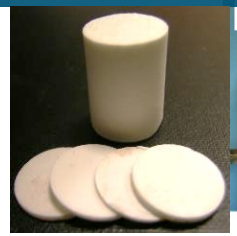
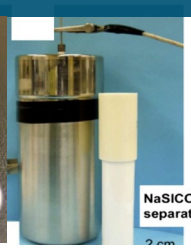
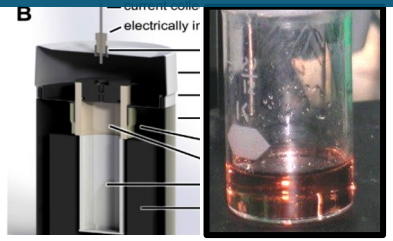
Materials Advances for Molten Sodium Batteries







Erik D. Spoerke

Stephen J. Percival, Leo J. Small,
Amanda Peretti, and Josh Lamb

Sandia National Laboratories, Albuquerque, NM

DOE Office of Electricity Delivery and Energy Reliability 2018 Peer Review
September 25-27, 2018
Santa Fe, NM

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SAND No.: SAND2018-10735 C

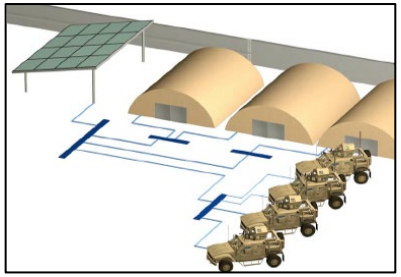
Key Design Criteria

There remains a need for grid-scale energy storage

Renewable/Remote Energy

Grid Reliability

National Defense



Emergency Aid

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

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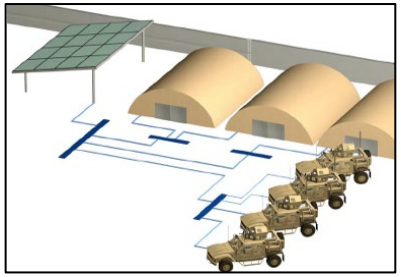
Emergency Aid

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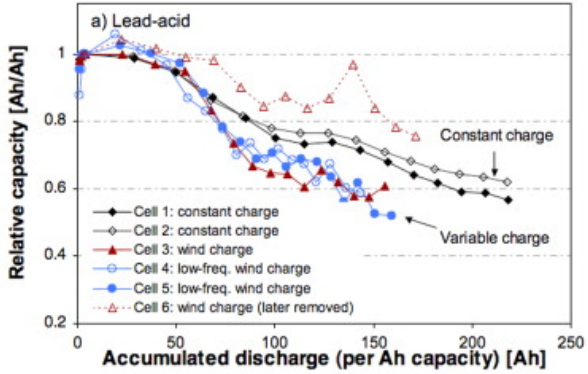
Pb-Acid (E_{cell} ~ 2.1V)

$$Pb + PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O$$

- Capacity fades quickly (typically 200-300 cycles)
- Temperature-sensitive function



E. Krieger, *et al.* (2013) *Energy* **60.** 492-500.

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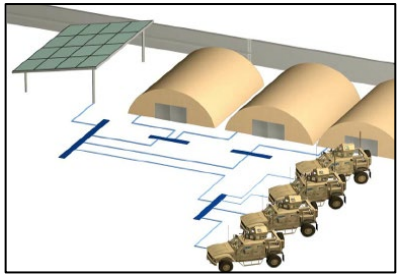

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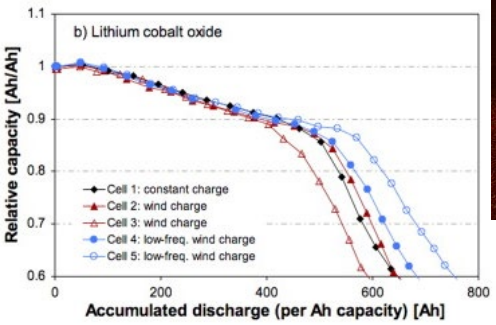
Li-ion (E_{cell} ~ 3.6V)

$$LiC_6 + CoO_2 \leftrightarrow C_6 + LiCoO_2$$

- Safety (flammable organic electrolytes
- Cycle lifetime limited
- Cost



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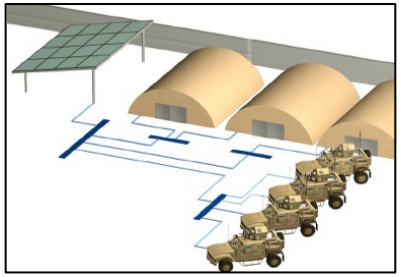


National Defense

Emergency Aid

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

Na-S ($E_{cell} \sim 2V$)

$2Na + 4S \leftrightarrow Na_2S_4$

- Safety: Violent, toxic reactions between molten Na and molten S – cascading runaway!
- Corrosive, toxic chemistries
- High temperature operation (270-350°C)

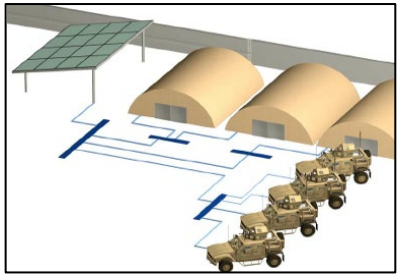
Key Design Criteria

There remains a need for grid-scale energy storage

Renewable/Remote Energy

Grid Reliability

National Defense



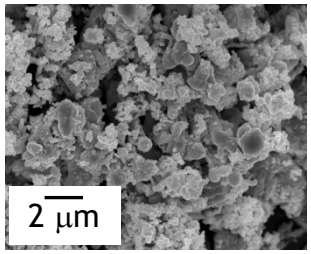
Emergency Aid

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

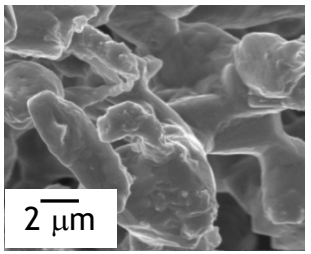
Na-$NiCl_2$ (E_{cell} ~ 2.6V)

$$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$$

- Cycle lifetime (solid cathode material
- Cost (related to cycle lifetime and material costs)
- High temperature operation (typically > 200°C)



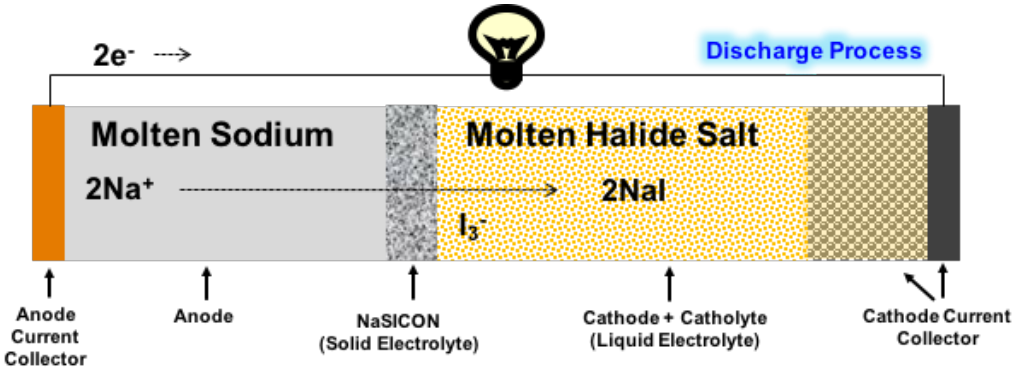
Particle Coarsening



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

Low Temperature Molten Na-Halide Batteries

Our Vision: A molten sodium-based battery that comprises a robust, highly Na^+-conductive, zero-crossover separator and a fully liquid, highly cyclable molten catholyte that operates at low temperatures.

