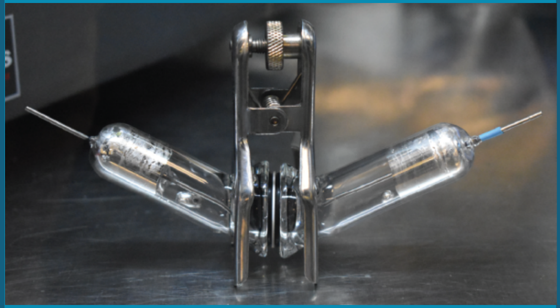
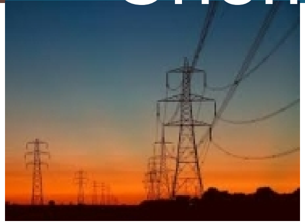
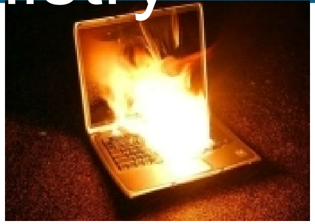
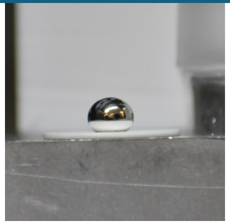
SAND2022-16259C

Sandia National Laboratories

Enabling Low-Cost Molten Sodium Batteries Through Engineered Catholyte-Separator Materials Chemistry

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Adam Maraschky
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Dan Lowry
Rose Lee
Leo J. Small

Materials Research Society Meeting, Fall 2022
Boston, MA
November 27-December 2, 2022

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This work at Sandia National Laboratories is supported by Dr. Imre Gyuk through the U.S. Department of Energy Office of Electricity.

U.S. DEPARTMENT OF ENERGY   NNSA National Nuclear Security Administration

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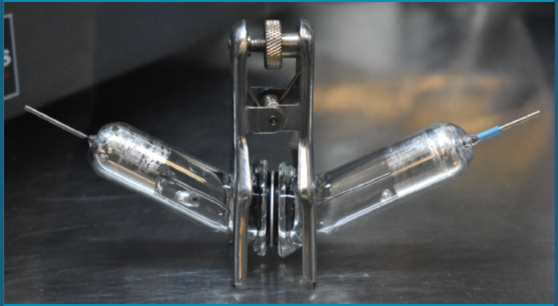
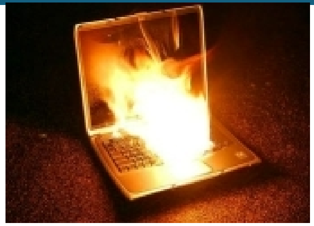
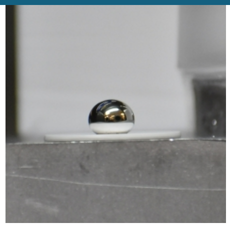
Creating a Battery Worth It's Salt!







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Low Temperature Molten Sodium (Na-NaI) Batteries: Not Your Grandmother's Sodium Battery!

Traditional Molten Sodium Batteries:

Na-S

$xS + 2Na \leftrightarrow Na_2Sx\ (3 \leq x \leq 5)$ E_{cell} ~2.08 V at 350°C

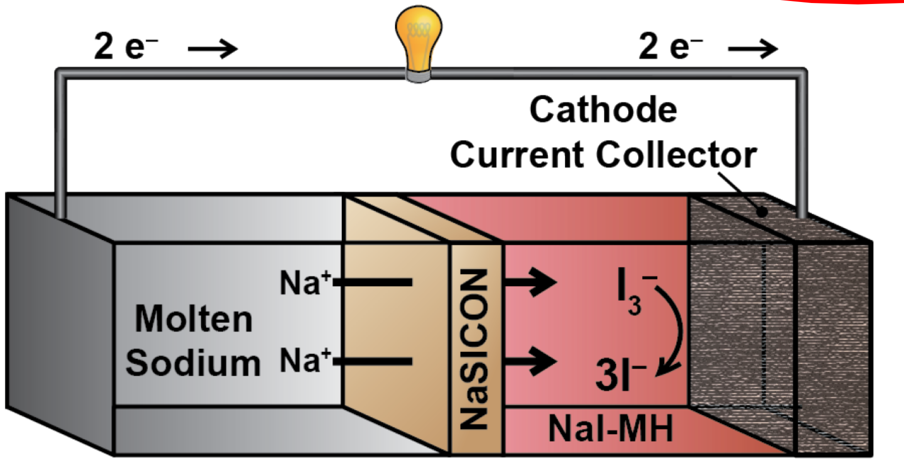
$Na\text{-}NiCl_2$

$NiCl_2\ (s) + 2Na\ (l) \leftrightarrow 2NaCl + Ni\ (s)$ E_{cell} ~2.58 V at 300°C

A Molten Sodium Battery at 110°C

- Molten Na anode (minimize dendrites?)
- Highly Na^+-conductive, physically robust separator (e.g., NaSICON)
- No complications from solid state electrodes

- 25 mol% NaI in MX_3 catholyte – no organic electrolytes
- Improved material lifetimes
  - *Lower cost reliability constraints*
- Lower cost materials
- Simplified heat management



Na-NaI battery:

$Na \rightarrow Na^+ + e^-$ $E^0 = 0V$

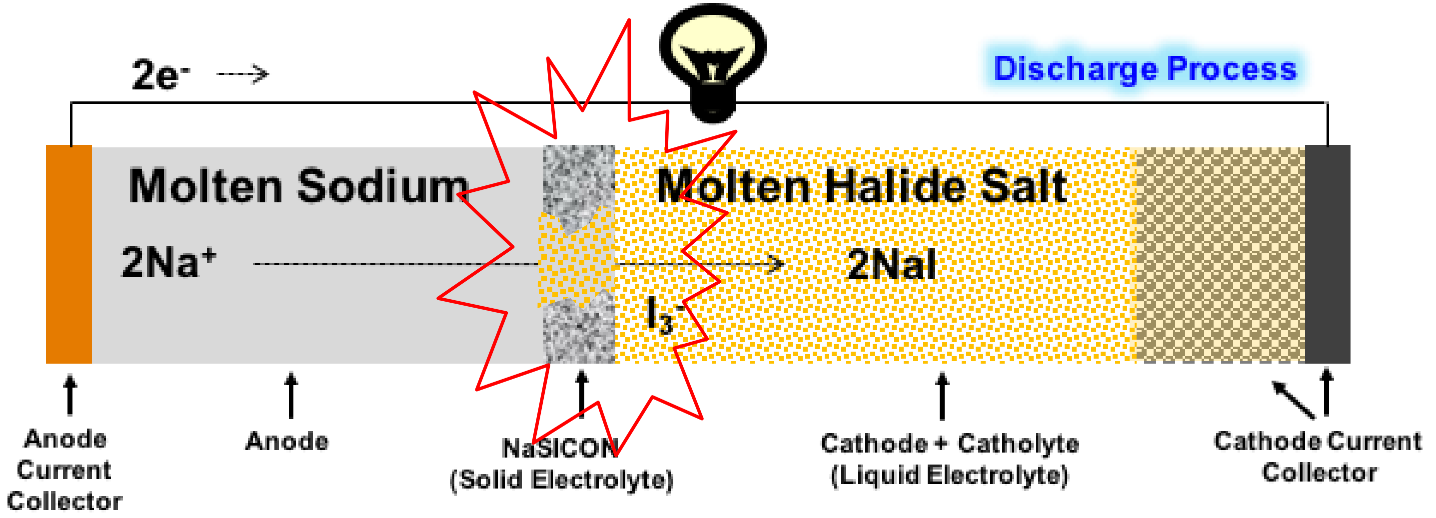
$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

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

Realizing a new, low temperature molten Na battery requires new battery materials and chemistries.

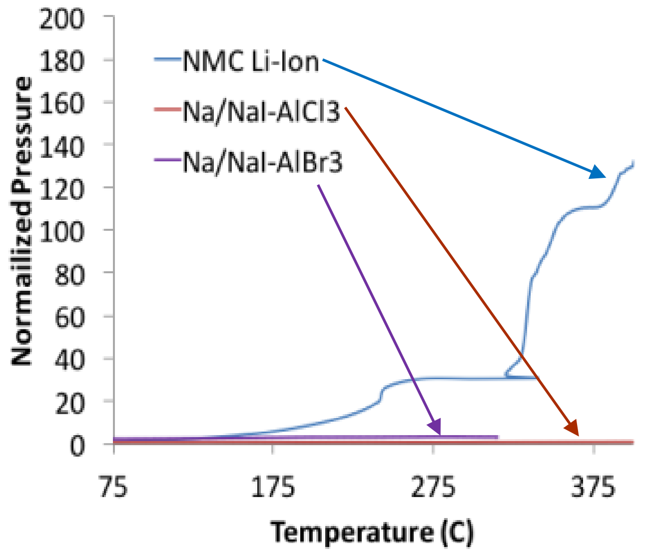
Small and Spoerke, *et al*. (2017) *J. Power Sources*. **360.** 569-574.

