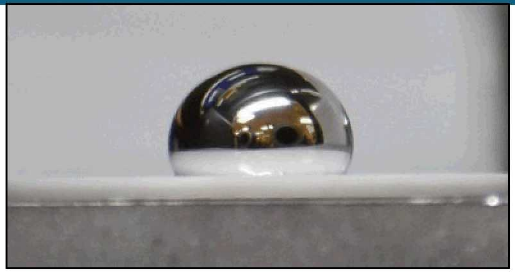
SAND2020-0733C

Synthetic Designs For Improved NaSICON-Based Sodium Ion Conductors



Amanda Peretti,
Eric Coker,
Mark Rodriguez,
Martha Gross,
Stephen Percival,
and Leo Small

PRESENTED BY

Erik D. Spoerke

Electronic Materials and Applications 2020
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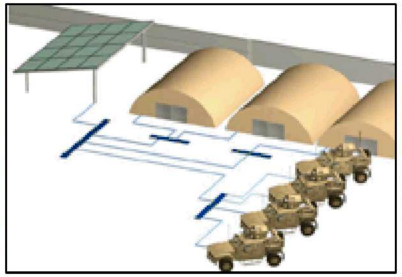
SAND No.: SAND

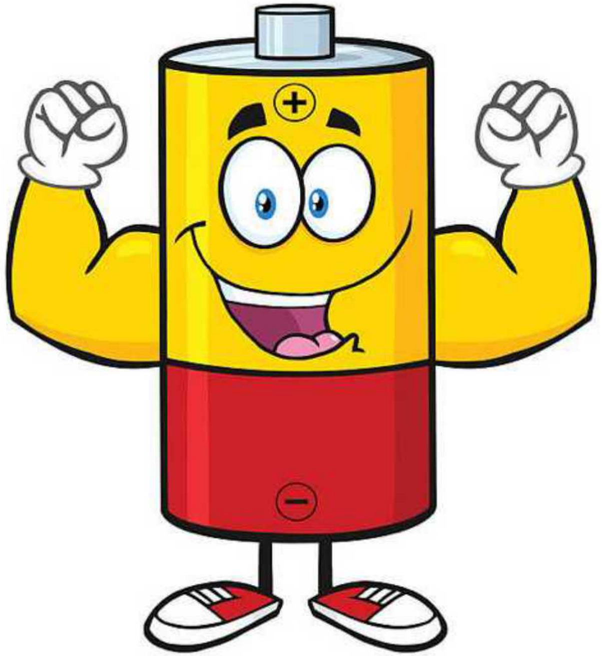
A Need for Grid-Scale Energy Storage



Renewable/Remote Energy | Grid Reliability | National Defense | Emergency Aid

As part of the DOE Office of Electricity efforts to create a modern, resilient, reliable, and agile grid system, we are developing new battery technology characterized by:

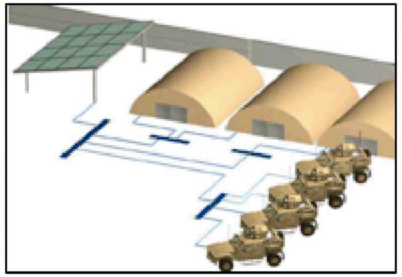
- Inherent Safety
- Long, Reliable Cycle Life
- Functional Energy Density (voltage, capacity)
- Low to Intermediate Temperature Operation
- Low Cost and Scalability



Sodium Batteries


Renewable/Remote Energy

Grid Reliability



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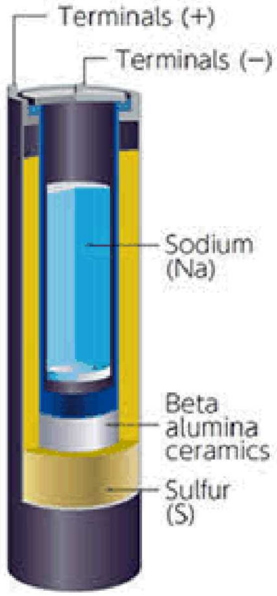
<u>Sodium-based batteries</u>

- 6th most abundant element on earth.
- 5X the annual production of aluminum.
- Proven technology base with NGK Sodium/Sulfur (NaS) and FzSoNick ZEBRA (Na-$NiCl_2$) systems.
- Utilize zero-crossover solid state separators.
- Favorable battery voltages (>2V).



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

$2Na + 4S \leftrightarrow Na_2S_4$

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

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

Sodium Batteries


Renewable/Remote Energy

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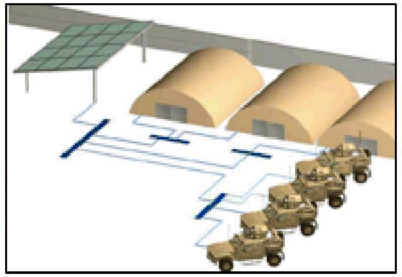

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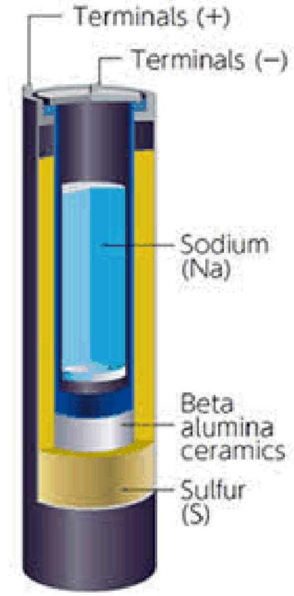


Na- ... **V)**

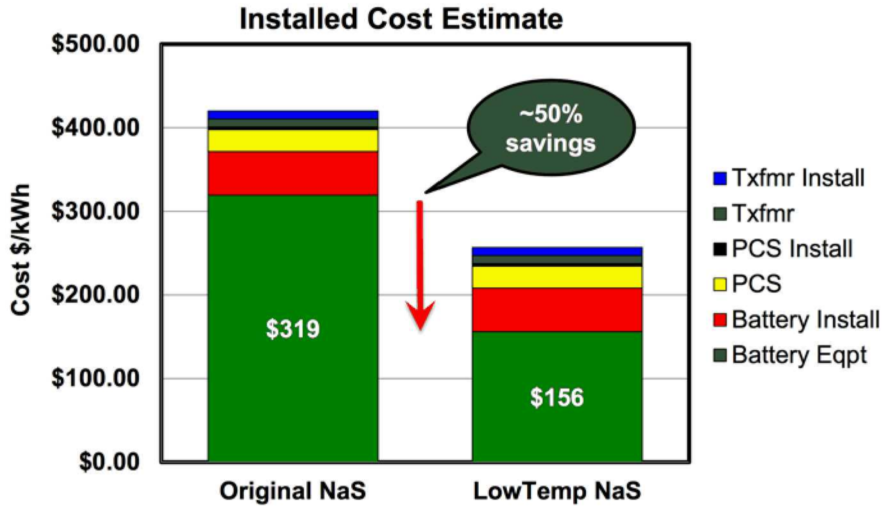
~300°C Operation!

2Na ... $Na^+ + 2Cl^- + Ni(s)$

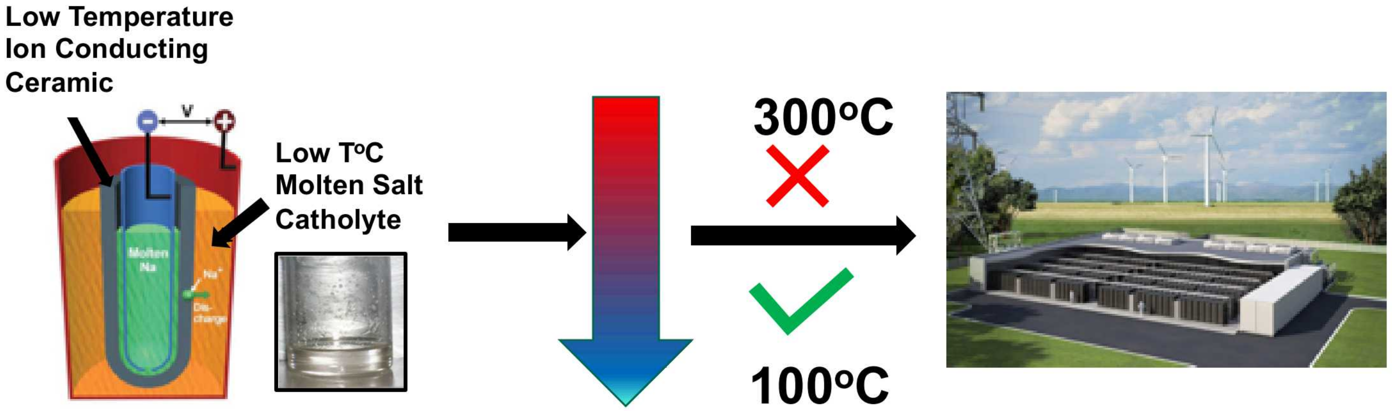
Lowering Battery Operating Temperature to Drive Down Cost

<u>Our Objective:</u> A safe, reliable, molten Na-based battery that operates at drastically reduced temperatures (near 100°C).

- 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

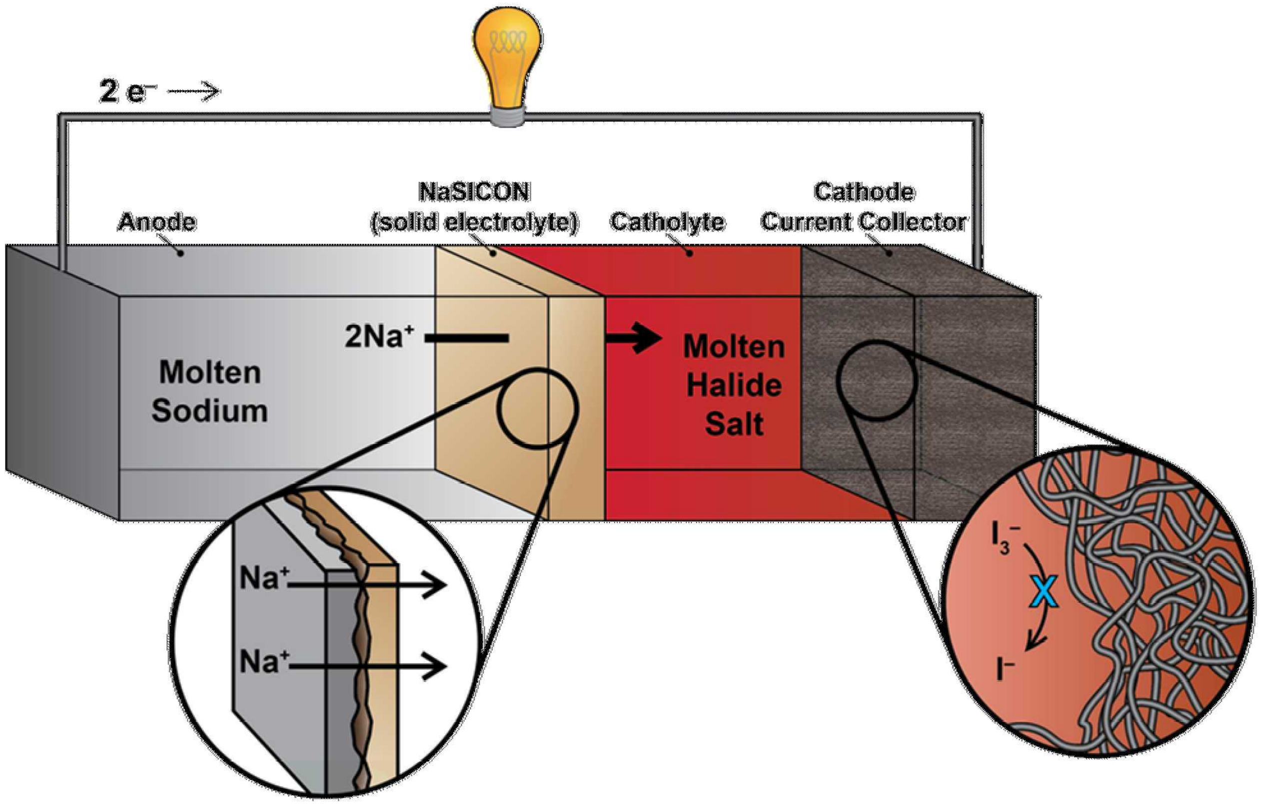


Low Temperature Molten Sodium (Na-NaI) Batteries

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

Ingredients for Success

- Molten Na anode
- 25 mol% NaI in AlX_3 catholyte
- Highly Na^+-conductive, zero-crossover separator (e.g., NaSICON)



Na-NaI battery:

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

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

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

Martha Gross

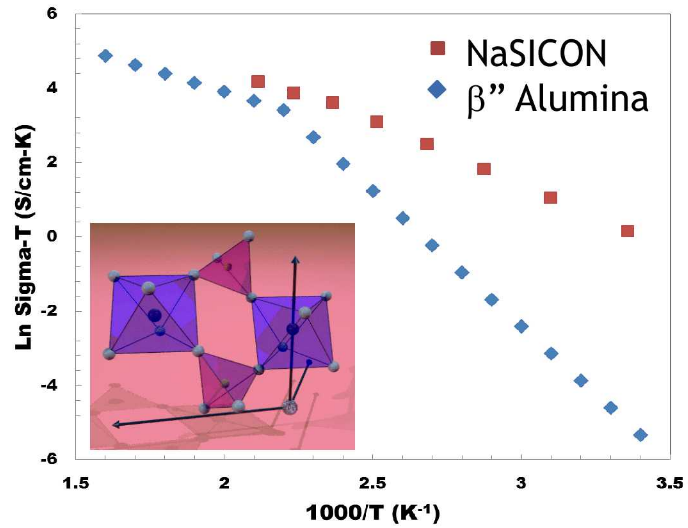
Desired Virtues of a Low Temperature Solid State Separator

What we want:

- High ionic conductivity at low temperatures
- Chemically compatible with anode and catholyte
- Zero-crossover
- Mechanically robust
- Cost-effective to produce at scale

A Promising Candidate: NaSICON

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



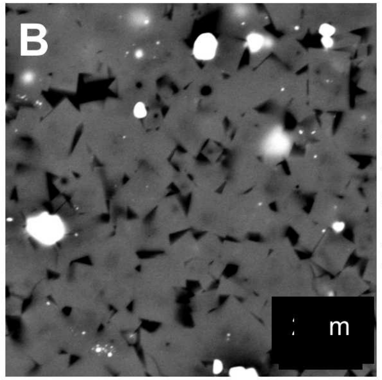
Small and Spoerke, et al. *J. Power Sources*. **360**. 569-574.