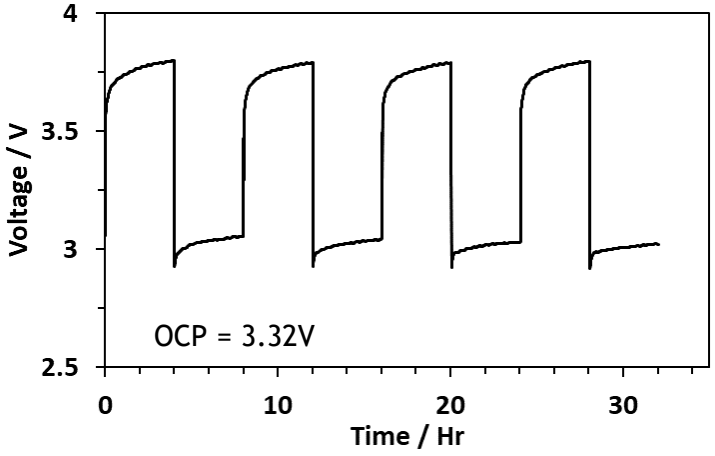


Na-NaI battery:

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

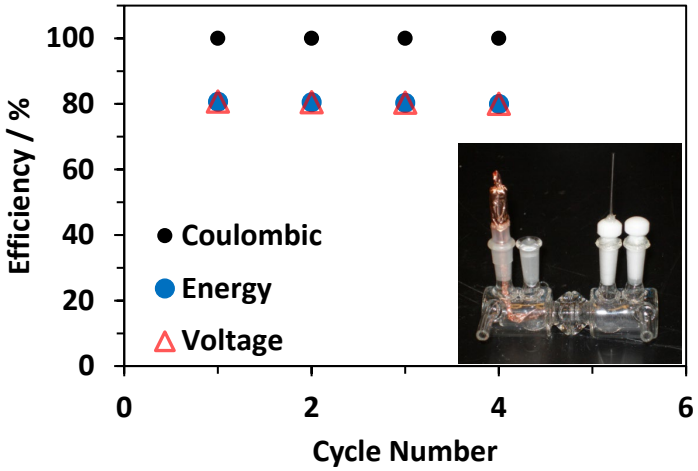
$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

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



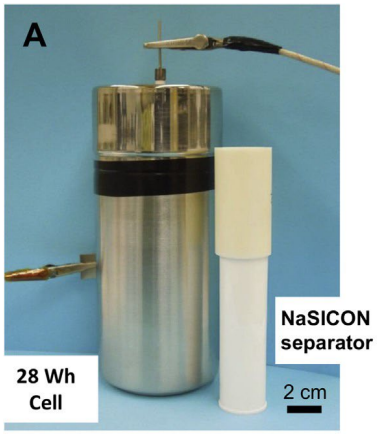
Battery cycling at 110°C!

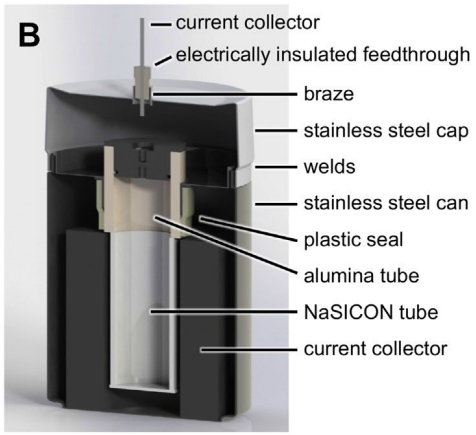
25 mol% NaI-$AlBr_3$ with NaSICON separator.

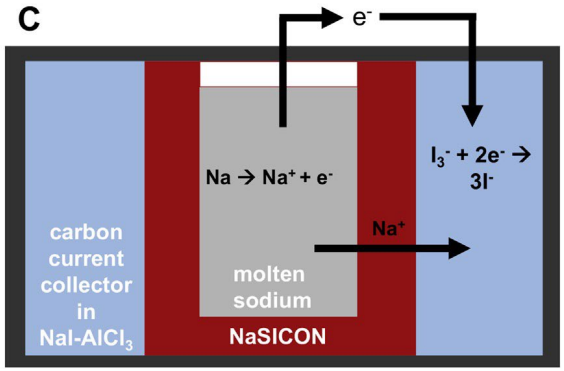


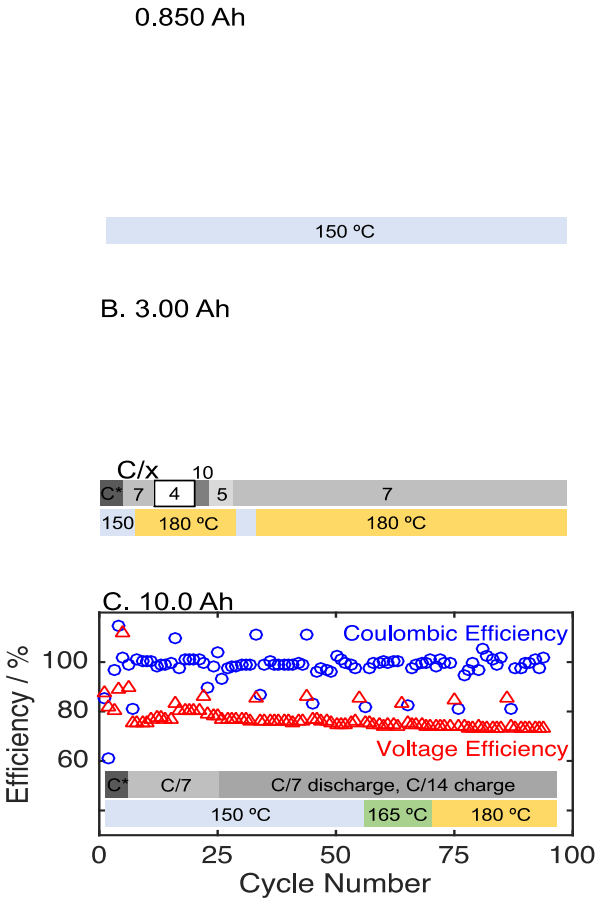
Effective Demonstration of Na-NaI Battery

Na-NaI battery was tested across several scales at 150-180°C.









The catholyte is 60 mol% NaI-$AlCl_3$ (with 5-10 mol% NaI added) – Significant undissolved solids at 150°C.

