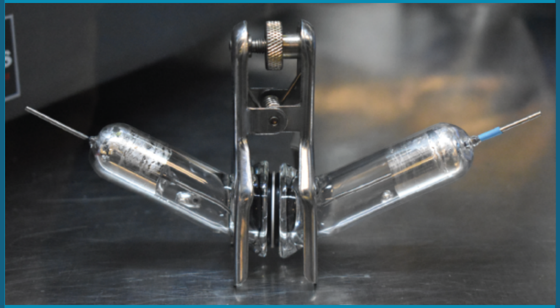
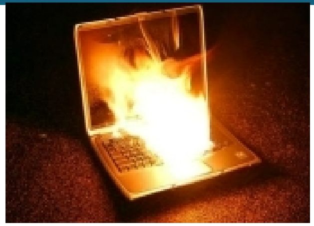
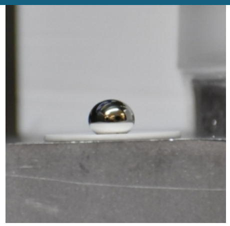
SAND2021-11315C

Sandia National Laboratories

Advancing the Promise of Low-Temperature Molten Sodium Batteries

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Stephen J. Percival
Leo J. Small
Mark A. Rodriguez

5th International Symposium on Materials for Energy Storage and Conversion

September 15, 2021

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U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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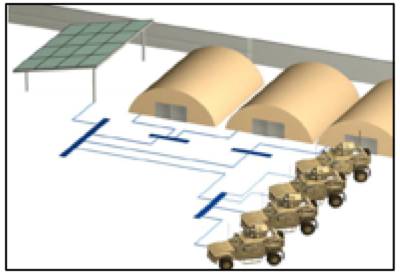
Sodium (Na) Batteries Can Help Meet a Growing Need


Renewable/Remote Energy

Grid Reliability



National Defense

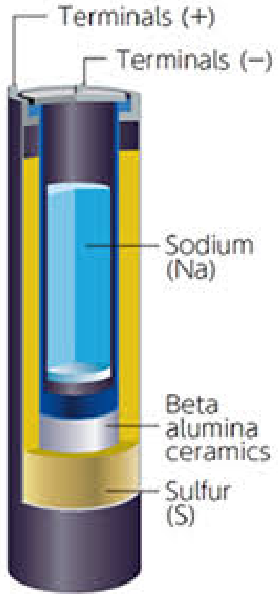
Emergency Aid

As part of the U.S. 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

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.
  - 580 MW/ 4GWh of NaS storage in 200 locations
  - ~130MWh of Na-$NiCl_2$ in telecon, utilities, and grid services
- Favorable battery voltages (>2V)
- Potential Longer Duration Storage (4-6 hours or more), 15-20 year lifetimes!



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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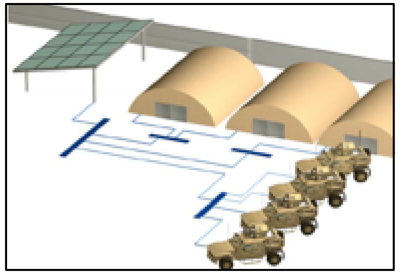

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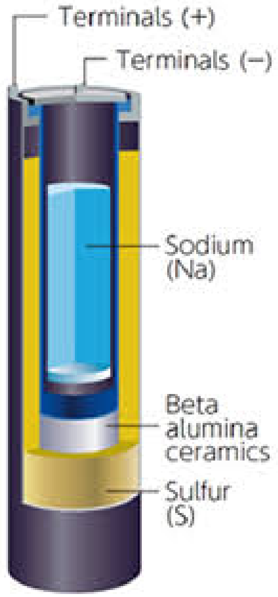


Na-S ... V)

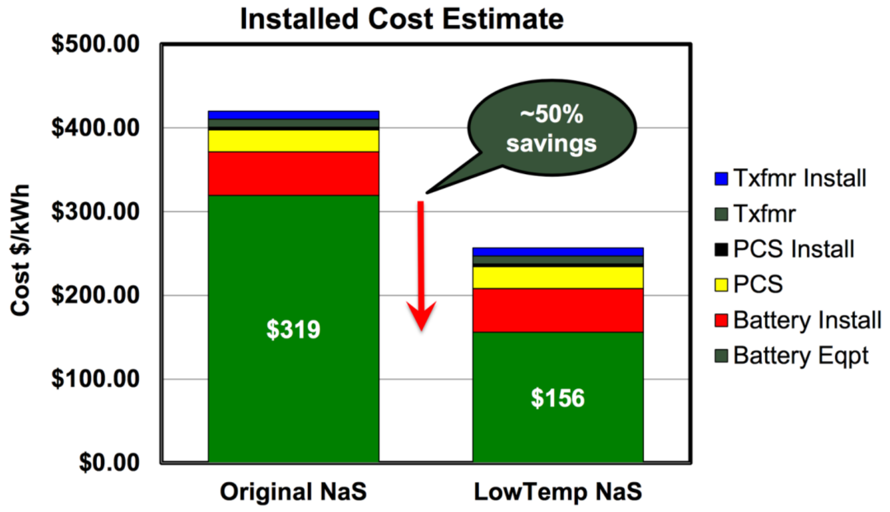
2Na ... $a^+ + 2Cl^- + Ni(s)$

~300°C Operation!

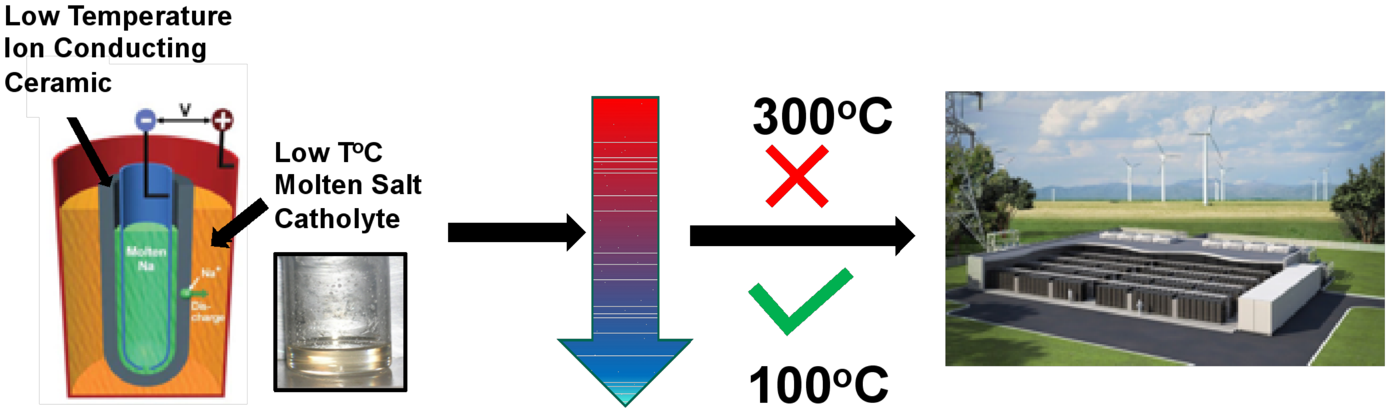
Lowering Battery Operating Temperature to Drive Down Cost

<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

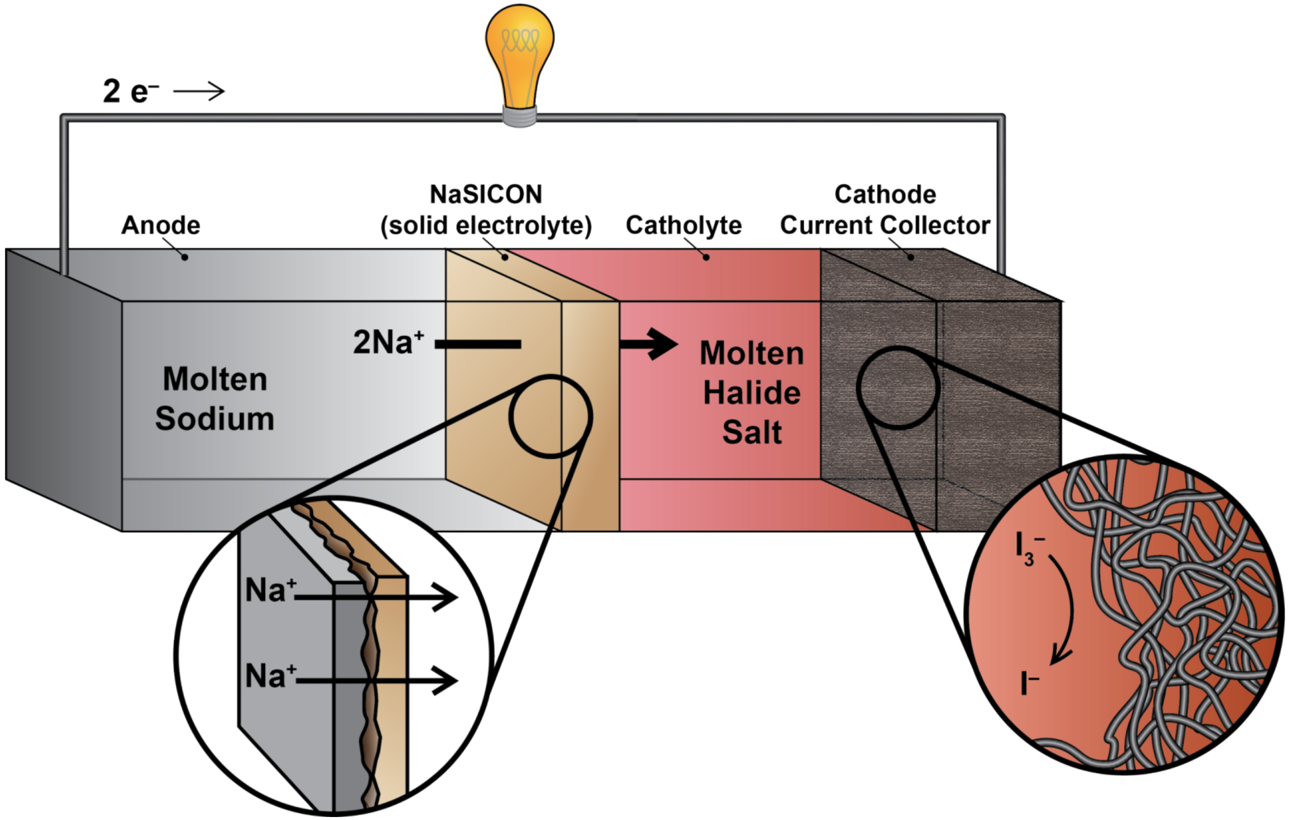


Low Temperature Molten Sodium (Na-NaI) Batteries: Not Your Grandfather's Sodium Battery!

