Mitigating Humidity Effects During NaSICON Processing

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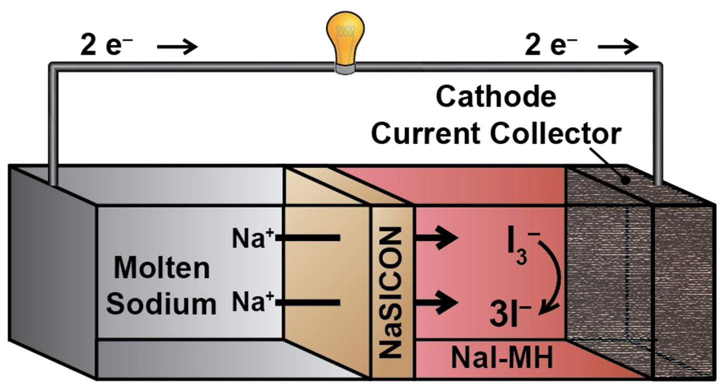
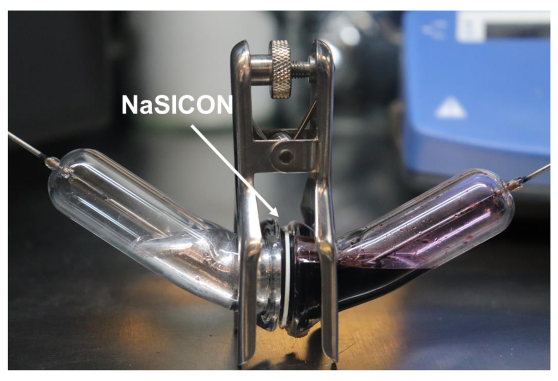
Background:

The Sodium (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

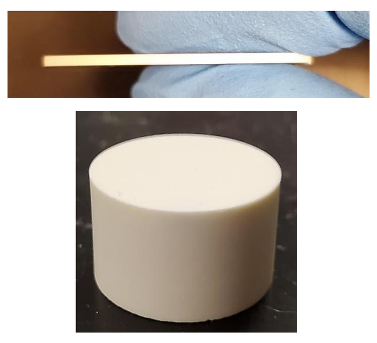
- High Na-ion conductivity at reduced temperatures (<150 °C)
- Chemical compatibility with molten Na and molten halide salts
- Mechanical robustness
- Low cost, scalable production



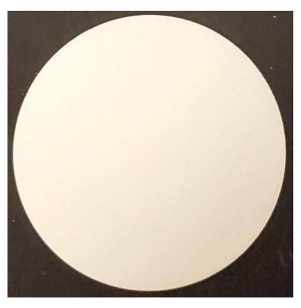
Photograph of a lab-scale molten sodium battery

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



Na^+ Conductivity: **3.75 mS cm^{-1}** (25 °C)
81.7 mS cm^{-1} (150 °C)
Density: **3.2 g cm^{-3}** (97% theoretical)



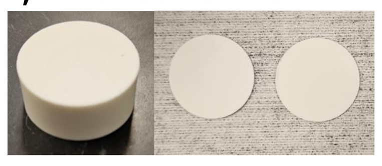
Problem: Variable laboratory humidity (10-50% RH) during NaSICON synthesis can impact NaSICON properties, with high humidity negatively influencing Na^+ conductivity, density, machineability, and scalability. Once synthesized, however, NaSICON is relatively immune to humidity effects.

Goal: Adapt our synthesis of high performance NaSICON to be less moisture sensitive and more amenable to other processing methodologies, without sacrificing key mechanical, chemical, and electrochemical properties.

NaSICON Synthesis Uses Two Hygroscopic Reagents

To synthesize NaSICON, inexpensive reagents – SiO_2, Na_2CO_3, $ZrSiO_4$, Na_3PO_4 - are used. Na_3PO_4 and, to a lesser extent, Na_2CO_3 readily absorb moisture from the air. The amount of water absorbed during processing can influence the resulting NaSICON.

20% RH, No calcine – Perfect!

