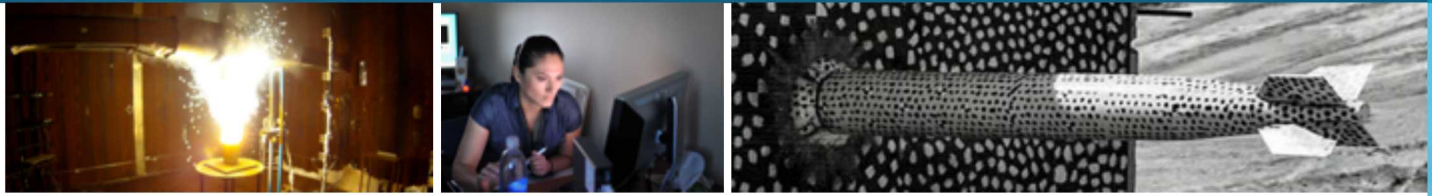
SAND2020-9498C

Low Temperature Molten Sodium Batteries



DOE Office of Electricity

Energy Storage Program Peer Review

Sep 29 – Oct 1, 2020

PRESENTED BY

Leo Small

Martha Gross, Rose Lee, Stephen Percival
Amanda Peretti, 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.

Team

Sandia

Martha Gross

Rose Lee

Stephen Percival

Amanda Peretti

Leo Small

Erik Spoerke

University of Kentucky

Prof. Y.T. Cheng – presenting next

Ryan Hill

See Posters By:

Martha Gross

Development of High-Performance Low-Temperature Molten Sodium Batteries

Ryan Hill

Mechanical and Microstructural Characterization of Montmorillonite Sodium Ion Conductors

Stephen Percival

Electrochemistry of the NaI-$AlBr_3$ Low Temperature Molten Salt System: Implications for Sodium Battery Performance

Erik Spoerke

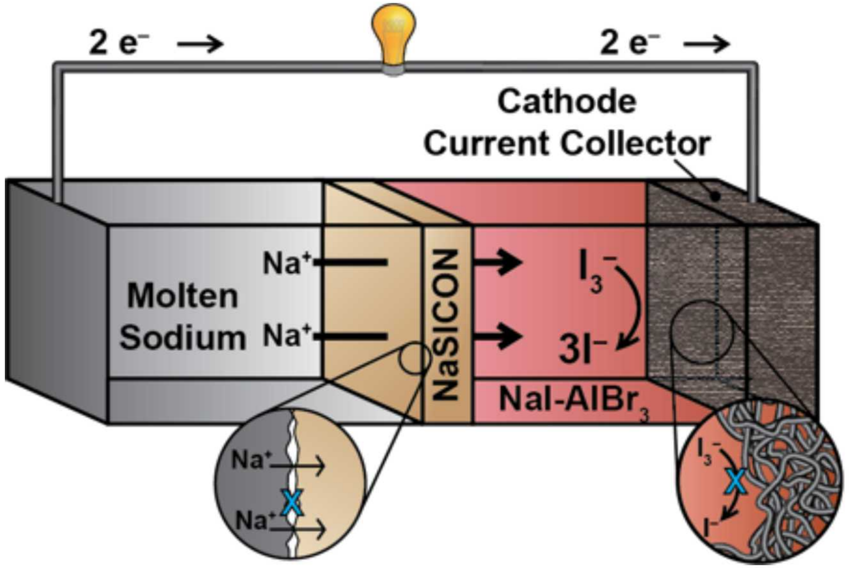
Solid State Separator Development

Program Objective

Develop enabling technologies for safe, low cost, *molten sodium batteries*

Molten sodium batteries are attractive for safe, reliable grid scale energy storage

- 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



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

Why Low Temperature?

Typical molten sodium batteries operate near 300 °C (Na-S) and 200 °C (ZEBRA). We are targeting battery operation near sodium's melting point (98 °C). 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.