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

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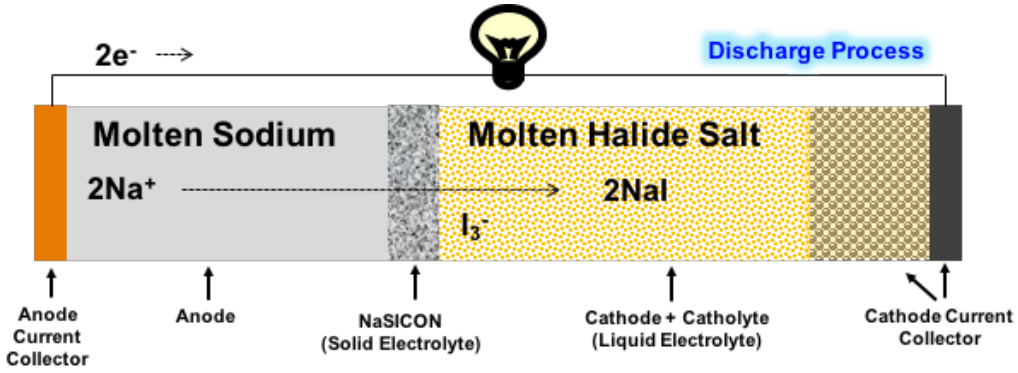
Molten Sodium Halide Batteries

Our Vision: A molten sodium-based battery that comprises a robust, highly Na^+-conductive, zero-crossover separator and a fully liquid, highly cyclable molten catholyte that operates at low temperatures.



Na-NaI battery:

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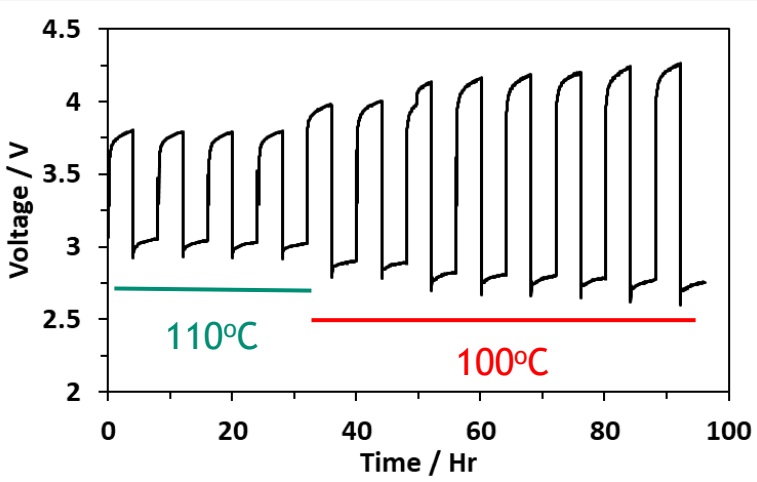
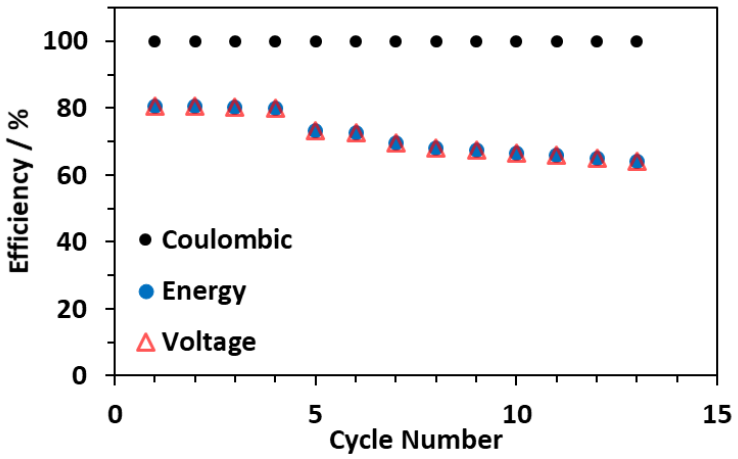
$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

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



Battery cycling at **100°C**!

25 mol% NaI-$AlBr_3$ with NaSICON separator.



Virtues of a Low Temperature Battery

Low Temperature Operation of a Molten Na Battery is Tremendously Enabling

- Improved Lifetime
  - Reduced material degradation
  - Decreased reagent volatility
  - Fewer side reactions
- Lower material cost and processing
  - Seals
  - Separators
  - Cell body
  - Polymer components become realistic!
- Reduced operating costs
- Simplified heat management costs

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

Na-NaI Battery Safety

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

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
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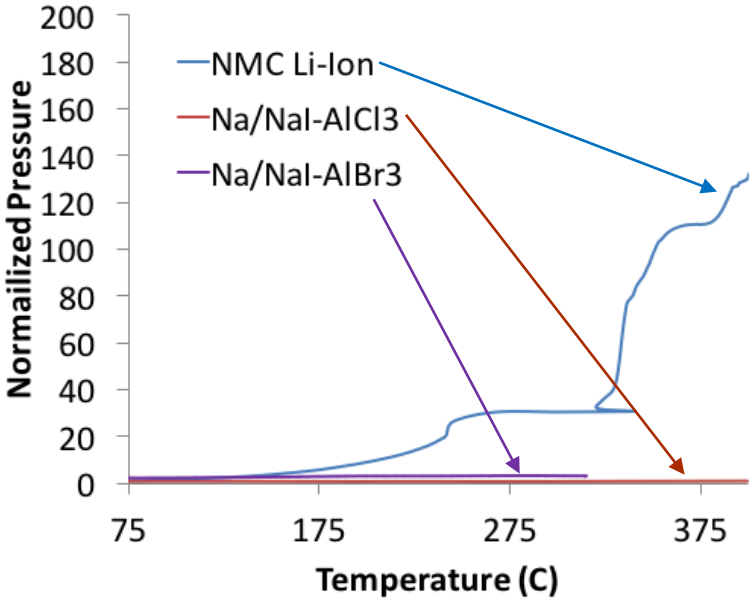
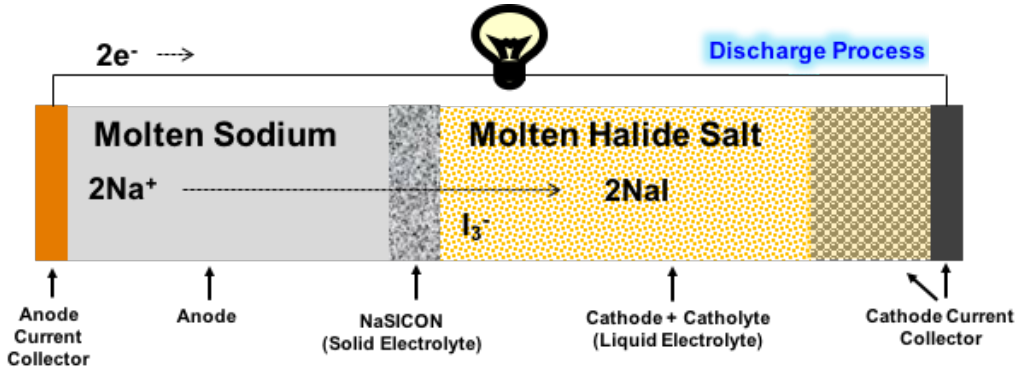
- Low Cost and Scalable





