Solid State Separator Development for Sodium-Based Batteries

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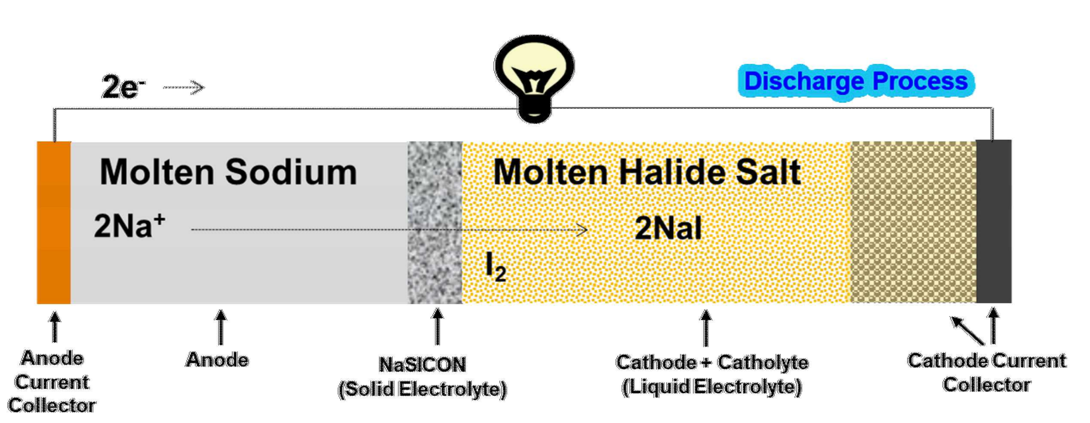
Objective: We aim to create zero-crossover solid state separators for safe, low cost, long cycle-life, low temperature (<150°C) grid-scale sodium-based batteries.

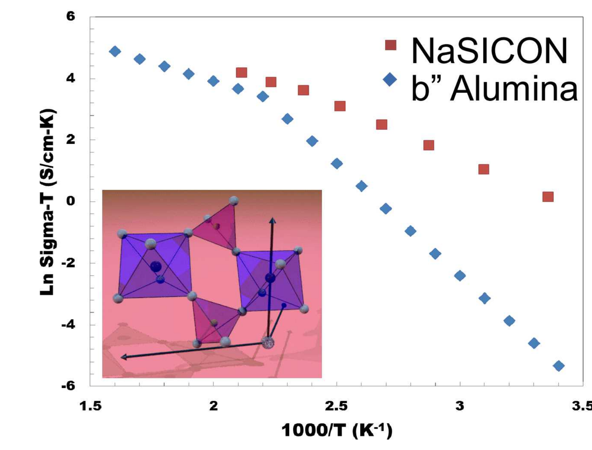


→ Na^+ E^0 = 0V
$2e^-$ → $3I^-$ E^0 = 3.24
+ I_3^- → $2Na^+ + 3I^-$ E^0_{cell} = 3.24V

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.

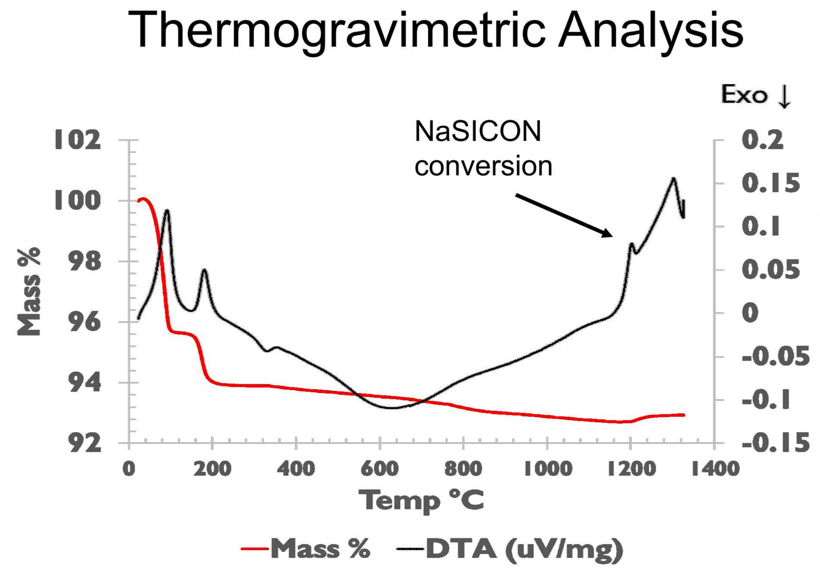


Thermal Analyses of Solid State Reaction

Goal: Inform low cost synthesis of high density, highly conductive NaSICON separators