Quick Recap of FY19

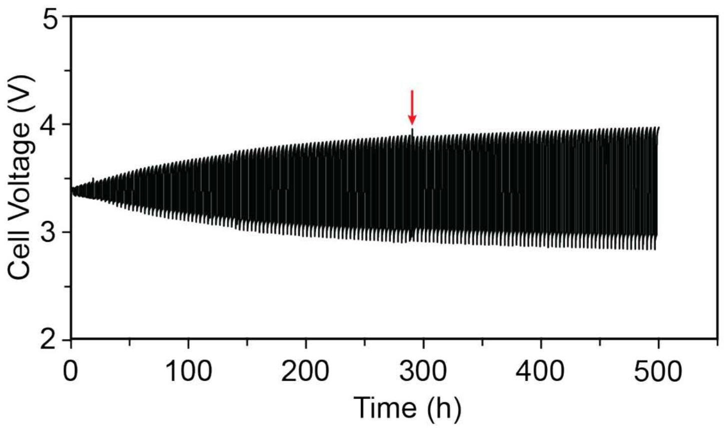
Sn-Coated NaSICON Anode

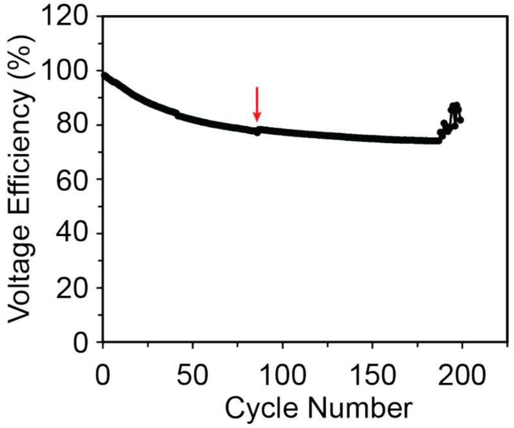
- Decreases interfacial resistance 6x to 1.01 Ω cm^2
- Enables currents up to 50 mA cm^{-2} in Na/NaSICON/Na cell

NaI-$AlBr_3$ Cathode

- Fully molten at 90 °C (25mol% NaI)
- Thermal activation of carbon felt lowers battery overpotential 5x.

Full Cell: Na/NaSICON/NaI-$AlBr_3$ at 110 °C





Demonstrated cycling of a molten sodium battery at 110 °C for 200 cycles (500 h) at >74% energy efficiency

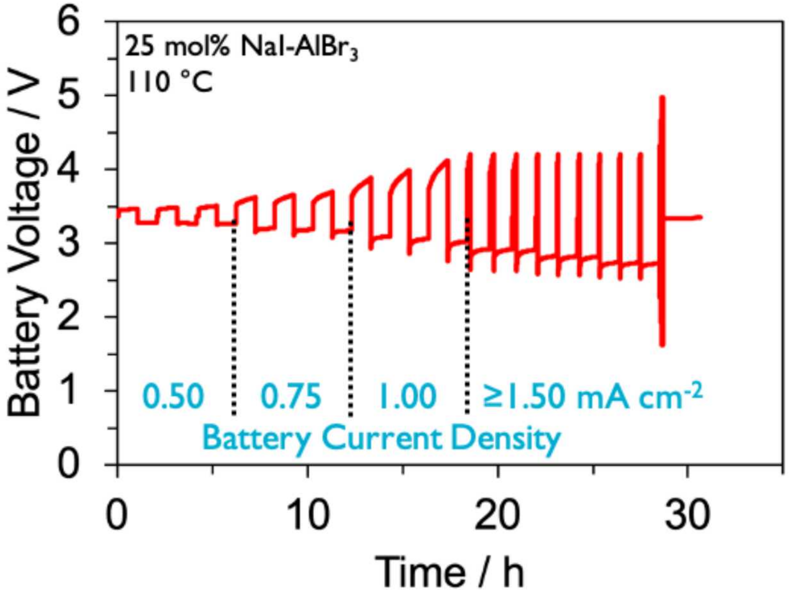
M.M. Gross, L.J. Small, A.S. Peretti, S.J. Percival, M. Rodriguez, E.D. Spoerke. *J. Mater. Chem. A*, **8** (2020) 17012.

