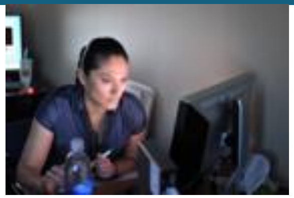
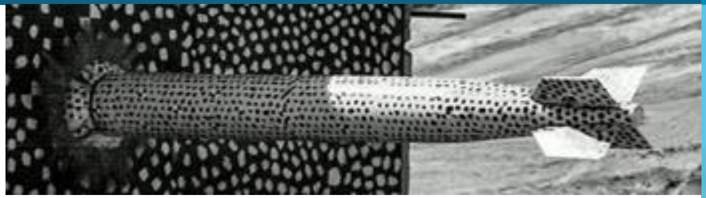
Low Temperature Molten Sodium Batteries

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

Sandia National Laboratories

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

U.S. DEPARTMENT OF ENERGY

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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

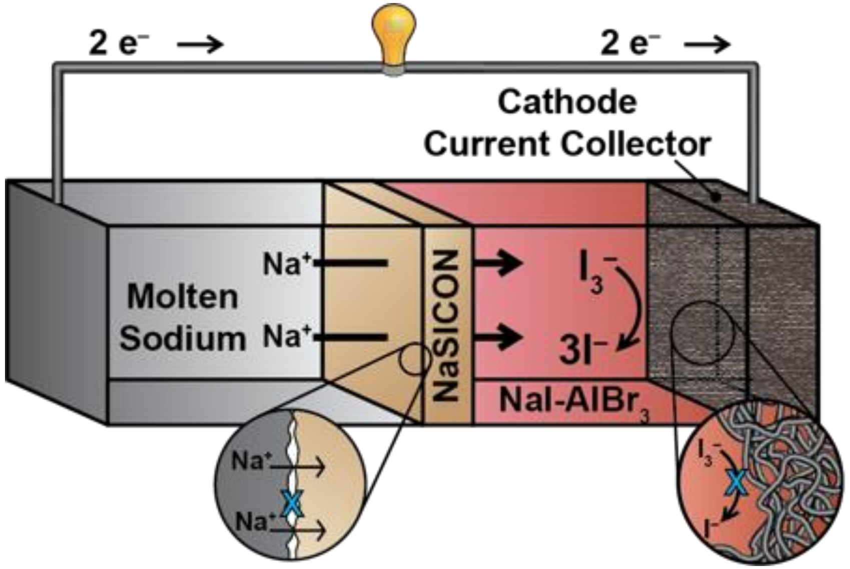
Solid State Separator Development

Program Objective

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

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



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.

Quick Recap of FY19

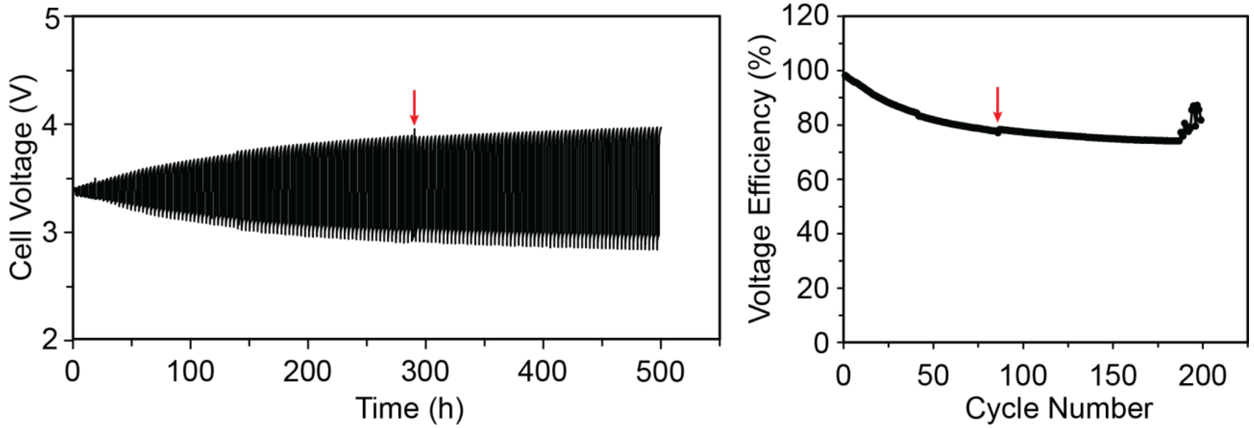
Sn-Coated NaSICON Anode

- 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 (25 mol% NaI)
- Thermal activation of carbon felt lowers battery overpotential 5x.

