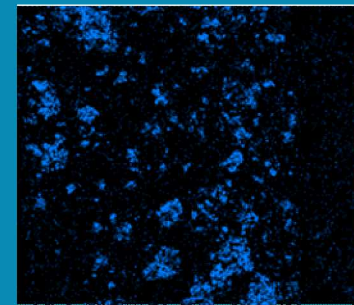
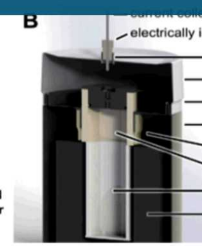
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2019-0748C

Rethinking Solid State Sodium Ion Conductors for Low Temperature Molten Sodium Batteries





<u>Erik D. Spoerke</u>

Amanda Peretti, Stephen Percival, Jonathan Bock, Harlan Brown-Shaklee, Leo J. Small, and Babu Chalamala

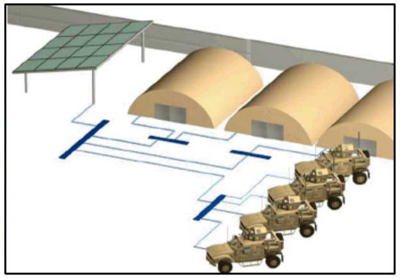
Sandia National Laboratories, Albuquerque, NM

Electronic Materials and Applications 2019 (EMA2019)
January 23-25, 2019
Orlando, FL