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

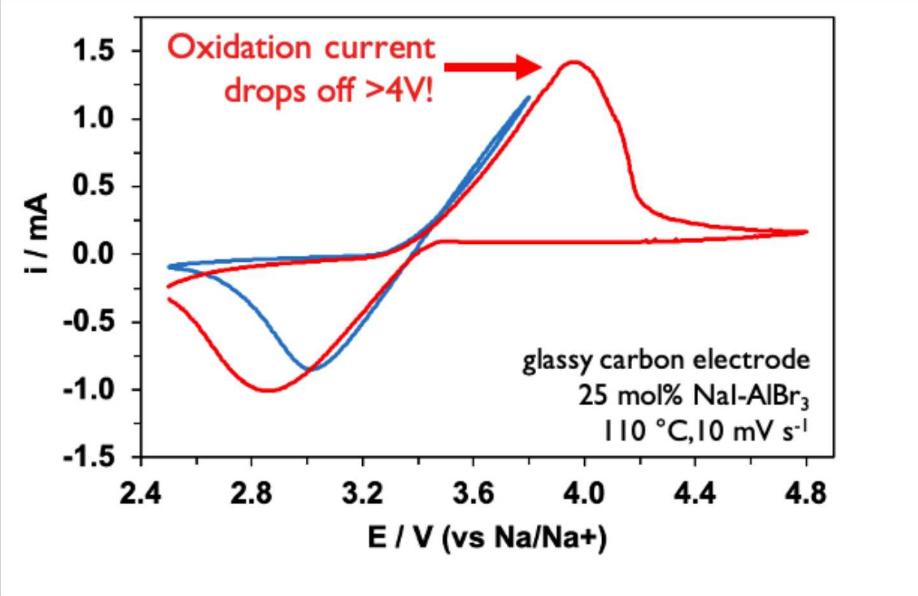
FY20: Pushing the NaI-$AlBr_3$ Catholyte to the Limit

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.

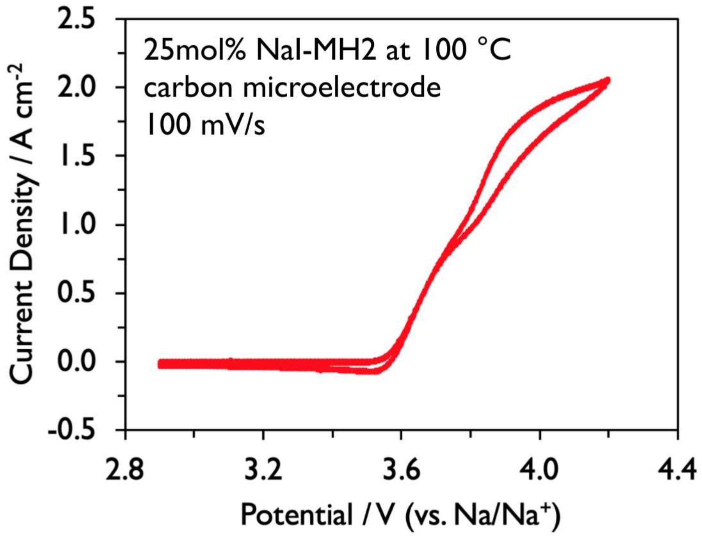
See Stephen Percival's poster for more details!

