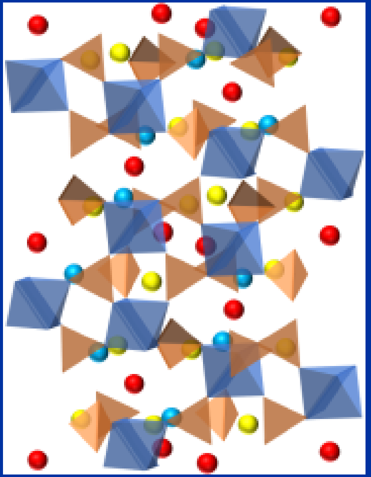
SAND2022-5968C

Characterization of NaSICON Solid Electrolytes Exposed to Thermal and Electrochemical Cycling in Molten Sodium Environment



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Part of SNL's Sodium Battery Program (PI: Leo Small)

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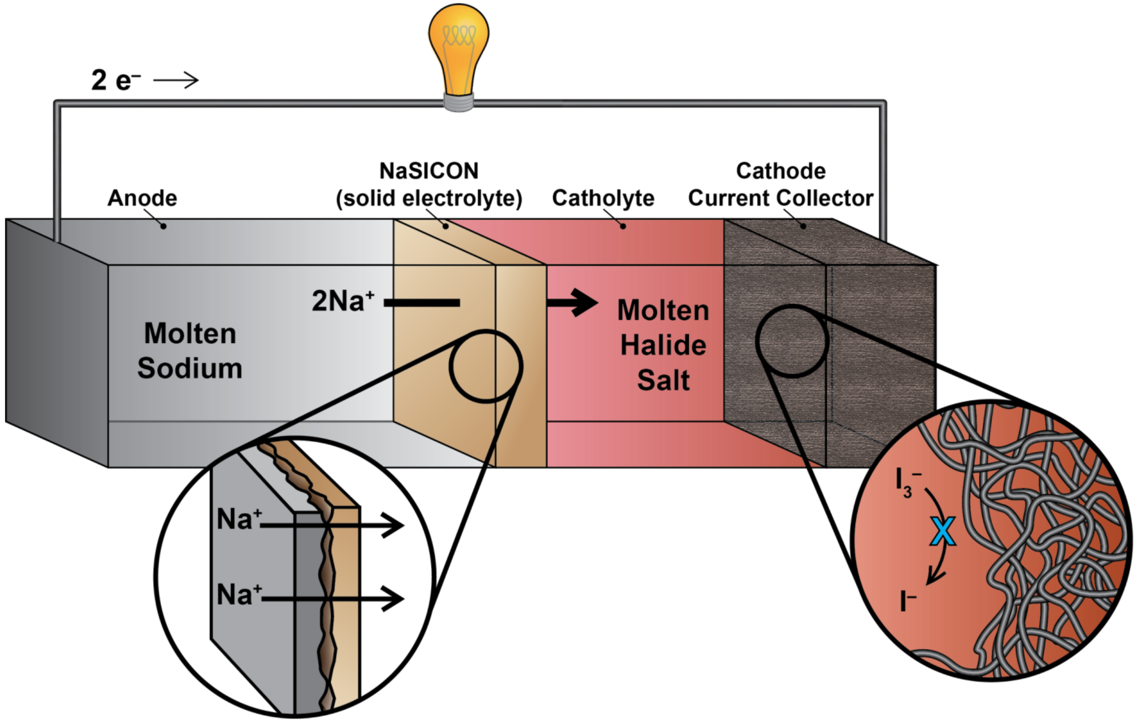
Motivation: Low Temperature Molten Sodium (Na-NaI) Batteries

*Realizing a new, low temperature molten Na battery requires new battery materials and chemistries – particularly in **sodium ion conductors***

Important electro-chemo-mechanical properties

- Highly Na^+-conductive
- Zero-crossover
- (Electro)chemical compatibility with Na and halide salts
- Mechanical integrity and "dendrite" suppression
  - ✓ Important for large-scale, long-duration, long-life applications