A Need for Grid-Scale Energy Storage Research


Renewable/Remote Energy

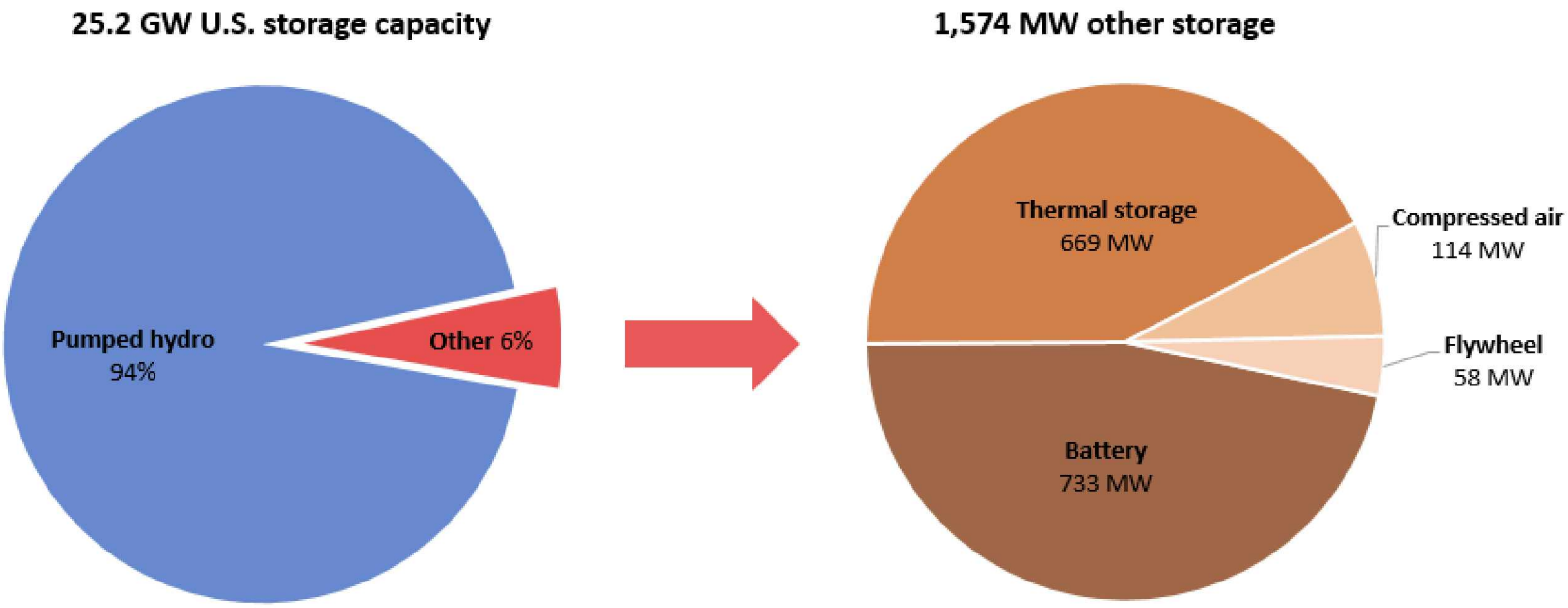
Grid Reliability



National Defense

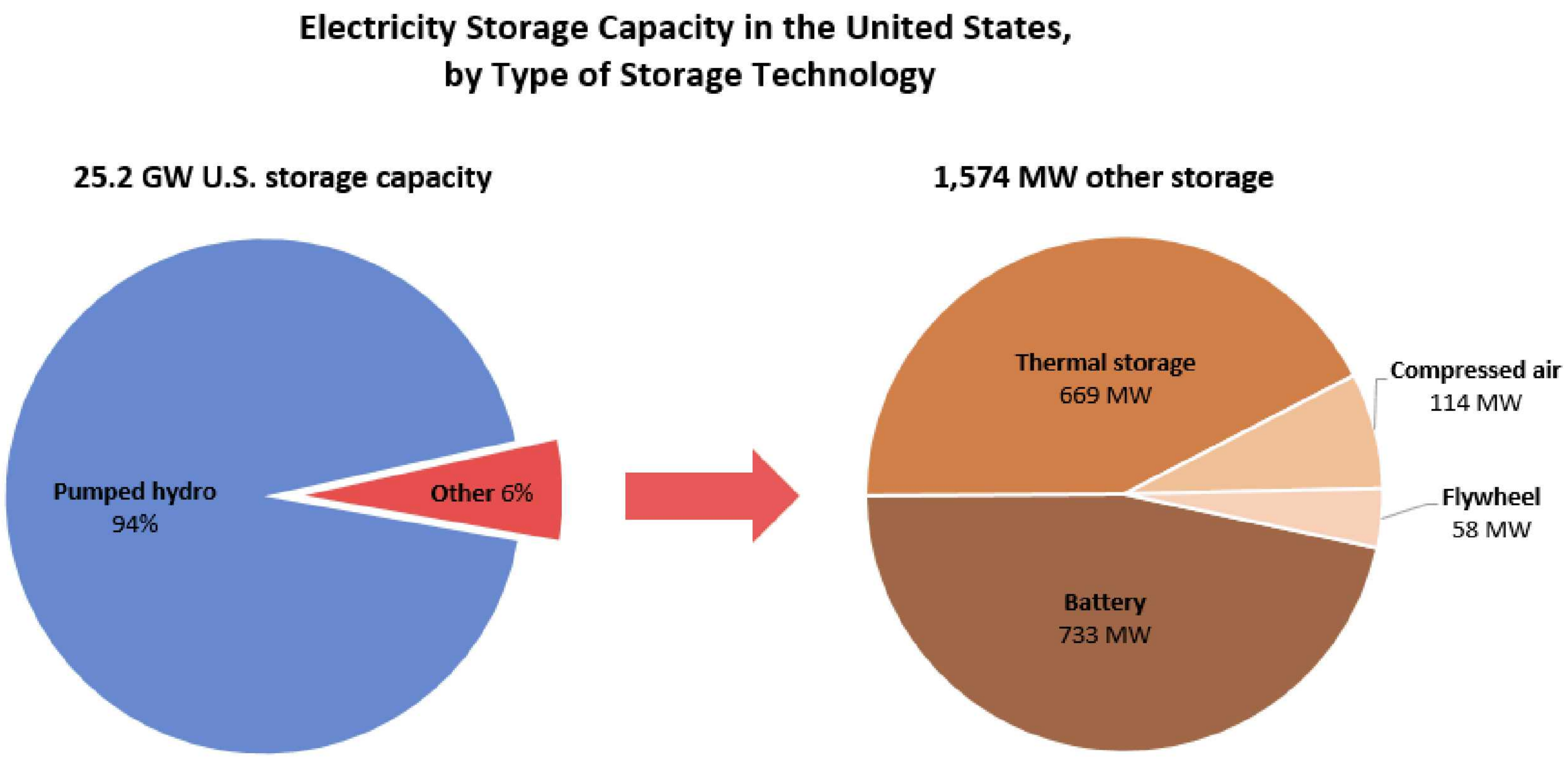
Emergency Aid

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*

Battery-based Energy Storage: Room to Grow!

Image from Can Stock Photo

Battery-based Energy Storage: Room to Grow!

Image from Can Stock Photo

Promise in Molten Sodium Batteries

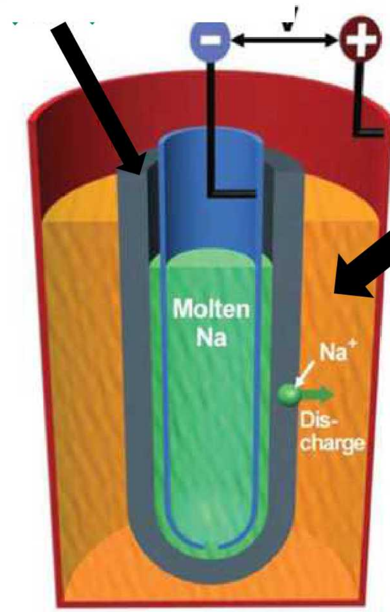
Sodium based Batteries

- 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.***

Traditional Na-Batteries operate ~300^{o}C

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

Ion Conducting Ceramic Separator



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

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

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

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

$2Na + 4S \leftrightarrow Na_2S_4$

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

Target Battery Properties

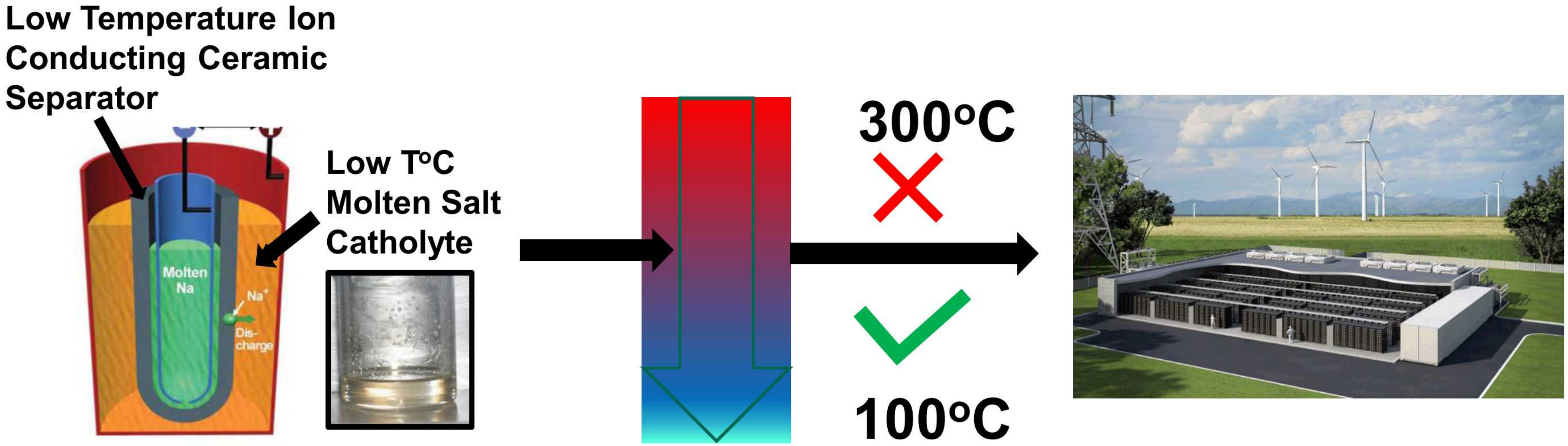
- Inherent Safety
- Long Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalable

Our Goal: Reduce Na-Battery Operating Temperature

We aim to develop materials chemistries that enable operation of sodium-based batteries at *reduced temperatures*.

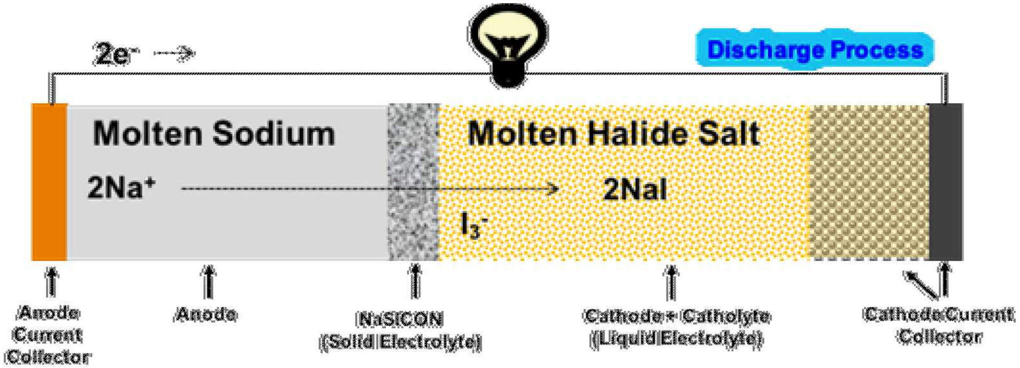
Reducing operating temperature requires innovation of several key battery components

- Catholyte
- Battery Seals and Packaging
- Separators



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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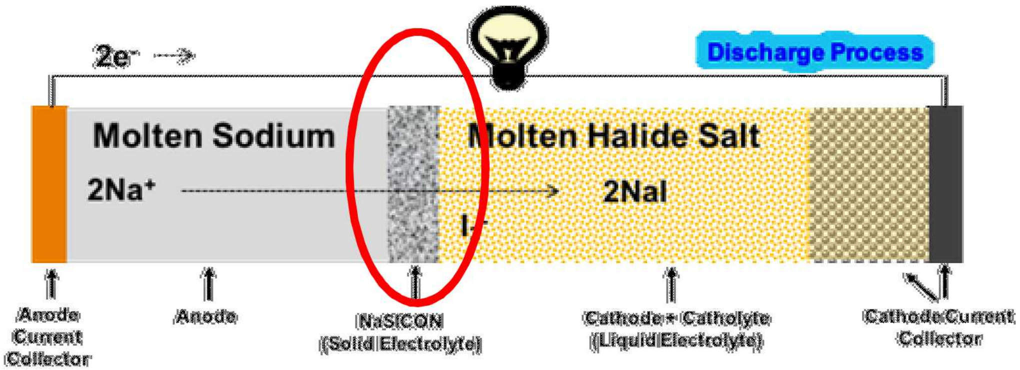

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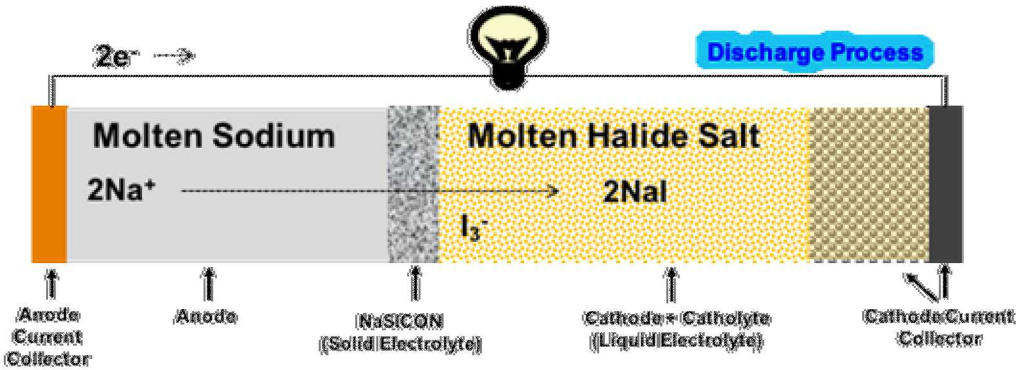

