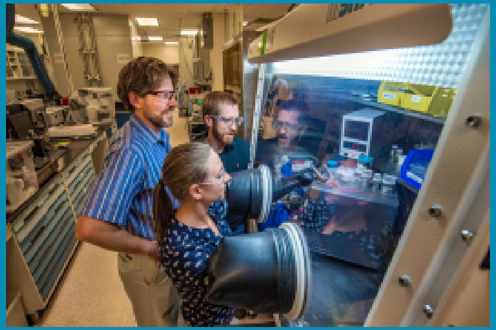
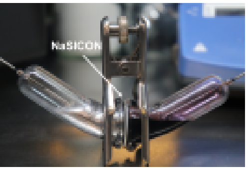
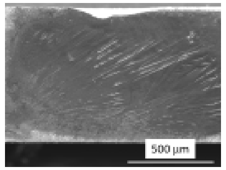
SAND2022-12988C

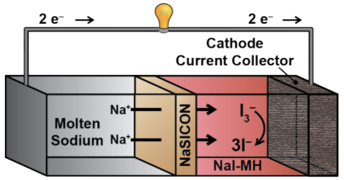
Sandia National Laboratories

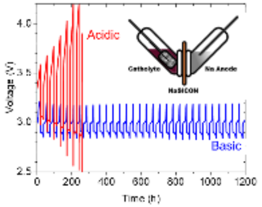
Low Temperature Molten Sodium Batteries

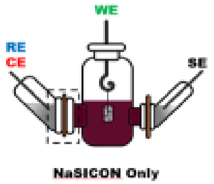


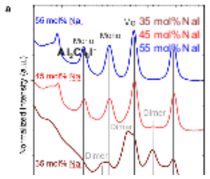












DOE Office of Electricity

Energy Storage Program Peer Review

Oct. 11-13, 2022

PRESENTED BY

Erik Spoerke

Adam Maraschky, Melissa Meyerson, Stephen Percival, Amanda Peretti, Martha Gross, Ryan C. Hill, Y.-T. Cheng, **Leo Small***

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

U.S. DEPARTMENT OF ENERGY

NNSA

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SAND2022-XXXX C

Our Team

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Erik Spoerke

Leo Small*

<u>University of Kentucky</u>

Prof. Y. T. Cheng

Ryan Hill

<u>Please See Posters:</u>

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

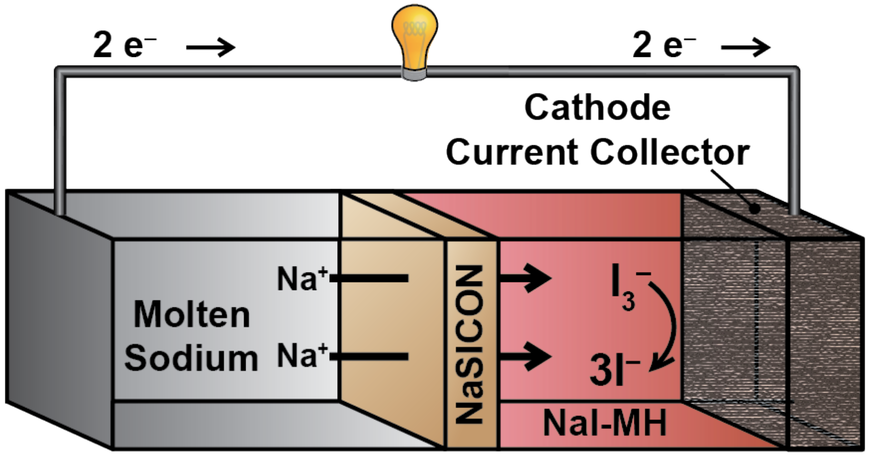
Al-Fe Based Molten Salts for Long Duration Energy Storage

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

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

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

Cathode

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

Why Low Temperature?

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

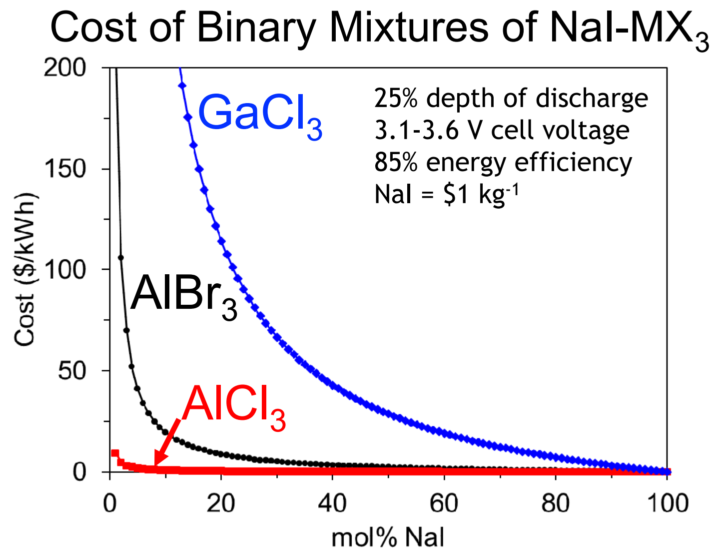
- Lower Cost
  - Plastic seals: below 150 °C, rubber o-rings can be used (<$0.1/each) vs. glass or metal seals.
  - Thinner and less expensive wiring materials
  - Less insulation
- Reliability
  - Lower temperatures → slower aging on all system components
  - System level heat management not as extensive
- Compatibility with higher voltage (>3V) chemistries (e.g., Na-NaI versus Na-$NiCl_2$)

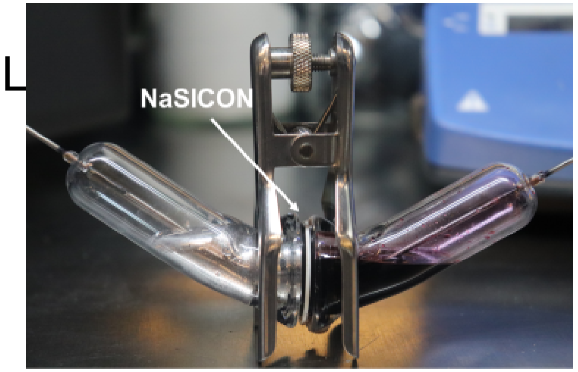
However, battery chemistries from higher temperatures will not work at low temperatures; they need to be reengineered.

