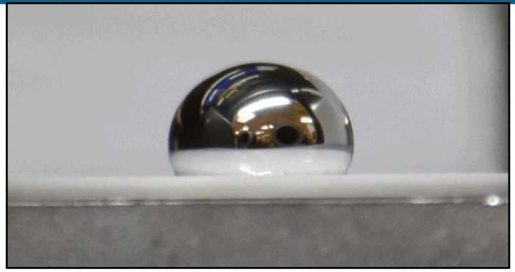
SAND2020-10071C

Implementing Low Temperature Strategies to Advance "Really Cool" Molten Sodium Batteries



Martha Gross
Stephen Percival
Amanda Peretti
Rose Lee
and Leo Small (PI)

PRESENTED BY

Erik D. Spoerke

PRIME 2020
October 4-9, 2020

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

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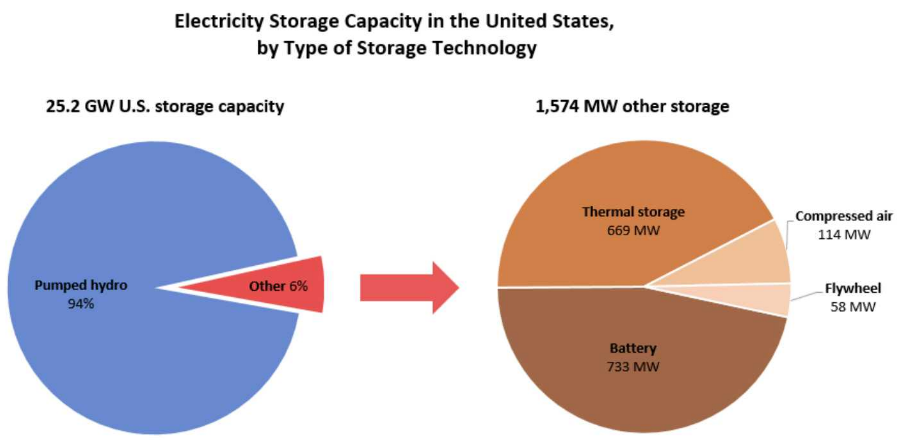
SAND No.: SAND

A Need for Grid-Scale Energy Storage

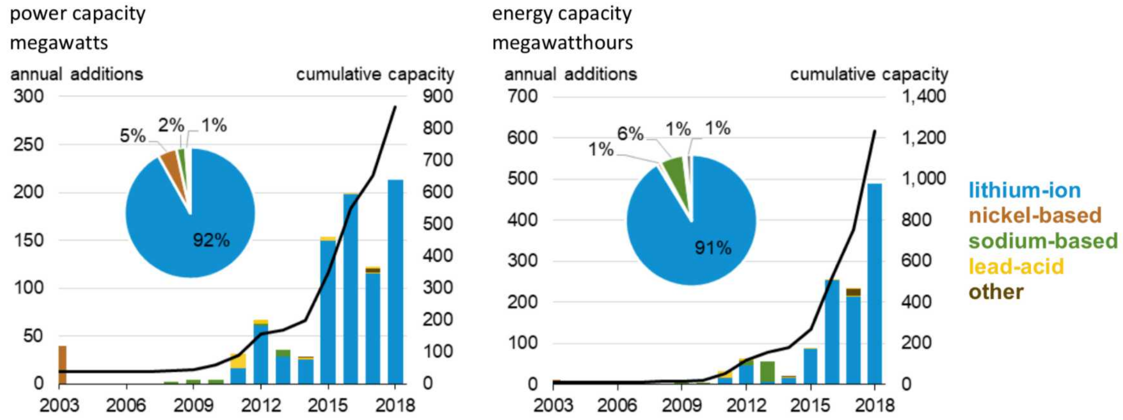
Renewable/Remote Energy Grid Reliability National Defense Emergency Aid

U.S. grid-scale energy storage is dominated by pumped hydroelectric storage, but battery storage is growing, largely through Li-ion batteries. Opportunities exist for other battery technologies to grow!



Source: *DOE Global Energy Storage Database http://www.energystorageexchange.org/ March, 2018*

U.S. Large-scale battery storage capacity by chemistry (2003-2018)

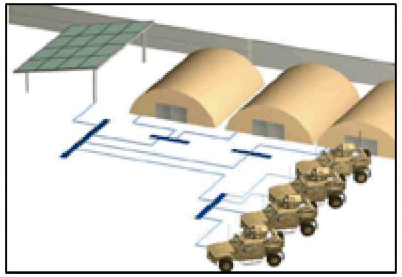


Source: U.S. Energy Information Administration, Form EIA-860, *Annual Electric Generator Report*

Figure adapted from: “Battery Storage in the United States: An Update on Market Trends.” EIA, 2020.

A Need for Grid-Scale Energy Storage




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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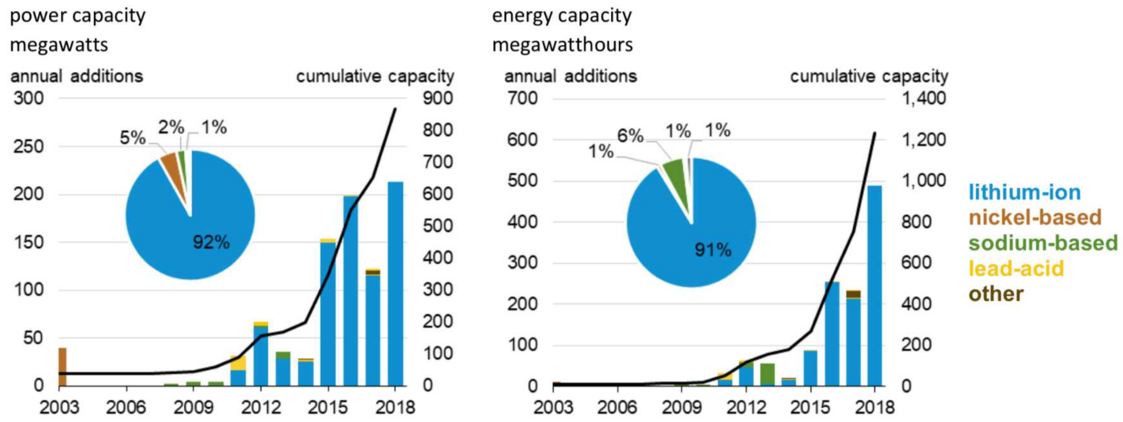

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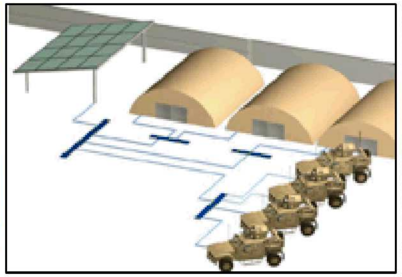
Grid-Scale Research at SNL