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!



Martha Gross

Na-NaI battery:

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

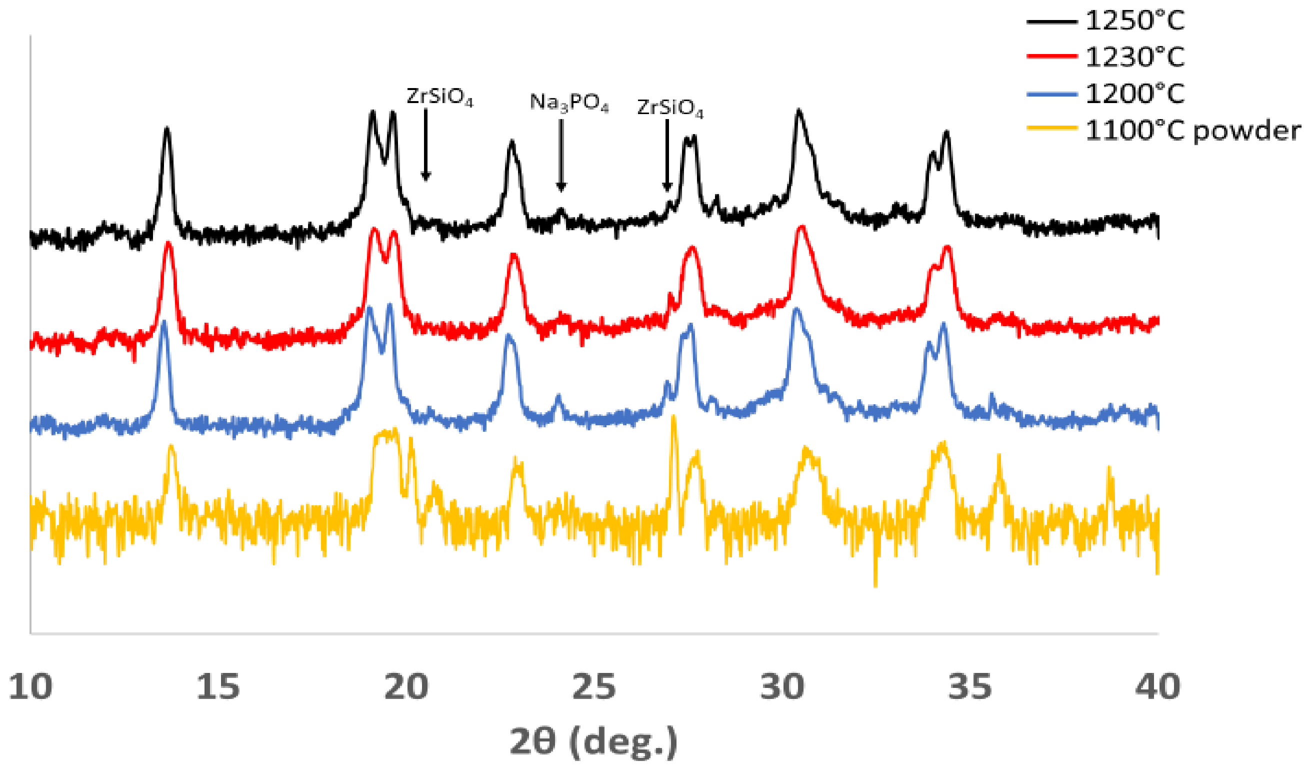
$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

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

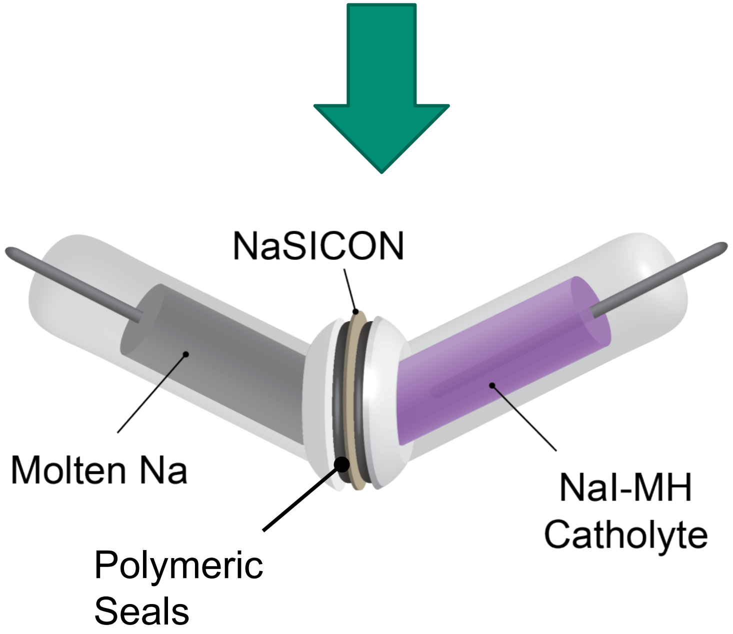
Small and Spoerke, *et al*. "Next Generation Molten NaI Batteries for Grid Scale Energy Storage." (2017) *J. Power Sources*. **360.** 569-574.

Solid State Synthesis Yields Effective NaSICON

Primary peaks reflect NaSICON phase: $Na_3Zr_2PSi_2O_{12}$



NaSICON cylinder and sectioned pellets.



NaSICON sintered at 1230°C yields >96% bulk density, acceptable phase purity, and ~10^{-3} S/cm at 25°C.

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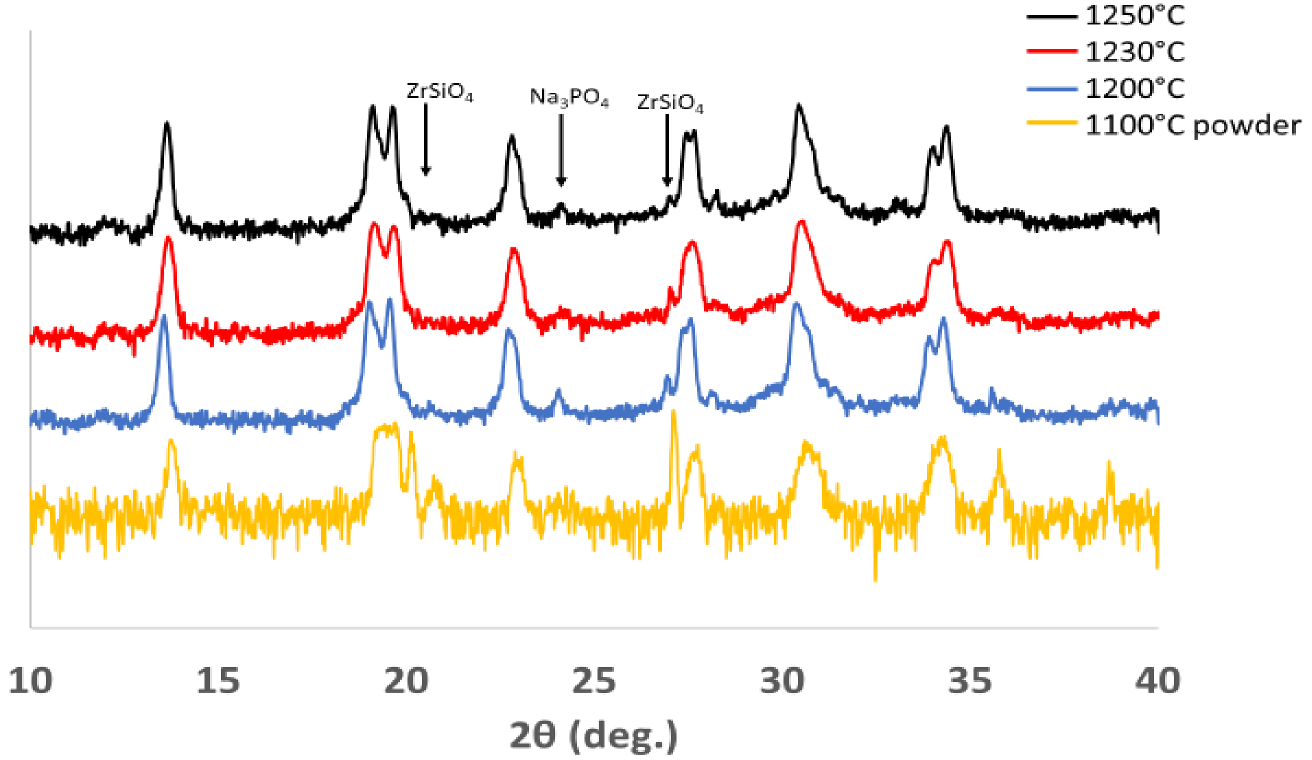