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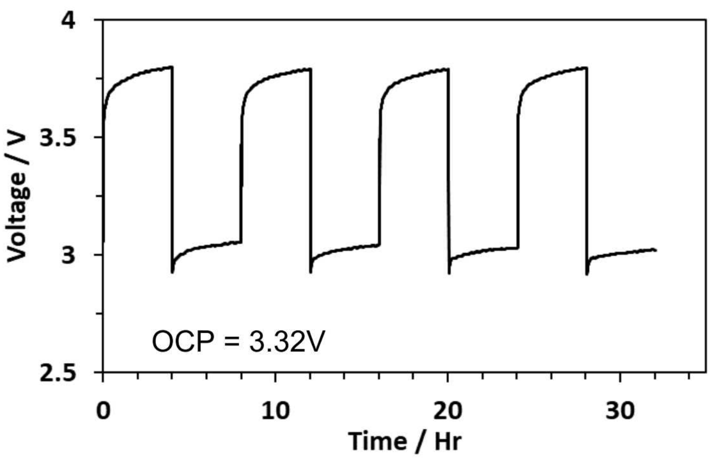
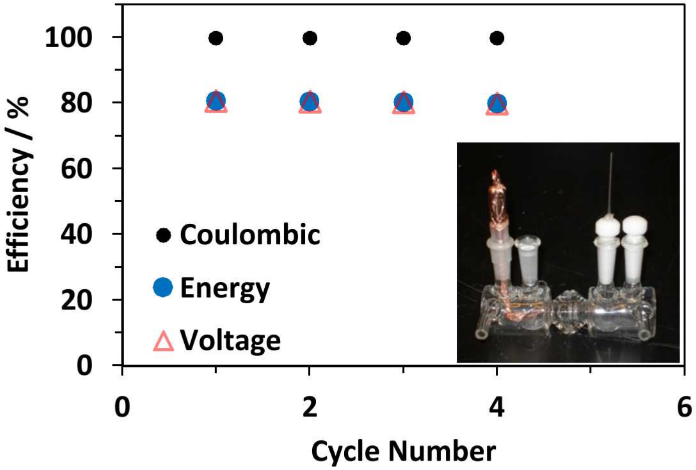


Battery cycling at 110°C!

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



Low*est* Temperature Molten Na-NaI Batteries

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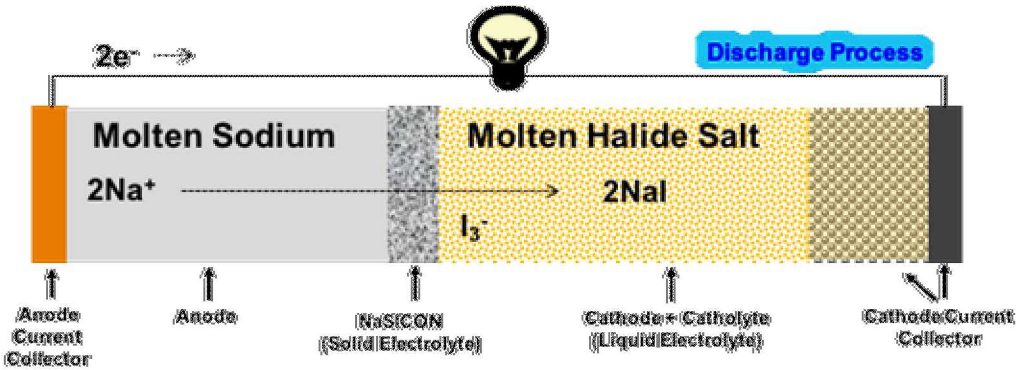

<u>Na-NaI battery:</u>

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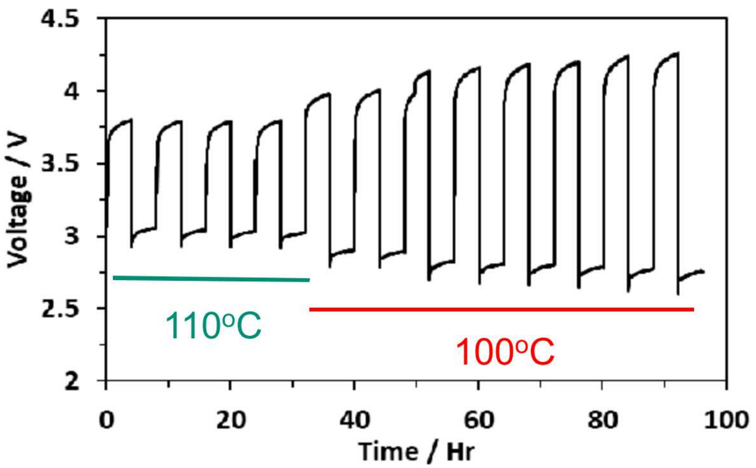
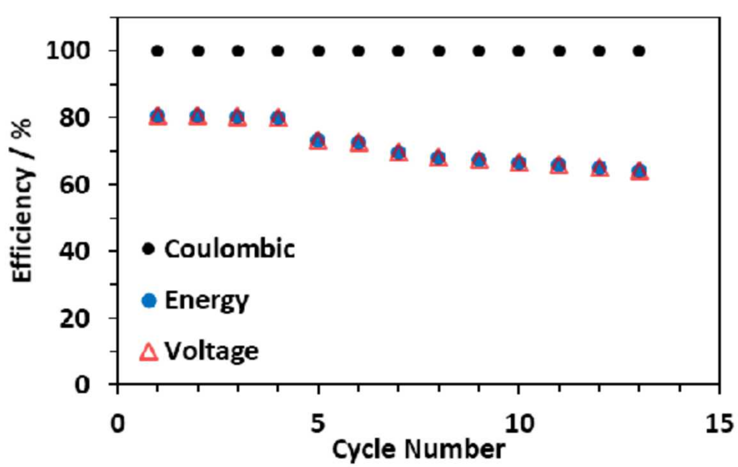


Battery cycling at **<u>100°C</u>**!

