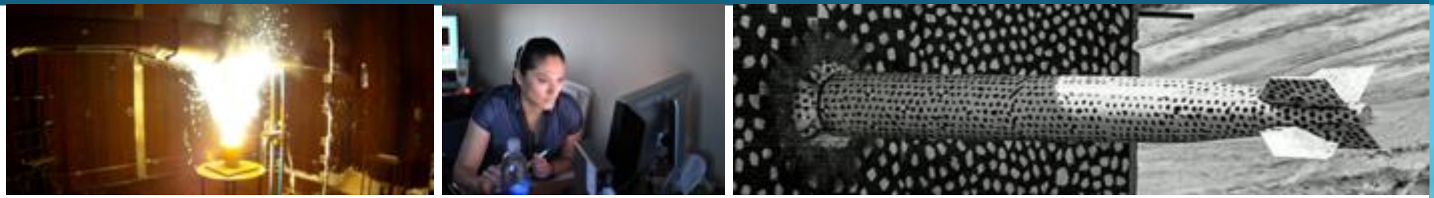
Sandia National Laboratories

Low Temperature Molten Sodium Batteries



DOE Office of Electricity

Energy Storage Program Peer Review

Oct. 26-28, 2021

PRESENTED BY

Leo Small

Martha Gross, Stephen Percival, Amanda Peretti, Rose Lee,
Adam Maraschky, Melissa Meyerson, Ryan C. Hill, Y.-T. Cheng, Erik Spoerke

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND2021-12666 C

Team

Sandia

Martha Gross

Rose Lee

Adam Maraschky

Melissa Meyerson

Stephen Percival

Amanda Peretti

Leo Small

Erik Spoerke

University of Kentucky

Prof. Y.T. Cheng – ***Presenting Next!***

Ryan Hill

See Posters:

Martha Gross

Low-Temperature Molten Sodium Batteries

Ryan Hill

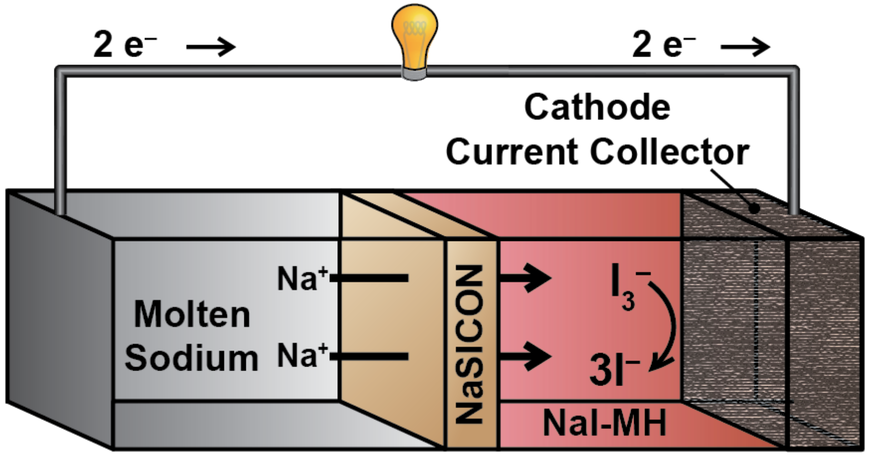
Mechanical, Microstructural, and Electrochemical Characterization of NaSICON Sodium Ion Conductors