Na-NaI battery:

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

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

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

Low Temperature Long Cycle Life

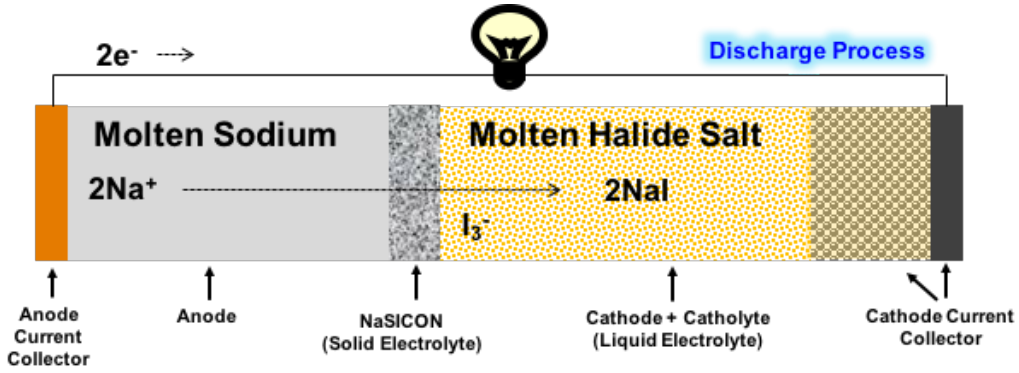
We envision that cycle life will be determined through
1) use of a zero-crossover separator (e.g., NaSICON or β"- Al_2O_3)
2) maintaining a fully liquid catholyte

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

SNL-synthesized NaSICON

Ionotec (β"- Al_2O_3)

NaSICON conductivity > 10^{-3} S/cm at 25°C



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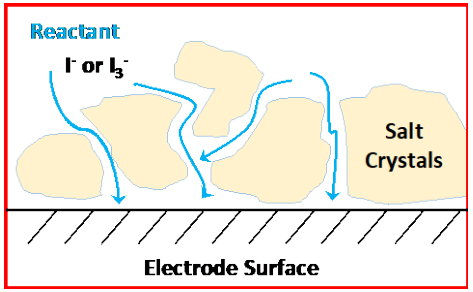
$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

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

Key to Low Temperature Battery Operation

We envision that cycle life will be determined through
1) use of a zero-crossover separator (e.g., NaSICON or β"- Al_2O_3)
2) maintaining a fully liquid catholyte

A fully molten catholyte avoids
a) Particle-hindered electrochemical processes
b) Particle-related loss of capacity



NaI-$AlCl_3$ at 150°C

NaI-$AlCl_3$ and NaI-$AlBr_3$ salts at 90°C

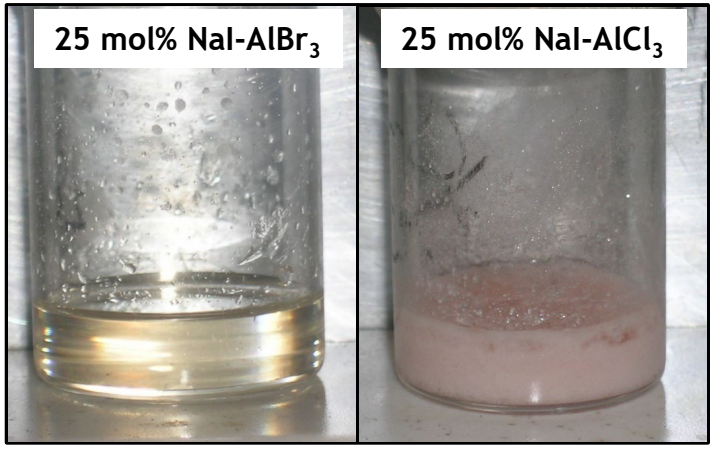
Molten NaI-$AlBr_3$ composition range spans 5-25% NaI and cell voltage is near or above 3V.

NaI-$AlBr_3$: A Low Temperature Molten Catholyte

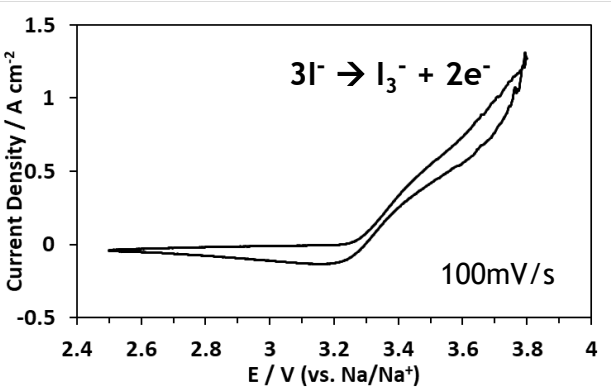
The NaI-$AlBr_3$ catholyte system exhibits excellent electrochemical behavior at reduced operating temperatures.

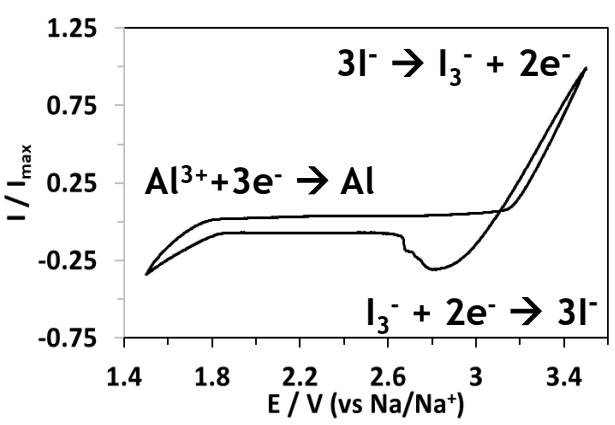
- 25:75 NaI-$AlBr_3$ salt completely molten at 90 °C
- Larger fully molten capacity range (~5-25 mol% NaI)

Samples at 90°C



- Carbon Fiber microelectrode shows excellent electrochemical behavior of 25 mol% NaI-$AlBr_3$ at 90°C



