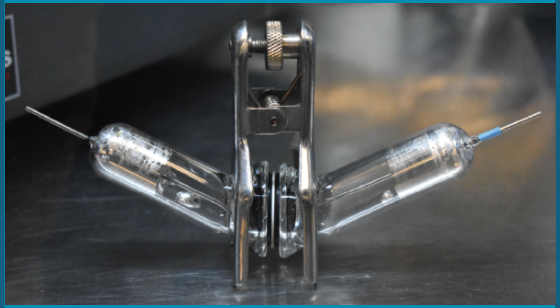
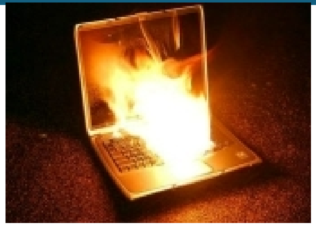
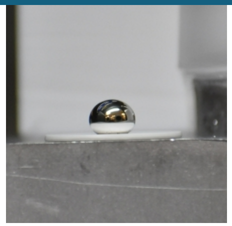
SAND2022-7866C

Sandia National Laboratories

"Dirt Cheap" Energy Storage: Clay-Based Separators for Solid State Storage







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U.S. DEPARTMENT OF ENERGY   NNSA National Nuclear Security Administration

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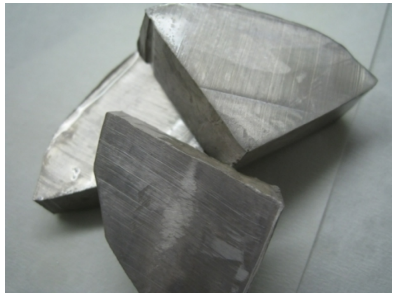
Sodium Batteries: Diverse Technologies

Sodium batteries…

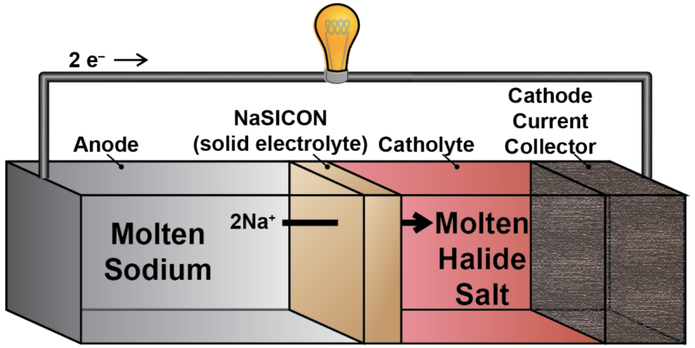
- Take advantage of globally abundant sodium…
  - 6th most abundant element in Earth's crust and 4th most abundant in the oceans.
  - 5X the annual production of aluminum
- Offer potential for safe, versatile, cost-effective energy storage
  - Grid-scale and backup power
  - Portable or vehicle storage

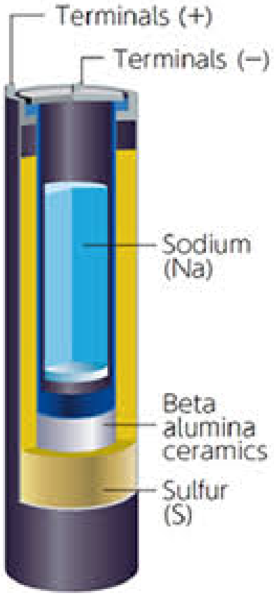


Sodium Metal

There are a number of sodium battery technologies in development or production:

1. Molten sodium (Na) batteries
   A. Sodium Sulfur (NaS)
   B. Sodium Metal Halide (Traditional ZEBRA Batteries)
2. Sodium Ion Batteries (NaIBs) – *PNNL, ORNL*
   A. "Li-Ion Analogs"
   B. Prussian Blue Analogs
   C. Salt-Water Batteries
3. Solid State Sodium Batteries (SSSBs)
4. Sodium Air Batteries ($Na\text{-}O_2$)





- Sodium Image from Dnn87 at English Wikipedia. - Transferred from en.wikipedia to Commons., CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=3831512
- NaS battery schematic from NGK Insulators.

Low Temperature Molten Sodium (Na-NaI) Batteries: Not Your Grandfather's Sodium Battery!

Realizing a new, low temperature molten Na battery requires new battery materials and chemistries.

Key Battery Attributes

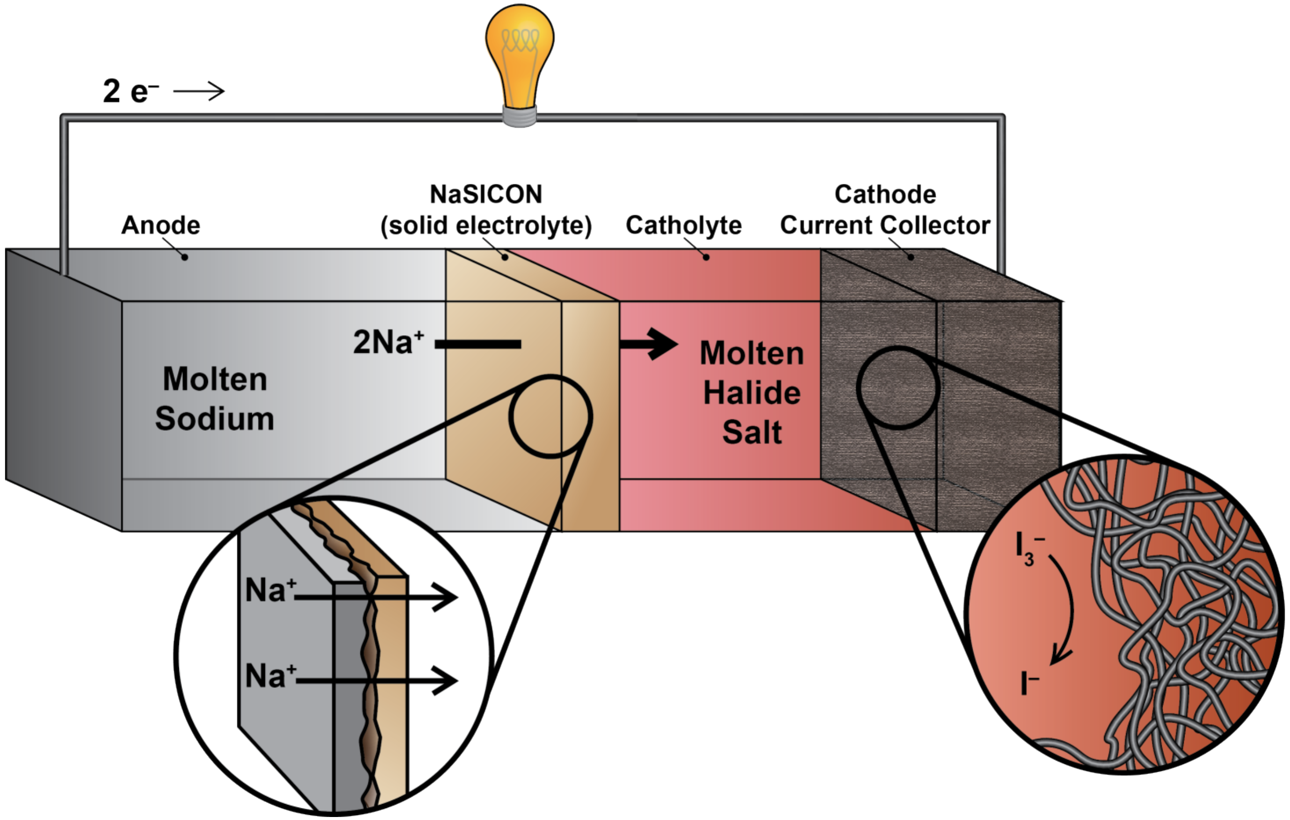
- Molten Na anode (minimize dendrites!)
- Highly Na^+-conductive, zero-crossover separator (e.g., NaSICON)
- 25 mol% NaI in MX_3 catholyte – no organic electrolytes
- No complications from solid state electrodes!