Methods for NaSICON Synthesis

- Solid State Synthesis from Oxides
- Sol-Gel Chemistry
- Spark-plasma Sintering

Challenges with NaSICON Synthesis: It's Never a Single Phase

- Na-volatility
- Densification
- Secondary Phase Formation
- Grain Size



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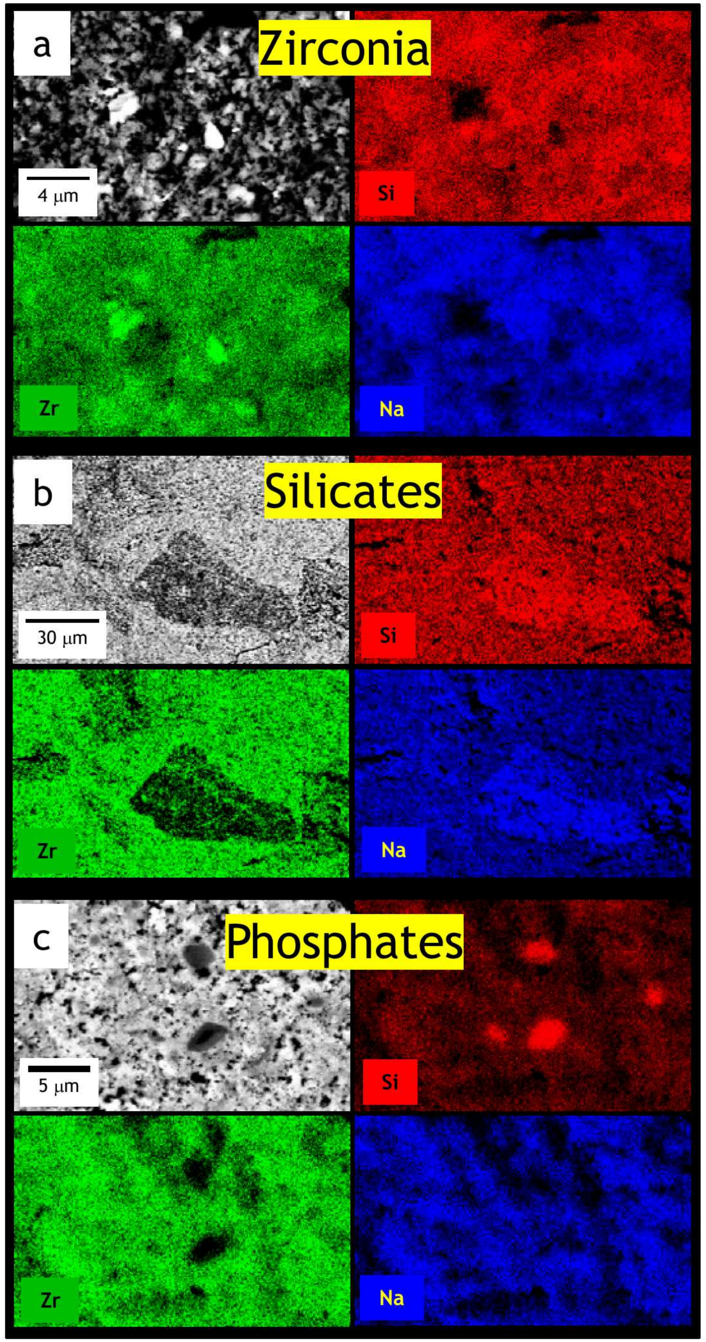

Our “Simple” Initial Synthetic Approach

Solid State Ceramic Synthesis (“Shake ‘n Bake”)

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

- Mill powders
- Press powders at 10-20 kSI
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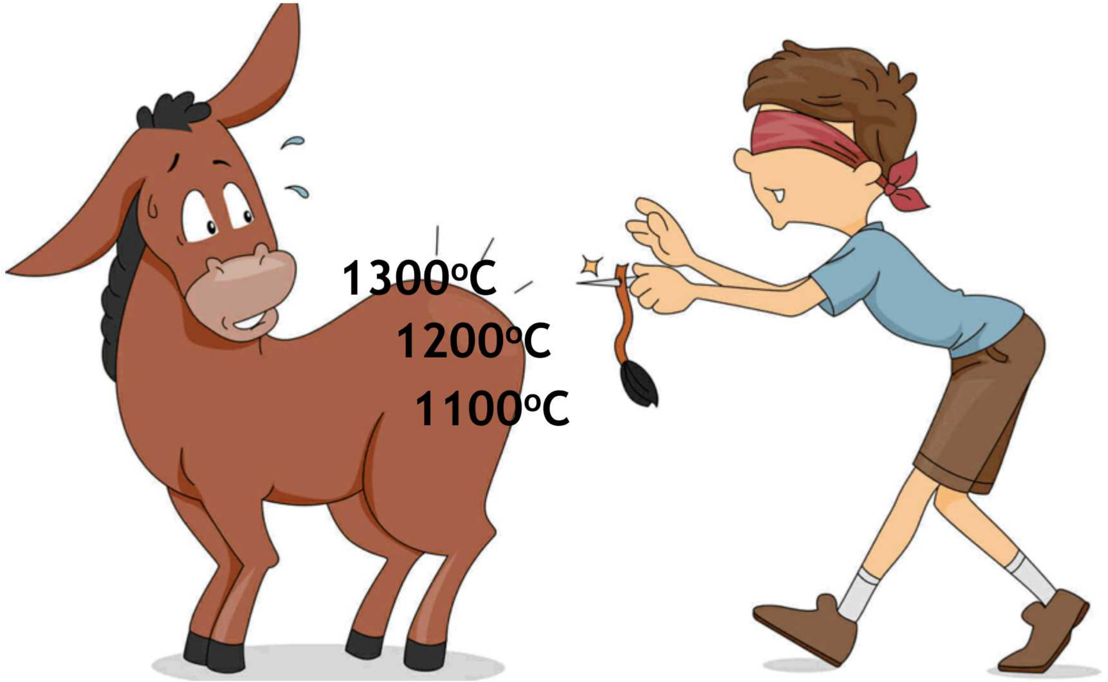

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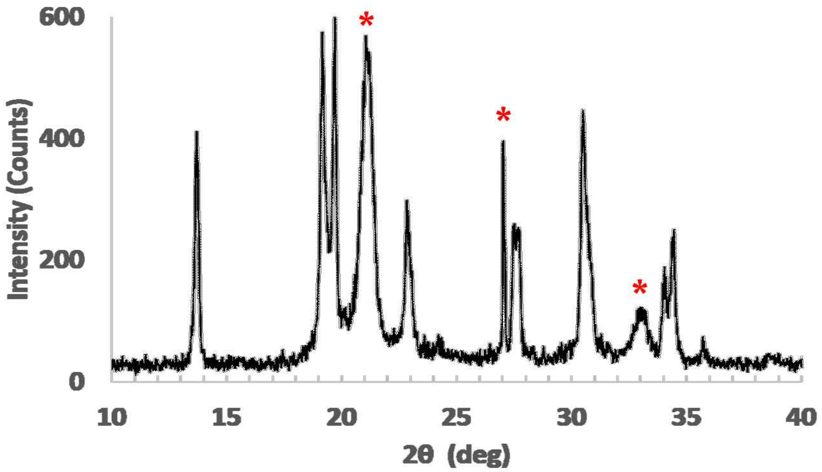

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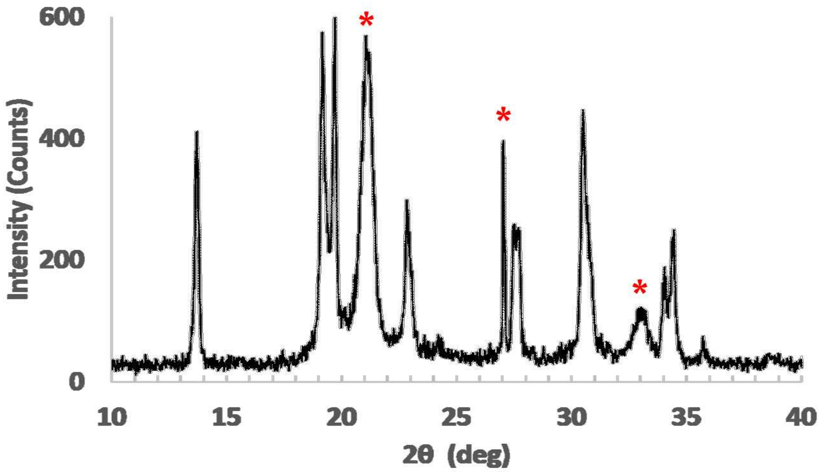

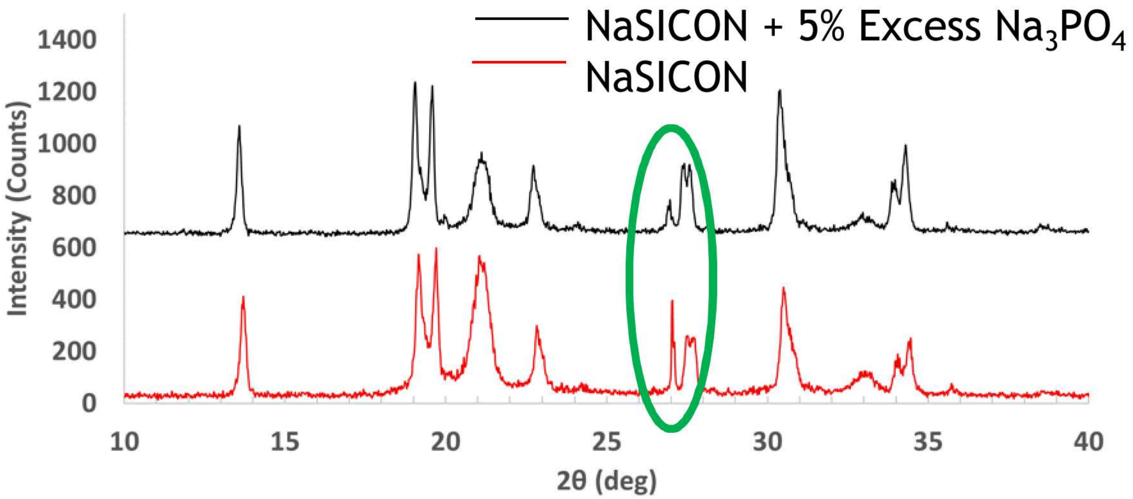

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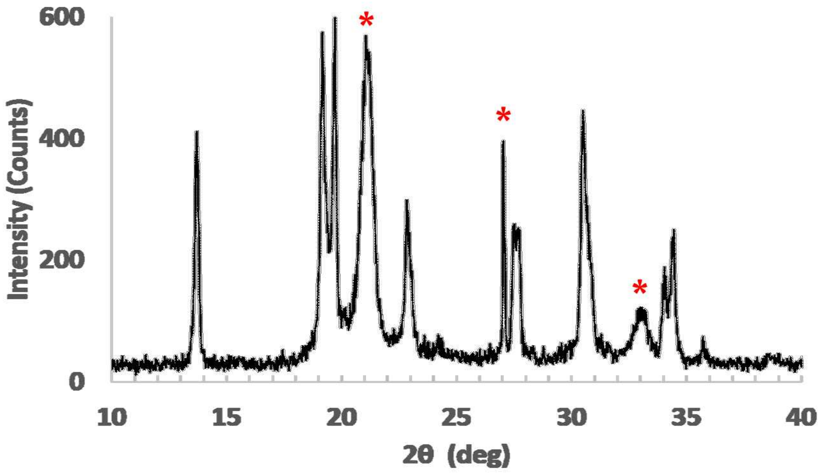

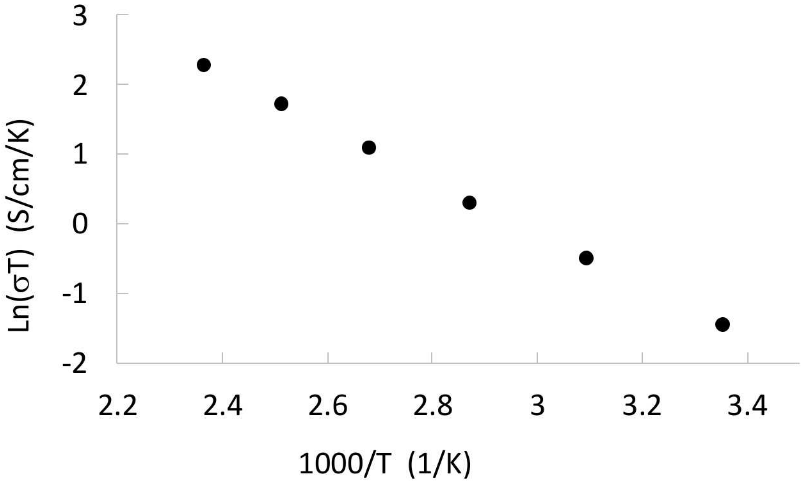

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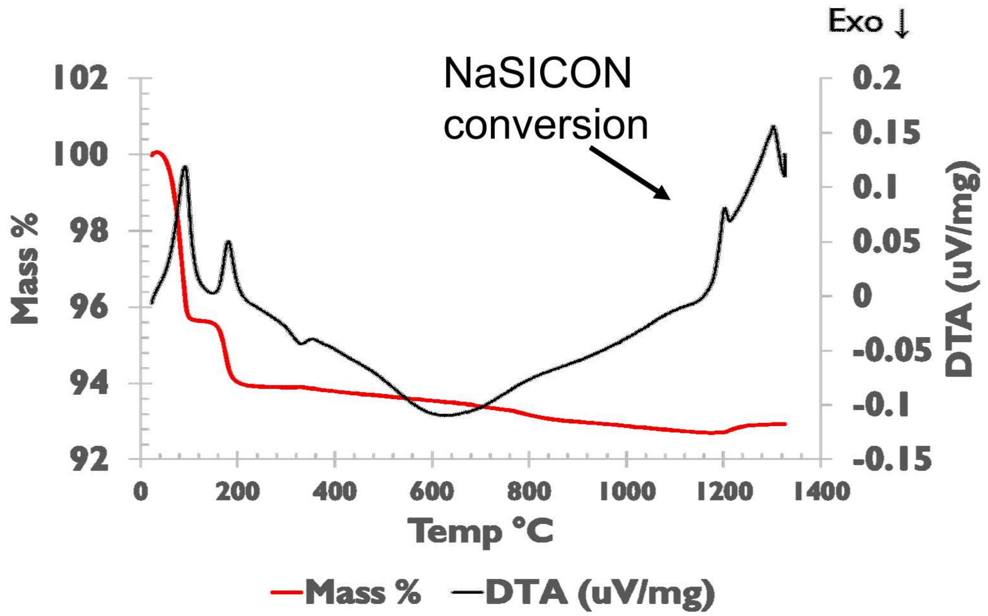
Unless it's raining…

Densities dropped to 70-80% during monsoon season.

