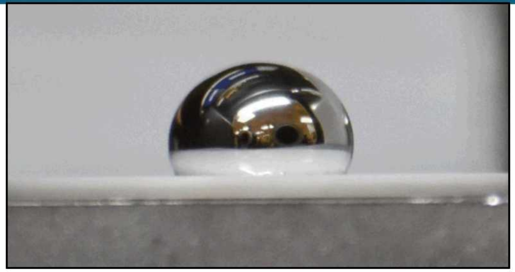
SAND2020-10070C

Solid State Ion Conductors to Enable Low Temperature Molten Sodium Batteries



SNL
Amanda Peretti,
Eric Coker,
Mark Rodriguez,
Martha Gross,
Stephen Percival, and
Leo Small (PI)

U. Kentucky
Ryan Hill
Prof. Yang-Tse Cheng

PRESENTED BY

Erik D. Spoerke

PRIME 2020
October 4-9, 2020

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

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.

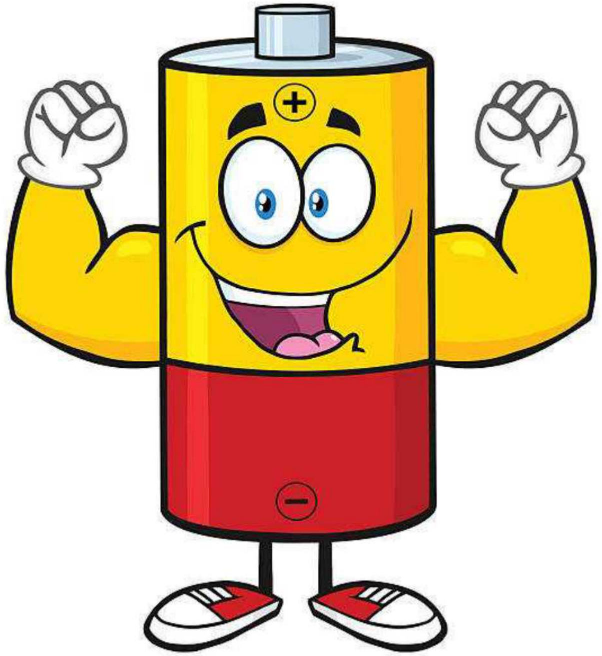
SAND No.: SAND

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

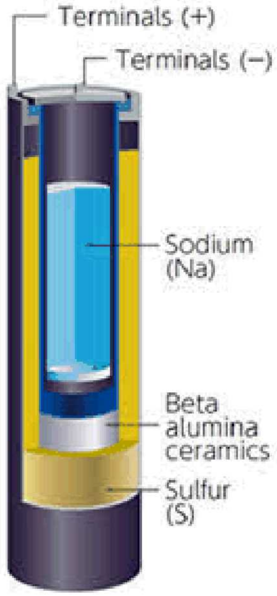
Renewable/Remote Energy Grid Reliability National Defense Emergency Aid

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

<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)

$2Na + 4S \leftrightarrow Na_2S_4$

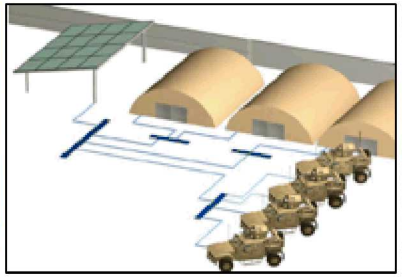
Na-$NiCl_2$ (E_{cell} ~ 2.6V)

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

Sodium Batteries


Renewable/Remote Energy

Grid Reliability



National Defense

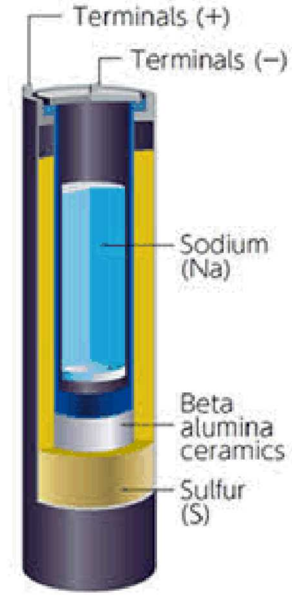
Emergency Aid

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

<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 ... V)

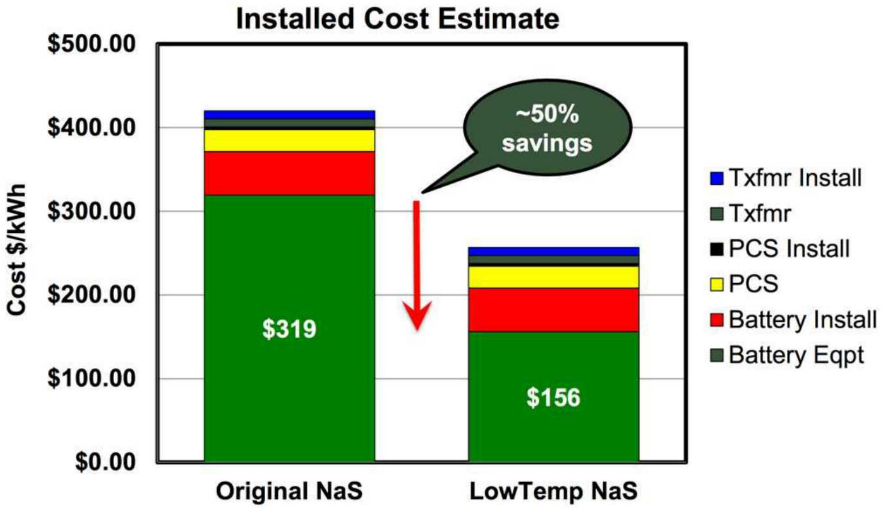
2Na ... $Na^+ + 2Cl^- + Ni(s)$

~300°C Operation!

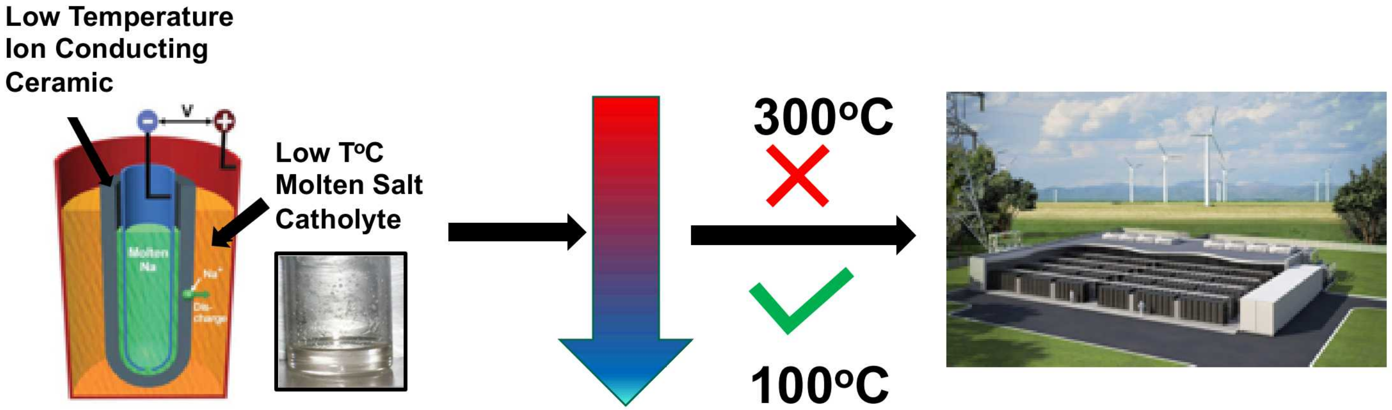
Lowering Battery Operating Temperature to Drive Down Cost

<u>Our Objective:</u> A safe, reliable, molten Na-based battery that operates at drastically reduced temperatures (near 100^{o}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

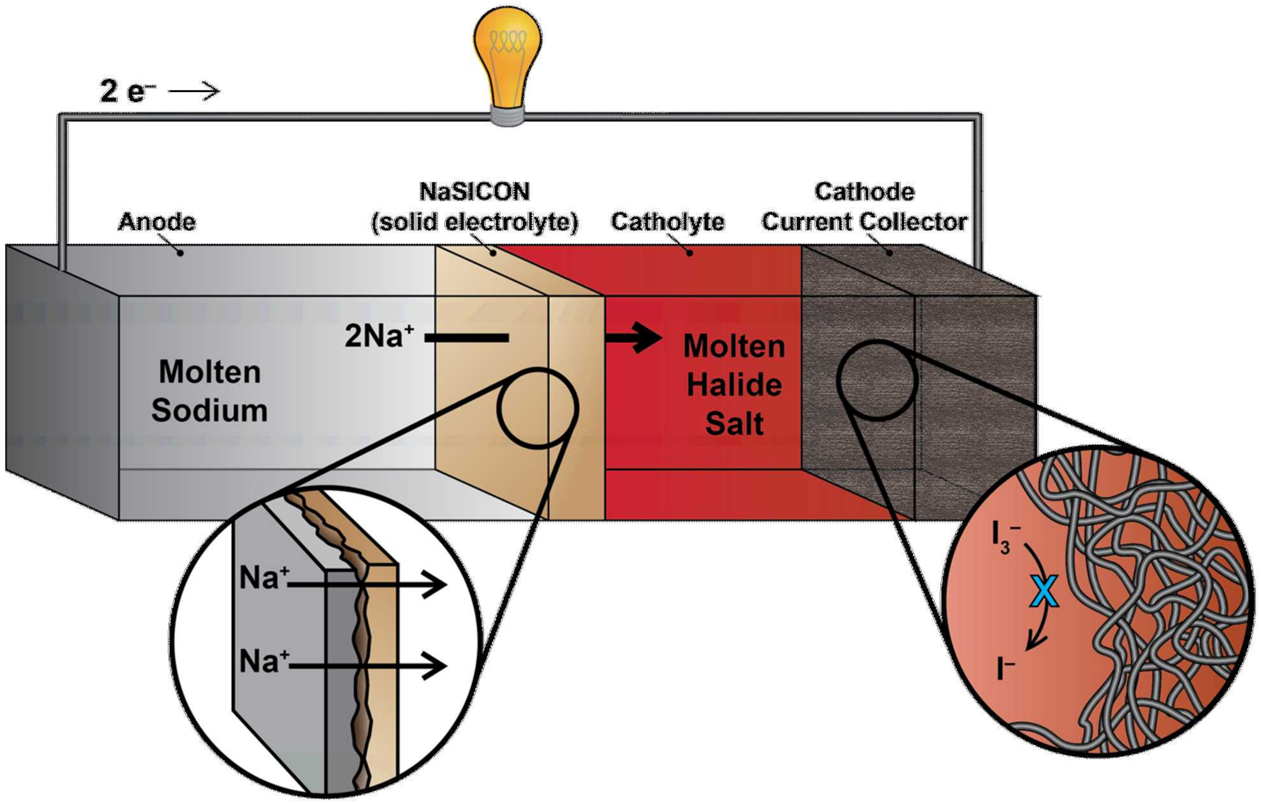


Low Temperature Molten Sodium (Na-NaI) Batteries

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:

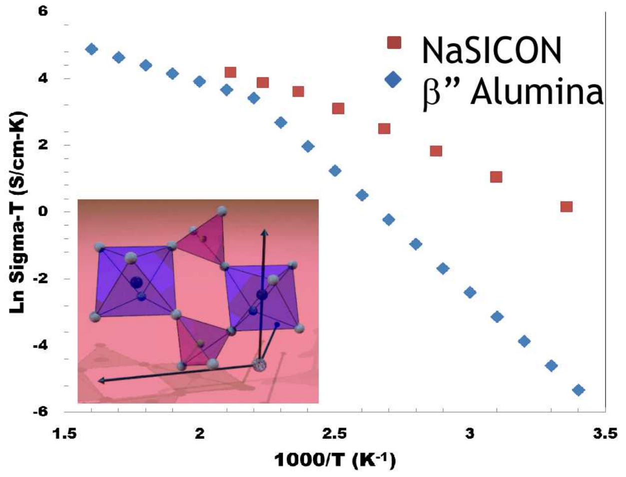
- High ionic conductivity at low temperatures
- Chemically compatible with anode and catholyte
- Zero-crossover
- Mechanically robust
- Cost-effective to produce at scale

A Promising Candidate: NaSICON

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

Chemical compatibility is a challenge:

✕ Conductive glasses – reactivity and/or low conductivity
✕ Sulfide-based conductors – reactivity
✕ Polymers - reactivity, low conductivity
- Oxides:
  - ? β”-Al_2O_3
    - atmospheric sensitivity
    - slightly lower conductivity *at lower temperatures*
  - ✓ *NaSICON*



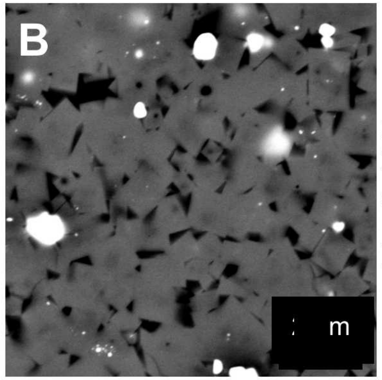
Small and Spoerke, et al. *J. Power Sources*. **360**. 569-574.

Methods for NaSICON Synthesis

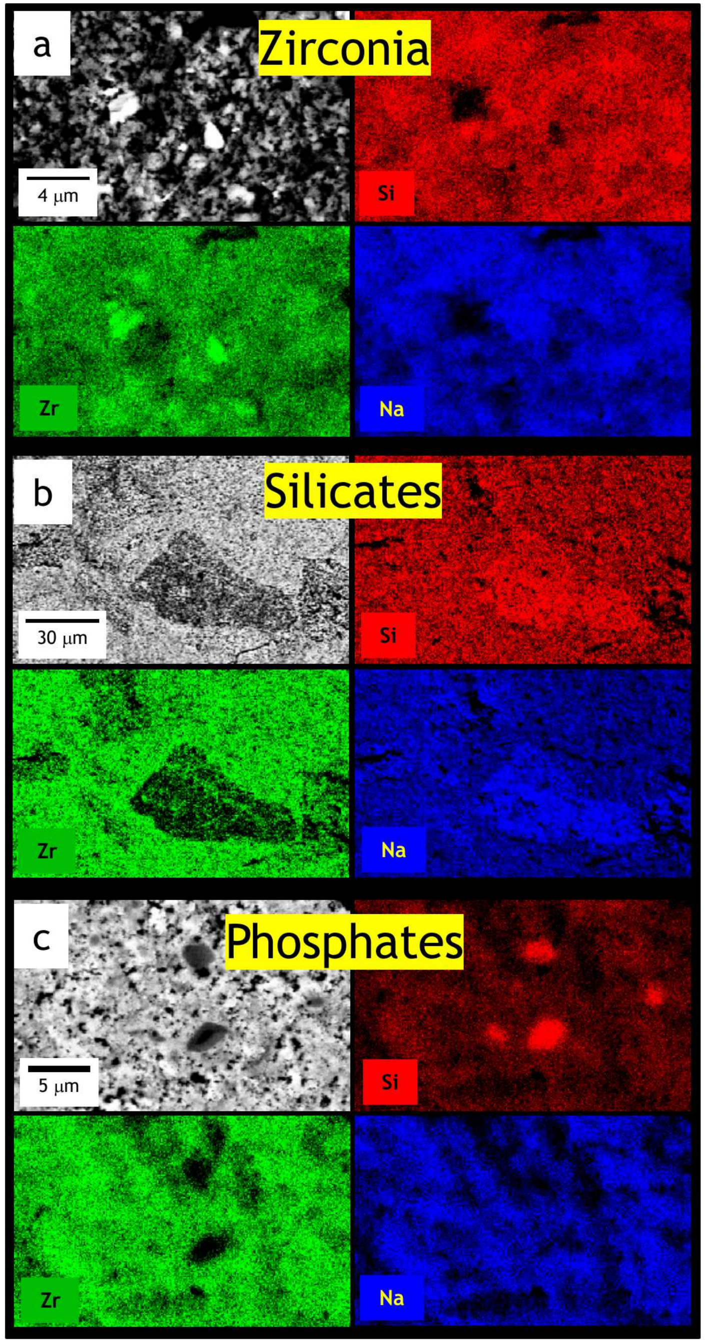
- Solid State Synthesis from Oxides
- Sol-Gel Chemistry
- Spark-plasma Sintering

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

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



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



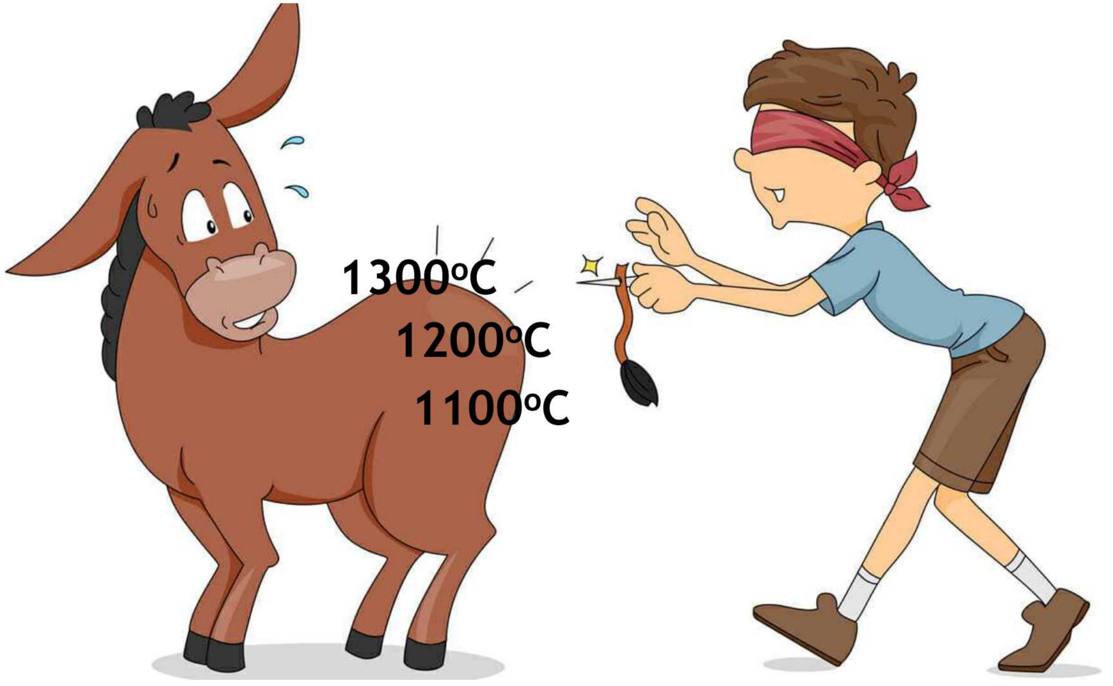
Our "Simple" Initial Synthetic Approach

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
- Fire at 1?00^{o}C in air

What thermal profile should we follow?



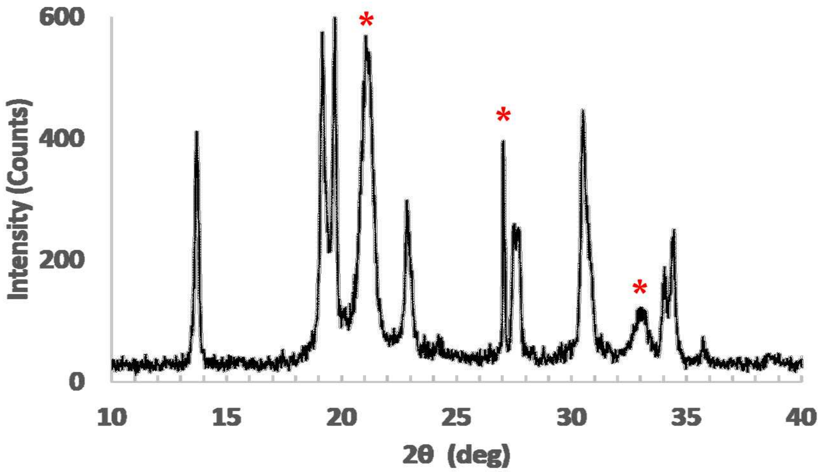
https://modernfarmer.com/2014/12/lets-stop-mean-donkeys-parties/

Our "Simple" Initial Synthetic Approach

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^oC in air
- X-ray diffraction confirms NaSICON synthesis with ZrO_2 and $ZrSiO_4$ secondary phases
  - Secondary phases can degrade conductivity
  - "Na" and "PO_4" volatility during sintering can lead to secondary phases

