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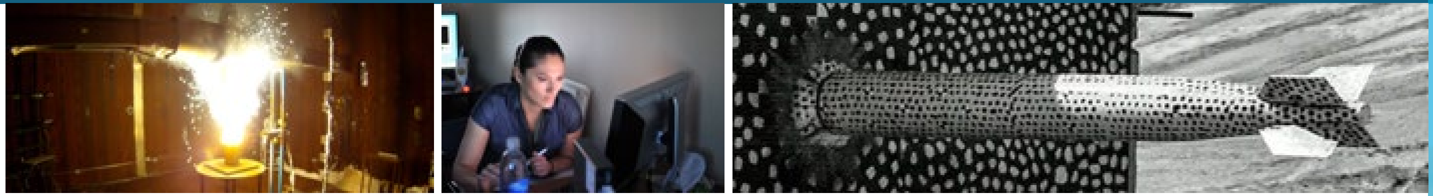
Low Temperature Molten Sodium Batteries



DOE Office of Electricity

Energy Storage Program Peer Review

Oct. 24-26, 2023

PRESENTED BY

Leo Small

Adam Maraschky, Melissa Meyerson, Stephen Percival, Amanda Peretti,
Ryan Hill, Y.-T. Cheng, Erik Spoerke

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

U.S. DEPARTMENT OF ENERGY

NNSA

SAND2023-10939C

Team

Sandia

Adam Maraschky
Melissa Meyerson
Stephen Percival
Amanda Peretti
Erik Spoerke
Leo Small

University of Kentucky

Prof. Y.T. Cheng
Ryan Hill (next)
"Shorting in Solid Electrolytes for Long Duration Sodium Batteries"

See Posters:

Stephen Percival
Molten Salt Speciation Affects Electrochemistry and Battery Cycling: Raman Spectroscopy and Modeling Analysis

Amanda Peretti
Current State of NaSICON for Molten Sodium Batteries

Leo Small
Low Temperature Molten Sodium Batteries

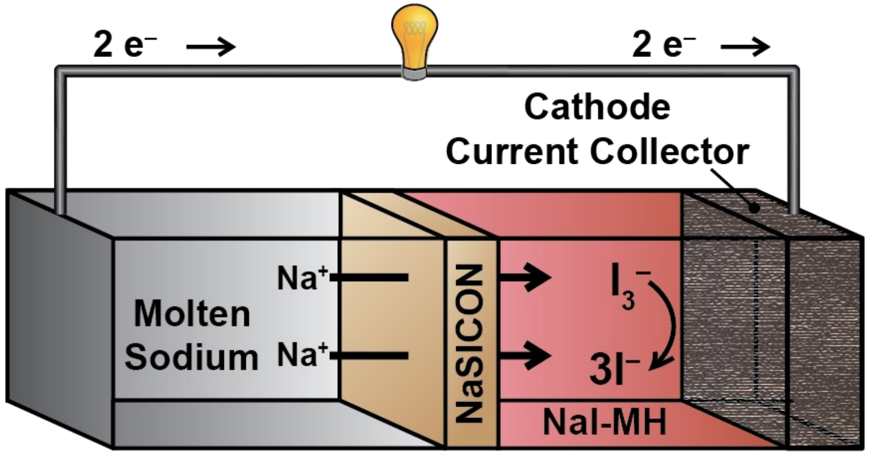
Acknowledgements (Sandia)
Will Bachman, Mia Blea, William Delmas, Philip Mantos, Steve Meserole, Zac Piontkowski, John Williard

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 350 °C (Na-S) and 250 °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:

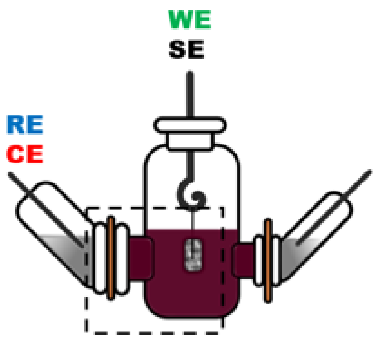
- Lower Cost
  - Plastic seals: below 150 °C, rubber o-rings can be used (<$0.1/each) vs. glass or metal seals.
  - Thinner and less expensive wiring materials
  - Less insulation
- Reliability
  - Lower temperatures → slower aging on all components
  - System level heat management not as extensive

20 kWh of each.
FZSoNick is a ZEBRA-style battery.
http://www.gridedge.com.au/sonick-battery.html

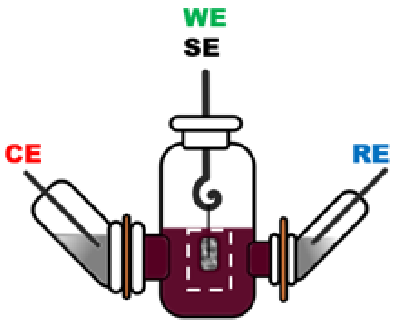
Battery chemistries from higher temperatures need to be reengineered to work at low temperatures.

FY22: Na^+ “Blockade” Identified at the NaSICON-Catholyte Interface

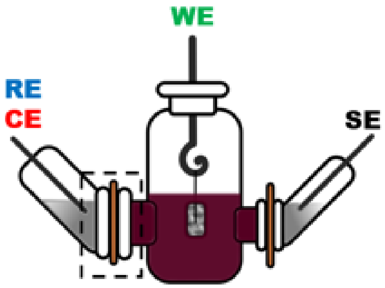
- Steady increase in battery overpotentials observed during cycling
- Custom 3-electrode cell developed to isolate individual interfaces present in a sodium battery
  - Increase in impedance identified at the NaSICON-catholyte interface
- Extensive materials characterization of the NaSICON surface (XRD, SEM, EDS, XPS) revealed no significant changes, except for a decrease in Na^+ content at the near surface (<10 nm).



