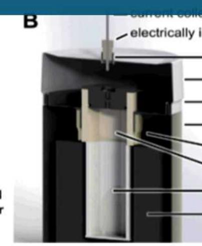
SAND2019-5929C

Low Temperature Molten Sodium-Based Batteries for Large Scale Electrical Energy Storage



<u>Erik D. Spoerke</u>

Stephen Percival, Leo Small, Amanda Peretti, Josh Lamb, and Babu Chalamala

Sandia National Laboratories, Albuquerque, NM

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

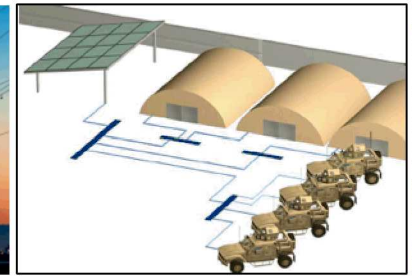
235th Electrochemical Society Meeting
May 26-30, 2019
Dallas, TX USA

SAND No.: SAND2019-

A Need for Grid-Scale Energy Storage Research


Renewable/Remote Energy

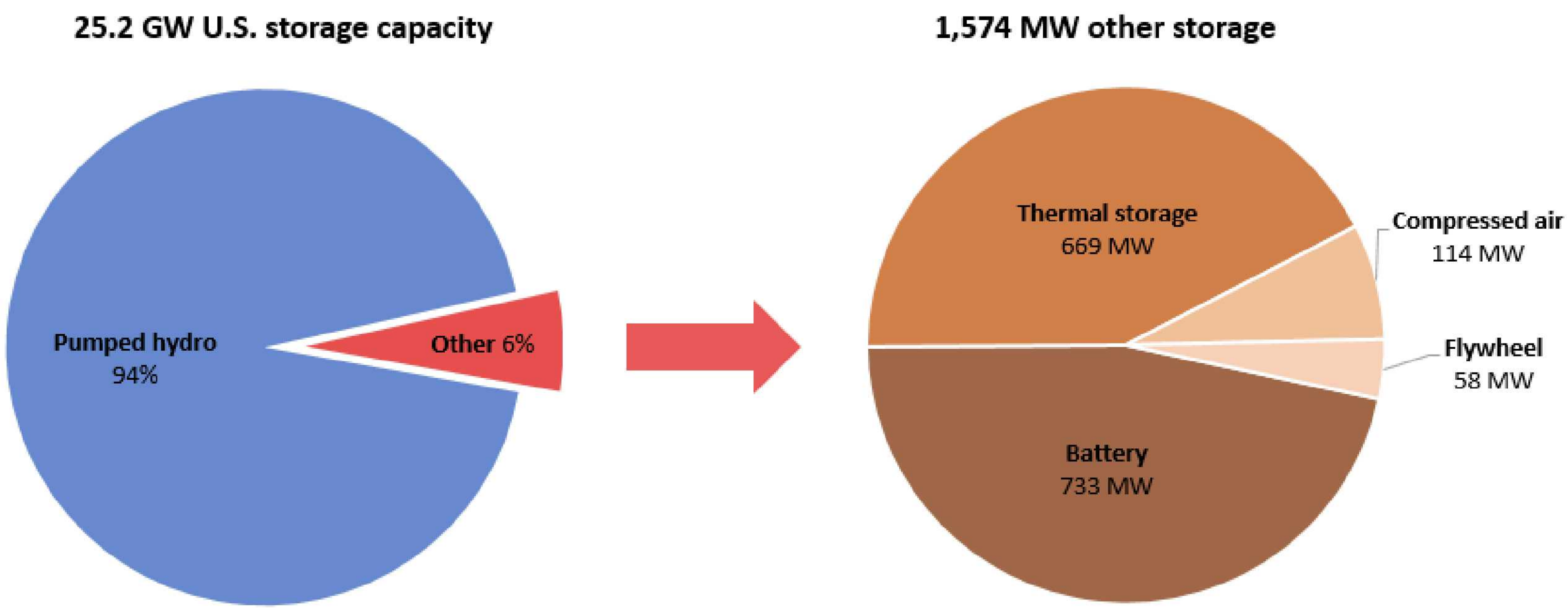
Grid Reliability



National Defense

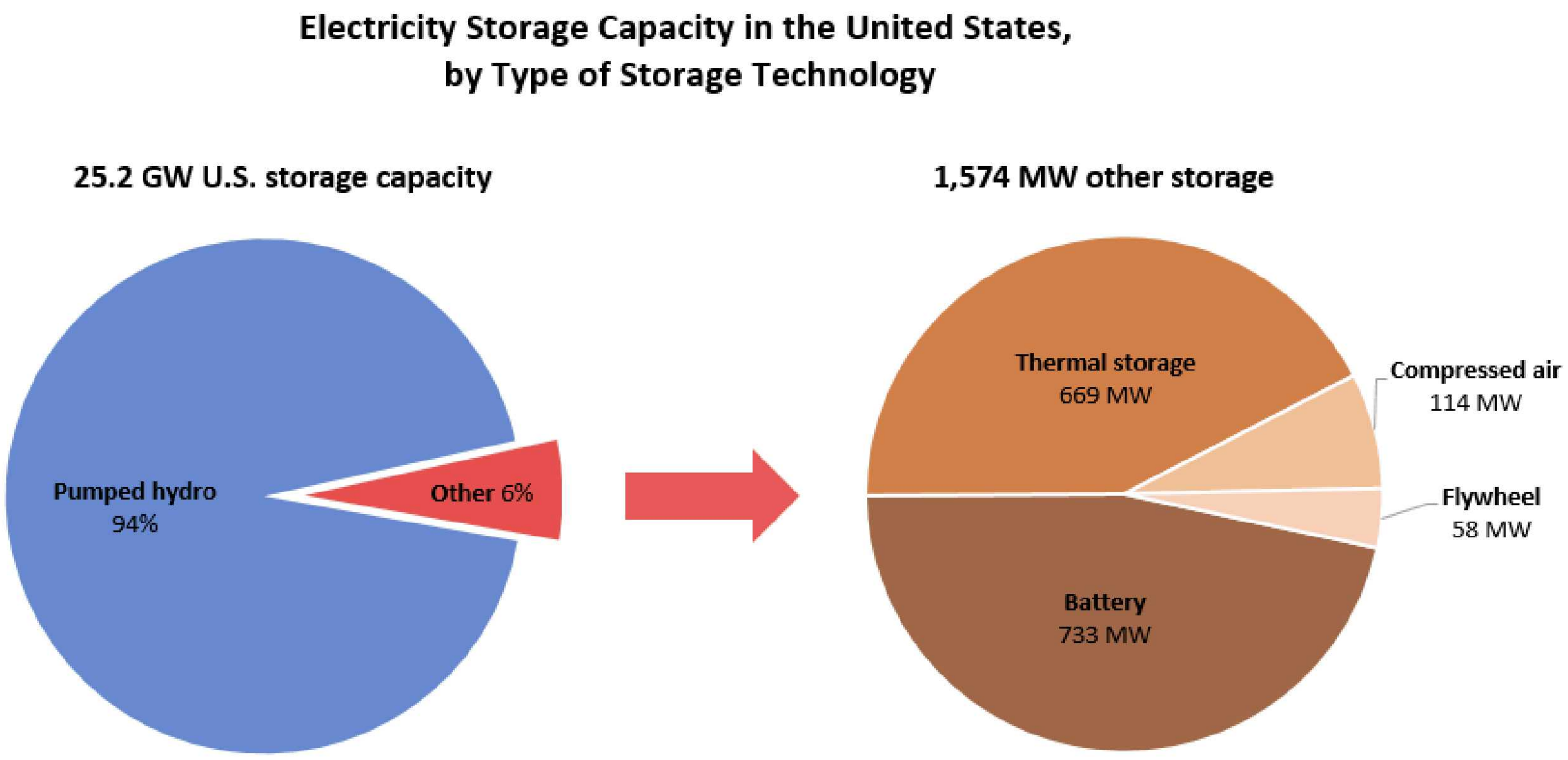
Emergency Aid

Electricity Storage Capacity in the United States, by Type of Storage Technology



Source: *DOE Global Energy Storage Database http://www.energystorageexchange.org/ March, 2018*

Battery-based Energy Storage: Room to Grow!