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)

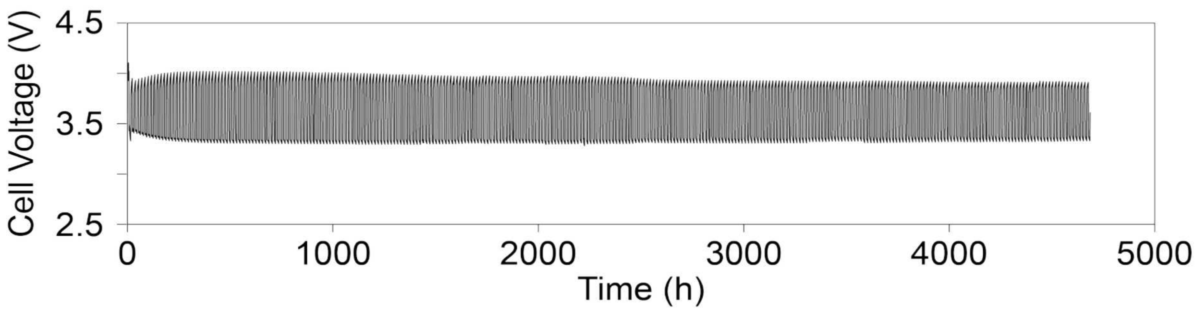
L=liquid
S=solid

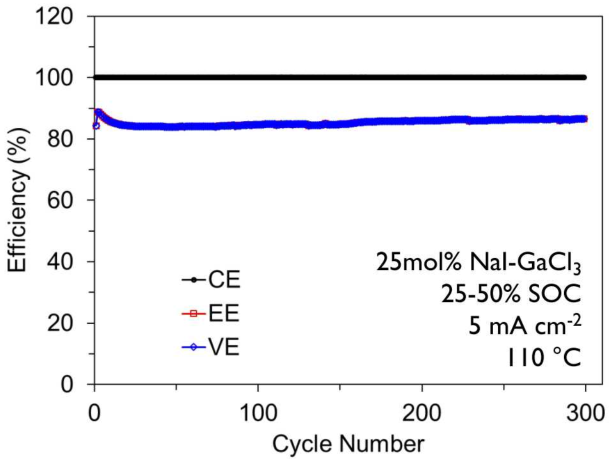
Redox-active molten salt NaI-MH2 was identified, with melting point near 50 °C.

Revised Catholyte Chemistry Increases Battery Performance at 110 °C

Integrated NaI-MH2 catholyte into molten Na batteries

- 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}.