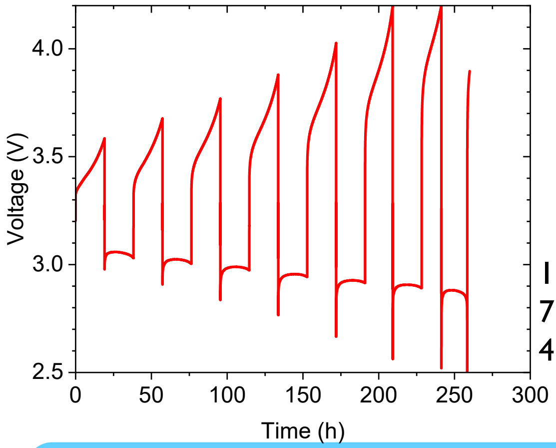
Full Cell



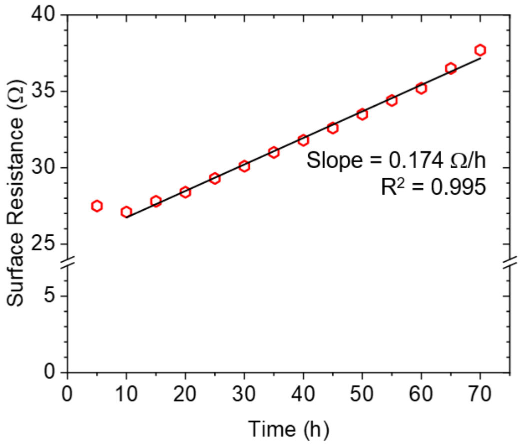
Graphite Felt Only



NaSICON Only



110 °C
7.5-37.5% SOC
45 mol% $NaI\text{-}AlCl_3$



Isolated NaSICON-catholyte interfacial resistance over time at open circuit

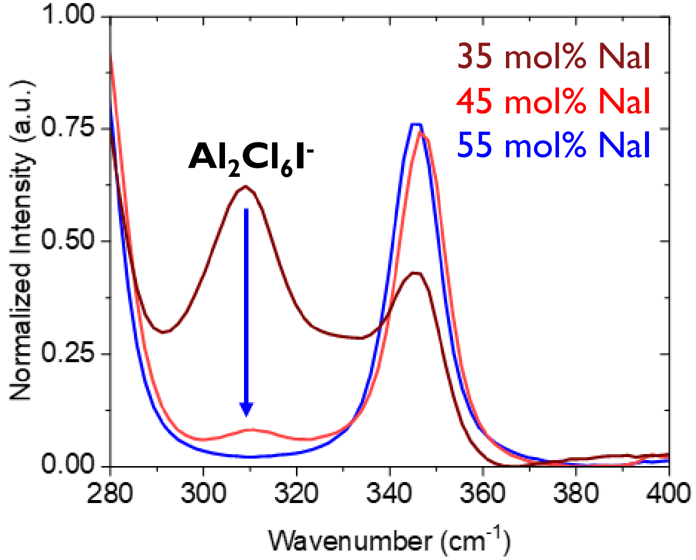
A significant, steadily increasing interfacial impedance was identified at the NaSICON-catholyte interface.

A.M. Maraschky et al. *J. Phys. Chem. C*, **127** (2023) 1293-1302. ***Invited Paper***.

FY22: "Blockade" Lifted by Controlling Salt Speciation

- 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 (>50 mol% NaI) eliminated acidic dimeric species, stabilizing the NaSICON-catholyte interface and, in turn, battery performance.

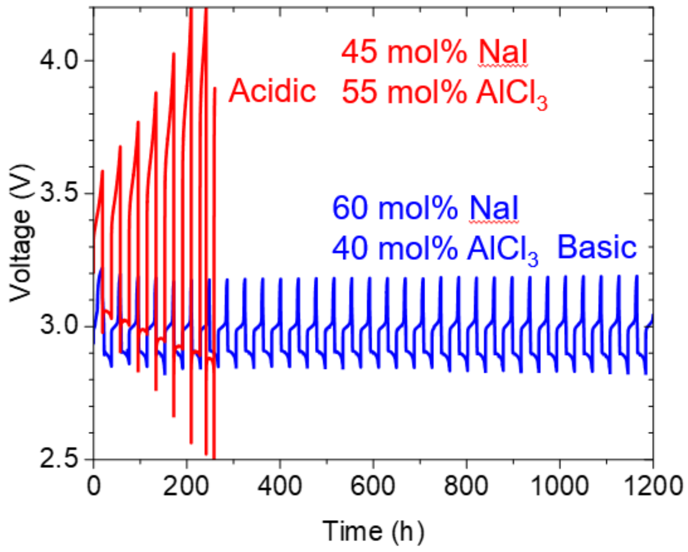
Raman Spectroscopy of NaI-$AlCl_3$ Catholytes



Eliminate acidic dimeric salt species.

Stabilize battery performance.

Battery Cycling Profiles



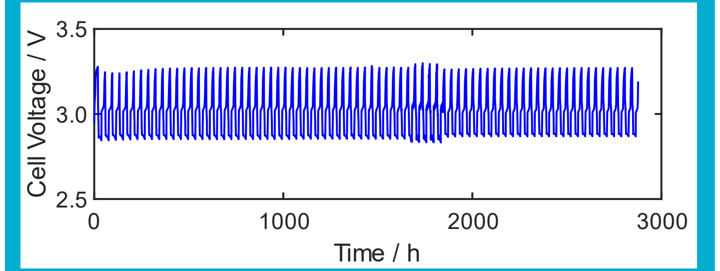
A.M. Maraschky et al. *J. Phys. Chem. C,* **127** (2023) 1293-1302. ***Invited Paper***.