<u>% of in service U.S. Generation Capacity</u>

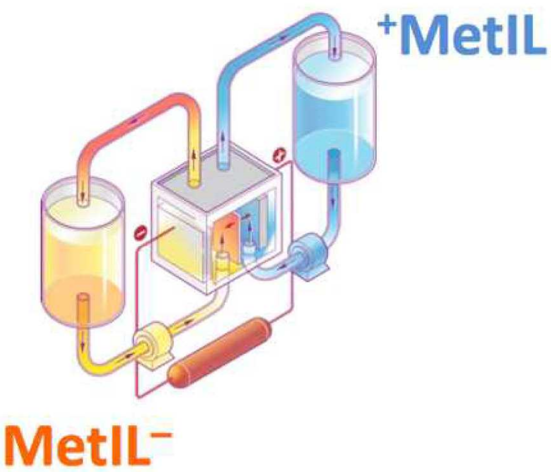
0.07% Battery Energy Storage

2.2% Battery Energy Storage and Pumped Hydro Storage

Source: *DOE Global Energy Storage Database http://www.energystorageexchange.org/ March, 2018*

Flow Batteries – Using Electroactive Fluids

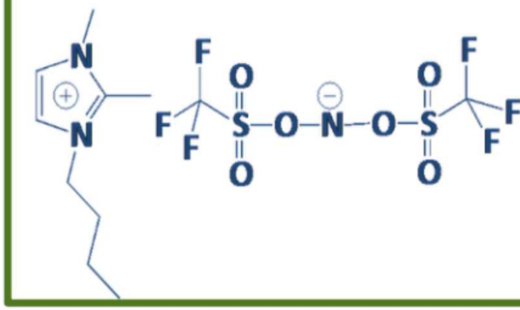
<u>Ionic Liquid Flow Batteries</u>: High energy densities possible through increased active species concentrations and and larger voltage windows.



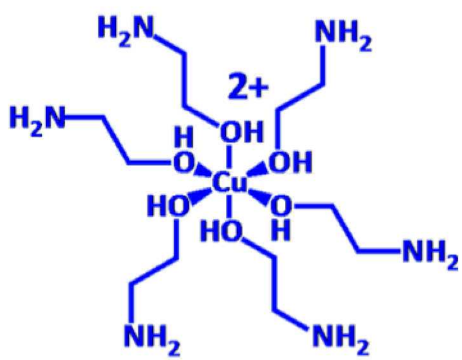
$$\text{Energy Density}_{RFB} \approx \tfrac{1}{2} n F V_{cell} c_{active}$$

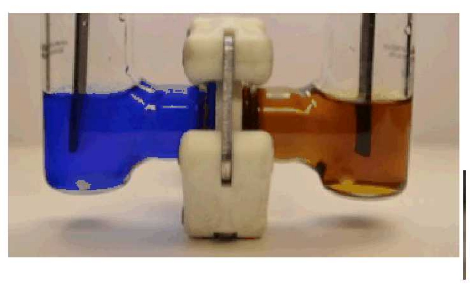
$$ED_{AQ} = \tfrac{1}{2} 1F 1.5_{cell} 2_{active} = \mathbf{1.5F}$$

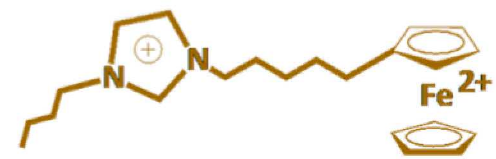
$$ED_{IL} = \tfrac{1}{2} 2F 2_{cell} 3_{active} = \mathbf{6.0F}$$



Four-Fold Improvement







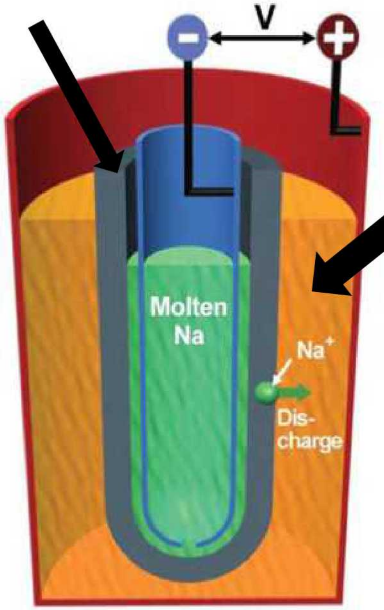
Pratt, *et al*, J. Electroanal. Chem. (2013) 153.

Promise in Molten Sodium Batteries

Sodium-based batteries

- 6th most abundant element on earth.
- 5X the annual production of aluminum.
- Proven technology base with NGK Sodium –Sulfur (NaS) Technology.
- Favorable battery voltages (>2V)
- ***Utilizes zero-crossover solid state separators.***

Ion Conducting Ceramic Separator



"Molten Catholyte"
- **Sulfur**
- **M-Halide Salts**

Traditional Na-Batteries operate at ~300°C

- Improves separator ionic conductivity
- Maintains molten phase chemistry
- Increases Cost
- Complicates Material Packaging
- Limits Battery Lifetime
- Introduces Freeze-thaw Hazards/Costs

Na-NiCl$_2$ (E_{cell} ~ 2.6V)

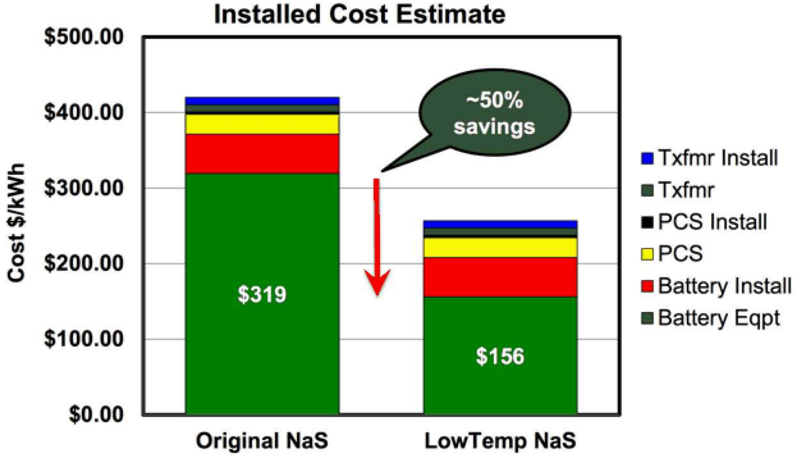
$2Na + NiCl_2 \leftrightarrow 2Na^+ + 2Cl^- + Ni(s)$

Na-S (E_{cell} ~ 2V)