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



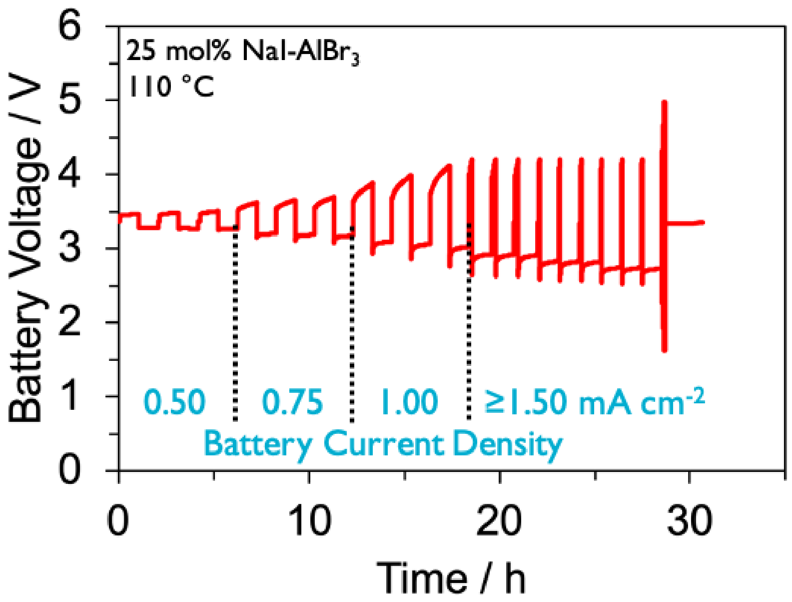
Demonstrated cycling of a molten sodium battery at 110 °C for 200 cycles (500 h) at >74% energy efficiency

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).

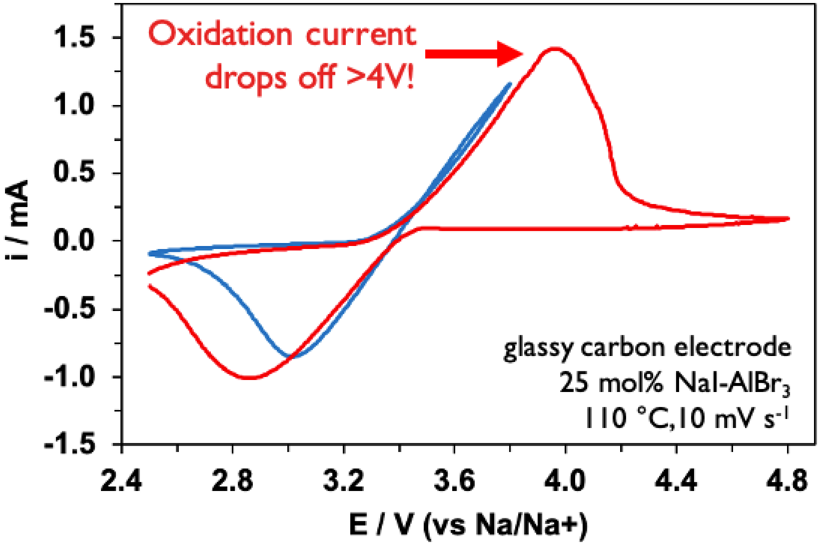
FY20: Pushing the NaI-$AlBr_3$ Catholyte to the Limit

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.



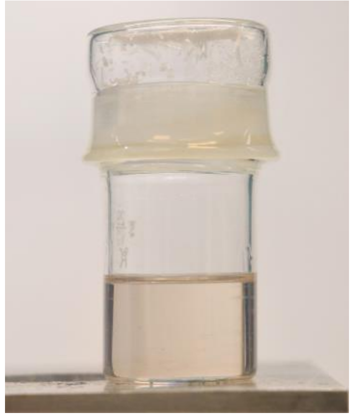
NaI-$AlBr_3$ catholyte cannot continuously cycle at more than 0.75 mA cm^{-2} due to passivation of carbon electrode.

See Stephen Percival's poster for more details!