Inherent Safety of a Molten Salt Catholyte



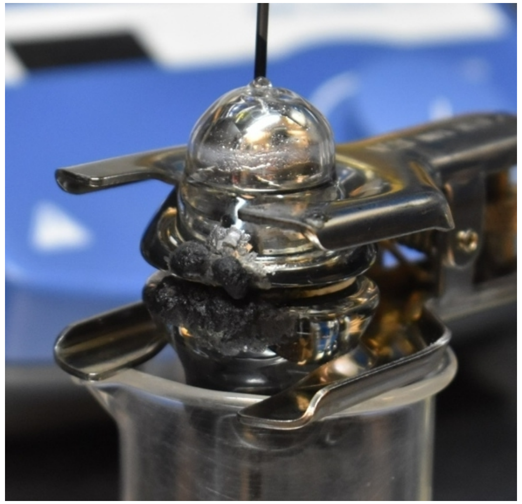
Simulating separator failure, metallic Na and NaI/AlX_3 were combined and heated.

Byproducts of reaction are aluminum metal and harmless sodium halide salts.



Accelerating rate calorimetry reveals that Na-NaI/AlX_3 mixtures exhibit:

1) *no significant exothermic behavior*
2) *no significant gas generation of pressurization*



Failed separator led to termination of battery, but no significant hazardous conditions.

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

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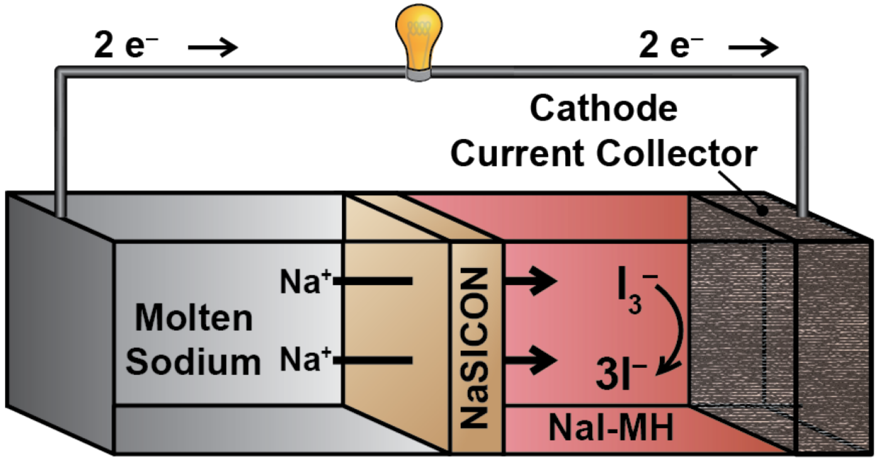

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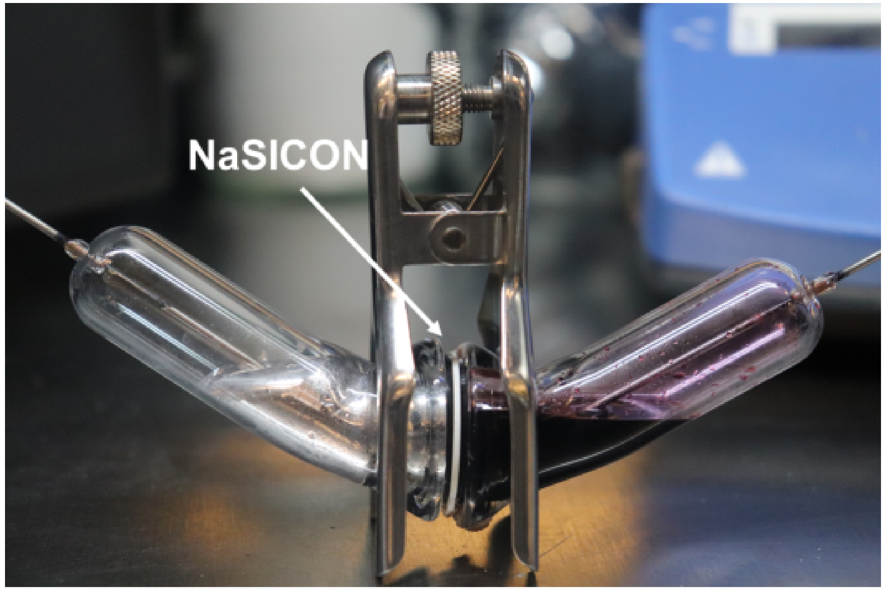
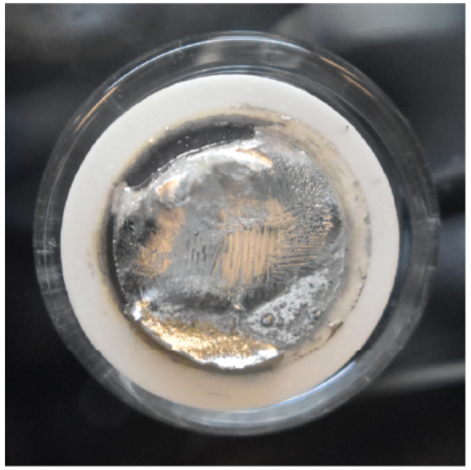
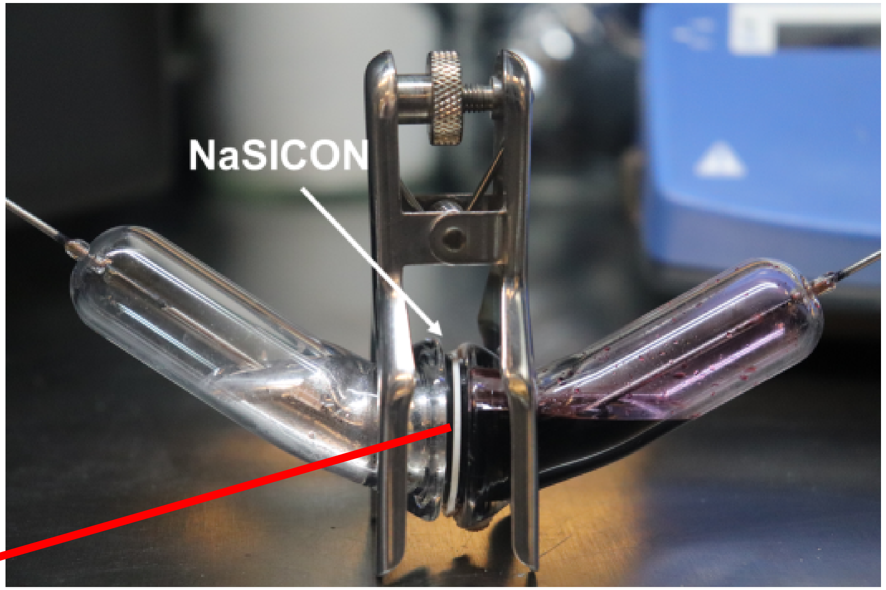
Inorganic, Molten-Salt Design is Robust!



Inorganic, Molten-Salt Design is Robust!

