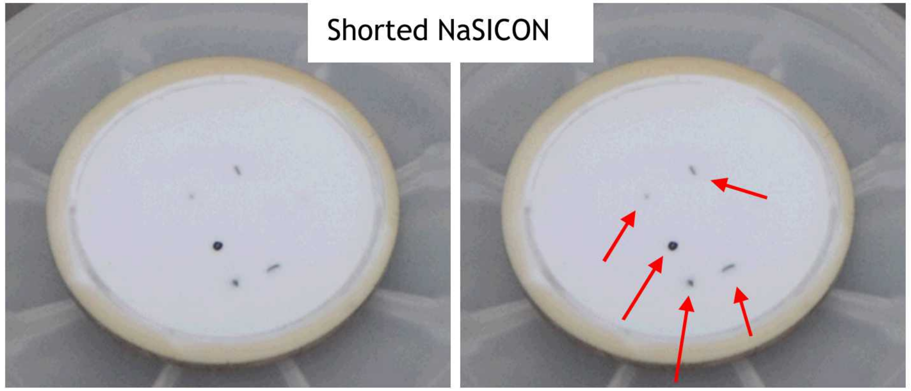
Poor sodium wetting on NaSICON is a problem.



Improper Na-wetting of NaSICON.

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

Red arrows pointing to shorts



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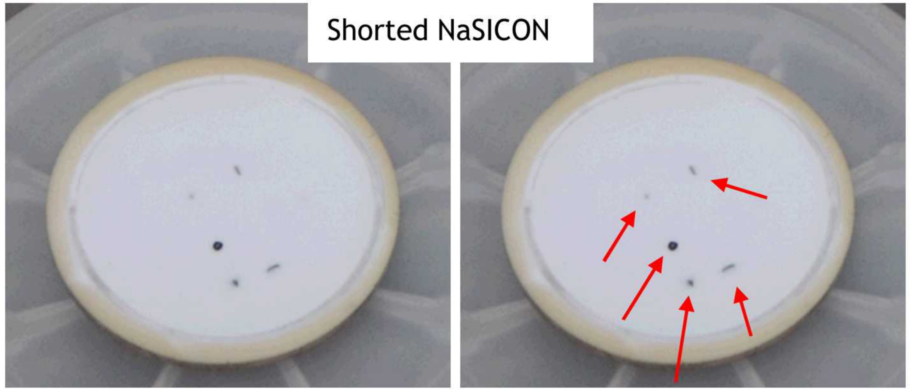
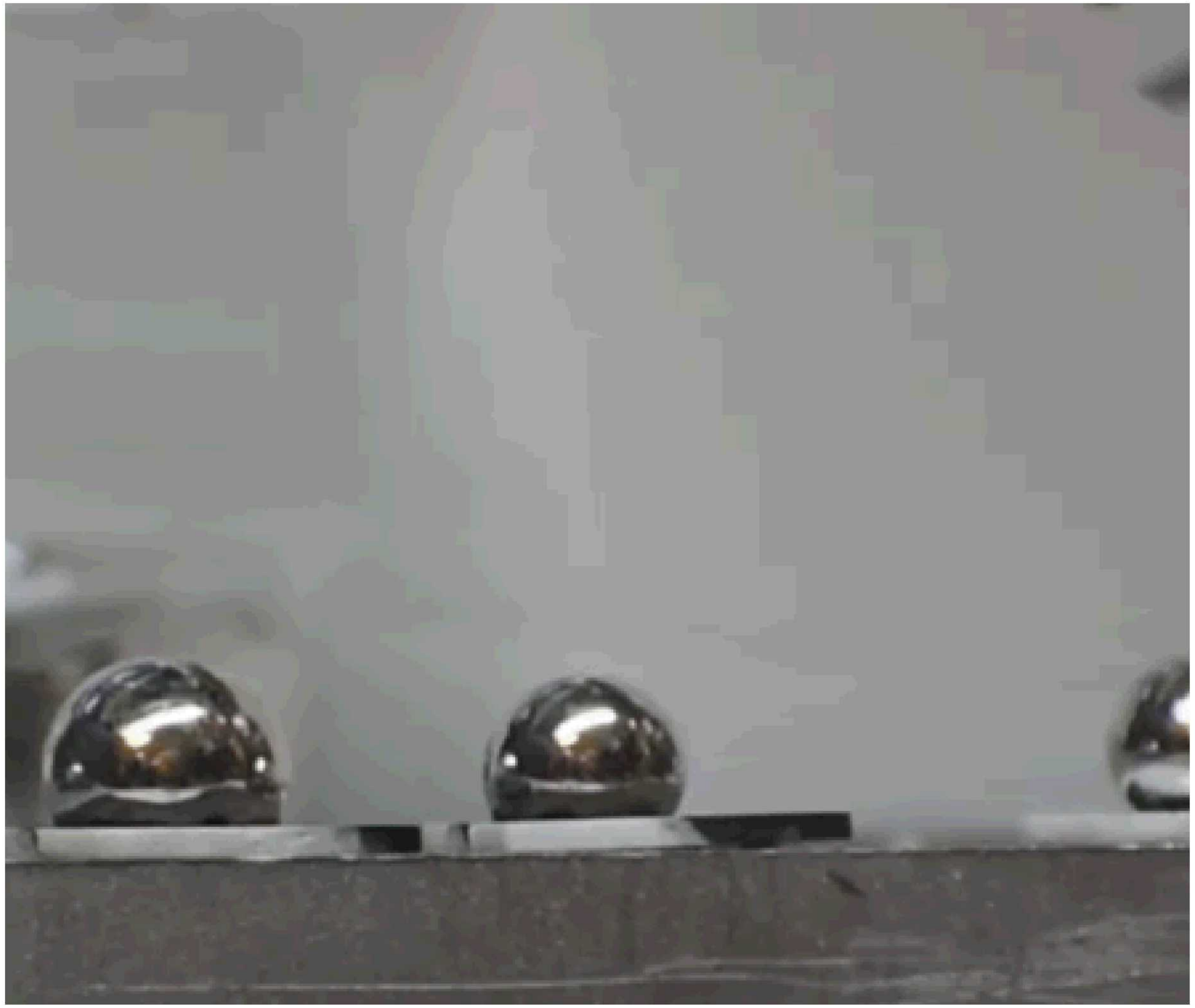