Martha Gross

<u>Na-NaI battery:</u>

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

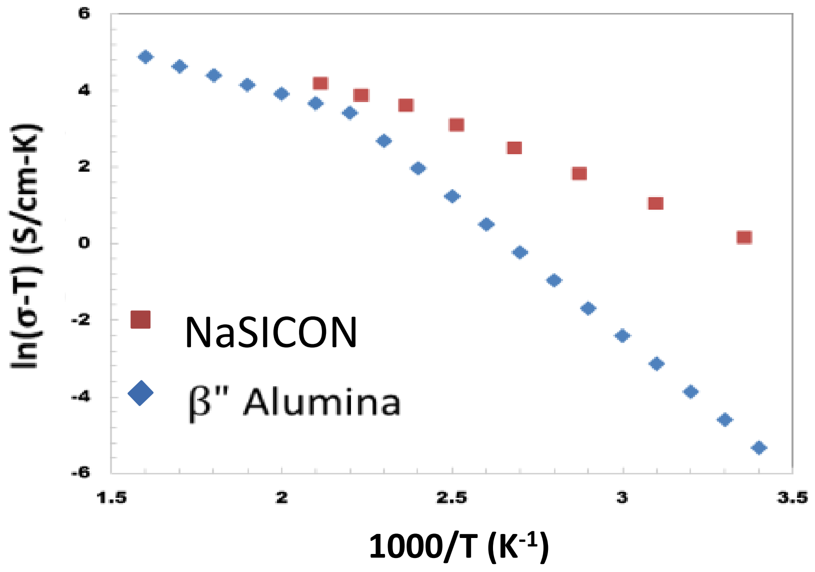
$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24$ V

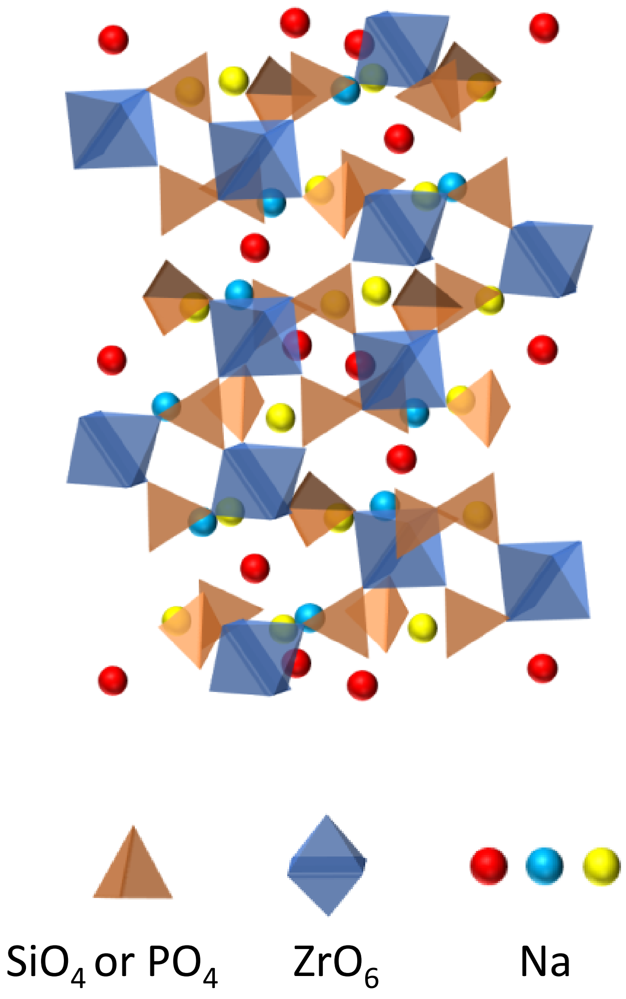
$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0_{cell} = 3.24$ V

NaSICON Solid Electrolytes

Key Qualities of NaSICON Ceramic Ion Conductors

- $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$
- High Na-ion conductivity (>10^{-3} S/cm at 25^{o}C)
- Zero-crossover (high-density after sintering)
- Chemically compatible with molten Na and halide salts (at low T!)
- Mechanical integrity? After exposure to battery materials?