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



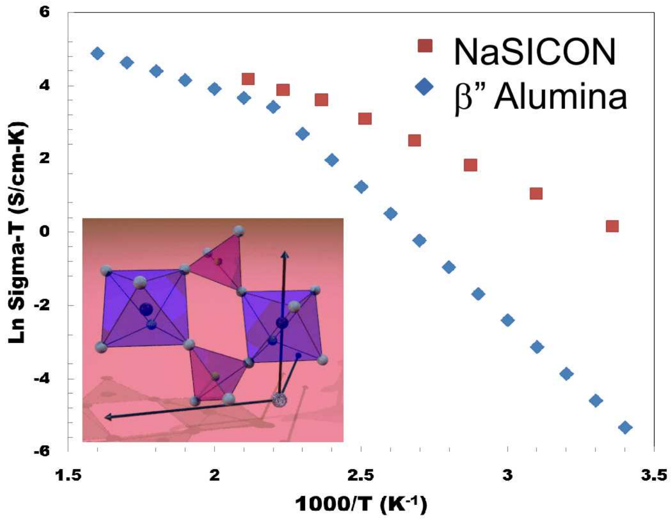
NaSICON Ceramic Separators

Key Separator Properties:

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

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



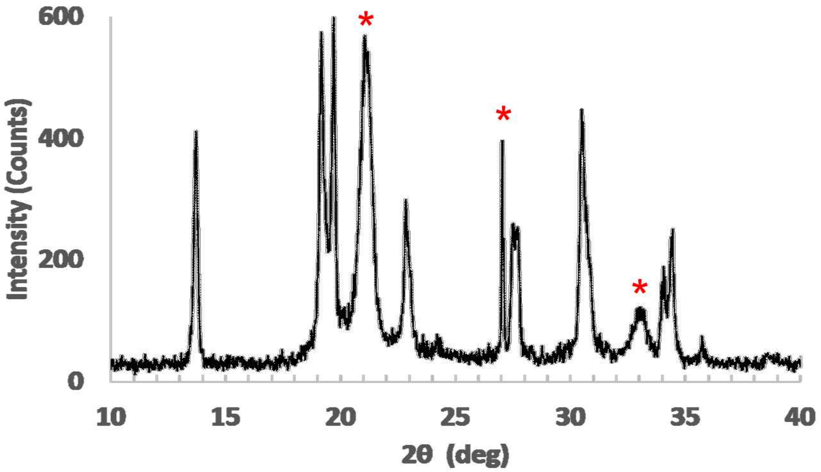
Small and Spoerke, et al. *J. Power Sources*. **360**. 569-574.

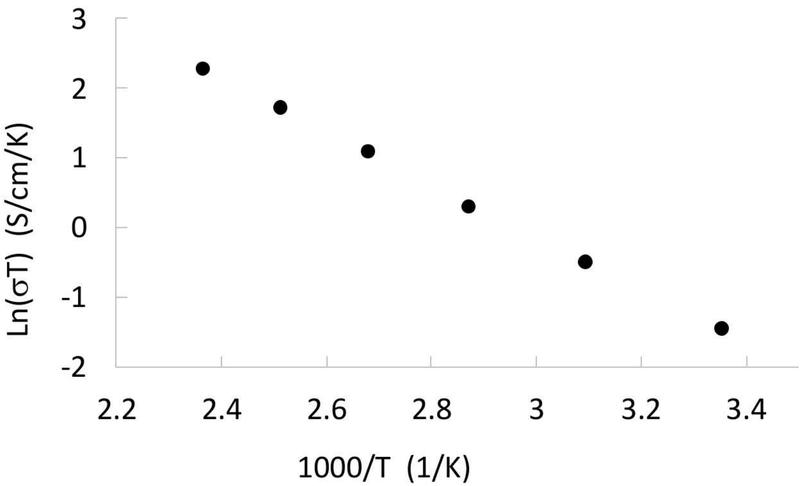
Conventional Synthesis

Solid State Ceramic Synthesis ("Shake 'n Bake")

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

- Milled powders pressed and fired at 1200°C in air
- Pellet densities >95%
- X-ray diffraction confirms NaSICON synthesis with ZrO_2 and $ZrSiO_4$ secondary phases
- Conductivities reasonable, but slightly less than commercial NaSICON





Key Processing Variables

Humidity

- Desired >95% theoretical density (3.2 g/cm^3)
- During monsoon season (high humidity) pellet density dropped from 98% to ~70-80%
- Drying or calcining powder at 600°C immediately before pellet pressing returned density to >95% density.

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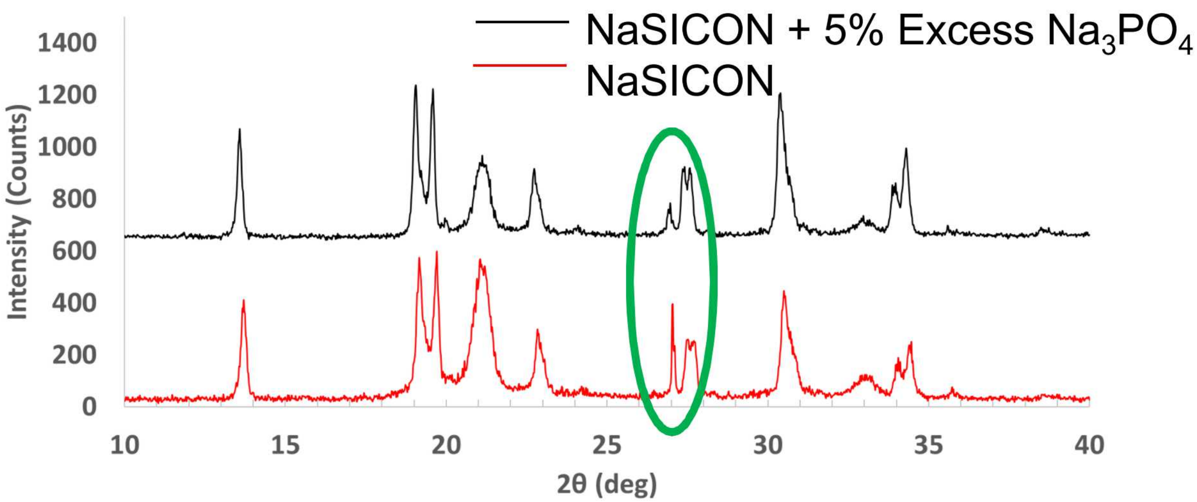
Secondary Phase Formation