Strong Anodic Interfaces





Na strongly wets Sn-coated separator

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

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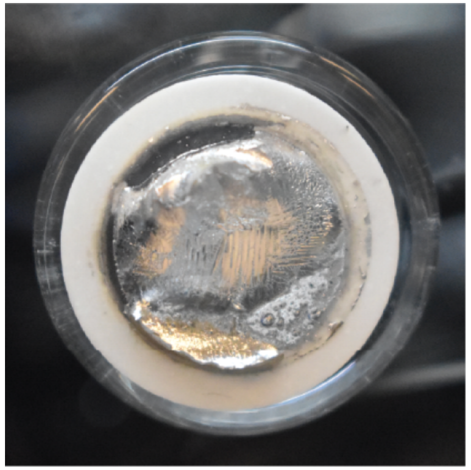

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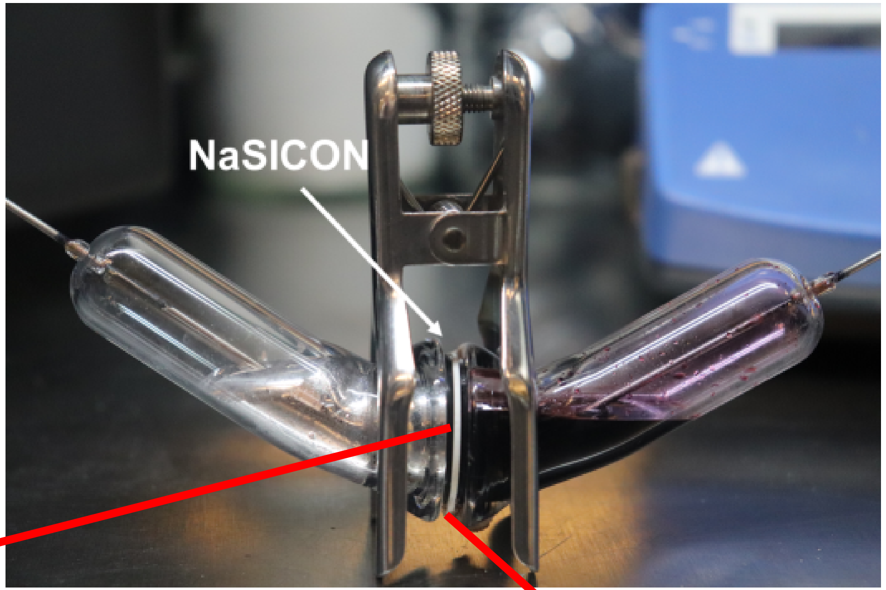
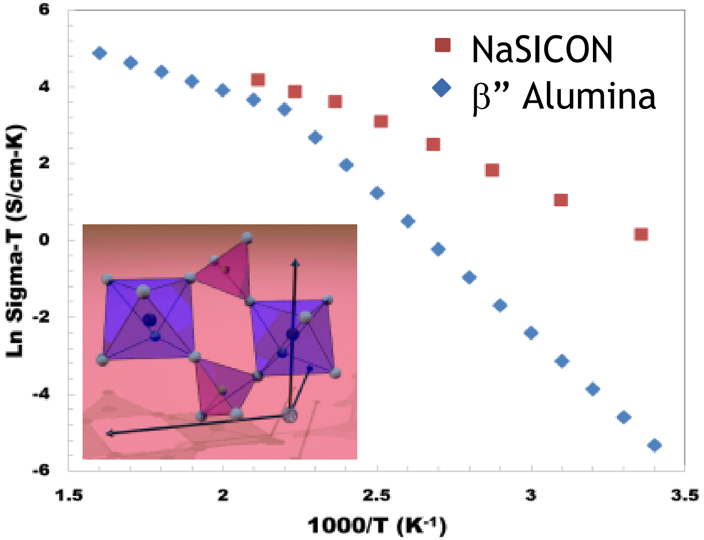


Stable, Highly Conductive NaSICON Separator



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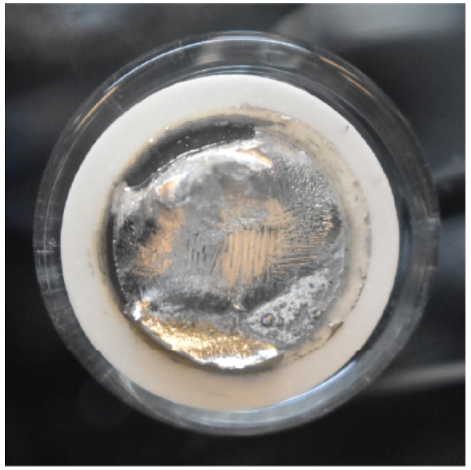

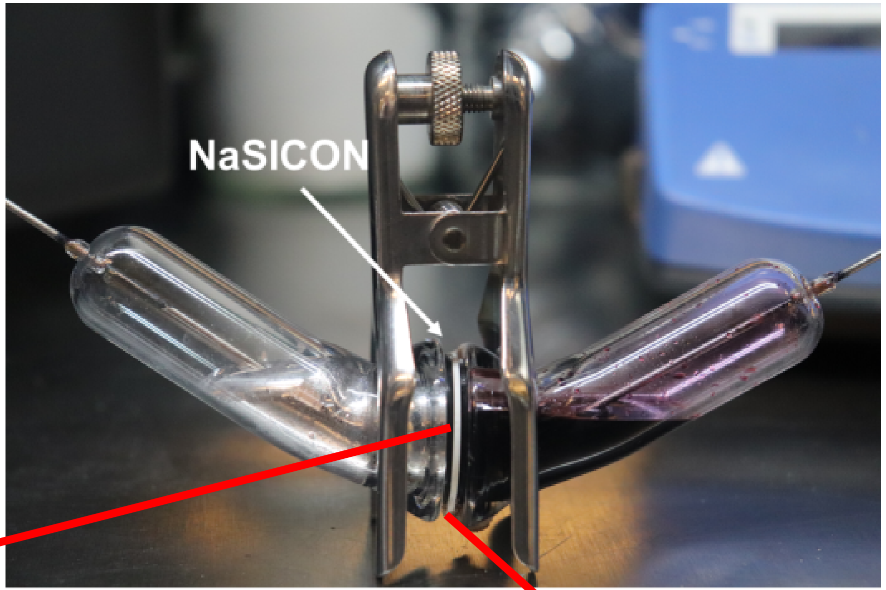

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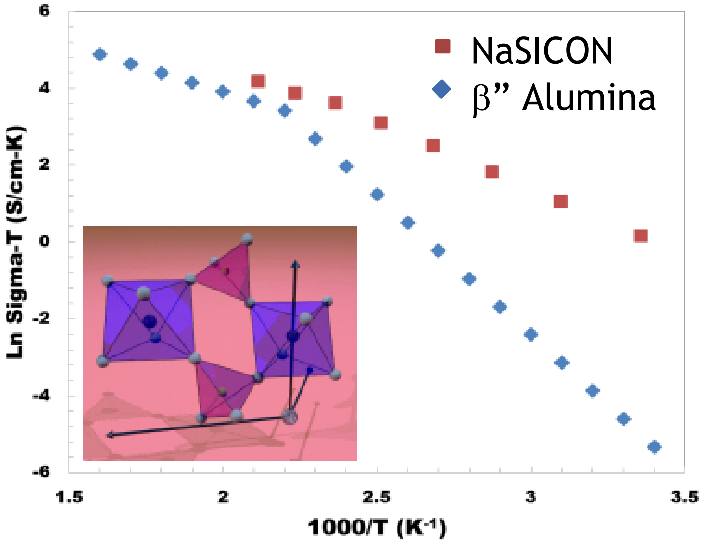
Stable, Highly Conductive NaSICON Separator

(Anodic Gasket: Inert rubber
Cathodic Gasket: Commercial Fluoropolymer)



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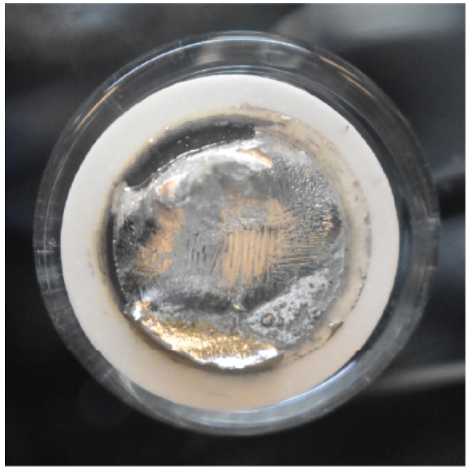

