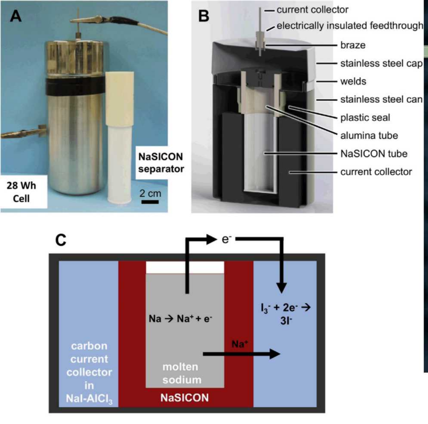

National Laboratories

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Sodium Ion-Conducting Separator Development

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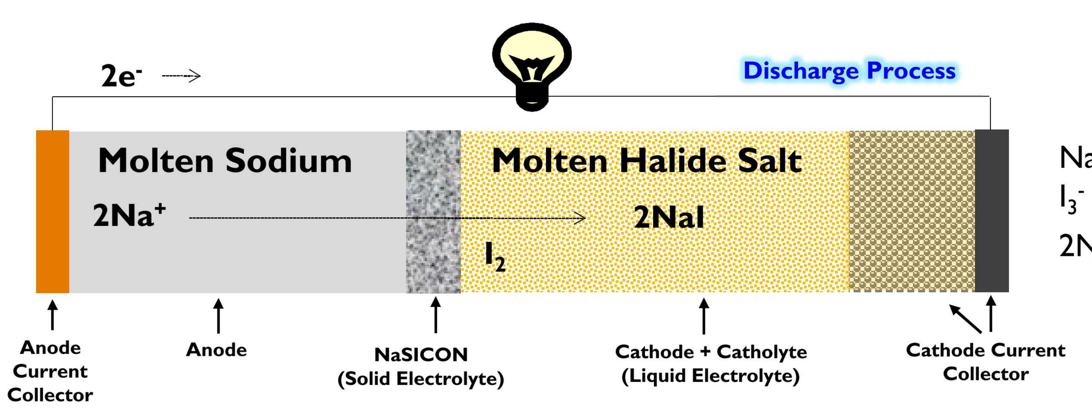
Motivation: We aim to develop safe, low cost, long cycle-life, low temperature (<150°C) grid-scale sodium-based batteries, enabled by zero-crossover solid state separators.

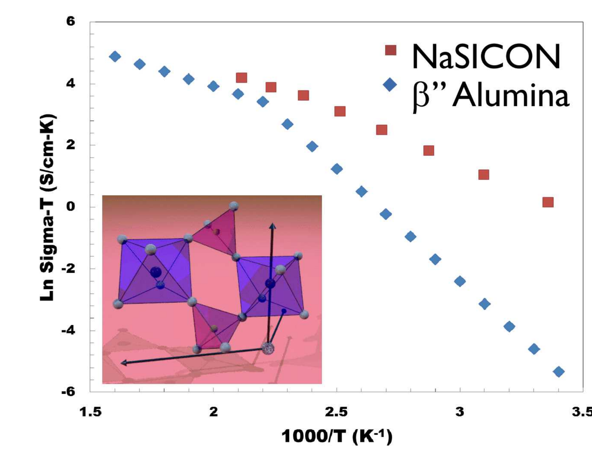


Na → Na^+ E^0 = 0V
I_3^- + 2e⁻ → 3I⁻ E^0 = 3.24
2Na + I_3^- → 2Na^+ + 3I⁻ E^0_{cell} = 3.24V

Key Separator Properties:

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

Based on its high Na-ionic conductivity (>10^{-3} S/cm at 25°C) and established chemical compatibility, NaSICON ceramics ($Na_3Zr_2PSi_2O_{12}$) are good candidates for development.