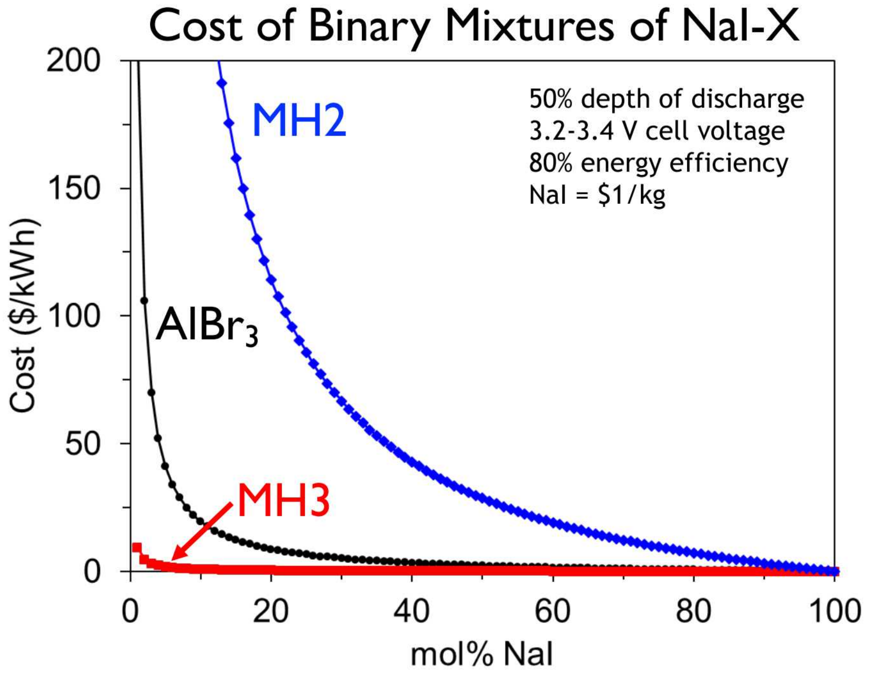


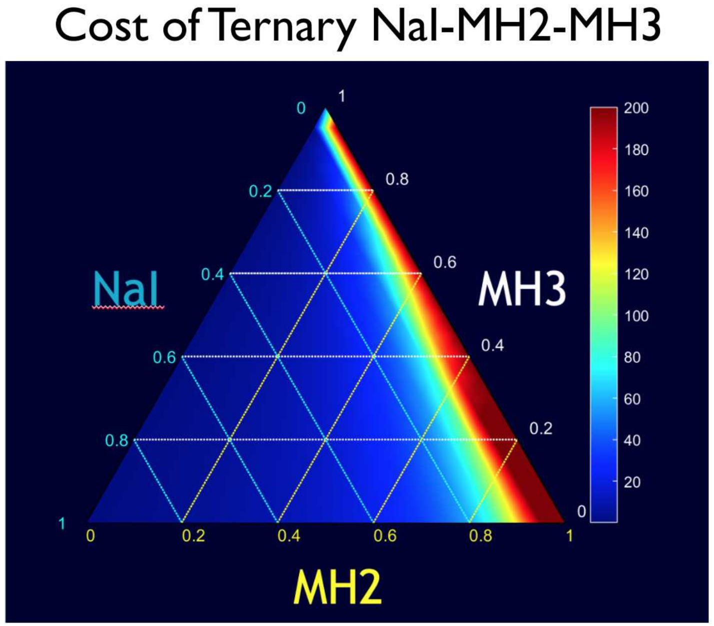
Cycled molten sodium battery with NaI-MH2 catholyte at 110 °C for >6 months with >85% energy efficiency, using 25x cycling capacity and 10x current density vs. NaI-$AlBr_3$ catholyte!

See Martha Gross' poster for more details!

Catholyte Cost Analysis

- 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.





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

Moving Forward: Leverage Cost Analysis to Identify New Catholytes

Use cost as first level screen for new catholytes

Catholyte Materials Cost

↓

Melting Temperature <100 °C

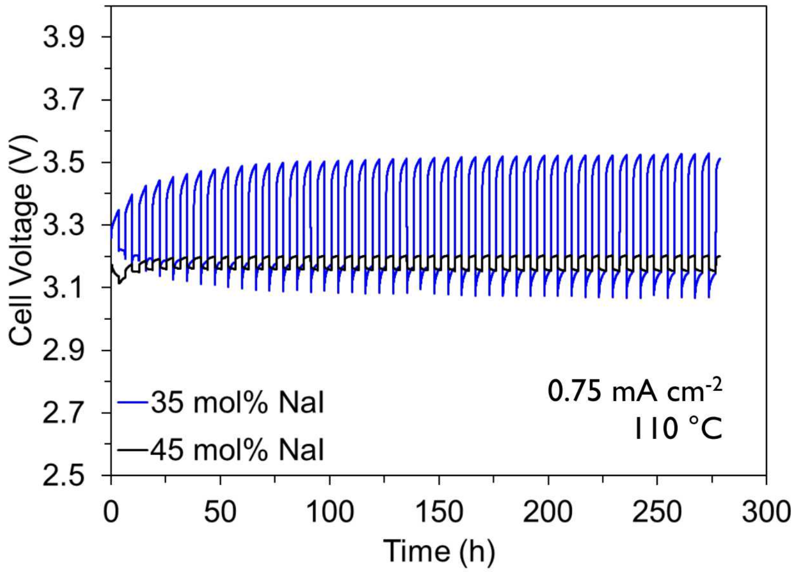
↓

Conductivity >10 mS cm^{-1}

↓

Test in Battery →

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.