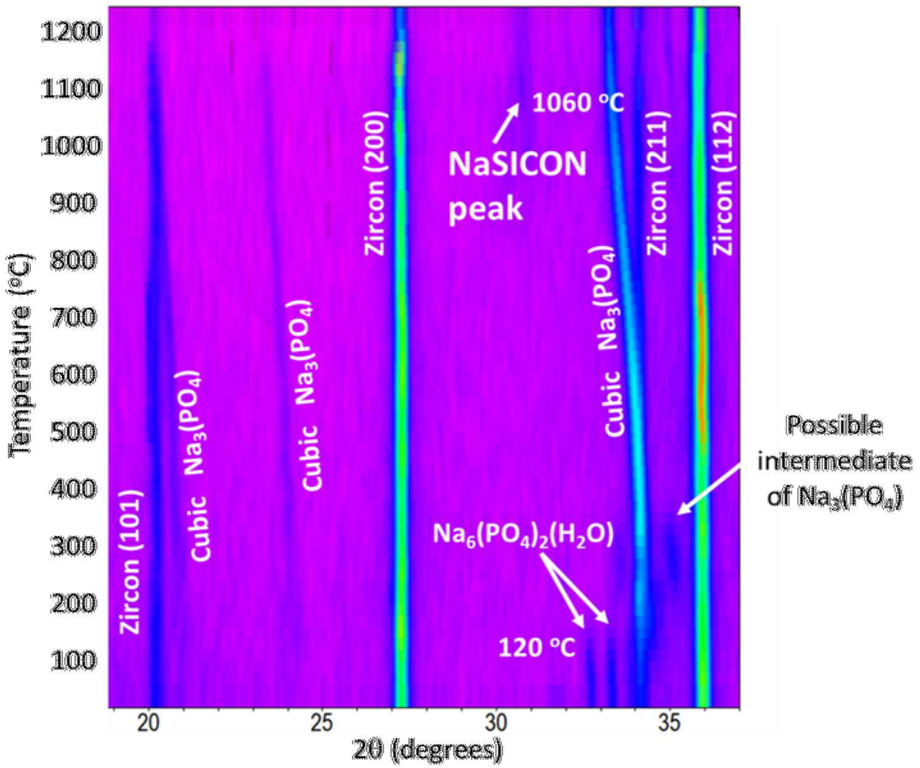
Hygroscopic Na_3PO_4 likely a problem…

Thermal Analyses to Address Humidity

Differential Thermal Analysis and Thermogravimetric Analysis



Variable Temperature X-Ray Diffraction

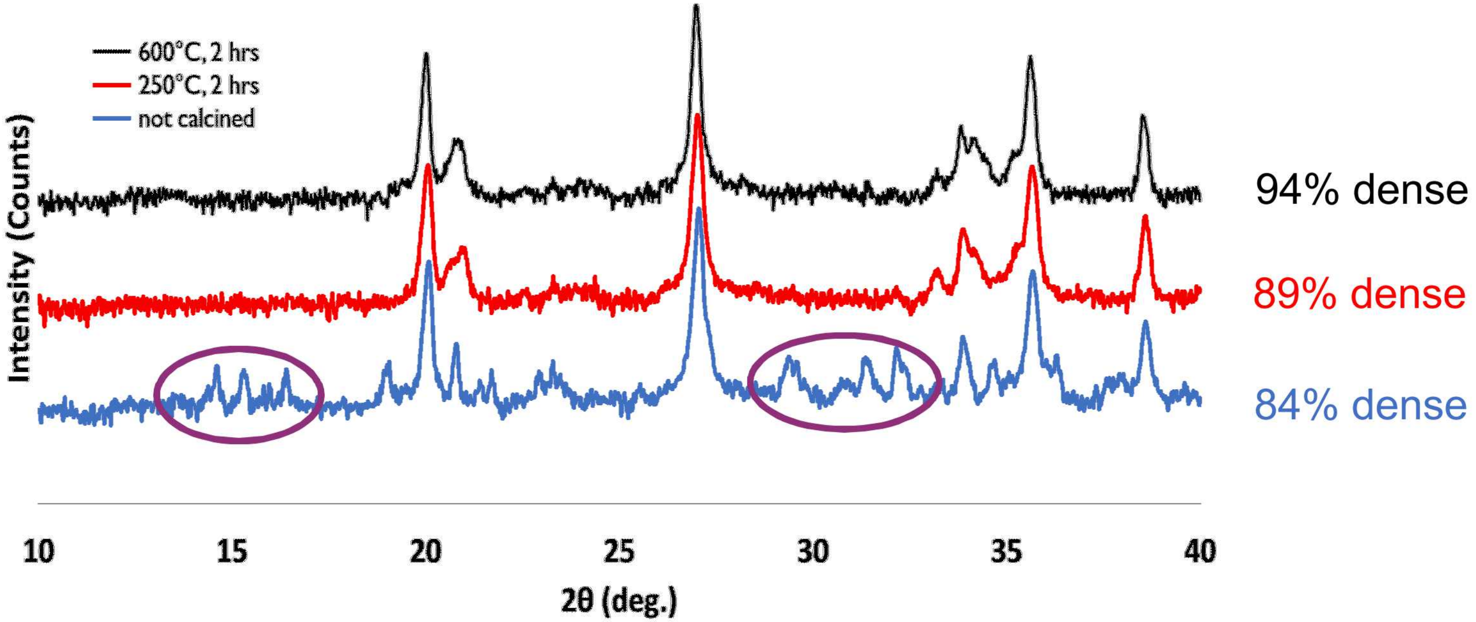


- DTA/TGA show water removed from precursor powder by ~250°C.
- NaSICON conversion reaction evident between 1150-1230 °C.

- VTXRD shows conversion of Zircon and cubic $Na_3(PO_4)$ to NaSICON starting near 1100°C
- Hydrate form of $Na_3(PO_4)$ up to 120°C, converts to cubic $Na_3(PO_4)$ at ~300°C.

Calcining Powder Improves NaSICON Synthesis

- XRD confirms that calcining precursor powder to at least 250°C eliminates sodium phosphate hydrates in precursor.
- Density measurements, though, show that higher calcining temperature (600°C) leads to still higher sintered ceramic density.



- Calcining also results in improved ionic conductivity, likely due to improved density.

*Sintered at 1200°C	σ (mS/cm) at 25°C
Calcine at 600°C	0.2
No Calcine	0.03

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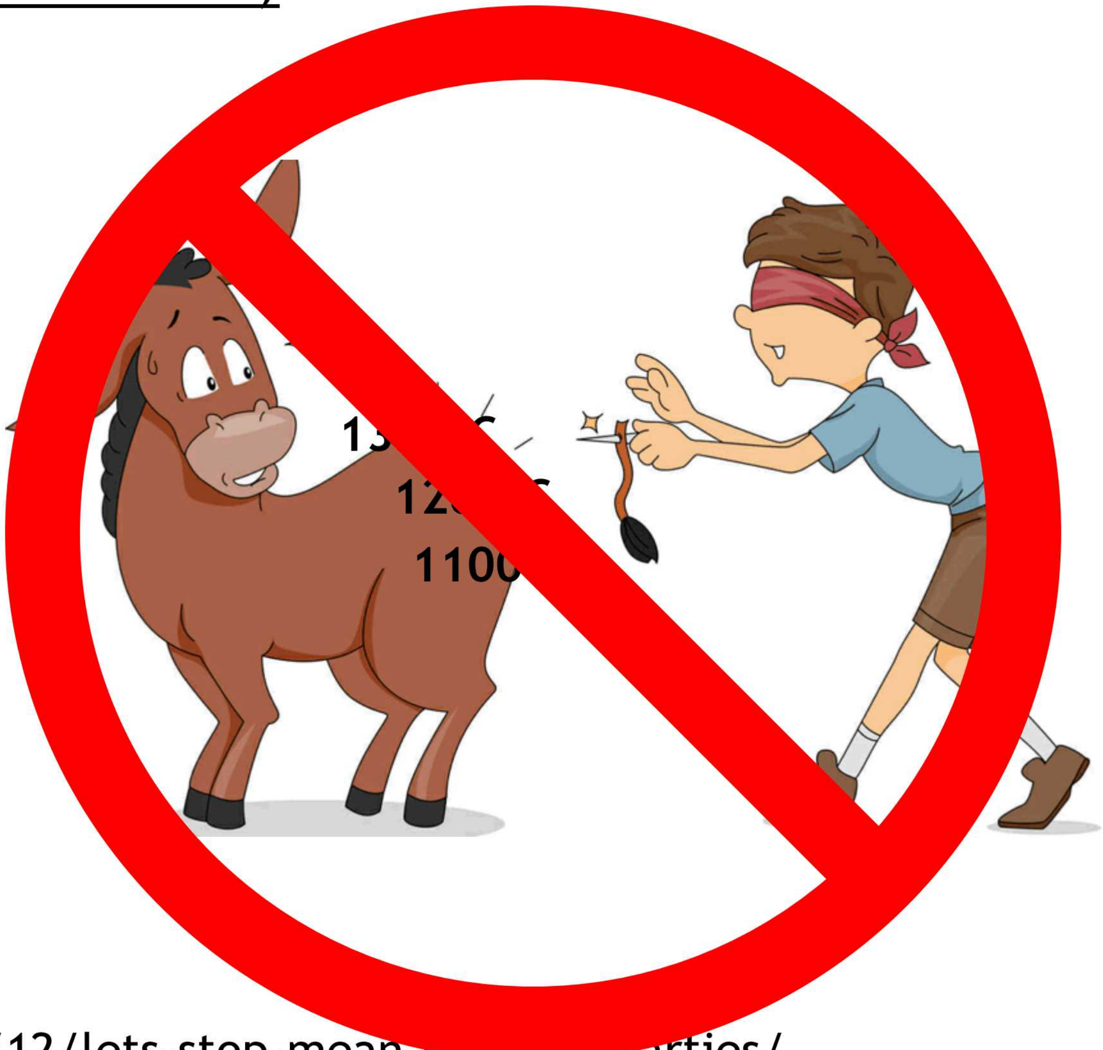

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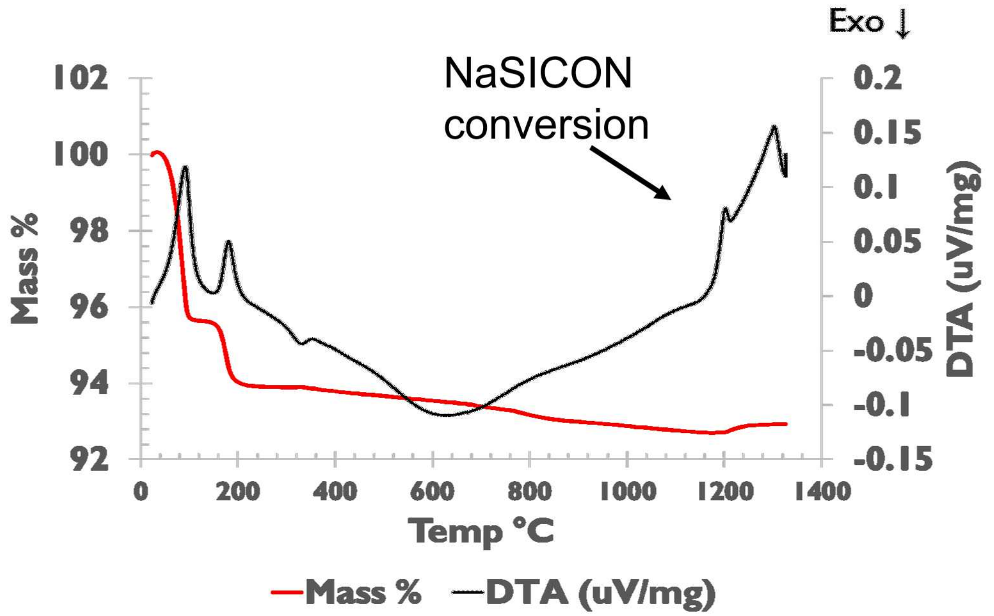
Thermal Analyses to Inform Solid State Reaction Conditions

Differential Thermal Analysis and Thermogravimetric Analysis



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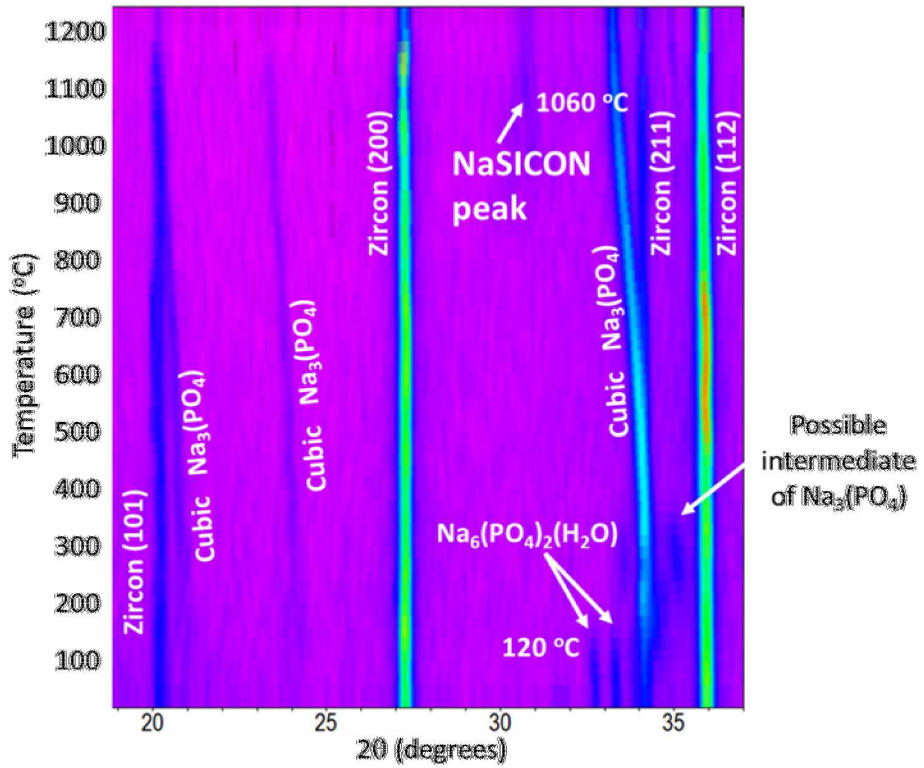