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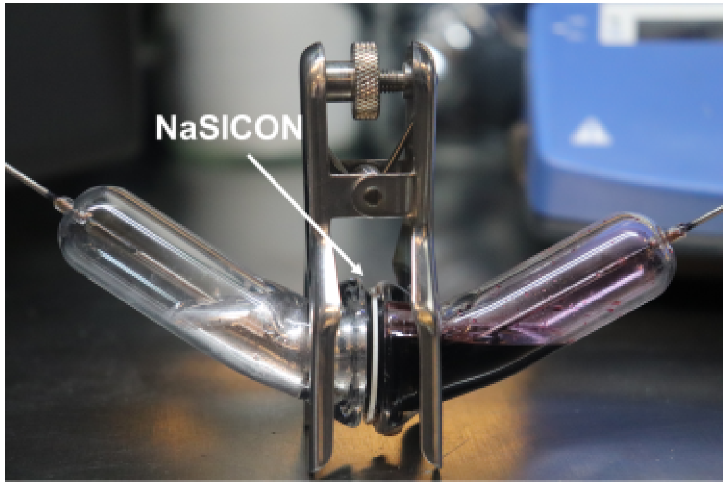
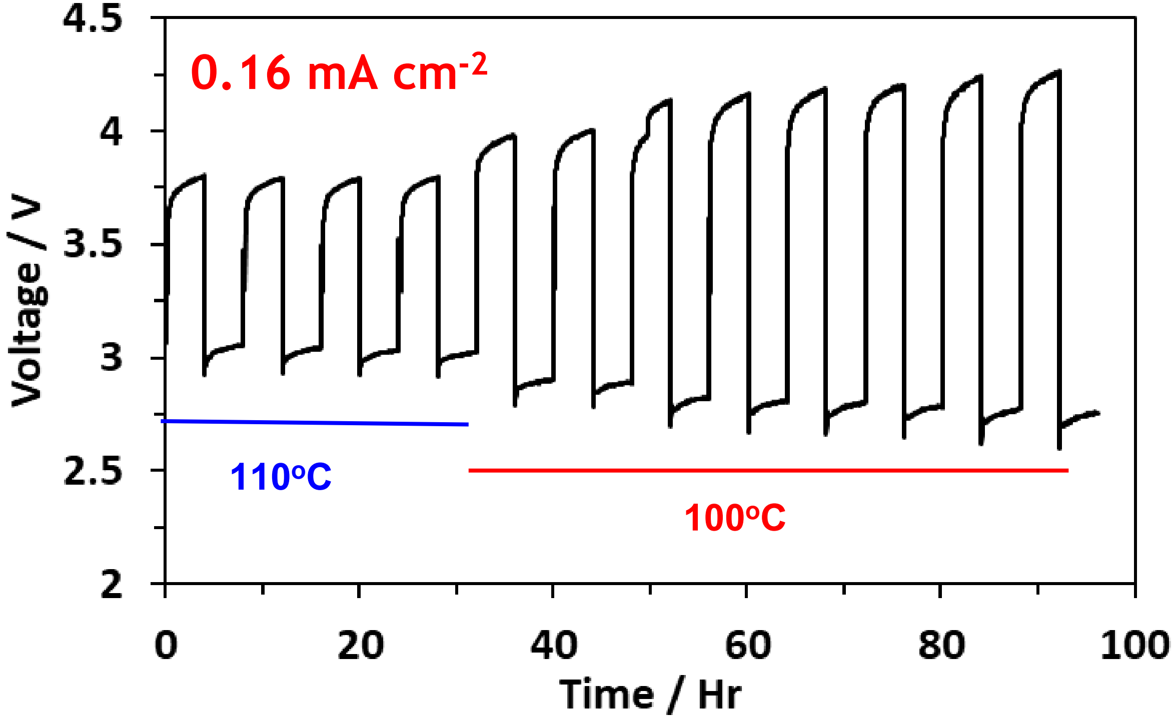


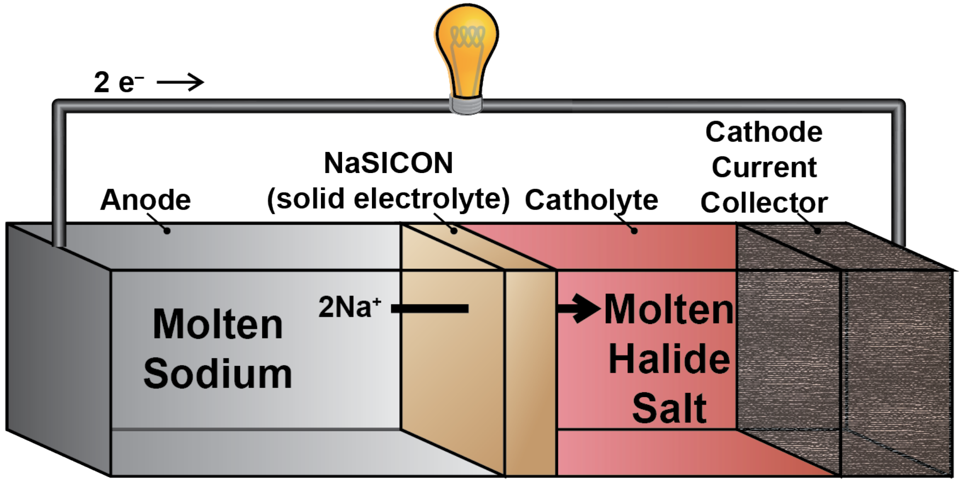
Molten Na Battery Cell Set-Up

Catholyte: 25 mol % NaI in $AlBr_3$ salt

NaSICON sintered at 1230°C yields >96% bulk density, acceptable phase purity, and ~10^{-3} S/cm at 25°C.

Na Wetting is a Key Interfacial Challenge to Lower Temperature Na-Battery Operation



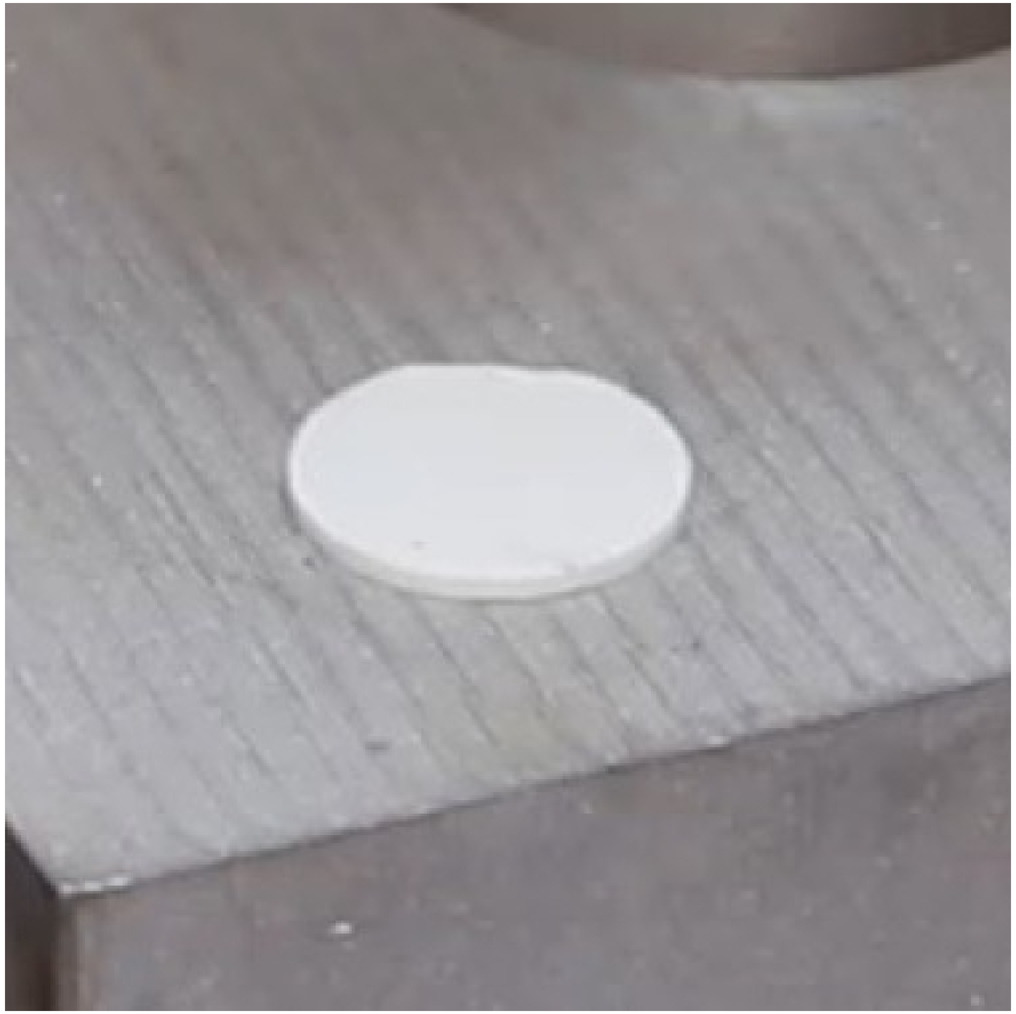


- High overpotential at low current density
  - > 1 V at 0.16 mA cm^{-2}
- Post Mortem: **Na wet poorly to NaSICON**

Data collected by Stephen J. Percival

Is the Sodium Supposed to Bounce?