Na-NaI battery:

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

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

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



Martha Gross

Small and Spoerke, *et al*. "Next Generation Molten NaI Batteries for Grid Scale Energy Storage." (2017) *J. Power Sources*. **360.** 569-574.

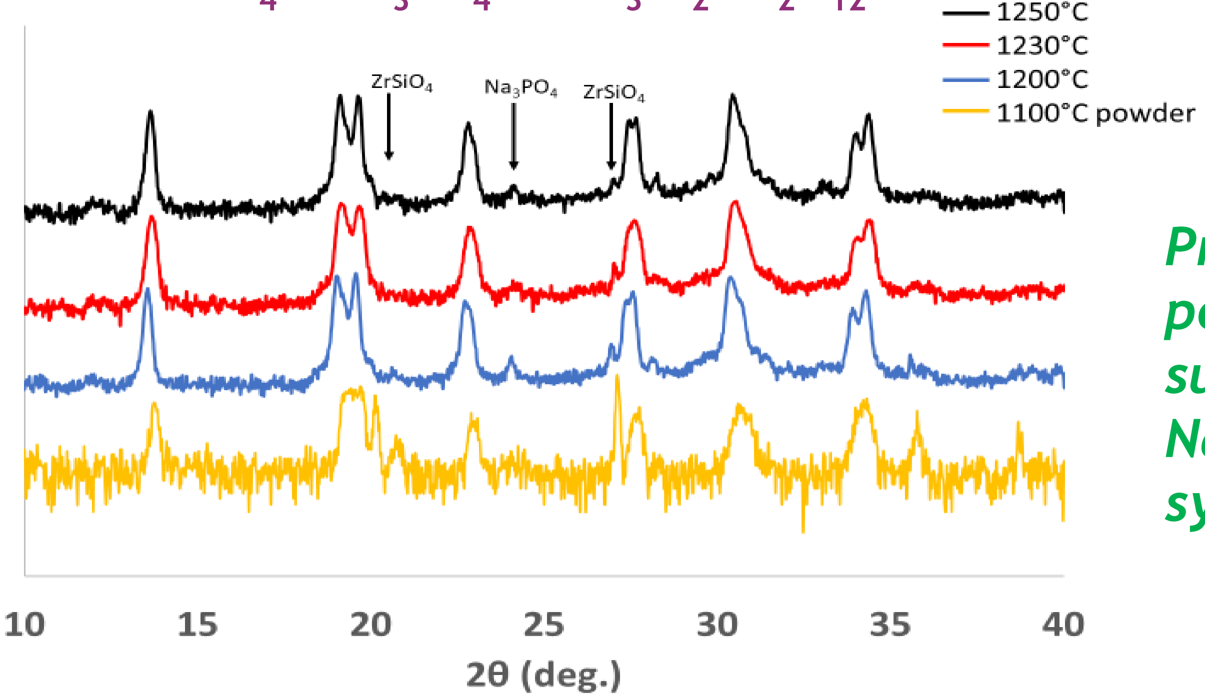
NaSICON - A Low-Temperature Solid-State Ion Conductor

NaSICON ($Na_3Zr_2PSi_2O_{12}$)

- High Na^+ conductivity at low temperatures
- "Compatible" with molten Na and molten salts

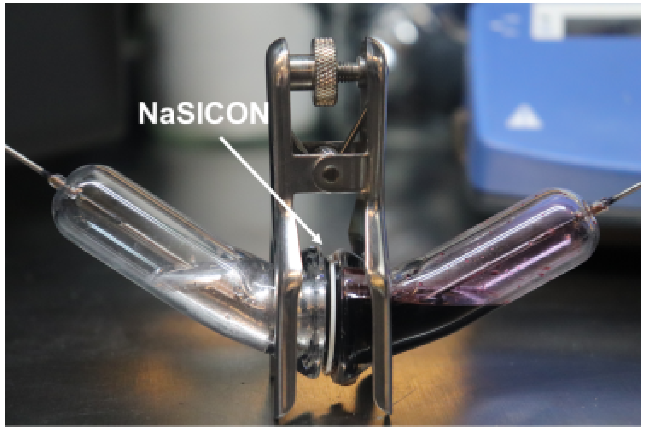
Solid state ceramic synthesis:

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



Primary XRD peaks reveal successful NaSICON synthesis.

NaSICON cylinder and sectioned pellets.



Molten Na Battery Cell Set-Up

NaSICON sintered at 1230°C yields >96% bulk density, acceptable phase purity, and ~10^{-3} S/cm at 25°C.

NaSICON may not be "Good Enough"

<u>Challenge</u>: *Can we find something less expensive and easier to produce than NaSICON?*

We must retain:

- *High ionic conductivity*
- *Good mechanical integrity*
- *Chemical Compatibility*

A Skier's Perspective on Ion Transport Materials Design

✓ Rapid transport on well-defined paths (conductive)

SFChronicle.com

A Skier's Perspective on Ion Transport Materials Design

❌ Impeded transport (resistive)

✓ Rapid transport on well-defined paths (conductive)

A Skier's Perspective on Ion Transport Materials Design

✗ Impeded transport (resistive)

✓ Rapid transport on well-defined paths (conductive)

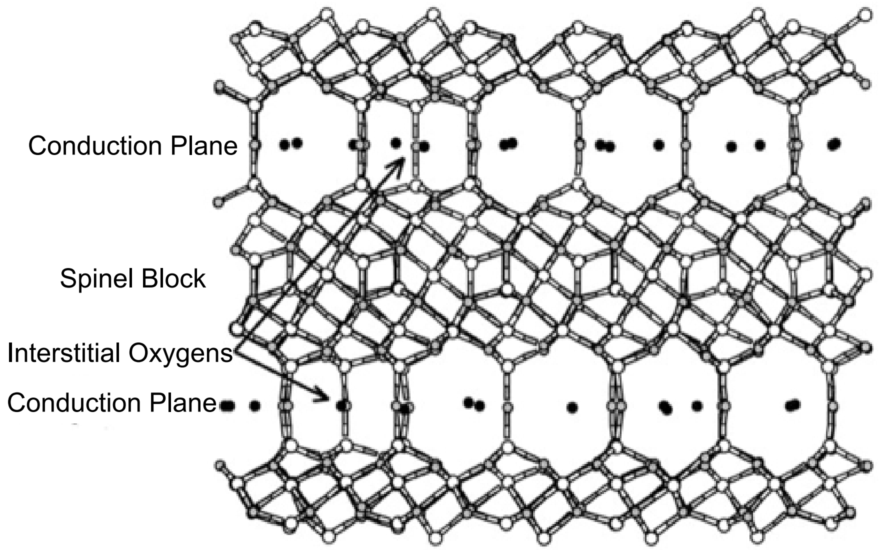
✓ Selective transport

Dirt: An Alternative Solid State Separator?

Goal: Identify new, highly conductive, low cost sodium ion conductors for energy storage applications.

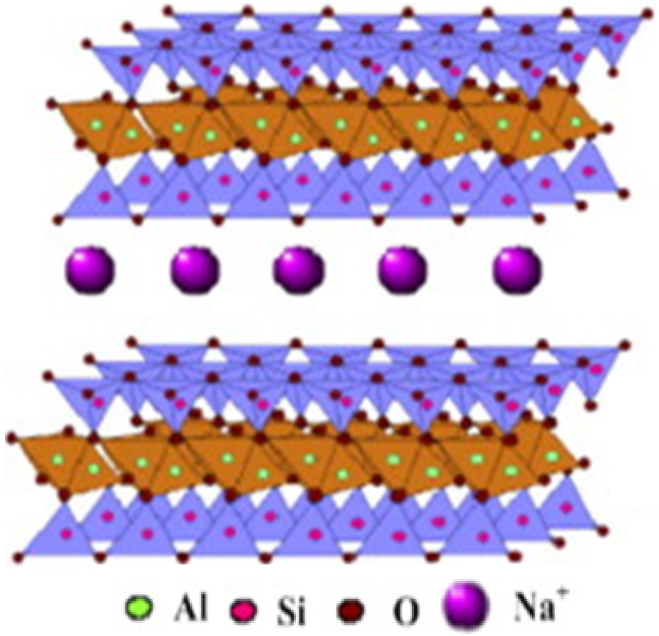
In the known Na-ion conductor β"-Al_2O_3, Na^+ conduction follows ordered conduction planes.