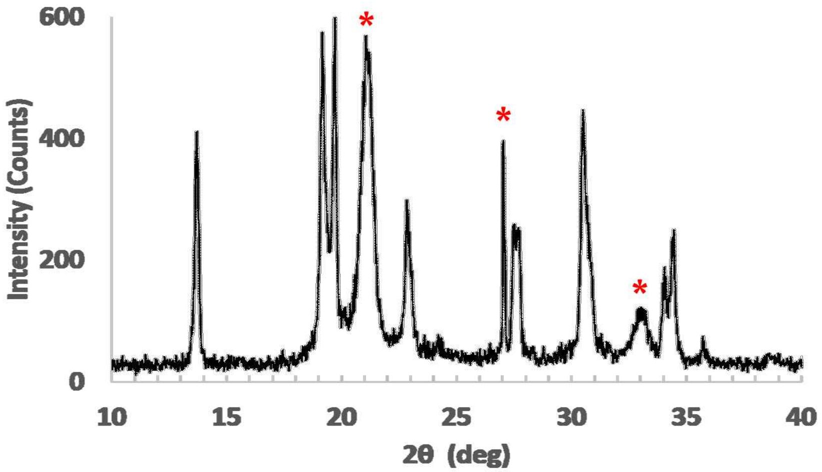


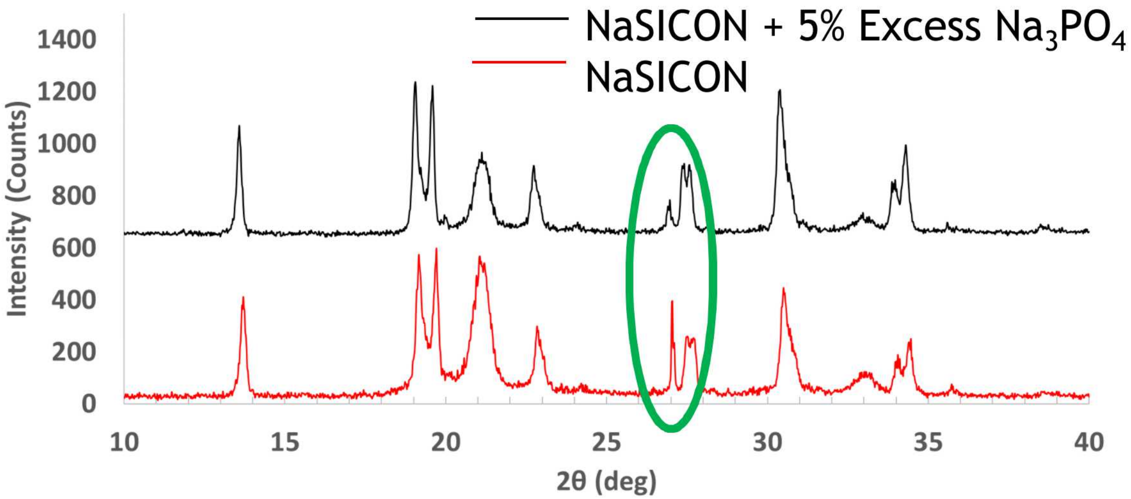
Our "Simple" Initial Synthetic Approach

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
- X-ray diffraction confirms NaSICON synthesis with ZrO_2 and $ZrSiO_4$ secondary phases
    - Secondary phases can degrade conductivity
    - "Na" and "PO_4" volatility during sintering can lead to secondary phases
    - 5% Excess Na_3PO_4 showed diminished secondary phases



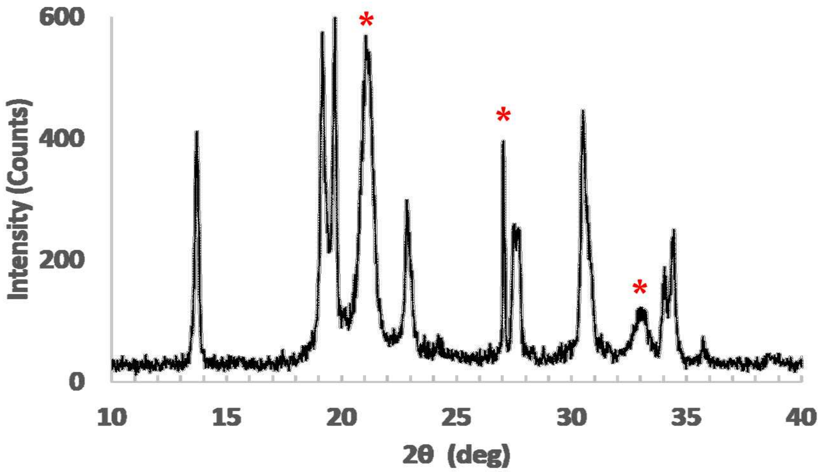


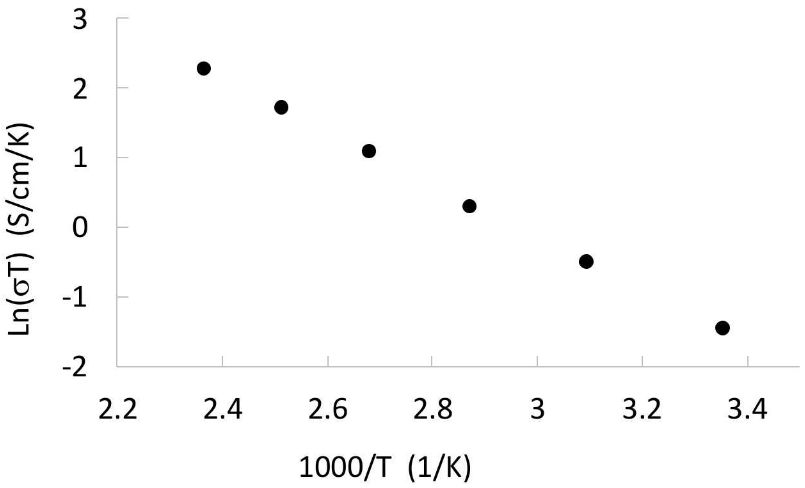
Our "Simple" Initial Synthetic Approach

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
- X-ray diffraction confirms NaSICON synthesis with ZrO_2 and $ZrSiO_4$ secondary phases
  - Secondary phases can degrade conductivity
  - "Na" and "PO_4" volatility during sintering can lead to secondary phases
  - 5% Excess Na_3PO_4 showed diminished secondary phases
- Conductivities reasonable, but slightly less than "commercial" NaSICON





Our "Simple" Initial Synthetic Approach

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
- X-ray diffraction confirms NaSICON synthesis with ZrO_2 and $ZrSiO_4$ secondary phases
    - Secondary phases can degrade conductivity
    - "Na" and "PO_4" volatility during sintering can lead to secondary phases
    - 5% Excess Na_3PO_4 showed diminished secondary phases
- Conductivities reasonable, but slightly less than "commercial" NaSICON
- Density ~ 92-95% theoretical (3.2 g/cc)

Our "Simple" Initial Synthetic Approach

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^{o}C in air
- X-ray diffraction confirms NaSICON synthesis with ZrO_2 and $ZrSiO_4$ secondary phases
    - Secondary phases can degrade conductivity
    - "Na" and "PO_4" volatility during sintering can lead to secondary phases
    - 5% Excess Na_3PO_4 showed diminished secondary phases
- Conductivities reasonable, but slightly less than "commercial" NaSICON
- Density ~ 92-95% theoretical (3.2 g/cc)

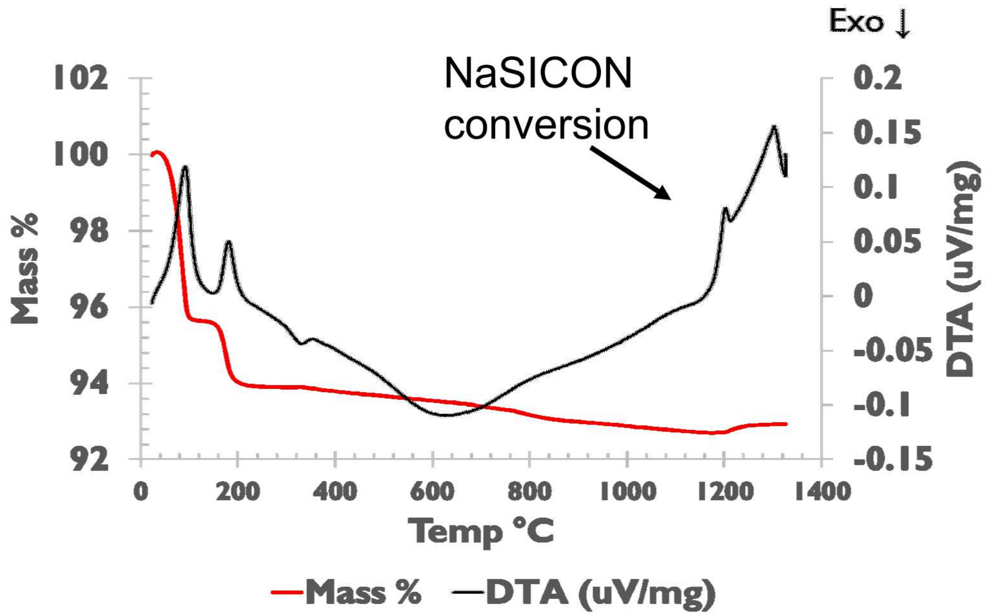
Unless it's raining…

Densities dropped to 70-80% during monsoon season.