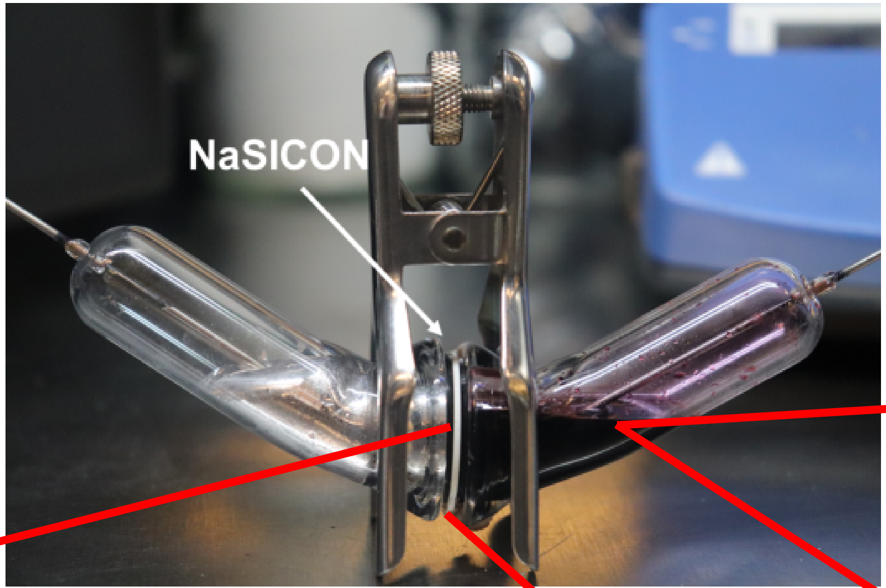

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Stable, Highly Conductive NaSICON Separator

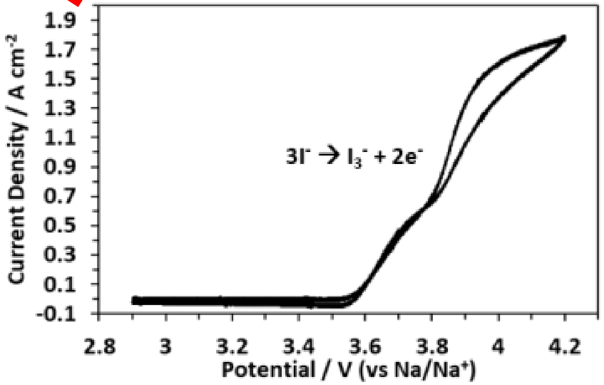
(Anodic Gasket: Inert rubber
Cathodic Gasket: Commercial Fluoropolymer)

Electroactive, Low Melting Temperature Molten Salt

NaI-$GaCl_3$ "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)



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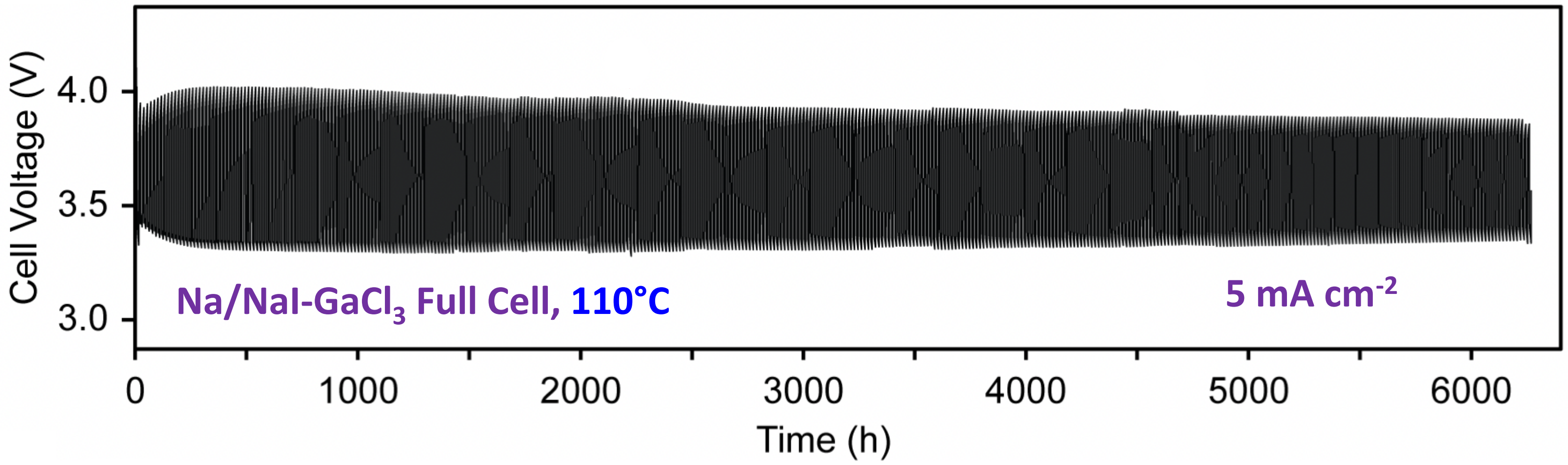
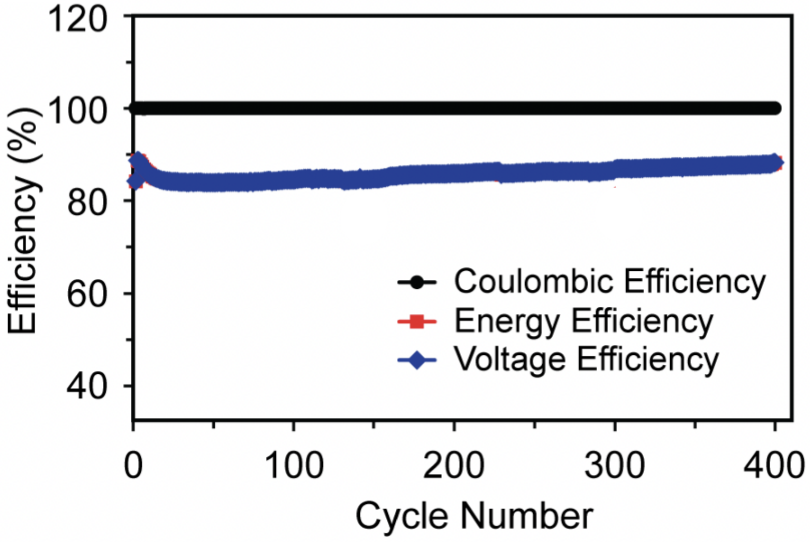
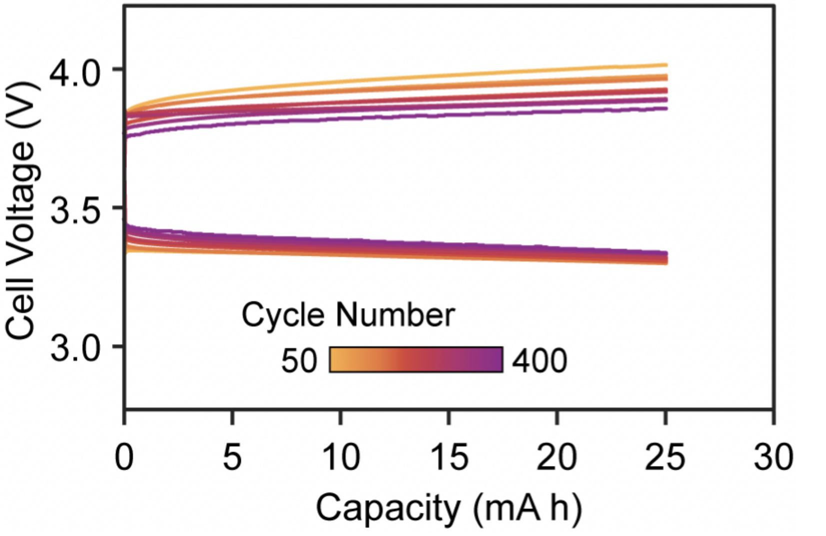
Robust Design Enables Robust Performance

Full Cells Demonstrated Unprecedented Performance at 110°C:

- Excellent, stable cycling for over 8 months!
- High voltage (3.6V)!