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



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

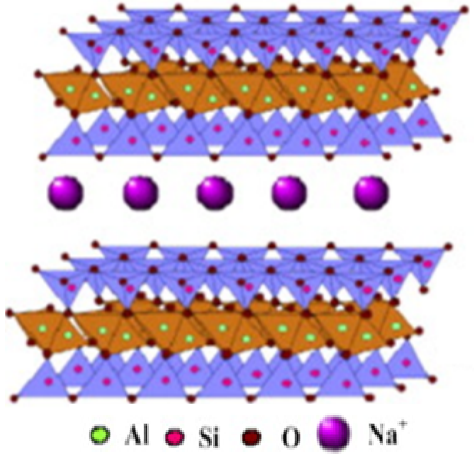
Challenge: Can we utilize MMT to create a low cost Na^+ ion conductor?



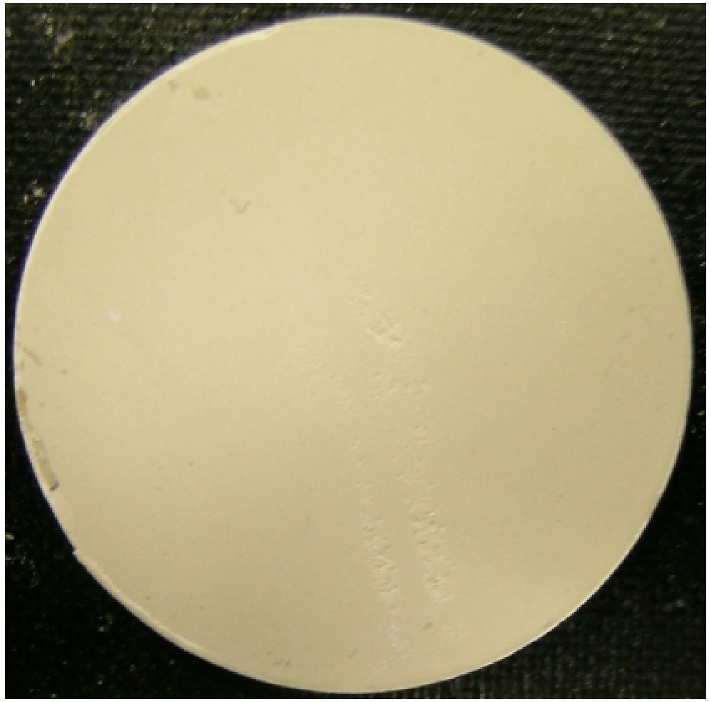
Motawie, *et al. Egypt. J. Petroleum* **23**(3)(2014), p331-338.

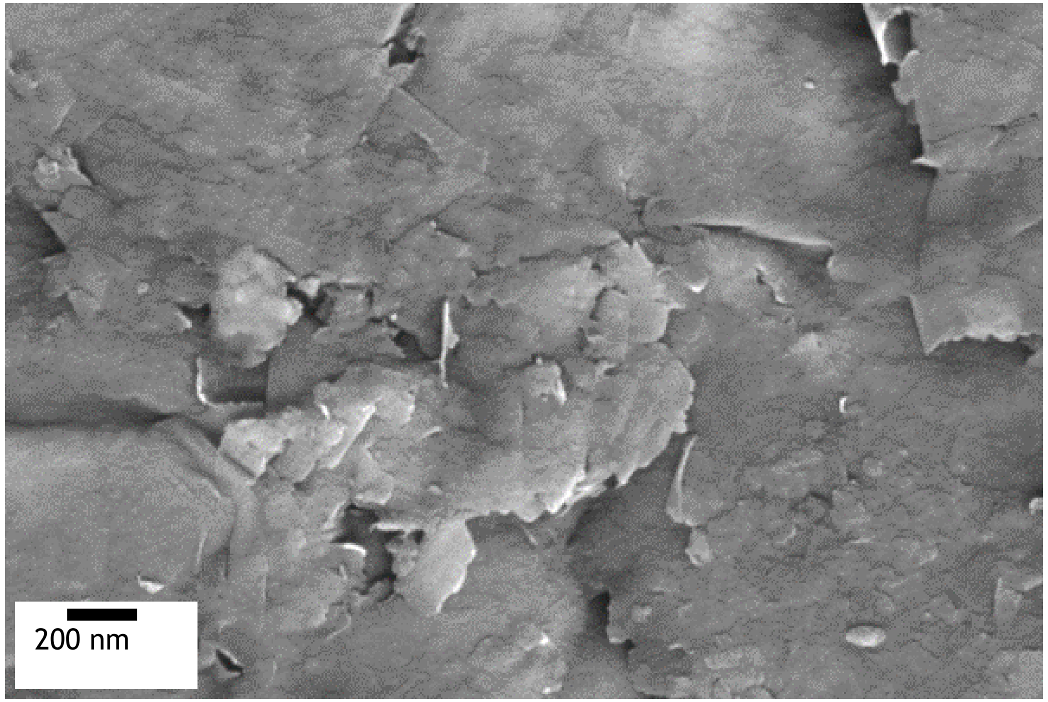
"Kitty Litter Konductors"

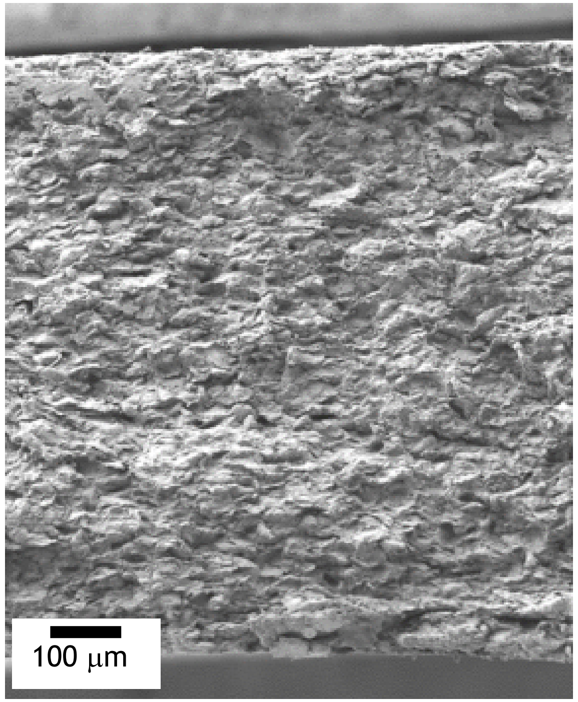
- MMT can be pressed into pellets suitable for assessment of ionic conductivity.
- Clay structure clearly evident in bulk pellet.



MMT Pellet (1")

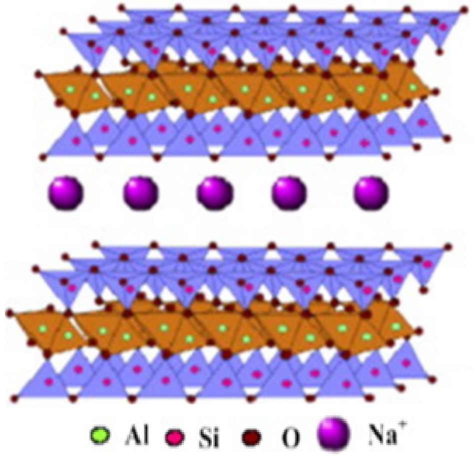






Multilayered Structure and Composition Matter!