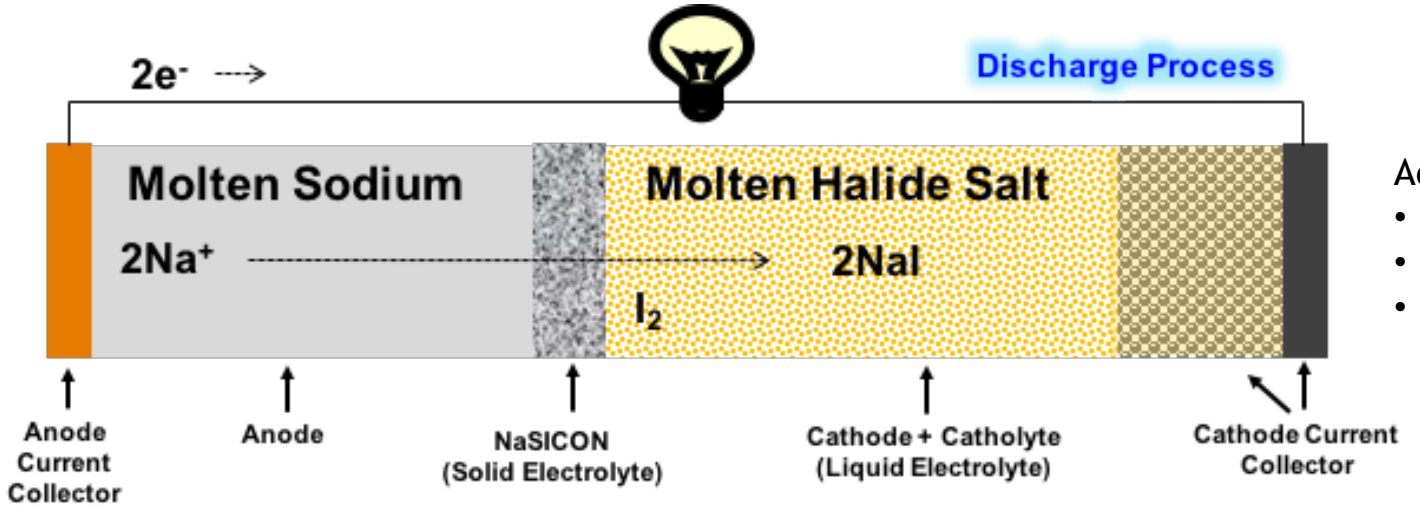


- NaI-$AlBr_3$ system shows good iodide electrochemical reversibility.
  - $AlBr_3$ (20mol% NaI) system at 120 °C and 1V/s

Poster presentation by Dr. Stephen Percival

“Molten Salt Catholyte Development for Low Temperature Na-Halide Batteries”

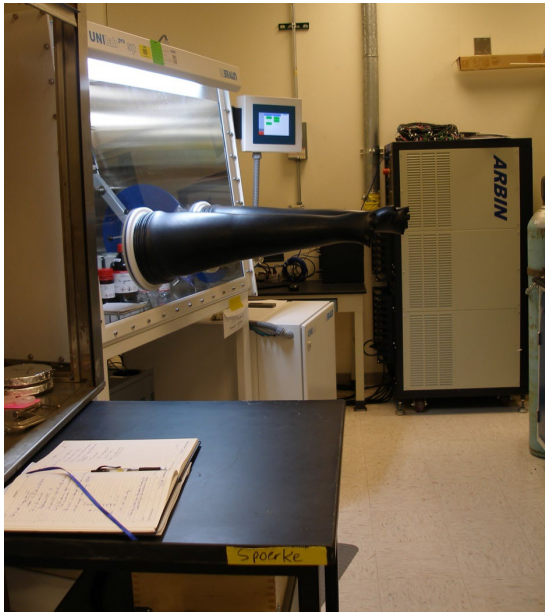
A New Materials Science-Driven Redesign



Additional Material Issues
- Seals
- Battery casings
- Electrical contacts

Facility Upgrades:

- New UniLab Glove Box with Atmospheric Controls (gas and temperature)
- Arbin Instruments LBT series battery tester with 40 channels. +/- 5A, +/- 5V per channel.
- Custom electrical cables shielded up to the point of measurement (battery), rated to 200 C, 5A.
- New test cell designs



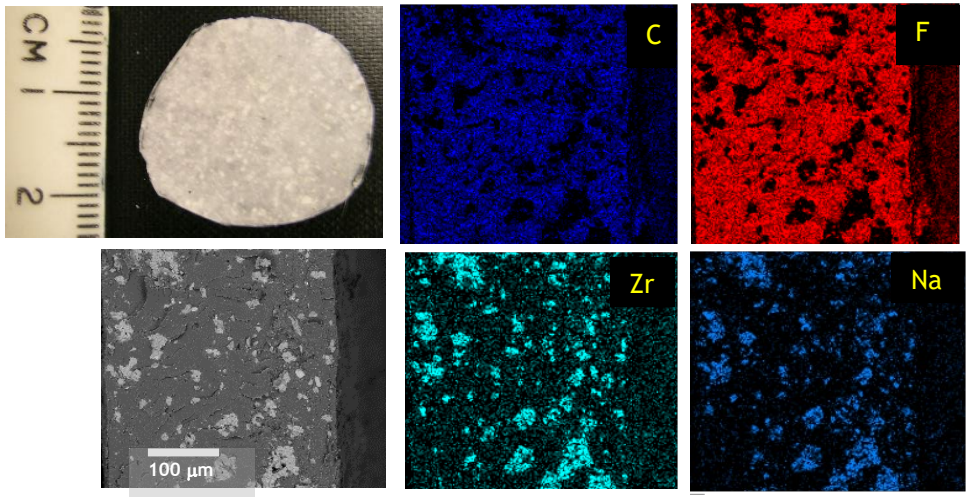
Composite Separator Innovation

Composite separators could enable thinner (higher conductance), mechanically robust separators.

Initial Approach

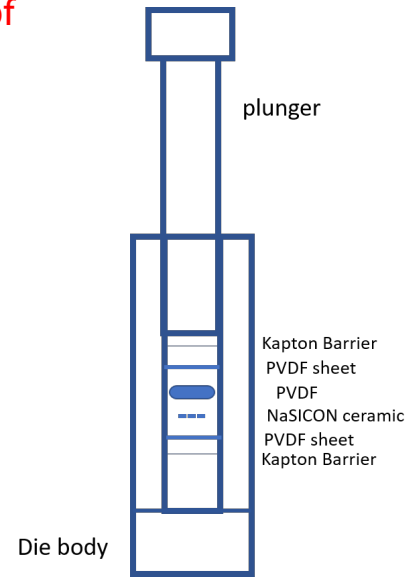
- Powdered NaSICON and powdered polymer (polyvinylidene difluoride: PVDF) were warm-pressed together
- Tough composite with reasonable distribution of NaSICON
- Good interfaces between NaSICON and polymer

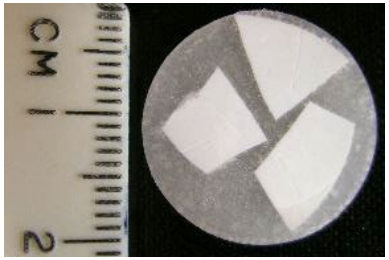
➢ Impractically low ionic conductivity. Poor connectivity of Na-conductive NaSICON is evident in cross-sectional elemental mapping.



An alternative approach

- NaSICON chips (1mm thick) enveloped in PVDF powder and warm-pressed
- NaSICON chips provide continuous conductive path through separator





Conductivity is determined by NaSICON ceramic.

σ_{RT} ~0.5 mS/cm for composite!