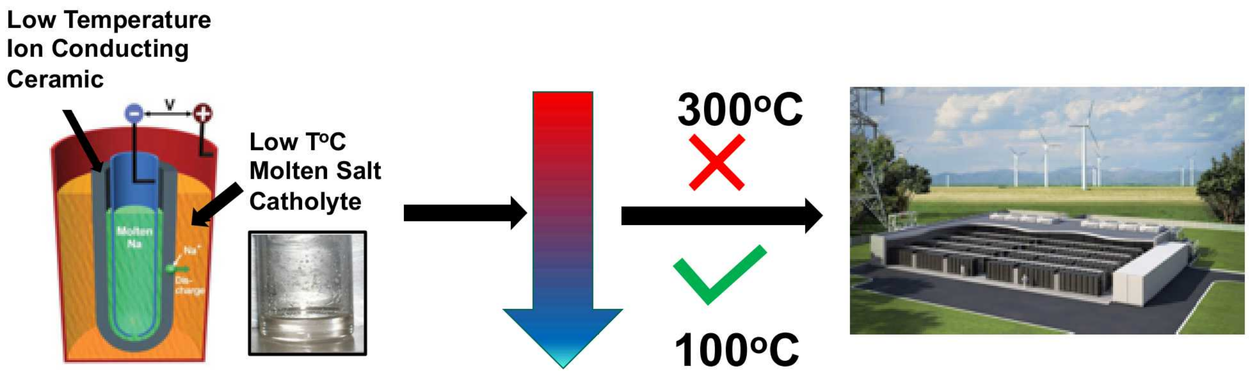
$2Na + 4S \leftrightarrow Na_2S_4$

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?
- Reduced operating costs
- Simplified heat management costs
  - Operation
  - Freeze-Thaw

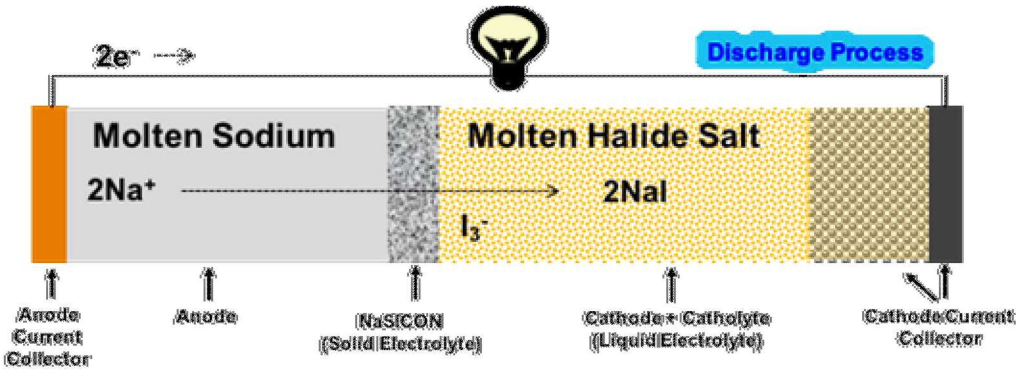


Gao Liu, et al. "A Storage Revolution." 12-Feb-2015 (online): https://ei.haas.berkeley.edu/education/c2m/docs/Sulfur%20and%20Sodium%20Metal%20Battery.pdf



Low Temperature Molten Na-NaI 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:

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

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

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

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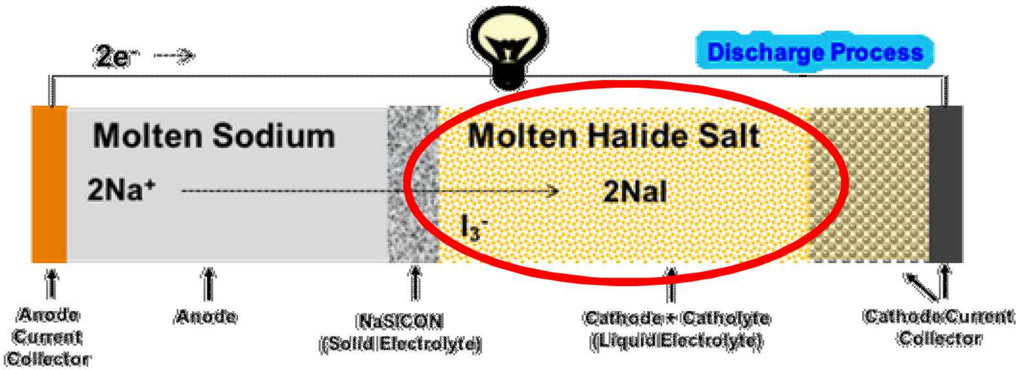

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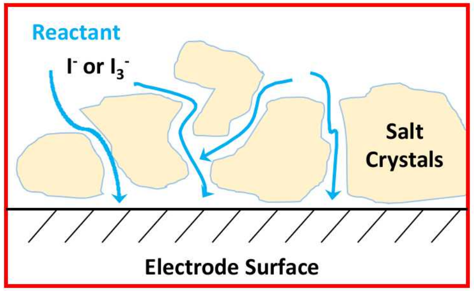
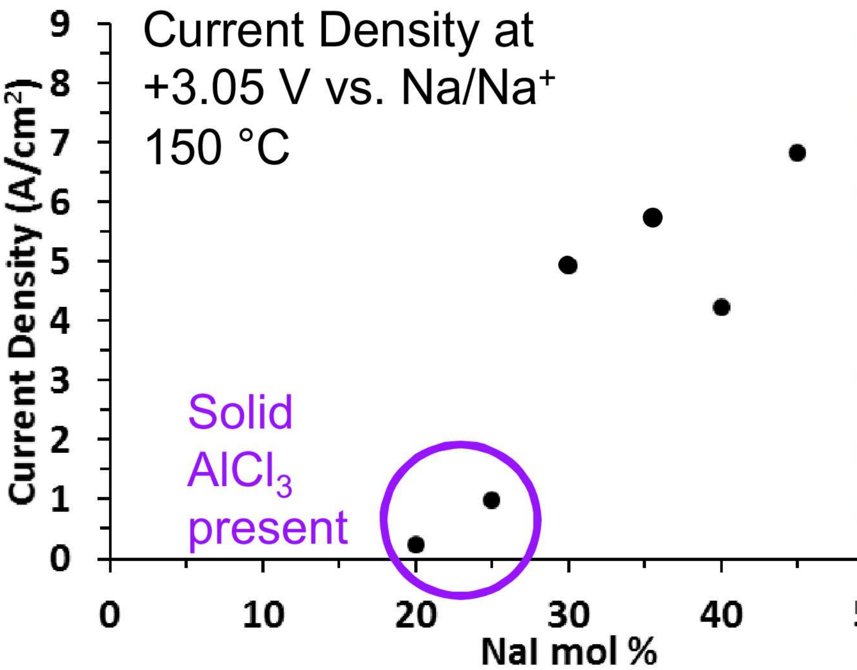
How important

Catholytes are Key to Low Temperature 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





Current Density is significantly lower when solid secondary phases are present.

S. Percival, L. Small, and E.D. Spoerke. *J. Electrochem. Soc.*, **165** (14) A3531-A3536 (2018)

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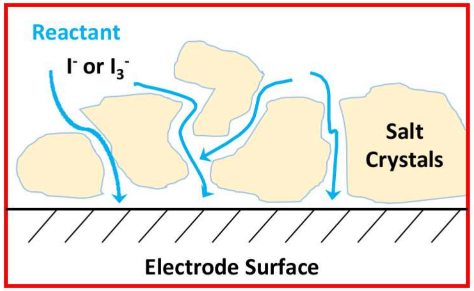
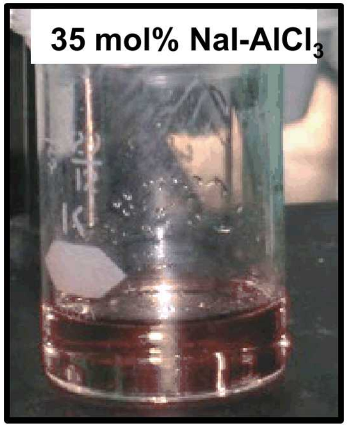


$NaI-AlCl_3$ at 150°C



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

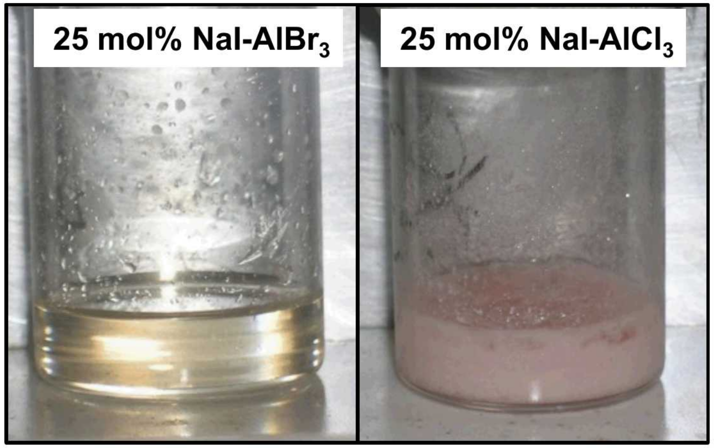
Molten $NaI-AlBr_3$ composition range spans 5-25% NaI and cell voltage is near or above 3V.