- MMT pellets exhibit excellent ionic conductivity! (~ 0.1 mS/cm)
- The layered structure of the clays plays a key role Na^+ mobility through the separator.
- H_2O content increases conductivity of composite.



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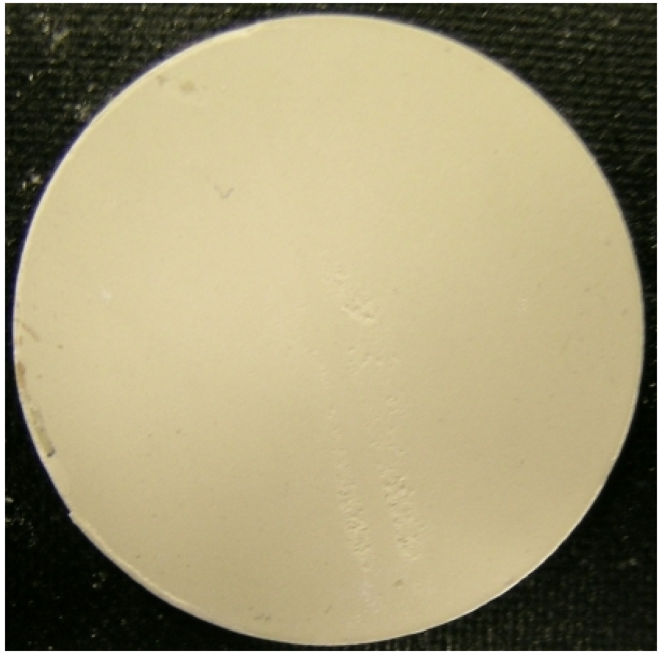

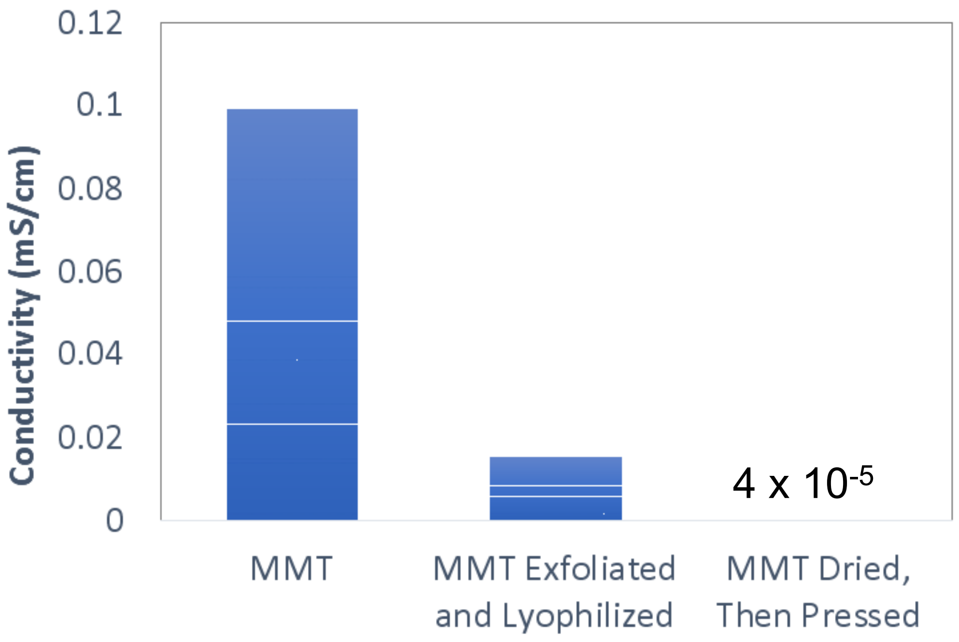

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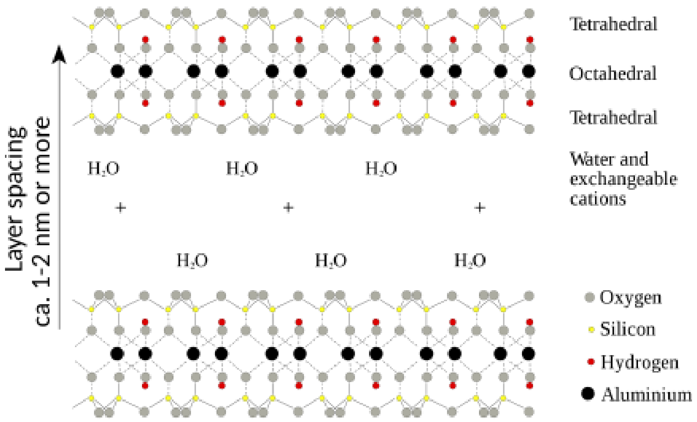

Image by Andreas Trepte, Wikipedia Commons

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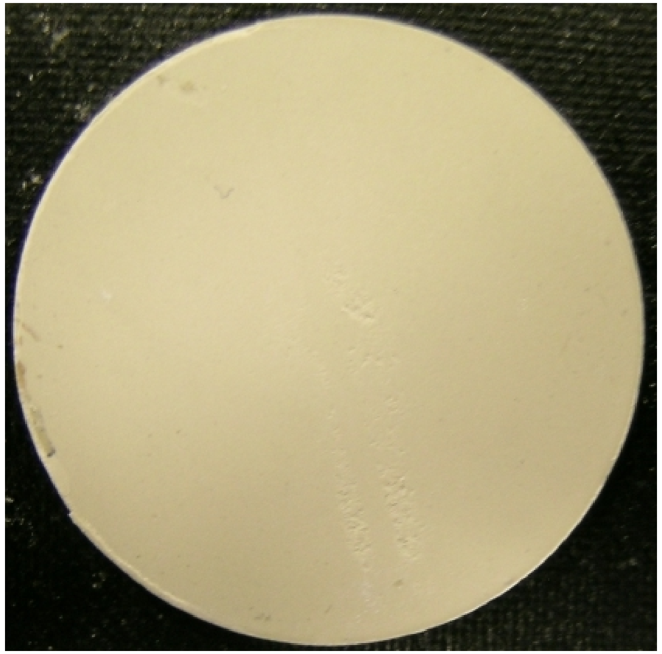
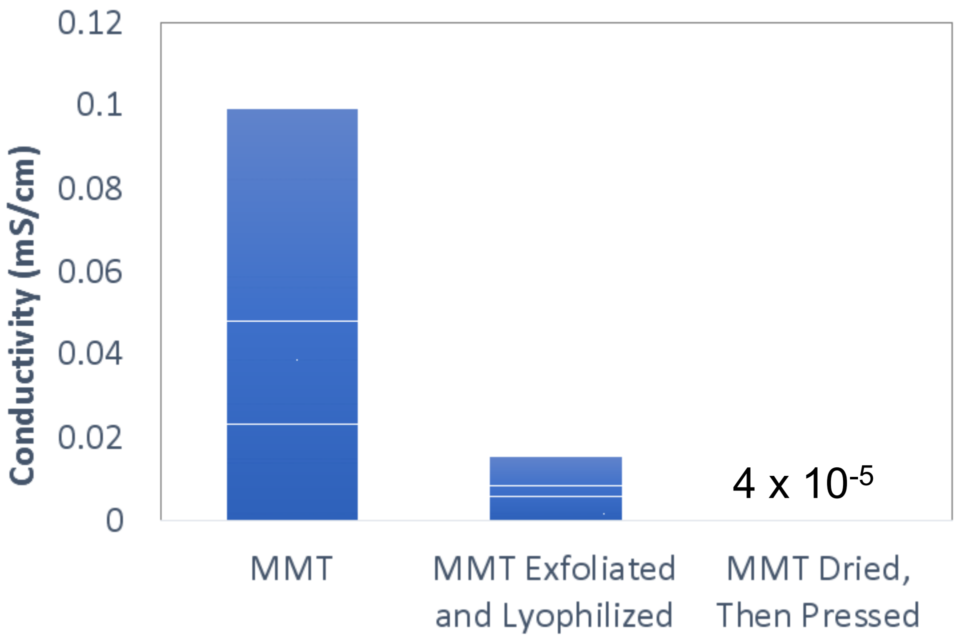