M.M. Gross, S.J. Percival, R.Y. Lee, A.S. Peretti, E.D. Spoerke, L.J. Small, *Cell Rep. Phys. Sci.,* 2 (2021) 100489

Robust Design Enables Robust Performance…at High Cost

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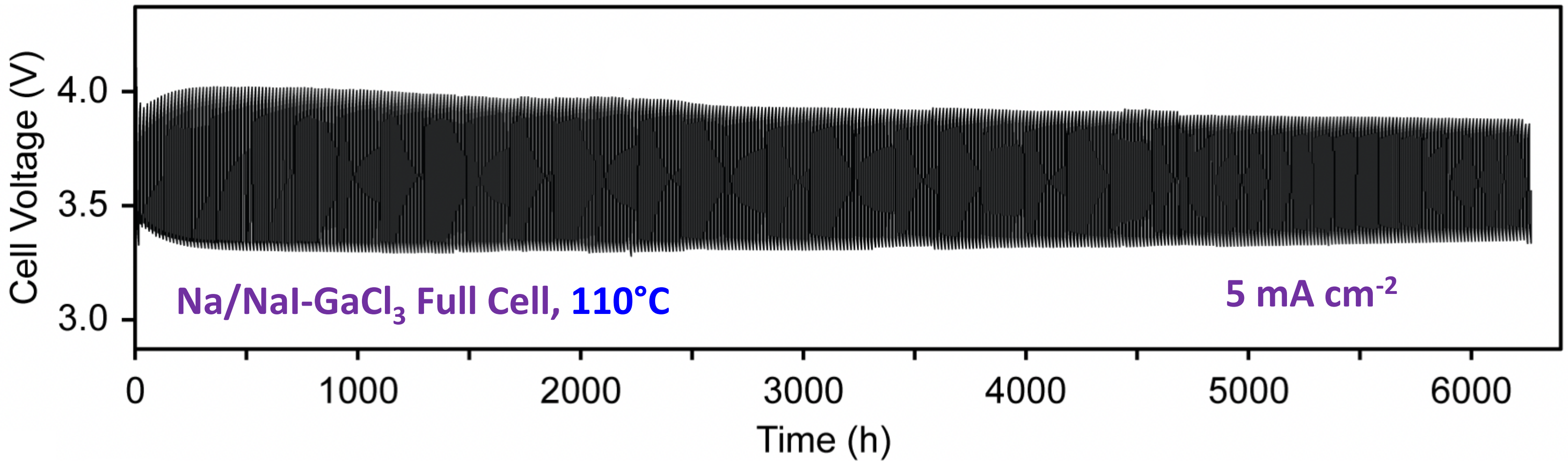

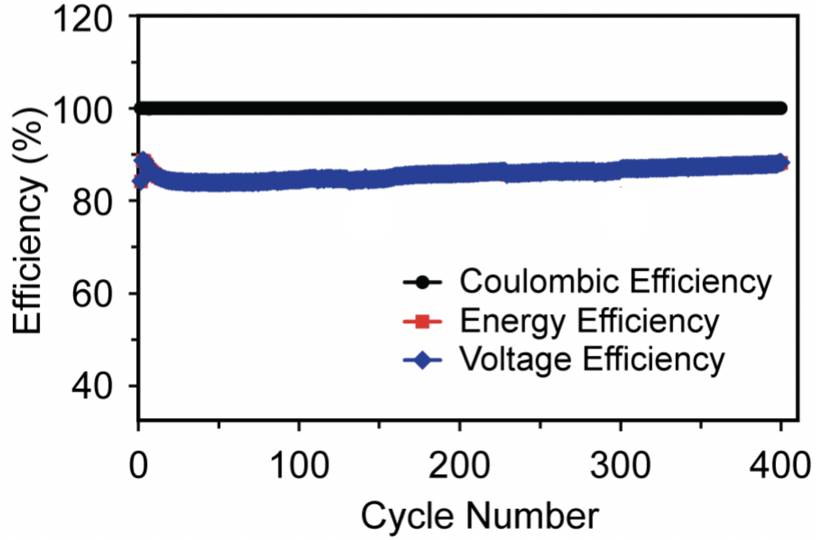

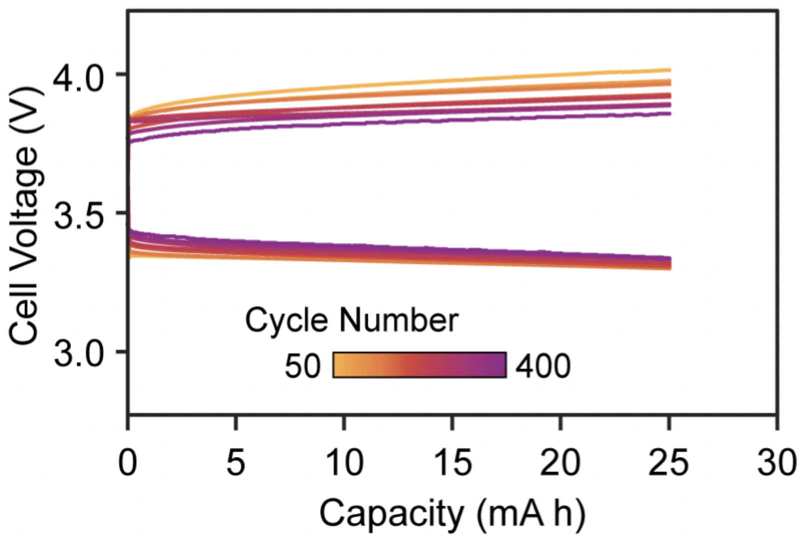

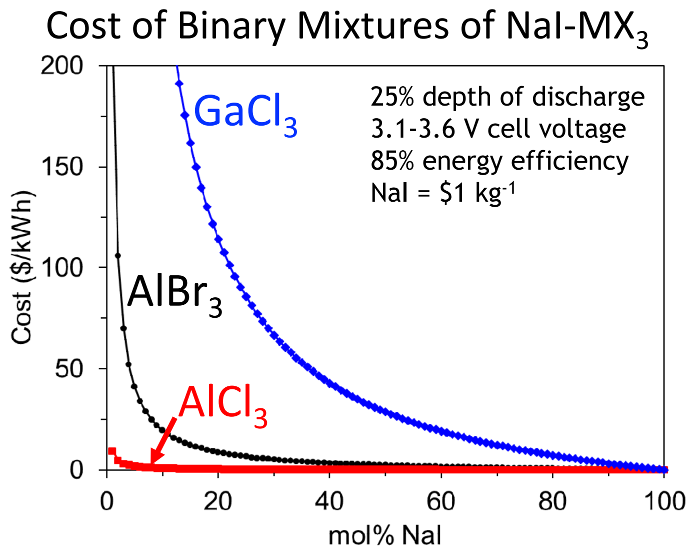

S.J. Percival, L.J. Small, and E.D. Spoerke, *J. Electrochem. Soc.*, 165 (2018) A3531

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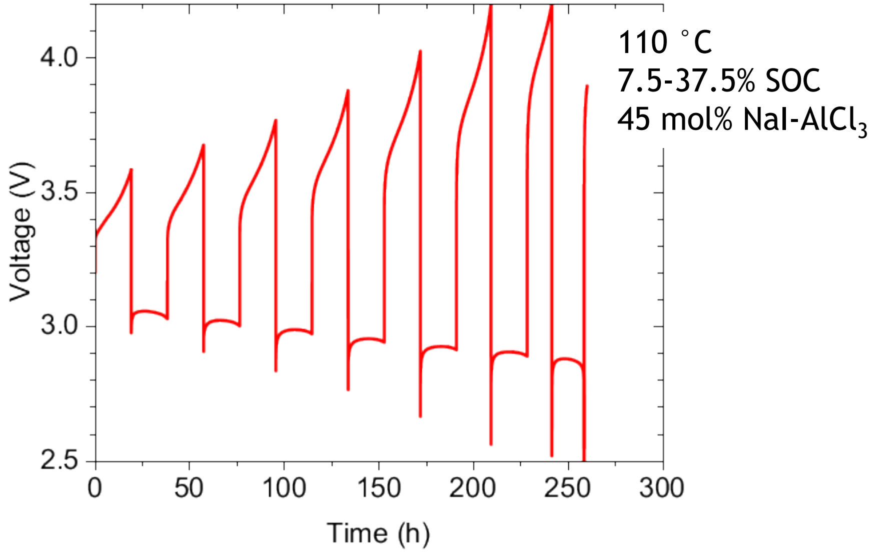
Poor Na^+ Battery Cycling with Lower-Cost Salt

Observed Problem: Steady increase in battery overpotentials observed during cycling.