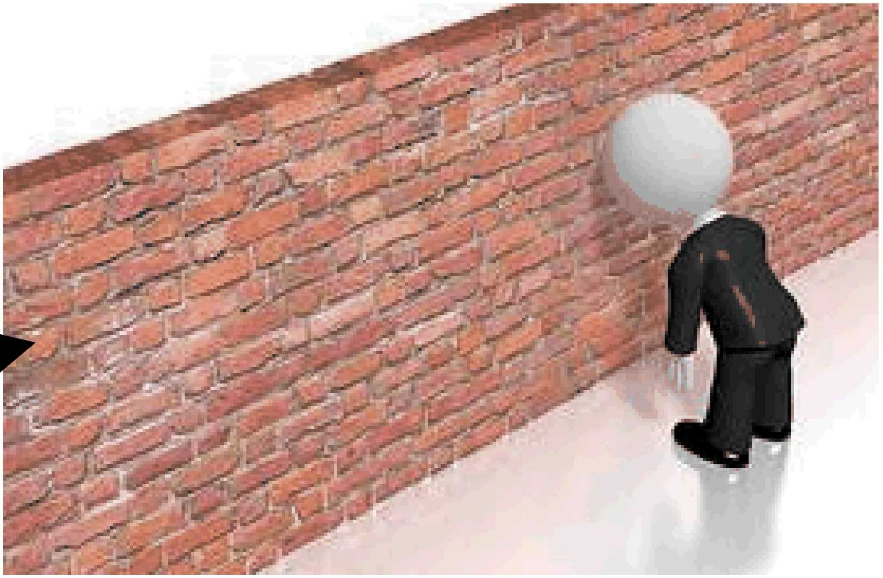
- Secondary phases, such as ZrO_2 and $ZrSiO_4$, can degrade conductivity.
- "Na" and "PO_4" volatility during sintering can lead to secondary phase formation.
- 5% Excess Na_3PO_4 showed diminished secondary phases



Conductivity increase by ~30% with excess Na_3PO_4!

Conventional Synthesis Can be a Headache!

Solid state synthesis of NaSICON?



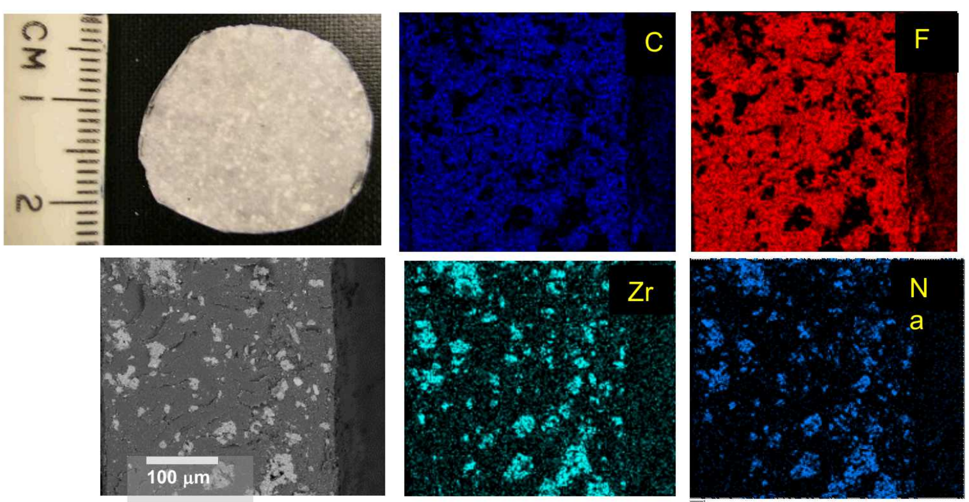
Composite Separator Innovation

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.



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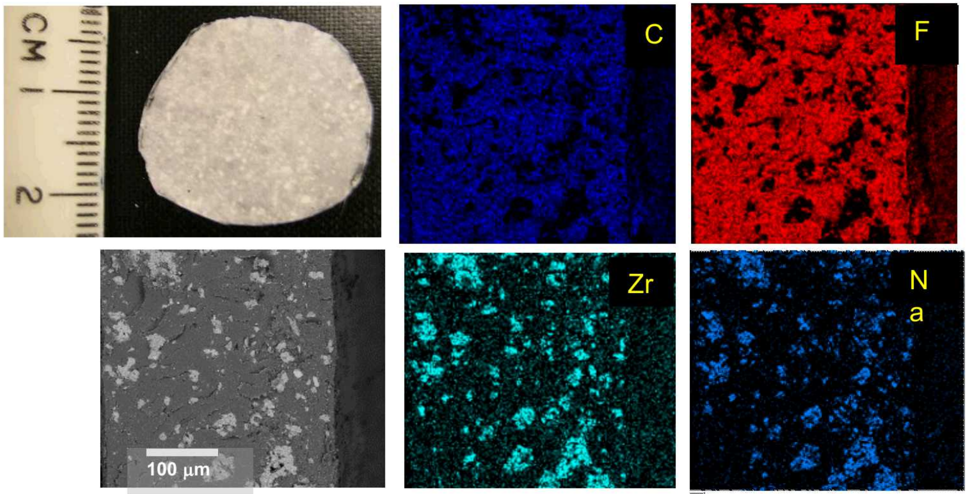
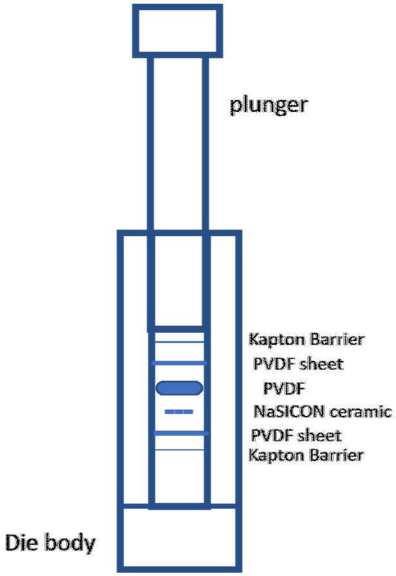
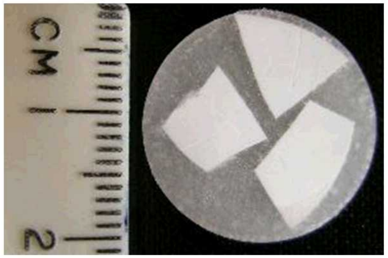