Ingredients for a Low-Cost Battery

Stability

>1 month cycling

$AlCl_3$-NaI Battery 110 °C



FY22

>6 months cycling[1]

2.5 mA cm^{-2}

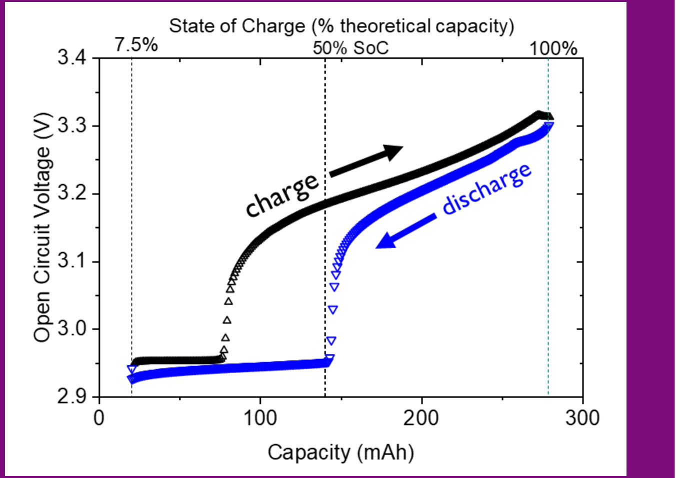
23% depth of discharge

>93% energy efficiency

polymer seals

Deep Discharge

>50% theoretical



FY23

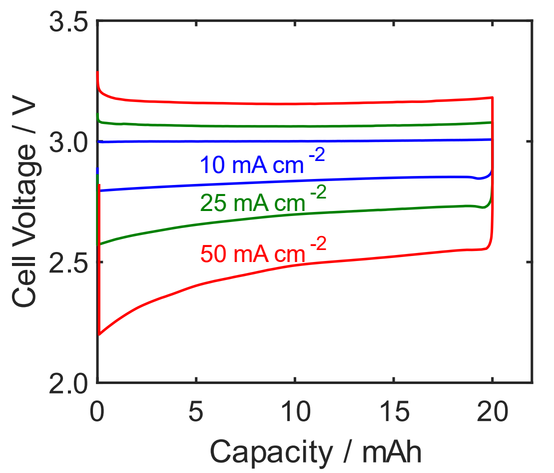
92.5% theoretical capacity accessed!

2.5 mA cm^{-2}

197 Wh kg^{-1}

High Current

>50 mA cm^{-2}



FY23

Up to 250 mA cm^{-2} charge

50 mA cm^{-2} discharge

Up to 100x increase in charge current!

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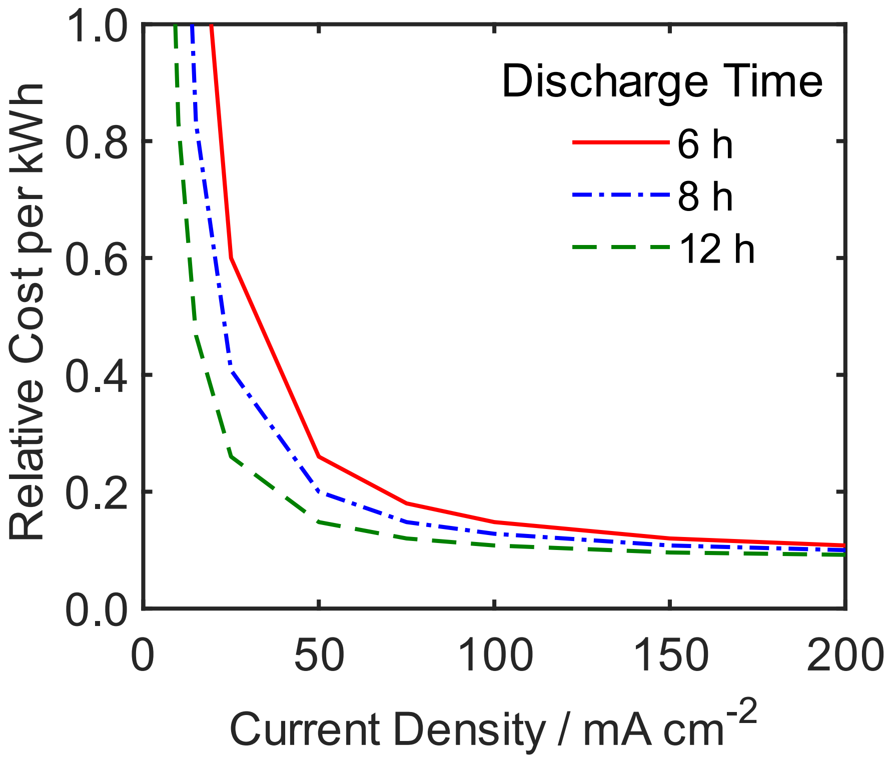
[1] A.M. Maraschky et al. *J. Phys. Chem. C*, **127** (2023) 1293-1302. ***Invited Paper***.