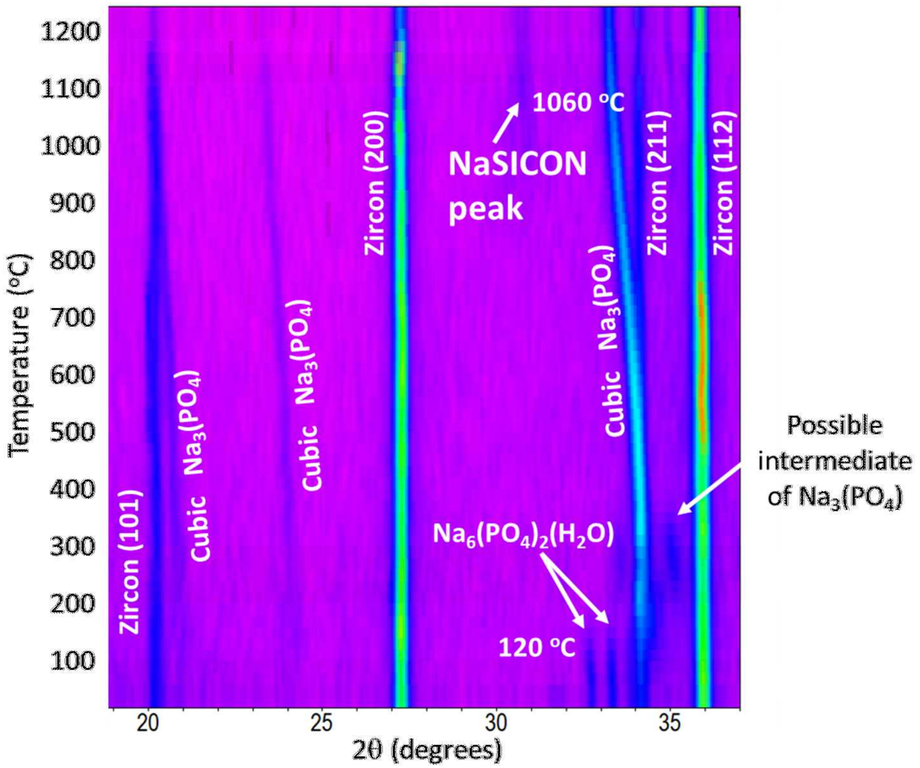
Hygroscopic Na_3PO_4 likely a problem…

Thermal Analyses to Address Humidity

Differential Thermal Analysis and Thermogravimetric Analysis



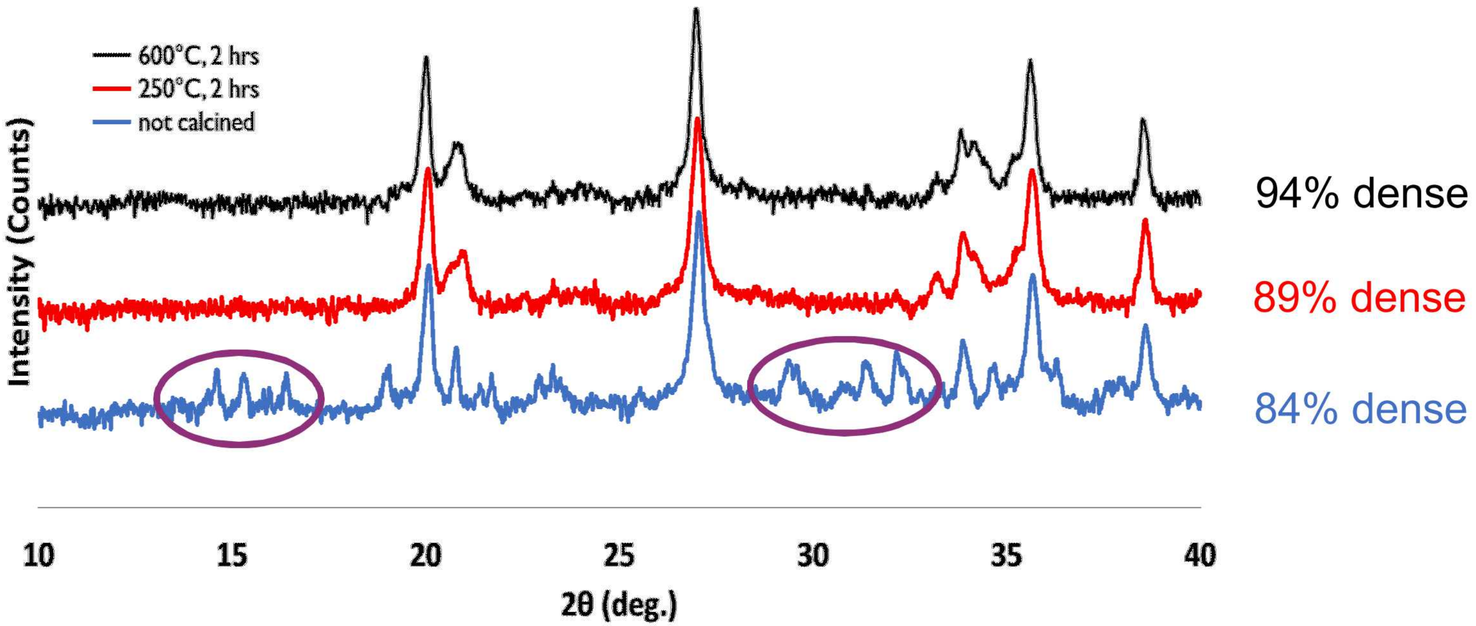
Variable Temperature X-Ray Diffraction



- 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

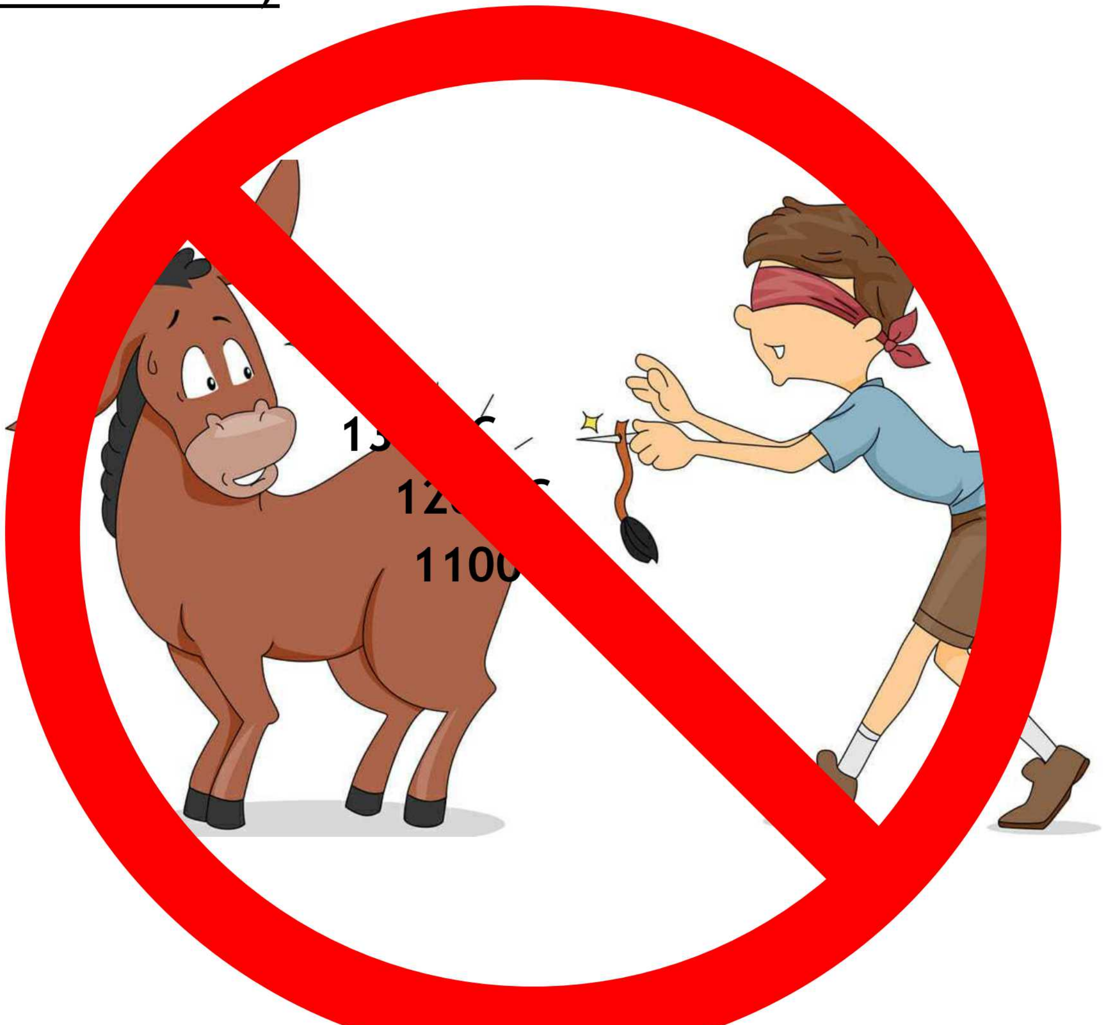
Our "Simple" Initial Synthetic Approach

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
- Fire at 1?00^{o}C in air

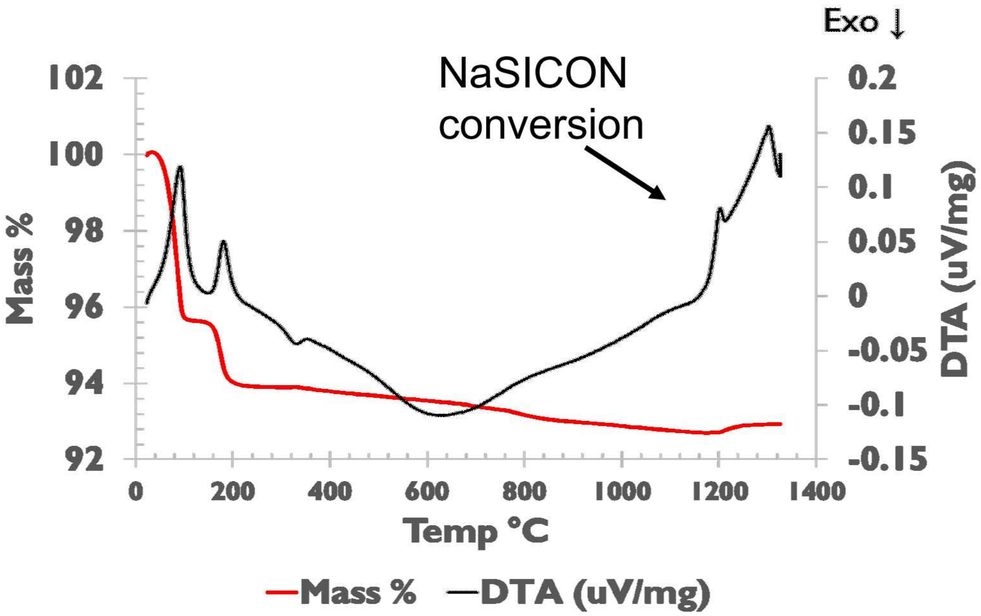
What thermal profile should we follow?