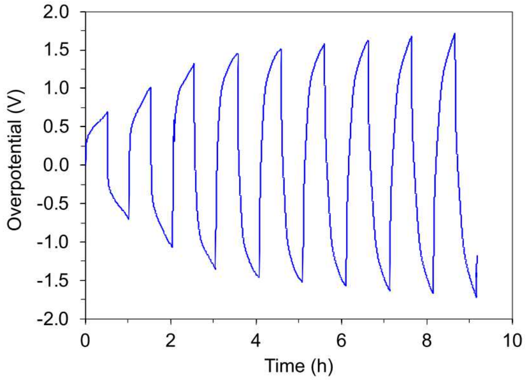
Solid State Separators for Molten Sodium Batteries

We have take a 2-pronged approach to separator development:

1) Improving processing to increase yield of high density, high conductivity NaSICON, free of cracks or pinholes.
   - Simple solid state chemistry: $Na_3PO_4 + 2ZrSiO_4 \rightarrow Na_3Zr_2PSi_2O_{12}$
   - Sintered at 1230 °C in air
   - Effective use of binder/lubricant during pressing
   - Controlled humidity
   - Optimized pressing conditions
   - Current NaSICON shows >96% density and ~5×10^{-4} S/cm RT

2) Identifying alternatives separator materials capable of robust performance and high conductance. Working with U. Kentucky, we have explored:
   - Clay-based separators
     - Recognized not suitable for molten sodium chemistry, but may be suitable for solid-state systems or Na-ion chemistries.
       - Ionic conductivity, mechanical properties are both important!
   - Engineered composites may offer pathway to mechanically robust systems – large focus of future work in this system!

NaSICON Pellets



Symmetric Na_xMnO_2 cell made with a clay-based separator.

Solid state sodium ion conductors are critical elements of molten sodium batteries and may impact other Na-based battery technologies (e.g., solid state sodium, sodium-ion batteries, alkaline Zn-batteries).

See presentation by YT Cheng and posters by Erik Spoerke and Ryan Hill for more details!

Accomplishments – Publications and Patents

Publications

- M. M. Gross, L. J. Small, A. S. Peretti, S. J. Percival, M. Rodriguez, and E. D. Spoerke. Tin-Based Ionic Chaperone Phases to Improve Low Temperature Molten Sodium-NaSICON Interfaces. *J. Mater. Chem. A,* **8** (2020) 17012. DOI: 10.1039/d0ta03571h
- E. D. Spoerke, M. M. Gross, S. J. Percival, and L. J. Small, "Molten Sodium Batteries," in *Energy-Sustainable Advanced Materials*, M. E. Alston and T. N. Lambert, Ed. Berlin, Germany: Springer Nature, *In Press* (2020).
- E. D. Spoerke, M. M. Gross, L. J. Small, and S. J. Percival, "Sodium-Based Battery Technologies for Grid-Scale Energy Storage," *DOE Energy Storage Handbook*, U.S. Dept. of Energy, *In press* (2020).
- S. J. Percival, R. Y. Lee, A. S. Peretti, M. M. Gross, L. J. Small, and E. D. Spoerke. "Electrochemistry of the $AlBr_3$-NaI Molten Salt System: Low Temperature Molten Salt for Energy Storage Applications." *In Review* (2020).
- 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." *In Review* (2020).
- M. M. Gross, S. J. Percival, L. J. Small, J. Lamb, A. S. Peretti, and E. D. Spoerke. "Advanced Low Temperature Molten Sodium Batteries with a NaI-$AlBr_3$ Catholyte." *In Review* (2020).