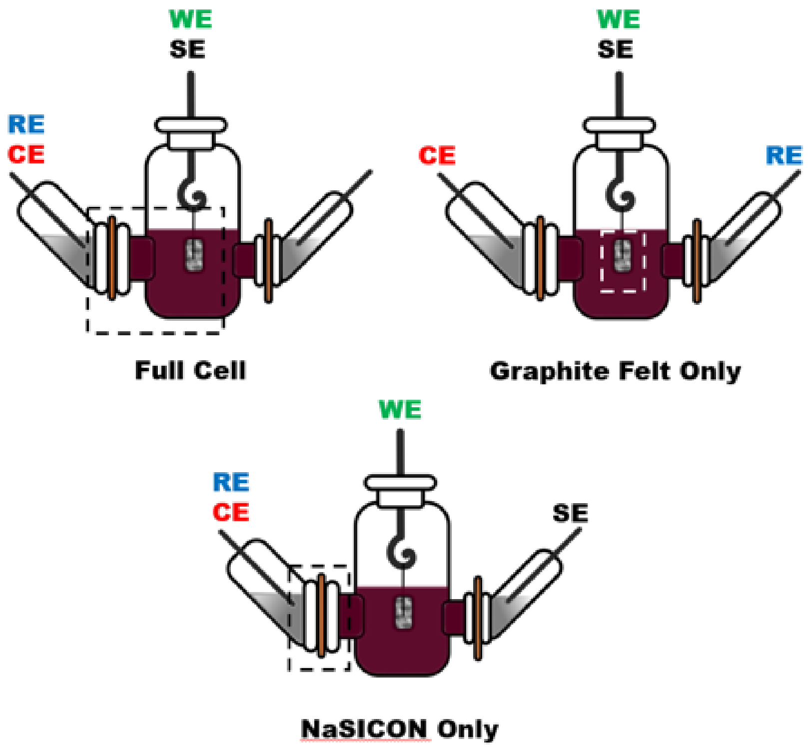


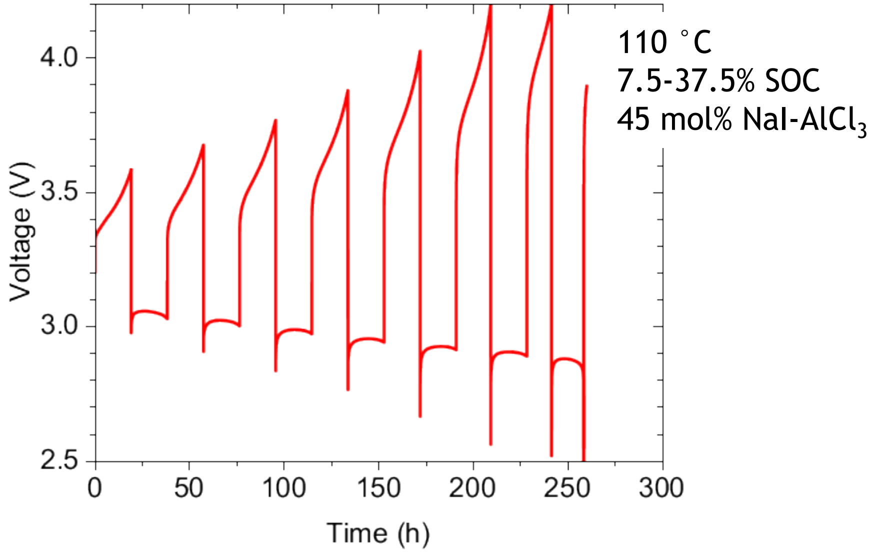
A.M. Maraschky, *et al*. “Impact of Catholyte Lewis Acidity at the Molten Salt-NaSICON Interface in Low-Temperature Molten Sodium Batteries.” (2022) J. Phys. Chem. C, *In Review*.

Characterizing Explicit Battery Interfaces

Observed Problem: Steady increase in battery overpotentials observed during cycling.

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





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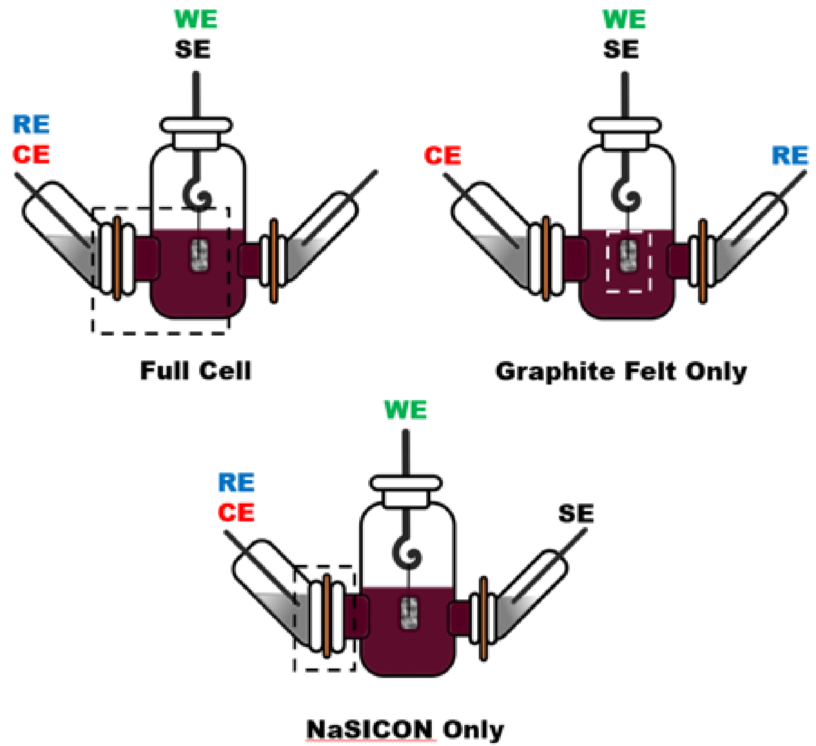
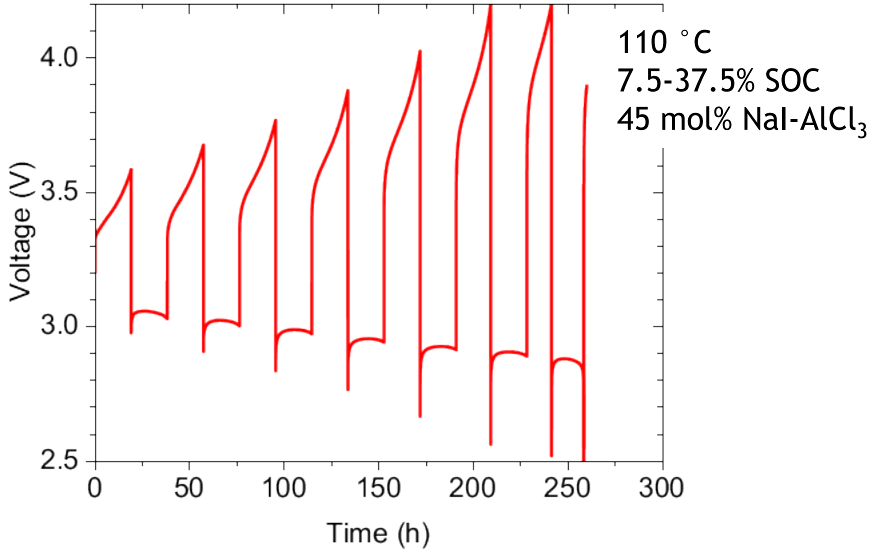
Na^+ "Blockade" Identified at the NaSICON-Catholyte Interface

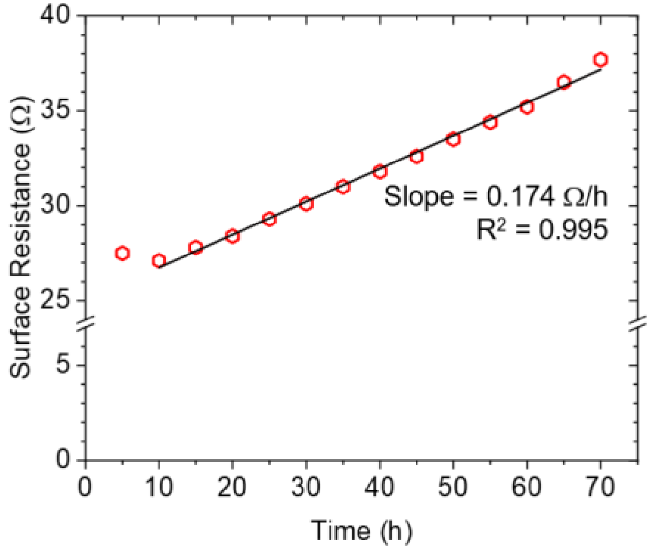
Observed Problem: Steady increase in battery overpotentials observed during cycling.