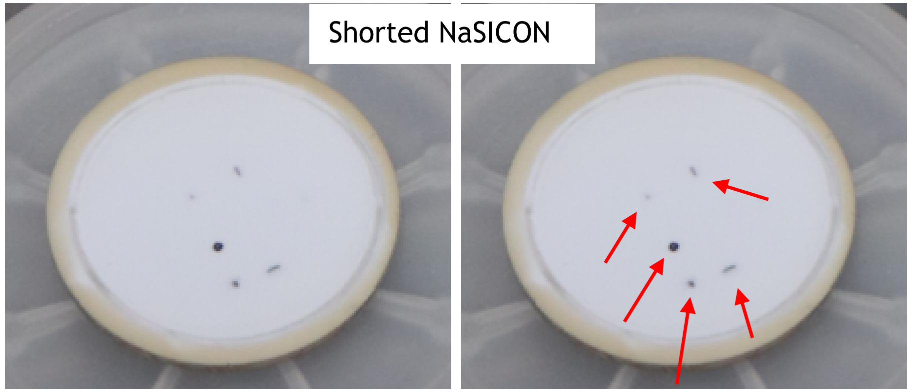
Bare NaSICON at 110°C



Improper Na-wetting of NaSICON.

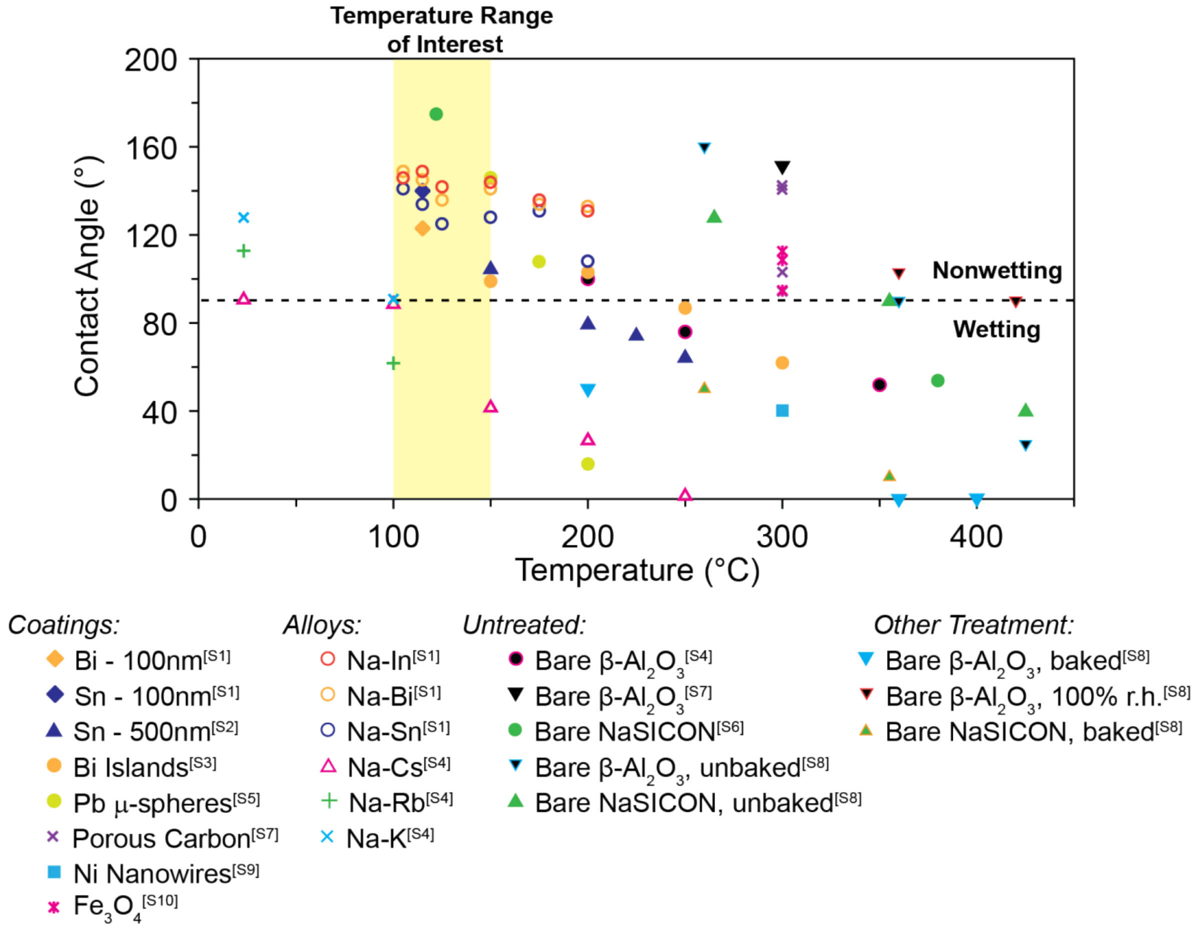
Improper wetting leads to current constriction through small active areas of NaSICON eventually forming shorts.

Red arrows pointing to shorts



Martha Gross, Stephen Percival

What About an Engineered Coating?



All previous work performed on β”-Al_2O_3 (100 - 150 °C)

- **Limited research in the temperature range of interest**
- **Previous work at low temperatures entirely on β”-Al_2O_3**
- **Sn shows promise as a coating material**
  - Alloys with Na
  - High Na^+ conductivity based on Na^+-ion anode work
- Sn is sparingly soluble in Na
- Solubility: ~ 6.7 x 10^{-3} wt% at 110 °C

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

The Amazing, Sticking Sodium...

Surface Temperature: 110°C

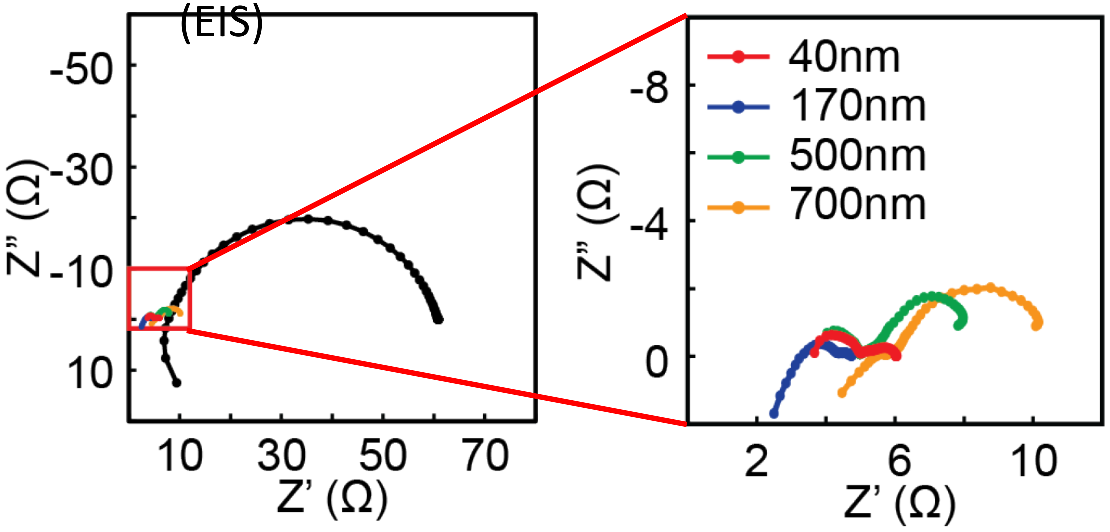
Sn-coated NaSICON

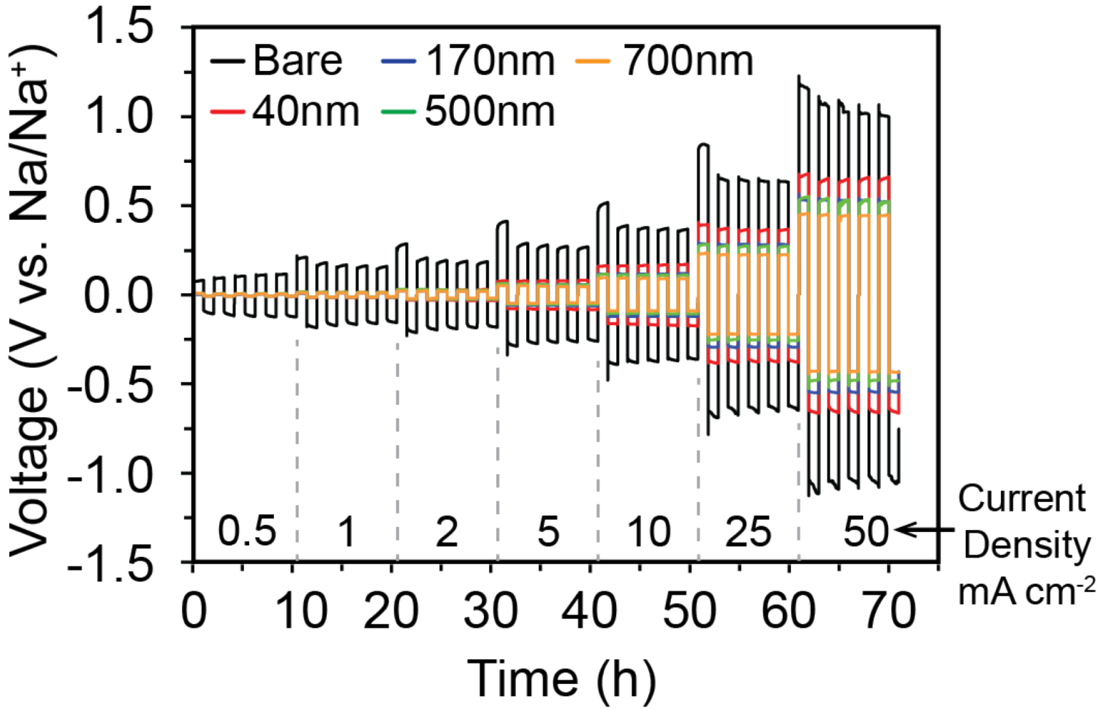
Sn-coated NaSICON

The Sn-based coating clearly enhances the adhesive interface between sodium and NaSICON.