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

$Na \rightarrow Na^{+} + e^{-}$

$E^{0}_{cell} = 3.24 V$

Cathode

$I_3^{-} + 2e^{-} \rightarrow 3I^{-}$

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

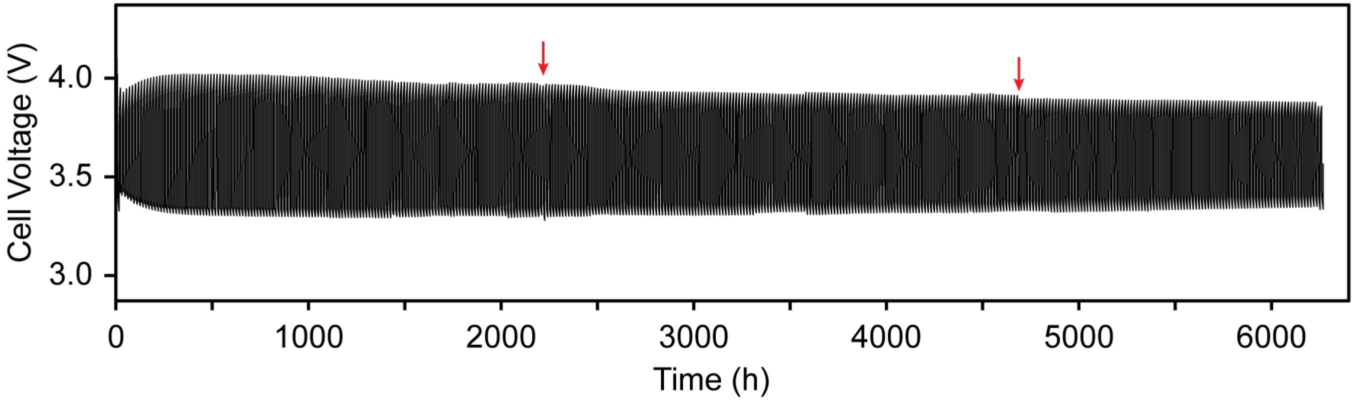
However, battery chemistries from higher temperatures will not work at low temperatures; they need to be reengineered.

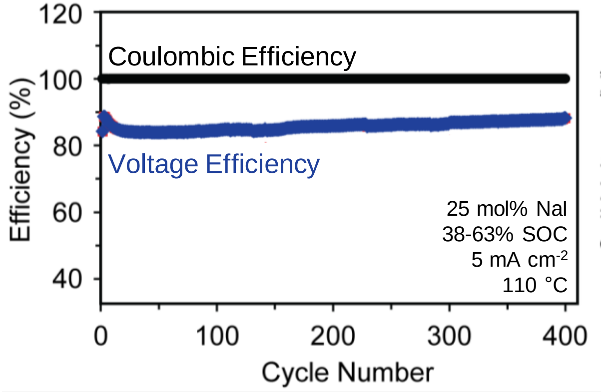
While low temperature (~100 °C) can improve cost and reliability, significant materials challenges arise.

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





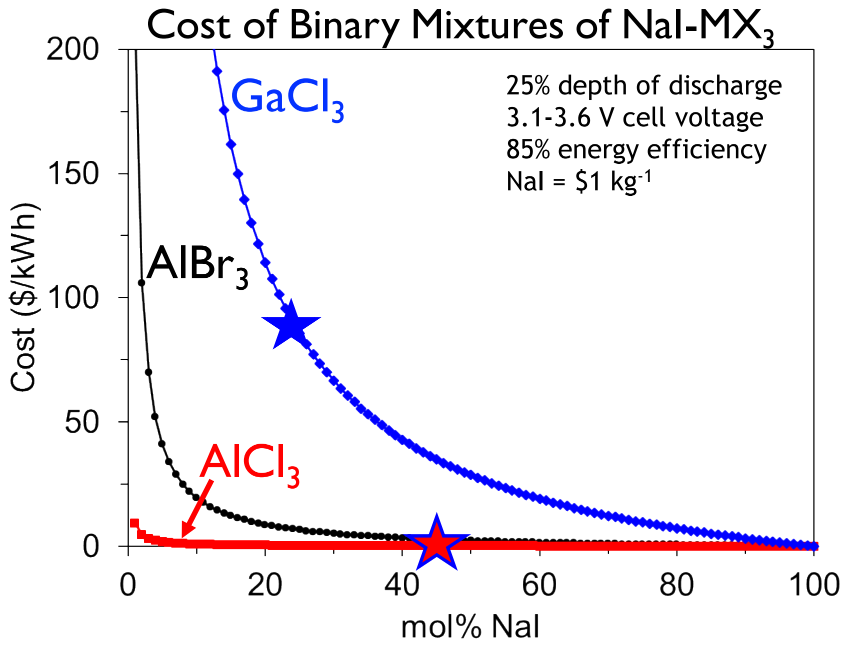
Cycled molten sodium battery with NaI-$GaCl_3$ catholyte at 110 °C for >8 months with >85% energy efficiency at 40% increase in cell voltage vs. ZEBRA.