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

Discovery: Increase in impedance identified at the NaSICON-catholyte interface





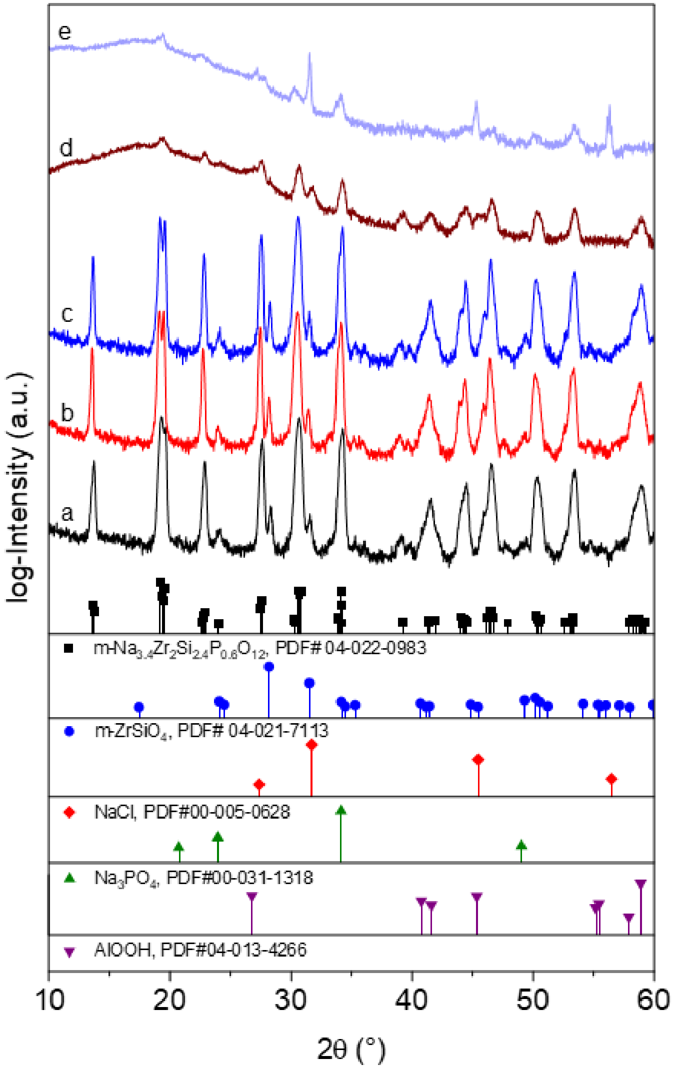


Isolated NaSICON-catholyte interfacial resistance over time at open circuit

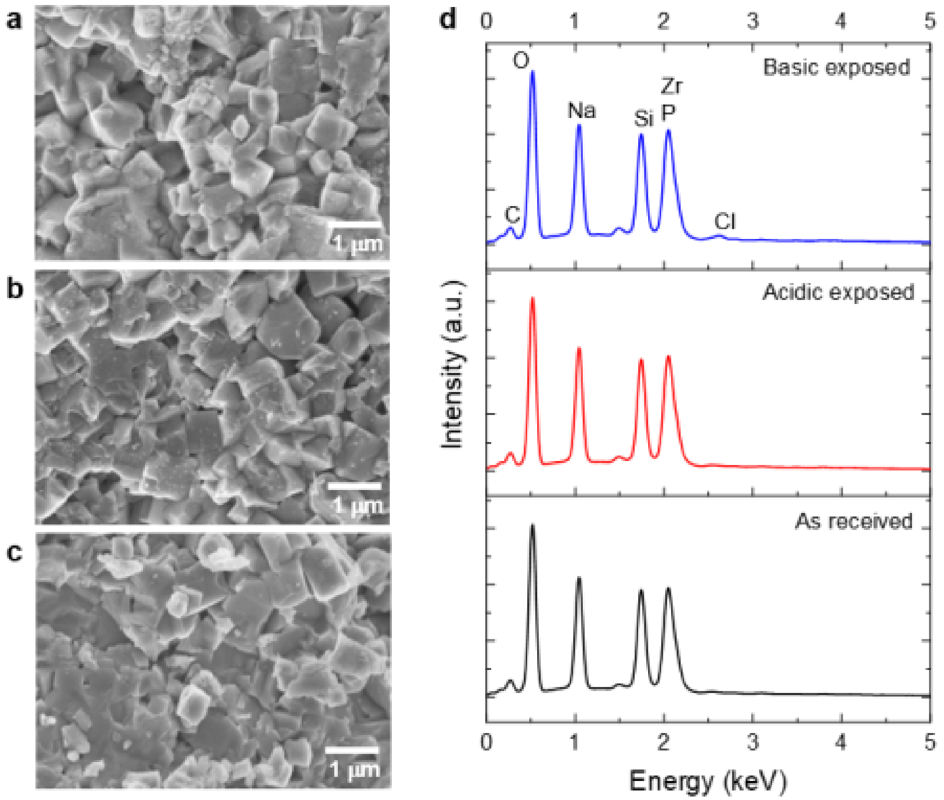
A.M. Maraschky, *et al*. "Impact of Catholyte Lewis Acidity at the Molten Salt-NaSICON Interface in Low-Temperature Molten Sodium Batteries." (2022) J. Phys. Chem. C, *In Review*.

Seeking the Source of the Performance Degradation

X-Ray Diffraction (XRD)



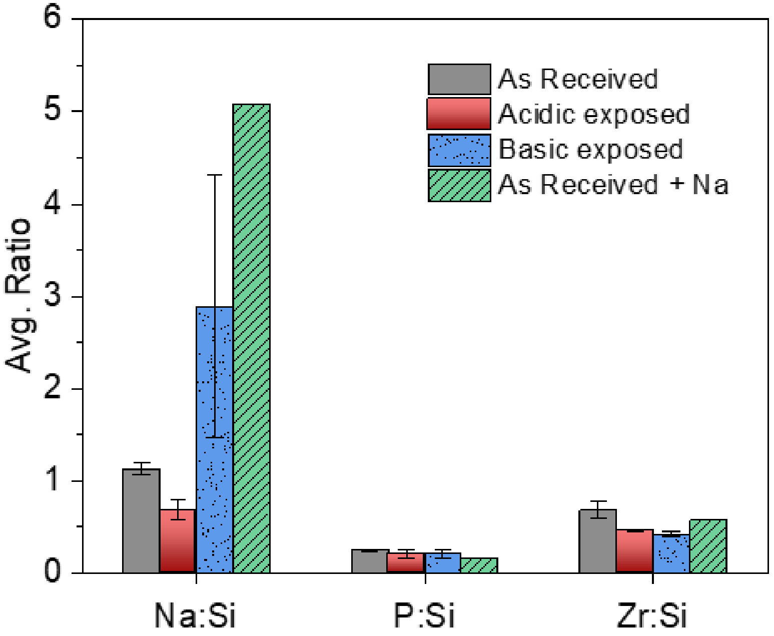
Scanning Electron Microscopy (SEM + EDS)



X-Ray Photoelectron Spectroscopy (XPS)

**values normalized to Si*

$Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$

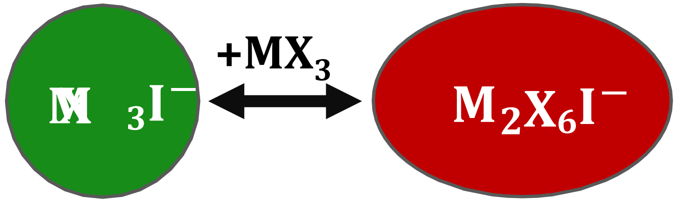


Extensive materials characterization of the NaSICON material and salt-exposed surface *revealed no significant changes*, except a slight decrease in Na^+ content at the near surface (<10 nm).

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*.

Understanding Molten Salt Catholyte Chemistry

Consider a mixed salt: NaI-MX_3



- I^- is a soft Lewis Base
- MX_3 is the Lewis acid (M = Al, Ga; X = Cl, Br)
- Together, these form a Lewis Acid-Base Adduct: MX_3I^-
- In the presence of excess Lewis Acids, dimeric adducts can also form ($M_2X_6I^-$)

Importantly, the nature of the Lewis acid and the ratio of the acid to base impact the the adduct bonding and speciation.