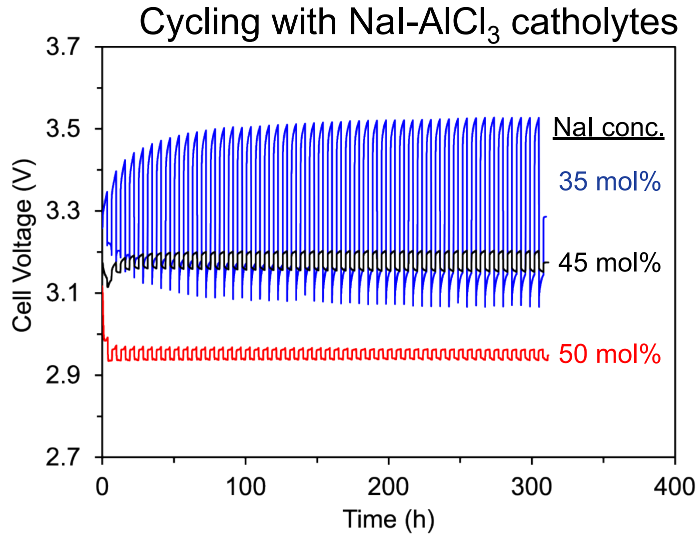
While low temperature (~100 °C) can improve cost and reliability, significant materials challenges arise.

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-$AlCl_3$ catholyte at 110 °C, using lessons learned previously from $GaCl_3$ and $AlBr_3$-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-$AlCl_3$ were limited
  - 5 mA cm^{-2}
  - 30% theoretical energy density (130 Wh L
  - unstable performance over long times







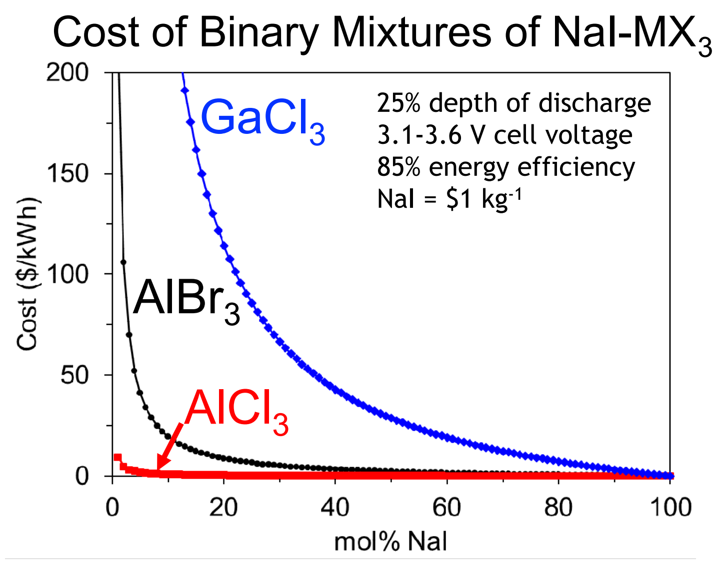
1. M.M. Gross, L.J. Small, A.S. Peretti, S.J. Percival, M. Rodriguez, E.D. Spoerke. *J. Mater. Chem. A,* **8** (2020) 17012.
3. R.Y. Lee, SJ. Percival, L.J. Small, *J. Electrochem. Soc.* **168** (2021) 126511.

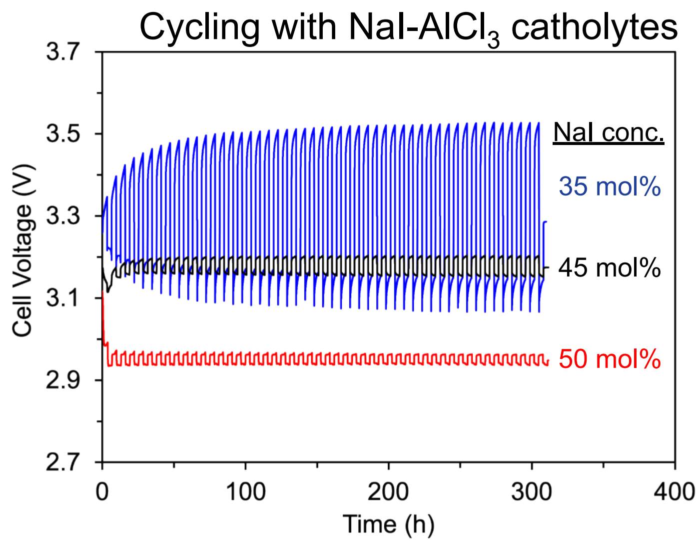
Targeting Catholyte Materials to Control Costs

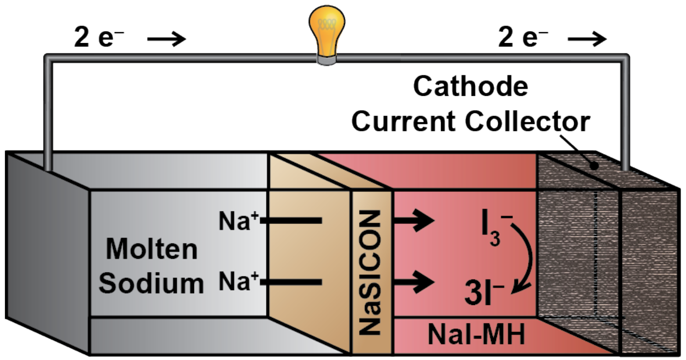
We are targeting a low cost, NaI-metal halide catholyte.

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







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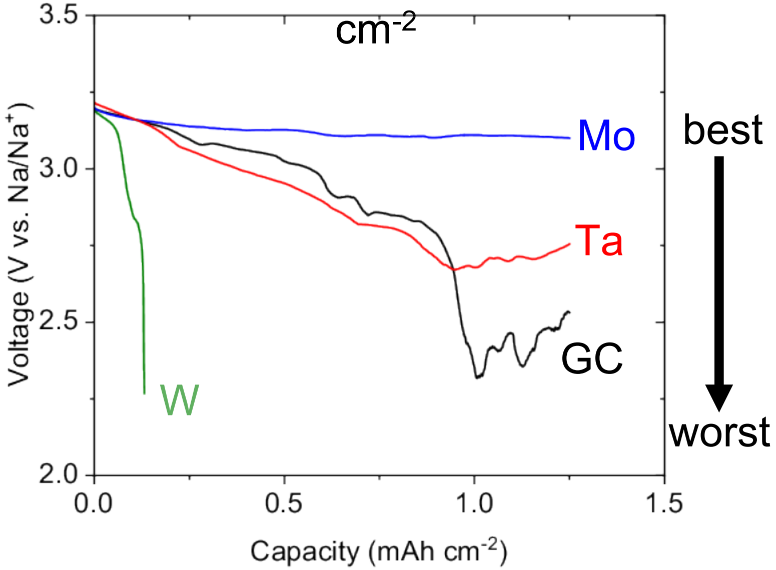
3. R.Y. Lee, SJ. Percival, L.J. Small, *J. Electrochem. Soc.* **168** (2021) 126511.