Sn Coating Dramatically Reduces Charge Transfer Resistance and Cell Overpotential

Electrochemical Impedance Spectroscopy (EIS)



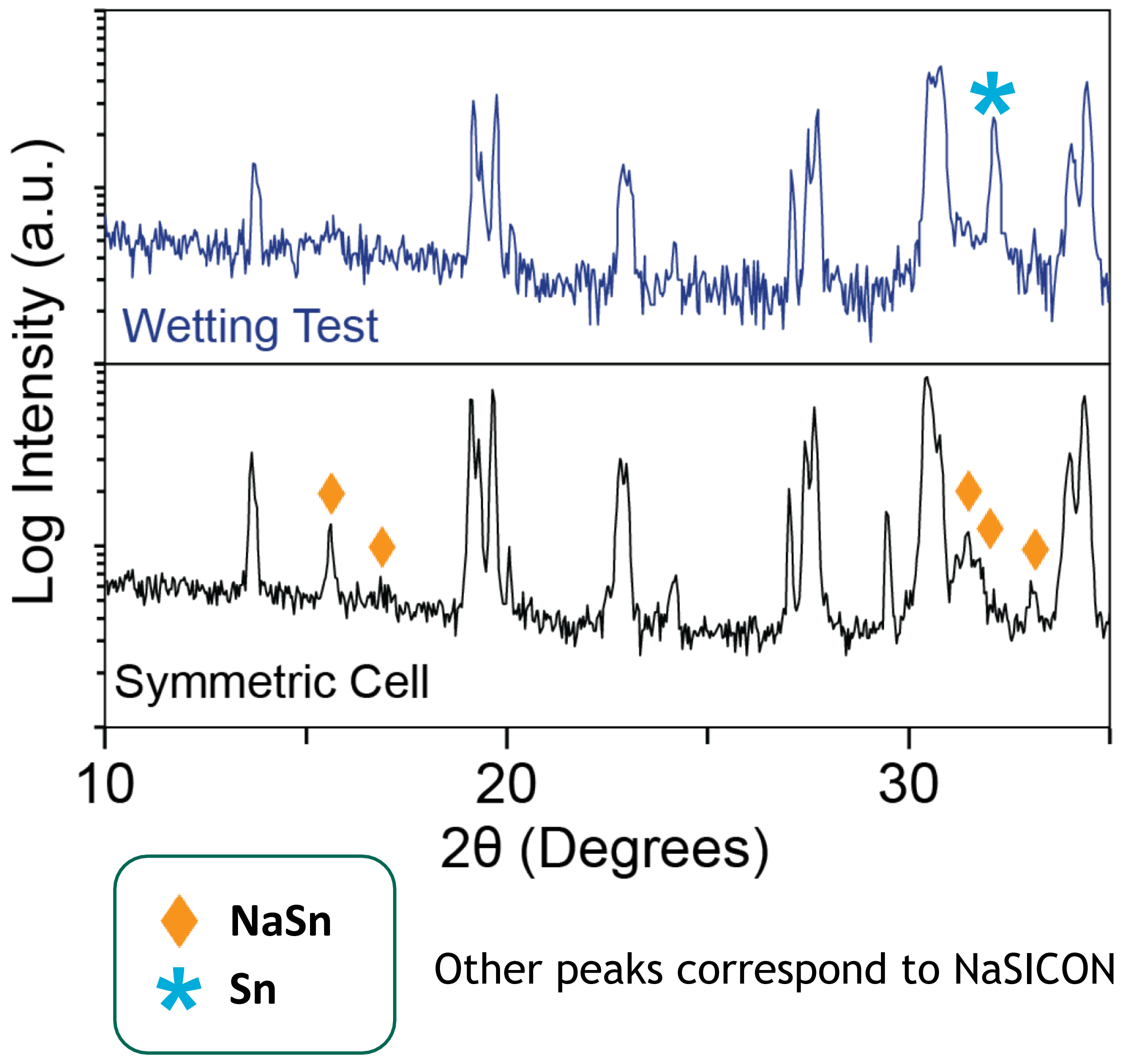


- Dramatically reduced electrochemical impedance indicates a much less resistive interface.
- Cells with Sn-coated NaSICON demonstrated lower overpotential at all current densities, regardless of Sn coating thickness
- **Sn coatings > t_{crit} performed better than coatings < t_{crit}**
  - **Contradicts results expected from contact angle testing**

Nearly 3X Reduction in Overpotential at 10x Current Density of Li-ion Batteries

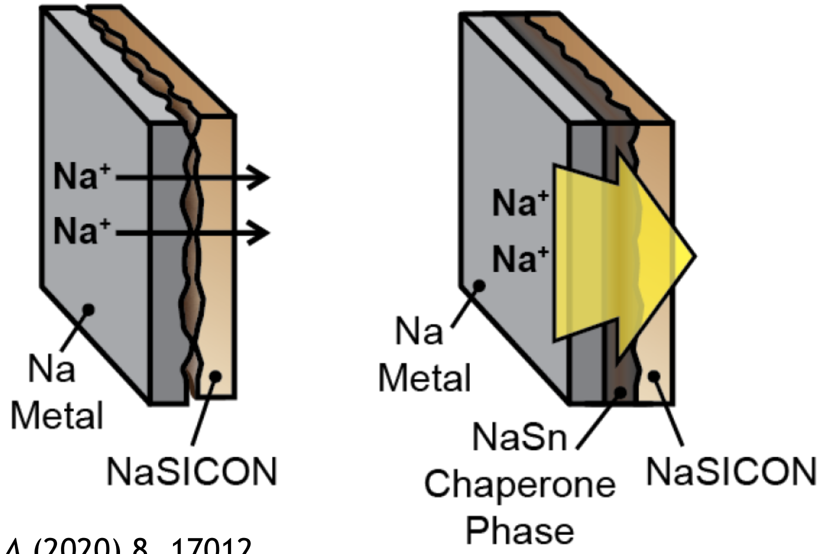
M.M. Gross, L.J. Small, A.S. Peretti, S.J. Percival, M.A. Rodriguez, E.D. Spoerke, *J. Mater. Chem. A* (2020) 8, 17012

During Cycling a Na^+-Conducting NaSn "Chaperone Phase" Forms



Other peaks correspond to NaSICON

- XRD analysis of uncycled & cycled Sn-coated NaSICON
- Intermetallic NaSn phase identified in cycled samples
  - Not identified in samples from static contact angle measurements
- **Na^+-ion conducting NaSn "chaperone phase" formed during cycling produces enhanced battery performance**



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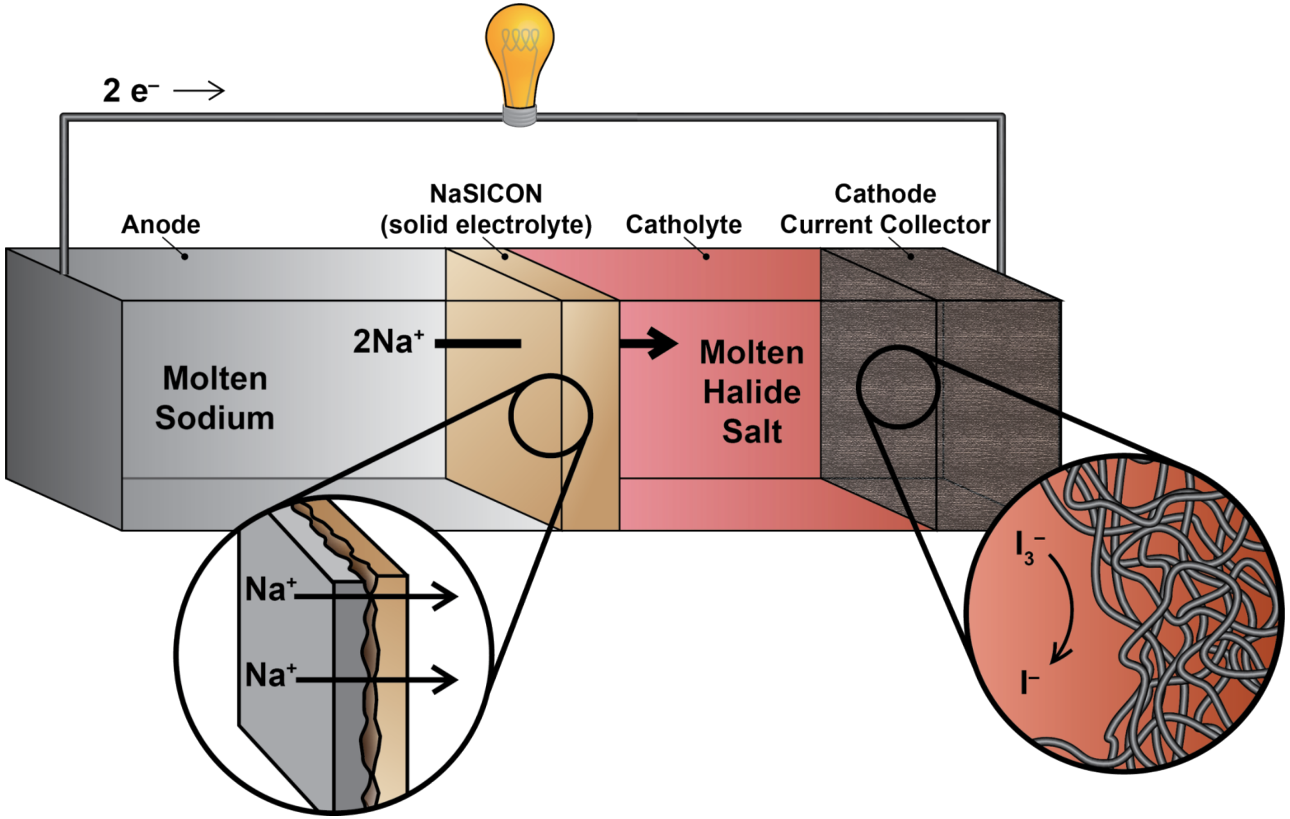

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Small and Spoerke, *et al*. "Next Generation Molten NaI Batteries for Grid Scale Energy Storage." (2017) *J. Power Sources*. **360.** 569-574.