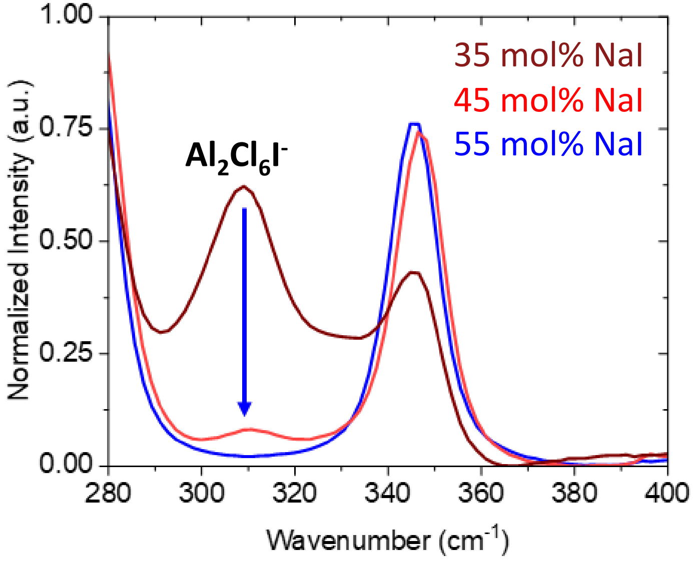
While MX_3I^- is important for electrochemical reactions at the electrode, $M_2X_6I^-$ is not believed to participate in active reactions.

Lee and Percival, *et al*. “Electrochemical Modeling of Iodide Oxidation in Metal-Halide Molten Salts.” *J. Electrochem. Soc*. (2021) **168** 126511.

Raman Spectroscopy Reveals Composition-Specific Changes in Salt Speciation

- Using Raman spectroscopy, Lewis acidic dimeric species, such as $Al_2Cl_6I^-$, were identified in 35% and 45 mol% NaI in $AlCl_3$.
- *Lewis acidic dimeric species were not observed under Lewis basic conditions (>50 mol% NaI).*

Raman Spectroscopy of NaI-$AlCl_3$ Catholytes



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"Blockade" Lifted by Controlling Salt Speciation

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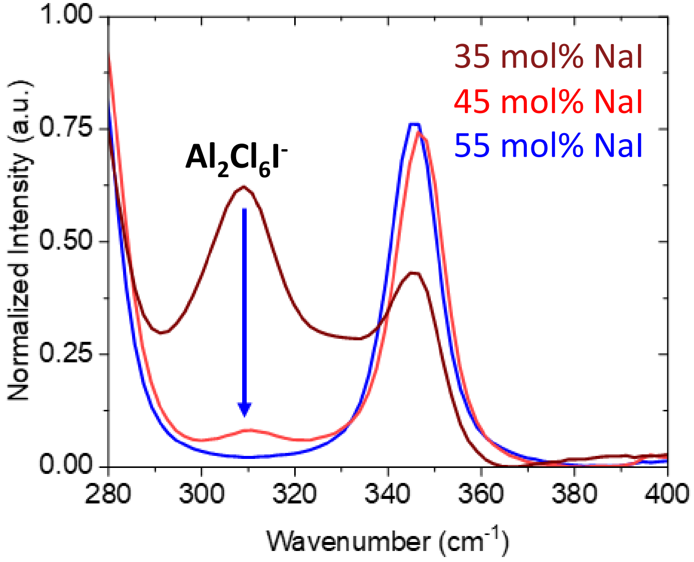
- *Lewis acidic dimeric species were not observed under Lewis basic conditions (>50 mol% NaI).*
- Hypothesize that these dimeric species interact negatively with the NaSICON interface.
- Shifting to Lewis basic catholytes (>50mol% NaI) eliminated acidic dimeric species, stabilizing the NaSICON-catholyte interface and, in turn, battery performance.

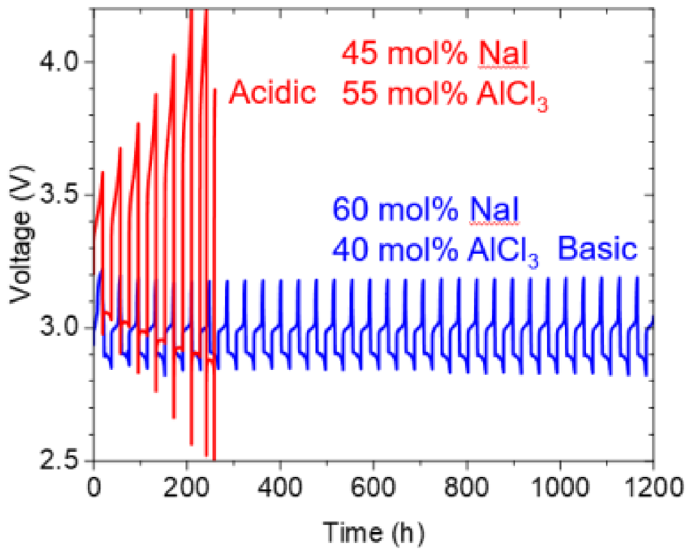
Raman Spectroscopy of NaI-$AlCl_3$ Catholytes



Eliminate acidic dimeric salt species.

Stabilize battery Performance.

Battery Cycling Profiles



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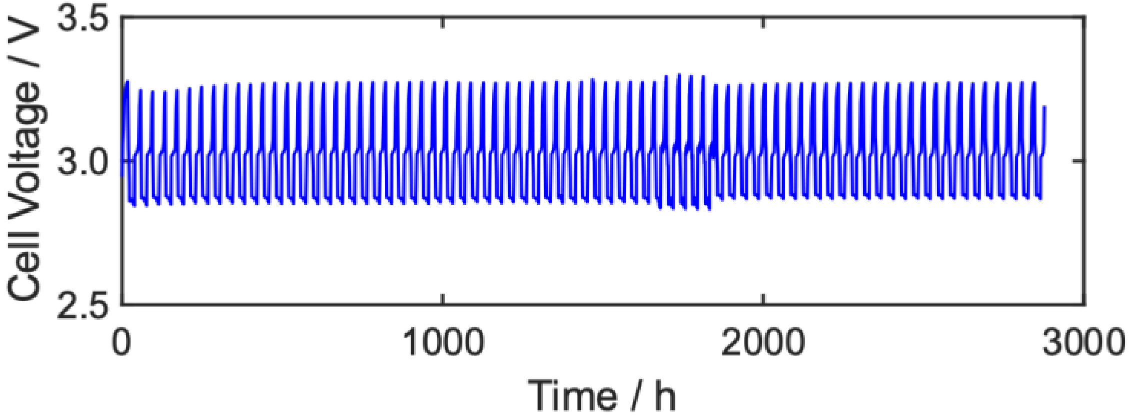
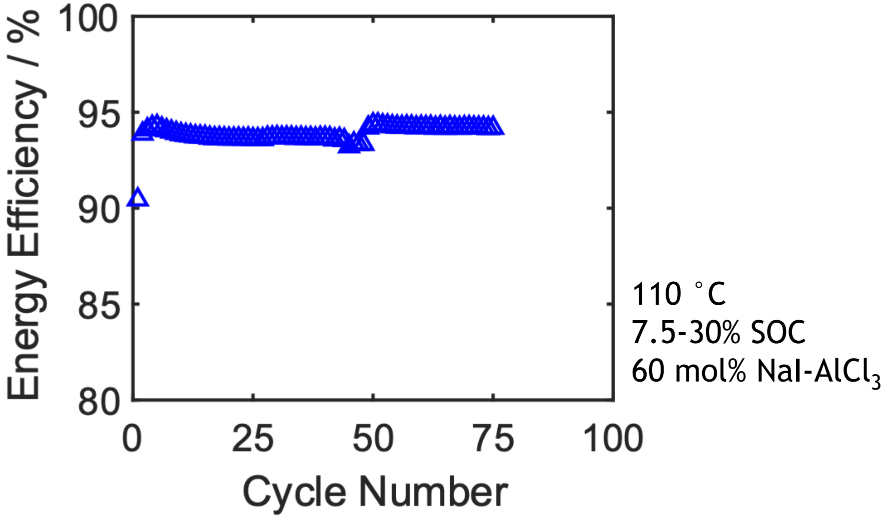
Finally, a Battery Worth Its Salt: Stable Cycling Performance Over 5 Months

Using a Lewis Basic molten salt catholyte 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.

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*.

Summary and Opportunities

- Low Temperature Molten Na-Batteries with molten salt catholytes have great potential for safe, reliable, cost-effective grid-scale storage storage…
  - Earth-Abundant Materials
  - No thermal runaway
  - Lower-cost materials
  - Long lifetime-operation
- …*but* materials challenges unique to low-temperature, low-cost chemistries remain.
  - Electrochemical salt speciation
  - Chemical compatibilities
  - Facile ionic and electronic interactions

Continued optimization of the materials in these evolving batteries will enable the ultimate development and deployment of low temperature molten sodium batteries!

Thank You!

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