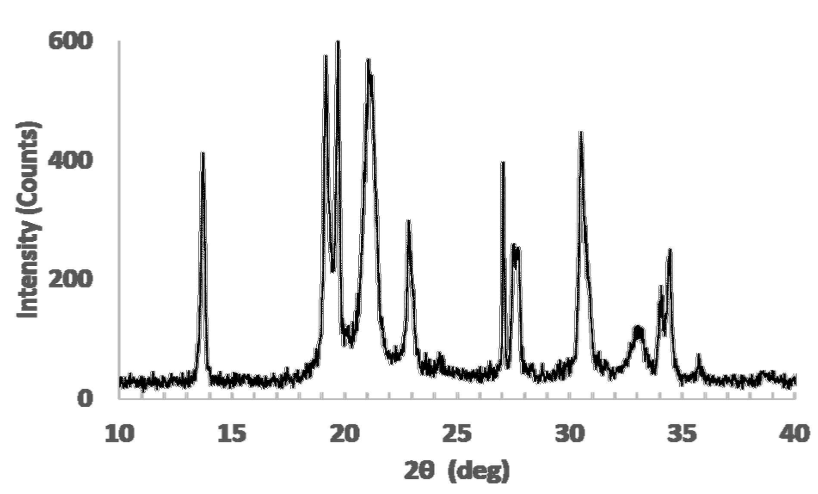


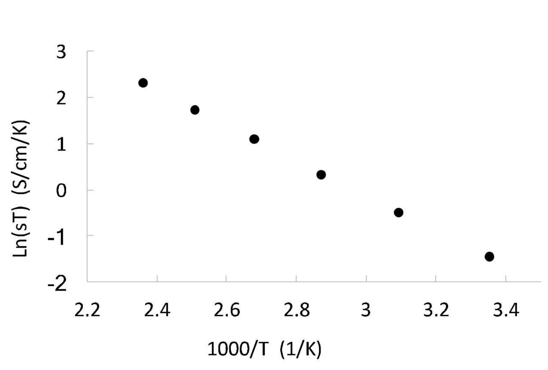
*Additional candidate battery chemistries include Zn-MnO_2 or aqueous Na-ion batteries.

NaSICON Solid State Synthesis

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

1. $ZrSiO_4$ and Na_3PO_4 milled (YSZ), vacuum dried, pressed, and fired at 1200°C for 12 hours.
2. Sintered parts (12-25mm diameter) sliced into discs (~1mm thick) for testing.





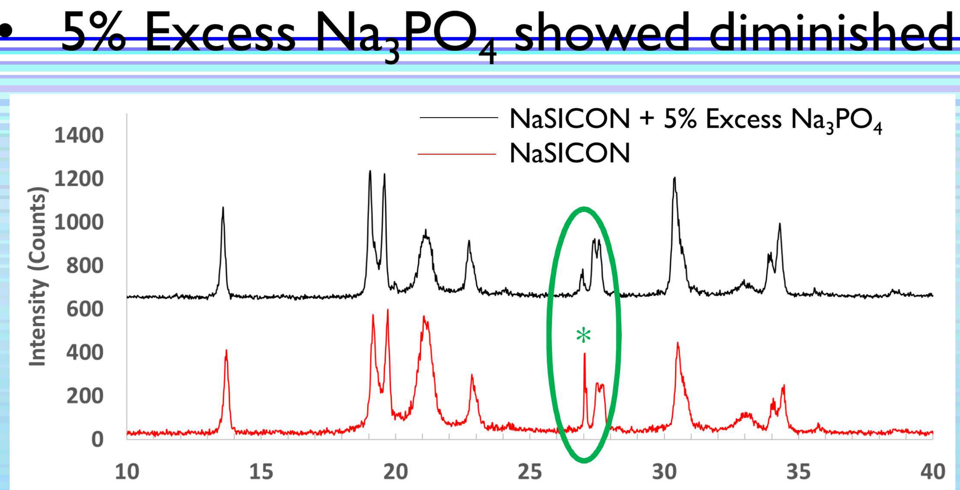
- Pellet densities ~ >95%
- X-ray diffraction confirm NaSICON synthesis
- Conductivities reasonable, but slightly less than commercial NaSICON

Key Processing Variable: Humidity

- Desired >95% theoretical density (3.2 g/cm³)
- 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.

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

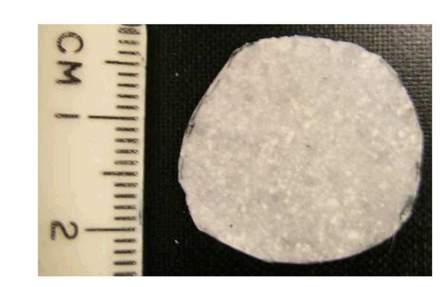


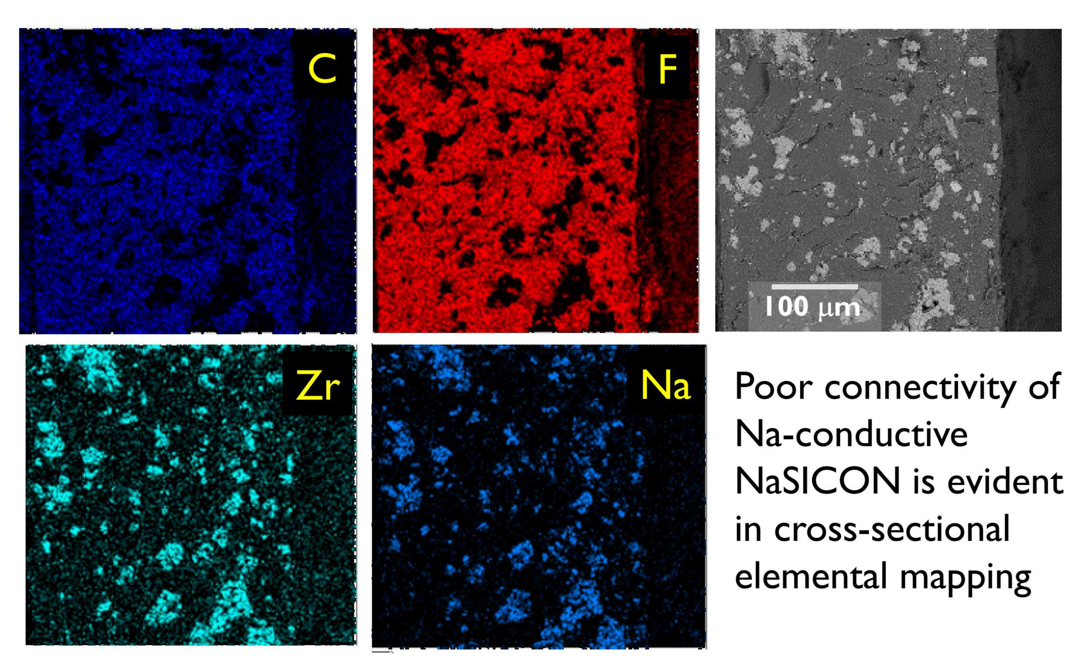
Conductivity increase by ~ 30% with excess Na_3PO_4!