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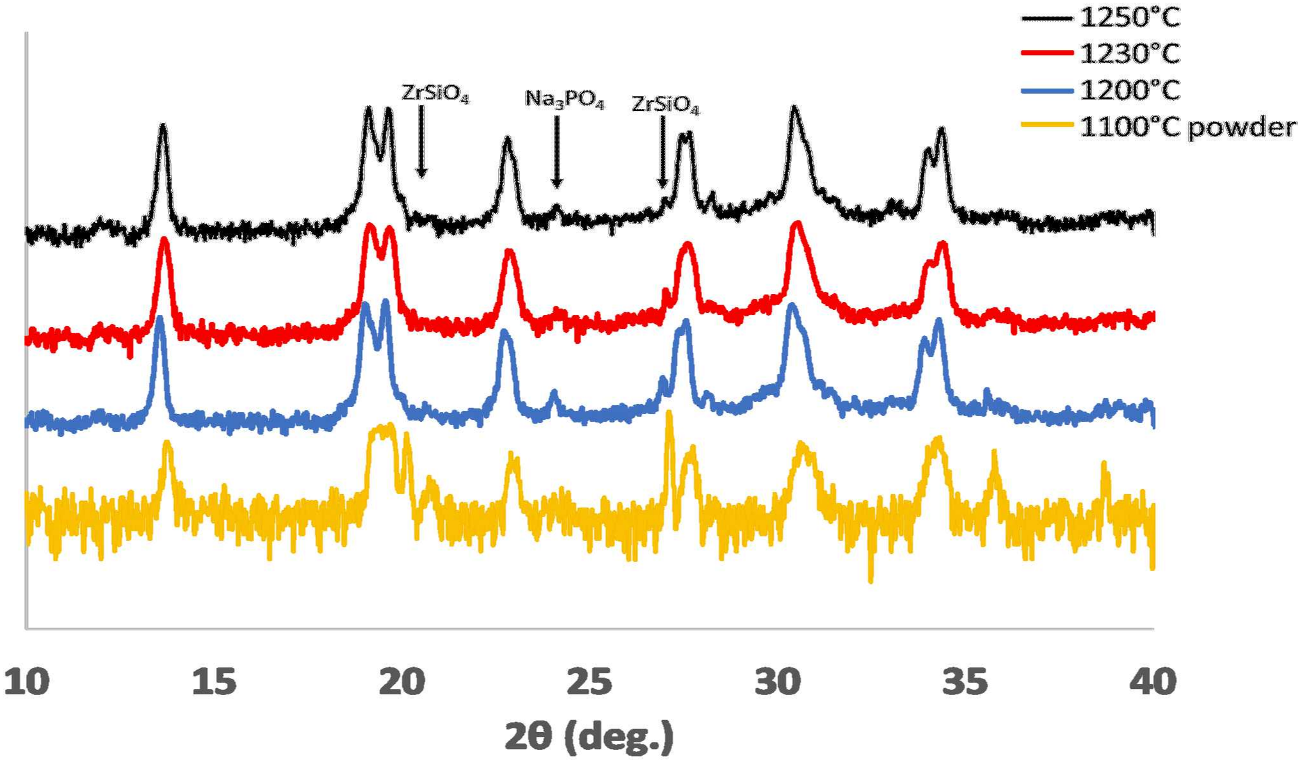
Sintering Temperature Affects NaSICON Conversion and Structure



Melted NaSICON sintered at 1250˚C

https://depositphotos.com/vector-images/goldilocks.html

- Reaction at 1100°C leads to incomplete conversion and poor densification.
- Sintering above 1230°C produces poorly formed, “melted” NaSICON.
- NaSICON calcined at 600°C, sintered at 1230°C, yields >94% bulk density, good phase purity, and >0.2 mS/cm at 25°C.

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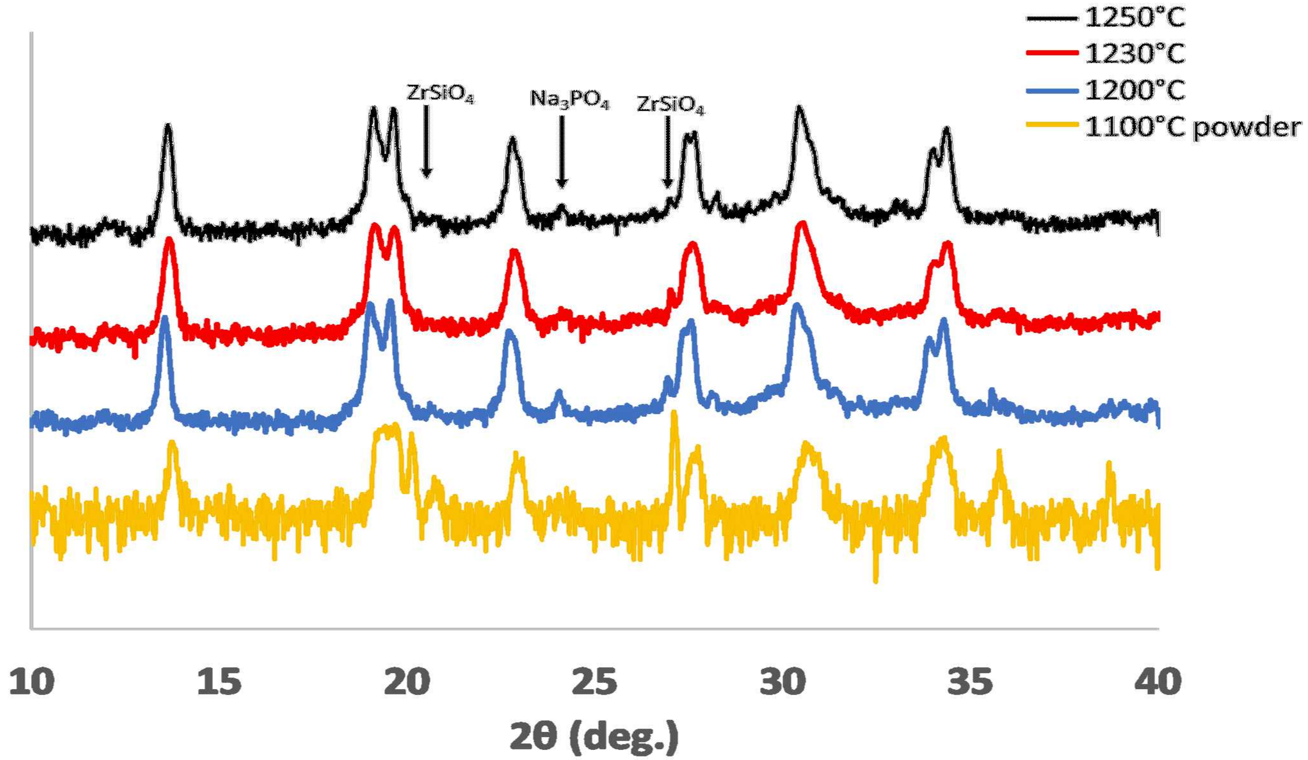

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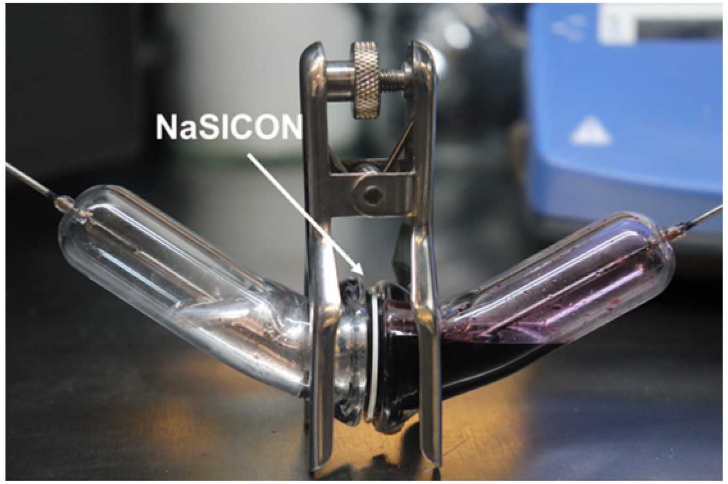

Molten Na Battery Cell Set-Up

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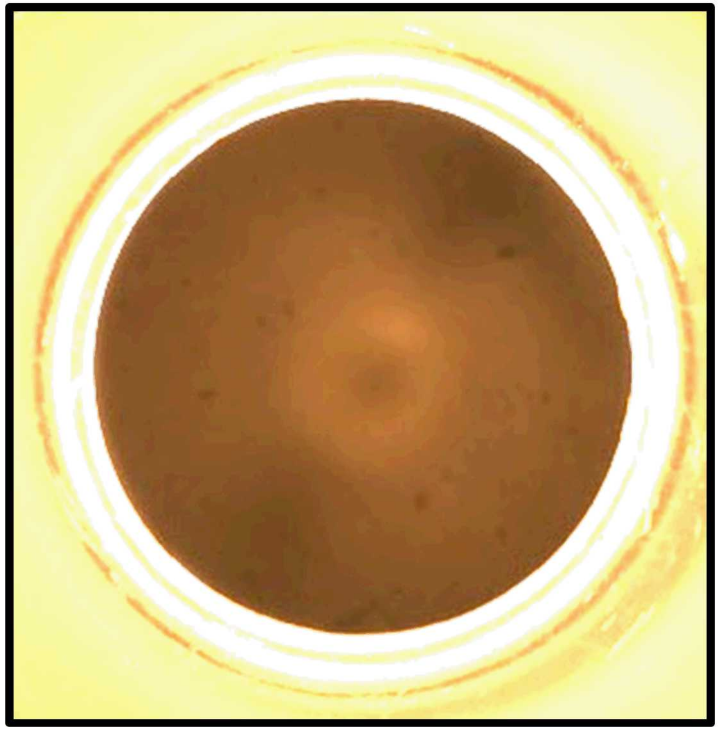
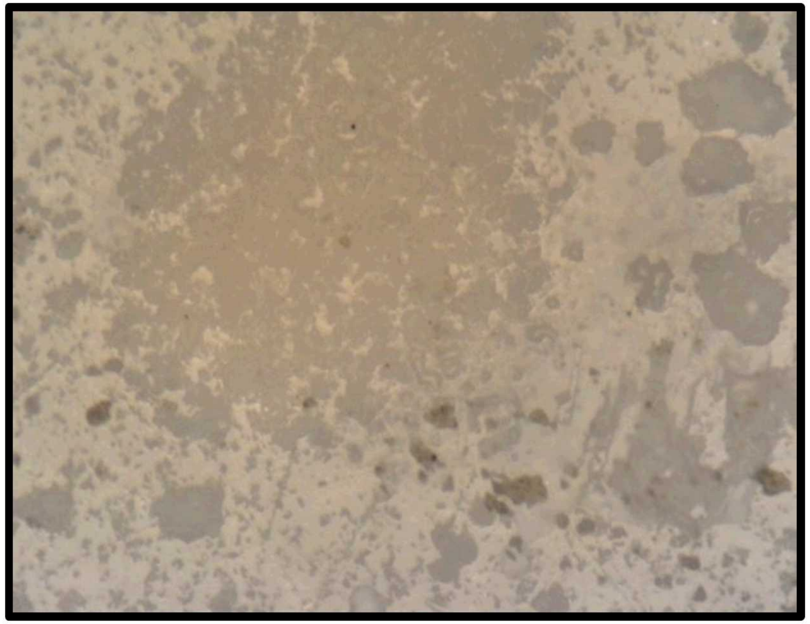
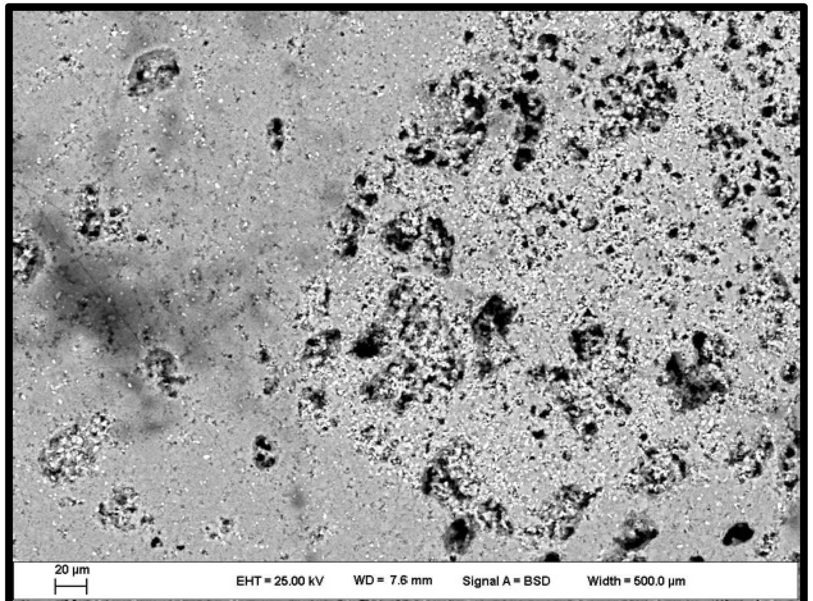
NaSICON Failures Reveal Inhomogeneities in Ceramic







"Speckles" and voids in NaSICON appear to be variations in density, texture, and composition that are susceptible to attack by molten halide salts.

Refining NaSICON Synthesis

Possible Problem: Poor particle packing during pressing leads to void formation and poor diffusion needed for NaSICON conversion.

Solution 1: Eliminate coarse aggregates from precursor powder.

Very slight improvement in NaSICON synthesis.