https://modernfarmer.com/2014/12/lets-stop-mean-donkeys-parties/

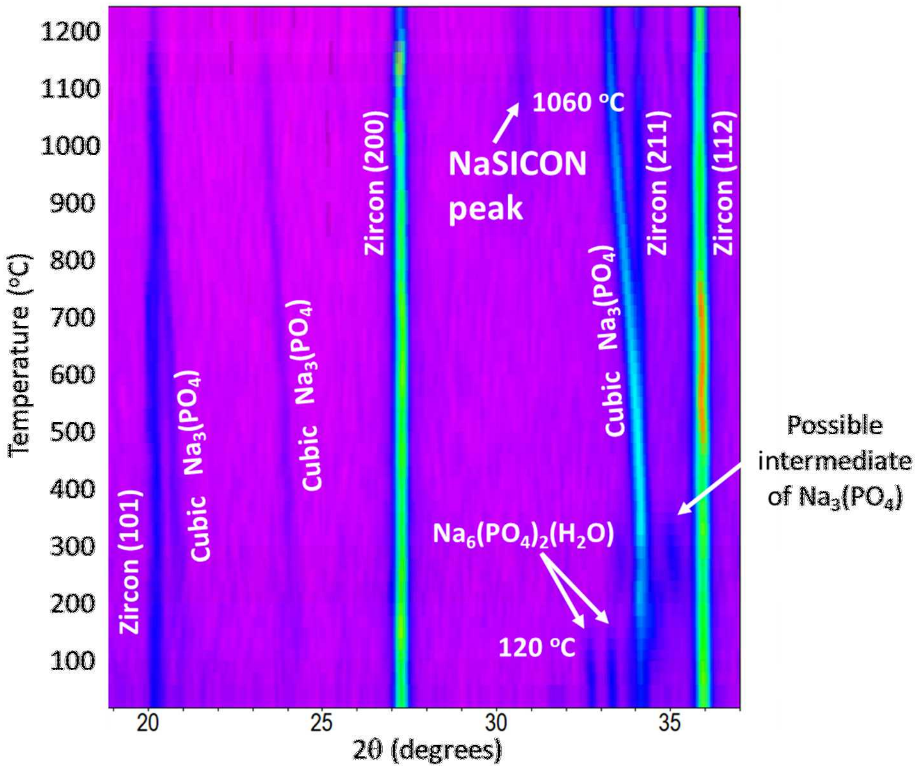
Thermal Analyses to Inform Solid State Reaction Conditions

Differential Thermal Analysis and Thermogravimetric Analysis



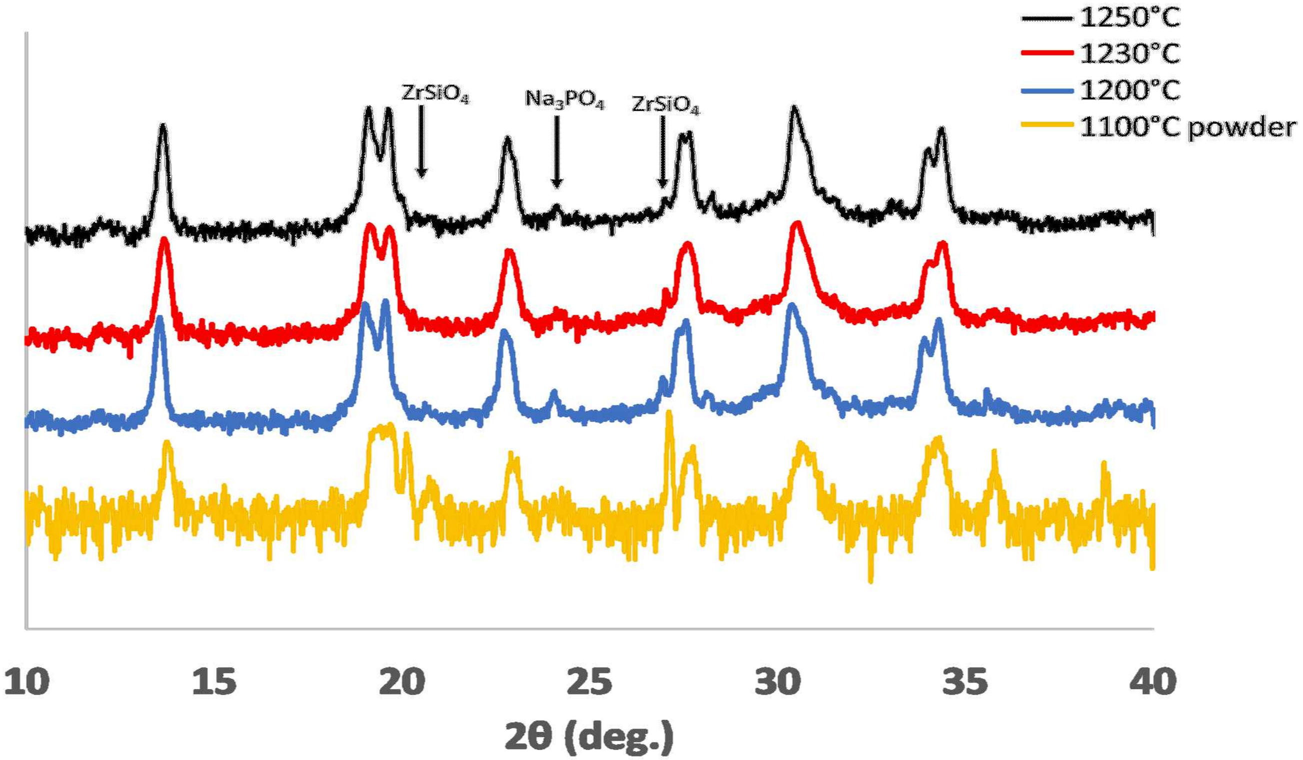
- DTA/TGA show water removed from precursor powder by ~250°C.
- NaSICON conversion reaction evident between 1150-1230 °C.

Variable Temperature X-Ray Diffraction



- 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.

Sintering Temperature Affects NaSICON Conversion and Structure

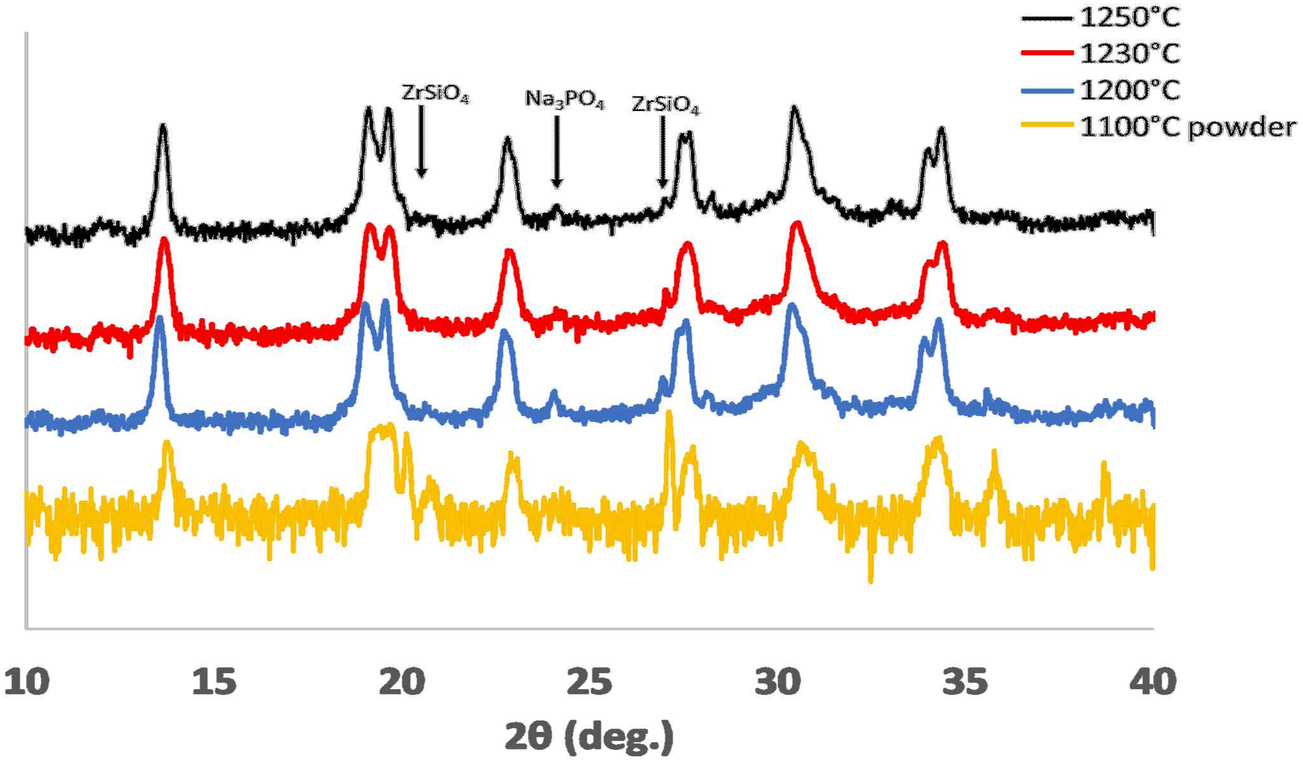


Melted NaSICON sintered at 1250˚C

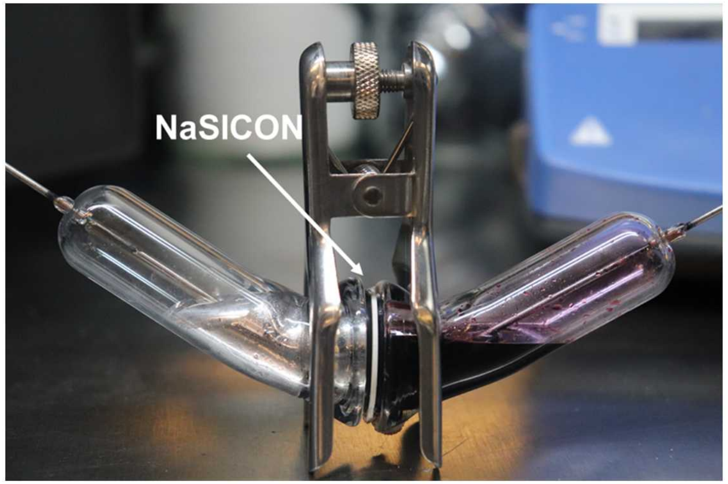
https://depositphotos.com/vector-images/goldilocks.html

- Reaction at $1100^{o}C$ leads to incomplete conversion and poor densification.
- Sintering above $1230^{o}C$ 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.