NaSICON Coated with Sn-Based Coating Shows Drastically Improved Adhesion!



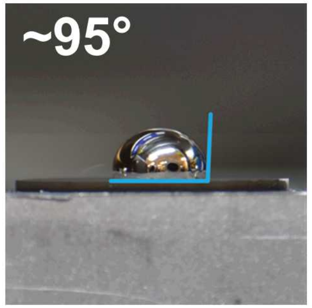
An Improved Na Interface

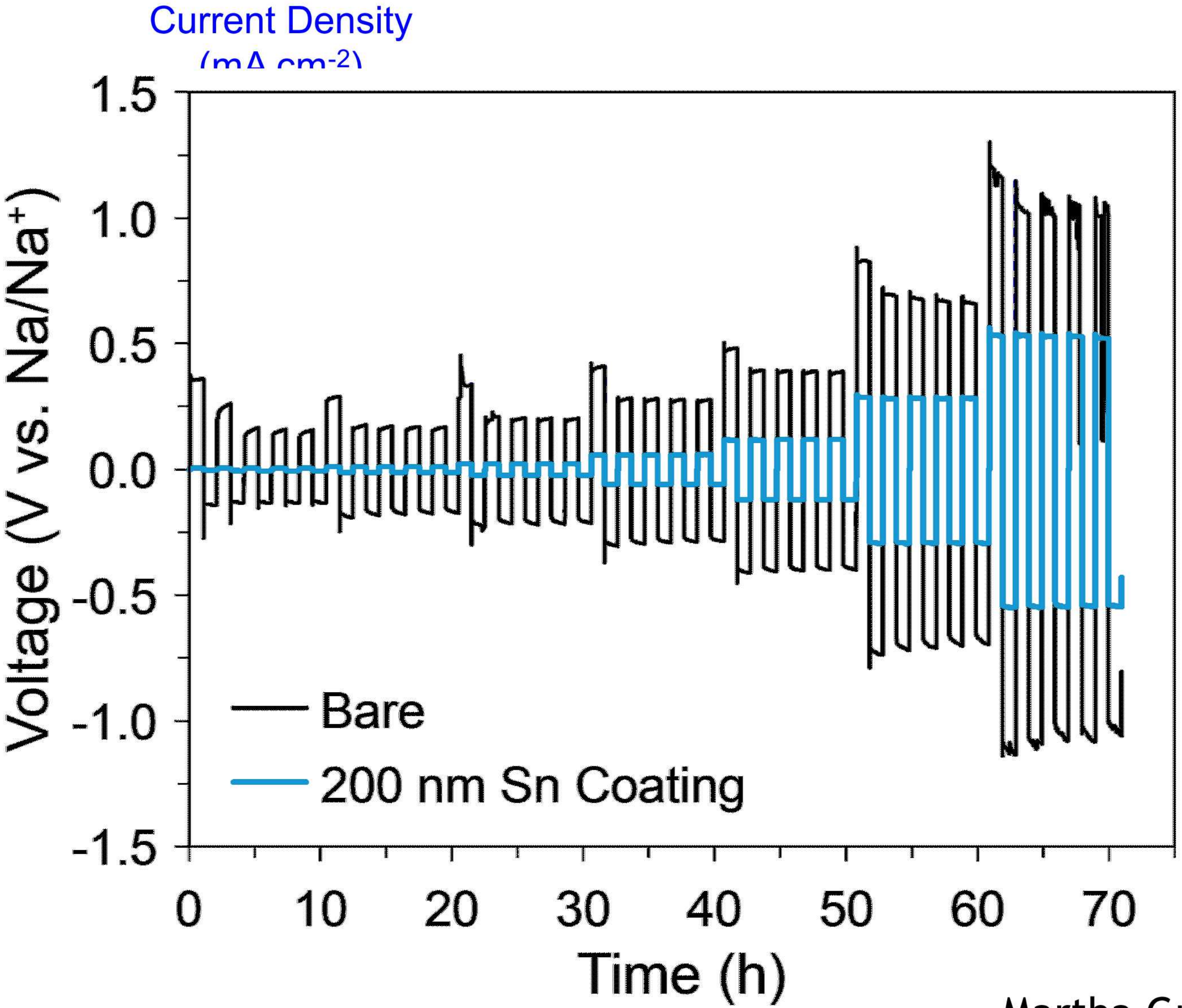
Symmetric cell cycling (Na on both sides) shows that the Sn-based coating improves wetting on