Poster presentation by Amanda Peretti

“Sodium Ion-Conducting Separator Development”

Project Dissemination and Publications

Peer-Reviewed Publications:

- L.J. Small, J.S. Wheeler, J.F. Ihlefeld, P.G. Clem, and E.D. Spoerke. "Enhanced alkaline stability in a hafnium-substituted NaSICON ion conductor." *J. Mater. Chem. A.* (2018) **6**, 9691-9698. DOI: 10.1039/C7TA09924J.
- E. Allcorn, G. Nagasubramanian, H.D. Pratt III, E. Spoerke, and D. Ingersoll. "Elimination of active species crossover in a room temperature, neutral pH, aqueous flow battery using a ceramic NaSICON membrane." *J. Power Sources.* (2018) **378**, 353-361.
- DOI: 10.1016/j.jpowsour.2017.12.041
- S.J. Percival, L.J. Small, and E.D. Spoerke. "Electrochemistry of the NaI-$AlCl_3$ Molten Salt System for Use as Catholyte in Sodium Metal Batteries." *J. Electrochem. Soc.* (2018) *In Review.*

- **Intellectual Property:**
- E.D. Spoerke, P.G. Clem, J.S. Wheeler, L.J. Small, J. Ihlefeld. "Cation-enhanced chemical stability of ion-conducting zirconium-based ceramics." US Patent No: 9988312. (6/5/2018).
- J.A. Bock, E.D. Spoerke, H. Brown-Shaklee, L.J. Small. "Solution-Assisted Densification of Sodium Ion Conducting Ceramics." SD# 14673 (April, 2018).
- S.J. Percival, L.J. Small, and E.D. Spoerke. "Molten Inorganic Electrolytes for Low Temperature Sodium Batteries." Sandia Technical Advance, SD# 14842. (Sept., 2018).

Conference Engagement:

- 9 Conference Presentations (2 invited)
- 2 organized conference symposia

Take Away Messages

We have demonstrated cycling behavior of a lab-scale molten Na-NaI battery at 100°C!

This demonstration utilized a materials system that addressed key requirements of a next generation grid-scale battery:

- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

Key achievements along the way:

- Updated laboratory facilities and testing prototypes
- Extensive characterization of molten salt phase behavior and electrochemistry
- Established capabilities to create NaSICON ion conducting ceramics
- Created new NaSICON-polymer composite separators
- Had an active year of research dissemination and community engagement.

Where are we going next?

Efforts will focus on the continued development, and improvement of low-temperature Na-based batteries.

- Continued optimization of molten salt composition and chemistry
- Exploit current NaSICON ceramics and PVDF-composites for aqueous battery applications
- Modify composite electrolyte structure and chemistry to reduce resistance and improve chemical compatibility for molten Na batteries
- Refine battery test designs to improve “engineering” issues with battery testing
  - System seals
  - Molten component wetting
  - Separator geometry
- Demonstrate extended cycling behavior of low-temperature molten Na-MX batteries!

Acknowledgements

SNL Team

Dr. Stephen Percival

Dr. Leo Small

Amanda Peretti

Dr. Josh Lamb

Dr. Eric Allcorn

Sara Dickens

Dr. Babu Chalamala

External Engagement

Advanced Manufactured Power Systems (AMPS)

- Battery test cell design

University of Kentucky (FY19)

- Professor Y-T Cheng (mechanical testing)

Enlighten Innovations (formerly Ceramatec)

- NaSICON Manufacturer

Work at Sandia National Laboratories is supported by Dr. Imre Gyuk through the Department of Energy Office of Electricity Delivery and Energy Reliability.

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Acknowledgements

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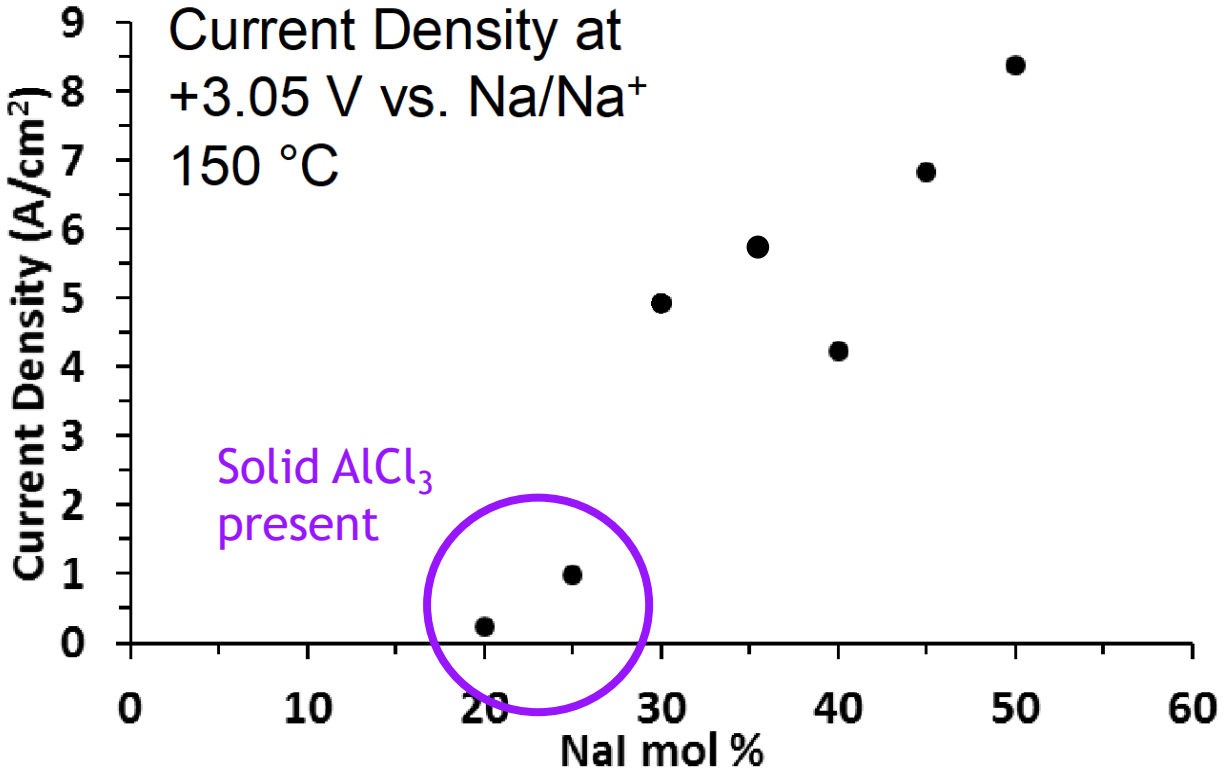
Backup Slides

