Low Temperature Molten Sodium Batteries

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PRESENTED BY
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Team

**Sandia**
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- Stephen Percival
- Amanda Peretti
- Leo Small
- Erik Spoerke

**University of Kentucky**
- Prof. Y.T. Cheng – *Presenting Next!*
- Ryan Hill

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**See Posters:**

**Martha Gross**
*Low-Temperature Molten Sodium Batteries*

**Ryan Hill**
*Mechanical, Microstructural, and Electrochemical Characterization of NaSICON Sodium Ion Conductors*
Program Objective

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
Na → Na⁺ + e⁻ 
E⁰_{cell} = 3.24 V

Cathode
I₃⁻ + 2e⁻ → 3I⁻
Why Low Temperature?

Typical molten sodium batteries operate near 300 °C (Na-S) and 200 °C (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 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

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.
Recent Accomplishments

Integrated high-voltage NaI-GaCl$_3$ catholyte into molten sodium batteries at 110 °C

- Ran >400 cycles (>8 months) at 5 mA cm$^{-2}$ (25% DoD) for 85.3% energy efficiency
- Successfully accessed all I$^-$/I$_3^-$ capacity (100% DoD) at 3.5 mA cm$^{-2}$
- Cycled currents as high as 30 mA cm$^{-2}$
- Nominal voltage of 3.62 V is 40% higher than standard ZEBRA chemistry

Cycled molten sodium battery with NaI-GaCl$_3$ catholyte at 110 °C for >8 months with >85% energy efficiency at 40% increase in cell voltage vs. ZEBRA.

https://www.sandia.gov/labnews/2021/08/02/better-batteries-for-grid-scale-energy-storage/
Catholyte Materials Control Costs

- NaI-GaCl$_3$ catholyte shows great performance, but $\text{GaCl}_3$ is expensive (>\$100 kg$^{-1}$).
- After evaluating costs across many binary and ternary NaI-MX$_3$ combinations, we decided to reinvestigate NaI-AlCl$_3$, a chemistry we used at higher temperatures in 2016.

Despite its great performance, NaI-GaCl$_3$ is too expensive! Reinvestigate NaI-AlCl$_3$, with materials cost <$1$ kWh$^{-1}$. 

Reinvented NaI-AlCl₃ to Cycle at 110 °C

NaI-AlCl₃ molten salts were integrated into molten sodium batteries at 110 °C, using lessons learned since our last attempts in 2016.

- Applied Sn coating to decrease Na-NaSICON interfacial resistance¹
- Controlled molten salt composition and conditioning to limit precipitation²³
- Cycled 5-35% SOC at 5 mA cm⁻² for 70% energy efficiency
- **Targeted 130 Wh/L usable capacity, <$1/kWh (materials)**

**But we want more…**

- The theoretical energy density of 45 mol% NaI-AlCl₃ is >430 Wh/L, phase limitations restrict capacity to 30% to maintain electrolyte.
- Limited to 5-10 mA cm⁻², why?

Low-cost NaI-AlCl₃ catholyte successfully cycled at 110 °C, but we want more power!

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Modeling NaI-MX₃ Speciation Reveals Kinetic Limitations

We coupled microelectrode studies with electrochemical simulations to understand the differences between NaI-AlCl₃, NaI-AlBr₃, and NaI-GaCl₃.

- Extracted chemical and electrochemical parameters
- NaI-AlCl₃ had slowest electron transfer rates, highest currents
- Multiple species exist in the molten salt—Al₂Cl₆, Al₂Cl₆I⁻, AlCl₃I⁻, etc.
- Some species “lock up” iodide, making it unavailable for energy storage.

Iodide oxidation consists of an electrochemical step, I₂ formation,

\[ 2\text{AlCl}_3\text{I}^- \rightarrow 2\text{AlCl}_3 + \text{I}_2 + 2e^- \]

followed by a chemical step, I₃⁻ formation.

\[ \text{AlCl}_3\text{I}^- + \text{I}_2 \rightarrow \text{AlCl}_3\text{I}_3^- \]

Trace GaCl$_3$ Improves NaI-AlCl$_3$ Kinetics

We hypothesized that the chemical step was rate-limiting at high potentials.

To enhance this chemical step, we added 1 mol% GaCl$_3$ to NaI-AlCl$_3$.

- $E^0$ for AlCl$_3$I$^-$ oxidation is 3.49 V vs. Na/Na$^+$
- $E^0$ for GaCl$_3$I$^-$ oxidation is 4.00 V vs. Na/Na$^+$
- GaCl$_3$I$^-$ is more stable against electrochemical oxidation, allowing it to react with I$_2$ on the electrode and speed up this chemical step.

$$2AlCl_3I^- \rightarrow 2AlCl_3 + I_2 + 2e^-$$

$$GaCl_3I^- + I_2 \rightarrow GaCl_3I_3^-$$

Addition of 1 mol% GaCl$_3$ increases steady state current 3x, and stabilizes electrode performance at long times in 3-electrode cells.

Estimated catholyte materials cost: $1 \text{ kWh}^{-1}$

Introduction of 1 mol% GaCl$_3$ significantly enhances iodide oxidation in NaI-AlCl$_3$ by removing rate-limiting I$_2$. 
Improved Conductivity in NaSICON Separator

Increased NaSICON conductivity by optimizing composition

- Old composition: $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$
- New composition: $\text{Na}_{3+x}\text{Zr}_2\text{Si}_{2+x}\text{P}_{1-x}\text{O}_{12}$, $0 \leq x \leq 0.6$
- Increased $\text{Na}^+$ conductivity from 7.8 to 20 mS cm$^{-1}$ at 110 °C

Equates to approximately

- 20% decrease in overall battery resistance
- 3-4% increase in energy efficiency, e.g. 86→90%

Under consideration in other battery systems such as Zn-MnO$_2$ batteries in development at UEP.

2.6x increase in NaSICON $\text{Na}^+$ conductivity increases battery efficiency!
Analysis of Mechanical Properties

Working with University of Kentucky, we have explored the mechanical properties of sodium ion conducting separators.

Nanoindentation of NaSICON reveals that

- Cycling NaSICON significantly changes its modulus of elasticity.
- Localized inhomogeneities in NaSICON under high currents can increase stiffness.

Mechanical properties of NaSICON ceramics are highly dependent on their cycling history.

See poster by Ryan Hill and presentation by Prof. Y.-T. Cheng for more details!
Accomplishments – Publications and Patents

Publications


Patents


Accomplishments – Presentations


Path Forward

This past year we applied our knowledge of low temperature molten sodium battery systems to decrease sodium battery active materials cost 100x, moving from a \( \text{GaCl}_3 \) to an \( \text{AlCl}_3 \)-based catholyte.

Next year, we will focus on developments for practical applications:

**Bigger** – increase NaSICON diameter from 25 to 50 mm

**Faster** – improved current collector design and material to increase battery power output

**Stronger** – characterization of NaSICON mechanical properties vs. cycling conditions

**Longer** – long duration energy storage – How well is capacity retained over month long periods?
Acknowledgements

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Questions?

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