NaSICON and drastically reduces overpotentials on cycling!

This improved interface is critical to realizing effective battery performance.

Untreated NaSICON

With Sn-Based Coating





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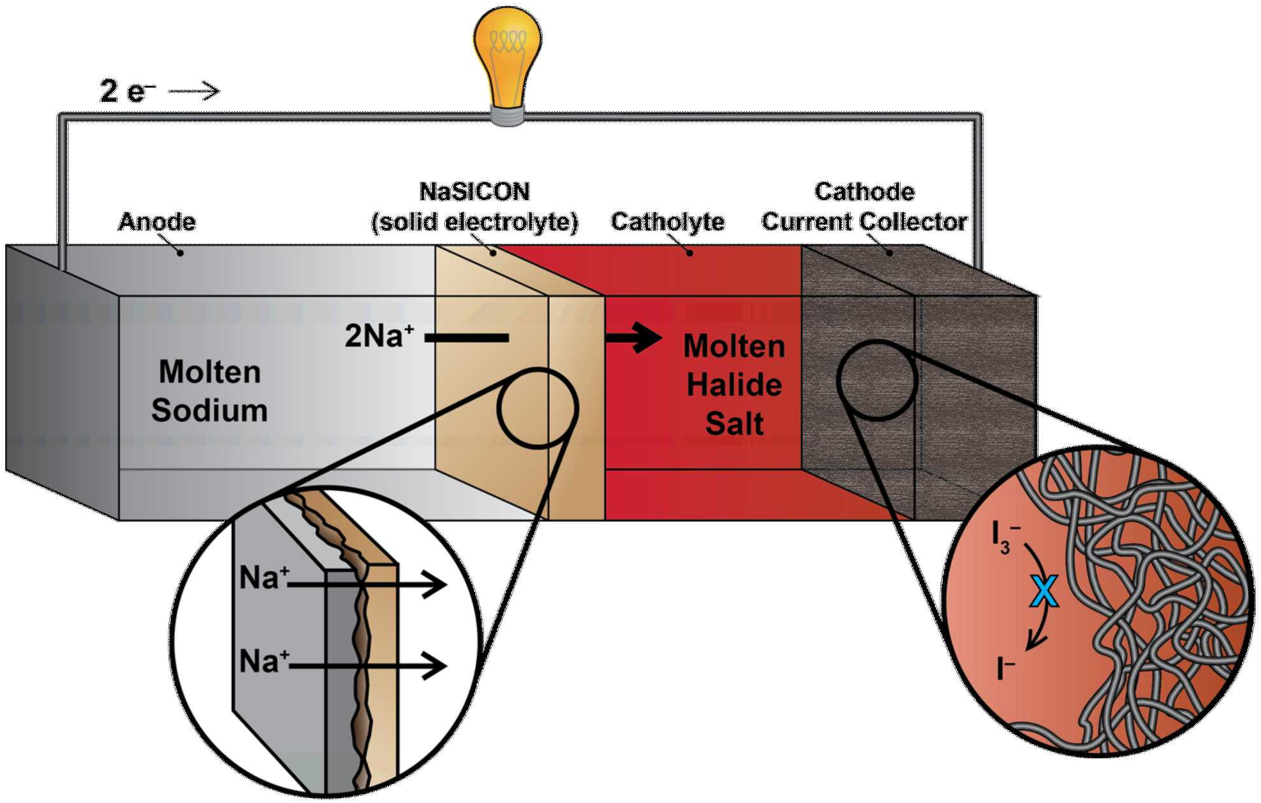