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

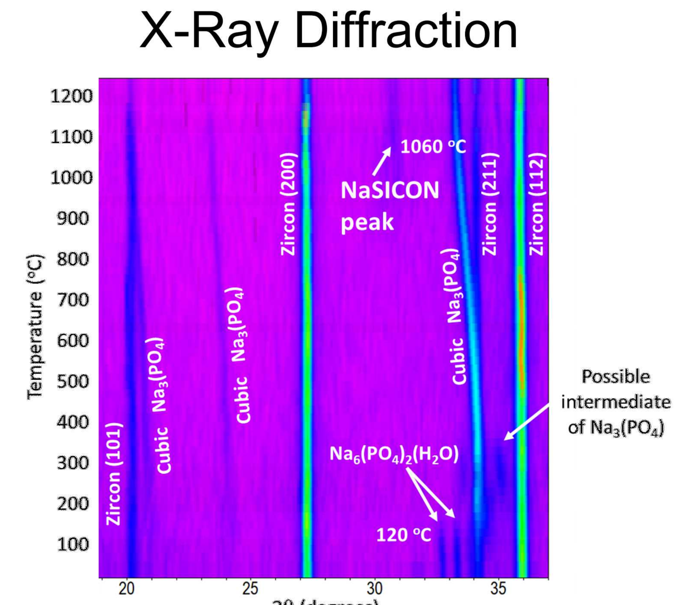
Differential Thermal Analysis and Thermogravimetric Analysis



- DTA/TGA show water removed from precursor powder by ~250°C.
- NaSICON conversion reaction evident between 1150-1230 °C.
- Sintering above 1230°C → poor ceramic integrity (melting?)

NaSICON Sintered at 1250°C

Variable Temperature X-Ray Diffraction

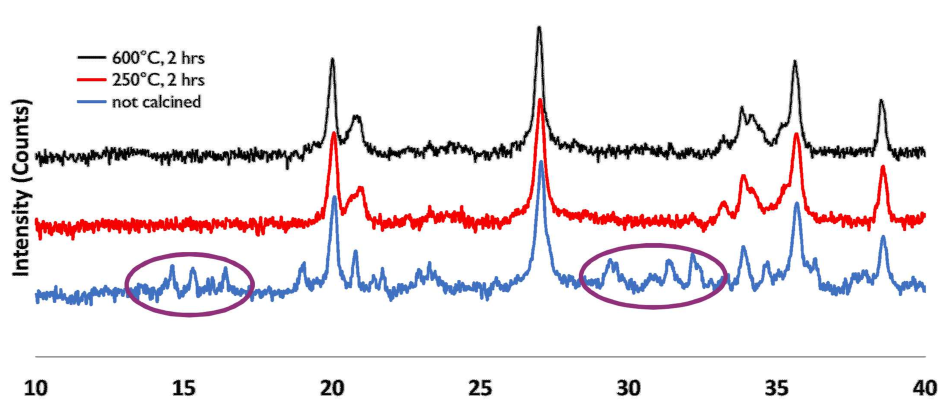


- VTXRD shows conversion of Zircon and cubic $Na_3(PO_4)$ to NaSICON starting near 1100°C
- Hydrate form of $Na_3(PO_4)$ up to 120°C, converts to cubic $Na_3(PO_4)$ at ~300°C.

Why is this important?