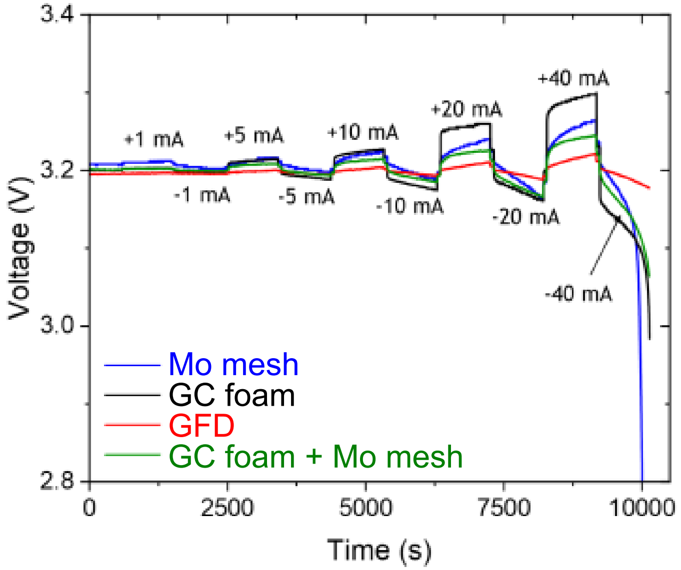
Optimizing (Cathode) Current Collector Material

- 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”

Disc Performance at -5 mA cm^{-2}



Rate Testing Meshes and Foams



110 °C
7.5% SOC
45 mol% $NaI-AlCl_3$

Mo shows best discharge, while GC shows best charging performance. *High available surface area* overcomes small differences in electrocatalytic activity.

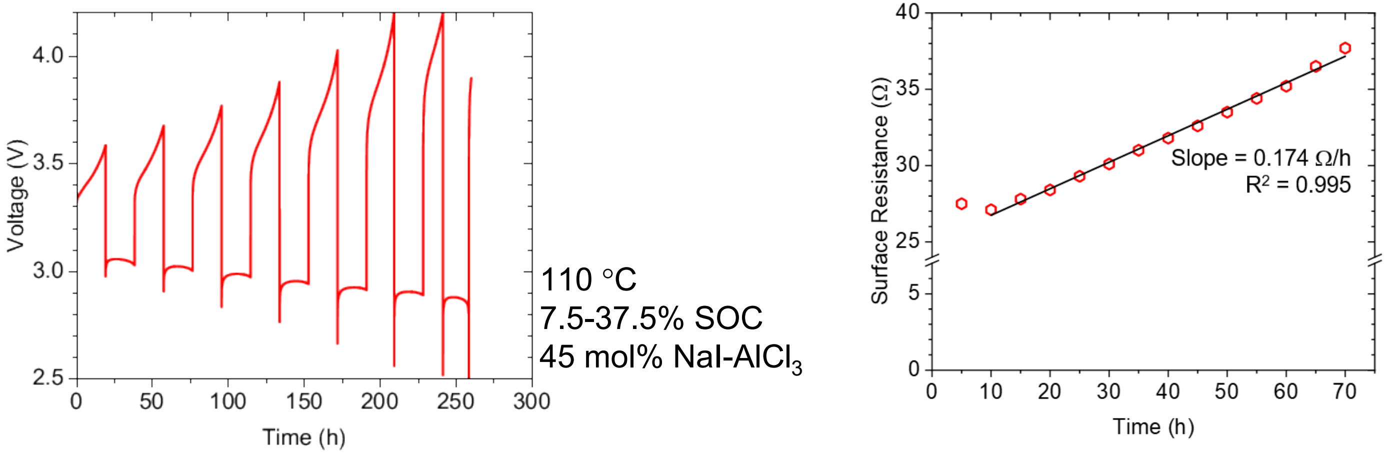
A.M. Maraschky et al. Tailoring Electrode Materials for Iodide/Triiodide Redox in Low-Temperature Molten Sodium Batteries. (2022)*In Preparation*.

Na^+ "Blockade" Identified at the NaSICON-Catholyte Interface

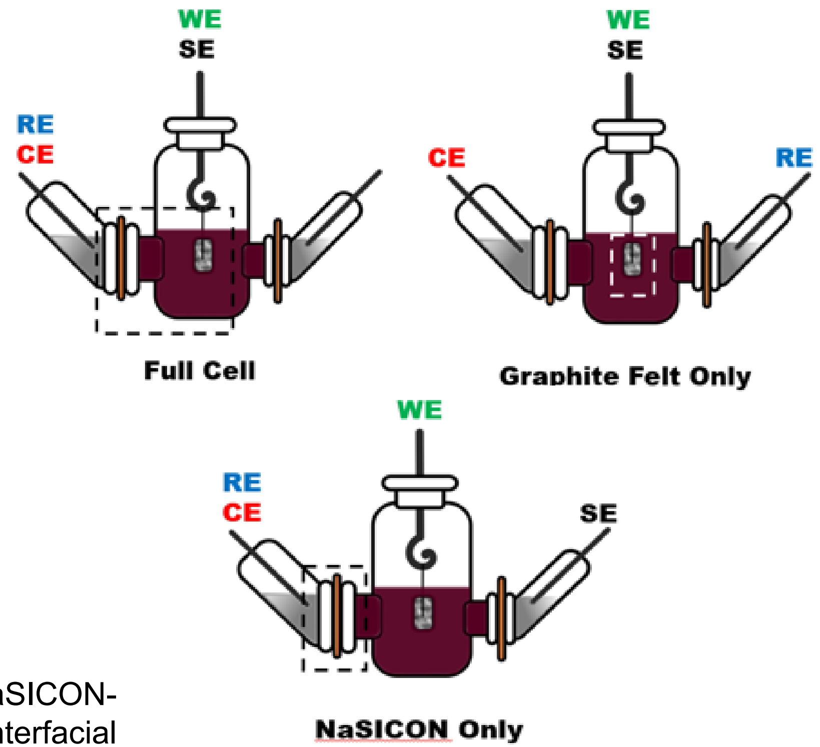
<u>Observed Problem</u>: Steady increase in battery overpotentials observed during cycling.

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

<u>Discovery</u>: Increase in impedance identified at the NaSICON-catholyte interface



Isolated NaSICON-catholyte interfacial resistance over time at open circuit



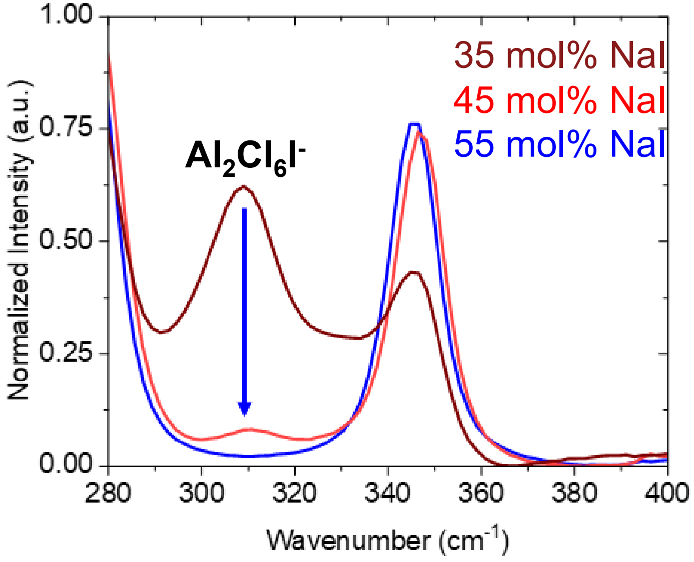
Extensive materials characterization of the NaSICON material and salt-exposed surface (XRD, SEM, EDS, XPS) *revealed no significant changes*, except for a decrease in Na^+ content at the near surface (<10 nm).