Renewable/Remote Energy

Grid Reliability



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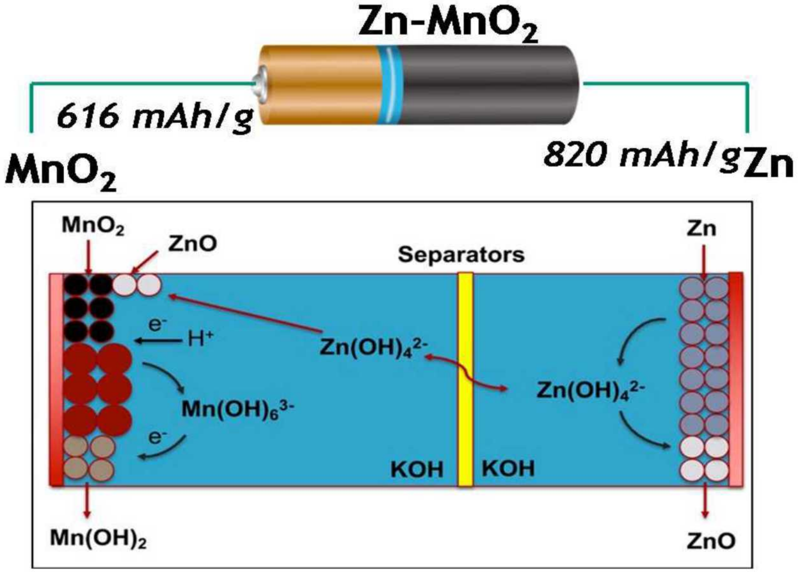


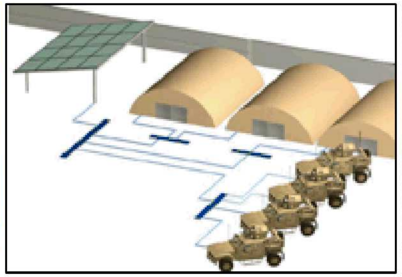
SNL work In collaboration with CUNY, Northeastern University, New Mexico State, Stony Brook University, Urban Electric Power.

SNL PI: Dr. Tim Lambert

Grid-Scale Research at SNL


Renewable/Remote Energy

Grid Reliability



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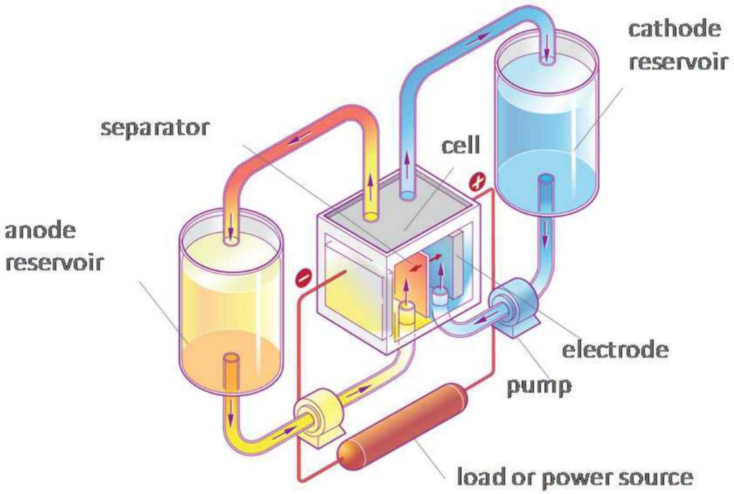


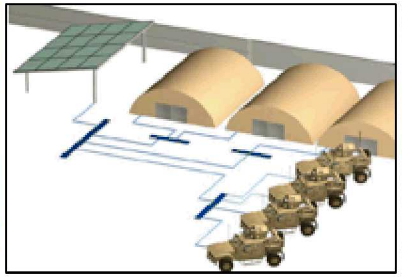
SNL work in collaboration with University of Washington/Texas, Davidson College, LANL, WattJoule, UET.

SNL PI: Dr. Travis Anderson
SNL Membrane PI: Dr. Cy Fujimoto

Sodium Batteries Can Help Meet a National Need


Renewable/Remote Energy

Grid Reliability



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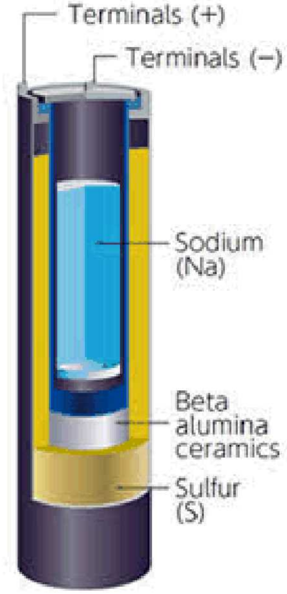
Sodium-based batteries

- 6th most abundant element on earth.
- 5X the annual production of aluminum.
- Proven technology base with NGK Sodium/Sulfur (NaS) and FzSoNick ZEBRA ($Na\text{-}NiCl_2$) systems.
    - 580 MW/ 4GWh of NaS storage in 200 locations
    - ~114MWh of $Na\text{-}NiCl_2$ in telecon, utilities, and grid services
- 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)

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

Sodium Batteries Can Help Meet a National Need

Renewable/Remote Energy Grid Reliability National Defense Emergency Aid

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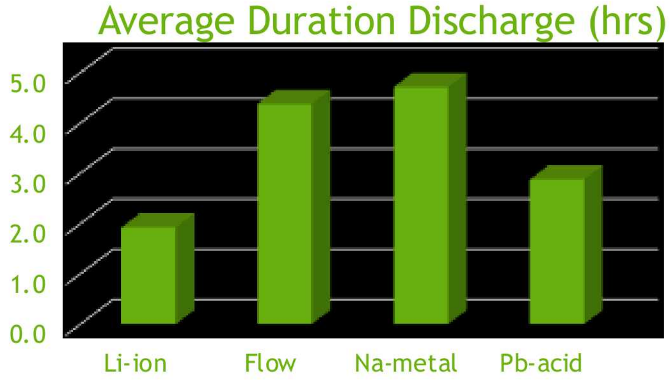

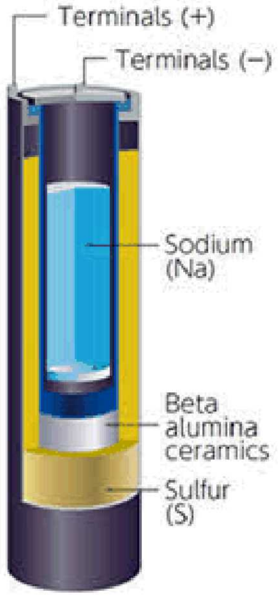

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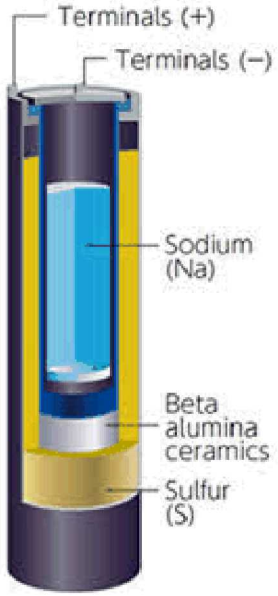