Battery Safety: Evaluating Potential Hazards of "Failed" Na-NaI Batteries

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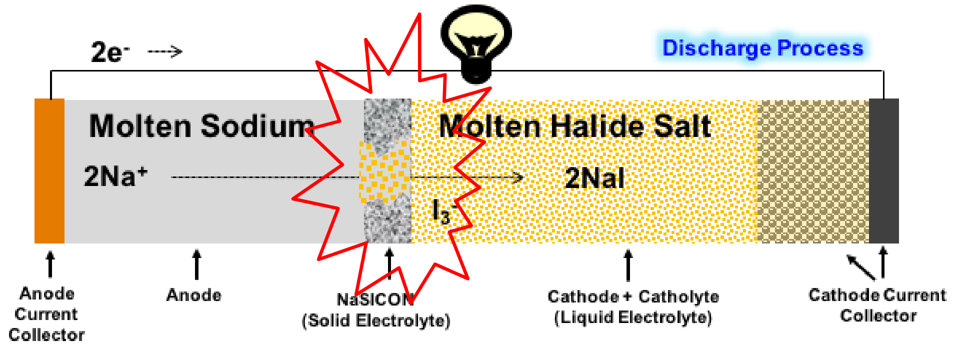
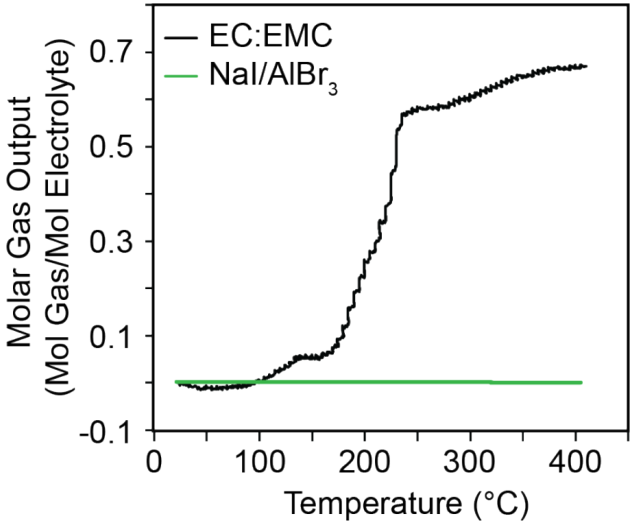


Simulating separator failure, metallic Na and NaI/AlX_3 were combined and heated.

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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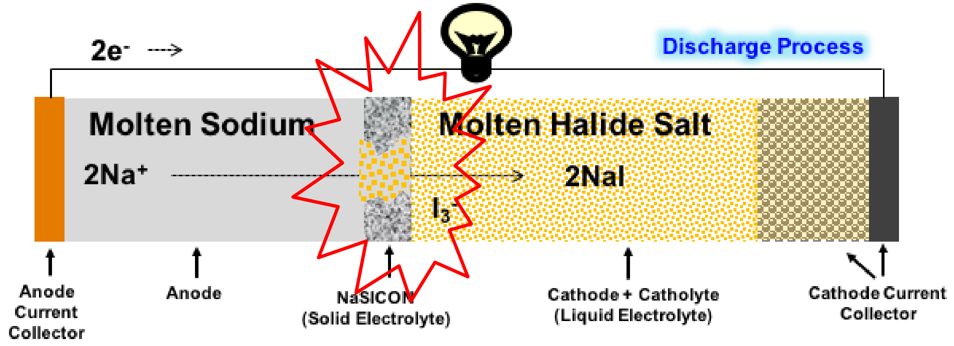

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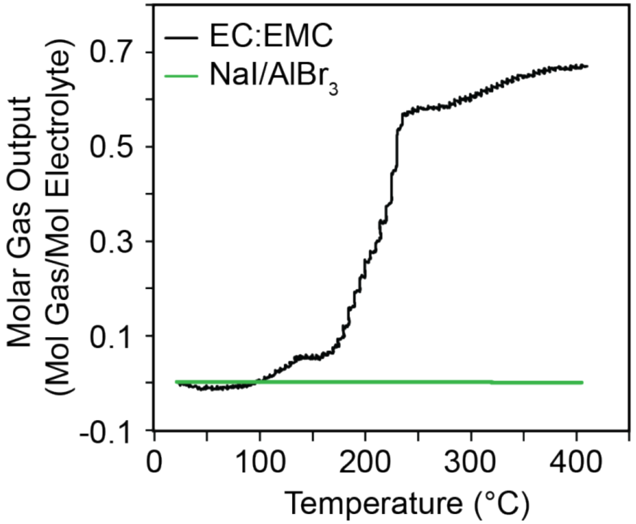
Byproducts of reaction are **aluminum metal and harmless sodium halide salts**.



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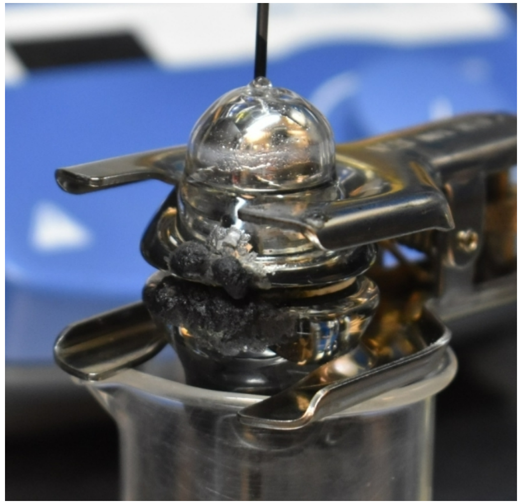
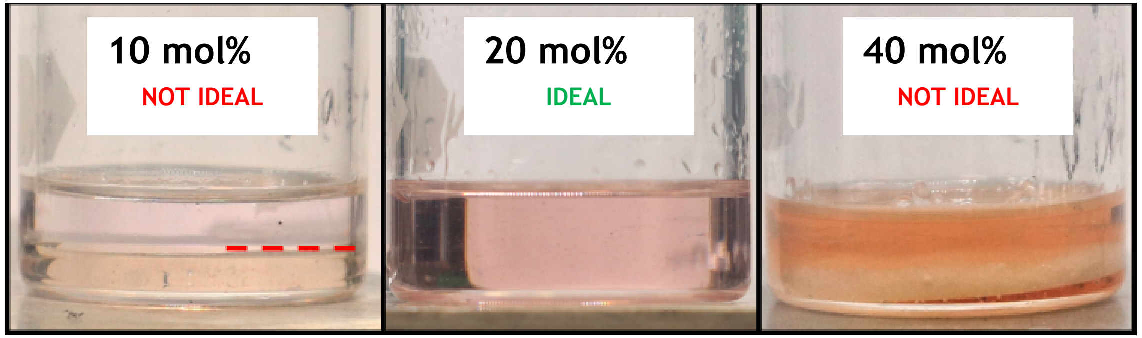


Failed separator led to termination of battery, but no significant hazardous conditions.

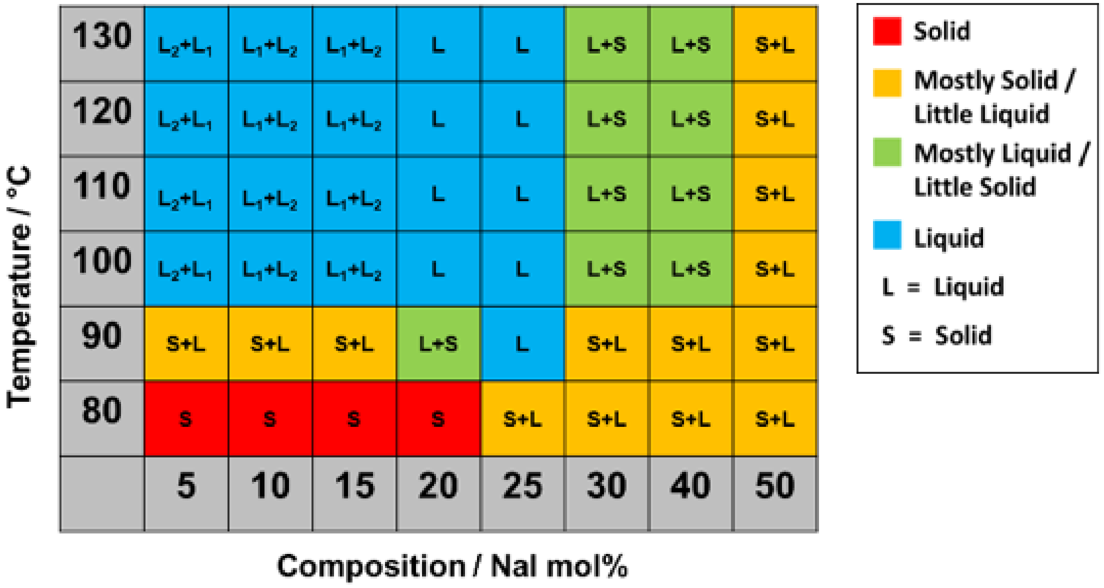
Catholyte Development: Phase Behavior

Effective catholytes must provide a combination of physical and electrochemical properties.

