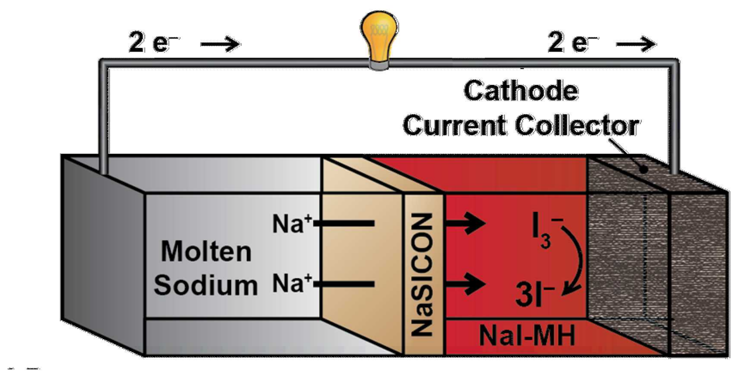
SAND2020-9881C

Solid State Separator Development for Sodium Batteries

Erik D. Spoerke,[1] Amanda Peretti,[1] Martha M. Gross,[1] Stephen J. Percival,[1] Ryan Hill,[2] Yang-Tse Cheng,[2] and Leo J. Small[1] (PI)
1. Sandia National Laboratories, Albuquerque, NM, USA; 2. University of Kentucky, Lexington, KY, USA
edspoer@sandia.gov and ljsmall@sandia.gov

Motivation: Sodium batteries hold significant potential as safe, low-cost, long cycle-life batteries. They are among of the DOE Office of Electricity's (OE) battery research priorities, part of the OE mission to ensure a resilient, reliable electrical grid. Effective zero-crossover solid state separators remain a critical part of sodium battery performance and represent a potential point of failure in these batteries

Objective: We aim to create zero-crossover solid state separators that enable low temperature (<150^{o}C) grid-scale sodium-based batteries.



Our molten Na battery chemistry:

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

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

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

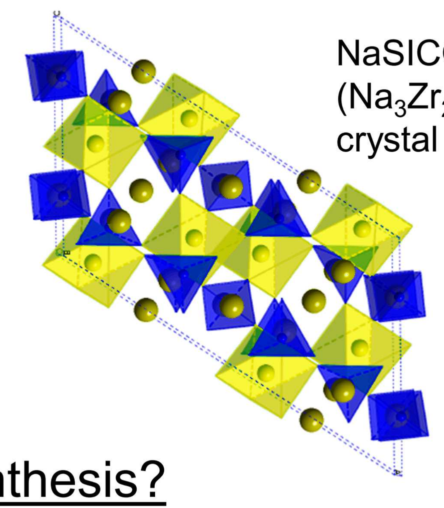
Key Separator Properties:

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

NaSICON Synthesis

Goal: Produce high density, highly conductive NaSICON separators

Based on high feasible Na-ionic conductivity (>10^{-3} S/cm at 25^{o}C, Ceramatec, Inc.) and established chemical compatibility, NaSICON ceramics remain attractive separators for Na-batteries.



NaSICON ($Na_3Zr_2PSi_2O_{12}$) crystal structure

Why we are working on NaSICON synthesis?

- Cost-effective, large scale manufacturing is still needed.
- Improved conductance is important for low temperature (~100^{o}C) operation.
- More robust mechanical properties are desired for long-term durability.
- NaSICON is *needed* for our low temperature sodium battery studies!

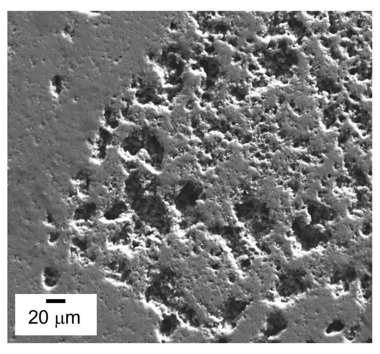
In our approach, we employ a solid state synthesis using low cost materials:

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

Toward Improved NaSICON Production

- In FY19, critical thermal processing conditions were identified to yield functional NaSICON with >94% density and >0.4 mS/cm at 25^{o}C using low cost materials.

- Unexpected pitting, cracking and void formation in the ceramics, however, periodically led to battery failures!



Pitting in the surface of a sintered, sectioned NaSICON pellet.

- **In FY20** we hypothesized these defects were related to poor compaction on pressing the green (unfired) ceramics.
- We systematically identified that 1) introducing 2% PVB binder, 2) controlling moisture content during processing, and 3) increasing pressing force helped *resolve this issue*.

Ceramic density increased to >96% density, and conductivity increased to 0.55 mS/cm.

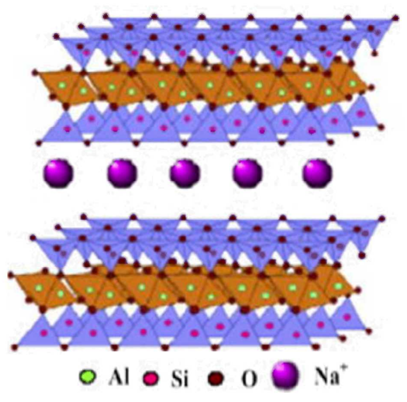
Key Result: High quality pellet yield was increased, producing a critical supply of NaSICON needed to sustain progress in the Na-battery program.

Future work will pursue 1) refinement of powder particle size distributions and 2) NaSICON integration in composites for thin, mechanically robust, high conductance separator performance.

Clay-Based Separator Development

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

In FY19, we recognized that sodium-based clays (e.g., montmorillonite) showed promising ionic conductivity.