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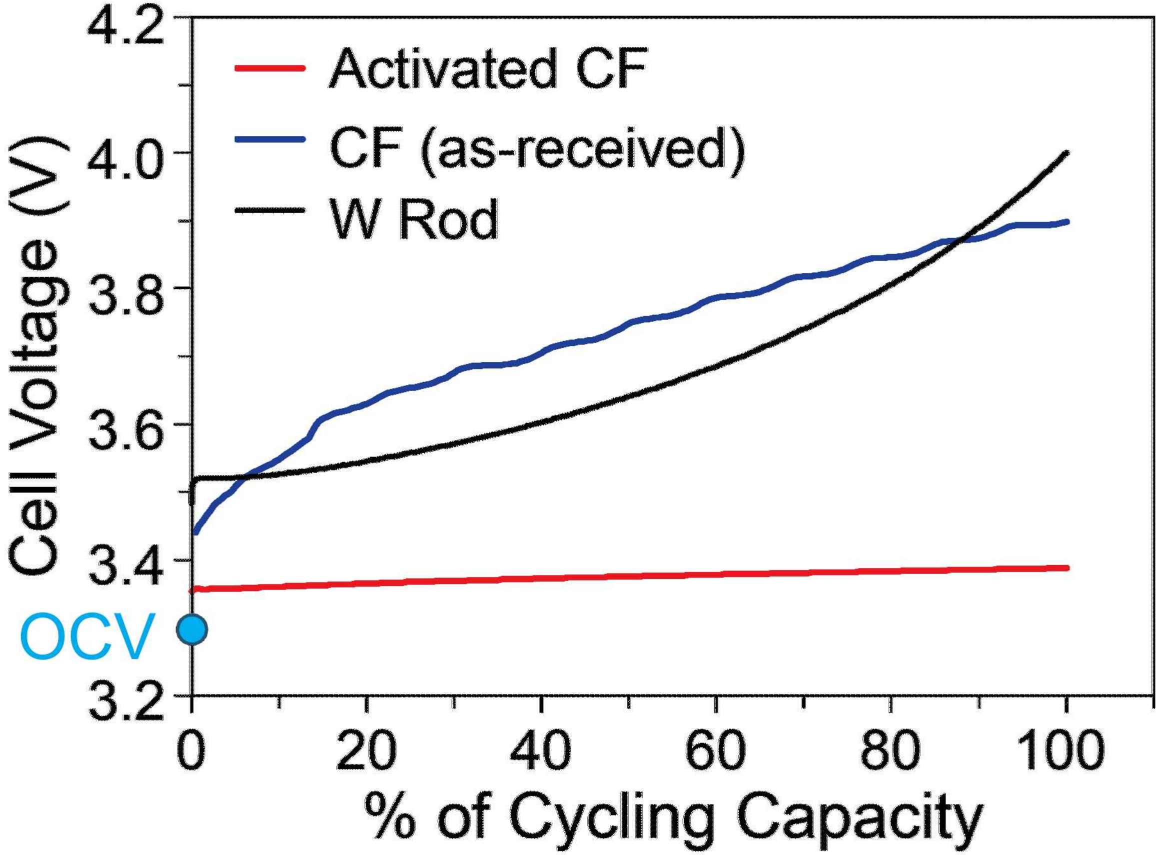
Improving Cathodic Current Collector