A.M. Maraschky et al. Impact of Catholyte Lewis Acidity at the Molten Salt-NaSICON Interface in Low-Temperature Molten Sodium Batteries. (2022) J. Phys. Chem. C,*In Review*.

“Blockade” Lifted by Controlling Salt Speciation

- Using Raman spectroscopy, Lewis acidic dimeric species, such as $Al_2Cl_6I^-$, were identified in 45 mol% $NaI\text{-}AlCl_3$.
- Lewis acidic dimeric species were not observed under Lewis basic conditions (>50 mol% NaI).

Raman Spectroscopy of $NaI\text{-}AlCl_3$ Catholytes



A.M. Maraschky et al. Impact of Catholyte Lewis Acidity at the Molten Salt-NaSICON Interface in Low-Temperature Molten Sodium Batteries. (2022) J. Phys. Chem. C,*In Review*.

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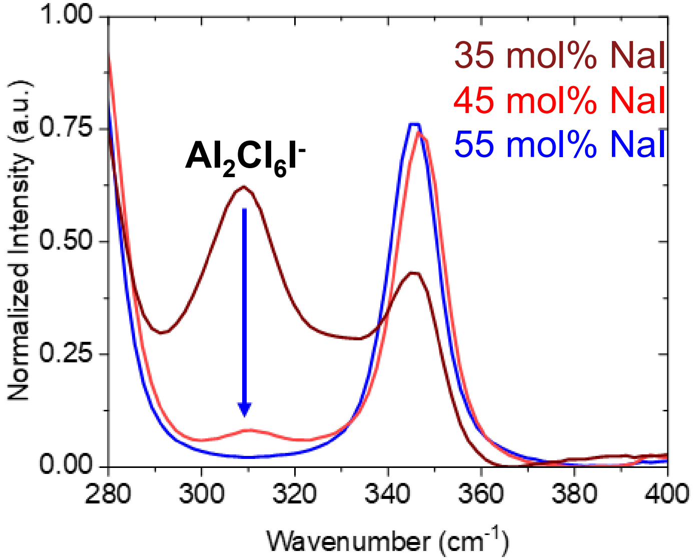
- Using Raman spectroscopy, Lewis acidic dimeric species, such as $Al_2Cl_6I^-$, were identified in 45 mol% NaI-$AlCl_3$.
- Lewis acidic dimeric species were not observed under Lewis basic conditions (>50 mol% NaI).
- Shifting to Lewis basic catholytes (>50mol% NaI) eliminated acidic dimeric species, stabilizing the NaSICON-catholyte interface and, in turn, battery performance.

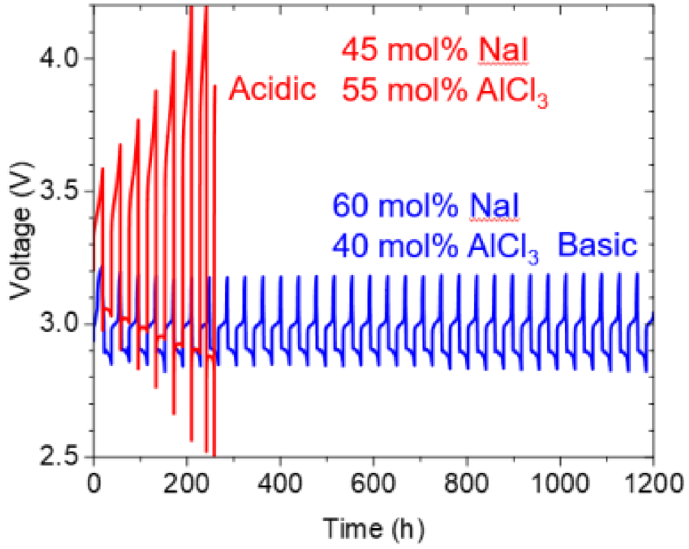
Raman Spectroscopy of NaI-$AlCl_3$ Catholytes



Eliminate acidic dimeric salt species.

Stabilize battery Performance.

Battery Cycling Profiles

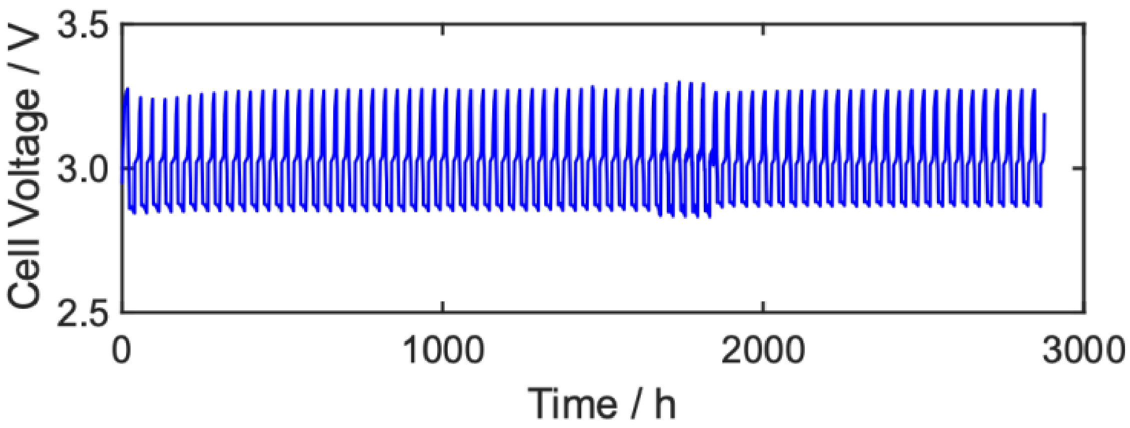


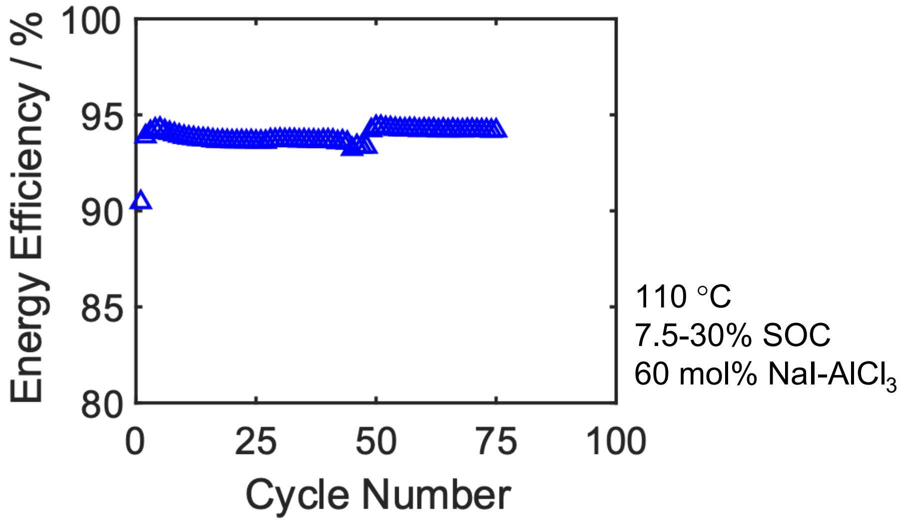
A.M. Maraschky et al. Impact of Catholyte Lewis Acidity at the Molten Salt-NaSICON Interface in Low-Temperature Molten Sodium Batteries. (2022) J. Phys. Chem. C, *In Review*.