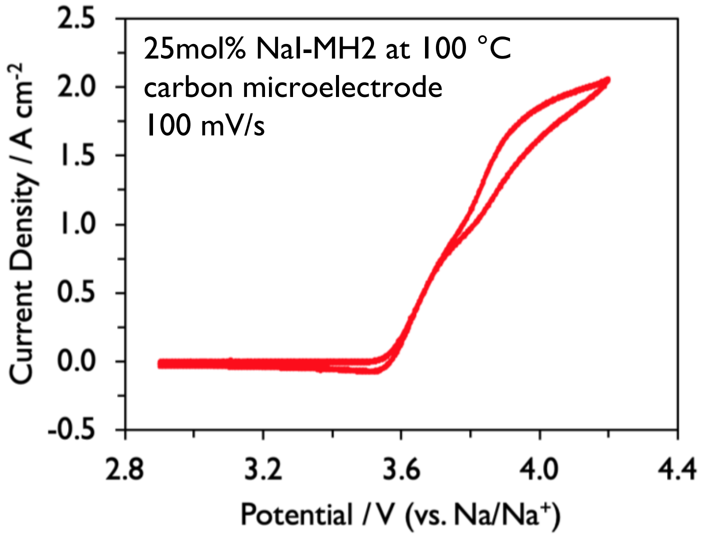
Revised Catholyte Chemistry MH2 – Even Lower Melting Point!

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)

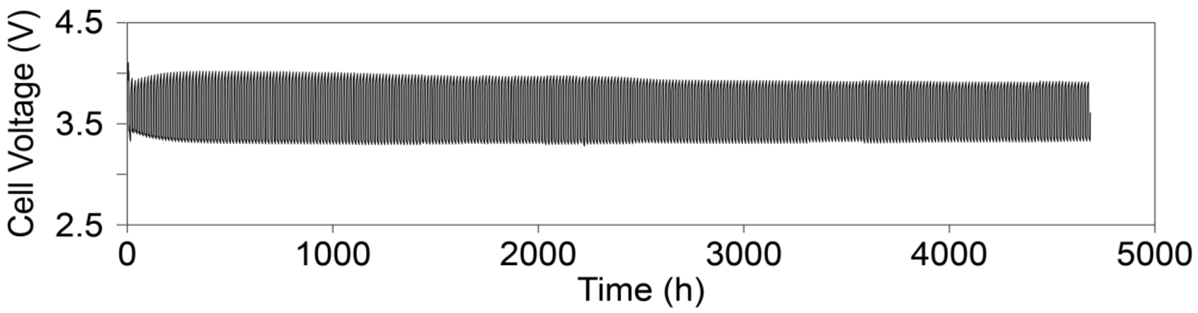
L=liquid
S=solid

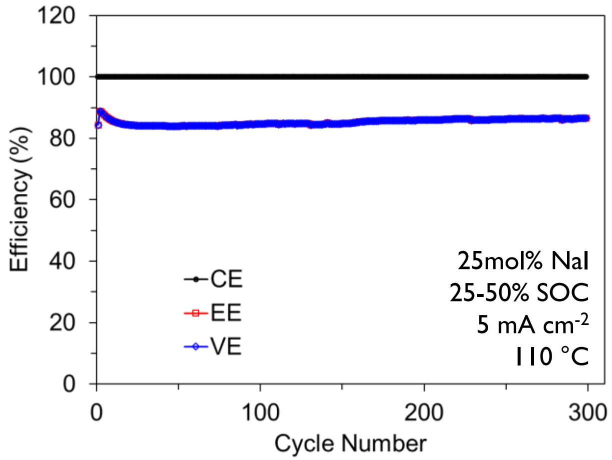
Redox-active molten salt NaI-MH2 was identified, with melting point near 50 °C.

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}.