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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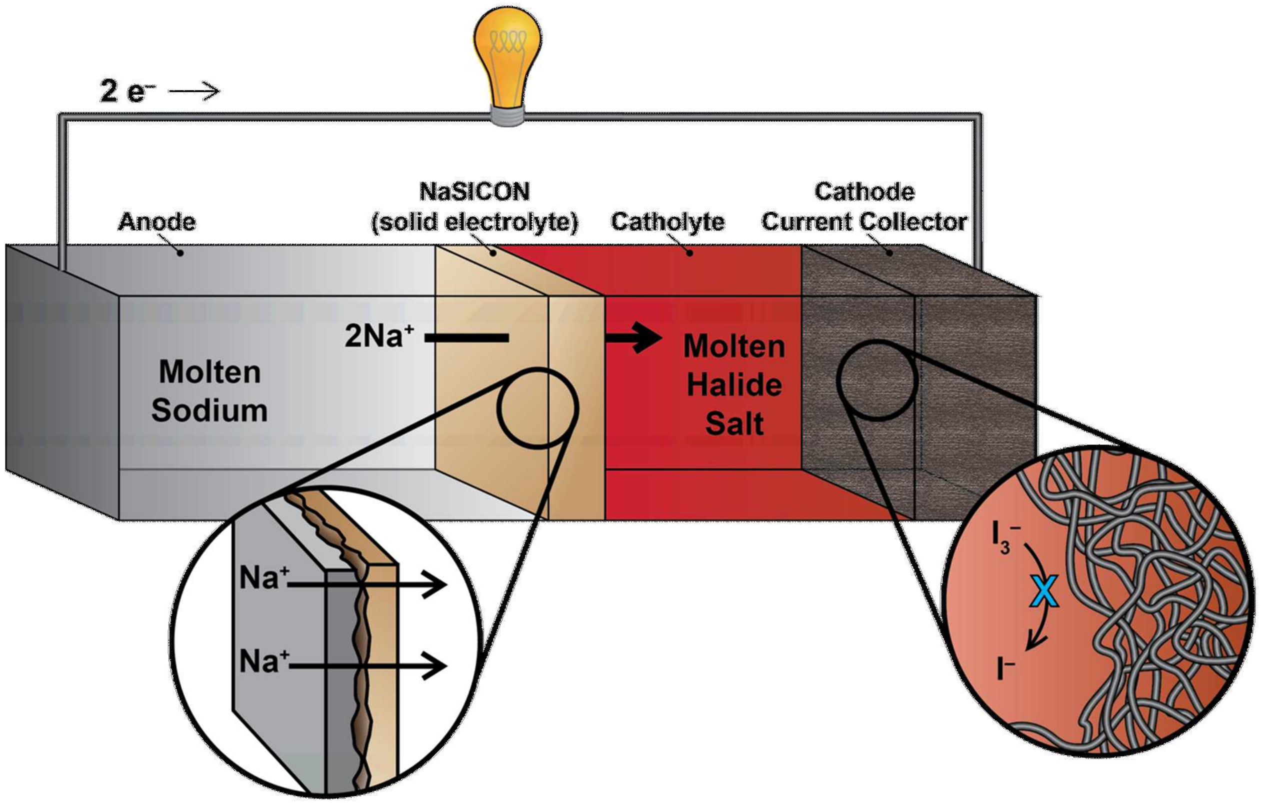