Confirming Na Conductivity

- Na-MMT pellets exhibit excellent ionic conductivity!
  (0.3 - 1 x 10^{-4} S/cm)
- Al-MMT: 8 x 10^{-11} S/cm
- K10-MMT (Acid-substituted): 7 x 10^{-9} S/cm
- Water content in each clay at least as high as in Na-MMT

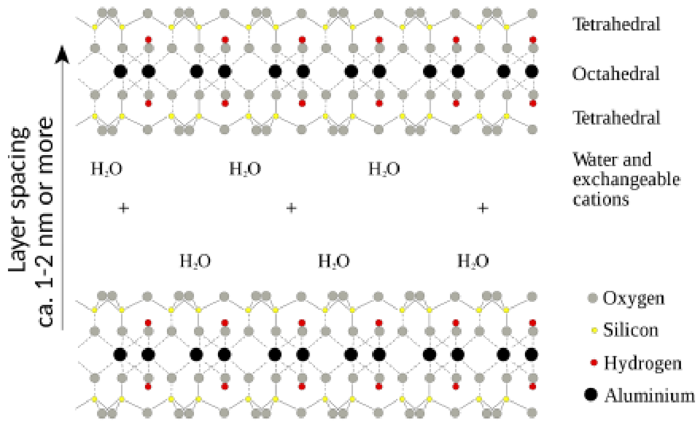
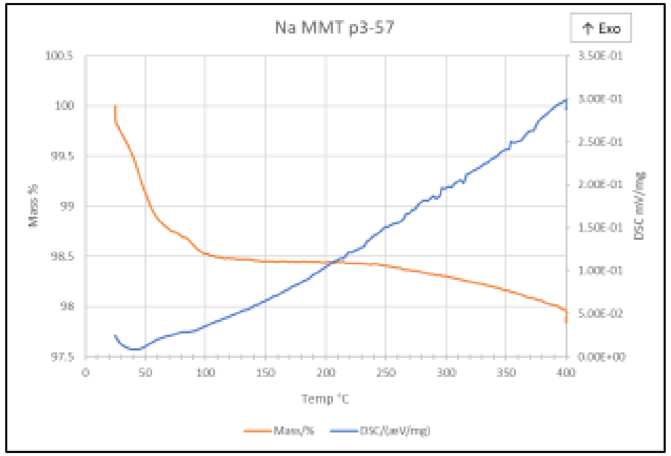
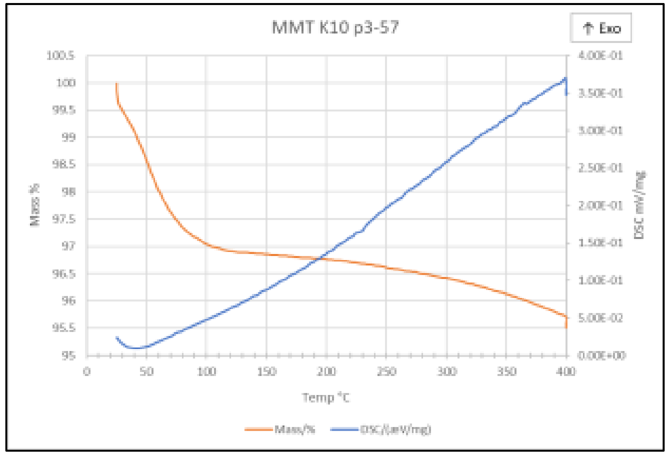


Image by Andreas Trepte, Wikipedia Commons

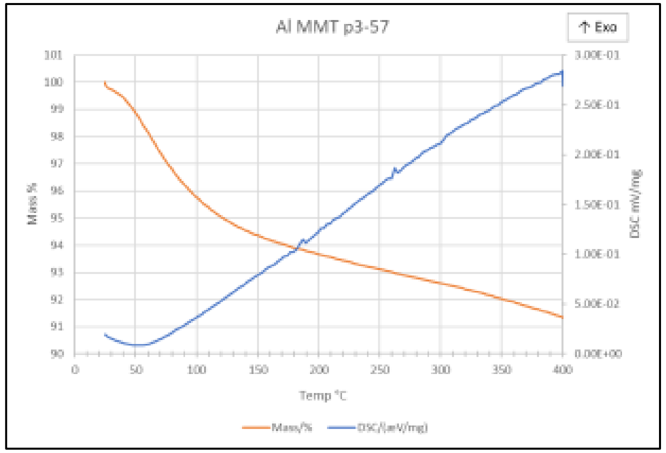
Na: ~1.5% H_2O



K10: ~3% H_2O



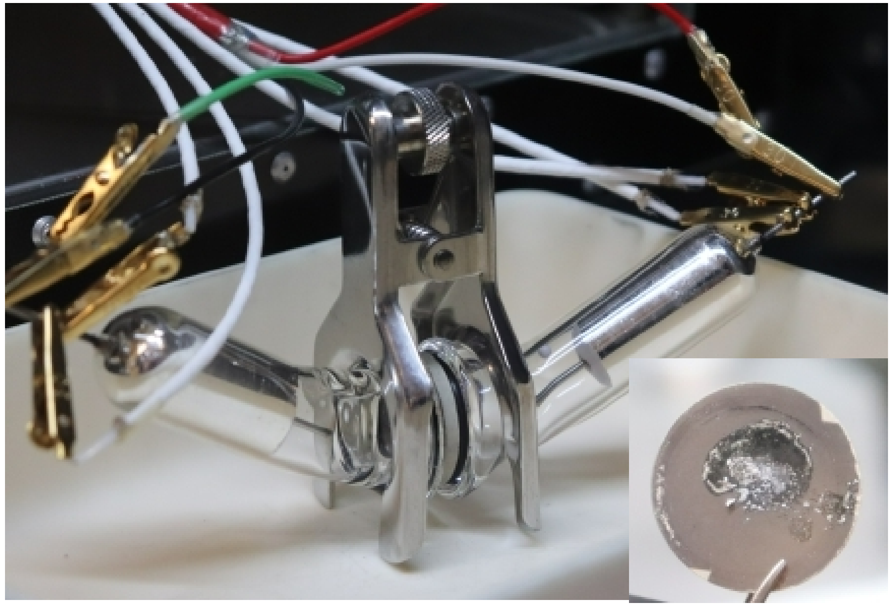
Al: ~6% H_2O



Are These Useful?

- Initial tests reveal high impedance across separator interfaces with Na metal.
  - ❖ Reactivity of water in clay with Na species is a problem!

- Application of protective surface coatings (Sn) stabilize MMT pellets for battery testing.
  - ❖ Still not sufficient chemical compatibility against molten sodium

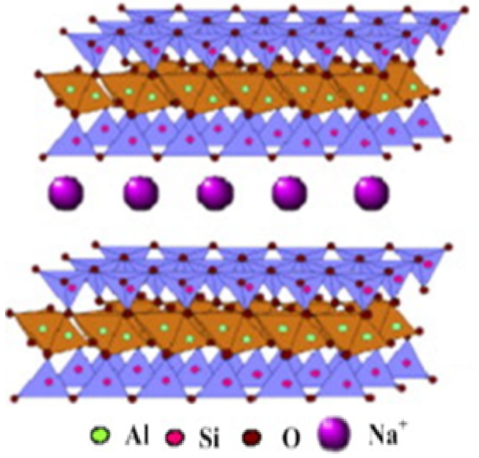


Symmetric molten Na cell with MMT separator (w/ Sn-based coating). Inset: separator after test.

Humpty Dumpty's Separators…

Despite promising conductivity…

- MMT pellets can be very fragile
- MMT is soluble in…well…everything useful!



