Current State of NaSICON for Molten Sodium Batteries

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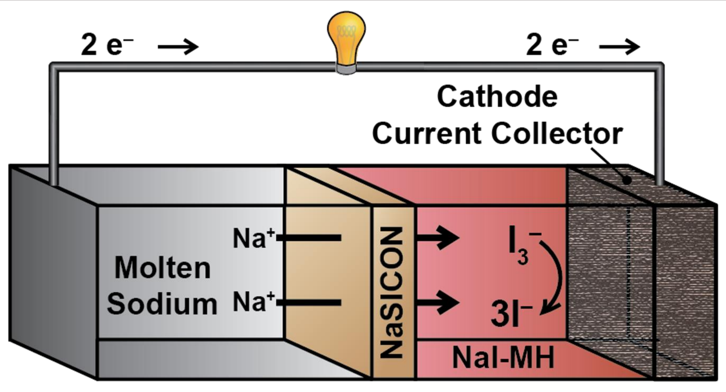
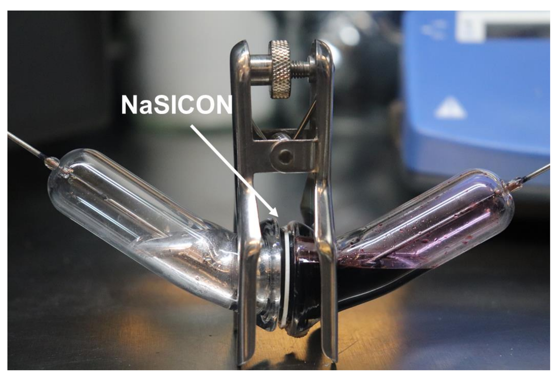
Background:
The Na Super Ion CONductor (NaSICON) is a solid-state ceramic separator with high sodium ion conductivity. Our team uses NaSICON in low-temperature molten sodium batteries to facilitate selective sodium ion transport between a molten sodium (Na) anode and a sodium-iodide (NaI)-based molten salt catholyte, while simultaneously preventing the two molten electrodes from mixing.

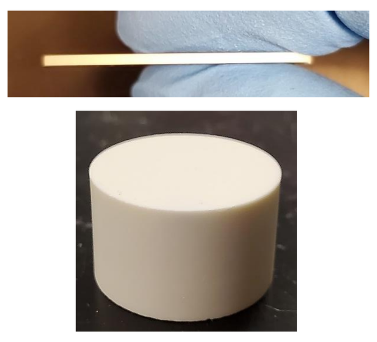


Key Separator Properties for NaSICON: $Na_{(1+x)}Zr_2Si_xP_{3-x}O_{12}$, 0<x<3
- High Na-ion conductivity at reduced temperatures (<150 °C)
- Chemical compatibility with molten Na and molten halide salts
- Mechanical robustness
- Low cost, scalable production

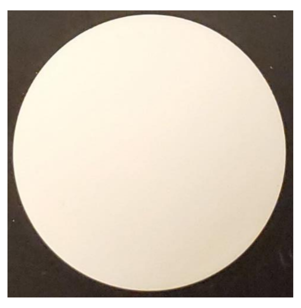


Photograph of a lab-scale molten sodium battery

We have developed a solid-state, reactive sintering process to create lab-scale NaSICON with high yield, high density, and high sodium ion conductivity by increasing sodium content (x>2), controlling particle aggregation, and critically, managing moisture uptake during powder processing.



Our NaSICON Standard (25°C)
Conductivity: ~**3.2 mS/cm**
Density: **3.2 g/cm³** (97% theoretical)



Our Problem: Current processing conditions for high performance limit the scalability and form-factor for NaSICON.

Our Challenge: Can we adapt our synthesis of high performance NaSICON to be less moisture sensitive and more amenable to other processing methodologies, without sacrificing high performance?

Illustrating Moisture Sensitivity in Conventional Syntheses:

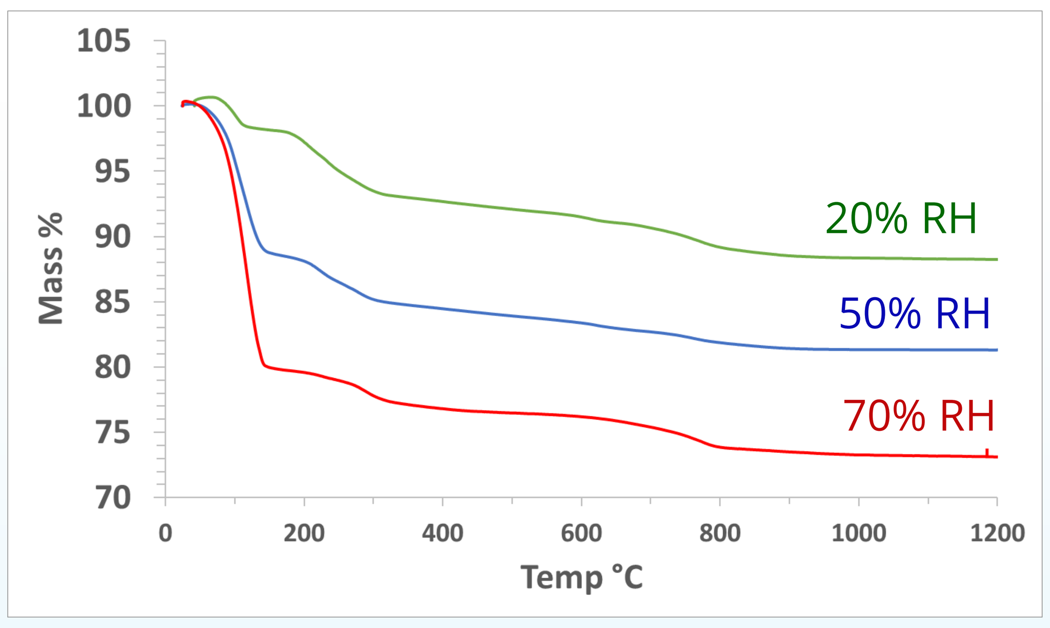
Many synthetic approaches use binders during ceramic processing. Here, we show that addition of polyvinyl butyral (PVB) picks up moisture and impacts NaSICON sintering.

- Inorganic precursors (solid state oxides and phosphates) were calcined to 600˚C to remove moisture.
- PVB was added as a binder/lubricant to dry powders to help with particle compaction during pressing.
- PVB-precursor mixture was exposed to variable atmospheric humidities before pressing and firing above 1200˚C.

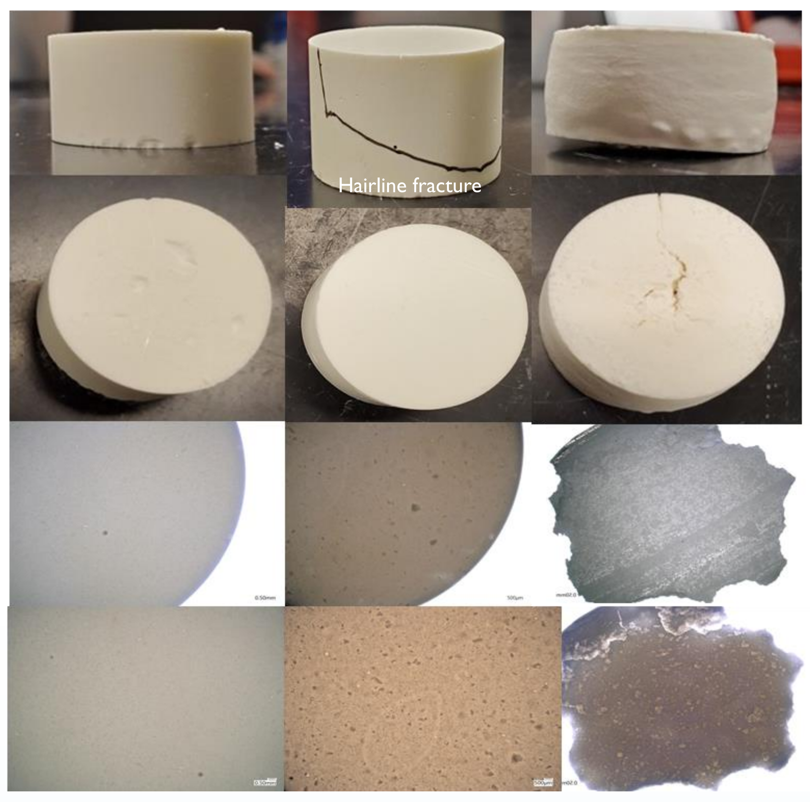
Results:

- Thermogravimetric Analysis of Pre-fired mixtures shows humidity-dependent water uptake.
- Evaluation of fired ceramics shows humidity-uptake decreased ceramic density, reduced conductivity and created critical flaws in NaSICON.

Thermogravimetric Analyses of PVB-Mixed Powder Precursor



Fired NaSICON with PVB Binder



NaSICON with PVB binder		
Humidity	Density %	Conductivity (mS/cm)
20%	97	1.97
50%	96	1.60
70%	89	0.74

Moisture sensitivity limits practical synthesis of high performance NaSICON!