Salts at 100 °C



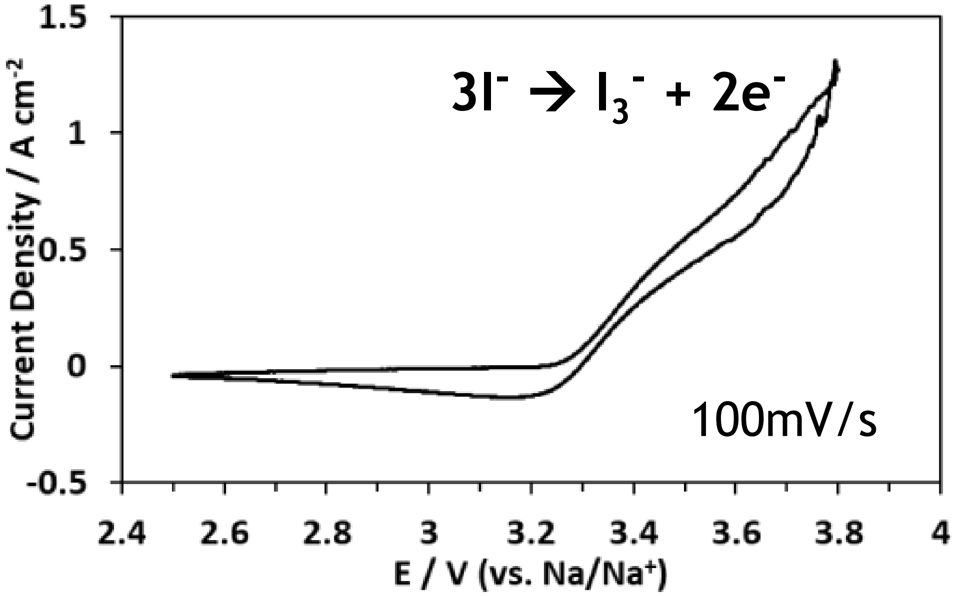
NaI-$AlBr_3$ salts



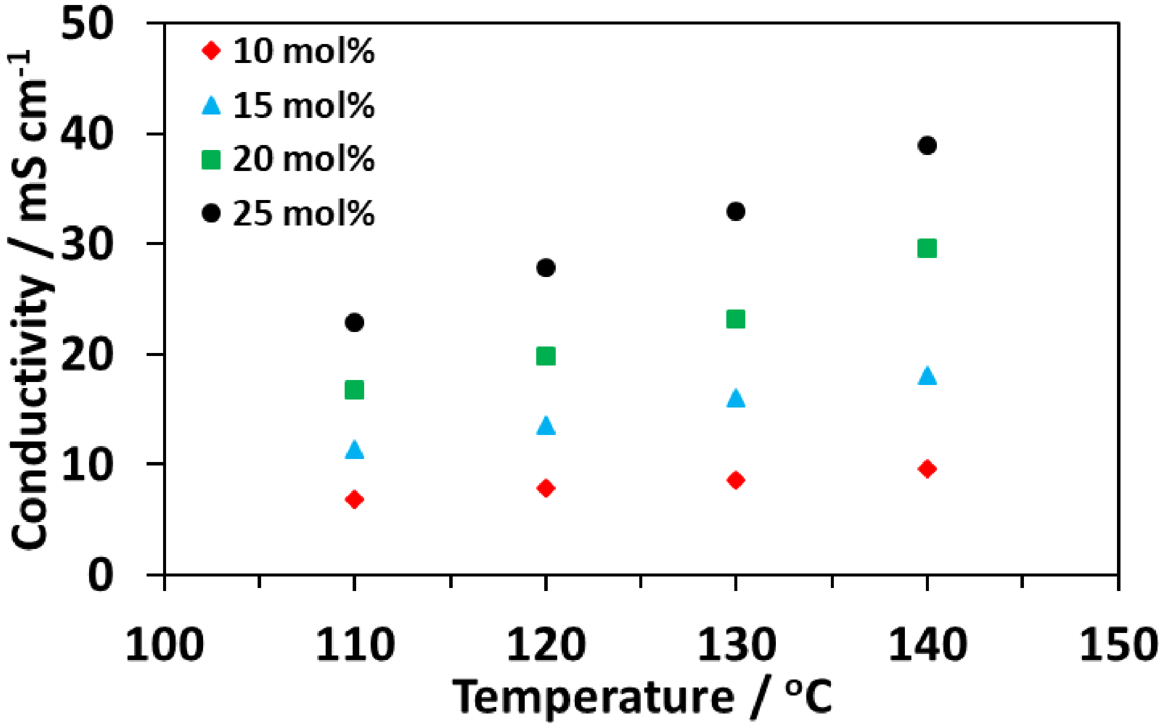
- Presence of solids will hinder reactant diffusion
- Lower NaI compositions show 2 immiscible liquid phases (red dashed line) – may be detrimental
- Composition range identified where catholyte is fully molten from phase diagram

Catholyte Development: Electrochemical Properties

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



Ionic conductivity increases with increasing NaI composition and temperature

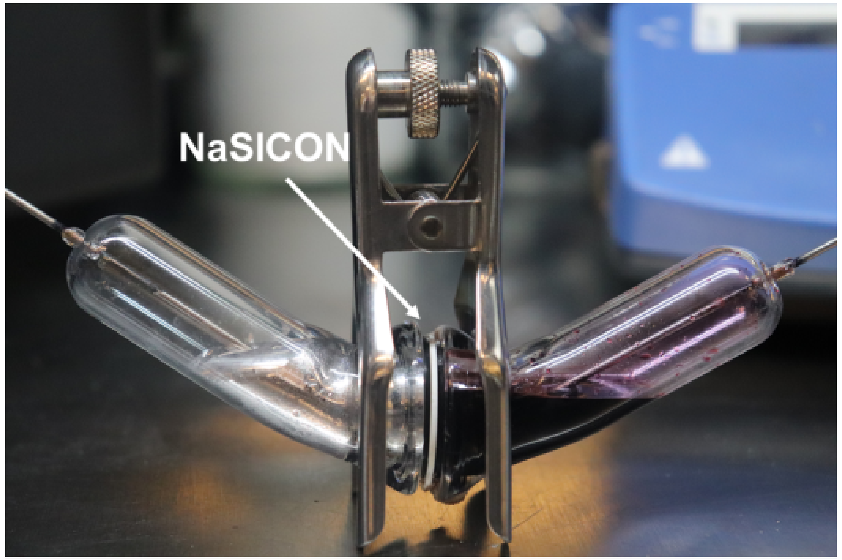


Conductivity on par with solid ceramic electrolyte, NaSICON, at 110 °C

<u>**Ionic conductivity is not believed to be a limiting factor**</u>

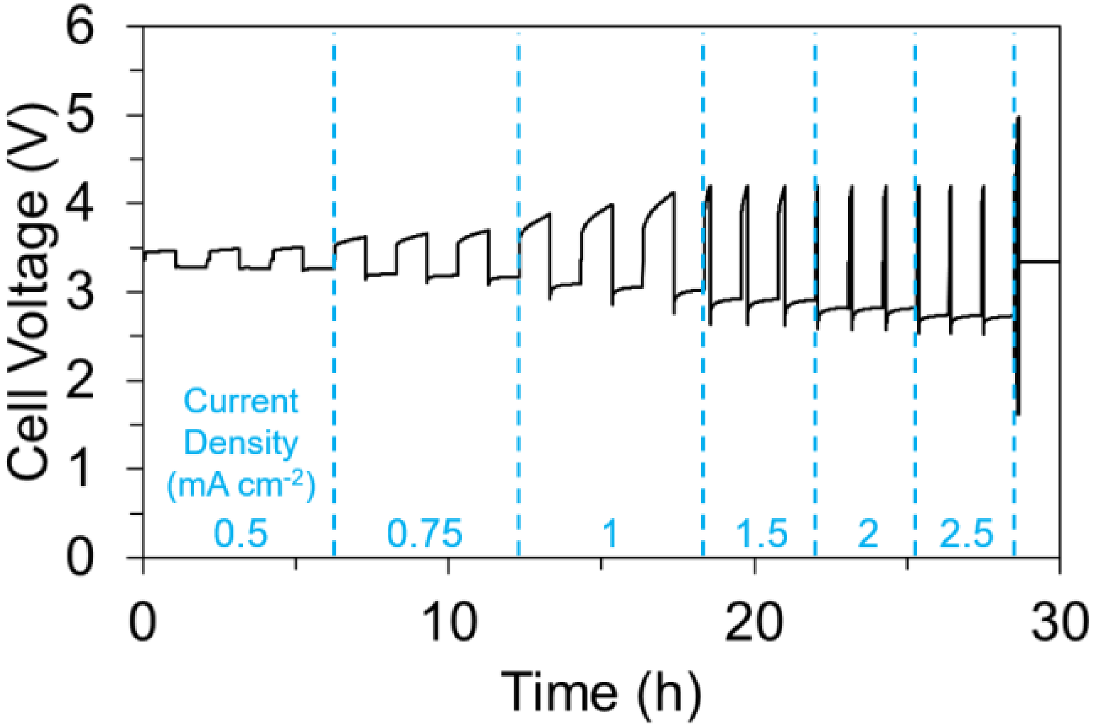
Evaluating Catholyte Performance in a Battery

Assembled cells show promisingly high voltages and first ever cycling at 110°C!