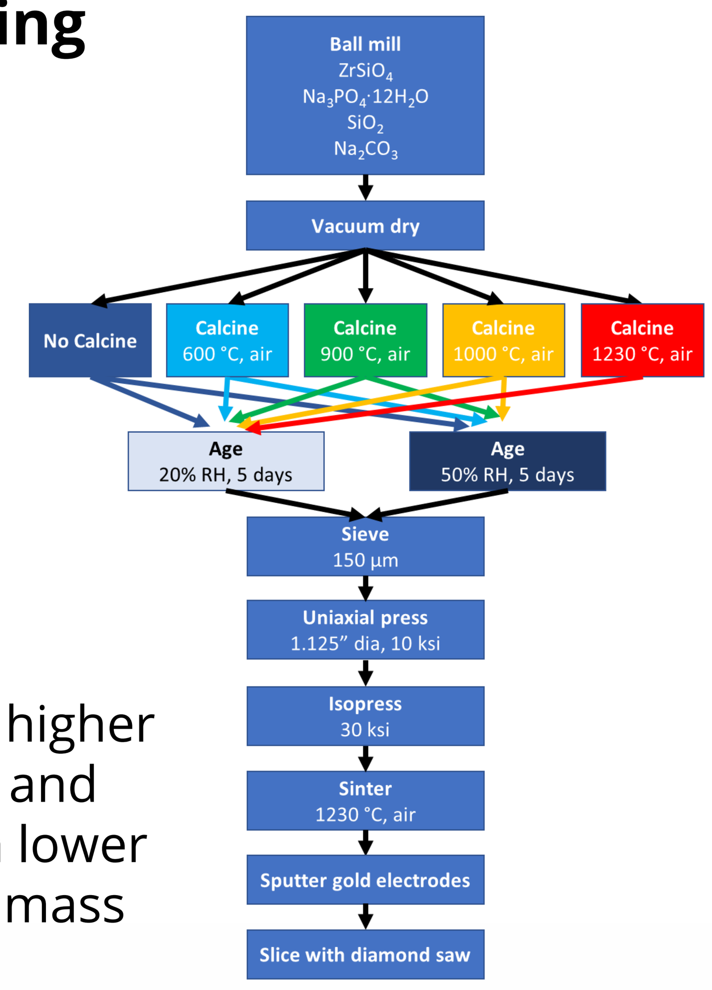


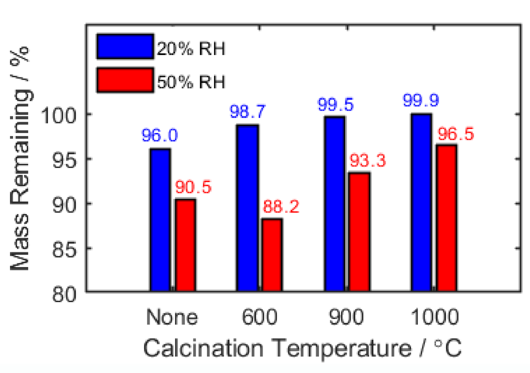
50% RH, No calcine – Disaster!

Varying Calcination Temperature to Eliminate Hygroscopic Reagents Before Sintering

We investigated the effect of two key processing parameters during NaSICON synthesis:

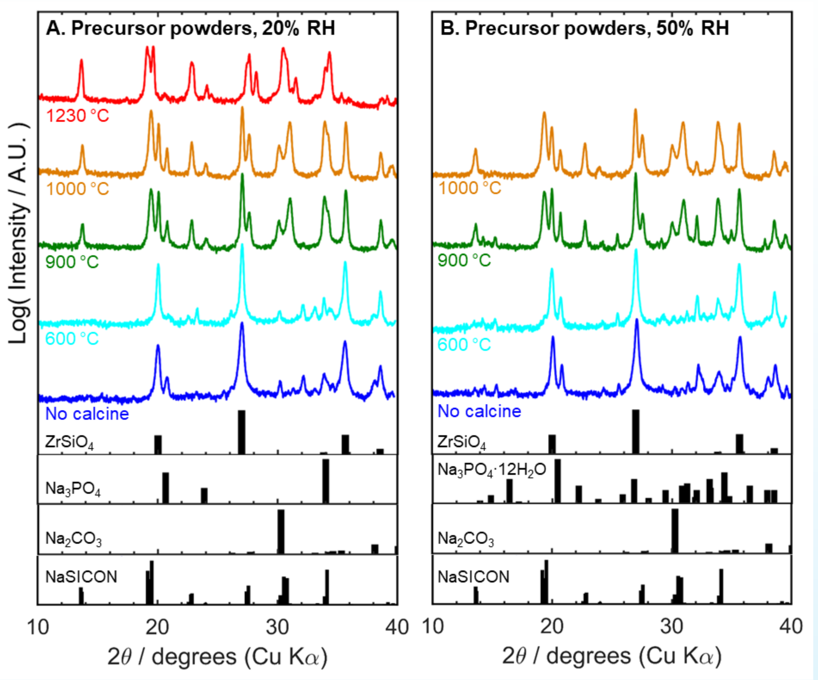
1. Calcination temperature: none, 600, 900, 1000, or 1230 °C
2. Humidity exposure after calcination 20% or 50% RH for 5 days





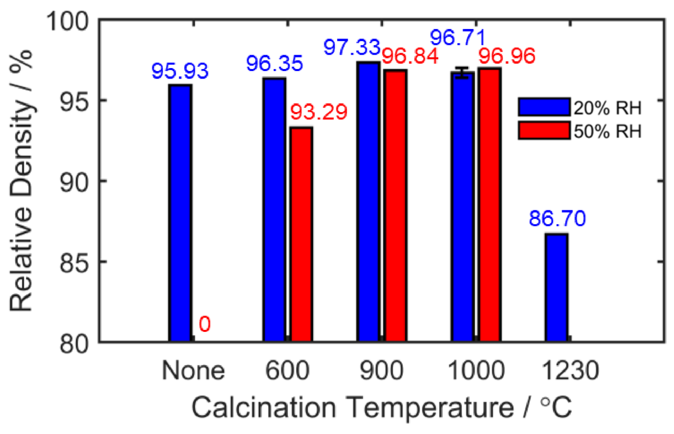
TGA analysis reveals that higher calcination temperatures and lower humidities result in lower water absorption (higher mass remaining).