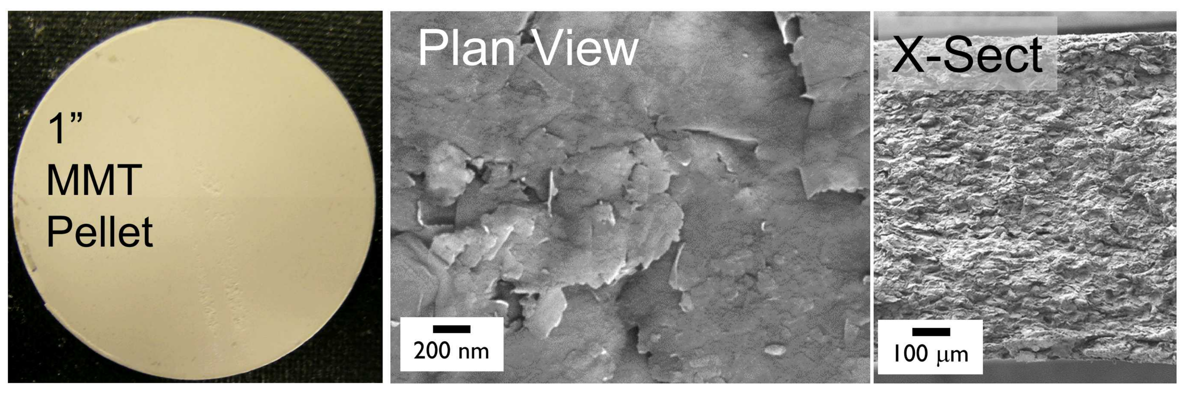
Motawie, *et al. Egypt. J. Petroleum* **23**(3) (2014), p331-338.

- The ordered layers in low-cost montmorillonite (MMT) clay create similar sodium-rich conduction planes.
- MMT can be pressed into pellets with
- promising ionic conductivity! (~ 0.1 mS/cm).
- The layered structure of the clays plays a key role Na$^+$ mobility through the separator.
- H_2O content is key to conductivity of the clay.

FY20 Objectives: 1) characterize pellet structure and mechanical properties* and 2) and explore clay use as electrochemical separators.

*Please see poster by Ryan Hill, "Mechanical and Microstructural characterization of Montmorillonite (MMT) Sodium Ion Conductors" for mechanical assessment of clays and clay-based composites.

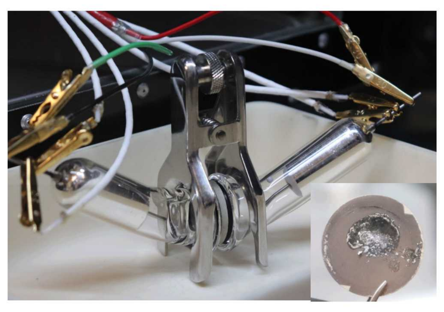
Microstructure Analysis:



Scanning electron micrographs clearly showed clay platelet on pellet surface and a dense, clay-packed cross-section needed for conductivity.

SEM image credit: Sara Dickens (SNL)

Separator Evaluation: Can the low temperature conductivity of the clay make it a useful electrochemical separator?



Symmetric molten Na cell with MMT separator (Inset: separator after test.

✕ The water content in clay, key to its conductivity, proved too reactive in molten sodium batteries.

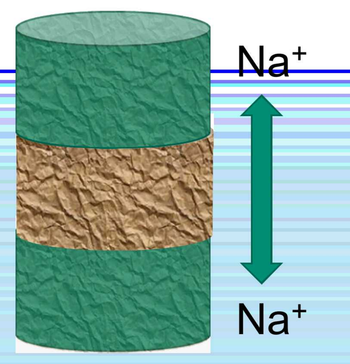
✕ The relative solubility of clay against common aqueous and polar non-aqueous solvents made it impractical to use in traditional sodium-ion systems.

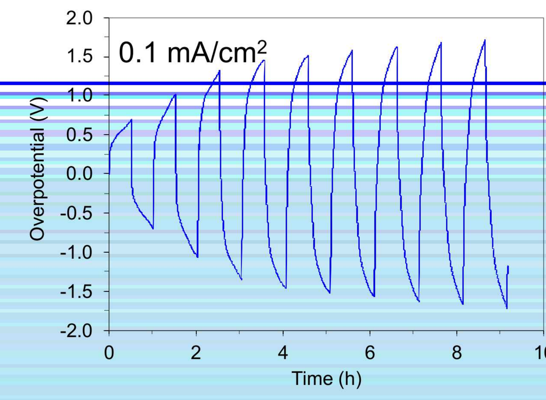
What about a solid state system?

"Anode":
Na_xMnO_2 + Hard Carbon

Solid State Electrolyte:
Na-MMT

"Cathode":
Na_xMnO_2 + Hard Carbon





Low current galvanostatic cycling in a symmetric pseudocapacitor shows MMT separator will facilitate reversible charge transport between the two symmetric MnO_2-based electrodes!

Improved electrode composition and interfaces are needed to reduce high overpotentials, though.

Programmatic Accomplishment: Spoerke, *et al.* "Clay based ion conductors: A dirt cheap separator?" In preparation for submission to *J. Mater. Chem. A.* (2020).

Conclusions and Outlook

- Continued refinement of NaSICON synthesis yielded material for a reliable source of lab-scale separators needed for Na-battery testing.
- Undesirable reactivity and solubility undermined the potential of low cost, high conductivity clay separators in molten sodium and solvent-based sodium ion batteries.
- Low current density cycling in a solid state symmetric pseudocapacitor shows a potential pathway toward utilizing clays as a low-cost next generation separator.

Future materials innovations built on these results promise new, low-cost, high conductance solid state separators!

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.:

This work was supported through the Energy Storage Program, managed by Dr. Imre Gyuk, within the U.S. Department of Energy's Office of Electricity.