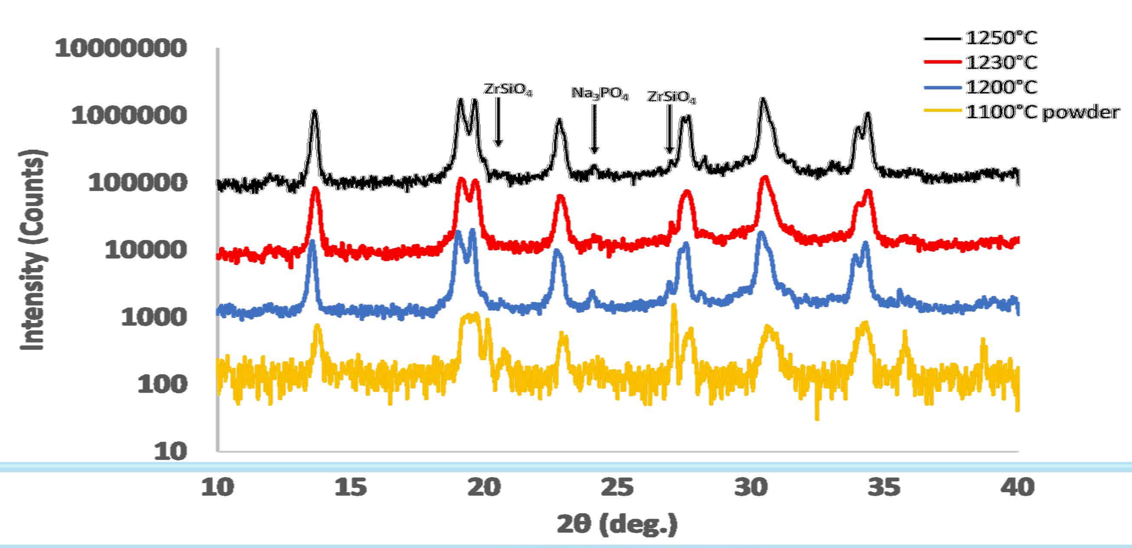
Effective NaSICON Conversion/Densification

- 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 better sintered ceramic density.



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

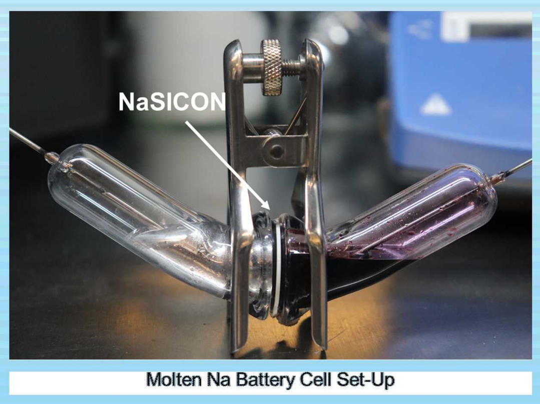
*Sintered at 1200°C	σ (mS/cm) at 25°C
Calcine at 600°C	0.2
No Calcine	0.03



- Sintering to at least 1230°C leads to more complete NaSICON conversion and suitable densities.
- Phase purity and density improve critical mechanical strength and ionic conductivity.

NaSICON calcined at 600°C, sintered at 1230°C yields >94% density and > 0.4 mS/cm at 25°C.

These ceramics are suitable for lab-scale testing of molten sodium batteries.

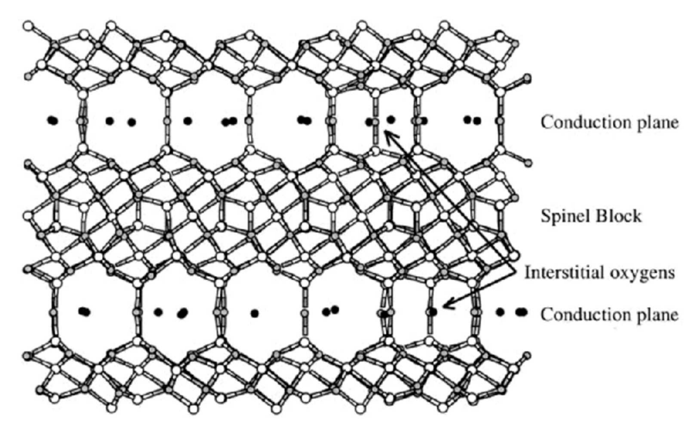


Molten Na Battery Cell Set-Up

Alternative Separator Materials

Goal: Identify new, highly conductive, low cost sodium ion conductors.

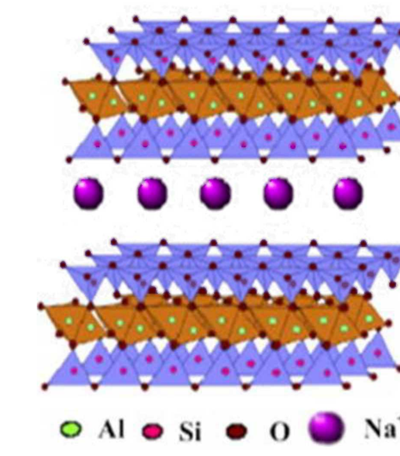
In the Na-ion conductor β"-Al_2O_3, Na^+ conduction follows ordered conduction planes.