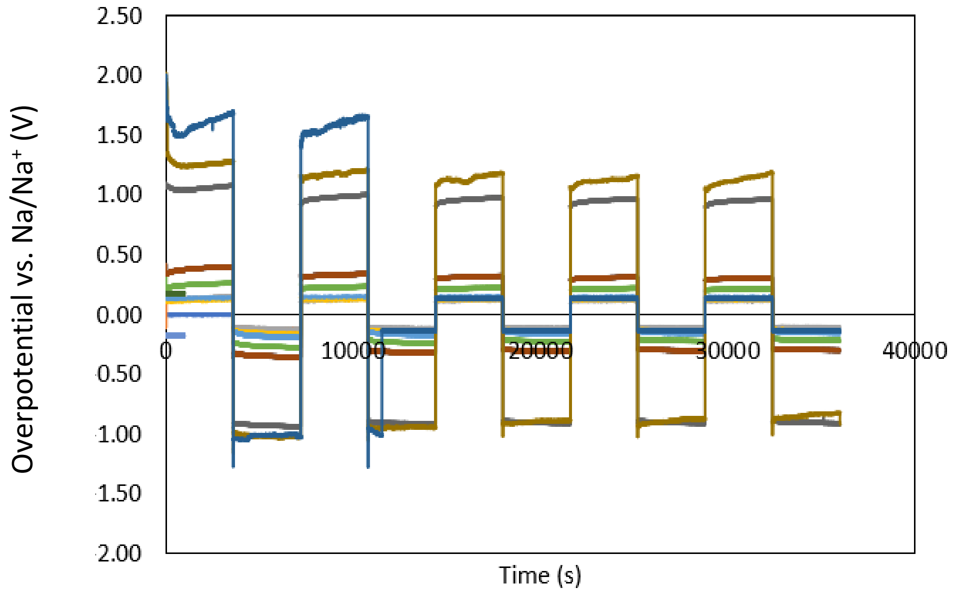


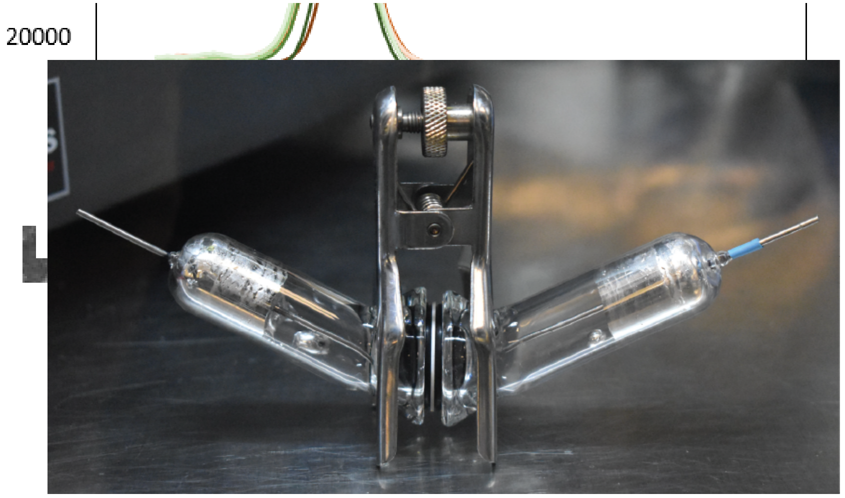


Understanding NaSICON Behavior in Na Batteries

- Electro-chemo-mechanical phenomenon
  - Must understand <u>all three</u> aspects

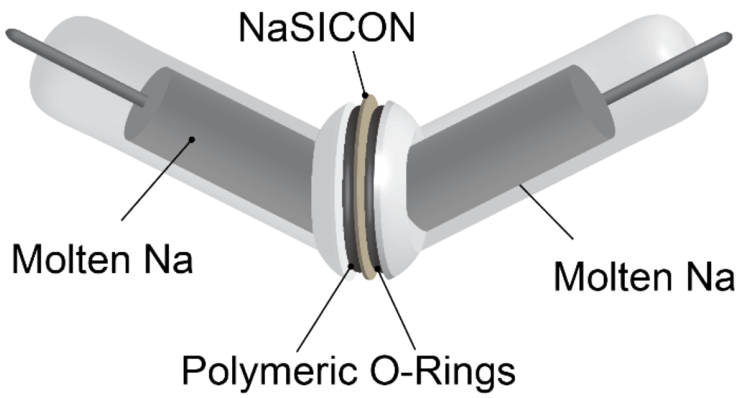
- UK-SNL team has the capability to explore these!
  - Cycling molten sodium batteries (electrochemical)
  - Compositional analysis (chemical)
  - Indentation (mechanical)
  - Microstructure analysis