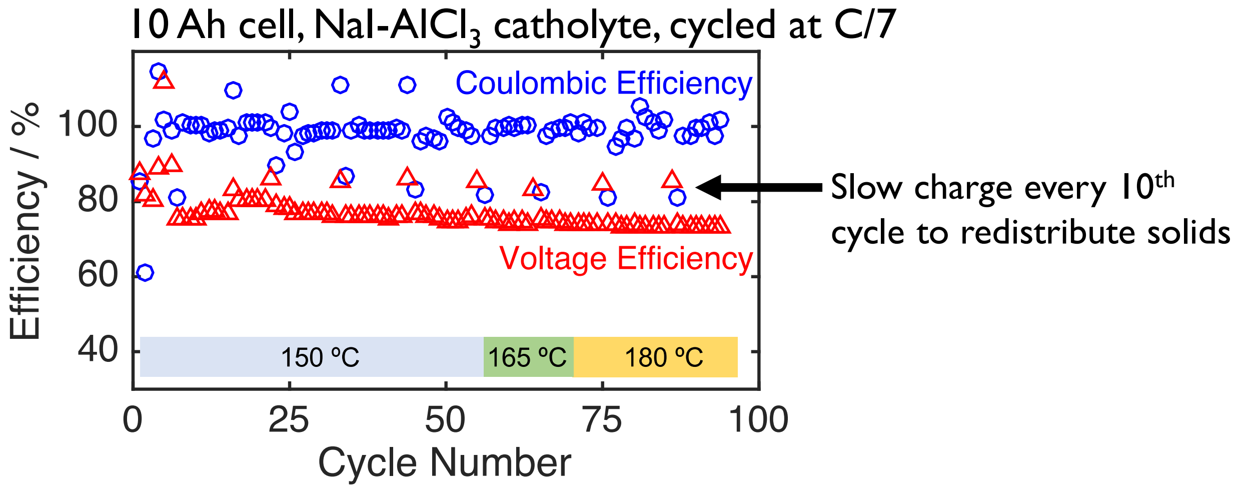
https://www.sandia.gov/labnews/2021/08/02/better-batteries-for-grid-scale-energy-storage/

M.M. Gross, S.J. Percival, R.Y. Lee, A.S. Peretti, E.D. Spoerke, and L.J. Small. *Cell Reports Physical Science* **2** (2021) 100489.

Catholyte Materials Control Costs

- NaI-$GaCl_3$ catholyte shows great performance, but ***$GaCl_3$ 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.





In 2016 we used 60 mol% NaI-$AlCl_3$ at 150-180 °C, but precipitation of solids prevented operation at lower temperatures.

Despite its great performance, NaI-$GaCl_3$ is too expensive! Reinvestigate NaI-$AlCl_3$, with materials cost <$1 kWh^{-1}.

L.J. Small, E.D. Spoerke et. al. *J. Power Sources* **360** (2017) 569-574.

Reinvented NaI-$AlCl_3$ to Cycle at 110 °C

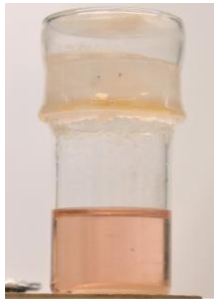
NaI-$AlCl_3$ molten salts were integrated into molten sodium batteries at 110 °C, using lessons learned since our last attempts in 2016.

- Applied Sn coating to decrease Na-NaSICON interfacial resistance[1]
- Controlled molten salt composition and conditioning to limit precipitation[2,3]
- Cycled 5-35% SOC at 5 mA cm^{-2} for 70% energy efficiency
- ***Targeted 130 Wh/L usable capacity, <$1/kWh (materials)***

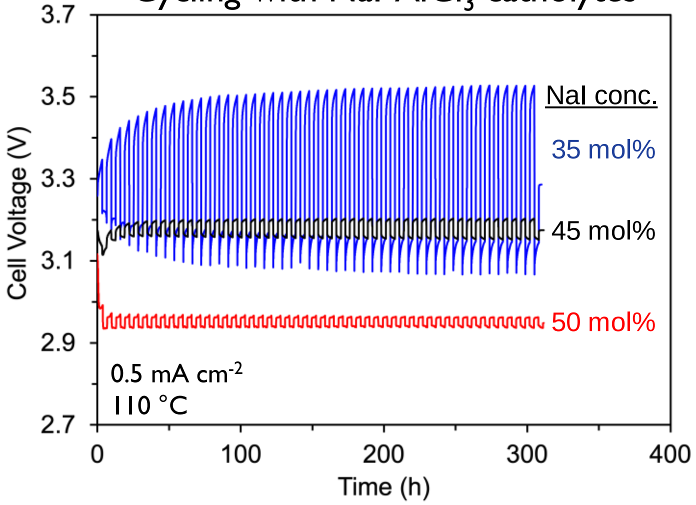
But we want more…

- The theoretical energy density of 45 mol% NaI-$AlCl_3$ is >430 Wh/L, phase limitations restrict capacity to 30% to maintain electrolyte.
- Limited to 5-10 mA cm^{-2}, why?