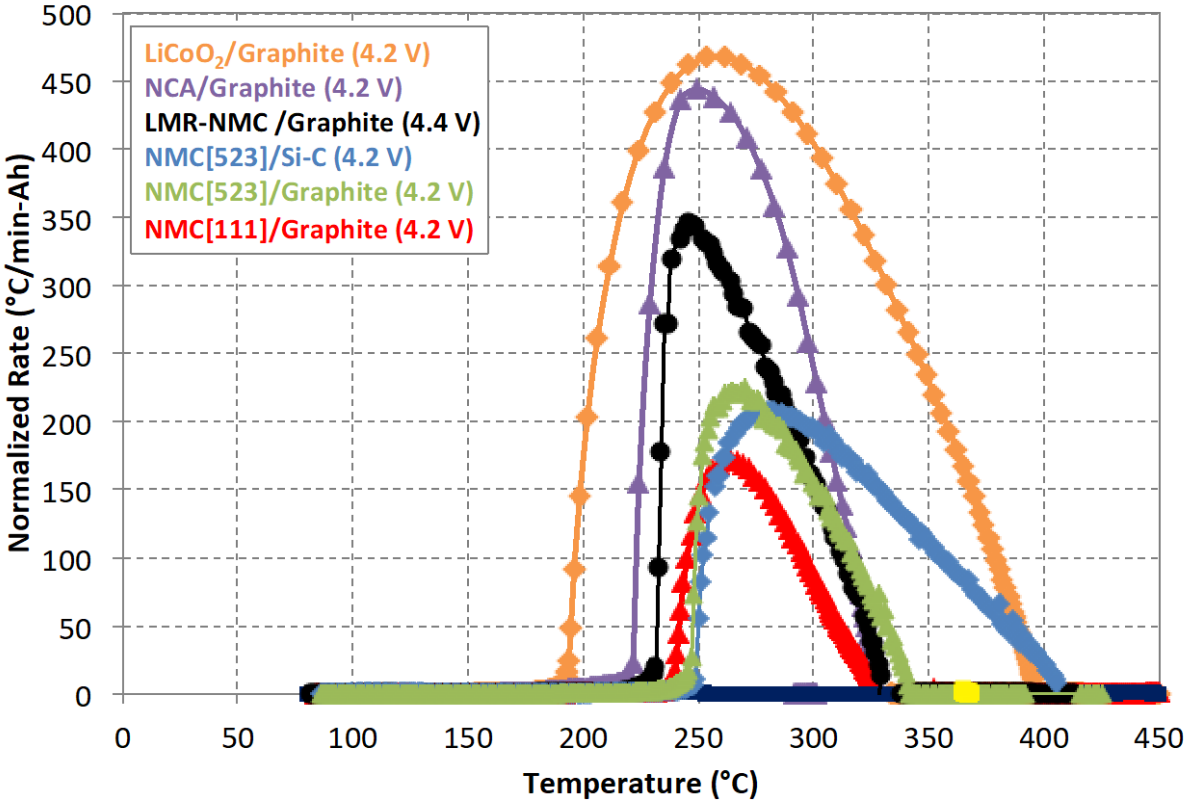
Current Density Variation

Highest current densities are observed at highest NaI concentrations. There is a significant drop in current density when solid $AlCl_3$ is formed.



Accelerating Rate Calorimetry (ARC) Shows No Significant Exotherms

When complete separator failure is simulated by mixing Na metal and NaI/$AlCl_3$ catholyte, ARC testing reveals no hazardous runaway exothermic behavior!



Hazards of Poor Material Selection

Polymer incorporation highlights the importance of careful material section.

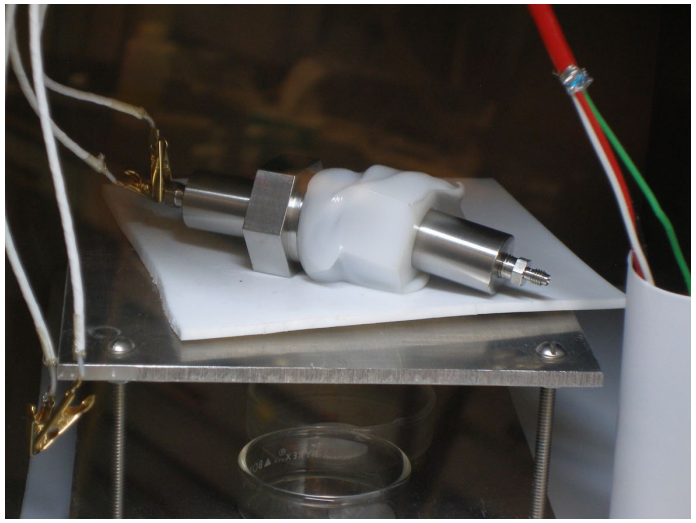
Compatibility must be considered for:

- Molten sodium
- Molten halide catholyte salts
- Non-ambient temperatures
- Electrochemical reactions
- Temperature
- Mechanical Properties (toughness, compliance, hermeticity, etc.)

Magnesium metal and Teflon (PTFE) are elements of decoy flares…Sodium has a similar reactivity.

Molten sodium and fluoropolymers should not be considered stable, especially for long-term use.

Thermal and mechanical stability



Chemical compatibility

NaSICON Solid State Separators

Key Separator Properties:

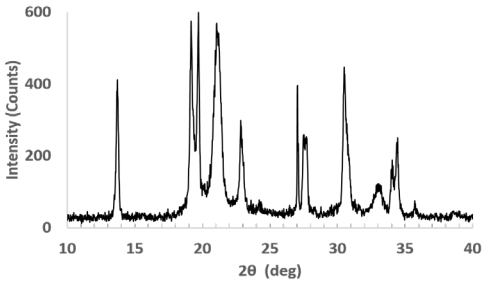
- Selective, high ionic conductivity at reduced temperature (<150°C)
- Chemical compatibility (molten Na, molten halide salts, strong base)
- Mechanical robustness
- Low cost, scalable production

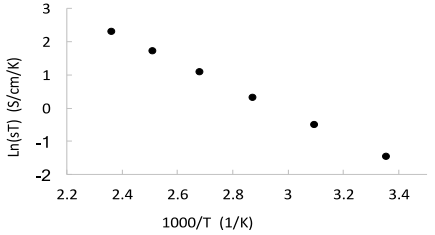
Based on its high Na-ionic conductivity (>10^{-3} S/cm at 25°C) and established chemical compatibility, NaSICON ceramics ($Na_3Zr_2PSi_2O_{12}$) are good candidates for development.

Solid State Ceramic Synthesis

$$2ZrSiO_4 + Na_3PO_4 \rightarrow Na_3Zr_2PSi_2O_{12}$$

- Pellet densities ~ >95%
- X-ray diffraction confirm NaSICON synthesis with minor ZrO_2 and $ZrSiO_4$ secondary phases
- Conductivities reasonable, but slightly less than commercial NaSICON
- Improved phase purity with Na_3PO_4
- Increased density with decreased humidity





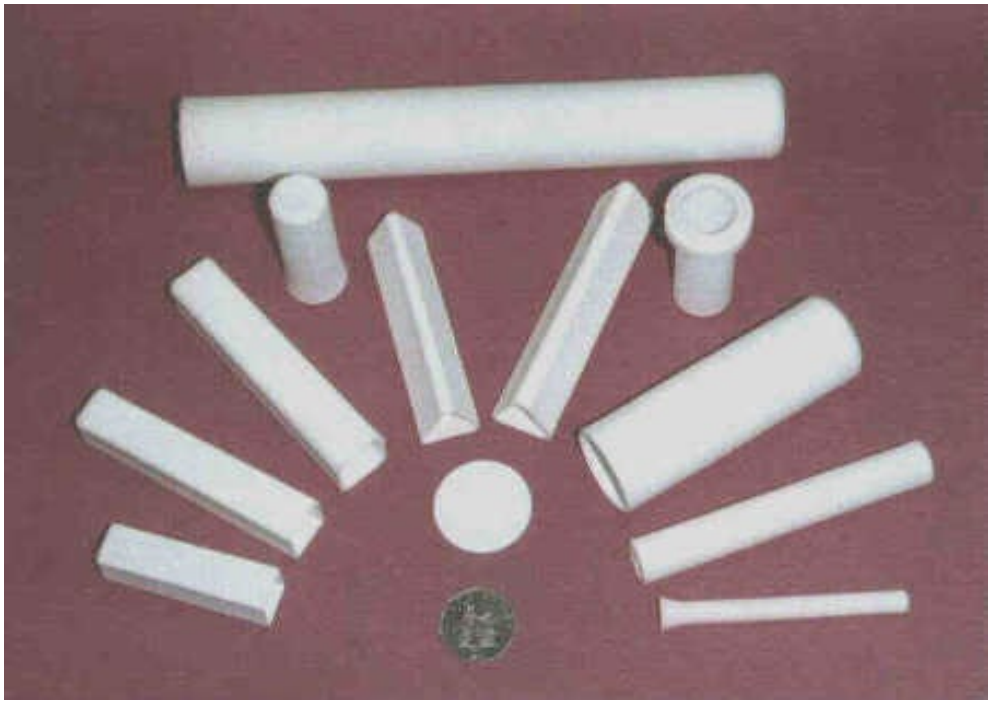
An Alternative Ceramic Separator Candidate