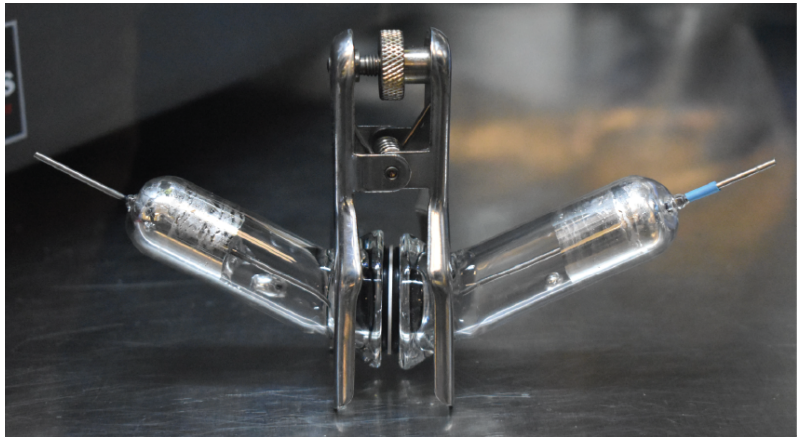




Mechanical Behavior of NaSICON

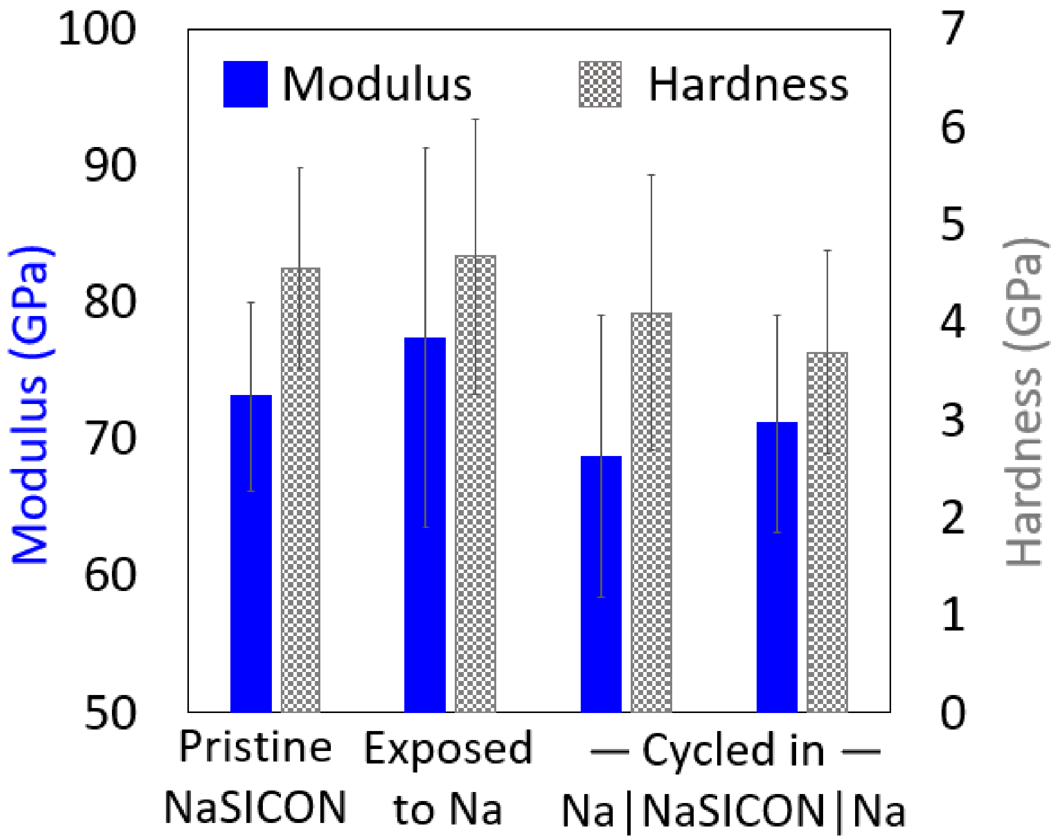
- Exploring mechanical properties after:
  - NaSICON heated to 110 °C
  - NaSICON exposed to molten Na at 110 °C
  - NaSICON (x2) cycled up to 50 mA/cm^2 in Na|NaSICON|Na cell at 110 °C