X-ray diffraction analysis demonstrates that low humidity (20%) or high calcination temperatures (1000, 1230 °C) prevent formation of hydrated phases in precursor powder that are later sintered into NaSICON.



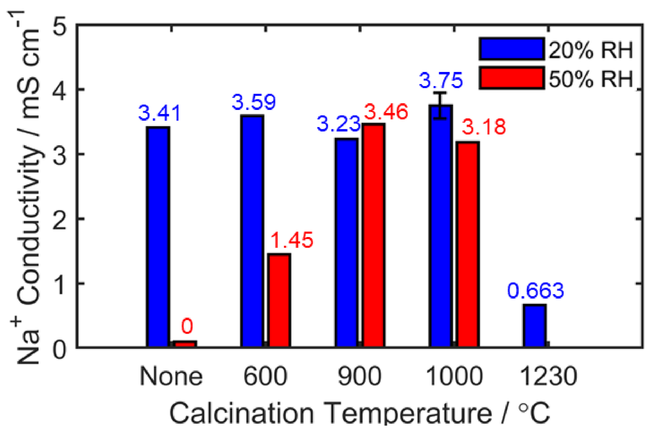
Optimized Calcination Temperature Improves Performance and Processing Resiliency to Humidity

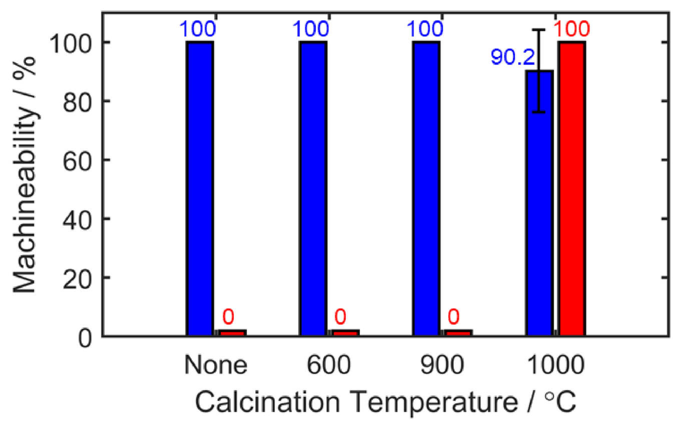
As-synthesized NaSICON was evaluated for 4 key properties:



Relative density was unaffected by precursor humidity exposure when a 900 or 1000 °C calcination was used. 1230 °C calcination produced extensive porosity.

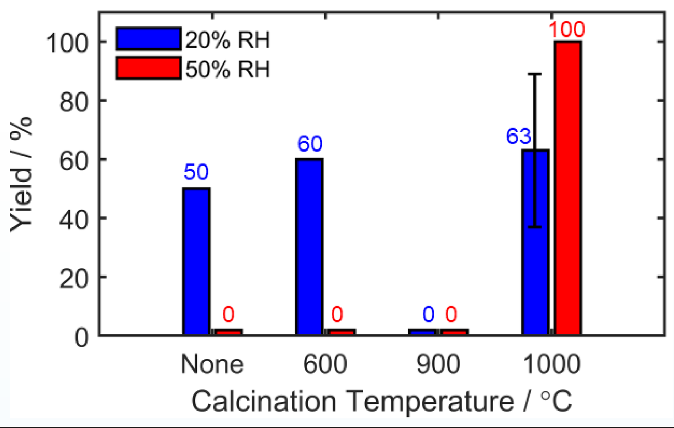
Na^+ conductivity was high when humidity was 20% RH during processing. To increase conductivity at 50% RH, a 900 or 1000 °C calcine must be used.





Machineability (% of full slices produced from NaSICON cylinder) was unaffected by calcination temperature at 20% RH processing, but at 50% RH only 1000 °C calcination produced full (unbroken) slices.

Yield was unacceptable at 50% RH unless a 1000 °C calcine was used. "Yield" represents the % of defect-free slices from a NaSICON cylinder.



Conclusions and Future Directions

- A calcination temperature of 1000 °C increases NaSICON performance and processing resiliency over 20-50% RH by eliminating hygroscopic phases present during sintering.
- When synthesized at moderate humidities (e.g. 50% RH), NaSICON parts exhibit good conductivities and densities, yet cannot be machined into useful shapes.
- Future work will focus on adapting humidity-resistant NaSICON precursor with alternative processes to expand our available NaSICON form factor and scale.

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