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Acceptable phase purity

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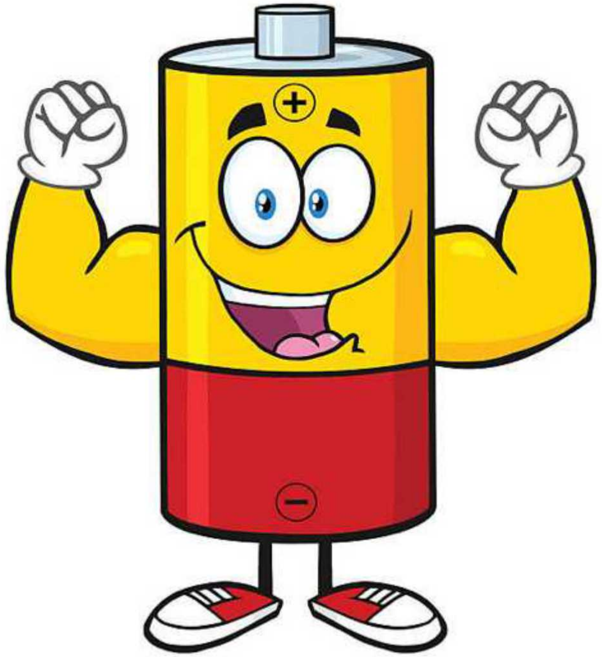

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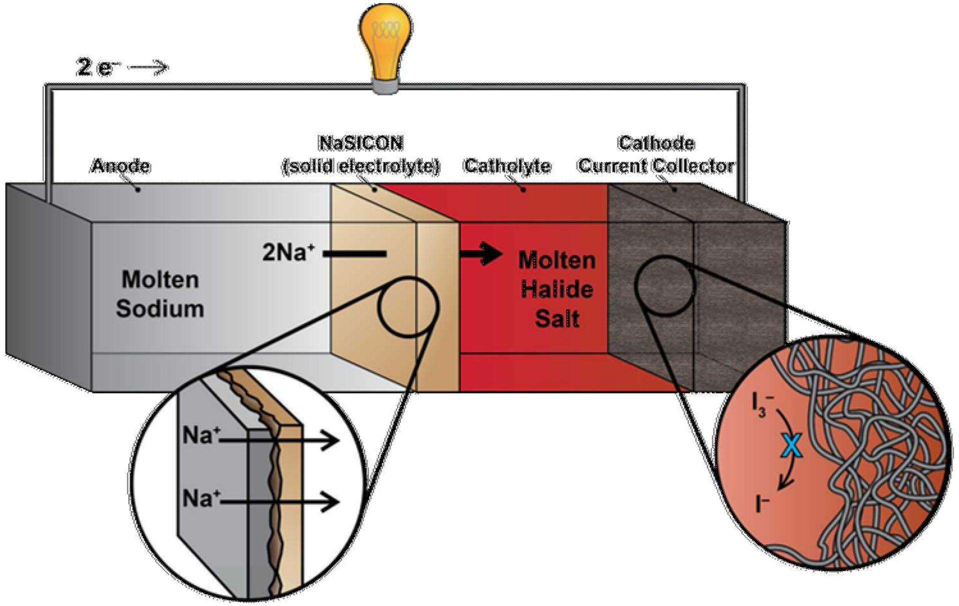

Ingredients for Success

- Molten Na anode
- Highly Na^+-conductive, zero-crossover separator (e.g., NaSICON)
- 25 mol% NaI in AlX_3 catholyte
- *No complications from solid state electrodes!*

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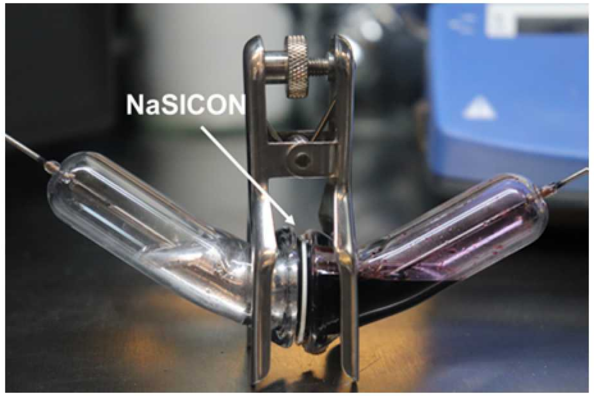


Molten Na Battery Cell Set-Up

Martha Gross

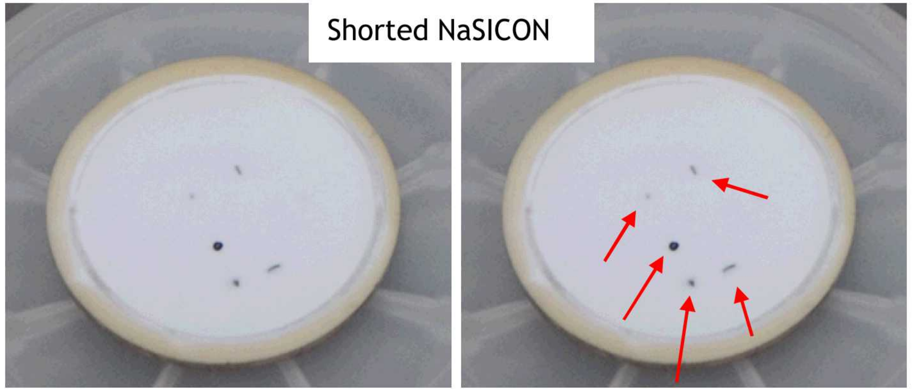
Follow the Bouncing...Sodium!

Poor sodium wetting on NaSICON is a problem.

Improper Na-wetting of NaSICON.

Red arrows pointing to shorts

Improper wetting leads to current constriction through small active areas of NaSICON eventually forming shorts.



Martha Gross, Stephen Percival

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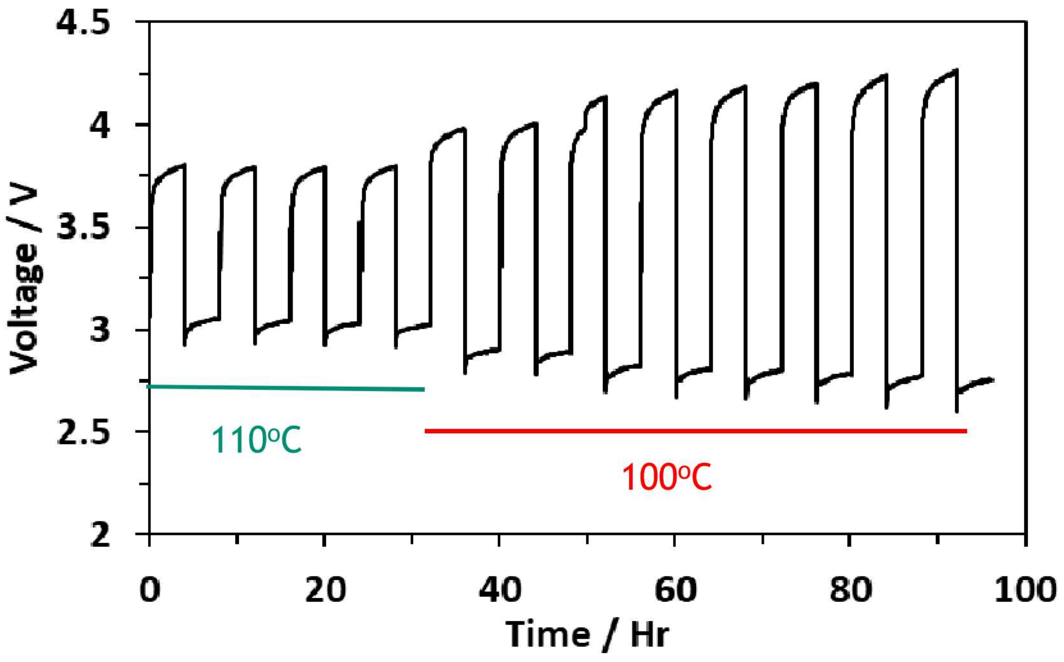

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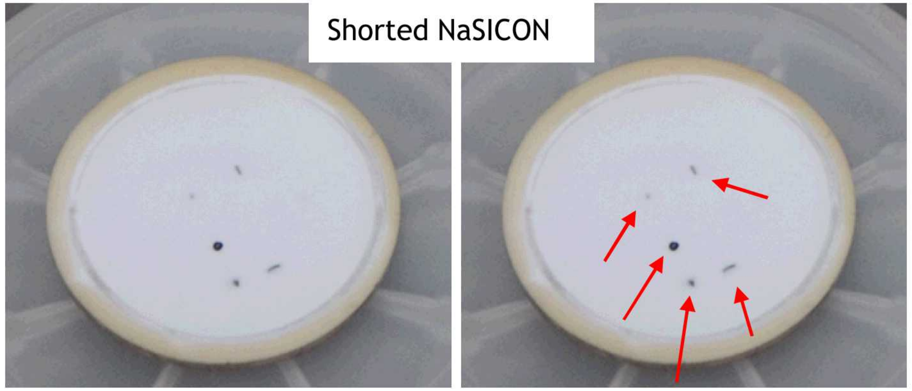
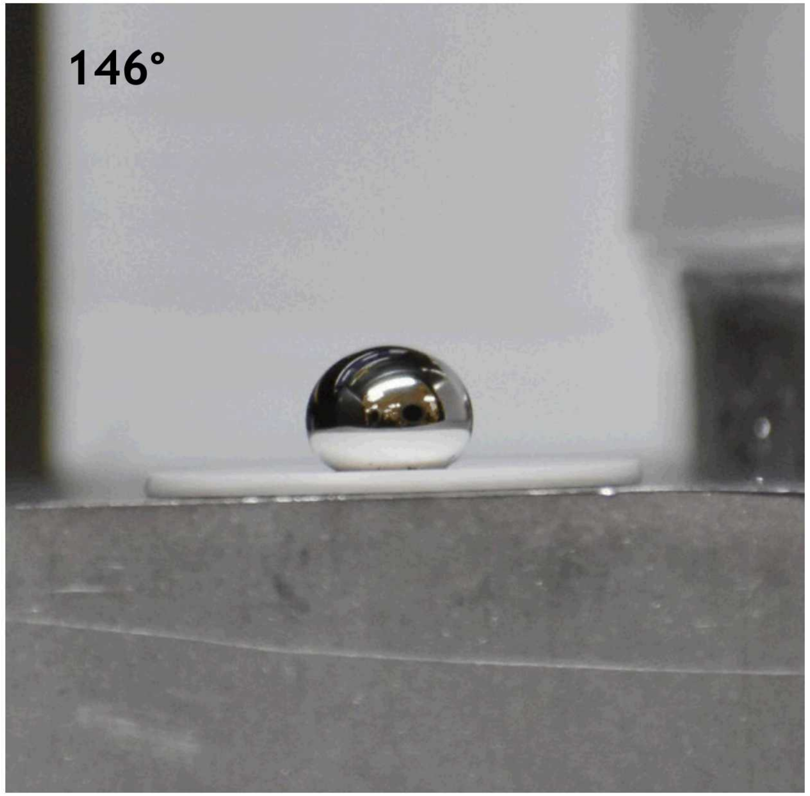


Stephen Percival

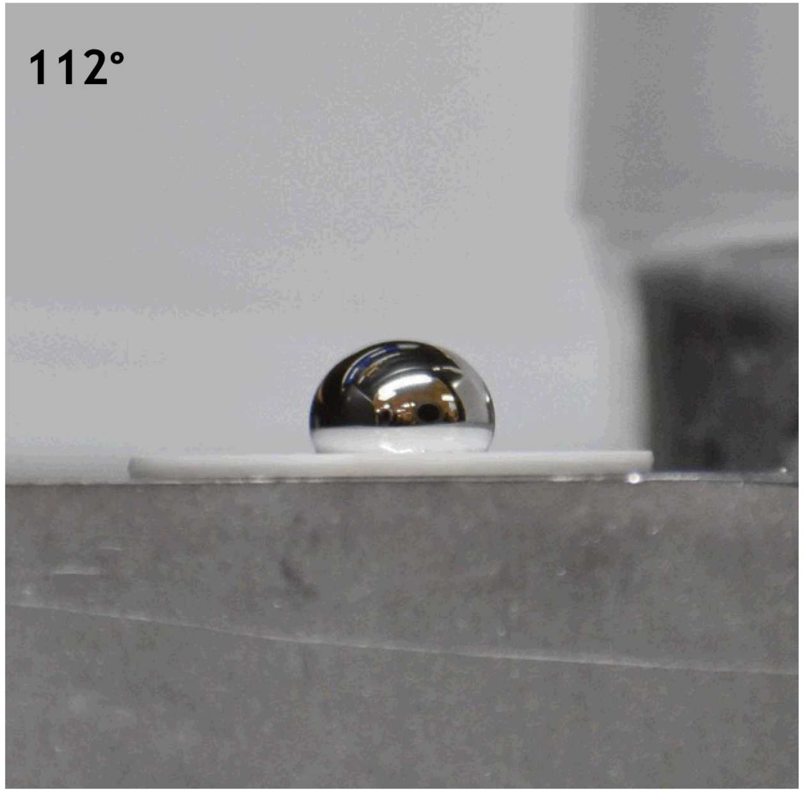
Modification of Electrolytes for Improved Wetting II

Polishing NaSICON surface significantly improves Na-wetting at 110°C.