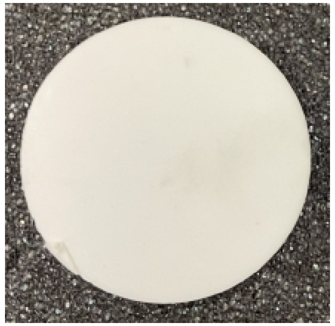




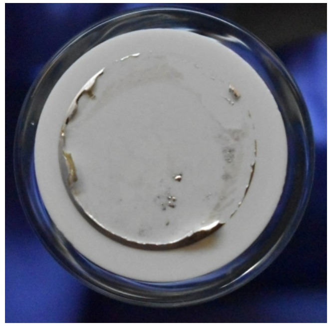
Mechanical Behavior of NaSICON

- Saw changes in NaSICON's mechanical response
  - Modulus increased after exposure to molten Na metal
  - Modulus and hardness decreased after cycling in Na|NaSICON|Na

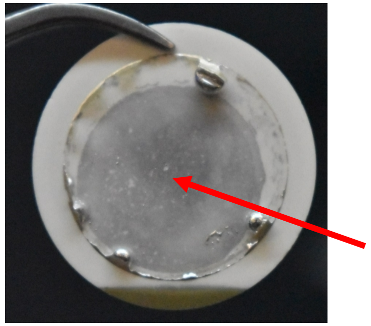




Pristine



Exposed to Na



Cycled

Color disappeared upon air exposure

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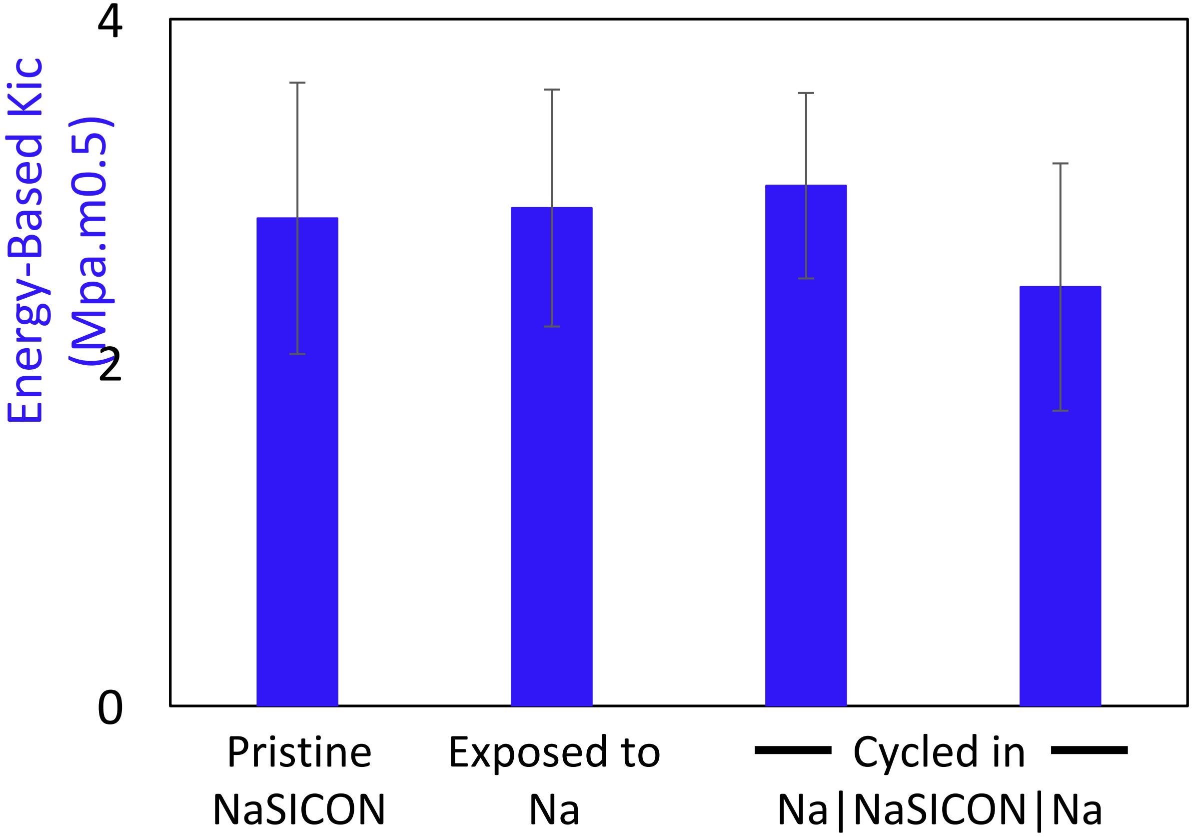
Fracture Toughness of NaSICON