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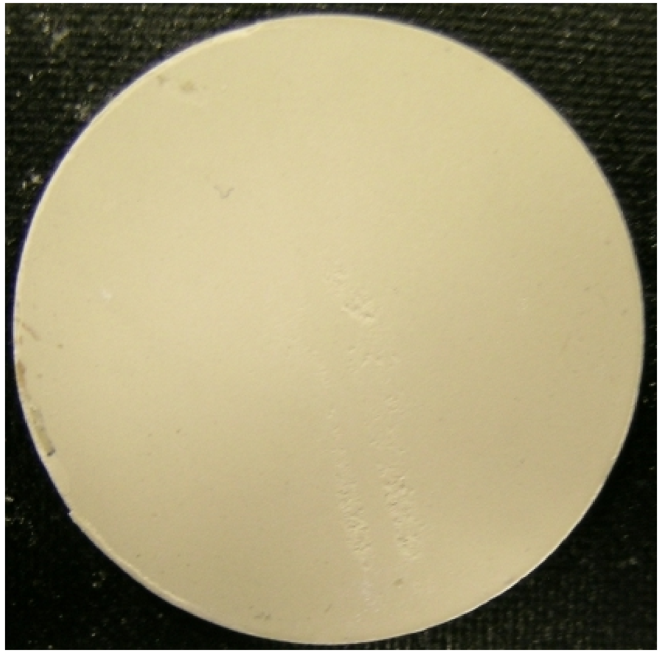
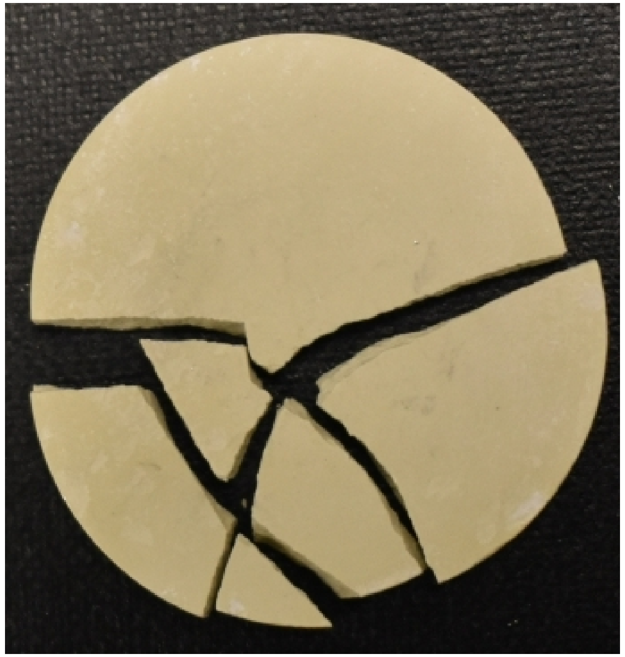


Broken MMT Pellet



Clay may not be "Good Enough" either!

Challenge: *Can we find something less expensive and easier to produce than NaSICON?*

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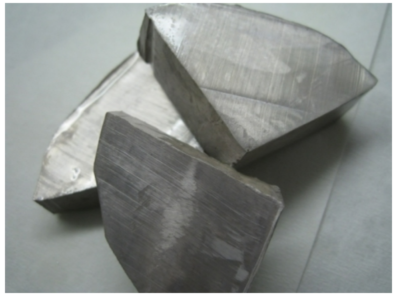

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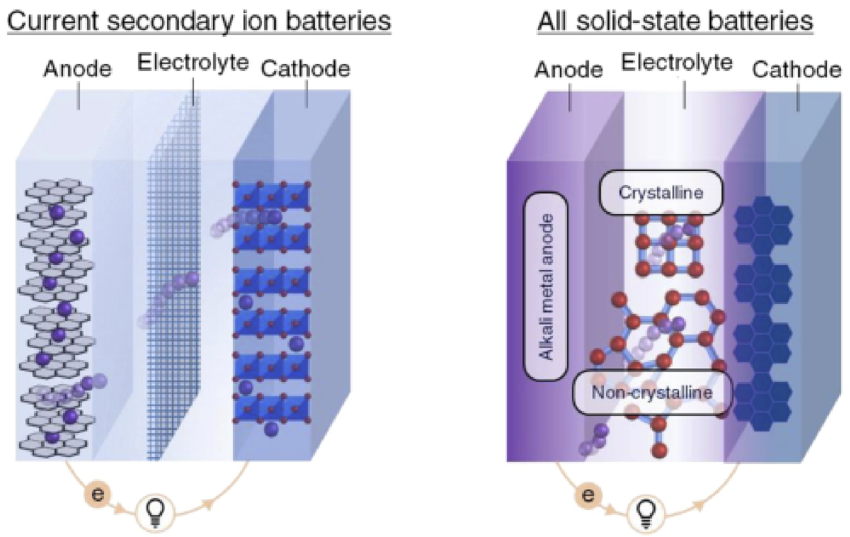

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- Battery Images from: Z. Grady, et al. (2020) Frontiers in Energy Research. doi: 10.3389/fenrg.2020.00218

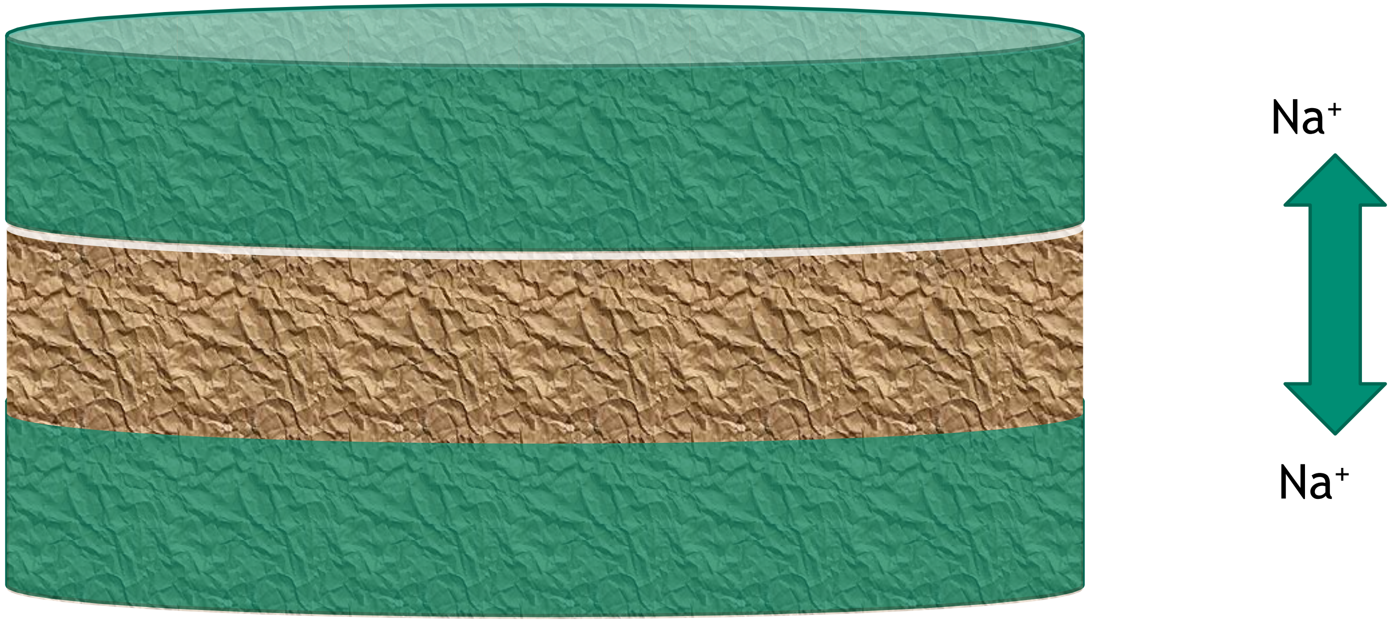
Dirt Pseudocapacitor: Proof of Concept

Using MMT as a solid state separator, we can press a sandwich an Na-MMT solid electrolyte between two MnO2-based electrodes.