Na- ... **V)**

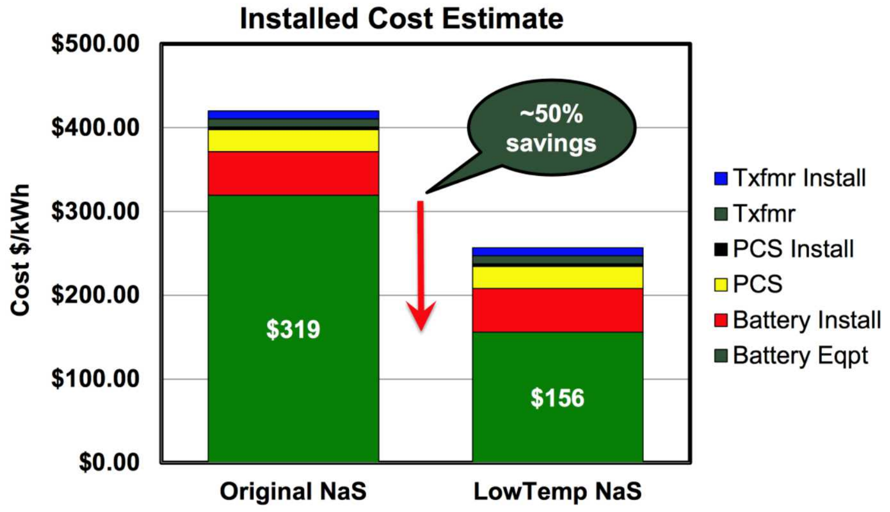
~300°C Operation!

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

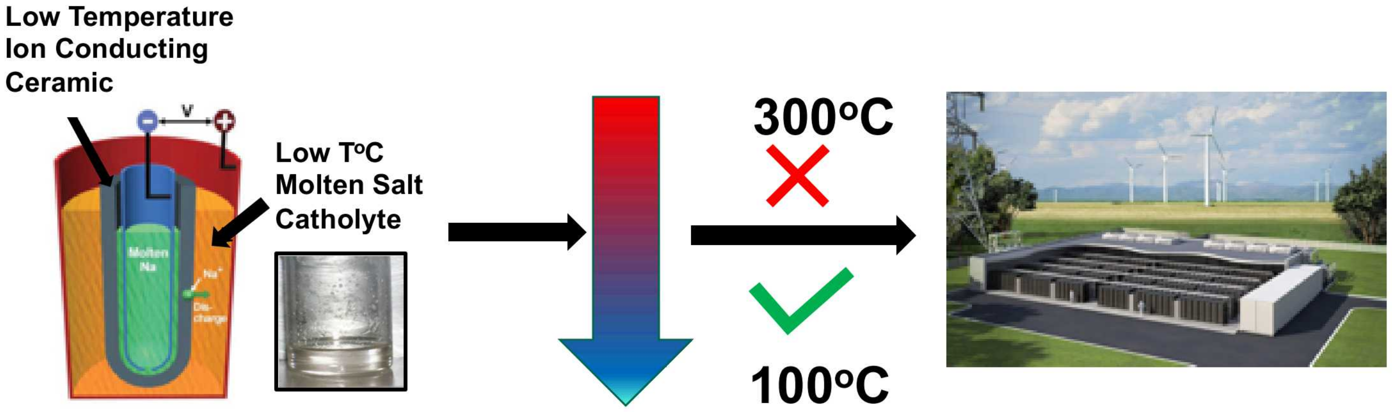
Lowering Battery Operating Temperature to Drive Down Cost

<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
  - Wiring!
  - 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

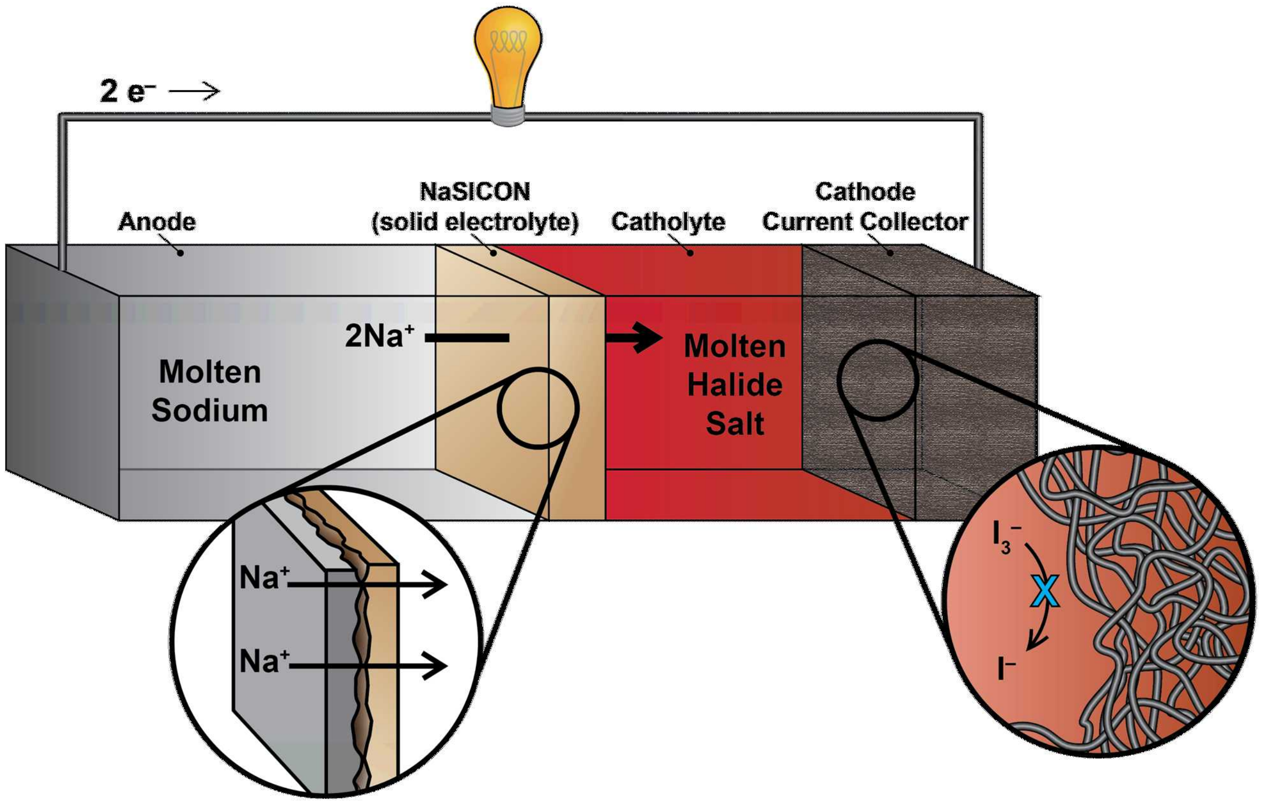


Low Temperature Molten Sodium (Na-NaI) Batteries

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

Key Battery Attributes

- Molten Na anode (minimize dendrites!)
- Highly Na^+-conductive, zero-crossover separator (e.g., NaSICON)
- 25 mol% NaI in MX_3 catholyte – no organic electrolytes
- *No complications from solid state electrodes!*