NaI-$AlBr_3$: A Low Temperature Molten Catholyte

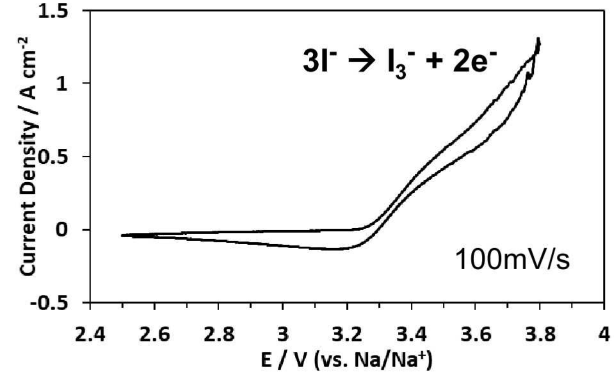
The NaI-$AlBr_3$ catholyte system exhibits excellent electrochemical behavior at reduced operating temperatures.

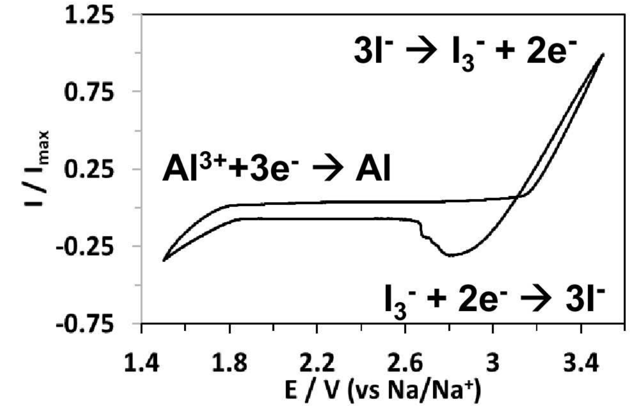
- 25:75 NaI-$AlBr_3$ salt <u>completely molten</u> at 90 °C
- Larger fully molten capacity range (~5-25 mol% NaI)

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

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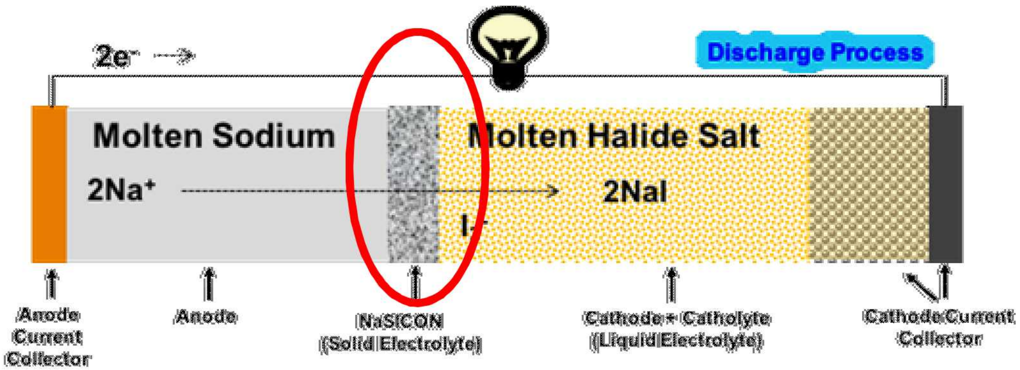

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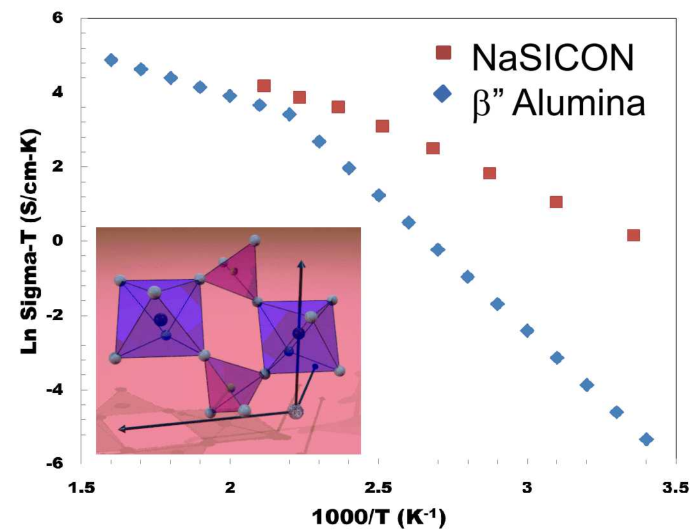
$I_3^{-} + 2e^{-} \rightarrow 3I^{-}$ $E^{0} = 3.24$

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

Key Qualities of NaSICON Ceramic Ion Conductors

- $Na_3Zr_2PSi_2O_{12}$
- High Na-ion conductivity ($>10^{-3}$ S/cm at $25^{o}C$)
- Chemical Compatibility with Molten Na and Halide salts
- Zero-crossover



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

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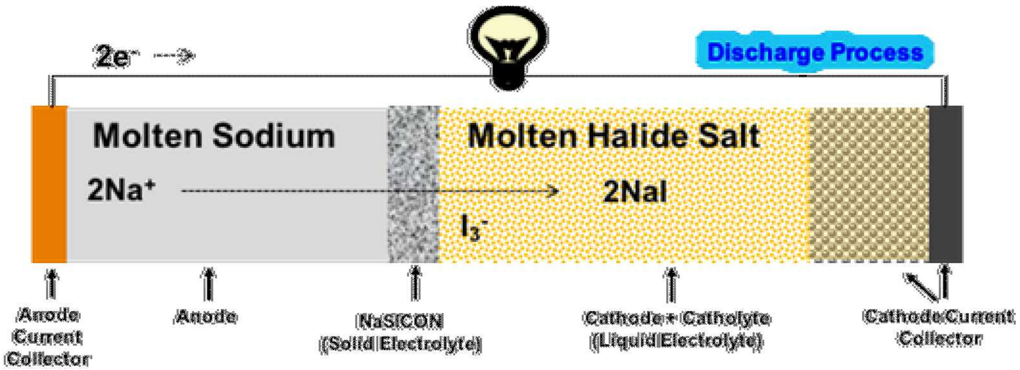