Higher Current Drives Down Cell Costs

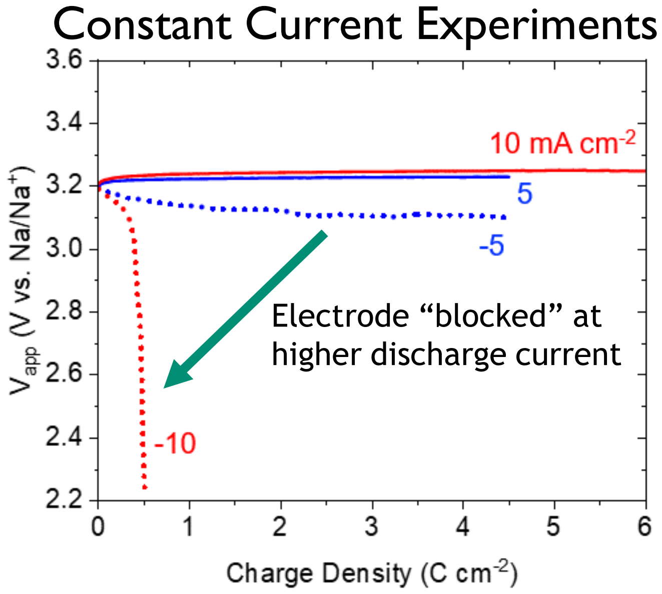


- Present applications for molten sodium batteries require 6-12 hour discharge times.
- The higher the current density, the more active material needed in each cell, resulting in larger electrodes.
- A cost model was developed using parameterized cell geometries and raw material costs for all cell components.
- Results show a decrease in cost per kWh as the electrodes are thickened, increasing the relative fraction of active material to inactive material (seals, housing, wiring, etc.)

Higher current density needed for lower costs!
Goal: ≥50 mA cm^{-2}, ≥80% Energy Efficiency

Cathode Limitations on Discharge

- At sustained high current on discharge, battery "turns off."
- Leveraged 3-electrode cell to isolate battery interfaces to understand the problem.
- We inferred that NaI precipitation, from reduction of I_3^- containing species, can accumulate and block the electrode on discharge at high current.
- Solutions
  - Scientific – identification of additives to enhance NaI solubility
  - Engineering – optimization of electrode surface area to NaSICON surface area



110 °C
7.5% SOC
Mo disk electrode
45 mol% NaI-$AlCl_3$

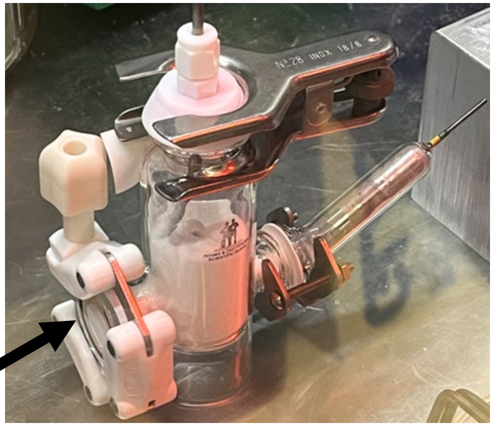
Electrode blocking is reversible and can be managed through scientific or engineering strategies.

A.M. Maraschky et al. *J. Electrochem. Soc.*, **170** (2023) 066504.
S.J. Percival et al. *J. Electrochem. Soc.*, **165** (2018) A3531-A3536.

In-Situ Raman to Monitor Salt Speciation

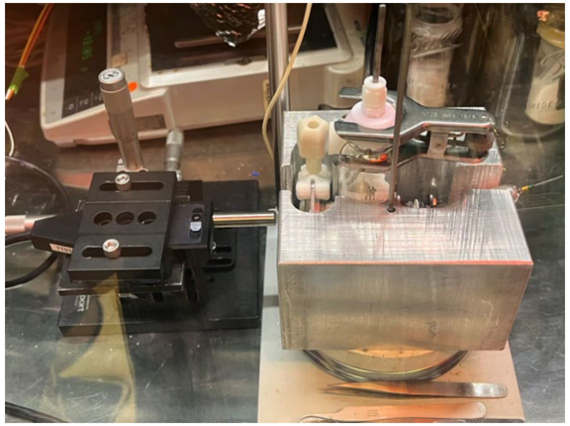
- System developed in argon glovebox to interrogate real-time behavior of both the bulk molten salt and the electrode-salt interface.
- Will enhance understanding of how additives influence salt speciation and NaI solubility at the electrode-salt interface.

Test Cell

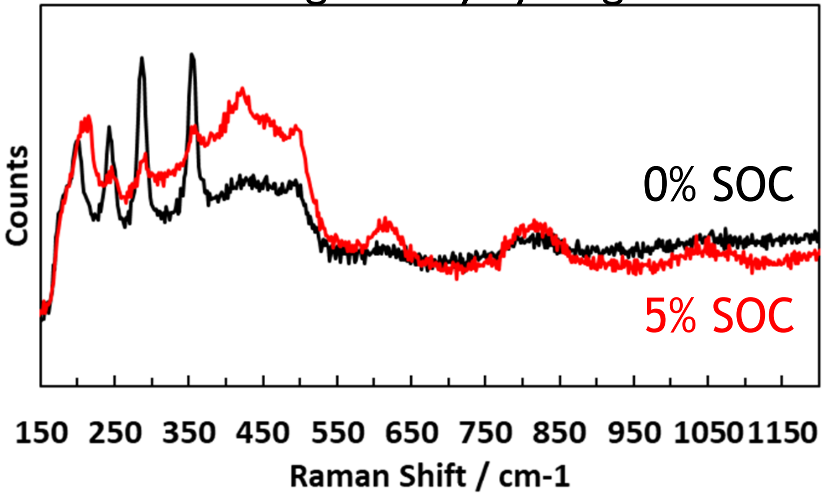


Quartz Window

Test Cell in Heating Mantle



Initial data show significant changes during battery cycling.