Unpolished

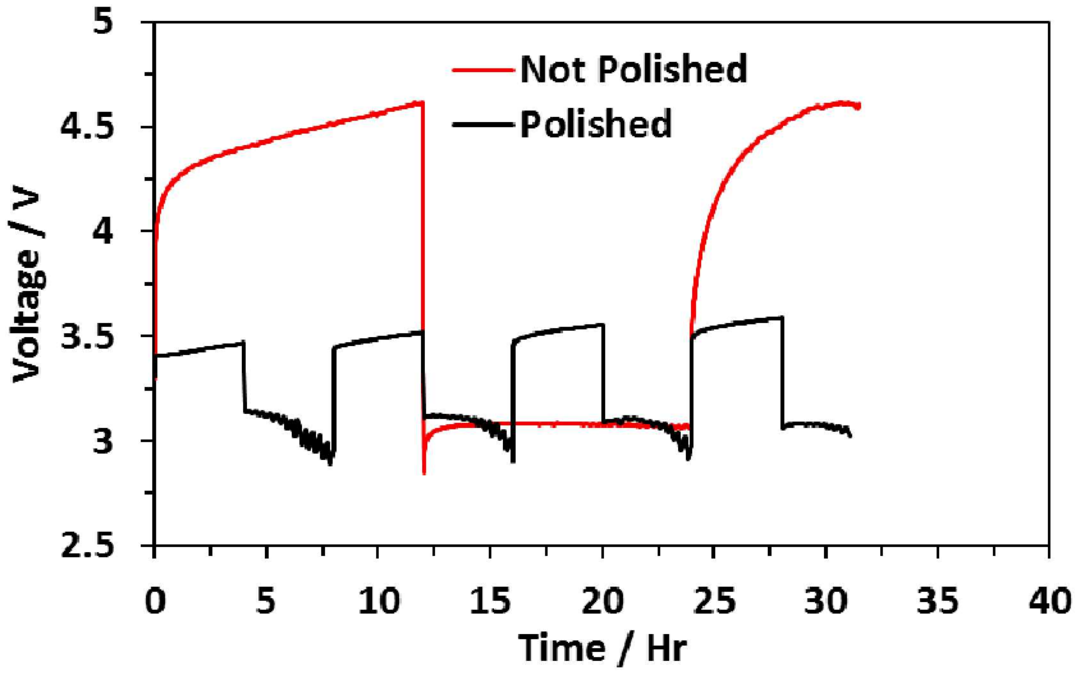


Polished



Separator Treatment Affects Cell Performance

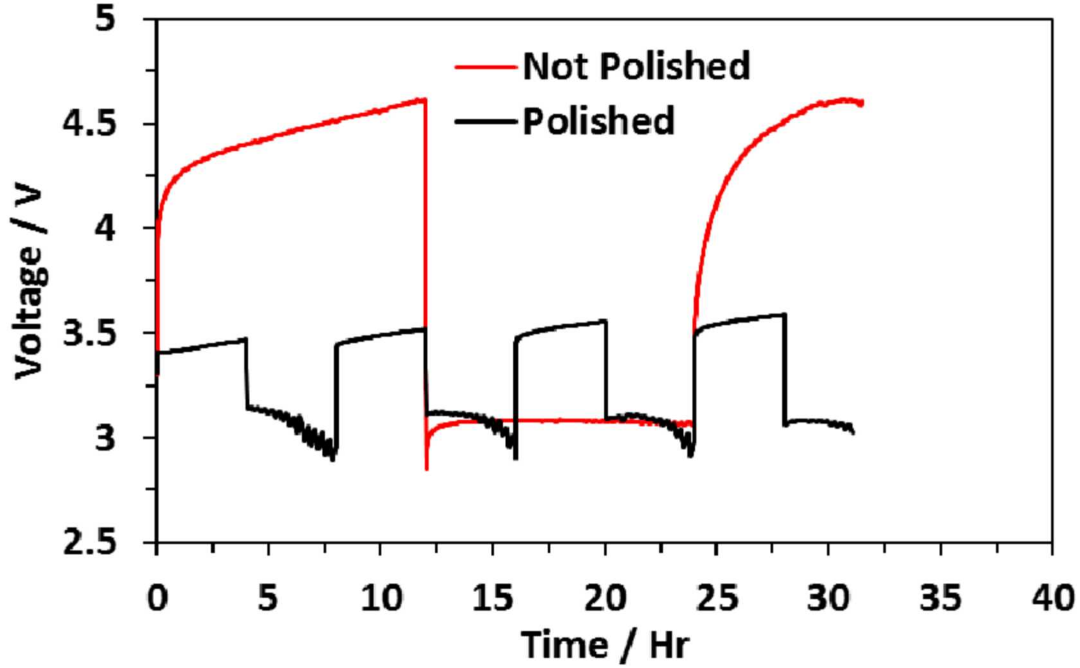
Removing "rough" NaSICON surface with a surface polish allowed higher operating current density and lower overpotentials.

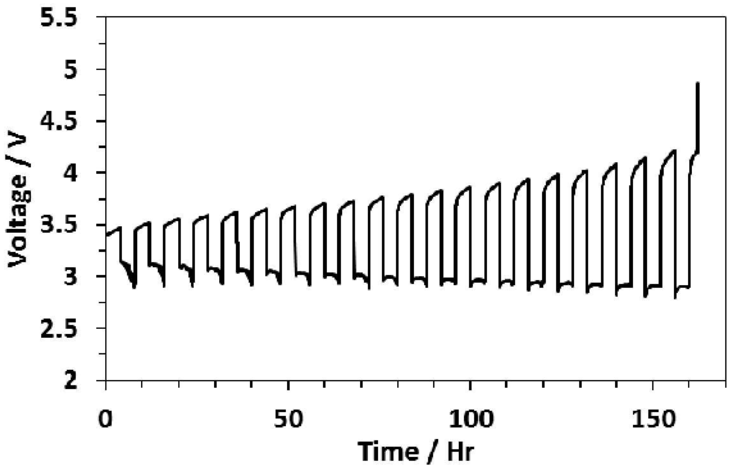


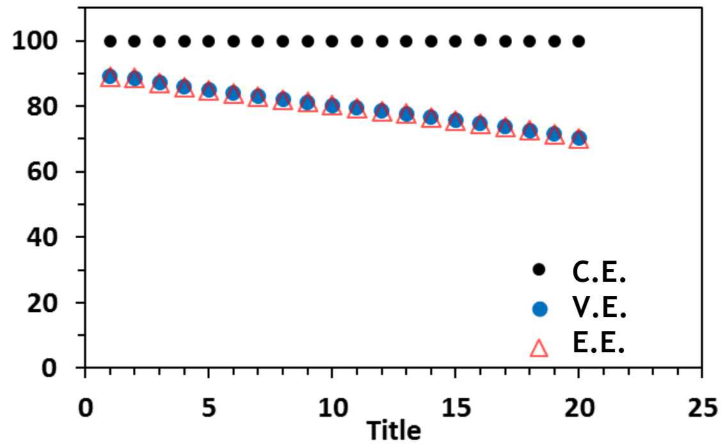
- **Un**polished NaSICON battery operated at ± 0.299 mA current C/12 1% DOD
- Polished NaSICON battery operated at ±0.897mA C/4 1% DOD

Separator Treatment Affects Cell Performance

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

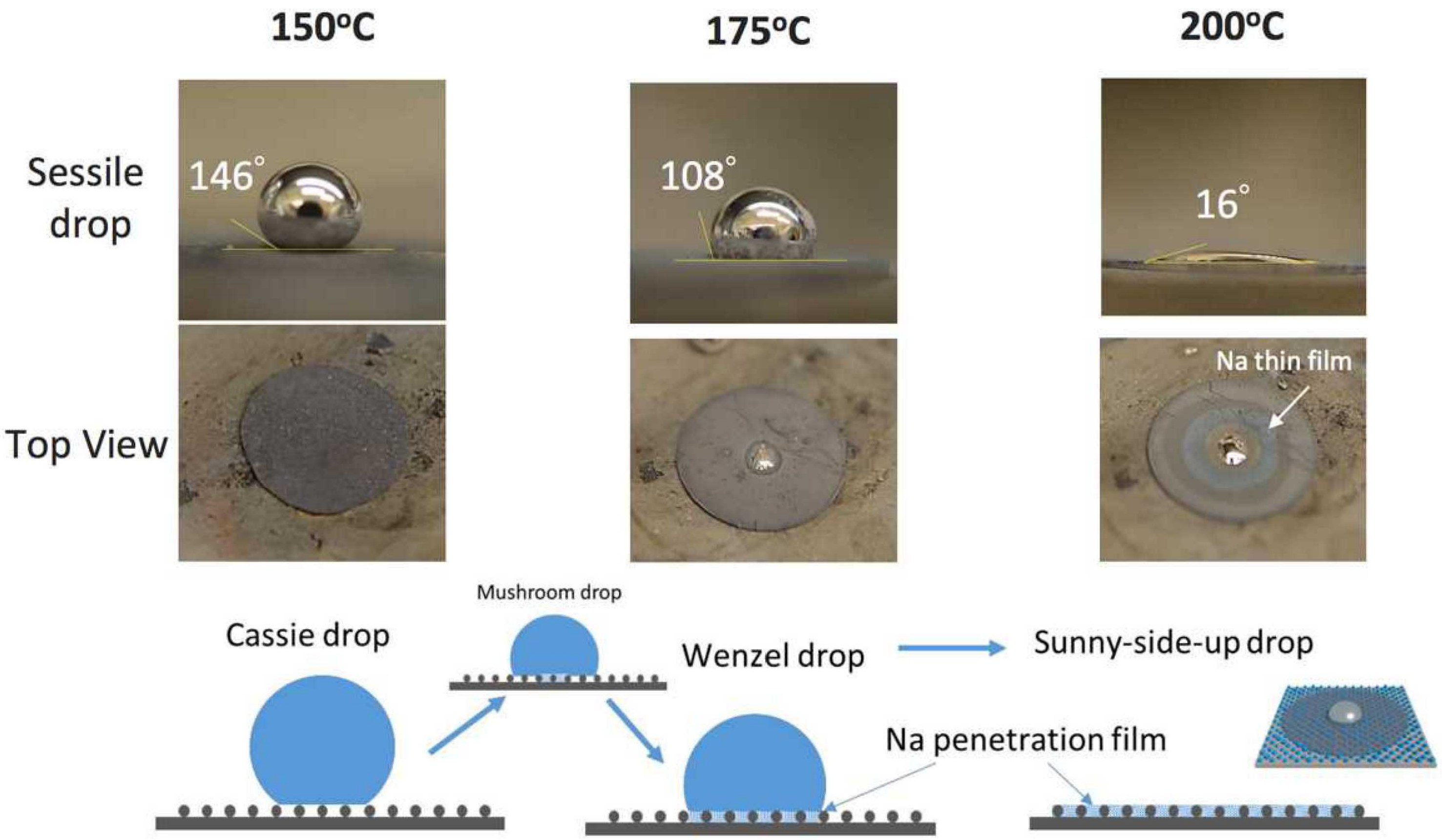






Polished NaSICON alone still shows relatively rapid performance fade.

Modification of Electrolytes for Improved Wetting?



Treatment of β"-Al_2O_3 with lead oxide leads to improved wetting…at higher temperatures!

- ❑ Na wetting in "sunny-side-up" shape is responsible for high battery performances

Pacific Northwest NATIONAL LABORATORY

G. Li, 2018 DOE OE Peer Review

Modification of Electrolytes for Improved Wetting III

At reduced temperatures, sodium wetting on NaSICON is not adequate.

Heated at 100-200^{o}C for 30 minutes

Modification of Electrolytes for Improved Wetting III

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

Heated at 100-200^{o}C for 30 minutes

Heated above 380^{o}C for 30 minutes

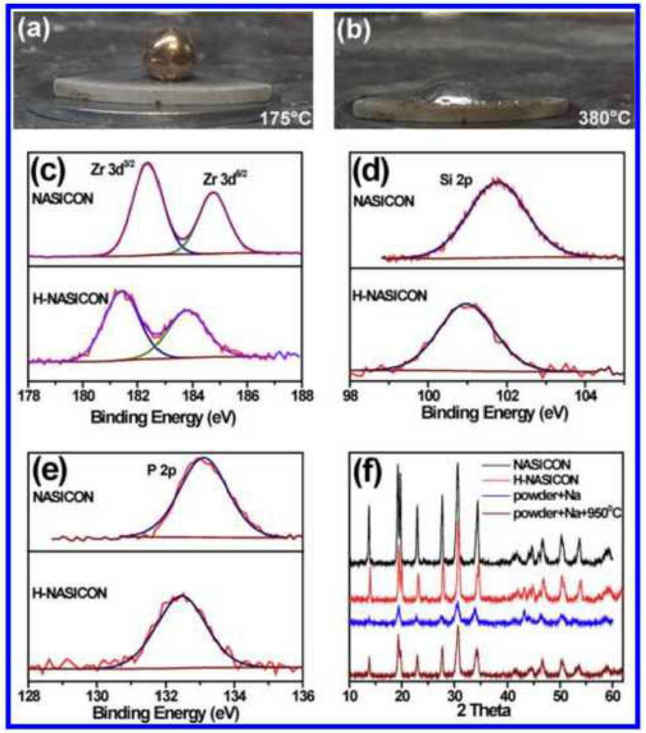
Modification of Electrolytes for Improved Wetting III

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

Heated at 100-200°C for 30 minutes

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.

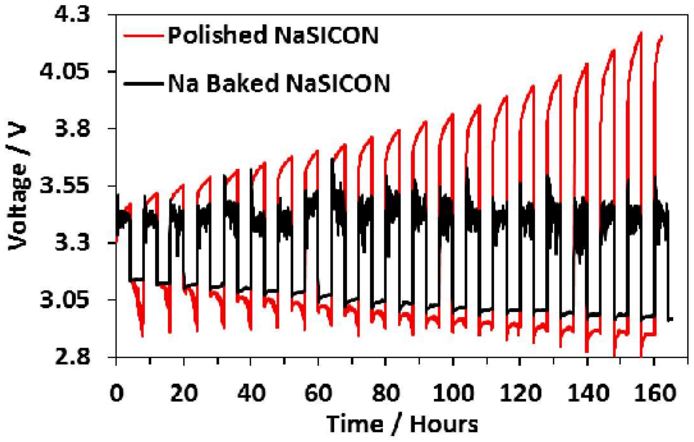
Separator Treatment Affects Cell Performance

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

Heated below 200°C for 30 minutes

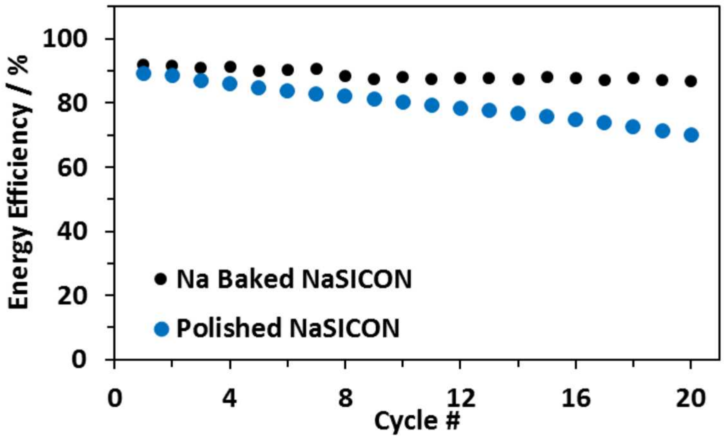
Heated above 380°C for 30 minutes

Na-treated NaSICON shows lower overpotentials on battery cycling.



Battery cycling at 110°C!