An alternative approach

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



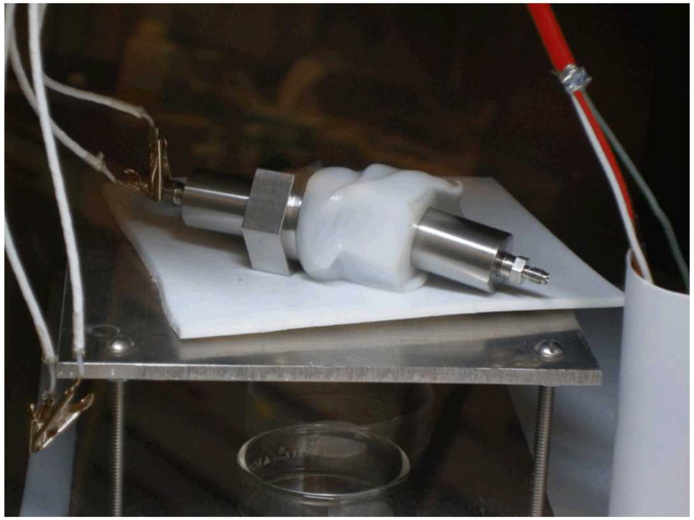


Conductivity is determined by NaSICON ceramic.

σ_{RT} ~0.5 mS/cm for composite!

Hazards of Poor Material Selection

Thermal and mechanical stability



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.)

Chemical compatibility

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.

One Quick Teaser…

Solution-Assisted Ceramic Densification (Cold Sintering)

NZP-1

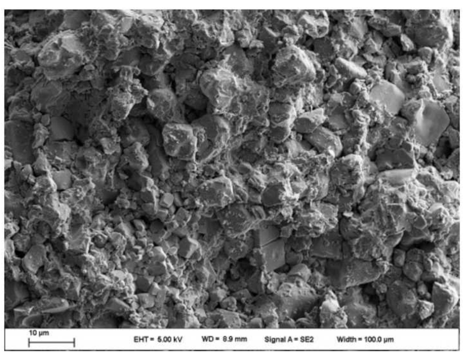
- $NaZr_2P_3O_{12}$ (From Sol-gel prep)
- 10wt% 10M NaOH
- 530MPa (75ksi)
- 25°C/min ramp rate
- Hold 150°C for 20 min

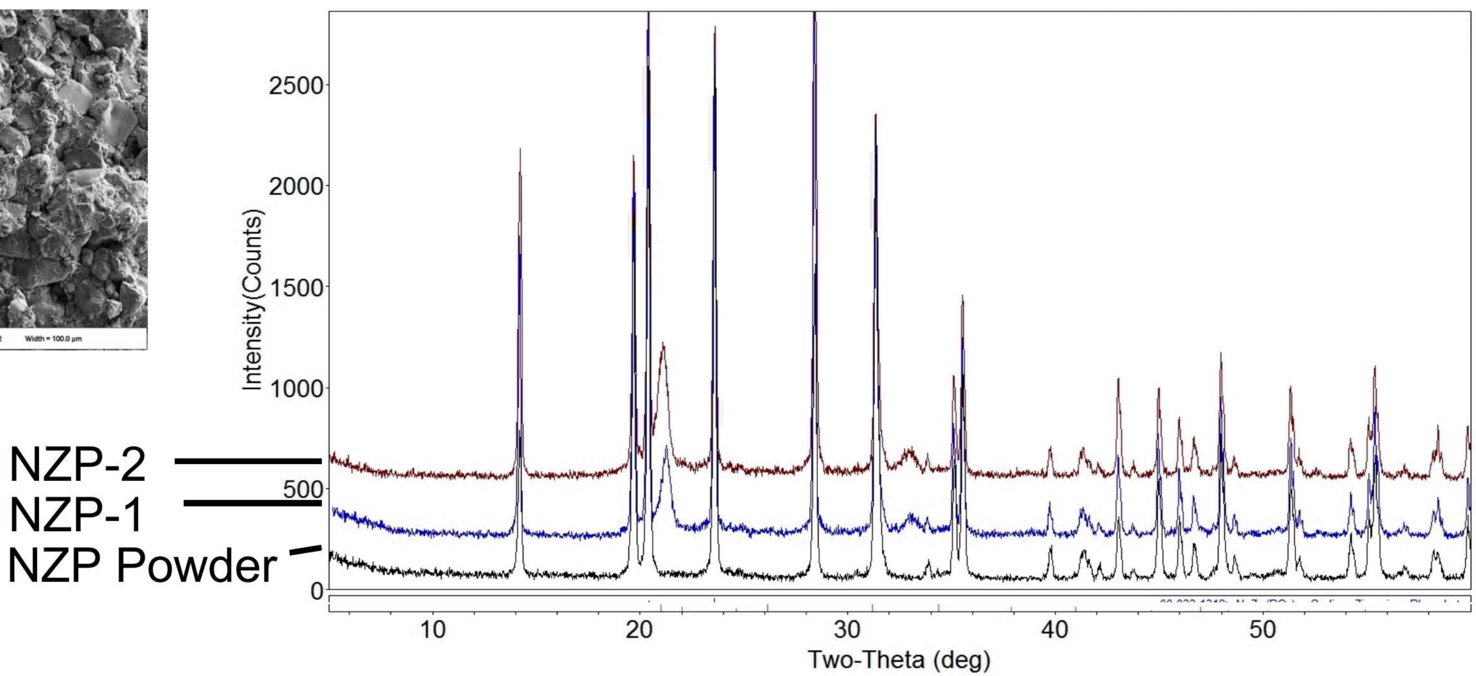
- **Geometric Density ~ 2.82g/cc**
- Relative Density ~89% (Theoretical assumed 3.2g/cc)