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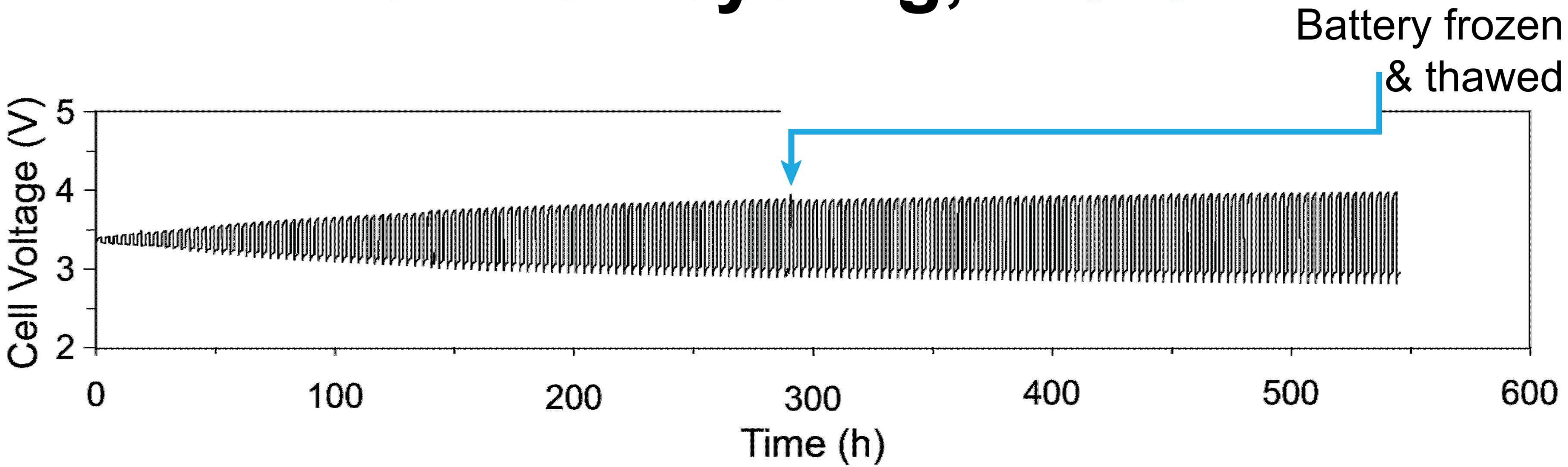
This Year's "Really Cool" Hurrah!

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)
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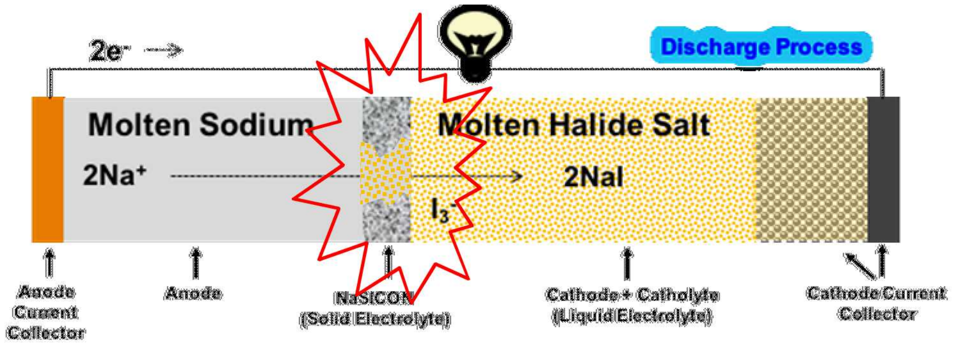
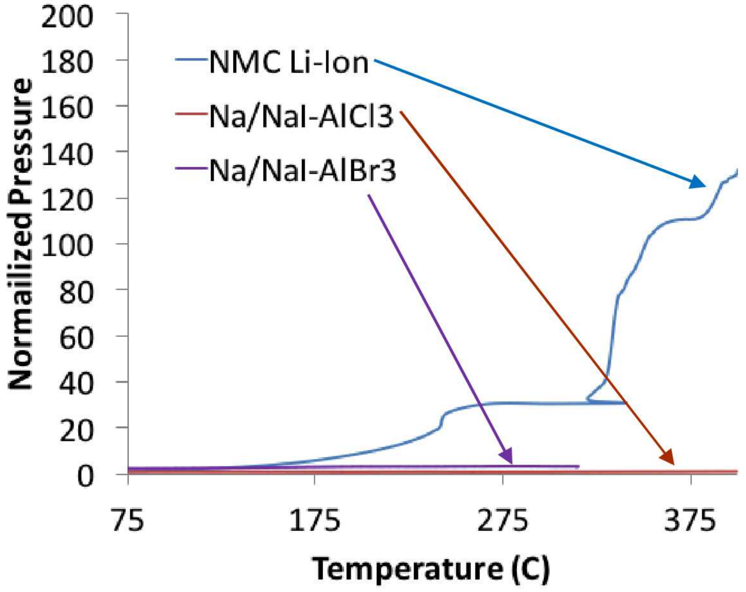


Simulating separator failure, metallic Na and NaI/AlX_3 were combined and heated.