Sintering Temperature Affects NaSICON Conversion and Structure



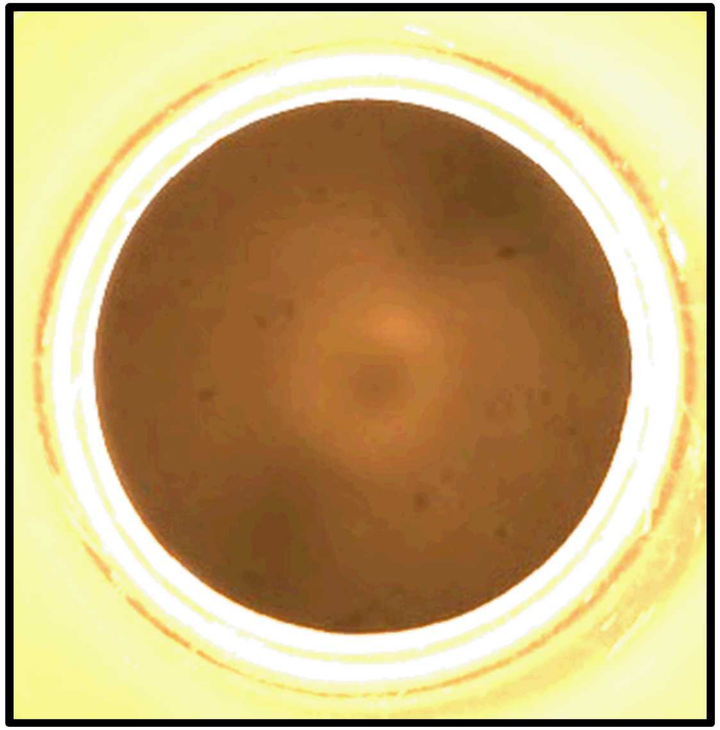
Melted NaSICON sintered at 1250˚C

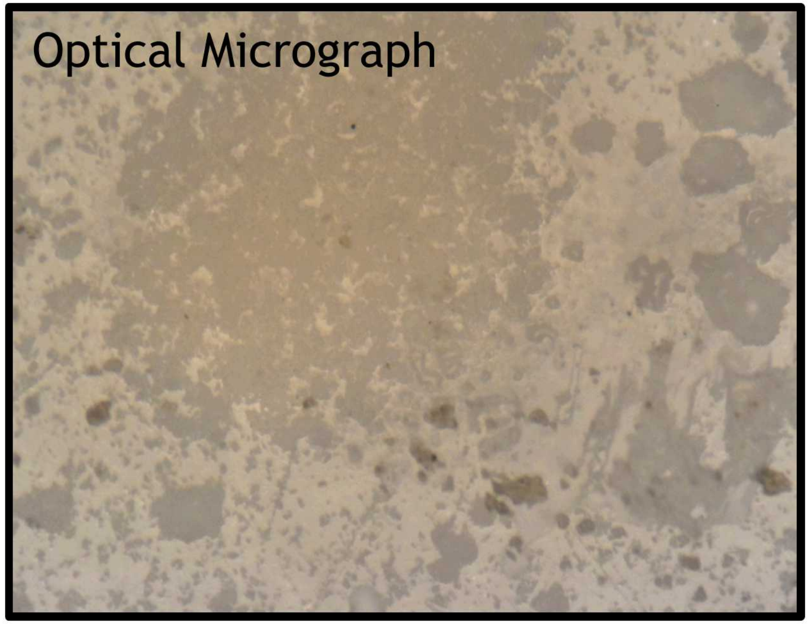


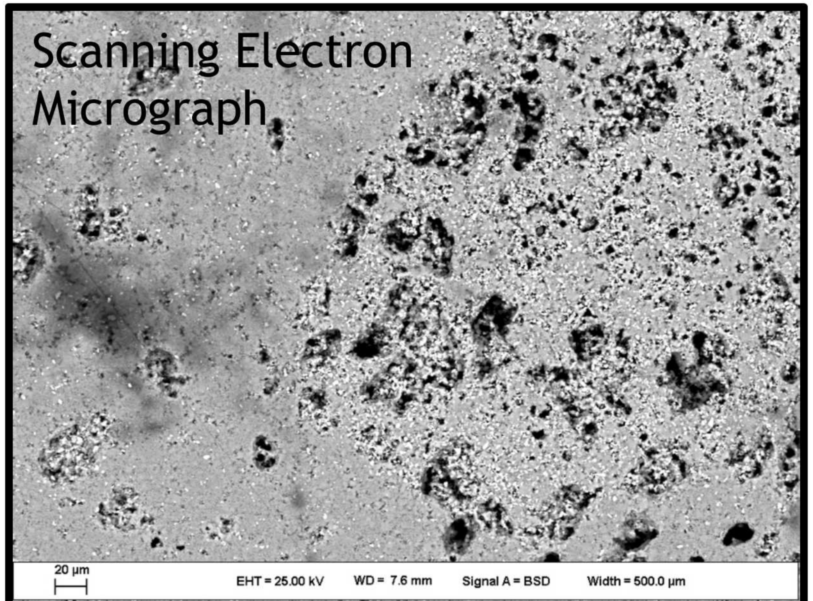
Molten Na Battery Cell Set-Up

- 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.

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.

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.

Solution 2: Increasing pressing force from 10 ksi to 20 ksi

Slightly bigger improvement in NaSICON synthesis.

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.

Solution 2: Increasing pressing force from 10 ksi to 20 ksi

Slightly bigger improvement in NaSICON synthesis.

Solution 3: Add polymeric binder to “lubricate” compacting particles during pressing

Significant improvement in NaSICON synthesis!

Density 94-96%

Acceptable phase purity

Conductivity increased to > 0.4 mS/cm

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.

Solution 2: Increasing pressing force from 10 ksi to 20 ksi

Slightly bigger improvement in NaSICON synthesis.

Solution 3: Add polymeric binder to “lubricate” compacting particles during pressing

Significant improvement in NaSICON synthesis!

- Density 94-96%
- Acceptable phase purity
- Conductivity increased to > 0.4 mS/cm

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.

Solution 2: Increasing pressing force from 10 ksi to 20 ksi

Slightly bigger improvement in NaSICON synthesis.

Solution 3: Add polymeric binder to “lubricate” compacting particles during pressing

Significant improvement in NaSICON synthesis!

Density 94-96%

Acceptable phase purity

Conductivity increased to > 0.4 mS/cm

Unless it’s raining…again!

Controlling moisture content during processing allows for still further improvement…

Density >96%

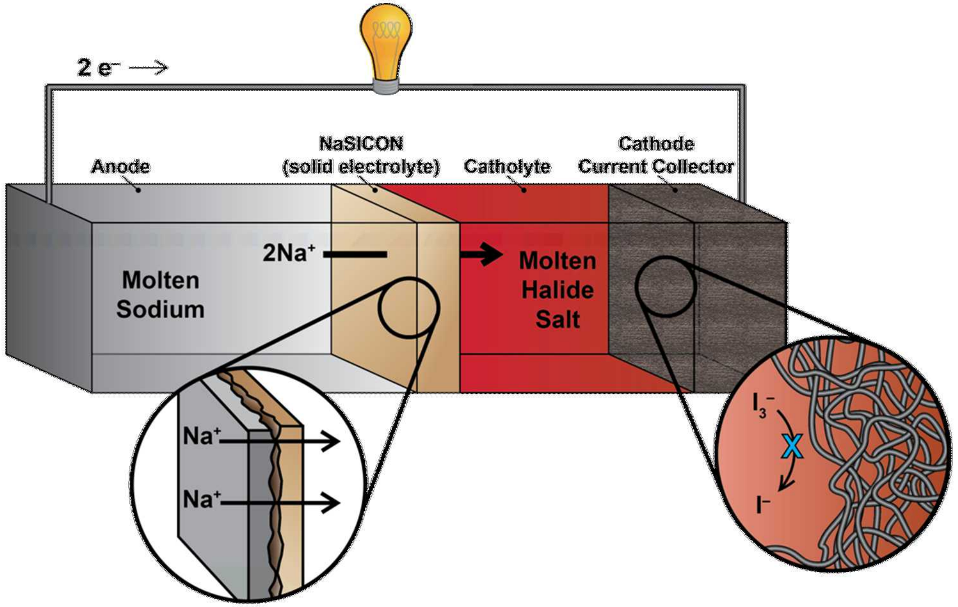
Conductivity increase >.5 mS/cm

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!*

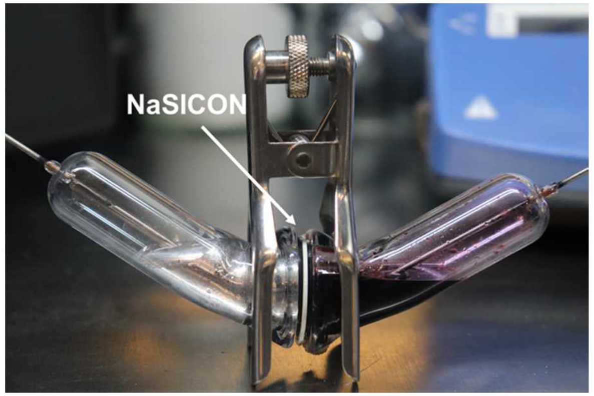


Na-NaI battery:

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

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

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



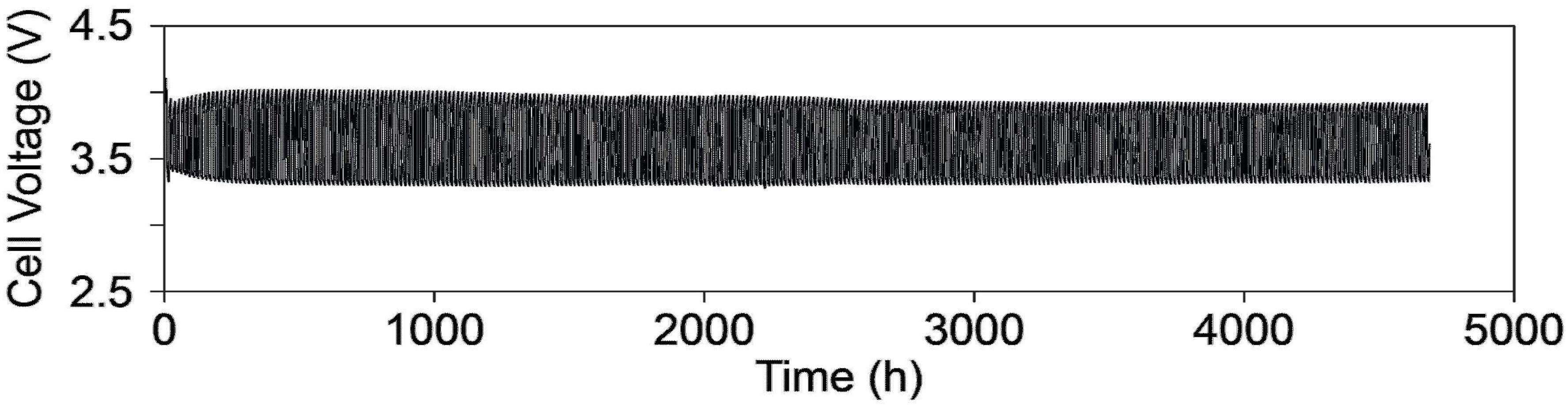
Molten Na Battery Cell Set-Up

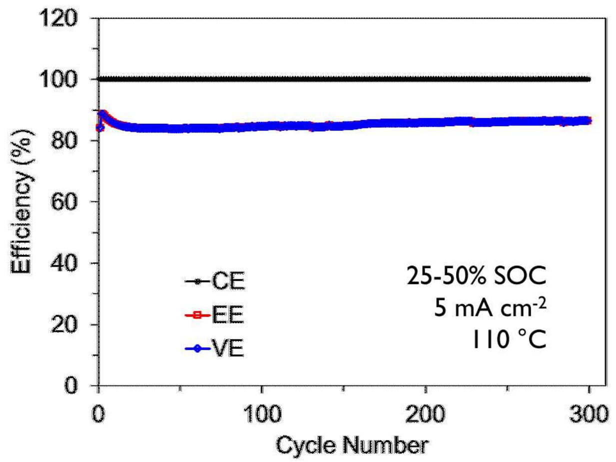
Martha Gross

Effective Battery Cycling with NaSICON

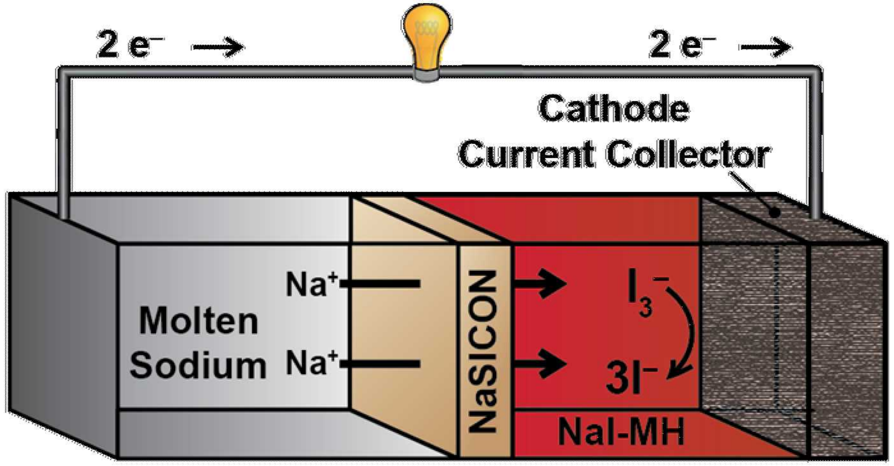
Integrated NaI-MH2 catholyte into molten Na batteries with NaSICON separator

- Successfully ran >300 cycles (>6 months) at 5 mA cm^{-2} (25% DoD) for 85.3% voltage efficiency. Still running!
- Successfully accessed all I^-/I_3^- capacity (100% DoD) at 3.5 mA cm^{-2}
- Cycled currents as high as 15 mA cm^{-2}.

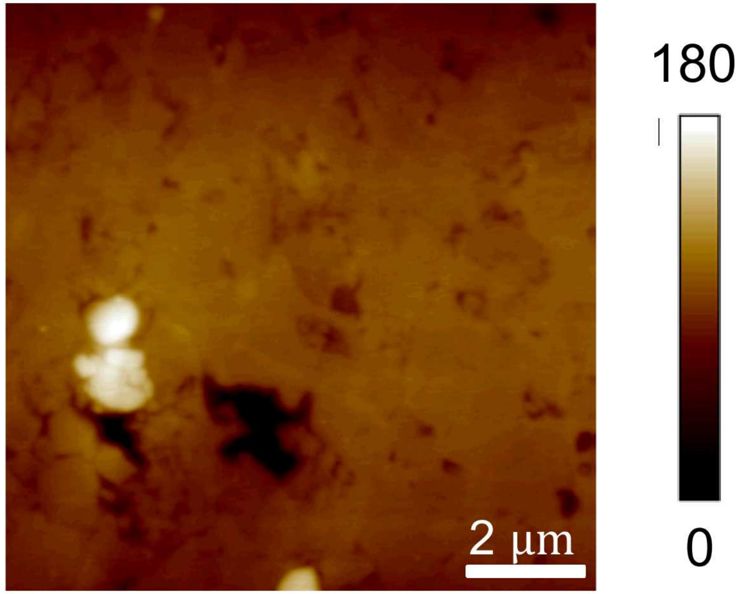




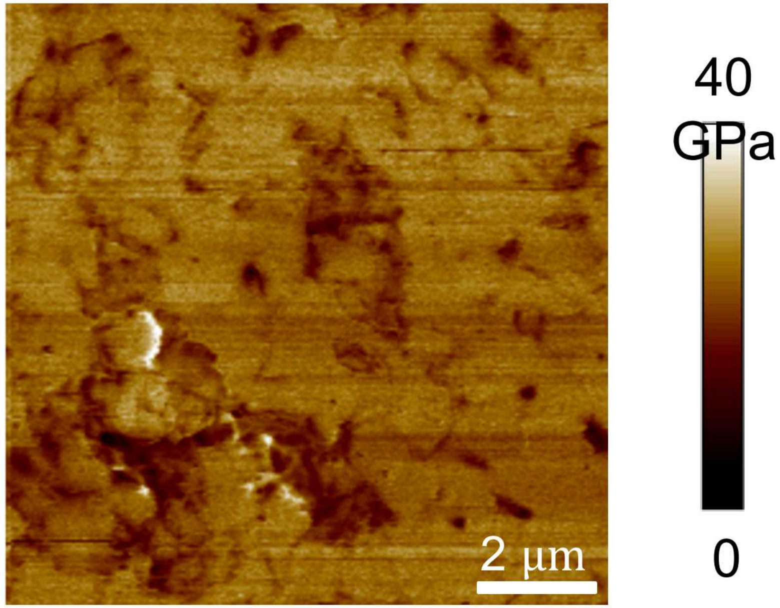
Mechanical integrity is important!



Mechanical and Microstructural Characterization of NaSICON



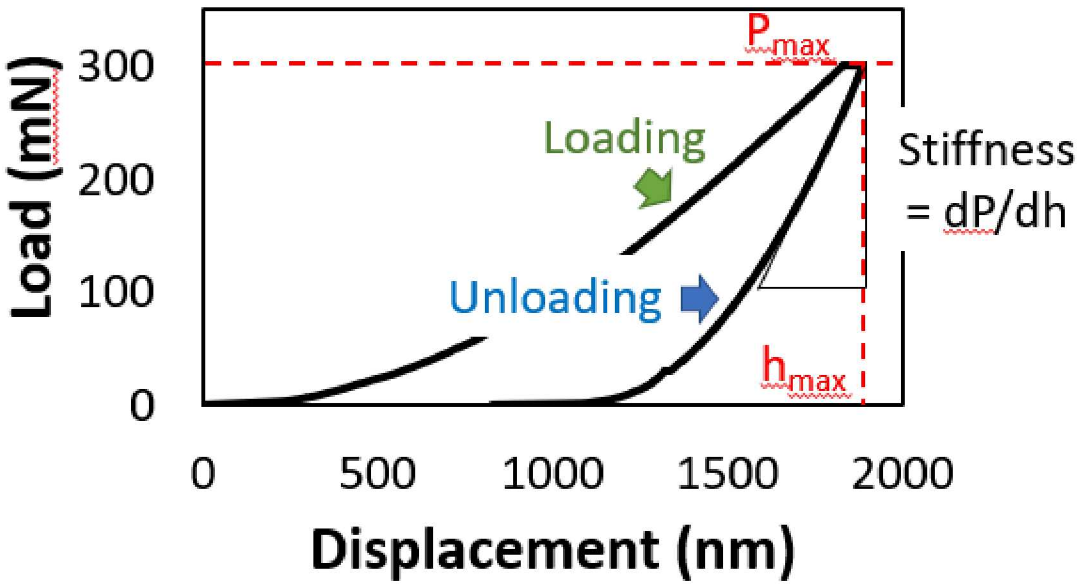
Surface Height



Elastic Modulus

Mechanically different regions can be visualized and reconciled with topographical features and phase differences

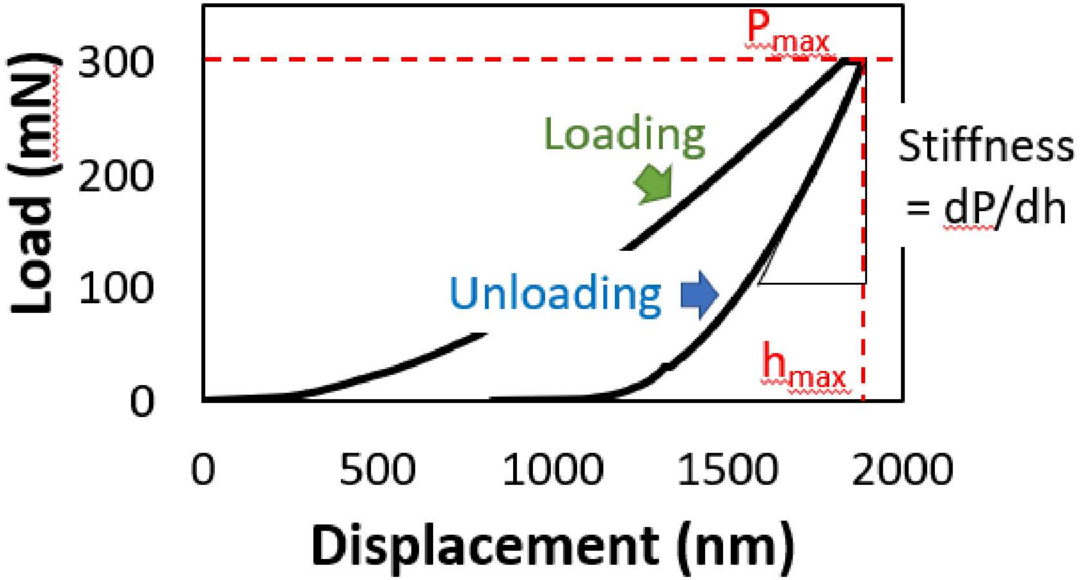
Basic Mechanical Metrics



Elastic Modulus (GPa)	Hardness (GPa)
76.32 ± 5.80	4.57 ± 0.55

Baseline mechanical properties of NaSICON are consistent with published values.