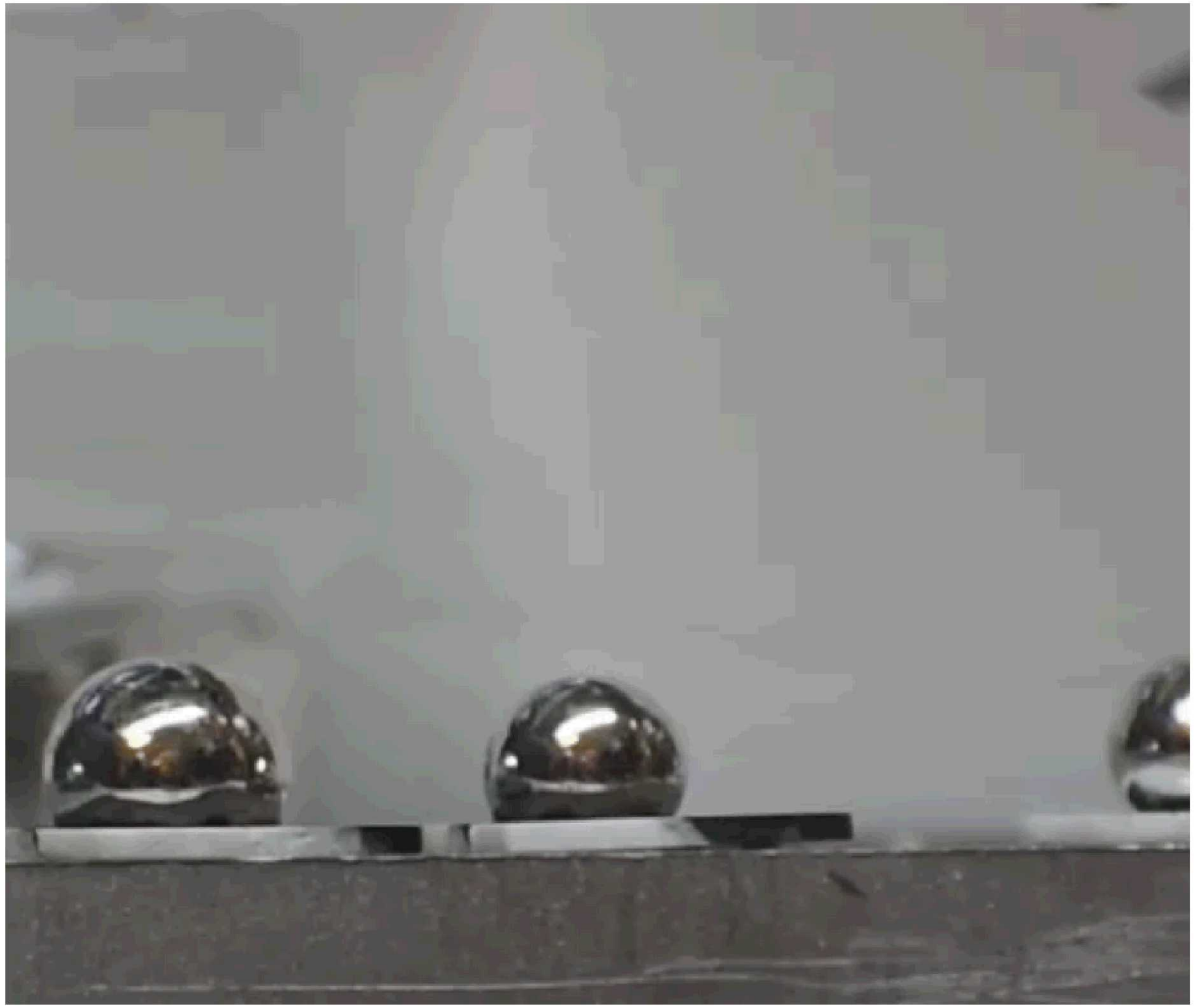
25 mol% NaI-$AlBr_3$ with NaSICON separator.



- 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

Is this “Good Enough?”

NaSICON Coated with Sn-Based Coating Shows Drastically Improved Adhesion!



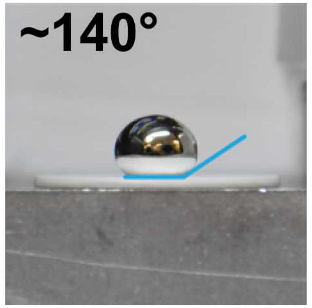
Martha Gross

An Improved Na Interface

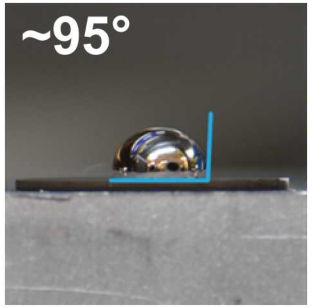
Symmetric cell cycling (Na on both sides) shows that the Sn-based coating improves wetting on NaSICON and drastically reduces overpotentials on cycling!

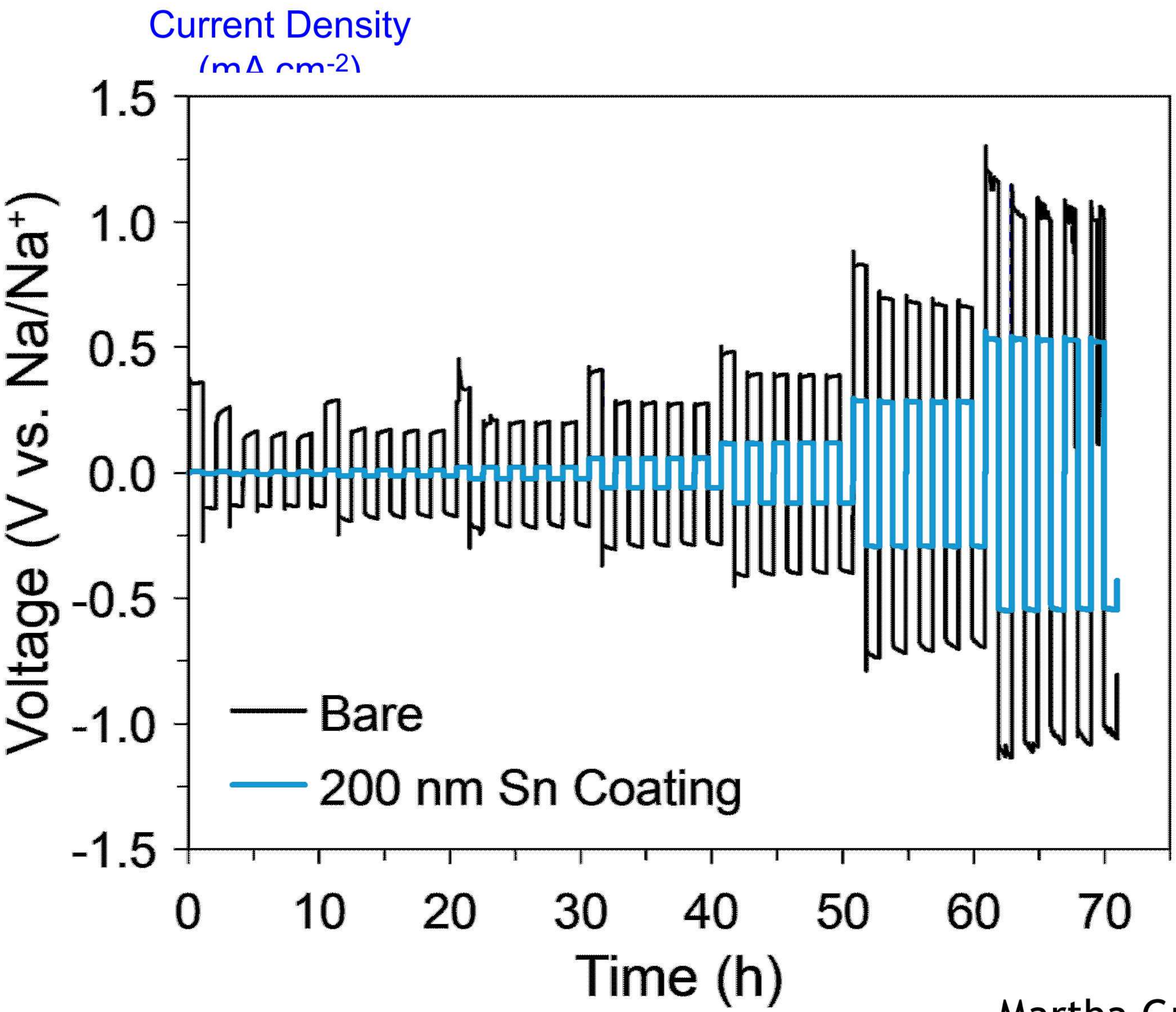
This improved interface is critical to realizing effective battery performance.

Untreated NaSICON



With Sn-Based Coating





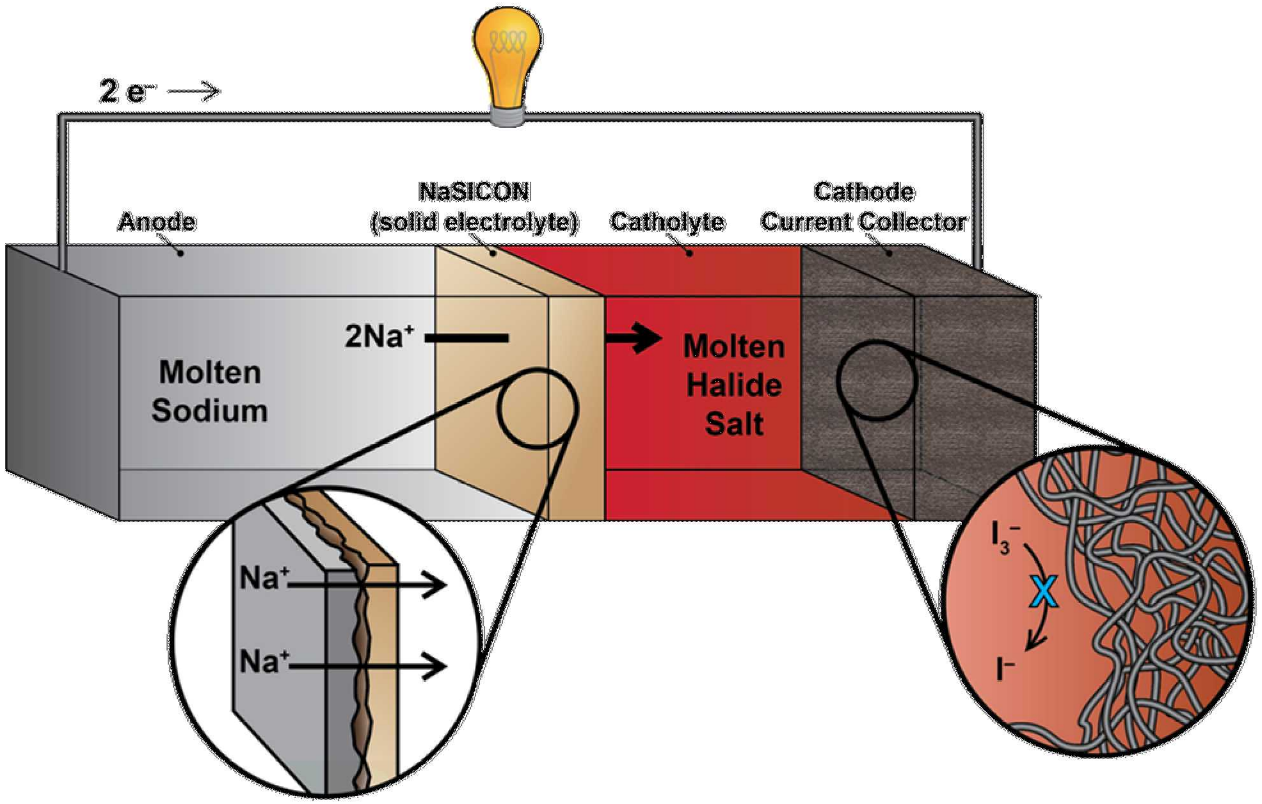
Martha Gross

Low Temperature Molten Sodium (Na-NaI) Batteries

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

Ingredients for Success

- Molten Na anode
- Highly Na^+-conductive, zero-crossover separator (e.g., NaSICON)
- 25 mol% NaI in AlX_3 catholyte
- *No complications from solid state electrodes!*



Na-NaI battery:

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

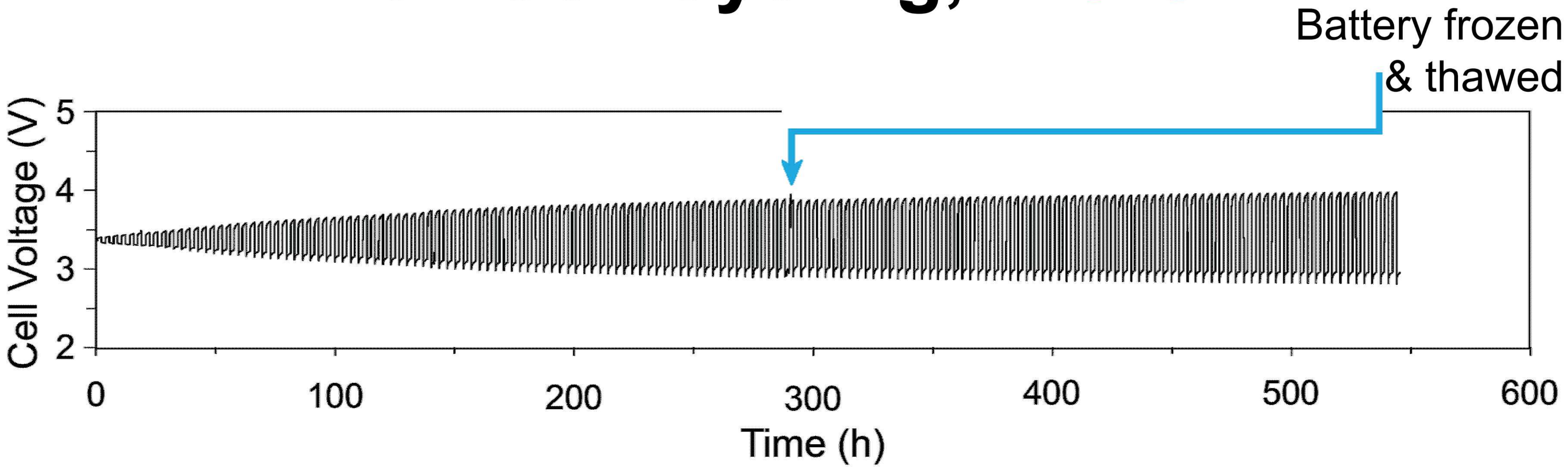
$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$

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

Martha Gross

This Year's "Really Cool" Hurrah!

Full Cell Cycling, 110°C



- Integration of Sn-based coating and activated CF enables long-term battery cycling: **Battery achieved 200 cycles!**
- Even after freeze/thaw, interfaces remain intact with uninterrupted cycling!

Martha Gross

Summary

Project Objective: Synthesis of a NaSICON-based solid state ion conducting separator for use in a novel ”low temperature” molten sodium battery.