Na-NaI battery:

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

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

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

A05-1006: Solid State Ion Conductors to Enable Low Temperature Molten Sodium Batteries by Erik Spoerke

A05-0933 Advancing Low Temperature Molten Sodium Batteries By Interfacial Engineering of Ceramic Electrolytes by Martha Gross

Martha Gross

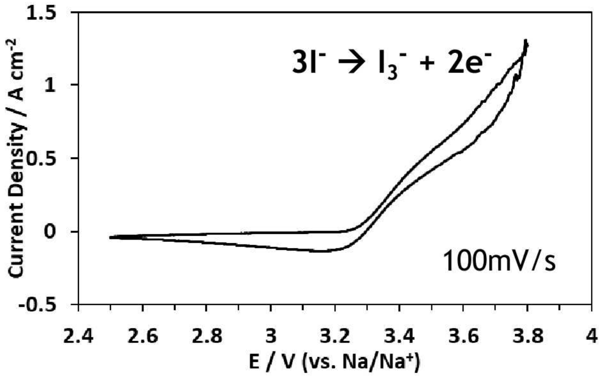
Early Low Temperature Na-Battery Performance

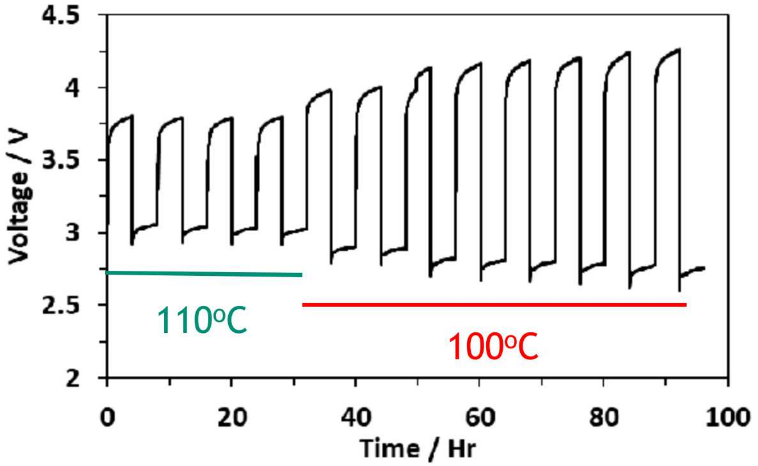
First demonstration of molten Na-NaI battery at 100-110°C.

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

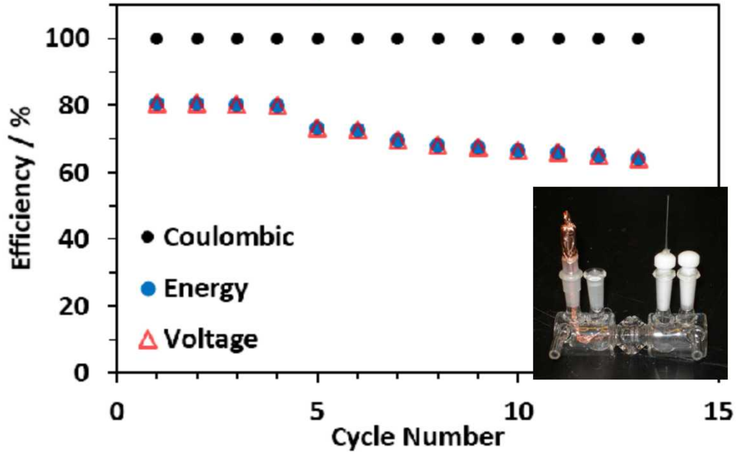
- 25:75 NaI-$AlBr_3$salt <u>completely molten </u>at 90 °C
- Large fully molten capacity range (~5-25 mol% NaI)

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.