"Anode":
Na_xMnO_2 + Carbon + MMT

Solid State Electrolyte:
Na-MMT

"Cathode":
Na_xMnO_2 + Carbon + MMT

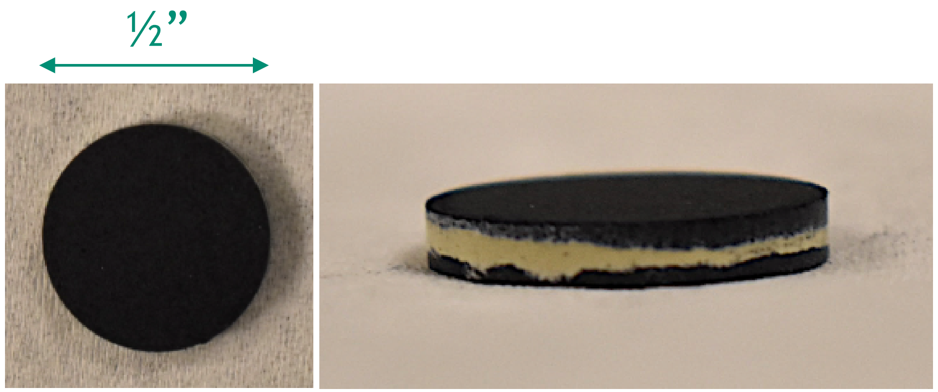


Promise, but a Materials Challenge!

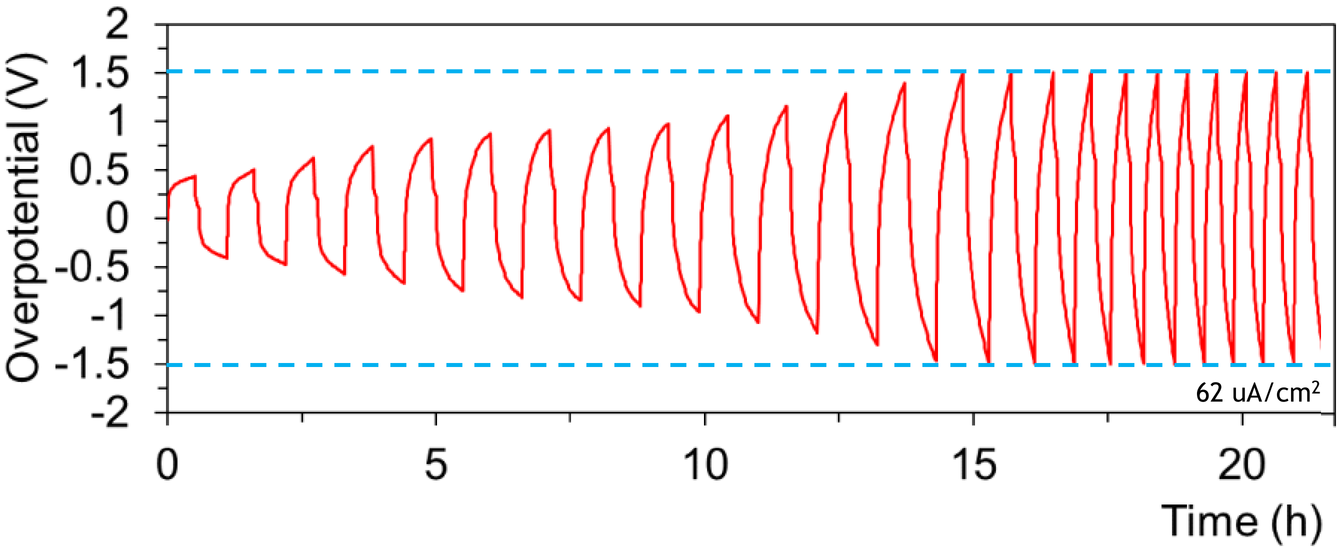
Electrochemical cycling shows promise!

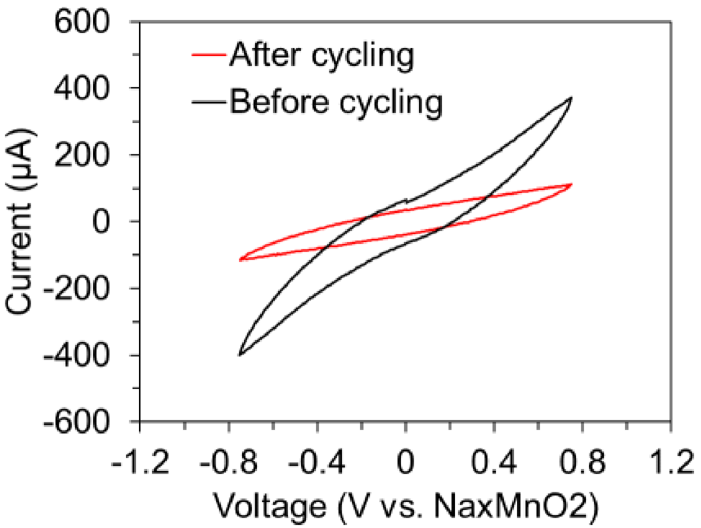
Cycling and cyclic voltammetry show signs of electrode degradation.

Need to improve electrode composition and interfaces.



Symmetric Galvanostatic Na_xMnO_2 cycling data. 1.5V limits (marked in blue dashed line)

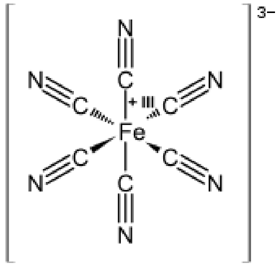


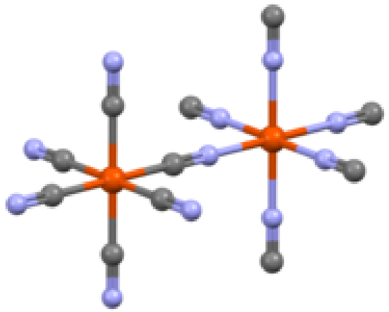


Cyclic voltammetry before and after testing shows loss of faradaic capacitance, indicating irreversible active material degradation.

Dirt Pseudocapacitor: Moving in the Right Direction?

Consider a different active sodium ion intercalation material: **Prussian Blue (PB)**