NaSICON Composite Assembly

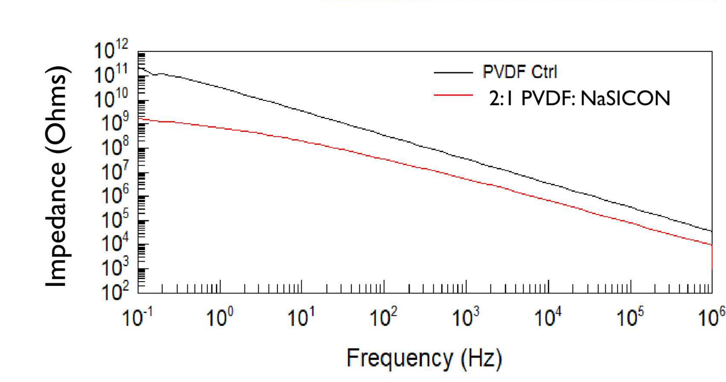
- Decreasing NaSICON thickness would reduce ionic resistance, but thin NaSICON can be mechanically fragile.
- We are working to develop NaSICON-Polymer composites that would provide the low temperature, high conductivity performance of NaSICON in a more mechanically robust structure that may enable thinner, less resistive separators.

- Powdered NaSICON and powdered polymer (polyvinylidene difluoride: PVDF) were combined (2:1PVDF:NaSICON) and pressed at 200°C for one minute to form a tough composite structure.
- Reasonably uniform bulk distribution of NaSICON
- Good interfaces between NaSICON and polymer



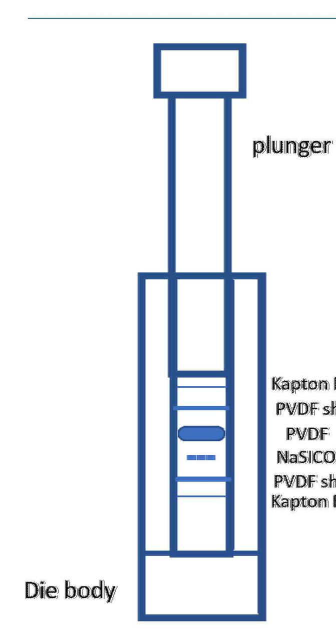


Poor connectivity of Na-conductive NaSICON is evident in cross-sectional elemental mapping

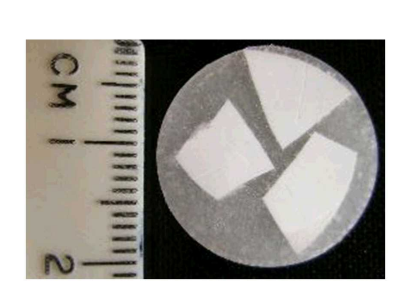


Although mechanically desirable, very high ionic resistance measured in composites makes these composites impractical.

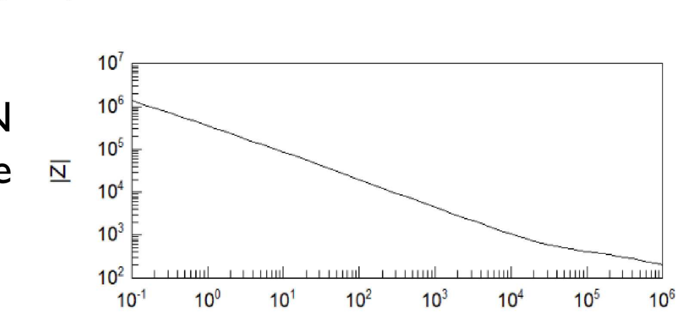
An Alternative Approach



- NaSICON chips (1mm thick) enveloped in PVDF powder and pressed in hot die (200°C)
- Excess polymer polished off, revealing NaSICON surfaces
- NaSICON chips provide continuous conductive path through separator



σ_{RT} ~0.95 mS/cm for NaSICON
σ_{RT} ~0.52 mS/cm for composite



Conclusions and Future Directions

- Solid State NaSICON was 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.
- Work is underway to integrate these ceramics and early composites into battery test structures.
- Though PVDF may work for aqueous applications, it is not chemically compatible with the molten sodium halide chemistries. We are currently using lessons learned with PVDF to explore alternative, chemically compatible polymer choices.
- Future work will focus on improving NaSICON ceramic conductivity and incorporation into composite structures.

Solid state synthesis, combined with composite processing can produce functional, mechanically robust sodium-ion conducting separators.

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