Stephen Percival

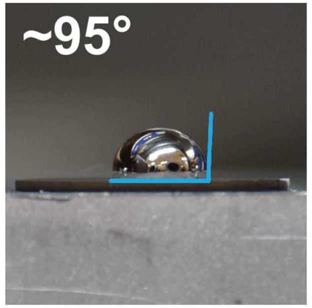
An Improved Na Interface

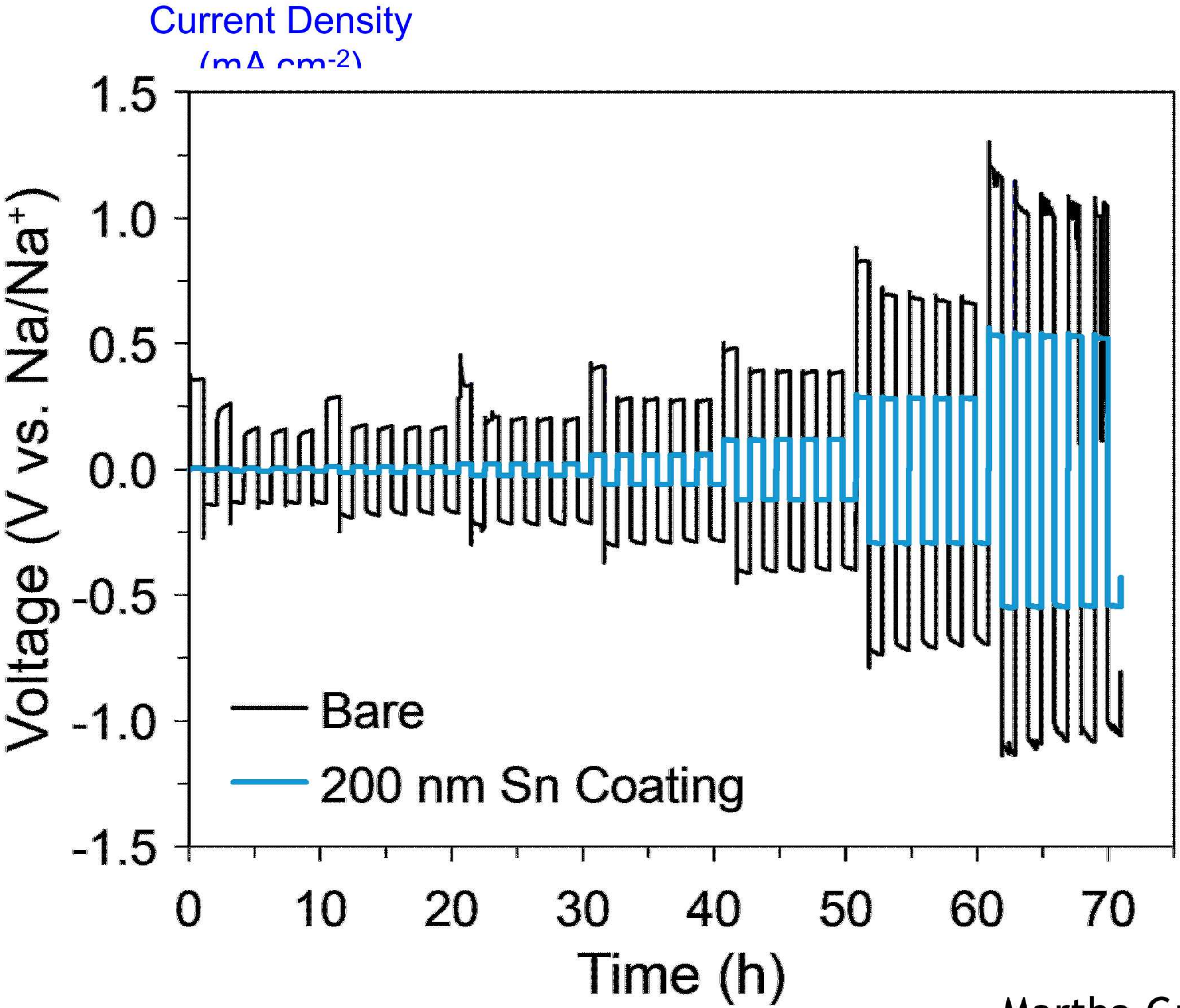
Symmetric cell cycling (Na on both sides) shows that the Sn-based coating improves wetting on NaSICON and drastically reduces overpotentials on cycling!

This improved interface is critical to realizing effective battery performance.

Untreated NaSICON

With Sn-Based Coating





Martha Gross

M.M. Gross, L.J. Small, A.S. Peretti, S.J. Percival, M. Rodriguez, E.D. Spoerke. *J. Mater. Chem. A*, **8** (2020) 17012.

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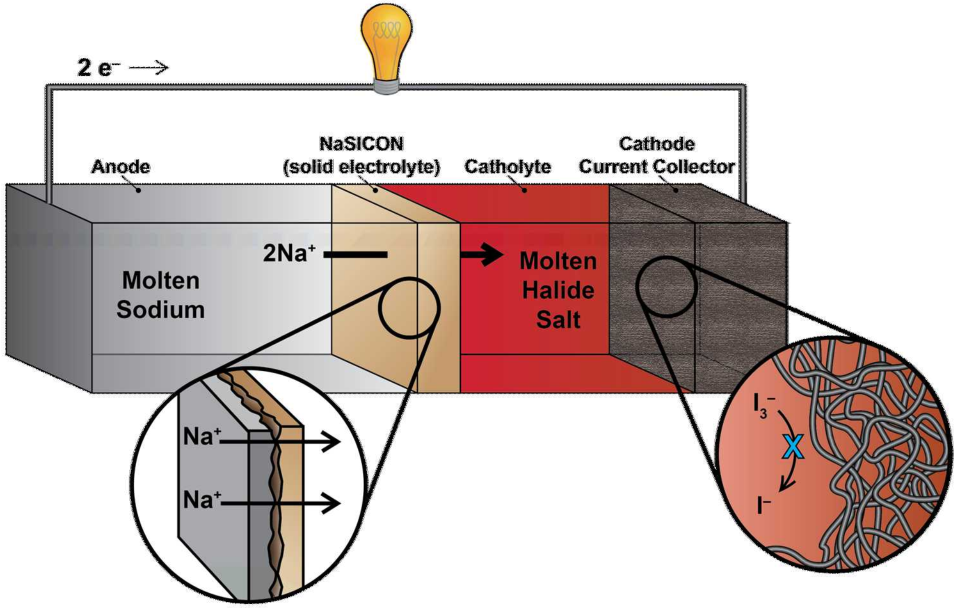

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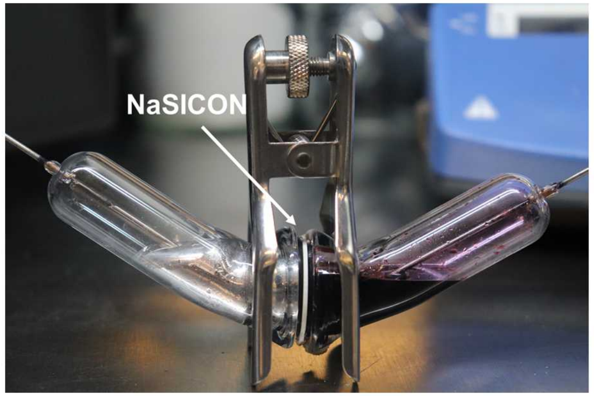
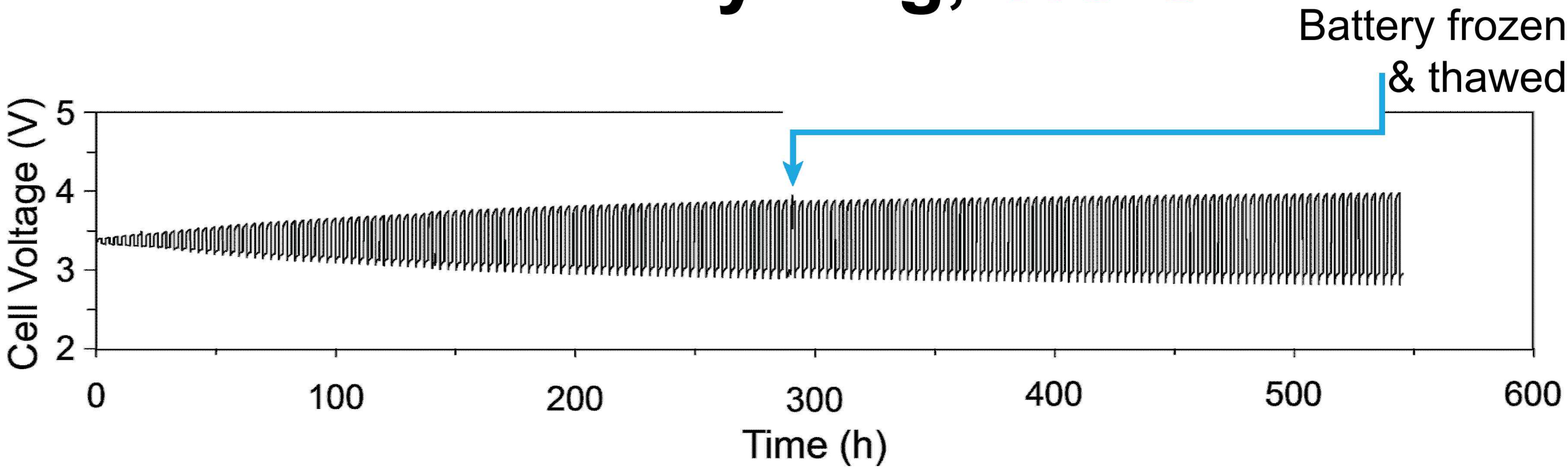