45 mol% NaI-$AlCl_3$ catholyte is fully molten at 110 °C



Cycling with NaI-$AlCl_3$ catholytes



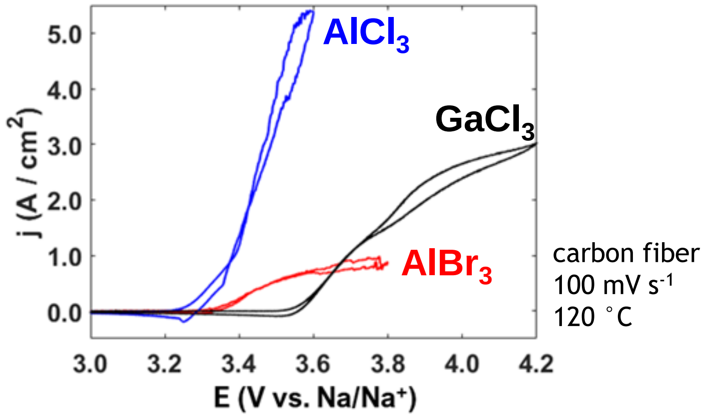
Low-cost NaI-$AlCl_3$ catholyte successfully cycled at 110 °C, but we want more power!

1. M.M. Gross, L.J. Small, A.S. Peretti, S.J. Percival, M. Rodriguez, E.D. Spoerke. *J. Mater. Chem. A,* **8** (2020) 17012.
2. S.J. Percival, L.J. Small, E.D. Spoerke. *J. Electrochem. Soc.,* ***165*** (2018) A3531-A3536.
3. S.J. Percival, R.Y. Lee, M.M. Gross, A.S. Peretti, L.J. Small, E.D. Spoerke. *J. Electrochem. Soc.,* ***168*** (2021) 036510.

Modeling NaI-MX_3 Speciation Reveals Kinetic Limitations

We coupled microelectrode studies with electrochemical simulations to understand the differences between NaI-$AlCl_3$, NaI-$AlBr_3$, and NaI-$GaCl_3$.

- Extracted chemical and electrochemical parameters
- NaI-$AlCl_3$ had slowest electron transfer rates, highest currents
- Multiple species exist in the molten salt – Al_2Cl_6, $Al_2Cl_6I^-$, $AlCl_3I^-$, etc.
- Some species "lock up" iodide, making it unavailable for energy storage.

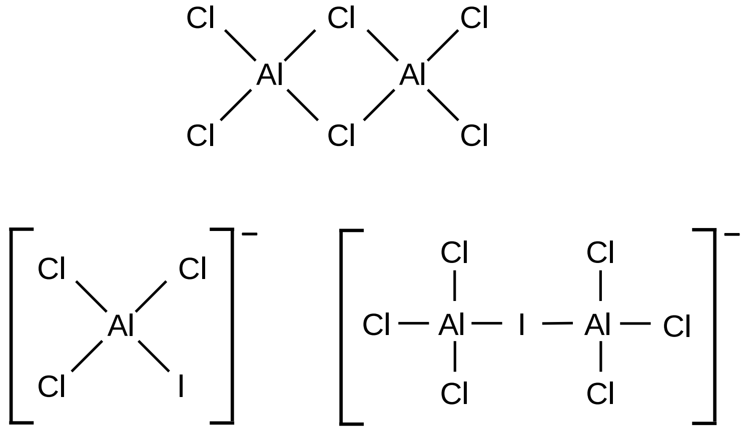


Iodide oxidation consists of an electrochemical step, I_2 formation,

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

followed by a chemical step, I_3^- formation.

$$AlCl_3I^- + I_2 \rightarrow AlCl_3I_3^-$$



Iodide oxidation consists of an electrochemical step followed by a chemical step.
We can leverage this to improve our catholyte.

R.Y. Lee, S.J. Percival, L.J. Small, *In Review* (2021).

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-$AlCl_3$.