β"-Al_2O_3 is commercially available from manufacturers, such as Ionotec Ltd (UK).

Available in a variety of shapes and sizes, including discs and closed-end tubes.

Report conductivity as high as 16 mS/cm at 100°C – comparable to high performing commercial NaSICON.

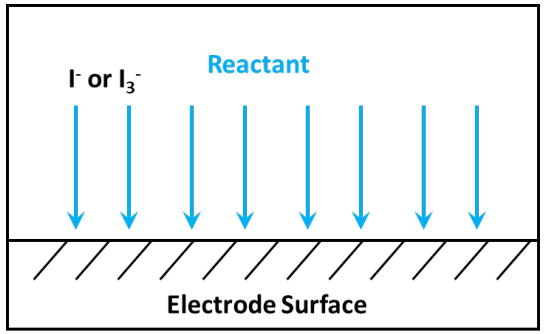
Some concerns about moisture sensitivity, sodium wetting, and mechanical strength.

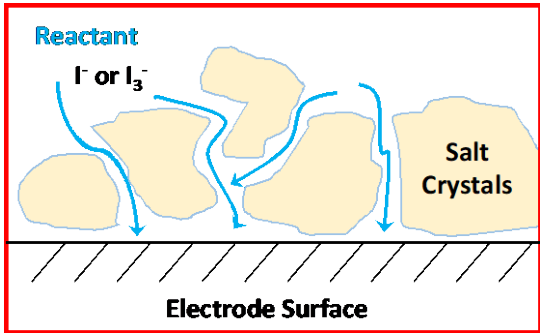


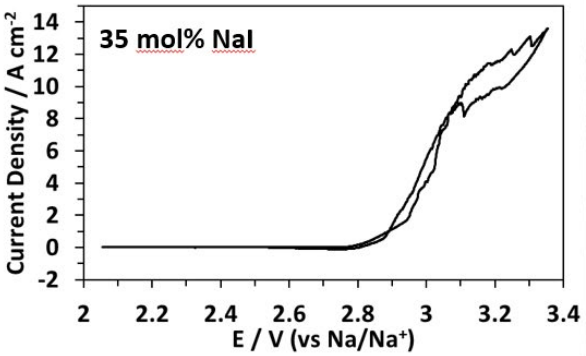
These materials provide the opportunity to explore fundamentals of electrochemistry while we continue our development of optimal solid state separators.

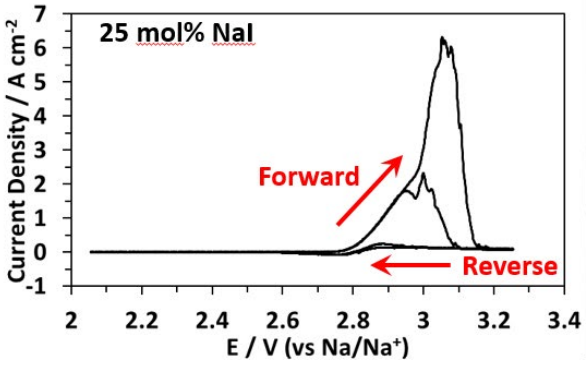
Controlling Molten Salt Melt Chemistry

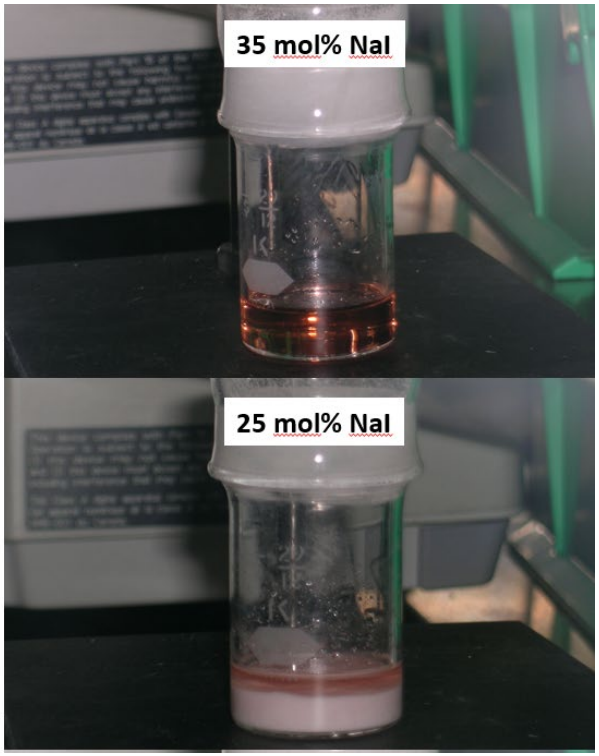
Hindered diffusion from solid-phases occluding electrode surfaces can impact electrochemical performance.









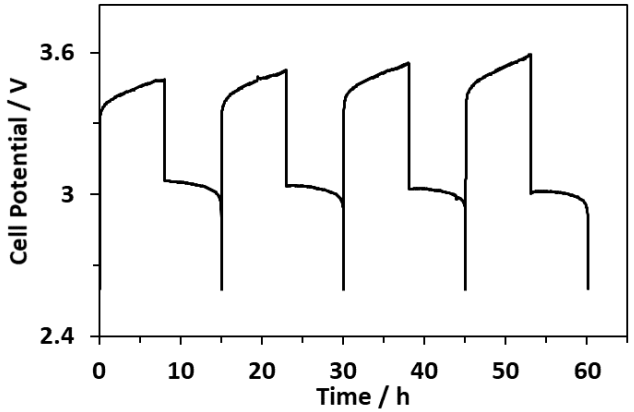


Salts at 150°C

Fully Molten Na/NaI-$AlCl_3$ Battery Cycling

1st iteration battery – β''-Al_2O_3 tube containing Na anode
40mol% NaI-$AlCl_3$ molten salt catholyte at 150 °C

- Fully molten state – 200 mAh capacity (lab scale)
- C/8 charge and discharge rate
- OCP = 3.14 V



Smooth charge discharge voltage curves

*Coulombic efficiency ~87% due to loss of I_2 from unsealed cell

Disassembled

Fully loaded and assembled