Molten Na Battery Cell Set-Up

Martha Gross

Excellent Initial Electrochemical Cycling at Low Temperatures

Full Cell Cycling, 110°C



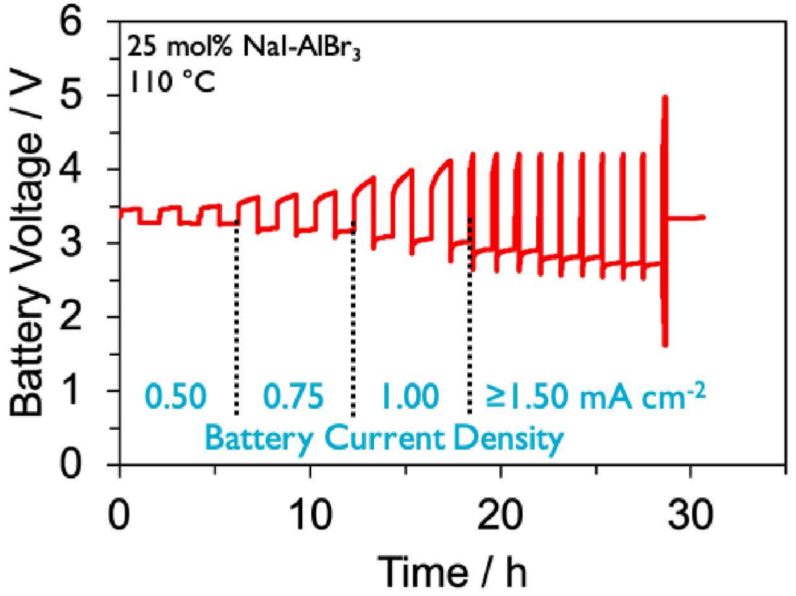
- Integration of Sn-based coating and activated CF enables long-term battery cycling: **Battery achieved 200 cycles!**
- Even after freeze/thaw, interfaces remain intact with uninterrupted cycling!

M.M. Gross, L.J. Small, A.S. Peretti, S.J. Percival, M. Rodriguez, E.D. Spoerke. *J. Mater. Chem. A,* **8** (2020) 17012.
M.M. Gross, S.J. Percival, L.J. Small, J. Lamb, A.S. Peretti, E.D. Spoerke. *In Review* (2020).

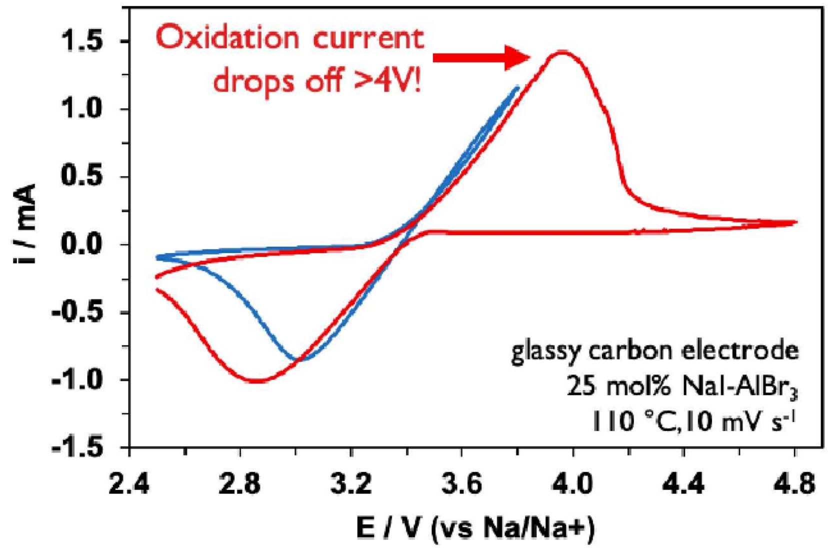
Testing the Limits of the NaI-$AlBr_3$ Catholyte

Previously ran NaI-$AlBr_3$ at 0.5 mA cm^{-2}, want to hit 50 mA cm^{-2} (shown in 2017 for NaI-$AlCl_3$ at 180 °C).

Increasing battery current density >0.75 mA cm^{-2} quickly results in failure



Cyclic voltammetry of the catholyte alone reveals that the carbon current collector passivates once the cell voltage exceeds 4V.



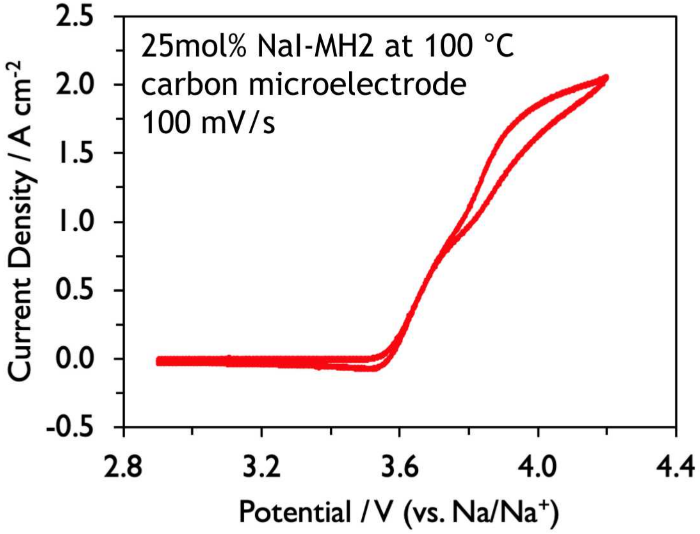
NaI-$AlBr_3$ catholyte cannot continuously cycle at more than 0.75 mA cm^{-2} due to passivation of carbon electrode.

Revised Catholyte Chemistry MH2 – Even Lower Melting Point!

