Low Temperature Molten Sodium Batteries

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PRESENTED BY
Erik Spoerke
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Adam Maraschky, Melissa Meyerson, Stephen Percival, Amanda Peretti, Martha Gross, Ryan C. Hill, Y.-T. Cheng, Leo Small*
Our Team

**Sandia**
Adam Maraschky
Melissa Meyerson
Stephen Percival
Amanda Peretti
Martha Gross
Erik Spoerke
Leo Small*

**University of Kentucky**
Prof. Y.T. Cheng
Ryan Hill

Please See Posters:

**Adam Maraschky**
*Experimental and Modeling Studies of Metal Halide Catholyte and Cathode Materials to Enable Low-Temperature Molten Sodium Batteries*

**Ryan Hill**
*Sodium Penetration through Solid State NaSICON Electrolytes under High Current*

**Stephen Percival**
*Al-Fe Based Molten Salts for Long Duration Energy Storage*
Program Objective and Approach

We aim to develop enabling technologies for safe, low cost, molten sodium batteries

Sodium batteries are attractive for resilient, reliable grid scale energy storage and are one of three key thrust areas in the OE Energy Storage materials portfolio.

- Utilize naturally abundant, energy-dense materials (Na, Al, Si)
- Minimize dendrite problems: molten sodium
- Prevent crossover due to NaSICON solid state separator
- Leverage inorganics to limit reactivity upon mechanical failure
- Enable applications for long duration energy storage

Anode: \[ \text{Na} \rightarrow \text{Na}^+ + e^- \]
Cathode: \[ \text{I}_3^- + 2e^- \rightarrow 3\text{I}^- \]

\[ E^0_{\text{cell}} = 3.24 \text{ V} \]
Why Low Temperature?

Typical molten sodium batteries operate near 300 °C (Na-S and ZEBRA). We are driving down battery operating temperature to near sodium’s melting point (98 °C) via innovative, low-temperature molten salt catholyte systems. This change enables:

• **Lower Cost**
  • Plastic seals: below 150 °C, rubber o-rings can be used (<$0.1/each) vs. glass or metal seals.
  • Thinner and less expensive wiring materials
  • Less insulation

• **Reliability**
  • Lower temperatures → slower aging on all system components
  • System level heat management not as extensive
  • Compatibility with higher voltage (>3V) chemistries (e.g., Na-Nal versus Na-NiCl₂)

However, battery chemistries from higher temperatures will not work at low temperatures; they need to be reengineered.

While low temperature (~100 °C) can improve cost and reliability, significant materials challenges arise.
Targeting Catholyte Materials to Control Costs

- We are targeting a low cost, NaI-metal halide catholyte.
- Last year, we demonstrated it was possible to cycle a NaI-AlCl₃ catholyte at 110 °C, using lessons learned previously from GaCl₃ and AlBr₃-based systems.¹⁻⁴
- Sn-coated NaSICON enables stable anode performance
- Phase control/precipitation of solid species
- However, initial tests at 110 °C with low-cost NaI-AlCl₃ were limited
  - 5 mA cm⁻²
  - 30% theoretical energy density (130 Wh L⁻¹)
  - unstable performance over long times

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Targeting Catholyte Materials to Control Costs

We are targeting a low cost, NaI-metal halide catholyte.

Goals this year (FY22):

• Understand Catholyte-Current Collector Interfaces
• Understand NaSICON-Catholyte Interfaces
• Demonstrate Stable Cycling (over months)
• Increase Current Density
• Increase Accessible Energy Density

Optimizing (Cathode) Current Collector Material

- Identified several candidate current collector materials – Mo, Ta, W, glassy carbon (GC), and graphite felt (GFD)
- Evaluated as idealized discs and more realistic high surface area materials in a 3-electrode cell
  - Ta passivated and was not reproducible
  - Mo showed best discharge performance, while glassy carbon (GC) exhibited best charge performance.
- (For more details, please see Poster: “Experimental and Modeling Studies of Metal Halide Catholyte and Cathode Materials to Enable Low-Temperature Molten Sodium Batteries”

Mo shows best discharge, while GC shows best charging performance. *High available surface area* overcomes small differences in electrocatalytic activity.
Na⁺ “Blockade” Identified at the NaSICON-Catholyte Interface

**Observed Problem:** Steady increase in battery overpotentials observed during cycling.

**Approach to Solution:** Custom 3-electrode cell developed to *isolate individual interfaces* present in a sodium battery.

**Discovery:** Increase in impedance identified at the NaSICON-catholyte interface

Extensive materials characterization of the NaSICON material and salt-exposed surface (XRD, SEM, EDS, XPS) revealed no significant changes, except for a decrease in Na⁺ content at the near surface (<10 nm).

“Blockade” Lifted by Controlling Salt Speciation

- Using Raman spectroscopy, Lewis acidic dimeric species, such as $\text{Al}_2\text{Cl}_6\text{I}^-$, were identified in 45 mol% NaI-AlCl$_3$.
- Lewis acidic dimeric species were not observed under Lewis basic conditions (>50 mol% NaI).