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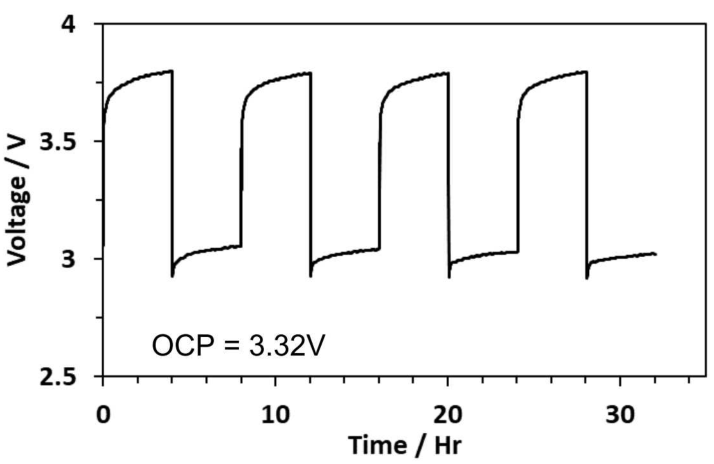
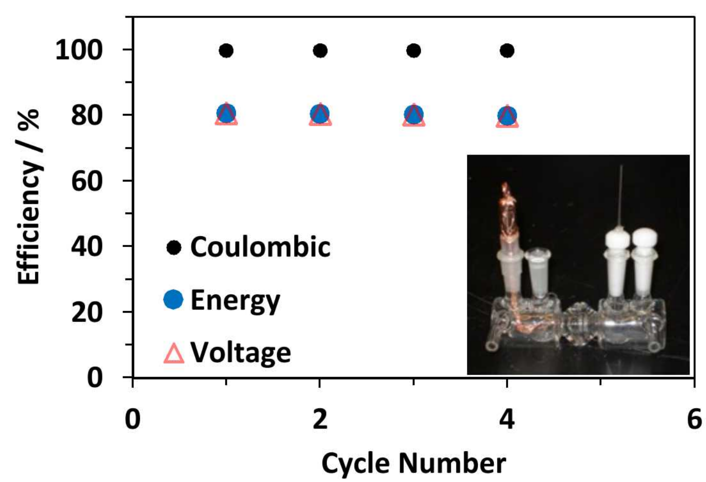


Battery cycling at 110°C!

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



How low can we go?

Low*est* Temperature Molten Na-NaI Batteries

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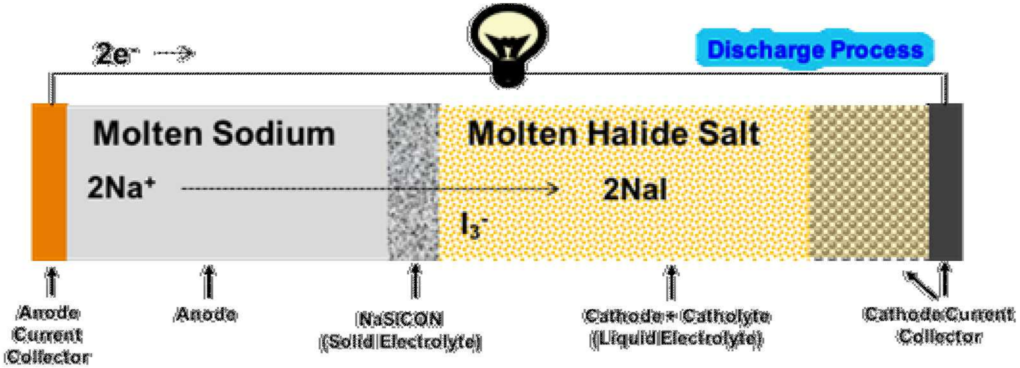

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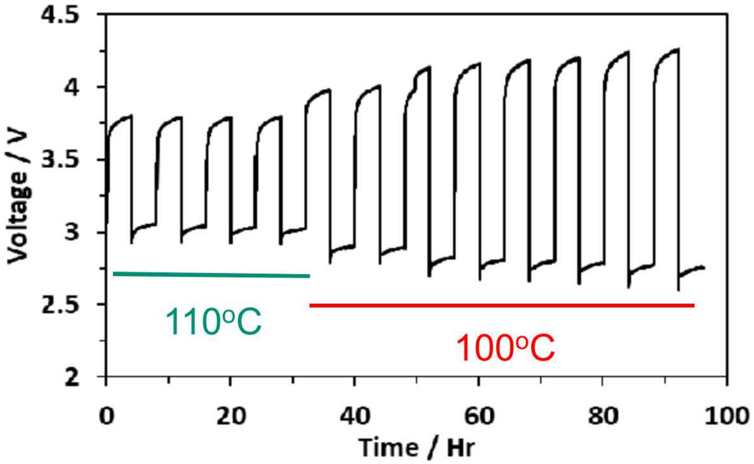
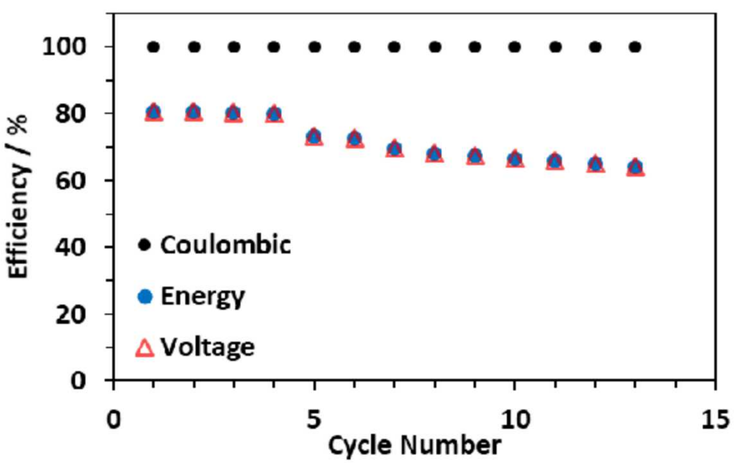


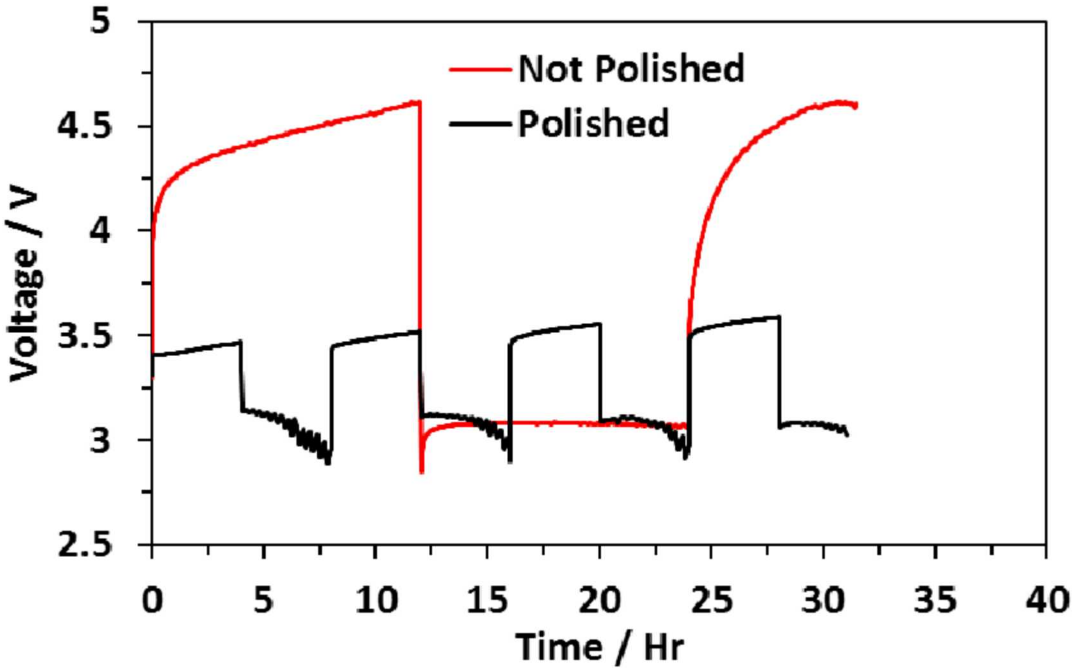
Battery cycling at **100°C**!