110 °C

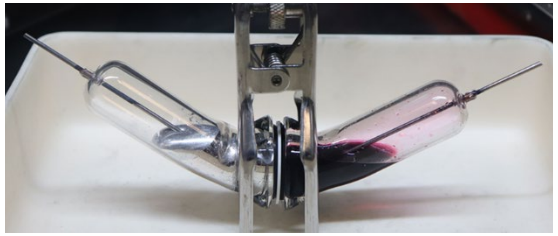
55 mol% NaI-$AlCl_3$

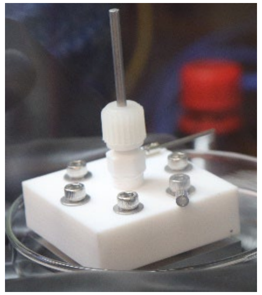
In-situ Raman system will improve understanding of molten salt speciation at the electrode-salt interface.

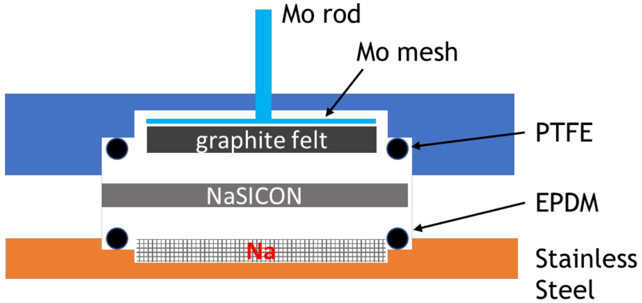
See poster by Stephen Percival for more details!

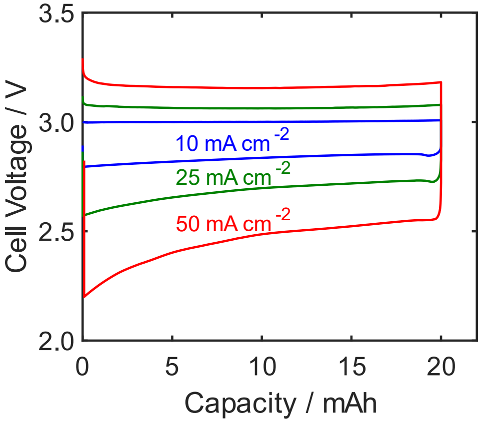
Cell Redesign Enables Increased Current Density

- The cell was redesigned to align the graphite felt parallel to NaSICON and uniformly compress the felt against the NaSICON
- Cell resistance decreased 2×, energy efficiency increased +10%, rate capability increased up to 50 mA cm^{-2}



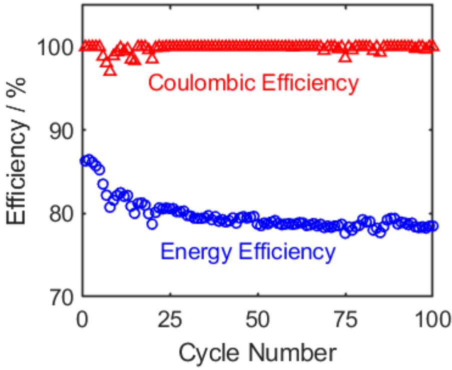






Cycling at up to 50 mA cm^{-2}.

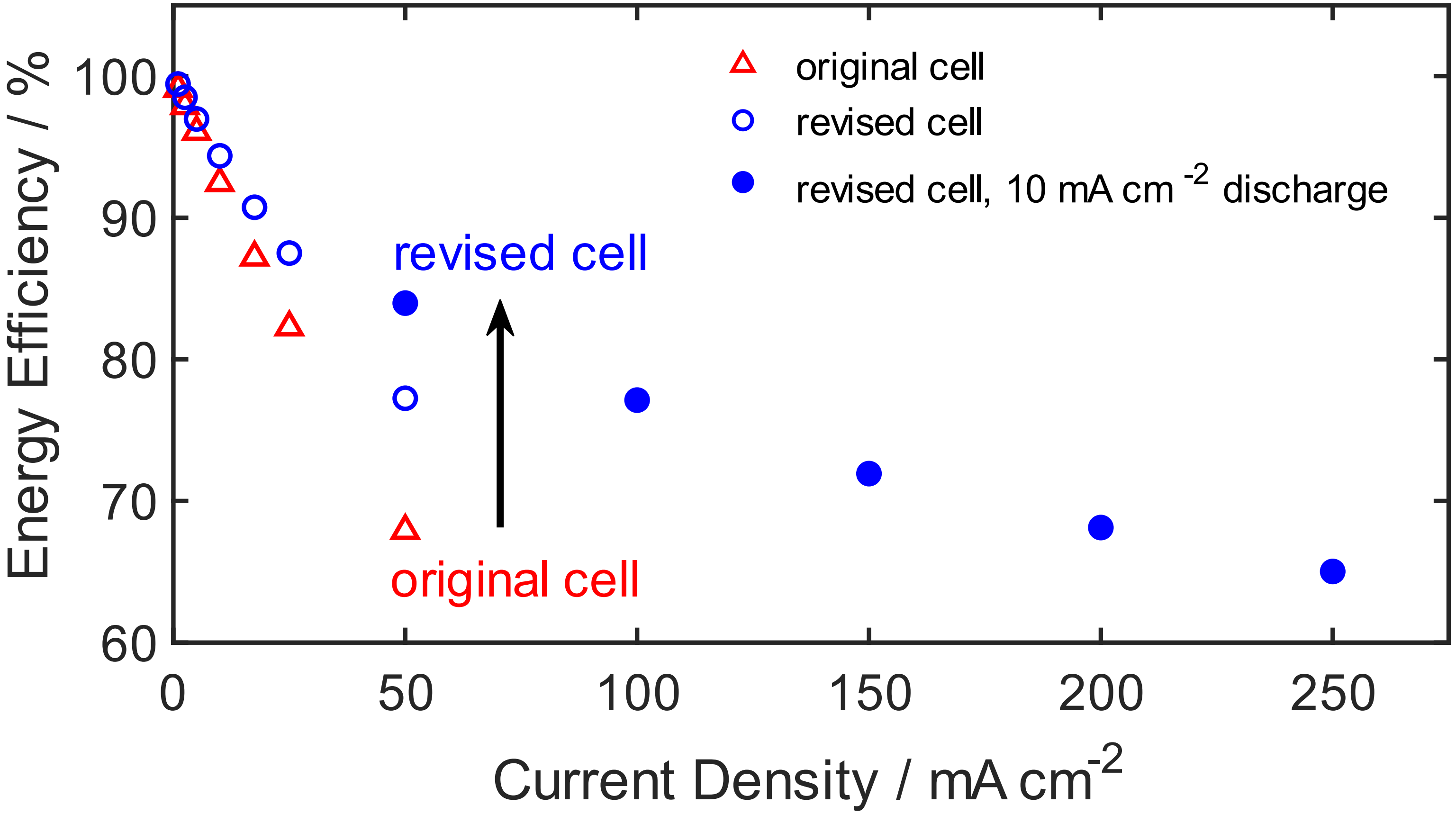
High Efficiency Cycling at 20× Higher Current!