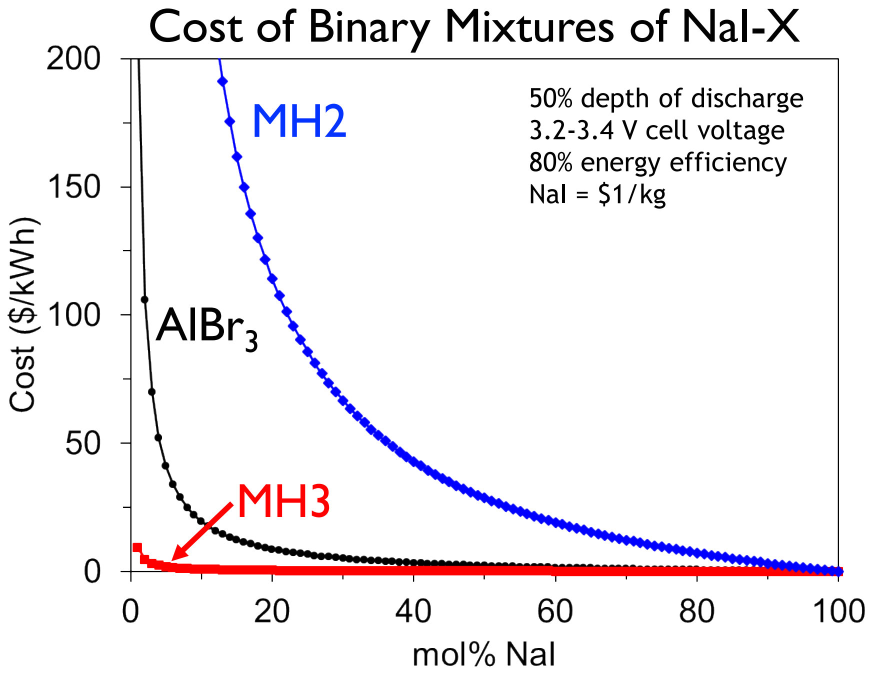


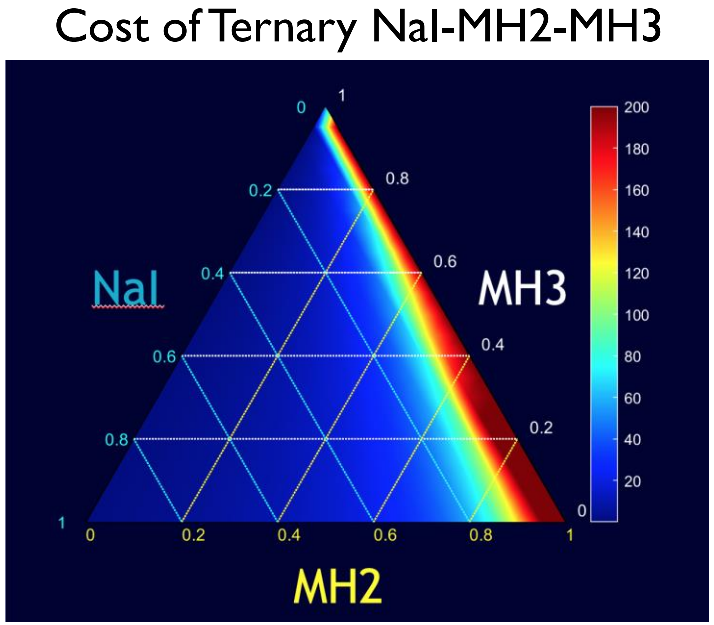
Cycled molten sodium battery with NaI-MH2 catholyte at 110 °C for >6 months with >85% energy efficiency, using 25x cycling capacity and 10x current density vs. NaI-$AlBr_3$ catholyte!

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

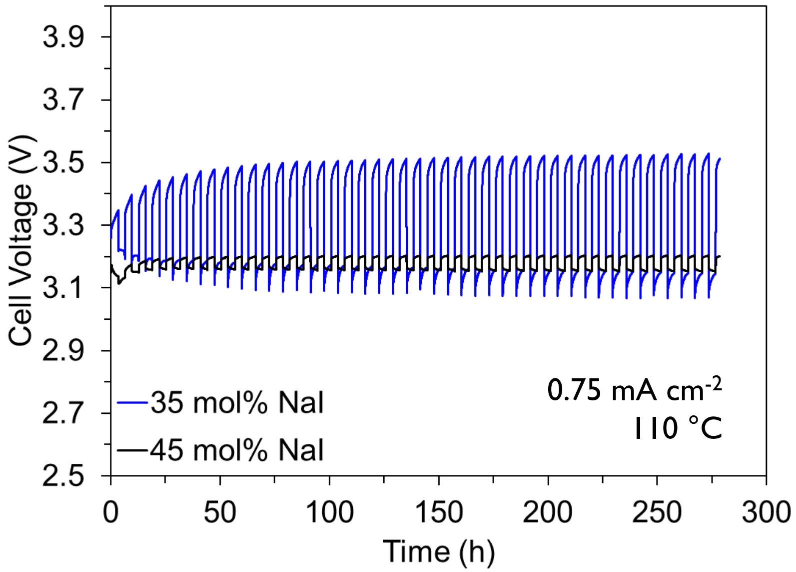
↓

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.

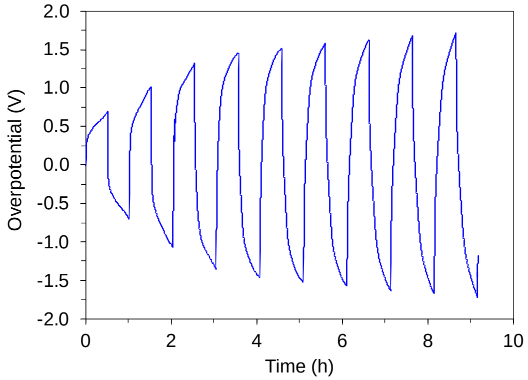
Solid State Separators for Molten Sodium Batteries

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 0.5 mS cm^{-1} (25 °C), 10 mS cm^{-1} (110 °C)

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.

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Questions?

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