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



Separator Treatment Affects Cell Performance

First, clearing roughening the NaSICON surface with a surface polish allowed higher operating current density and lower overpotentials.



- Not polished NaSICON battery operated at ± 0.299 mA current C/12 1% DOD
- Polished NaSICON battery operated at ±0.897mA C/4 1% DOD

Separator Treatment Affects Cell Performance

A high temperature soak of Na metal on the NaSICON modifies interfacial wetting.

Heated at 100-200°C for 30 minutes

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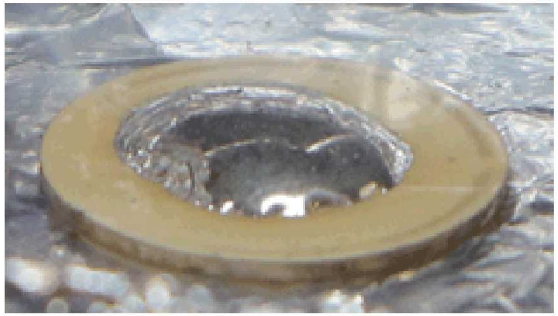

Heated above 380^{o}C for 30 minutes

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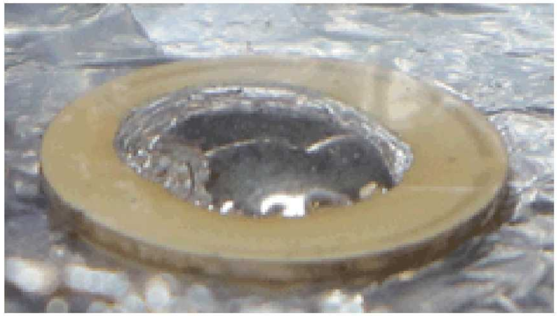
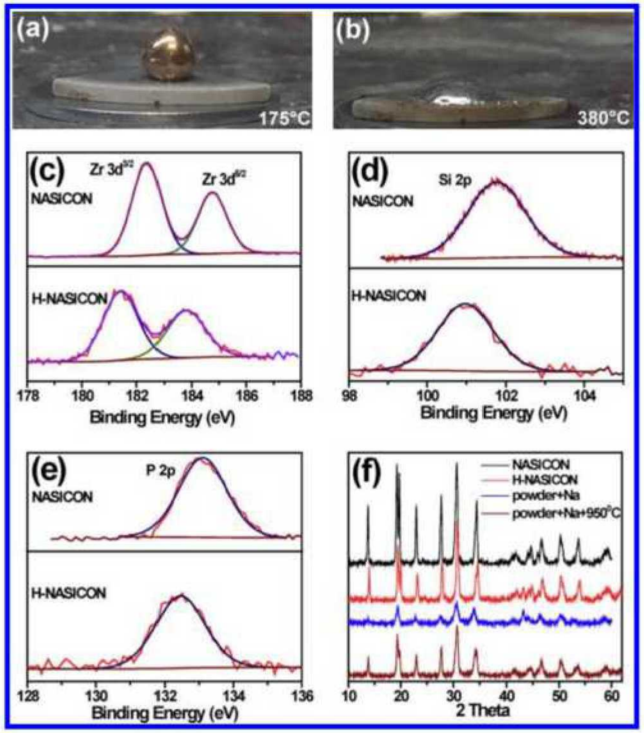


Heated above 380°C for 30 minutes

Based on treatments applied to NaSICON in a solid-state system, the change in pellet surface is believed due to formation of an amorphous, reduced NaSICON surface.



W. Zhou, *et al. ACS Cent. Sci.* (2017) **3**, 52-57.

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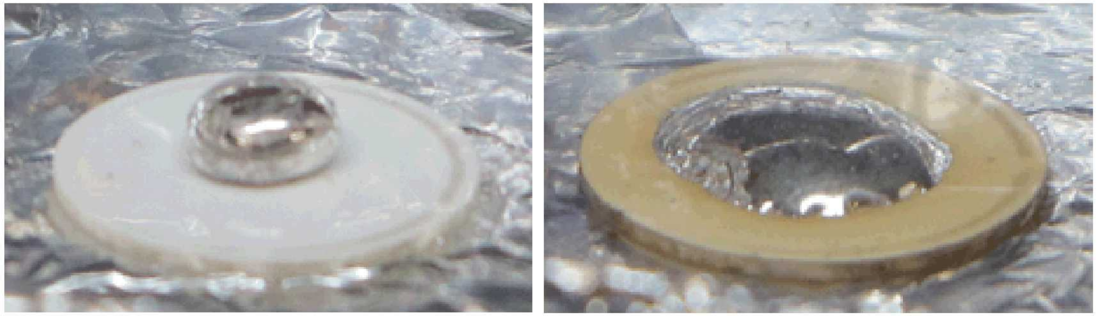
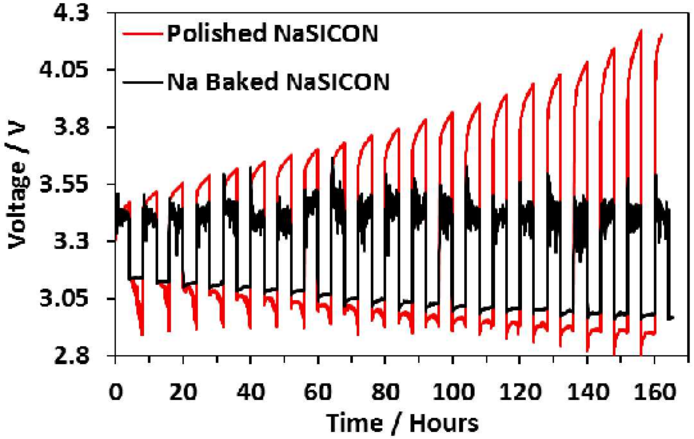
Heated below 200°C for 30 minutes



Heated above 380°C for 30 minutes

Na-treated NaSICON shows lower overpotentials on battery cycling.



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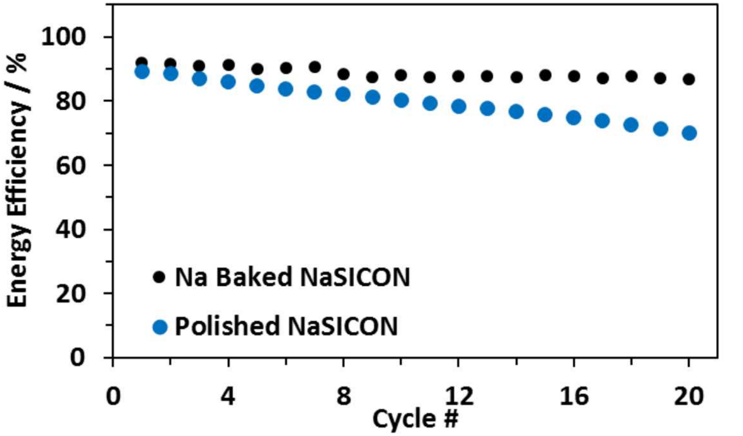


- Polished NaSICON battery operated at ±0.897 mA C/4 1% DOD
- Na Baked NaSICON battery operated at ±0.894 mA C/4 1% DOD

Will this be good enough?
(No pun intended)