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. 21, 2020.
- E. D. Spoerke, M. M. Gross, S. J. Percival, and L. J. Small, "Surface Treatments of NaSICON Ceramics for Improved Sodium Electrochemical Interfaces," US Patent Application # 62/940,697, Nov. 26, 2019.
- E. D. Spoerke, S. J. Percival and L. J. Small, "Molten Inorganic Electrolytes for Low Temperature Sodium Batteries," US Patent Application # 16/564,751. Sep. 2019.
- L. J. Small and E. D. Spoerke, "Alternating Current Electrodialysis," US Application # 16/691,333, Nov. 21, 2019.
- L. J. Small, S. J. Percival, and E. D. Spoerke, "Nanostructured polyelectrolytes for electrodialysis membranes," US Application # 16/128,081, Granted Jun. 10, 2020.

Accomplishments - Presentations

Invited

- E. D. Spoerke, "Materials Chemistry to Advance Na-Batteries." Materials Science & Engineering Department Seminar, University of North Texas, Denton, TX, Sep., 2019.
- S. J. Percival, M. M. Gross, L. J. Small, and E. D. Spoerke "Advances in Low Temperature Molten Sodium Halide Catholytes for Sodium Batteries," ACS Southwest & Rocky Mountain Regional Meeting (SWRM/RMRM) 2019, El Paso, TX, Nov. 2019.
- E. D. Spoerke, A. S. Peretti, S. J. Percival, L. J. Small, M. M. Gross, E. Schindelholz, M. Melia, S. B. Rempe, D. Nelson, and S. Russo, "The Ions Seeps Tonight: Assessing Ionic Transport in Multilayered Nanocomposites," Composites at Lake Louise 2019, Lake Louise, Alberta, Canada, Nov. 2019.
- E. D. Spoerke, "Toward Lower Temperature Molten Sodium Batteries for Grid Scale Applications," International Conference on Sodium Batteries (ICNaB-2019), Naperville, IL, Nov. 2019.
- E. D. Spoerke, A. S. Peretti, S. J. Percival, L. J. Small, M. M. Gross, E. Schindelholz, M. Melia, S. B. Rempe, D. Nelson, S. Russo, R. Hill, and Y.-T. Cheng, "Controlling Ion Transport in Multilayered Polymer Composites." Layered Polymeric Systems (ACS Polymer Division) – 2020, Windsor, CA, Feb. 2020.
- E. D. Spoerke and B. Chalamala, "What Role Will Innovation & Grid Modernization Play in Renewable Energy Development Nationally?" Renewable Energy Development, Grid Modernization & Distributed Generation Workshop, Milwaukee, WI, Mar., 2020.

Contributed

- E. D. Spoerke, M. M. Gross, S. J. Percival, L. J. Small, A. S. Peretti, J. Lamb, and B. Chalamala, "Tailoring Materials Chemistry to Advance Low Temperature Molten Sodium Batteries," 236th Electrochemical Society Meeting in Atlanta, GA, Oct. 2019.
- M. M. Gross, A. S. Peretti, S. J. Percival, L. J. Small, B. Chalamala, and E. D. Spoerke, "Interfacial Engineering in Sodium Batteries," Sandia National Laboratories and Los Alamos National Laboratories 2019 Postdoctoral Technical Showcase, Albuquerque, NM, Dec 2019, **[Best Poster Award]**
- E. D. Spoerke, A. S. Peretti, E. Coker, M. Rodriguez, M. M. Gross, S. J. Percival and L. J. Small, "Synthetic Designs for Improved NaSICON-Based Sodium Ion Conductors," American Ceramic Society's Electronic Materials and Applications meeting, Orlando, FL, Jan. 2020.
- M. M. Gross, A. S. Peretti, S. J. Percival, L. J. Small, M. Rodriguez, and E. D. Spoerke, "Interfacial Engineering of Ceramic Separators in Sodium Batteries," American Ceramic Society's Electronic Materials and Applications meeting, Orlando, FL, Jan. 2020.

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