135 °C
50 mA cm^{-2} charge
10 mA cm^{-2} discharge
30% DoD
60 mol% NaI-AlCl$_3$

20× Improvement in current density. ≥50 mA cm^{-2} goal achieved!

Cell Redesign: Charging Currents Increased 100×

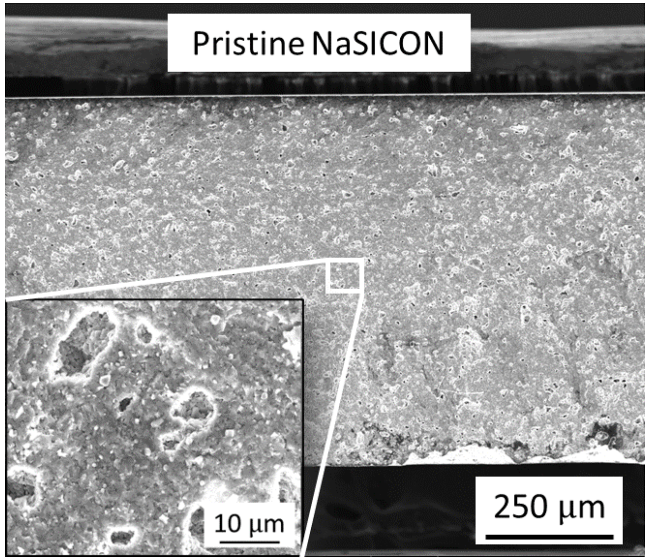


135 °C
10% DoD
60 mol% NaI-$AlCl_3$

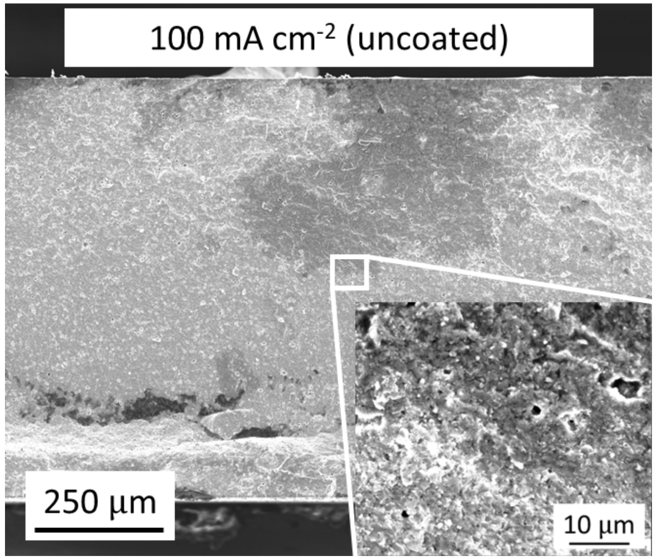
Charging Currents up to 250 mA cm^{-2} enabled by new cell design.

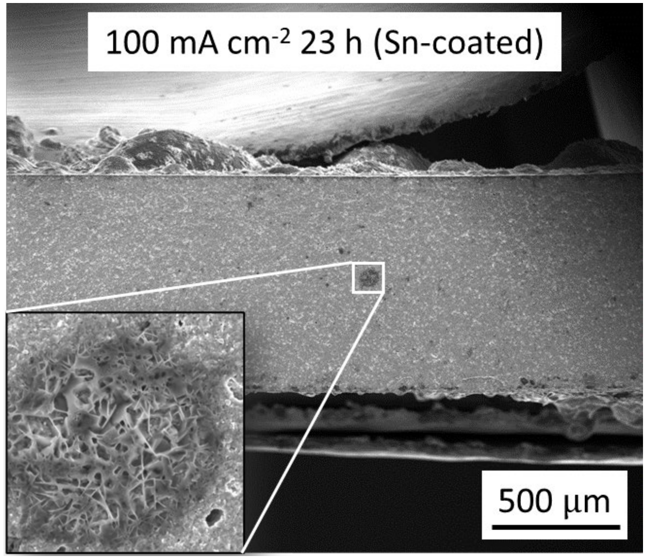
University of Kentucky: Limiting Current?

- As we push to >100 mA cm^{-2}, 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, with engineered interfaces.