NZP-2

- $NaZr_2P_3O_{12}$ ('1100C pg 6 NBI')
- 8wt% 10M NaOH
- 530MPa
- 10°C/min ramp rate
- Hold 150°C for 30 min

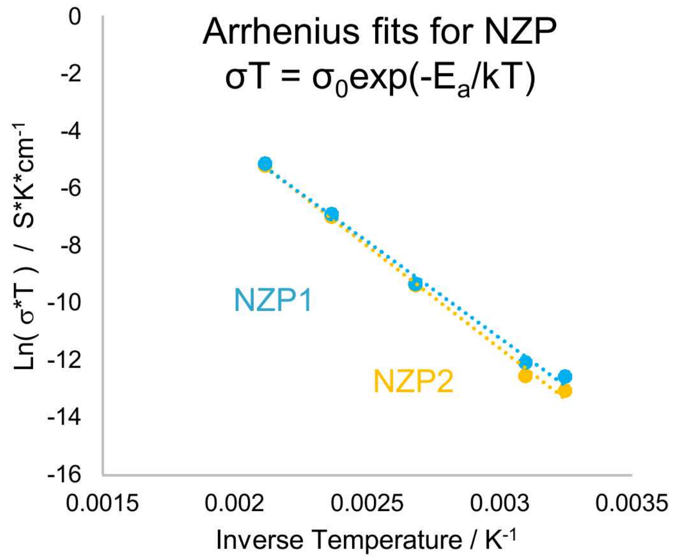
- **Geometric Density ~ 2.85g/cc**
- Relative Density ~90% (Theoretical assumed 3.2g/cc)





Na^+ Conductivity of CSP NZP + NZSP

	Na^+ Conductivity for (Grains + Grain Boundaries) / S cm^{-1}					
Sample	**200 °C**	**150 °C**	**100 °C**	**50 °C**	**35 °C**	**E_a (eV)**
NZP1	1.17E-05	2.19E-06	2.26E-07	1.10E-08	6.87E-09	0.62
NZP2	1.26E-05	2.38E-06	2.39E-07	1.76E-08	1.13E-08	0.58



>2.5 h equilibration time before each measurement
1 MHz – 10 mHz, 100 mV AC, 0 V DC using Solartron 1260+1296
NZP lost 0.2-0.3% mass after measurement.

For reference:

NZP: 10^{-5}-10^{-4} S/cm @200 °C, activation energy 0.51-0.61 eV
(900°C sinter + excess Na_2O from Aono, *JACerS*, 1996, 79, 2786-2788)

NZSP: ~4 mS/cm at 25 °C (Ceramatec)

Though not yet optimal, these results indicate promise toward the application of this process for NaSICON production.

Take Away Messages

- Low temperature sodium batteries, enabled by next generation solid state separators, may help address a huge need for increased grid-scale energy storage.
- Solid State NaSICON can be successfully synthesized with high density and reasonable conductivity
    - Humidity and secondary phase formation can affect NaSICON ceramic properties, but can be managed through synthetic modifications.
- Composite separators comprising NaSICON powder and polymer are tough and durable, but have insufficient NaSICON connectivity and thus very low conductivity.
- Composites comprising NaSICON “chips” with “through-connectivity” showed functional conductivity in a tougher, compliant separator.
- Chemical compatibility of composite components is IMPORTANT!
- Future work will focus on improving NaSICON ceramic conductivity and incorporation into hybrid or composite separator structures, including the use of alternative processing methods, such as solution-assisted ceramic densification.

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

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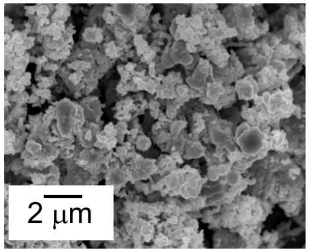
Backup Slides

Challenges with Existing Na-Batteries

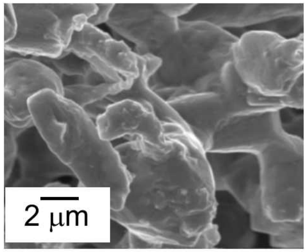
$Na\text{-}NiCl_2$ (E_{cell} ~ 2.6V)

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

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



Particle Coarsening →



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°C)