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

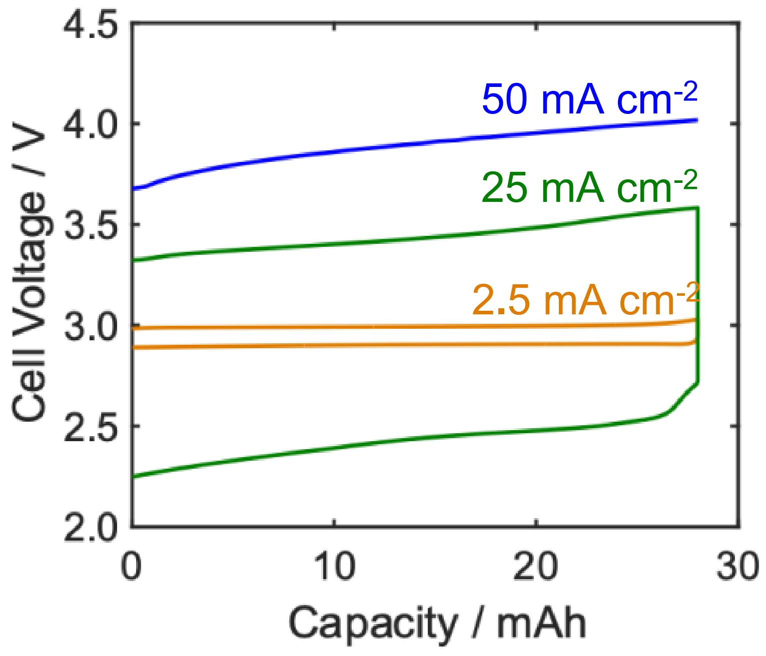


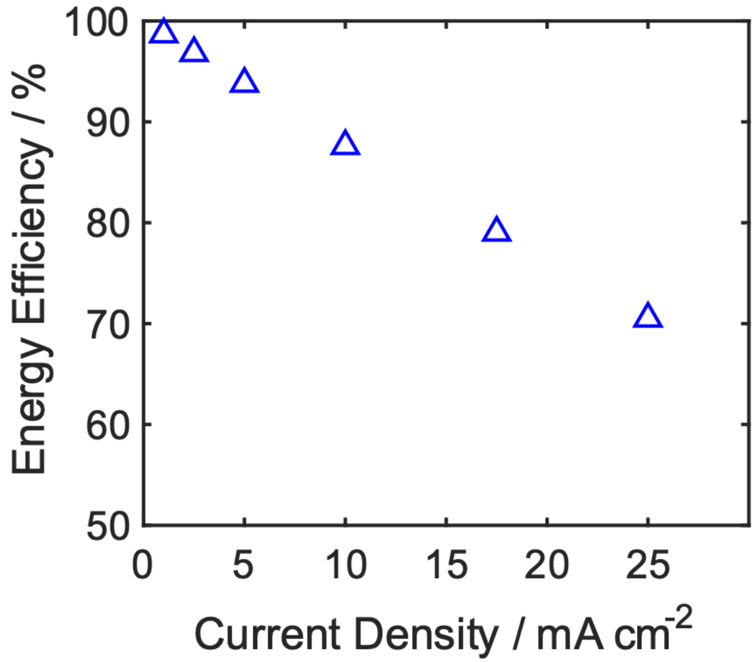


Low cost, Lewis basic NaI-$AlCl_3$ catholyte successfully cycled at 110 °C for >5 months.

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.



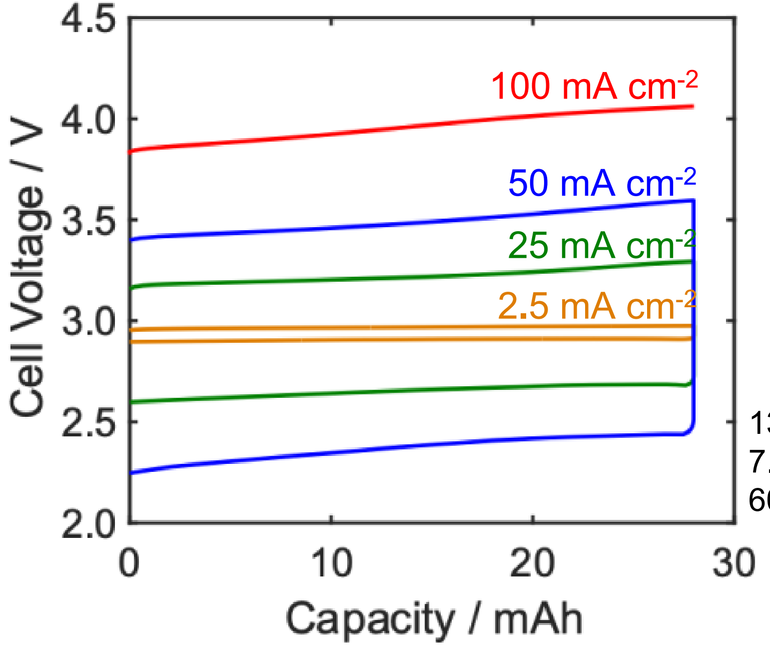


110 °C
7.5-17.5% SOC
60 mol% NaI-$AlCl_3$

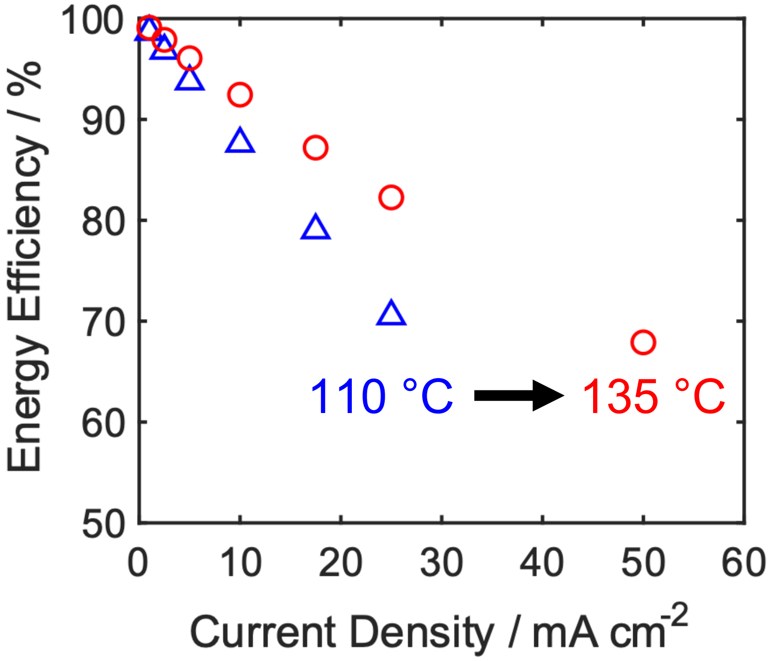
Charging currents up to 50 mA cm^{-2} were achieved at 110 °C.