Galvanostatic 100 mA cm^{-2} for 23 h at 110 °C





At high currents and low temperatures, interfacial engineering, such as our Sn coating, plays a key role in preventing Na-induced failure of NaSICON.

R.C. Hill et al. (2023) *In Review*.

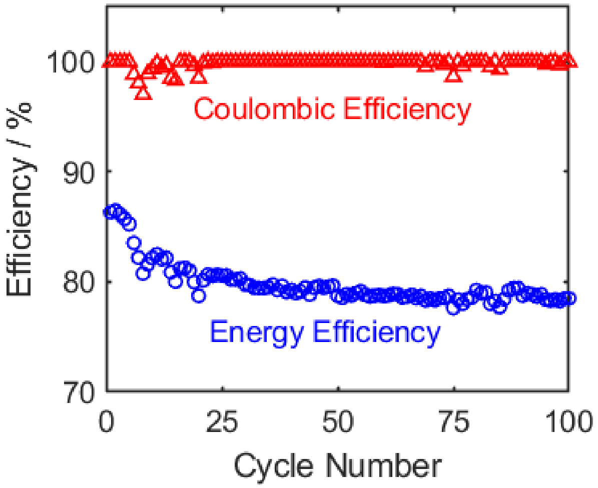
See talk by Ryan Hill for more details!

Path Forward

This past year we…

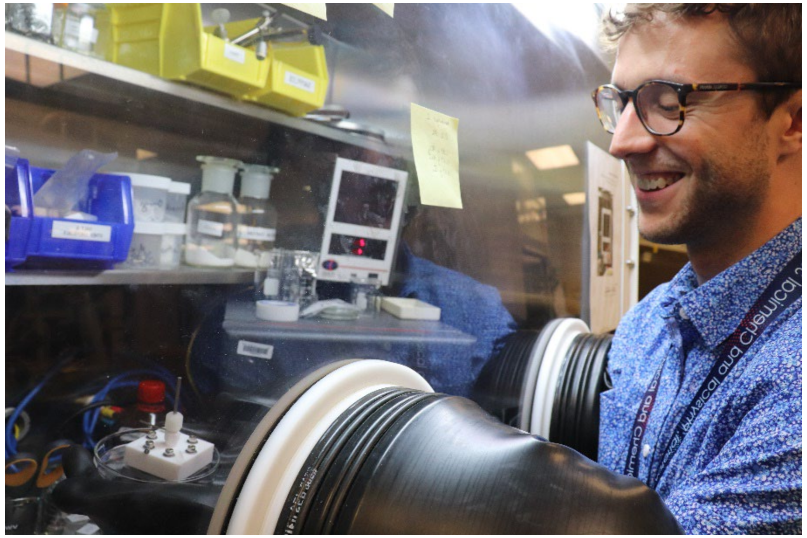
- demonstrated that >92.5% theoretical capacity of our NaI-$AlCl_3$ catholyte is accessible at low rates.
- identified that ≥50 mA cm^{-2} is ideal for cost-competitiveness.
- redesigned the cell to increase cycling current 20×, with charging currents up to 250 mA cm^{-2}.
- stood up in-situ Raman system to better understand catholyte speciation.

Cycling at 135 °C
50 mA cm^{-2} charging



Next year we will…

- increase discharge current density performance by
  - optimizing cell design.
  - identifying additives to improve NaI solubility.
  - leveraging the in-situ Raman cell to understand speciation and intermediates limiting discharge.
- demonstrate increased current density at deep discharge.
- improve NaSICON processibility for new form factors.



Accomplishments – Publications, Patents, Awards

Publications

- A.M. Maraschky, M.L. Meyerson, S.J. Percival, D.R. Lowry, S. Meserole, J.N. Williard, A.S. Peretti, M. Gross, L.J. Small, and E.D. Spoerke. "Impact of Catholyte Lewis Acidity at the Molten Salt-NaSICON Interface in Low-Temperature Molten Sodium Batteries." *Journal of Physical Chemistry C*. **127** (2023) 1293-1302.
- R.C. Hill, A.S. Peretti, L.J. Small, E.D. Spoerke, Y.-T. Cheng, "Molten Sodium Penetration in NaSICON Electrolytes at 0.1 A/cm^2." *ACS Applied Energy Materials*. **6** (2023) 2515-2523.
- A.M. Maraschky, S.J. Percival, R.Y Lee, M.L. Meyerson, A.S. Peretti, E.D. Spoerke, and L.J. Small. Electrode Blocking Due to Redox Reactions in Aluminum Chloride-Sodium Iodide Molten Salts. *Journal of the Electrochemical Society* **170** (2023) 066504.
- R.C. Hill, A.S. Peretti, A.M. Maraschky, L.J. Small, E.D. Spoerke, and Y.-T. Cheng. Can a Coating Mitigate Molten Na Dendrite Growth in NaSICON under High Current Density? (2023) *In Review*.
- R.C. Hill, A.S. Peretti, L.J. Small, E.D. Spoerke, and Y.-T. Cheng. Shorting at Long Duration: Critical Capacities in Battery Solid Electrolytes. (2023) *In Preparation*.