New low temperature molten salt system NaI-MH2 identified

- 20 mol% NaI is fully molten at 50 °C.
- Good conductivity: 46 mS cm^{-1} at 110 °C
- I^-/I_3^- redox observed

20 mol% NaI at 50 °C



MH2-NaI "Phase Diagram"

Temperature (°C)	10	20	25	30	40
130	L	L	L	L	L+S
120	L	L	L	L	L+S
110	L	L	L	L	L+S
100	L	L	L	L+S	L+S
90	L	L	L	L+S	L+S
80	L	L	L	L+S	L+S
70	S+L	L	L+S	L+S	S
60	S+L	L	L+S	S+L	S
50	S+L	L	S+L	S+L	S
40	S	S+L	S	S	S
30	S	S	S	S	S

Composition (mol% NaI)

L=liquid
S=solid

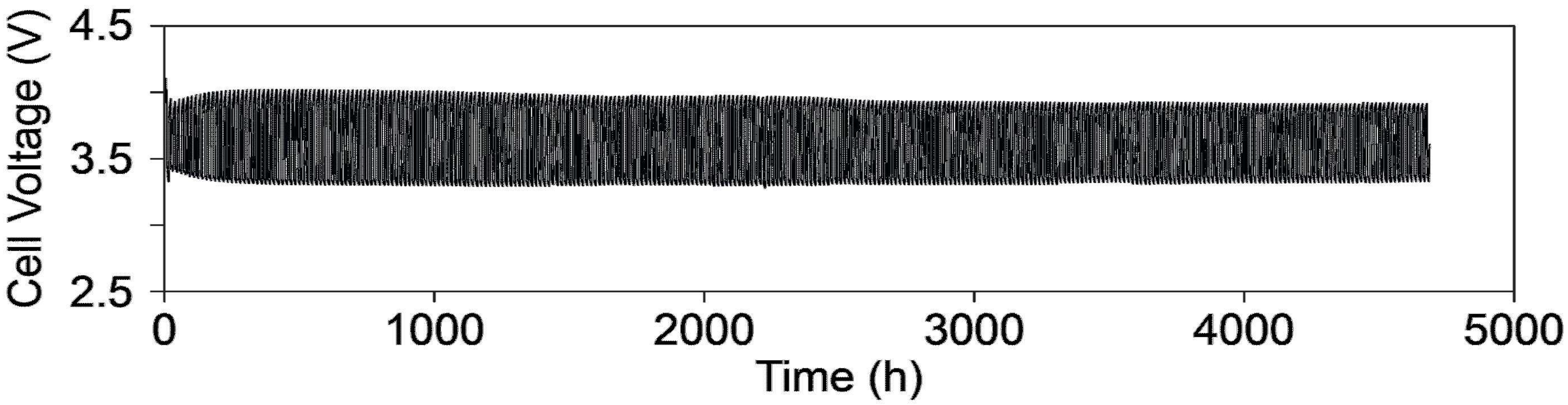
Redox-active molten salt NaI-MH2 was identified, with melting point near 50 °C.

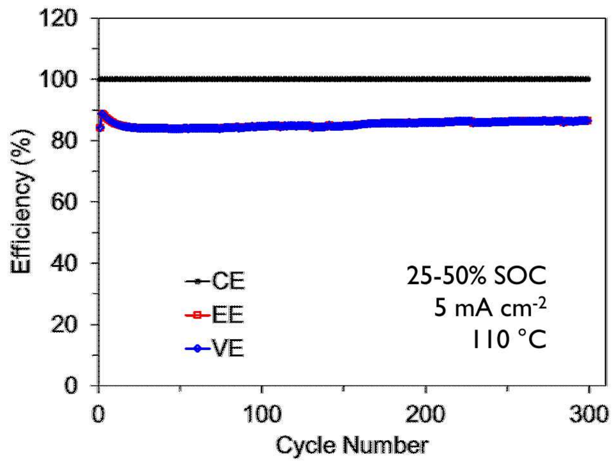
Rose Lee and Stephen Percival

Effective Cycling of a "Really Cool" Na-NaI Battery!

Integrated NaI-MH2 catholyte into molten Na batteries with NaSICON separator

- Successfully ran >300 cycles (>6 months) at 5 mA cm^{-2} (25% DoD) for 85.3% voltage efficiency. Still running!
- Successfully accessed all I^-/I_3^- capacity (100% DoD) at 3.5 mA cm^{-2}
- Cycled currents as high as 15 mA cm^{-2}.
- Battery voltage increased by about 400 mV over the $AlBr_3$ system!