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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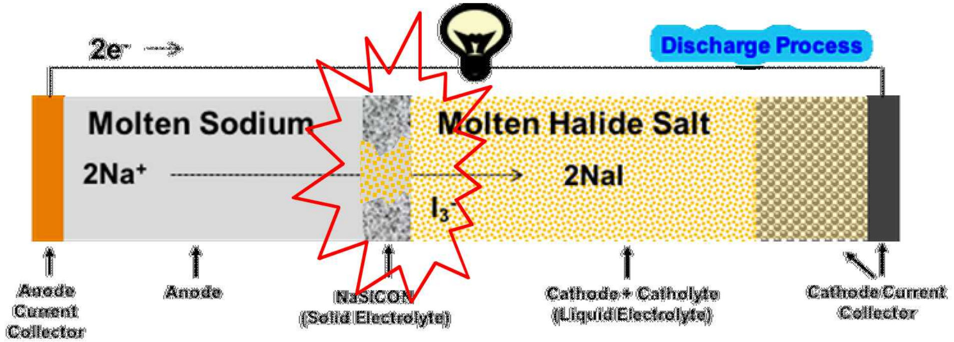

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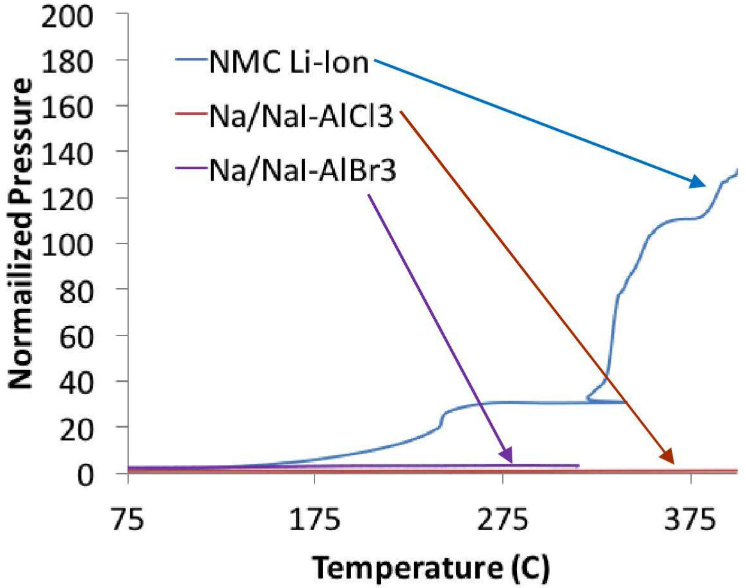

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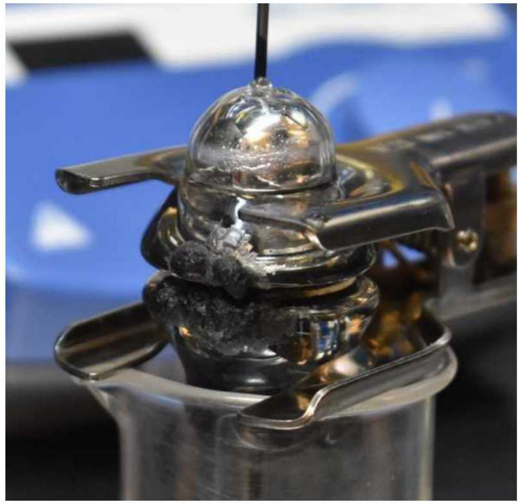

Failed separator led to termination of battery, but no significant hazardous conditions.

Summary

Project Objective: A safe, reliable, molten Na-based battery that operates at drastically reduced temperatures (near 100^{o}C).

Identified a low temperature, functional NaI-based molten catholyte and demonstrating initial battery cycling at 100^{o}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^{o}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^{o}C.

Acknowledgments and Thanks

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?

Erik Spoerke

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