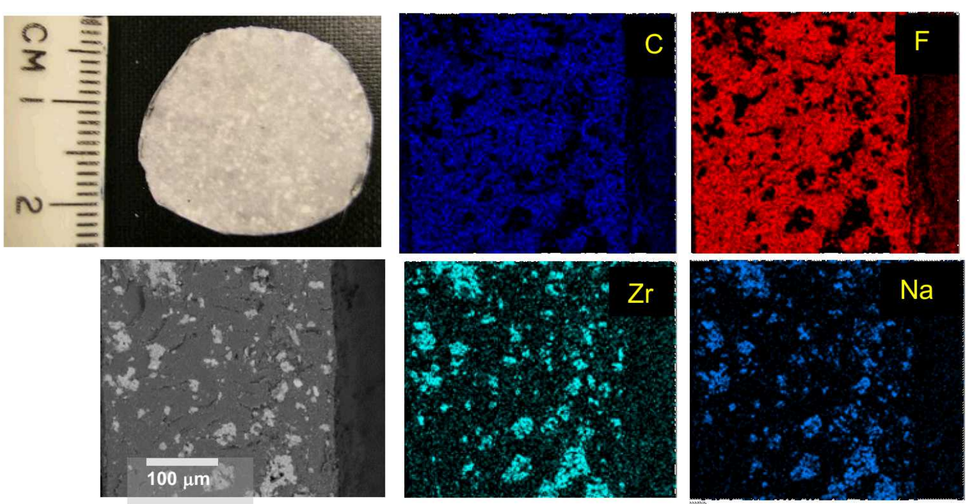
Composite Separator Innovation

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 ($4x10^{-10}$). Poor connectivity of Na-conductive NaSICON is evident in cross-sectional elemental mapping.



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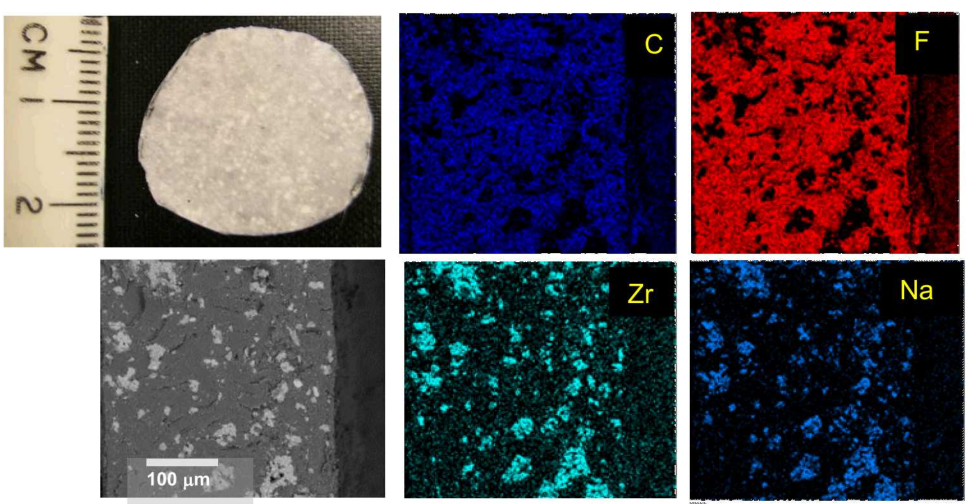
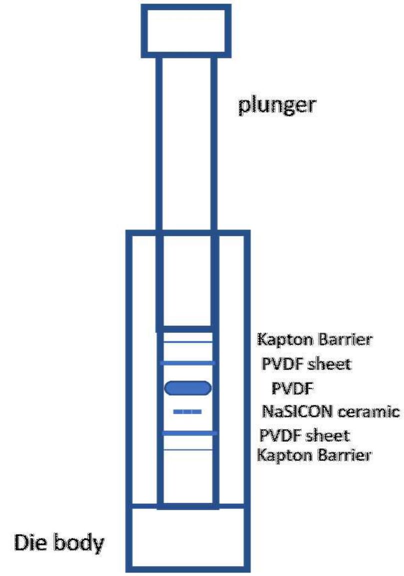
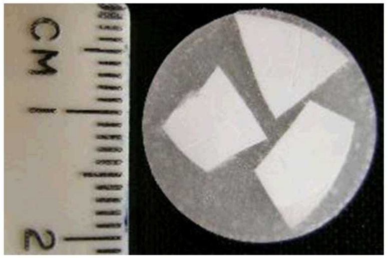


An alternative approach

- 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!

Take Away Messages

- Batteries are significantly under-represented in grid-scale electrical energy storage.

- Low temperature molten sodium batteries offer promise for safe, cost effective, long-life grid scale energy storage.

- Molten state anodes and catholytes are expected to improve battery performance, but require attention to materials chemistry.

- Separator performance is important and may be affected by significant interfacial interactions with molten components. Surface preparation of NaSICON will affect battery performance
  - Cleaning/polishing
  - High temperature Na-treatment

Continued materials development, and specific emphasis on interfaces, will be key to developing a new generation of molten-sodium 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.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Acknowledgements

Thank you!

We are currently seeking qualified postdoctoral candidates to work on battery technologies. (Eligibility for a US security clearance, which includes US citizenship, is required.)

Please contact me with questions: edspoer@sandia.gov

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

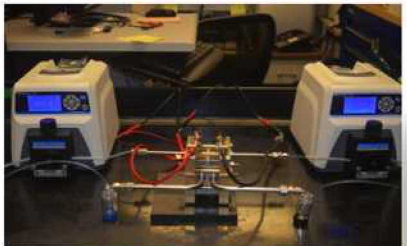
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Backup Slides

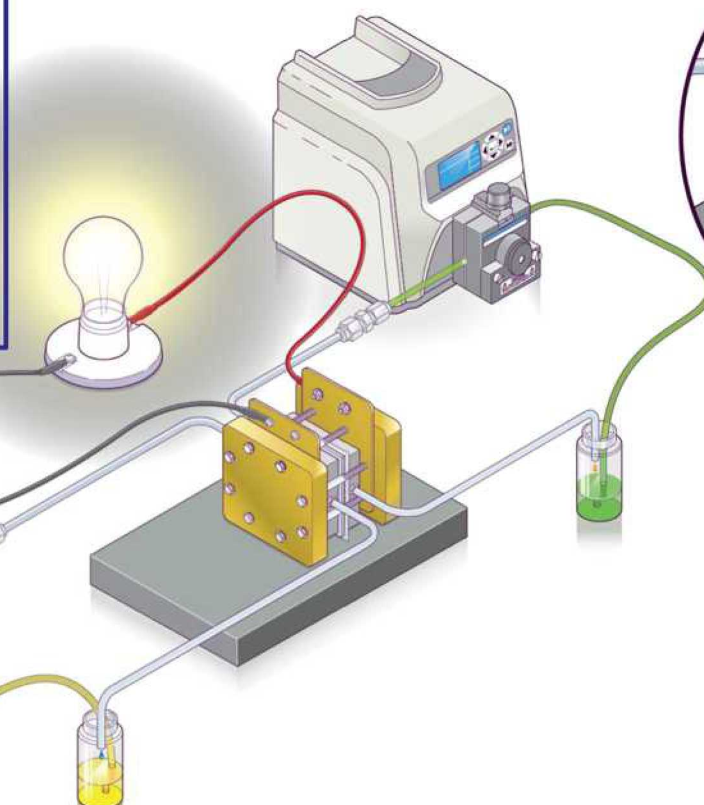
Flow Batteries – Using Electroactive Fluids