Patents

- **Patent Issued:** E.D. Spoerke, M.M. Gross, S.J. Percival, M.A. Rodriguez, and L.J. Small. Sodium Electrochemical Interfaces with NaSICON-Type Ceramics. US Patent No. 11,545,723 B2. Jan. 3, 2023.
- **Patent Issued:** J.A. Bock, E.D. Spoerke, H.J. Brown-Shaklee, and L.J. Small. Solution-Assisted Densification of NaSICON Ceramics. US Patent No. 11,600856 B2. Mar 7, 2023.
- **Patent Application:** A.M. Maraschky, M.L. Meyerson, S.J. Percival, E.D. Spoerke, L.J. Small. Bi-material Electrode for Molten Sodium Batteries. US Application # 63/420,515. Oct. 28, 2022.
- **CIP Patent Application**: E.D. Spoerke, M.M. Gross, S.J. Percival, and L.J. Small. Method to Improve Sodium Electrochemical Interfaces of Sodium Ion-Conducting Ceramics. US Application # 18/092,373. Jan 2, 2023.
- **Patent Application:** A.M. Maraschky, M.L. Meyerson, S.J. Percival, E.D. Spoerke, L.J. Small. Passive Gas Phase Cell Balancing Scheme for Molten Salt Batteries. US Application # 63/449,093. Mar. 1, 2023.

Awards

- S. Percival "Excellence in Review" Award from I&ECR (ACS)

Accomplishments – Presentations

Invited Presentations and Symposium Chairs

- E.D. Spoerke, L.J. Small, M. Gross, S.J. Percival, A.S. Peretti, R. Lee, J. Lamb. "Toward Large-Scale, Long Duration Energy Storage: Big Materials Challenges for a Big Energy Future. 2022 Dept. of Materials Science and Engineering Colloquium at University of Texas at Dallas. Feb 10, 2023.
- E.D. Spoerke Co-chaired the "Ion-Conducting Ceramics" symposium at the Electronic Materials and Applications 2023 Conference. Jan 17-20, Orlando, FL.
- E.D. Spoerke Co-chaired the "Energy Storage: Beyond Lithium" symposium at TechConnect World Innovation Conference & Expo. June 19-21, 2023. Washington, D.C.

Contributed Presentations

- A.M. Maraschky, M.L. Meyerson, S.J. Percival, A.S. Peretti, M.S. Gross, E.D. Spoerke, L.J. Small. "Optimizing the Current Collector for Sodium Iodide-Metal Halide Catholytes in Low-Temperature Molten Sodium Batteries." 242nd Electrochemical Society Meeting, Atlanta, GA, 10/9-13/2022.
- E.D. Spoerke, A.M. Maraschky, M.L. Meyerson, A.S. Peretti, S.J. Percival, M.S. Gross, S. Meserole, D. Lowry, R.Y. Lee, L.J. Small, "Exploring a Battery Worth Its Salt: Ceramic-Salt Interactions in a Low-Temperature Molten Sodium Battery." 32nd Rio Grande Symposium on Advanced Materials, Albuquerque, NM 10/24/2022.
- E.D. Spoerke, A.M. Maraschky, M.L. Meyerson, A.S. Peretti, S.J. Percival, M.S. Gross, S. Meserole, D. Lowry, R.Y. Lee, L.J. Small, "Enabling Low-Cost Molten Sodium Batteries Through Engineered Catholyte-Separator Materials Chemistry." 2022 MRS Fall Meeting, Boston, MA, 11/27/2022 – 12/2/2022.
- E.D. Spoerke, A.M Maraschky, M. Meyerson, A. Peretti, S. Percial, M. Gross, S. Meserole, D. Lowry, and L. Small. "sTable Salt Batteries: Understanding Materials Challenges to NaSICON Ceramics in Low-Temperature Molten Sodium Batteries." Electronic Materials and Applications, 2023. Orlando, FL. Jan, 2023.
- A.M. Maraschky, M.L. Meyerson, S.J. Percival, A.S. Peretti, D. Lowry, S. Meserole, R.Y. Lee, J. Williard, E.D. Spoerke, L.J. Small, "Keep It Lewis-Basic: Stability of NaSICON Separators in $AlCl_3$-NaI Catholytes for Molten Sodium Batteries." TMS 2023, San Diego, CA. 3/20-23/2023.
- R.C. Hill, A.S. Peretti, A.M. Maraschky, L.J. Small, E.D. Spoerke, Y.T. Cheng. "Molten Sodium Penetration Through NaSICON Electrolytes Under High Current." Spring Materials Research Society Meeting. San Francisco, CA. 4/10-14//2023.
- E.D. Spoerke, M. Gross, A.S. Peretti, S.J. Percival, L.J. Small, Y.T. Cheng, R.C. Hill. "'Dirt Cheap' Energy Storage: Clay-Based Separators for Solid State Storage." Spring Materials Research Society Meeting. San Francisco, CA. 4/10-14//2023.
- A.M. Maraschky, M.L. Meyerson, S.J. Percival, A.S. Peretti, D. Lowry, S. Meserole, R.Y. Lee, J. Williard, E.D. Spoerke, L.J. Small, "Molten Sodium Batteries – Lewis Acidity of $AlCl_3$/NaI Catholyte Impedes NaSICON Interface." 243rd Electrochemical Society Meeting, Boston, MA. 5/28-6/2/2023.
- R.C. Hill, A.S. Peretti, A.M. Maraschky, L.J. Small, E.D. Spoerke, Y.T. Cheng. "Molten Sodium Penetration Through Solid-State NaSICON Electrolytes Under High Current." 243rd Electrochemical Society Meeting, Boston, MA. 5/28-6/2/2023.
- E.D. Spoerke, A.M Maraschky, M. Meyerson, A. Peretti, S. Percival, M. Gross, S. Meserole, D. Lowry, and L. Small. "Developing Batteries Worth Their Salt: Technical Advances for Cost Effective Molten Sodium Batteries." TechConnect World Innovation Conference and Expo 2023. Washington, D.C. June, 2023.

Acknowledgements

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OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

Questions?

Leo Small
ljsmall@sandia.gov