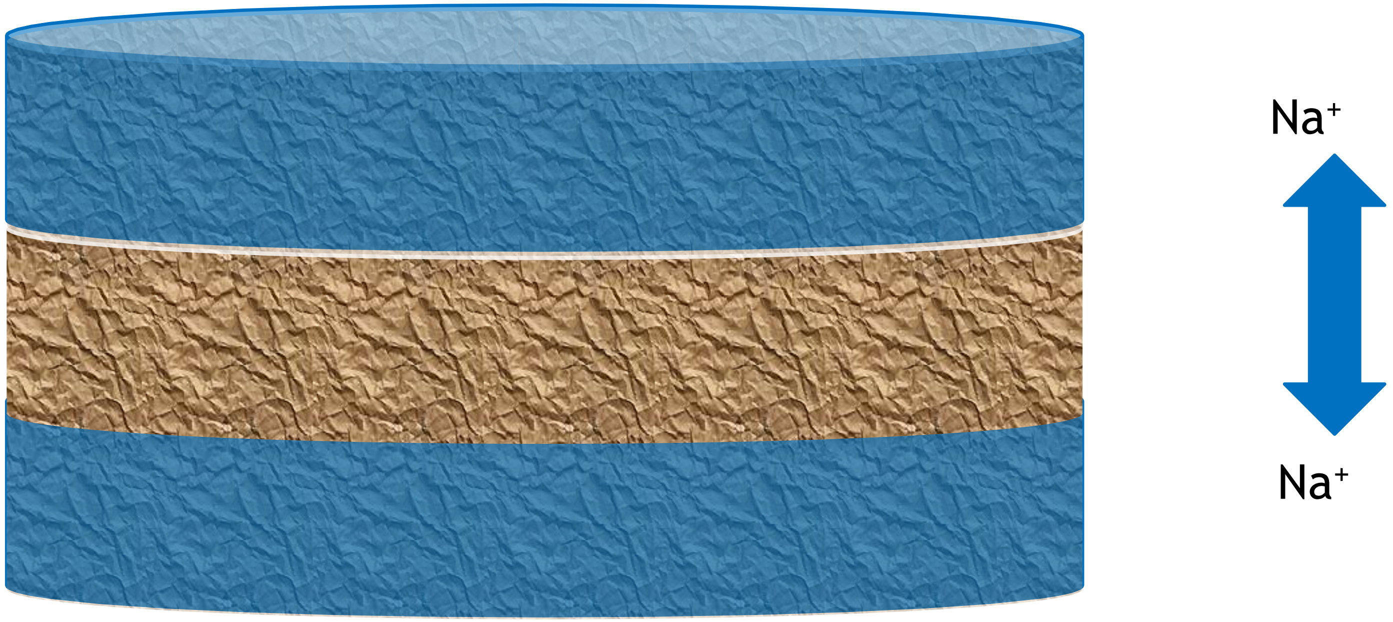




“Anode”:
Prussian Blue + Carbon + MMT

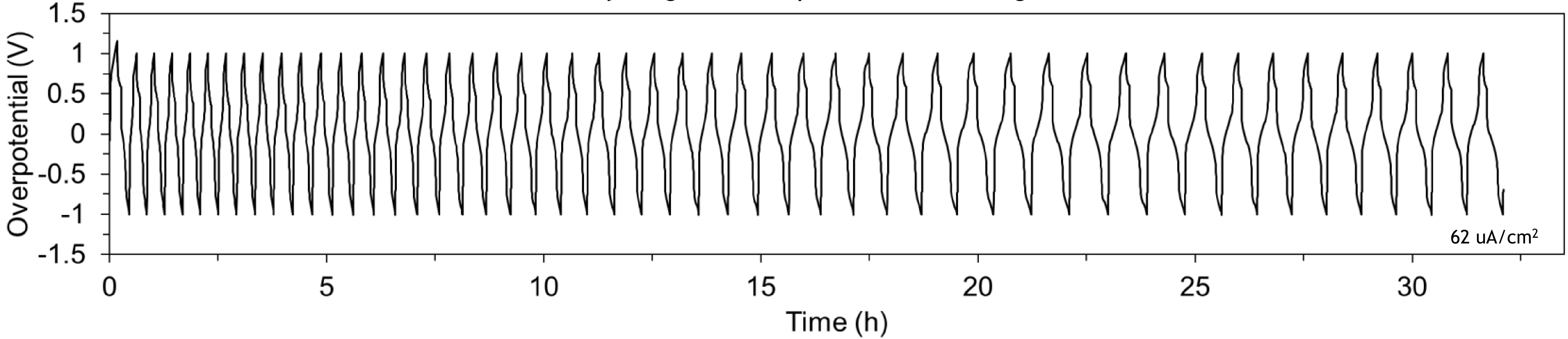
Solid State Electrolyte:
Na-MMT

“Cathode”:
Prussian Blue + Carbon + MMT

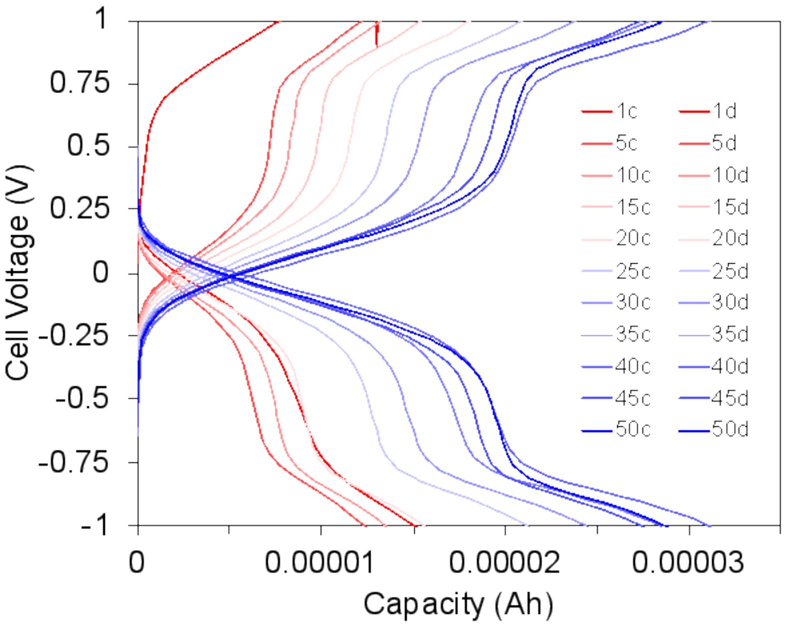


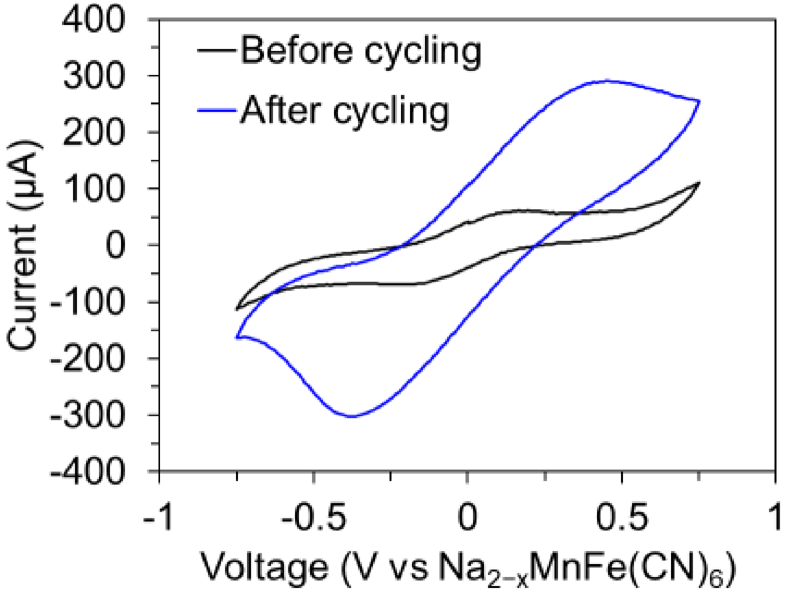
PB Improves Electrochemical Cycling!

Galvanostatic PB cycling shows improvements…and gets better over time!



Charge-Discharge curves and cycling profile show two electrochemical plateaus (high and low iron spin states) and improvements over time.





Cyclic voltammetry before and after testing shows increase in faradaic capacitance, indicating increased activity in PB material.

Take Home Messages and Path Forward

Solid State Ion Conductors are Hard.
Sometimes Literally (Ceramics).
Other times Figuratively (Clay).

- Following the example of layered ceramic sodium ion conductors, identified sodiated clay as a potential new “dirt-cheap” ion-conducting separator/electrolyte.
- Clay structure and water content are important to ion conduction.
- Chemical and mechanical may be challenges to traditional batteries.
- Solid-state systems (Dirt Pseudocapacitors) may be suitable homes for these layered separator alternatives!

- Future work will consider anisotropic systems (e.g., Dirt Batteries)
- Improvements in electrode composition and interfaces may improve higher rate performance.

Understanding of basic material structure/property relationships can help identify new classes of ion conductors with potential to impact emerging energy storage technologies.

Think outside the box!

Thanks!

This work at Sandia National Laboratories is supported through the Energy Storage Program, managed by Dr. Imre Gyuk, in the U.S. Department of Energy's Office of Electricity.

Contact: Erik Spoerke (edspoer@sandia.gov)

Thanks to those who actually did (most of) this work!

- Dr. Martha Gross
- Dr. Leo Small
- Amanda Peretti
- Dr. Stephen Percival
- Sara Dickens

- Professor Yang-Tse Cheng (U. Kentucky)
- Ryan Hill (U. Kentucky)

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