![Raman Spectroscopy of NaI-AlCl$_3$ Catholytes](image)

“Blockade” Lifted by Controlling Salt Speciation

- Using Raman spectroscopy, Lewis acidic dimeric species, such as Al$_2$Cl$_6$I$^-$, were identified in 45 mol% NaI-AlCl$_3$.
- Lewis acidic dimeric species were not observed under Lewis basic conditions (>50 mol% NaI).
- Shifting to Lewis basic catholytes (>50mol% NaI) eliminated acidic dimeric species, stabilizing the NaSICON-catholyte interface and, in turn, battery performance.

Raman Spectroscopy of NaI-AlCl$_3$ Catholytes

Eliminate acidic dimeric salt species.

Stabilize battery performance.

Battery Cycling Profiles

Stable Cycling Performance Over 5 Months

Combining a Lewis basic molten salt catholyte with a high surface area graphite felt current collector yielded stable batteries cycling over >5 months at 110 °C.

- 3.1 V nominal voltage (50% SOC)
- 22% depth of discharge, 2.5 mA cm⁻²
- >93% energy efficiency
- polymer seals

Low cost, Lewis basic NaI-AlCl₃ catholyte successfully cycled at 110 °C for >5 months.
Higher Currents: Charging up to 50 mA cm\(^{-2}\) at 110 °C

- Cycling up to 25 mA cm\(^{-2}\) and charging up to 50 mA cm\(^{-2}\) are readily achieved.
- Cell impedance needs to be optimized to increase energy efficiency >80% at high current.

![Graph showing cell voltage and energy efficiency vs. capacity and current density.](image)

Charging currents up to 50 mA cm\(^{-2}\) were achieved at 110 °C.
Slightly Higher Temperature Enables Even Higher Currents

- Increasing temperature from 110 to 135 °C decreased cell impedance and increased rate capabilities.
- Further optimization needed to enable higher currents at >80% energy efficiency.
- In other tests, up to 47.5% theoretical capacity achieved at 50 mA cm\(^{-2}\) charging.

Charging currents of 100 mA cm\(^{-2}\) achieved at 135 °C.

*We are approaching performance levels of higher temperature, commercialized ZEBRA batteries!*
As we push to 100 mA cm\(^{-2}\) and beyond, Na-induced NaSICON failure is of concern at low temperature (110 °C).

- We are working to understand, prevent, and non-destructively detect these failure mechanisms in symmetric Na-NaSICON-Na cells.

At high currents and low temperatures, interfacial engineering, such as our Sn coating, plays a key role in controlling Na-induced failure of NaSICON.

See poster by Ryan Hill for more details!
We are targeting a low cost, NaI-metal halide catholyte.

Goals this year (FY22):

• Understand Catholyte-Current Collector Interfaces
  ✓ Determined value of current collector *composition and structure* on battery performance.

• Understand NaSICON-Catholyte Interfaces
  ✓ Developed new electrochemical tool to characterize interfaces *in-situ*.
  ✓ Identified a Na⁺ “blockade” at the NaSICON-catholyte interface caused by salt species present only in Lewis-acidic catholytes.
  ✓ Resolved this blockade through understanding of catholyte chemistry.

• Demonstrate Stable Cycling (over months)
  ✓ Enabled stable battery performance > 5 months at 110°C.

• Increase Current Density
  ✓ Increased battery charging current densities 20X, from 5 to 100 mA cm⁻²

• Increase Accessible Energy Density
  ✓ Doubled accessible energy density from 130 to 254 Wh L⁻¹
Next year we will increase current density on discharge, targeting >80% energy efficiency at even higher energy densities. We will achieve this by:

- further improving ion-transport across the NaSICON-catholyte interface
- integrating cathode current collector materials to minimize overpotentials on discharge
- further understanding salt speciation under varying states of charge

In addition, we will work toward commercially-important materials optimization:

- long-duration seals
- improved NaSICON performance/stability/manufacturability
- larger-format cells
Accomplishments – Publications and Patents

Publications


Patents


Awards and Symposium Chairs

- L.J. Small was recognized for “Excellence in Review” by the American Chemical Society’s journal Industrial and Engineering Chemistry (I&EC).

- L.J. Small was named an “Outstanding Reviewer” for the 5th year in a row by the Royal Society of Chemistry’s journal *RSC Advances*.

- S.J. Percival was nominated for the Sandia Postdoc Development Distinguished Mentorship Award.


Accomplishments – Presentations

Invited Presentations


Contributed Presentations

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Questions?

Erik Spoerke
edsSpoer@sandia.gov

Leo Small
ljsmall@sandia.gov
• Identified several candidate current collector materials – Mo, Ta, W, glassy carbon (GC), and graphite felt (GFD)
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