Molten Na Battery Cell Set-Up

Catholyte: 25 mol % NaI in $AlBr_3$ salt



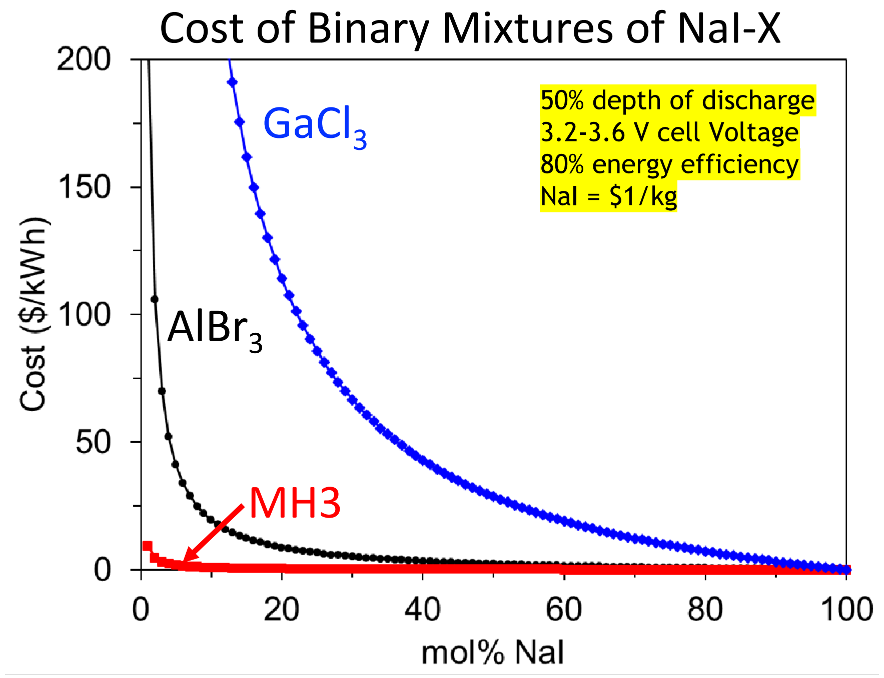
As the current densities increase, however, they fail rapidly.

M.M. Gross, E.D. Spoerke, et al. "Low Temperature Molten Sodium Batteries." (2020) *ACS Appl. Energy Mater.* **3** (11), 11456-11462.

Not All Low Temperature Catholytes are the Same

NaI-MH2 catholyte shows great performance, but ***MH2 is very expensive (>$100/kg)***.

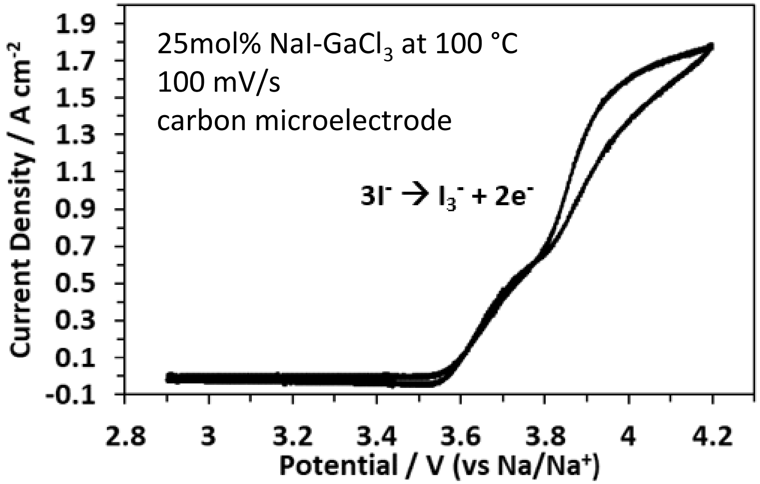
We evaluated costs across a large phase space of binary and ternary MH-NaI salt combinations to identify underlying cost trends, with goal of <$20/kWh for catholyte materials costs.

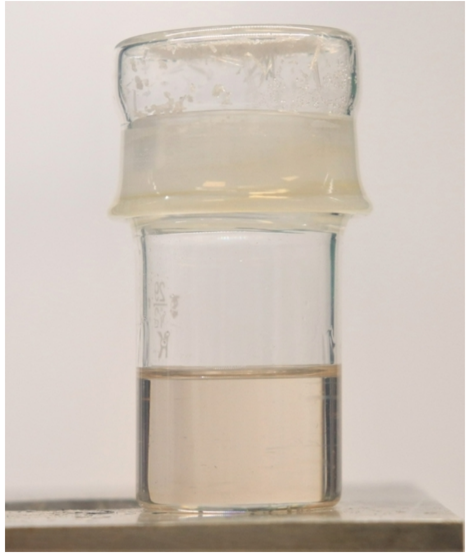


Not All Low Temperature Catholytes are the Same

New low temperature molten salt system NaI-$GaCl_3$ 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

NaI-$GaCl_3$ "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

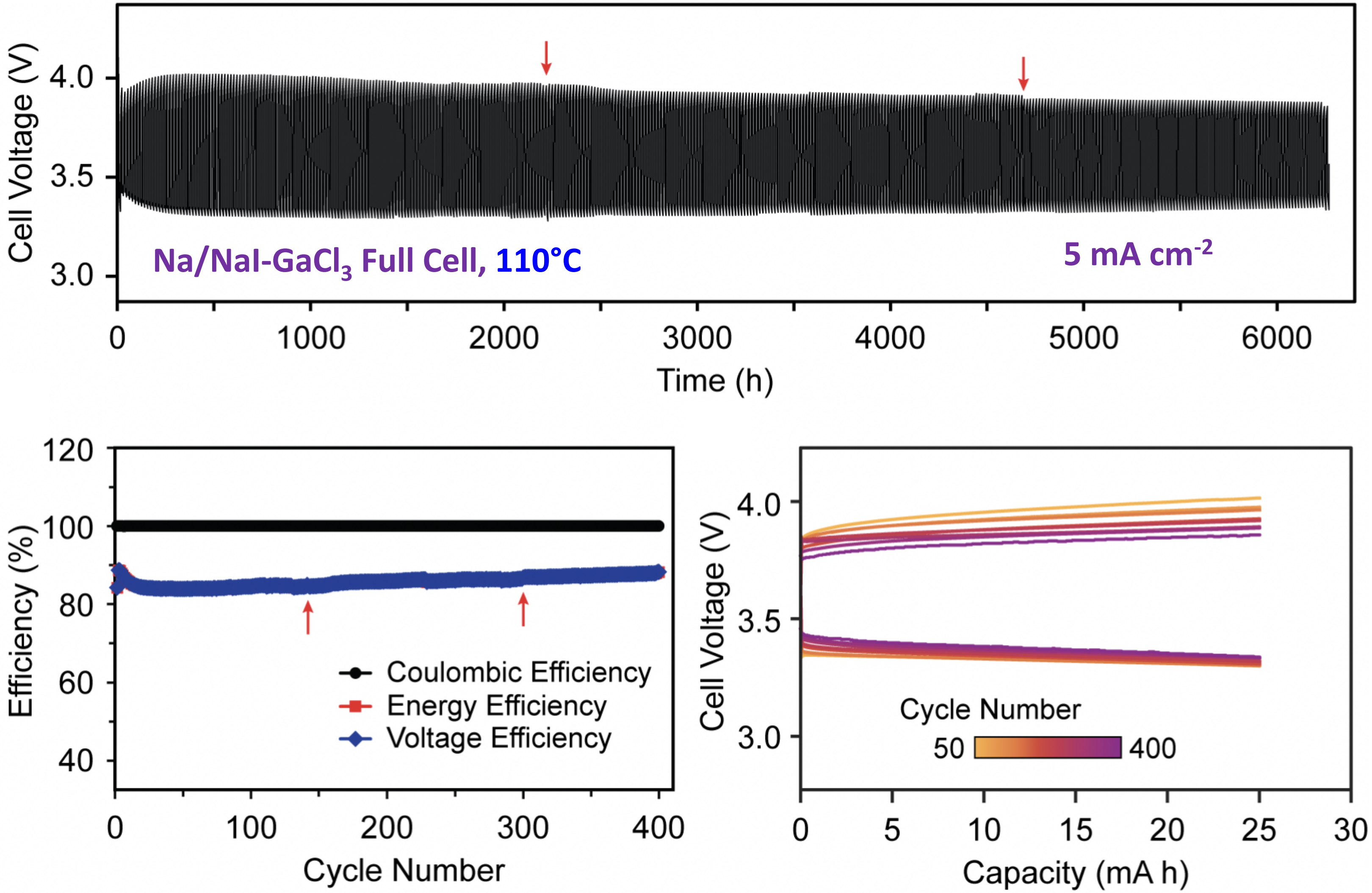
Composition (mol% NaI)

Ljsmall@sandia.gov

Sn Coating on NaSICON Enables Long Battery Lifetime!

With modified $GaCl_3$-based salt catholyte, cells exhibit:

- Excellent, stable cycling for over 8 months!
- High voltage (3.6V)!
- Resilience to “freezing” (relevant to long-duration applications)



M.M. Gross, et al. “A High Voltage, Low Temperature Molten Sodium Battery Enabled by Molten Halide Catholyte Chemistry.” (2021) *Cell Rep. Phys. Sci*. **2** (7), 100489.

Take Home Messages

- Reducing the operating temperature of molten sodium batteries promises cost-effective, reliable, safe storage technology.
- But…this change requires engineering and materials advances across the battery!
  - Separator Development
  - Interfacial Engineering
  - Catholyte Innovation
  - Battery Testing and Optimization

Continued advances in component optimization and scalable production of systems will make low-temperature molten sodium batteries potentially valuable tools to meet emerging grid-scale and long-duration energy storage needs.

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's Office of Electricity.

Contact: Erik Spoerke (edspoer@sandia.gov)

Thanks to those who actually did this work!

- Dr. Martha Gross
- Dr. Leo Small
- Amanda Peretti
- Dr. Stephen Percival
- Dr. Mark Rodriguez
- Sara Dickens
- Luis Jauregui
- Dr. Babu Chalamala