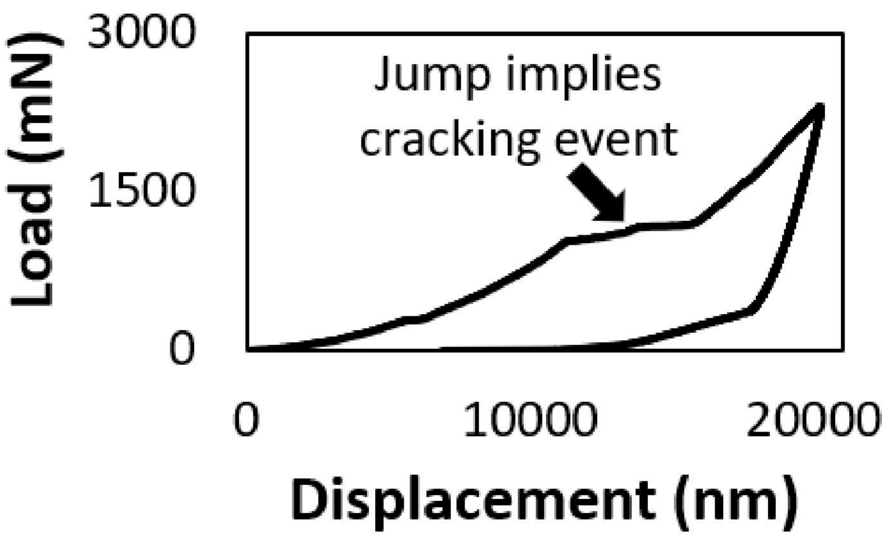
Basic Mechanical Metrics

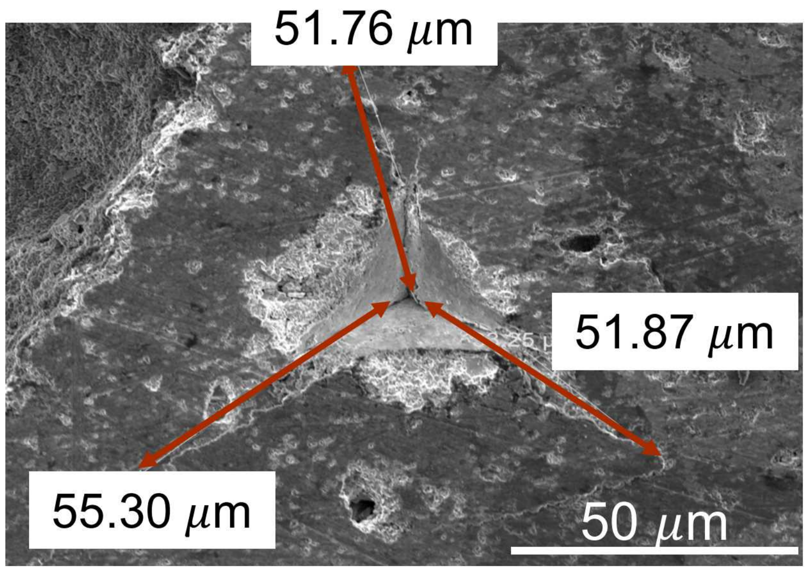


	Elastic Modulus (GPa)	Hardness (GPa)
NaSICON	76.32 ± 5.80	4.57 ± 0.55
β”-Al_2O_3 (with ZrO_2)[1]	0.185-0.199	~11-14

1. Sheng, J. Mater. Sci. (1988) **23,** 958-967.

Fracture Toughness of NaSICON





Cracks can be measured by SEM

Fracture toughness then calculated by:

$$K_c = A\left(\frac{E}{H}\right)^{\frac{1}{2}}\left(\frac{P}{c^{\frac{3}{2}}}\right)$$

A: Material independent constant = 0.040 ± 0.004
E: Young's Modulus
H: Hardness
P: Maximum load during indentation
c: Length of crack measured by SEM

Material	K_{Ic} (MPa√m)
SiC	3.00-6.00
MgO	2.50
Fused Silica	0.80
WC	6.00-20.00
β''-Al_2O_3 (w/ ZrO_2)[1]	2.3-4.5
NaSICON (measured)	1.90 ± 0.60

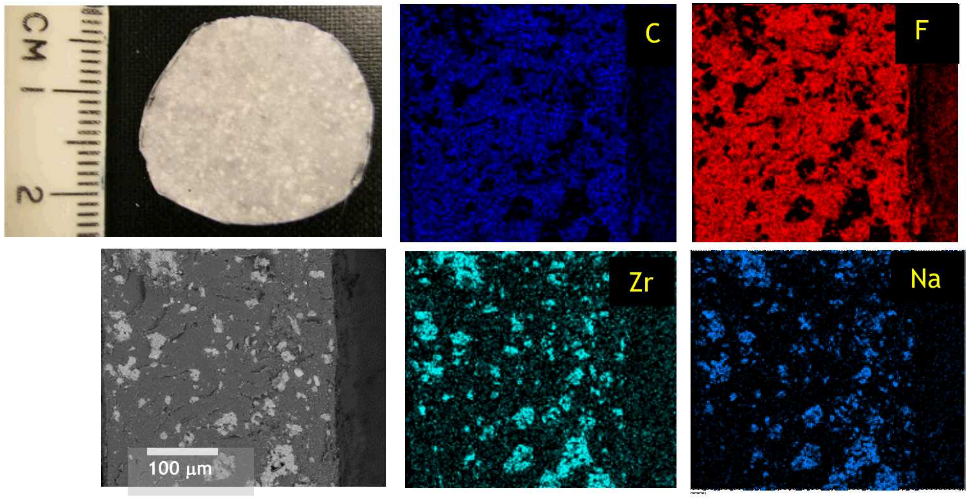
1. Sheng, J. Mater. Sci. (1988) **23**, 958-967.

A More Compliant NaSICON

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.

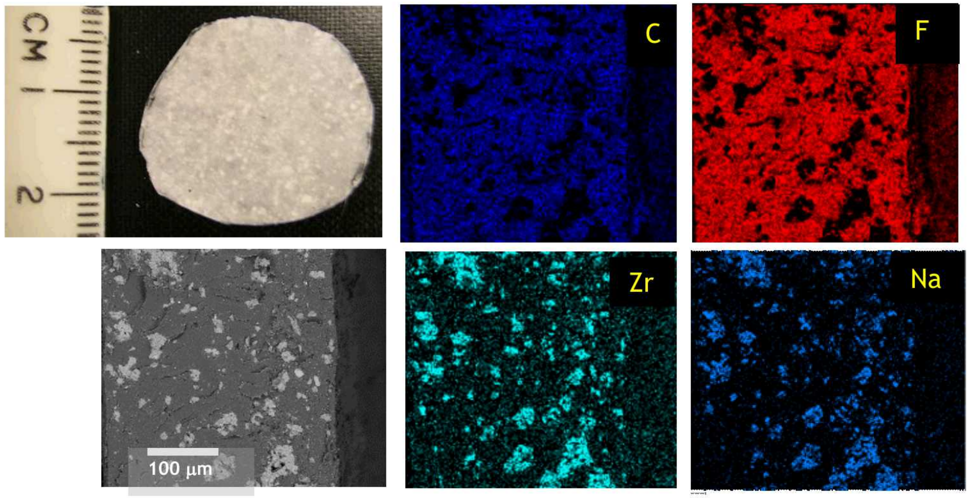


A More Compliant NaSICON

Initial Approach

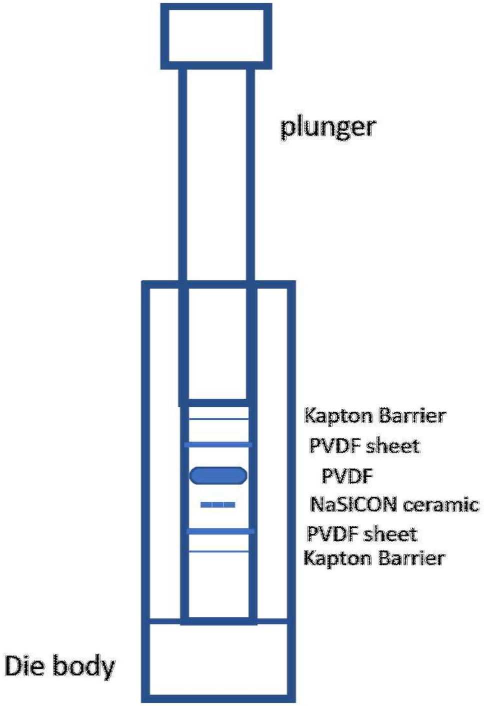
- Powdered NaSICON and powdered polymer (polyvinylidene difluoride: PVDF) were warm-pressed together
- Tough composite with reasonable distribution of NaSICON
- Good interfaces between NaSICON and polymer

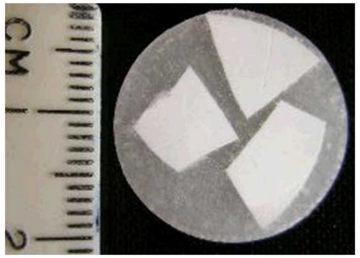
➢ Impractically low ionic conductivity. Poor connectivity of Na-conductive NaSICON is evident in cross-sectional elemental mapping.



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} ~0.25 mS/cm for composite!

- This is a “low tech,” but promising approach.
- Interfaces must be engineered for thin separator applications.
- Polymer selection is critical!

Hazards of Poor Material Selection

Polymer incorporation highlights the importance of careful material section.

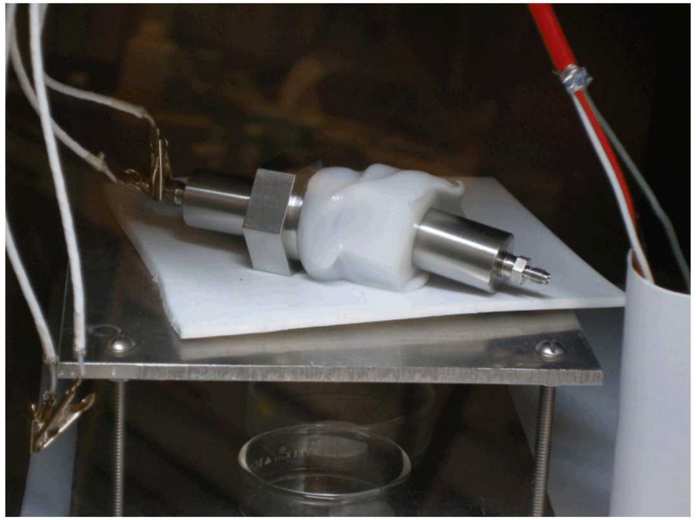
Compatibility must be considered for:

- 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

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

Summary

<u>Project Objective:</u> 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.

- Mechanical properties of NaSICON are important
  - Measured mechanical properties are comparable to literature values
  - Fracture toughness needs to be higher for reliable performance
  - Composite structures may offer new avenues to reliable performance, if chemical compatibility and structural integration can be optimized.

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

Title