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.



135 °C
7.5-17.5% SOC
60 mol% NaI-$AlCl_3$



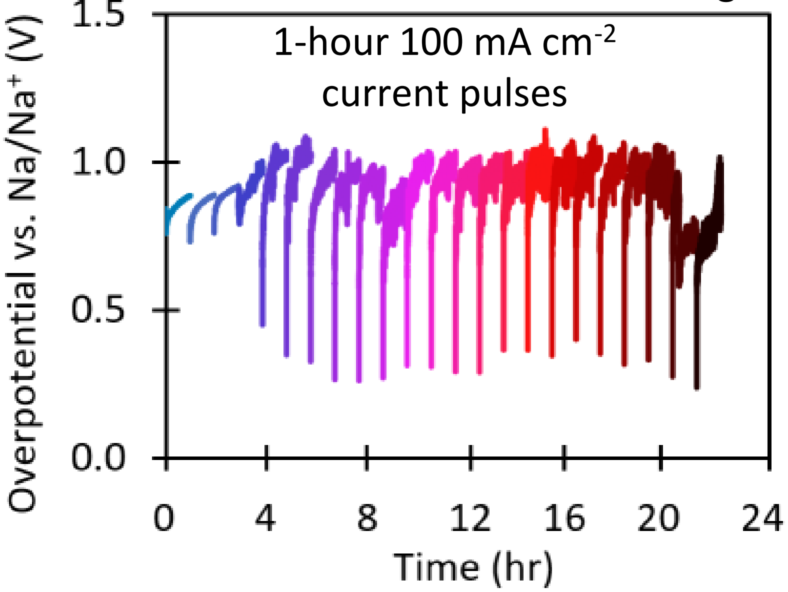
Charging currents of 100 mA cm^{-2} achieved at 135 °C.

We are approaching performance levels of higher temperature, commercialized ZEBRA batteries!

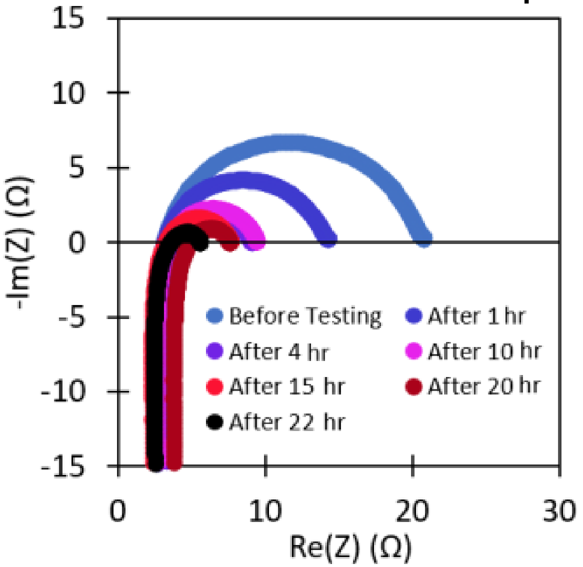
UKentucky: To 100 mA cm^{-2} and Beyond

- 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.

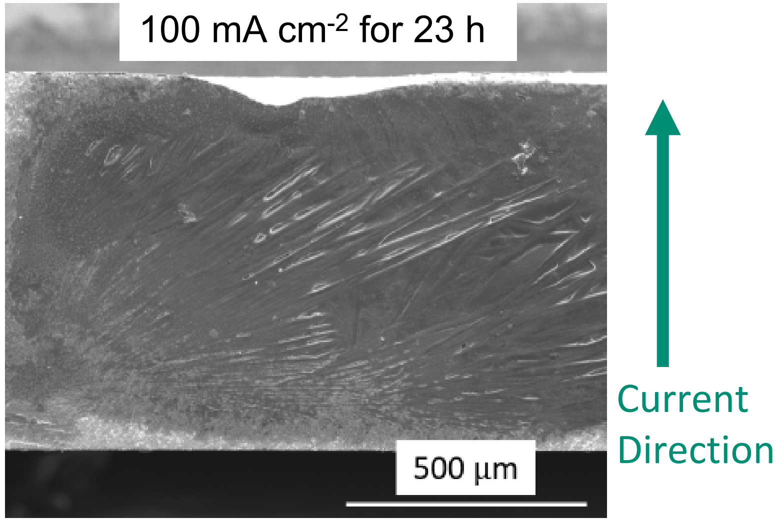
NaSICON without Sn coating shows Na-induced failure at low temperature



EIS between intervals



Post-mortem Imaging



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!

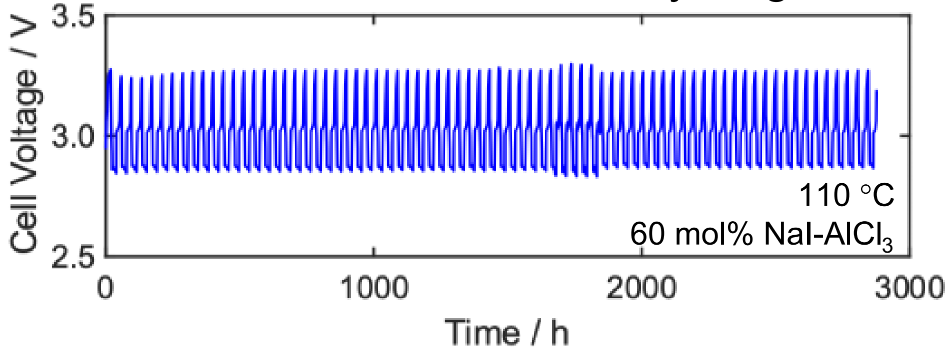
A Year of Progress: Science Enabling Performance

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 110C.
- 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}