Fracture toughness is intimately related to critical current density (CCD)



$$W_{crack} = W_{irrev} - W_{pp}$$

$$K_{ic} = \sqrt{\frac{E_r W_{crack}}{A_m}}$$

K_{ic}: Fracture Toughness
W_{irrev}: Total irreversible indentation work
W_{pp}: Purely plastic indentation work
W_{crack}: Work done to create cracks
E_r: Material reduced modulus
A_m: Indent contact area

Fracture toughness not significantly impacted by Na^+ conduction

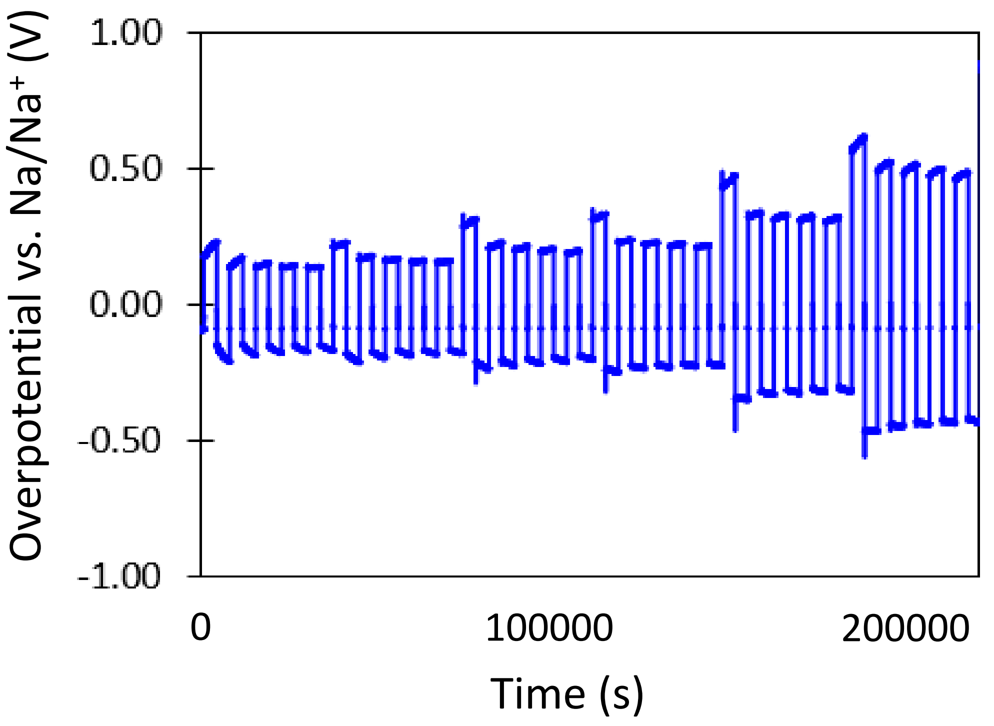
Cycling NaSICON should not affect ability to handle higher current densities