Beckers, van der Bent, and Leeuw. *Solid State Ionics* **133**(3-4)(2000), p217-231.

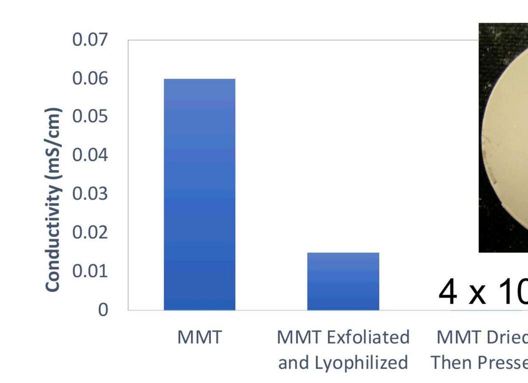
The ordered layers in low cost montmorillonite (MMT)clay create similar sodium-rich conduction planes.

Challenge: Can we utilize MMT to create a low cost sodium ion conductor?



Motawie, *et al. Egypt. J. Petroleum* **23** (3)(2014), p331-338.

- MMT can be pressed into pellets with excellent ionic conductivity!
- The layered structure of the clays plays a key role Na^+ mobility through the separator..
- H_2O content increases conductivity of composite.
- Clay pellets can be fragile, though!



MMT Pellet

Broken MMT Pellet

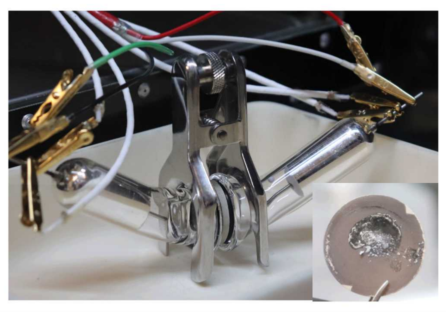
Can we integrate MMT into a composite with high conductivity and improved mechanical integrity?

Initial Composite Assessment

	σ (S/cm)	Qualitative Mechanical Properties
MMT	1 x 10^{-4}	Brittle, breaks with little effort
MMT: PE-block-PEG (1:1)	9 x 10^{-11}	Soft, crumbly
MMT:PEG (1:1)	5 x 10^{-8}	Pliable, but crumbly
MMT: PEG:NaTFSI (1:1:0.05)	4 x 10^{-6}	Pliable, but crumbly
MMT pressed at 150°C	5 x 10^{-5}	Very fragile
MMT: HDPE (3% HDPE, 150°C)	6 x 10^{-5}	Rigid and stronger

- Doping with sodium trifluoromethanesulfonimide (NaTFSI) can recover some of the conductivity lost through addition of insulating polymer matrix.
- Low temperature, functional polymers (e.g., PEG), do not significantly improve pellet integrity and are not suitable for molten Na-batteries, but inform composite design.
- Heating MMT decreases conductivity (likely through water loss).
- Adding a small amount of HDPE significantly improves pellet integrity, without significant impact to conductivity, beyond thermal treatment.

- Alternatively, increasing pellet thickness and application of sputtered metallic surface coatings stabilize MMT pellets for battery testing.
- Initial tests show promise, but reveal high impedance across separator interfaces with Na.



Symmetric molten Na cell with MMT separator (w/ Sn-based coating). Inset: separator after test.

Conclusions and Future Directions

- Thermal analyses informed key thermal processing that enabled dense, functionally conductive NaSICON separators for lab-scale testing.
- Ionic conductivity in novel MMT separators is depends on H_2O content and retention of layered clay structure.
- MMT composites show promise toward reducing pellet brittleness, but insulating polymer content or processing treatment (e.g., heating) can degrade performance.
- Initial tests indicate that MMT could prove useful as a novel ion conductor for Na-based batteries.
- Future work will expand these results toward improving NaSICON ceramic conductivity through ionic doping and synthesis of clay-based or NaSICON-based composites with high conductivity and robust mechanical properties.

Enhanced understanding of materials/properties relationships inform improved separator development!

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