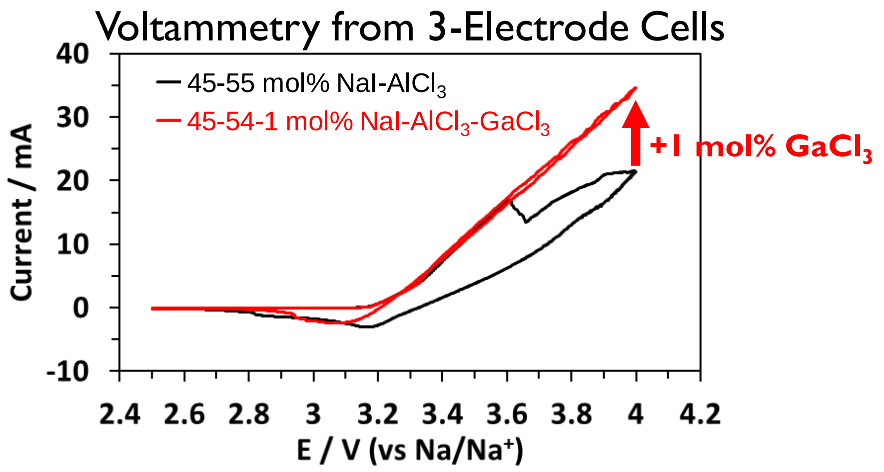
- E^0 for $AlCl_3I^-$ oxidation is 3.49 V vs. Na/Na^+
- E^0 for $GaCl_3I^-$ oxidation is 4.00 V vs. Na/Na^+
- $GaCl_3I^-$ is more stable against electrochemical oxidation, allowing it to react with I_2 on the electrode and speed up this chemical step.

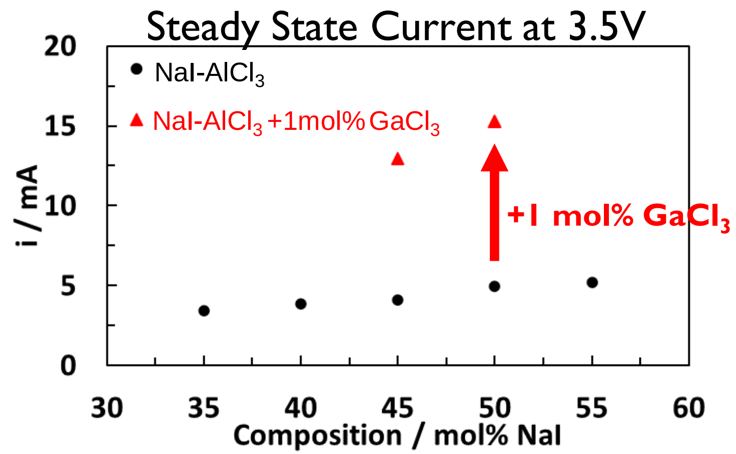
$$2AlCl_3I^- \rightarrow 2AlCl_3 + I_2 + 2e^-$$

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

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 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

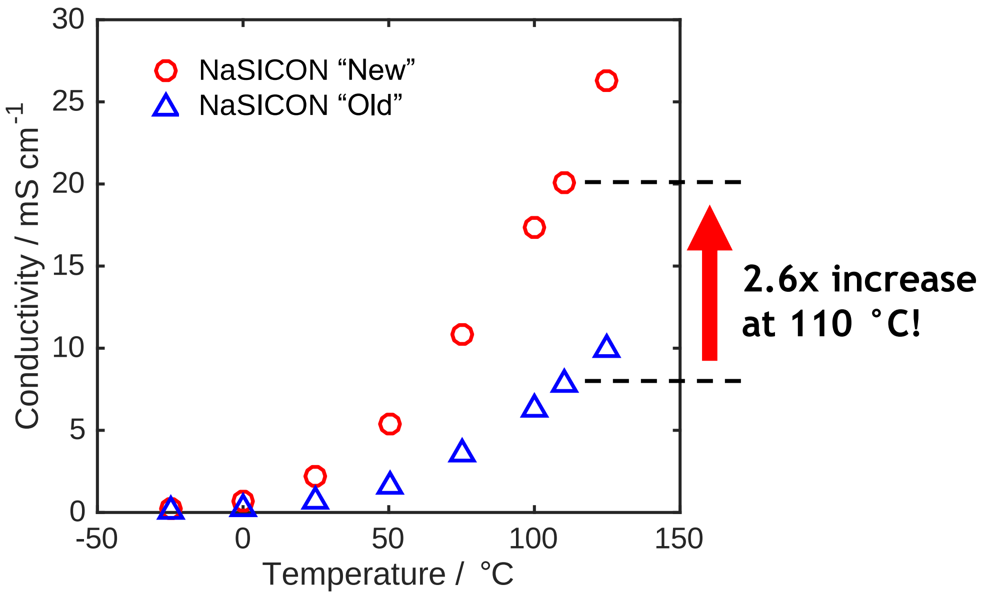
Increased NaSICON conductivity by optimizing composition