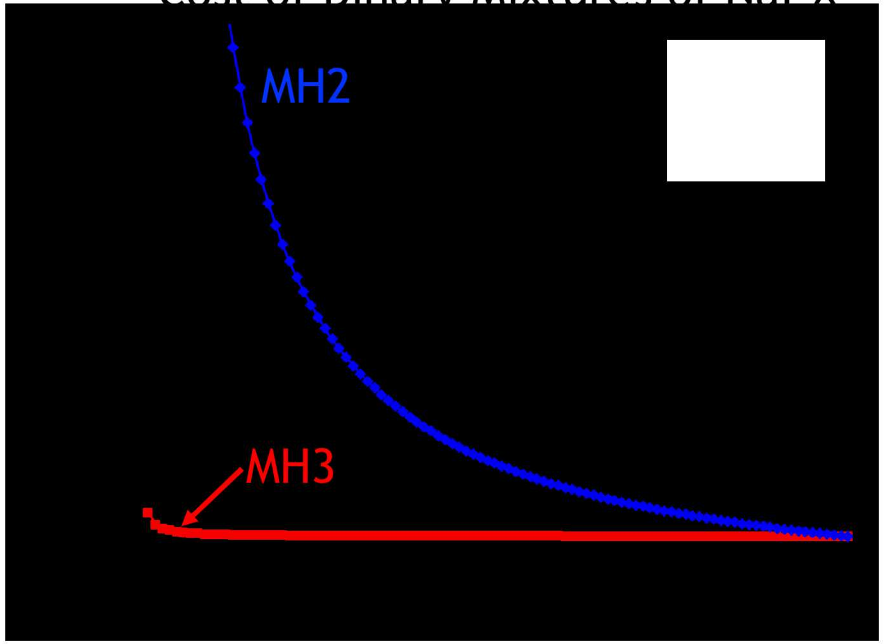


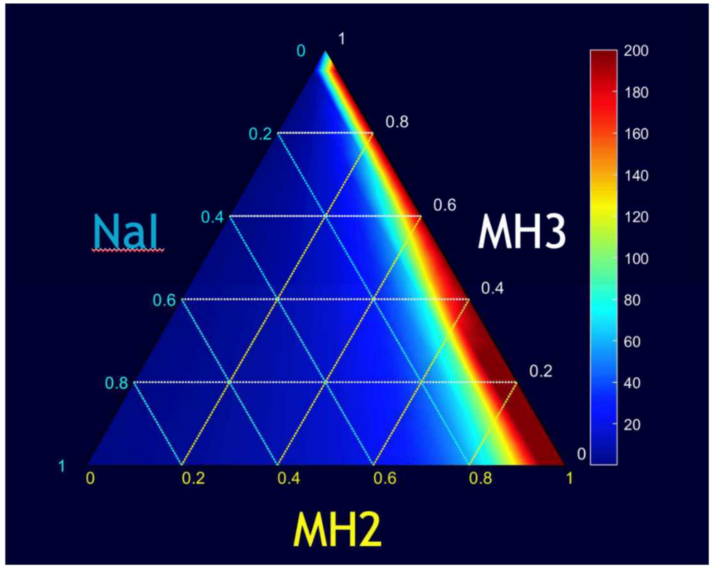
Cycled molten sodium battery with NaI-MH2 catholyte at 110 °C for >6 months with >85% energy efficiency, using 25x cycling capacity and 10x current density vs. NaI-$AlBr_3$ catholyte!

Catholyte Cost Analysis

- NaI-MH2 catholyte shows great performance, but ***MH2 is expensive (>$100/kg)*.**
- We evaluated costs across a large phase space of binary and ternary MH-NaI salt combinations to identify underlying cost trends, with goal of <$20/kWh for catholyte materials costs.

Cost of Binary Mixtures of NaI-X



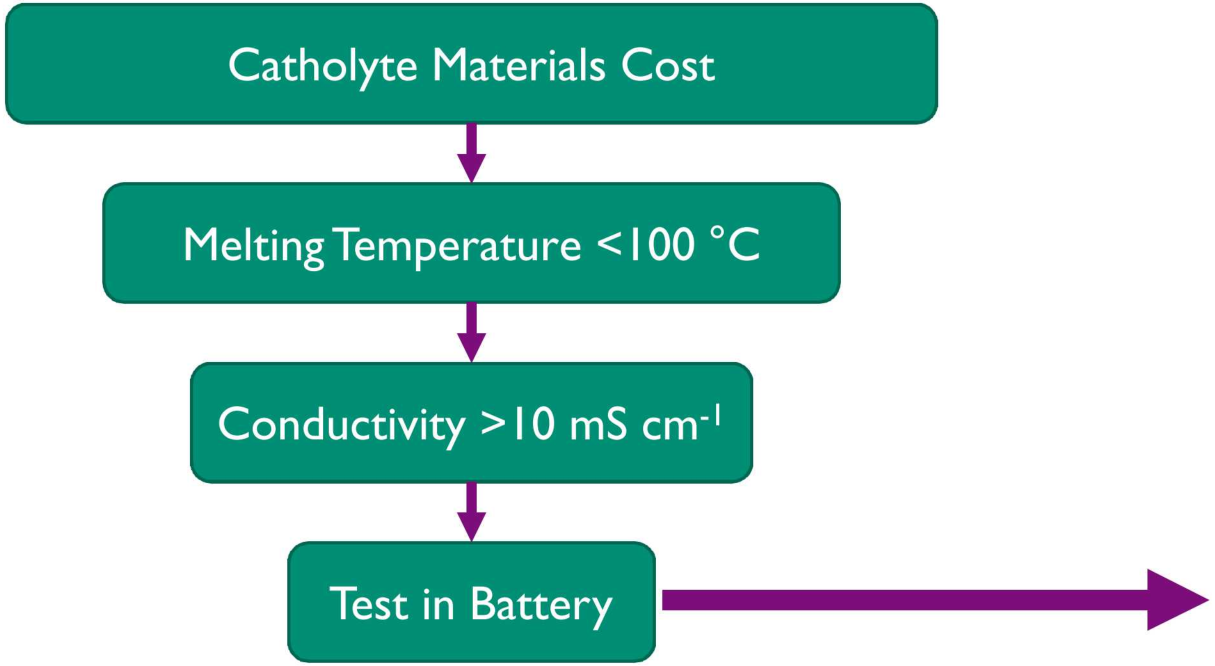


Increased NaI content and select metal-halide (MH) salts readily enable catholyte ***materials costs*** <$20 kWh, with <$5 kWh feasible.

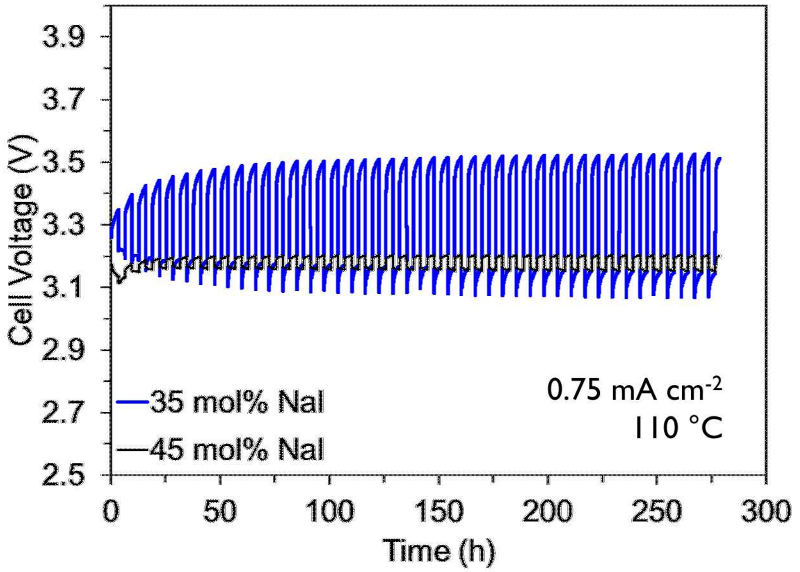
Martha Gross

Leveraging Cost Analysis to Identify New Catholytes

Use cost as first level screen for new catholytes



Batteries using NaI-MH3 Catholytes, <$5/kWh



45 mol% NaI-MH3 looks very promising

Use of catholyte screening process yielded promising initial battery performance with NaI-MH3 ***materials costs*** <$5 kWh.

Summary

The national need for energy storage is creating opportunities for grid-scale technologies! We are working to advance the development of low temperature molten Na batteries using Na-NaI chemistry.

- Controlling interfaces can enable strong cycling behavior at 110°C!
- Molten salt composition can have a significant impact on the electrochemical and physical properties of the catholyte.
- The electrochemical and interfacial materials chemistry of the molten salt catholyte chemistry can have a strong impact on battery performance.
- Optimization of these materials challenges has led to unprecedented low temperature battery cycling for over 6 months!
- Using cost analyses to help guide materials design may accelerate practical system designs, balancing tradeoffs between performance and materials costs.

Promising materials advances show that these low temperature batteries have the potential impact the evolving grid-scale energy storage landscape!

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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