- Solid State NaSICON can be successfully synthesized with high density and reasonable conductivity
  - Humidity and secondary phase formation can affect NaSICON ceramic properties (can be managed through synthetic modifications?)
  - Incomplete pressing can lead to inhomogeneous NaSICON synthesis
  - Improved ”green” densification can improve NaSICON uniformity and performance.

- Surface preparation of NaSICON will affect battery performance
  - Cleaning/polishing
  - High temperature Na-treatment
  - Sn-based coating

NaSICON-based solid electrolytes have the potential to impact a wide range of battery technologies as highly conductive, zero-crossover separators!

Acknowledgments and Thanks

THANK YOU!

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

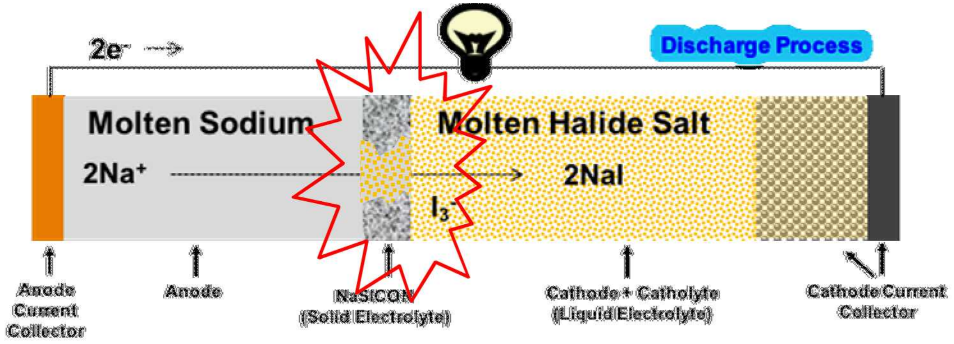
Questions?

Erik Spoerke

edspoer@sandia.gov

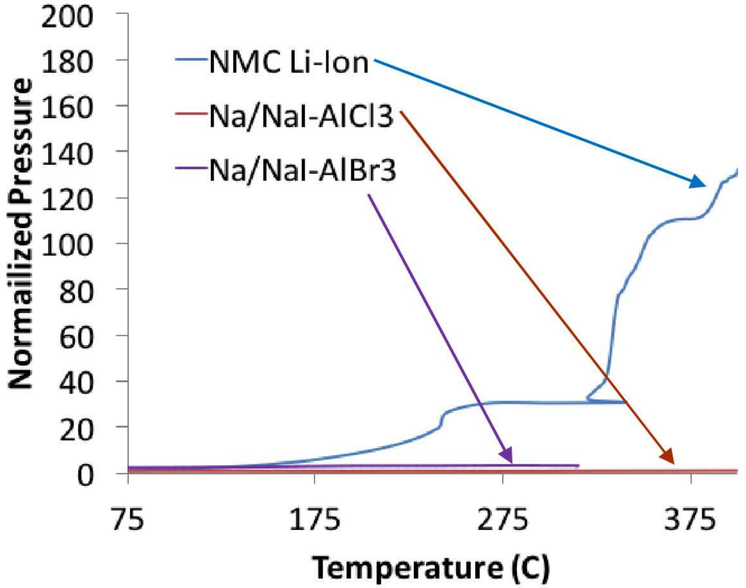
Evaluating Potential Hazards of "Failed" Na-NaI Batteries

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



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*

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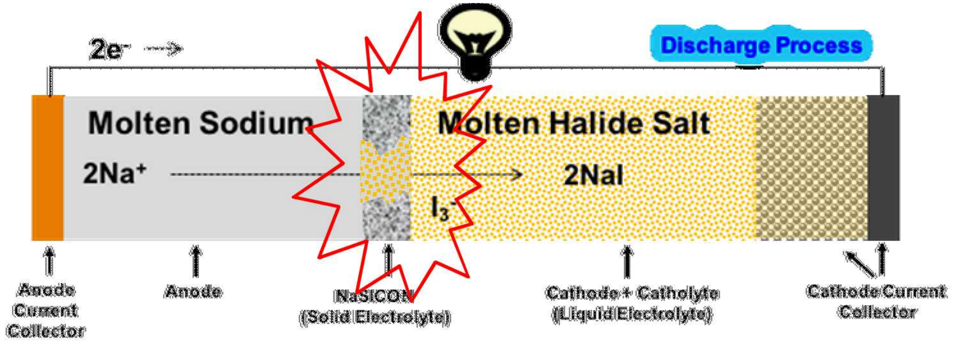

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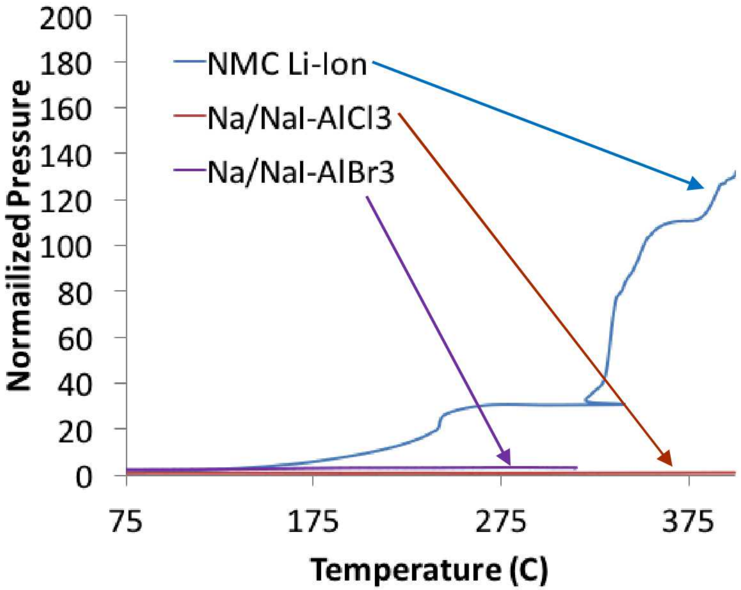

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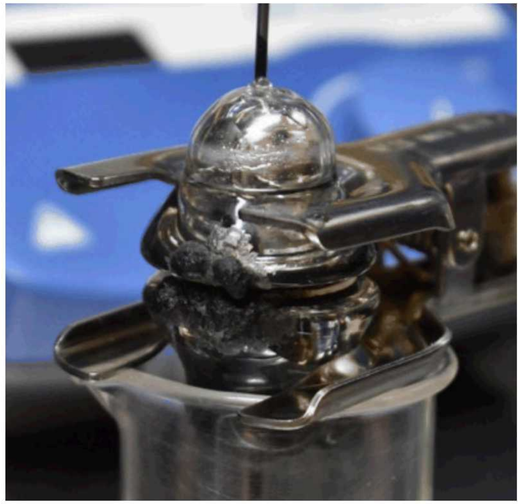
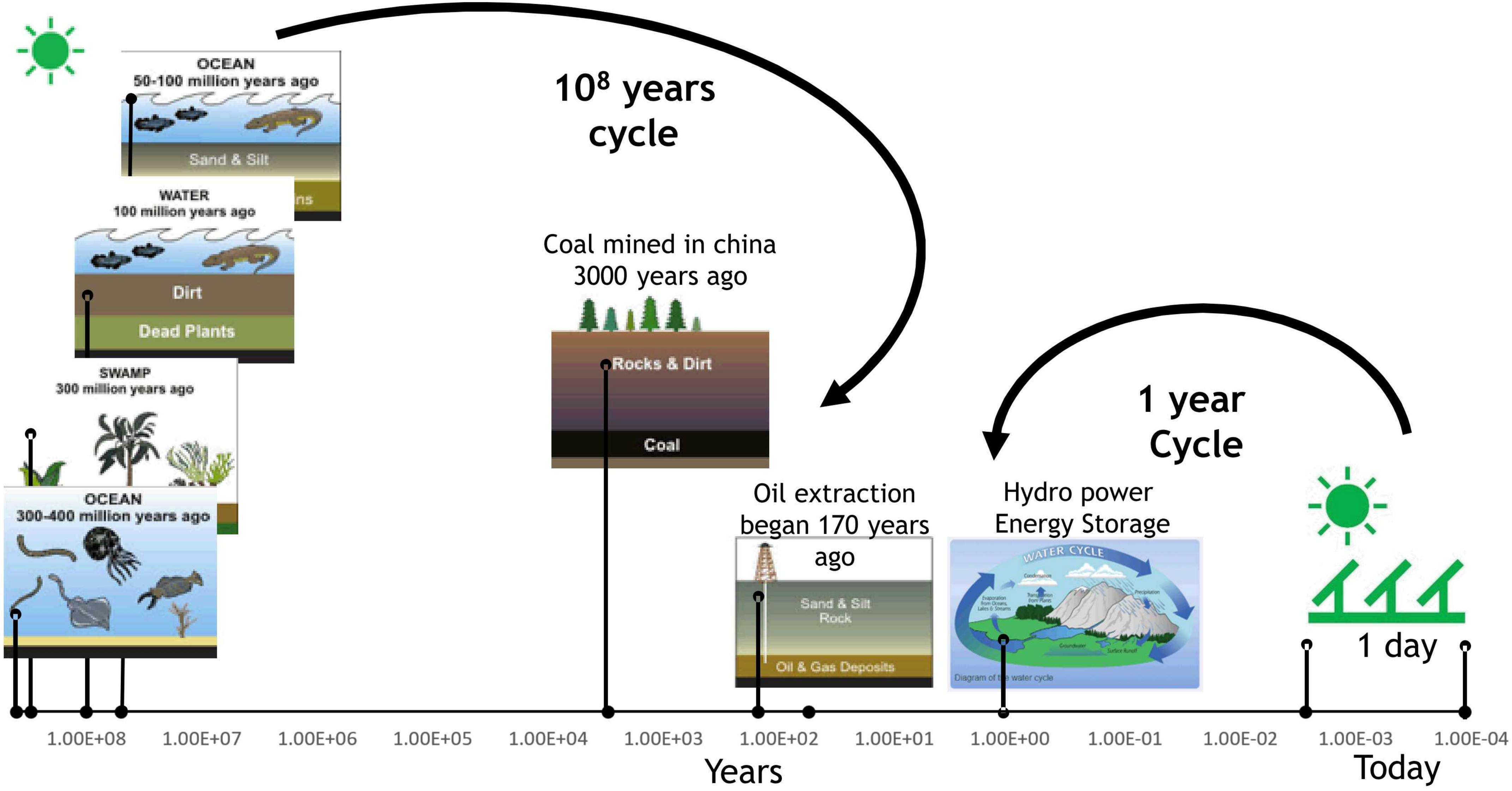


Failed separator led to termination of battery, but no significant hazardous conditions.

Where Does Our Energy Come From?



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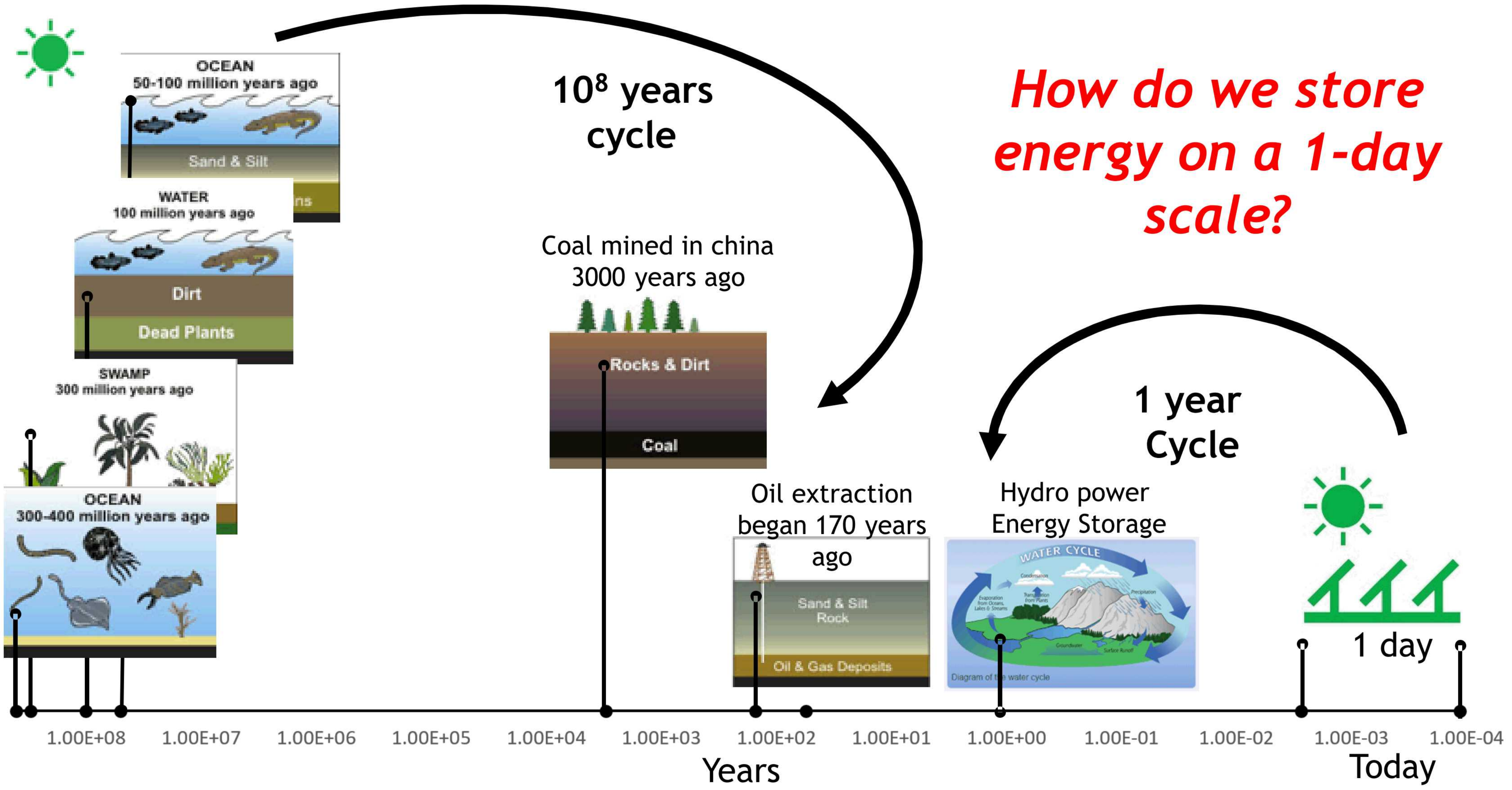

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Title