>5 Months Stable Cycling



New 3-Electrode Interface Isolating Tester

Path Forward: Science Enabling Performance

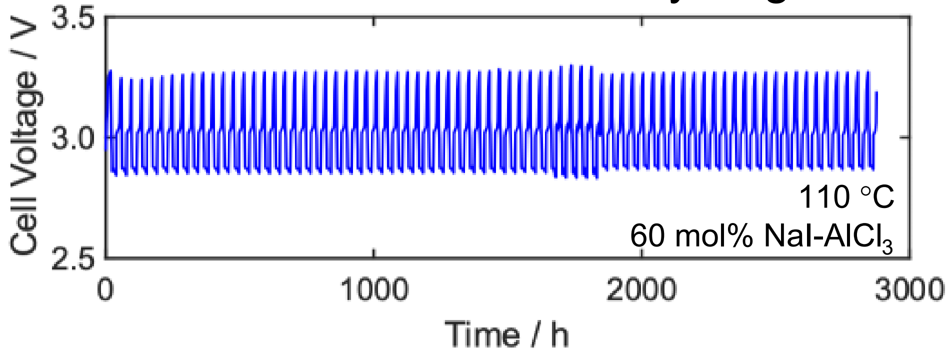
Next year we will increase current density on discharge, targeting >80% energy efficiency at even higher energy densities. We will achieve this by:

- 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

>5 Months Stable Cycling



New 3-Electrode Interface Isolating Tester

Accomplishments – Publications and Patents

Publications

- 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.org/10.1007/s10853-021-06562-1
- R.Y. Lee, S.J. Percival, and L.J. Small. Electrochemical Modeling of Iodide Oxidation in Metal-Halide Molten Salts. *Journal of the Electrochemical Society* **168** (2021) 126511. Doi.org/10.1149/1945-7111/ac3e7a
- 2021 paper named one of most influential in *Cell Reports Physical Science*. 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. Doi.org/10.1016/j.xcrp.2021.100489
- A.M. Maraschky, M.L. Meyerson, S.J. Percival, S. Meserole, J.N. Williard, A.S. Peretti, M.M. Gross, L.J. Small, E.D. Spoerke, Impact of Catholyte Lewis Acidity at the Molten Salt-NaSICON Interface in Low-Temperature Molten Sodium Batteries. (2022) *J. Phys. Chem. C.* (*Invited submission to Esther Sans Takeuchi Festschrift*) *In Review*.
- A.M. Maraschky, M.L. Meyerson, S.J. Percival, A.S. Peretti, E.D. Spoerke, L.J. Small. Tailoring Electrode Materials for Iodide/Triiodide Redox in Low-Temperature Molten Sodium Batteries. (2022) *In Preparation.*

Patents

- A.M. Maraschky, M.L. Meyerson, S.J. Percival, E.D. Spoerke, L.J. Small. Bi-material Electrode for Molten Sodium Battery. Sandia Technical Advance.
- E.D. Spoerke, S.J. Percival, and L.J. Small. *Molten Inorganic Electrolytes for Low Temperature Sodium Batteries*. US Patent No. 11,258,096 B2. Feb 22, 2022.

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.
- E.D. Spoerke Co-Chair with Dr. Imre Gyuk: "Energy Storage Symposium" at TechConnect World Innovation Conference & Expo 2021, Washington, D.C., October 18-21, 2021.
- E.D. Spoerke Co-Chair with Dr. Imre Gyuk: "Energy Storage Symposium" at TechConnect World Innovation Conference & Expo 2022, Washington, D.C., June 13-15, 2022.
- E.D. Spoerke Co-organizer for "Large Scale Energy Storage" Symposium, 241st Electrochemical Society Meeting, Vancouver, BC, Canada, May

Accomplishments – Presentations

Invited Presentations

- E.D. Spoerke, M.M. Gross, A.S. Peretti, S.J. Percival, R. Lee, J. Lamb, M. Rodriguez, L.J. Small. “Developing ‘Really Cool’ Low Temperature Molten Sodium Batteries.” TechConnect World Innovation Conference & Expo. Washington, D.C., Oct. 18-20, 2021.
- E.D. Spoerke. “Long-Duration Energy Storage: Emerging Technologies and Applications.” 13th Annual IEEE Energy Conversion Congress & Expo. Virtual Meeting. Oct. 10-14, 2021.
- E.D. Spoerke, M.M. Gross, A.S. Peretti, S.J. Percival, R. Lee, J. Lamb, M. Rodriguez, L.J. Small. “Materials Chemistry in *Battery* Energy Storage: A Key to Unlocking Our “Potential” Energy Future.” Fall Chemical & Materials Engineering Department Seminar at University of Kentucky, Sept. 22, 2021.
- M. M. Gross, S. J. Percival, R.Y. Lee, A.S. Peretti, M.A. Rodriguez, J. Lamb, E.D. Spoerke, and L.J. Small. “Development of a High-Voltage, Low Temperature Molten Sodium Battery.” Technical Presentation to Ambri Corp. Sept 20, 2021.
- E.D. Spoerke, M.M. Gross, A.S. Peretti, S.J. Percival, R. Lee, J. Lamb, M. Rodriguez, L.J. Small. “Advancing the Promise of Low-Temperature Molten Sodium Batteries.” *5th International Symposium on Materials for Energy Storage and Conversion.* Virtual. Sept 15, 2021.
- E.D. Spoerke. Materials Chemistry in Large-Scale Energy Storage: A Key to Unlocking our “Potential” Energy Future. Spring 2022 Department of Materials Science and Engineering Colloquium (Virtual) at The Ohio State University. January 28, 2022.
- A.M. Maraschky, R.Y. Lee, M.L. Meyerson, M.M. Gross, S.J. Percival, A.S. Peretti, E.D. Spoerke, L.J. Small. “Low-Temperature Molten Sodium Batteries for Large-Scale Storage: Fundamental Studies of Metal Halide Catholyte and Cathode Materials.” 241st Electrochemical Society Meeting, Vancouver, CA, 5/29/2022.
- A.M. Maraschky, M.L. Meyerson, S.J. Percival, D. Lowry, A.M. Peretti, M.M. Gross, E.D. Spoerke, L.J. Small. “Impact of Current Collector Material and Catholyte Lewis Acidity in Low-Temperature Molten Sodium Batteries.” Presentation to Akolkar Group at Case Western Reserve University, Cleveland, OH, 8/19/2022.