- Old composition: $Na_3Zr_2Si_2PO_{12}$
- New composition: $Na_{3+x}Zr_2Si_{2+x}P_{1-x}O_{12}$, $0 \leq x \leq 0.6$
- Increased 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 $Zn\text{-}MnO_2$ batteries in development at UEP.



2.6x increase in NaSICON Na^+ conductivity increases battery efficiency!

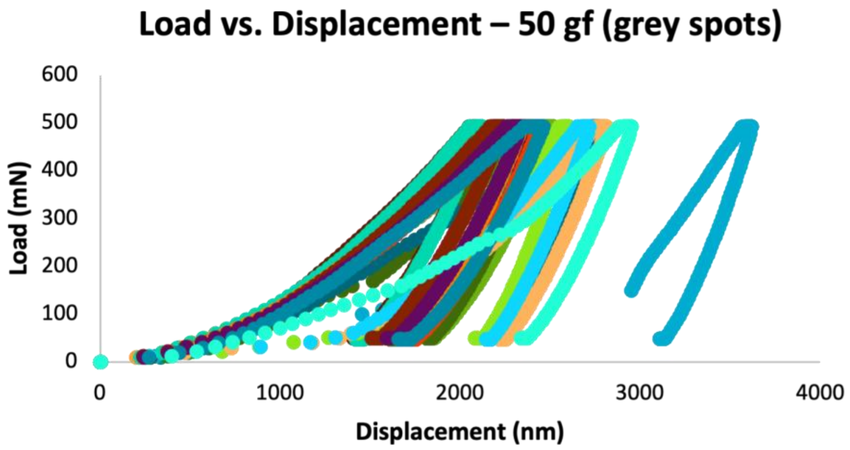
Analysis of Mechanical Properties

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.

A cycled NaSICON separator *not* coated in Sn



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

- M.M. Gross, S.J. Percival, R.Y. Lee, A.S. Peretti, E.D. Spoerke, and L.J. Small. A High Voltage, Low Temperature Molten Sodium Battery Enabled by Metal Halide Catholyte Chemistry. *Cell Reports Physical Science* **2** (2021) 100489.
- S.J. Percival, S. Russo, C. Priest, R.C. Hill, J.A. Ohlhausen, L.J. Small, E.D. Spoerke, and S.B. Rempe. Bio-Inspired Incorporation of Phenylalanine Enhances Ionic Selectivity in Layer-by-Layer Deposited Polyelectrolyte Films. *Soft Mater* **17** (2021) 6315-6325. ***Featured on Cover.***
- S.J. Percival, R.Y. Lee, M.M. Gross, A.S. Peretti, L.J. Small, and E.D Spoerke. Electrochemistry of the $AlBr_3$-NaI Molten Salt System: Low Temperature Molten Salt for Energy Storage Applications. *Journal of the Electrochemical Society* **168** (2021) 036510.
- R. Hill, A.S. Peretti, L.J. Small, E.D. Spoerke, and Y.-T. Cheng. Characterizing Mechanical and Microstructural Properties of Novel Montmorillonite-Rich Polyethylene Composites. *Journal of Materials Science* (2021). DOI: 10.1007/s10853-021-06562-1.
- R.Y. Lee, S.J. Percival, and L.J. Small. Molten Salt Electrochemical Modeling Reveals Speciation Rivals Kinetics for Iodide Oxidation. *In Review* (2021).

Patents

- J.A. Bock, E. D. Spoerke, H. J. Brown-Shaklee, and L. J. Small, "Solution-Assisted Densification of NaSICON Ceramics," US Patent Application, # 62/963,980, Jan. 2021.
- E.D. Spoerke, M.M. Gross, S.J. Percival, and L.J. Small, "Sodium Electrochemical Interfaces with NaSICON-Type Ceramics," US Patent Application # 17/104,306, Nov. 25, 2020.
- E.D. Spoerke, S.J. Percival, M.M. Gross, R.Y. Lee, and L.J. Small, "Low temperature sodium battery comprising an electrochemically active molten inorganic catholyte," Provisional US Patent Application. Oct 2021.