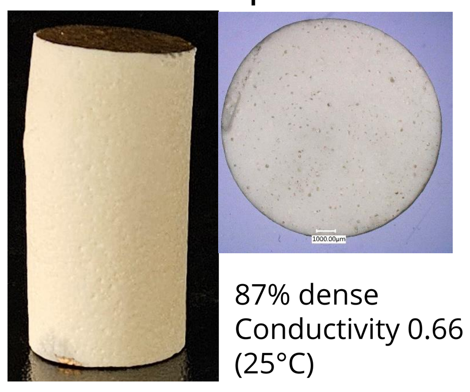
Modifying NaSICON Precursor to Reduce Moisture Sensitivity:

Moisture uptake is believed to impact the reactive sintering of NaSICON by binding to hygroscopic materials (e.g., phosphates) in the unreacted precursors.

Can we eliminate this problem using "fully converted" NaSICON powder? (Fired above 1200˚C)?

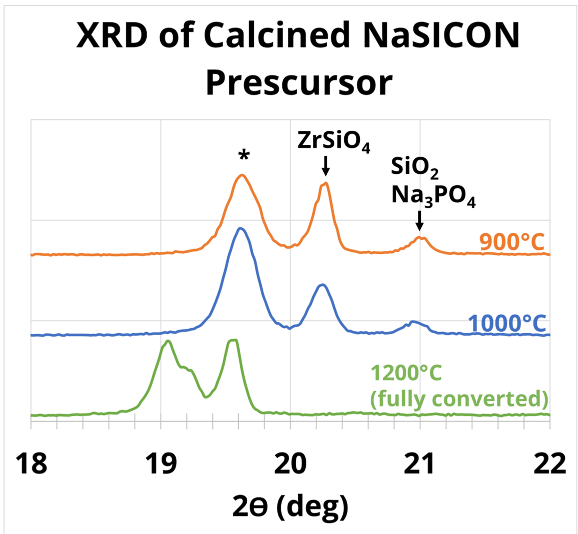
- Fully converted NaSICON precursor was ground and sieved before pressing and firing again above 1200ºC.
  - ✗ Resulting cylinder was deformed and sectioned discs contained spot defects.
  - ✗ Conductivity and density were also low.

NaSICON ceramic from fully-converted precursor.



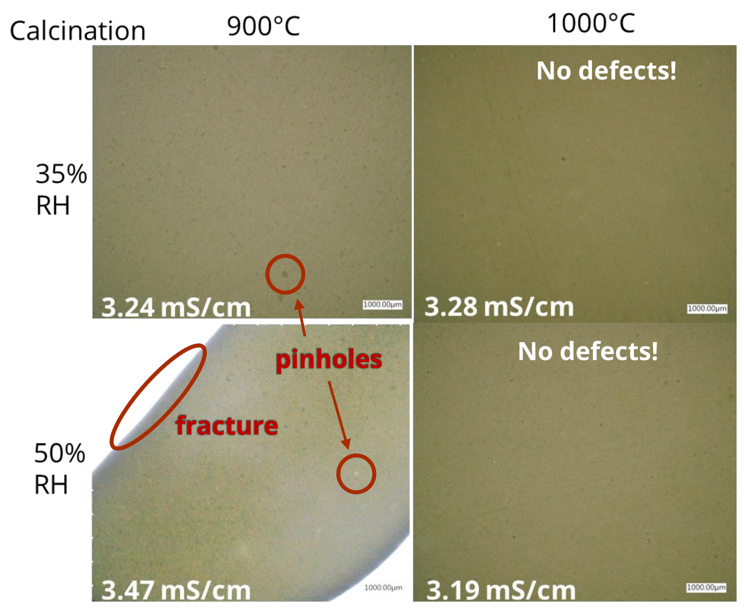
87% dense
Conductivity 0.66 mS/cm (25°C)

What about partially-converted NaSICON precursors?



Higher calcine temperature (900-1000˚C, (below full conversion (~1200˚C)) shows consumption of initial reagents (e.g., $ZrSiO_2$) and increase in silicon-rich precursor NaSICON phase (*).

- 1000˚C calcine showed most "pre-conversion," but still not full NaSICON conversion.
- These "partially converted" materials were exposed to elevated humidity before pressing and firing into ceramics.



All samples had 97% density

- ✓ Both 900˚C and 1000˚C showed good ionic conductivities (25˚C)
- ✓ 1000˚C calcination showed fewest defects.

Higher temperature calcine and formation of silicon-rich precursor NaSICON phase appears to decrease NaSICON moisture sensitivity!

Conclusions and Future Directions

- PVB binder improves particle compaction during pressing, but facilitates moisture uptake from the atmosphere, resulting in lower density, lower conductivity, and structurally-flawed NaSICON.
- Calcination to partially convert NaSICON stabilizes the precursor, decreasing the uptake of ambient moisture and allowing for NaSICON to be produced in more humid environment.
- Future work will focus on adapting moisture-resistant NaSICON precursor with alternative processes to expand our available NaSICON form factor and scale.

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