Contributed Presentations

- L.J. Small, R.Y. Lee, S.J. Percival, M.M. Gross, A.S. Peretti, M.L. Meyerson, E.D. Spoerke. “Understanding Electrochemical Processes in Molten Salt Catholytes for Low-Temperature Molten Sodium Batteries.” Fall 2021 Materials Research Society Meeting, Boston, MA/Virtual. December, 2021.
- E.D. Spoerke M.M. Gross, M. Meyerson, L.J. Small, S.J. Percival. “Low Temperature Molten Sodium Batteries for Long-Duration Energy Storage.” Fall 2021 Materials Research Society Meeting, Boston, MA/Virtual. December, 2021.
- M. M. Gross, S. J. Percival, R.Y. Lee, A.S. Peretti, E.D. Spoerke, and L.J. Small. “Lower Temperature, Lower Cost Molten Sodium Batteries.” Fall 2021 Materials Research Society Meeting, Boston, MA/Virtual. December, 2021.
- R. Hill, M.M. Gross, A.S. Peretti, L.J. Small, E.D. Spoerke, Y.T. Cheng. “Structural and Mechanical Characterization of NASICON Solid Electrolytes Upon Cycling in Molten Sodium.” Fall 2021 Materials Research Society Meeting, Boston, MA/Virtual. December, 2021.
- S.J. Percival, R.Y. Lee, L.J. Small. ”Electrochemical Simulations of Molten Salt Catholytes Reveal Speciation can Surpass Kinetics for Iodide Oxidation Rates.” ACS 2022 Spring Meeting, San Diego, CA and Virtual March 2022.
- R. Hill, J. Hempel, A.S. Peretti, L.J. Small, E.D. Spoerke, Y.-T. Cheng. “Electro-chemo-mechanical Behavior of NaSICON Solid Electrolytes in Molten Sodium Batteries. University of Kentucky 2022 Materials and Chemical Engineering Symposium in Lexington, KY. May 5, 2022.
- A.M. Maraschky, R.Y. Lee, S.J. Percival, M.M. Gross, A.S. Peretti, E.D. Spoerke, L.J. Small. “Experimental and Modeling Studies of Metal Halide Catholyte and Cathode Materials to Enable Low-Temperature Molten Sodium Batteries.” 2022 Materials Research Society Spring Meeting, Honolulu, HI, May 2022.
- E.D. Spoerke, M.L. Meyerson, A.M. Maraschky, A.S. Peretti, S.J. Percival, M.M. Gross, R.Y. Lee, J. Lamb, L.J. Small, “Molten Salt-Based Batteries for Safe, Reliable, Long-Duration Energy Storage.” 2022 Materials Research Society Spring Meeting, Honolulu, HI, May 2022.
- R. Hill, Y-T. Cheng, J. Hempel, E.D. Spoerke, L.J. Small, M.M. Gross, A.S. Peretti, “Characterization of NaSICON Solid Electrolyte Exposed to Thermal and Electrochemical Cycling in Molten Sodium Environment.” 2022 Materials Research Society Spring Meeting, Honolulu, HI, May 2022

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ENERGY STORAGE PROGRAM

Questions?

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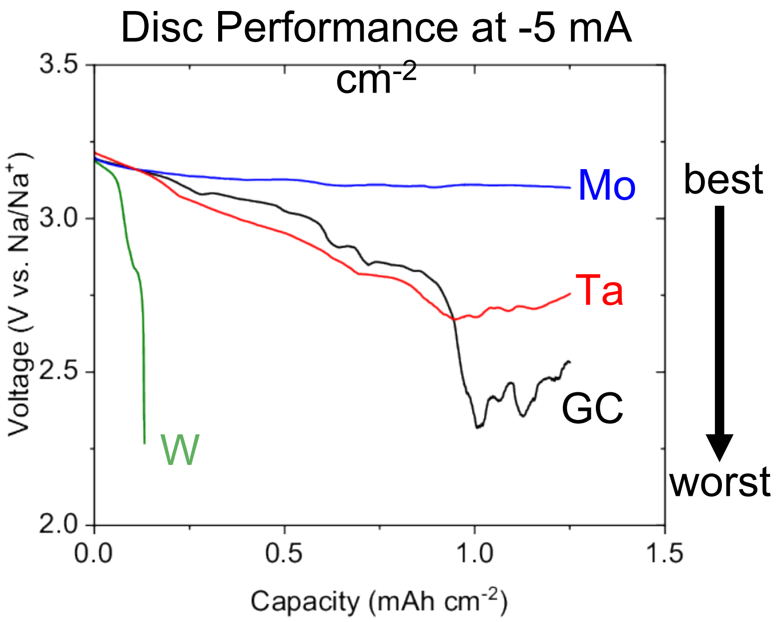
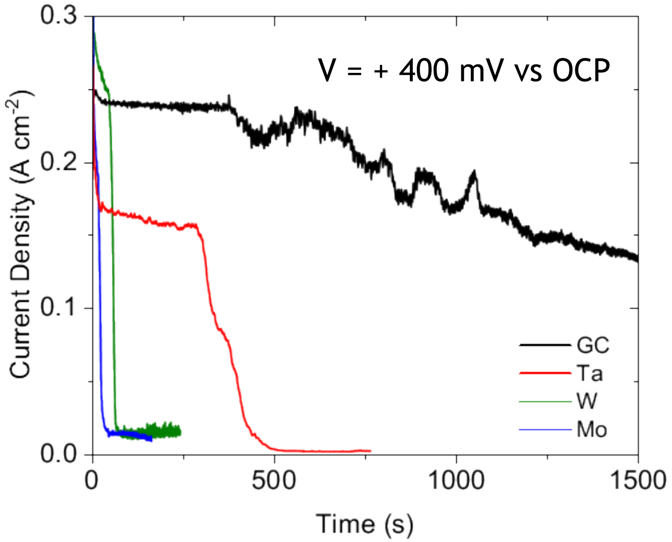
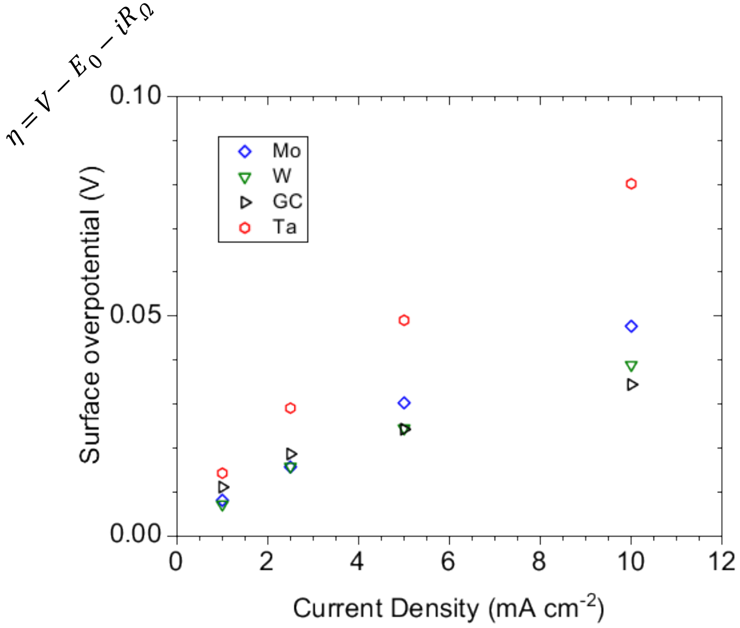
Backup Slide:

- Identified several candidate current collector materials – Mo, Ta, W, glassy carbon (GC), and graphite felt (GFD)
  - 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.

A.M. Maraschky et al. Tailoring Electrode Materials for Iodide/Triiodide Redox in Low-Temperature Molten Sodium Batteries. (2022)*In Preparation*.