Accomplishments – Presentations

- E.D. Spoerke, M.M. Gross, S.J. Percival, R.Y. Lee, L.J. Small. “Implementing Low Temperature Strategies to Advances “Really Cool” Molten Sodium Batteries.” Electrochemical Society PRiME 2020. (Virtual) Oct 2020.
- E.D. Spoerke, A.S. Peretti, E. Coker, M. Rodriguez, M.M. Gross, S.J. Percival, L.J. Small, R. Hill, Y.T. Cheng. “Solid State Ion Conductors to Enable Low Temperature Molten Sodium Batteries.” Electrochemical Society PRiME 2020. (Virtual) Oct 2020.
- M.M. Gross, A.S. Peretti, S.J. Percival, L.J. Small, M. Rodriguez, E.D. Spoerke. “Advancing Low temperature Molten Sodium Batteries by Interfacial Engineering of Ceramic Electrolytes.” Electrochemical Society PRiME 2020. (Virtual) Oct 2020.
- E.D. Spoerke, A.S. Peretti, E. Coker, M. Rodriguez, M.M. Gross, S.J. Percival, L.J. Small. “Solid State Materials to Enable Molten Sodium Batteries.” Materials Research Society Spring/Fall Meeting, (Virtual), Nov 2020.
- R. Hill, Y.-T. Cheng, A.S. Peretti, E.D. Spoerke, L.J. Small. “Mechanical Characterization of Montmorillonite Sodium Ion Conductors.” Materials Research Society Spring/Fall Meeting, (Virtual), Nov 2020.
- L.J. Small, S.J. Percival, R.Y. Lee, M.M. Gross, A.S. Peretti, E.D. Spoerke. “Molten Salt Catholyte for Low-Temperature Molten Sodium Batteries.” Materials Research Society Spring/Fall Meeting, (Virtual), Nov 2020.
- M.M. Gross, A.S. Peretti, S.J. Percival, L.J. Small, M. Rodriguez, E.D. Spoerke. “Engineering Ceramic Electrolyte Interfaces for Low-Temperature Molten Sodium Batteries.” Materials Research Society Spring/Fall Meeting, (Virtual), Nov 2020.
- M.M. Gross, S. Percival, R.Y. Lee, A. Peretti, M. Rodriguez, E.D. Spoerke, L.J. Small “High-Performance Low-Temperature Molten Sodium Batteries Enabled by Improved Charge Transfer Across Interfaces” 2021 MRS Spring Meeting & Exhibit, (Virtual) April 17-23, 2021.
- S.J. Percival, R.Y. Lee, M.M. Gross, A.S. Peretti, E.D. Spoerke, L.J. Small “Electrochemistry of the NaI-$AlBr_3$ Low Temperature Molten Salt System: Implications for Applied Battery Performance” American Chemical Society (ACS) Spring Meeting, (Virtual) April 5-30, 2021.
- S.J. Percival, R.Y. Lee, M.M. Gross, L.J. Small, A. Peretti, E.D. Spoerke “Electrochemistry of the NaI-$AlBr_3$ Low Temperature Molten Salt System: Implications for Applied Battery Performance” 2021 MRS Spring Meeting & Exhibit, (Virtual) April 17-23, 2021.
- L.J. Small, M.M. Gross, S.J. Percival, R.Y. Lee, A.S. Peretti, E.D. Spoerke “Materials Development for High-Performance Interfaces in Low-Temperature Sodium Batteries” American Chemical Society (ACS) Spring Meeting, (Virtual) April 5-30, 2021.
- E.D. Spoerke, M.M. Gross, A.S. Peretti, S.J. Percival, L.J. Small “Hybrid Solid State ‘Chaperone’ Phases to Improve Solid State Sodium Electrolytes” 239th Meeting of Electrochemical Society (ECS), (Virtual) May 30 – June 3, 2021.

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 $GaCl_3$ to an $AlCl_3$-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

We thank the DOE Office of Electricity, Energy Storage Program managed by Dr. Imre Gyuk for funding this work!

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

Questions?

Leo Small
ljsmall@sandia.gov