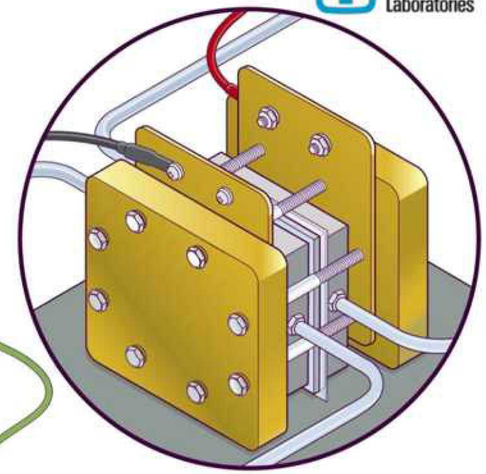
Ionic Liquid RFB Prototype

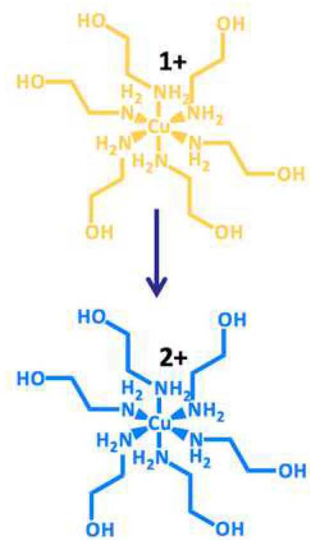
Sandia National Laboratories



Lab Scale Prototype







FY14 Focus: Non-aqueous electrolyte/membrane compatibility

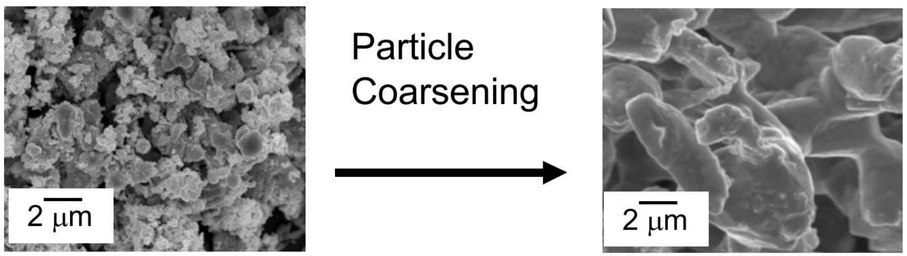
Anderson, Pratt, Small (SNL)

Challenges with Existing Na-Batteries

Na-NiCl$_2$ (E_{cell} ~ 2.6V)

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

- High temperature operation (typically > 270^{o}C)
- Cycle lifetime (solid cathode phase)
- Cost (related to cycle lifetime and material costs)



Na-S (E_{cell} ~ 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^{o}C)

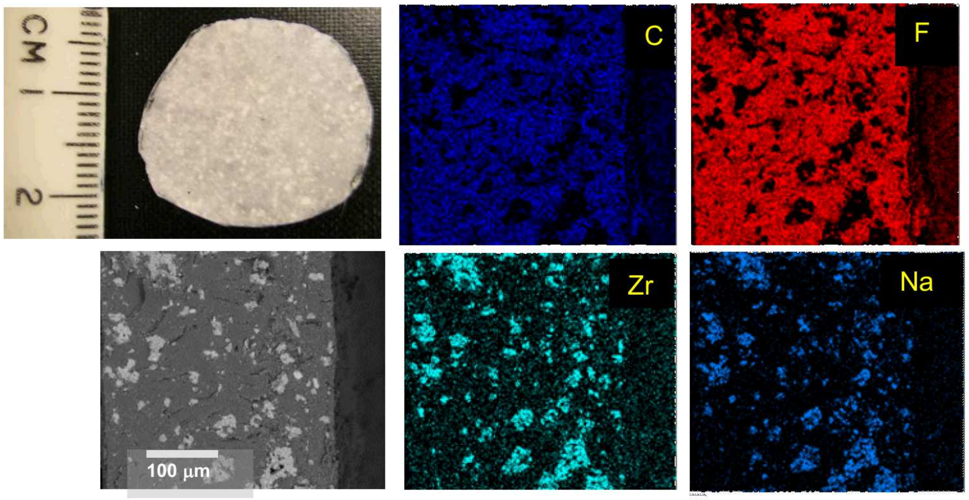
Composite Separator Innovation

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 (4×10^{-10}). Poor connectivity of Na-conductive NaSICON is evident in cross-sectional elemental mapping.



Hazards of Poor Material Selection

Polymer incorporation highlights the importance of careful material section.

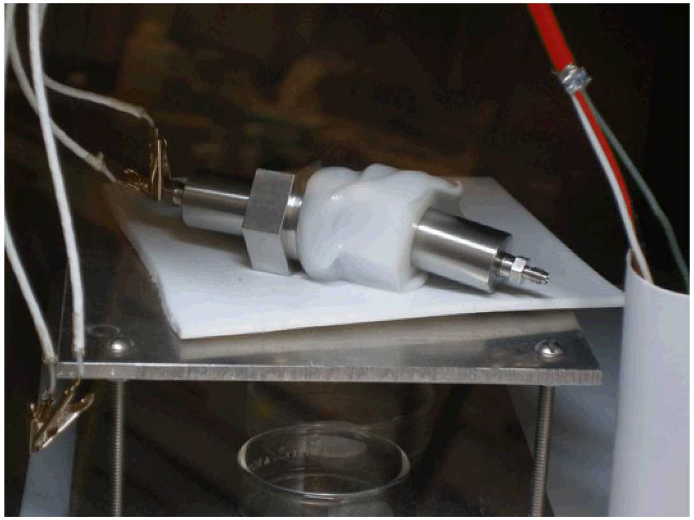
Compatibility must be considered for:

- 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

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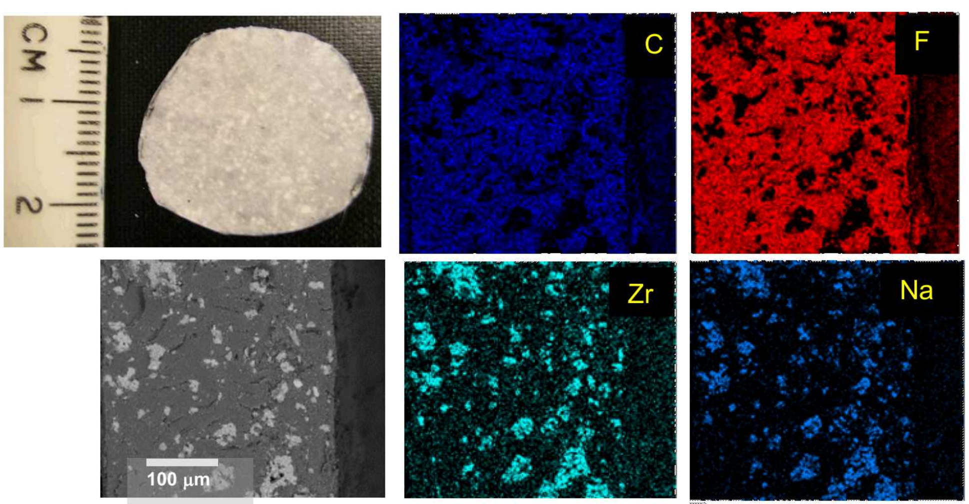
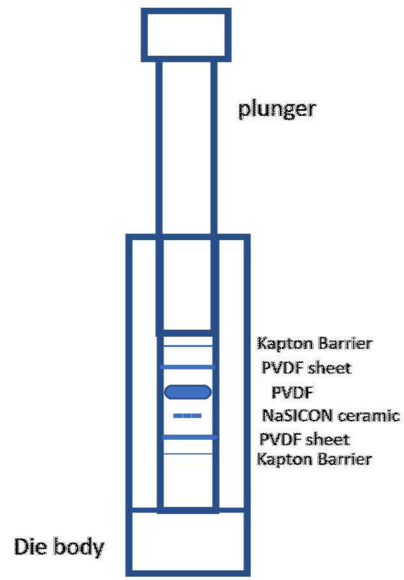
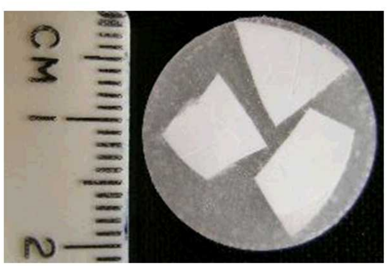


An alternative approach

- 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!