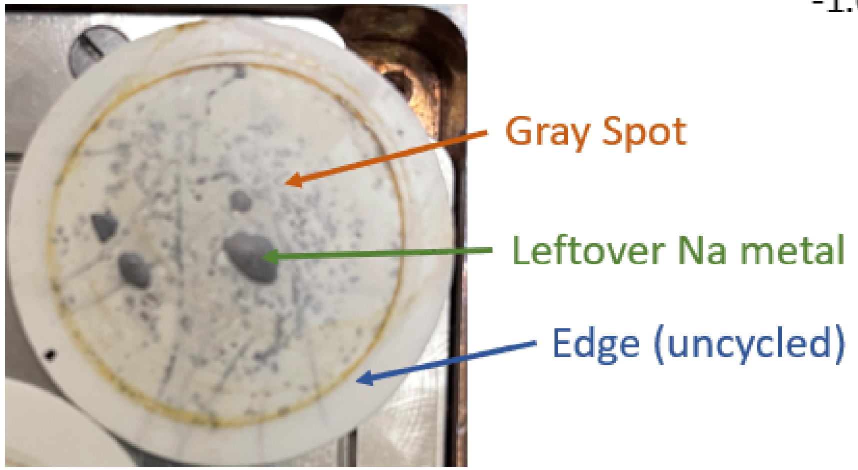
Hempel, J. L.; Meyer, A.; Hill, R.; Cheng, Y.-T. *MRS Commun. 2022 122* **2022**, *12* (2), 279–282.

Chemical Changes in NaSICON

- NaSICON cycled up to 225 mA/cm^2 in Na|NaSICON|Na symmetric cell at 110 °C
  - High current density to induce chemical changes
  - Typical CCD in SEs @ RT is ~0.1-1 mA/cm^2

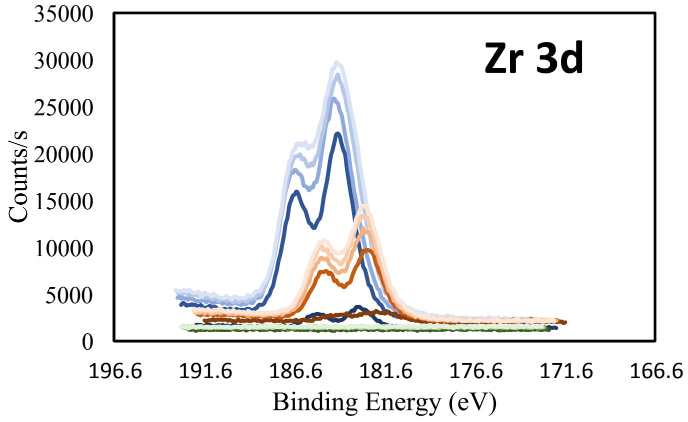
- Permanent gray spots (and lines) appeared across NaSICON surface

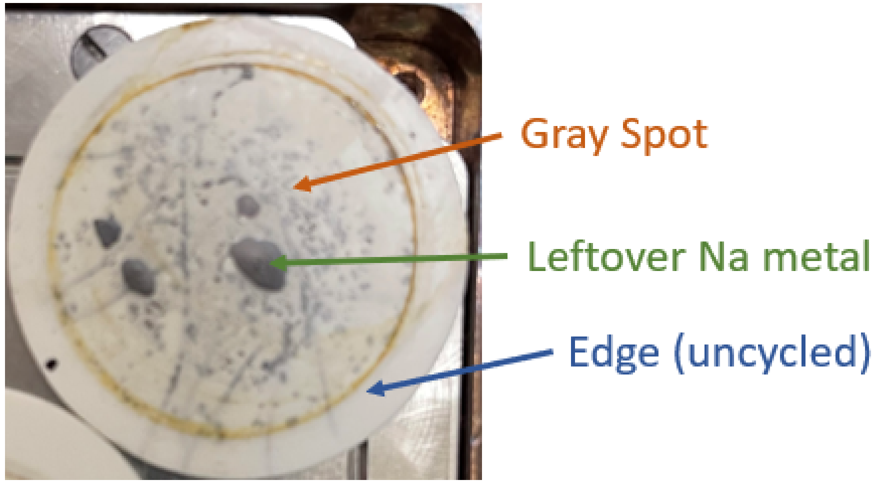


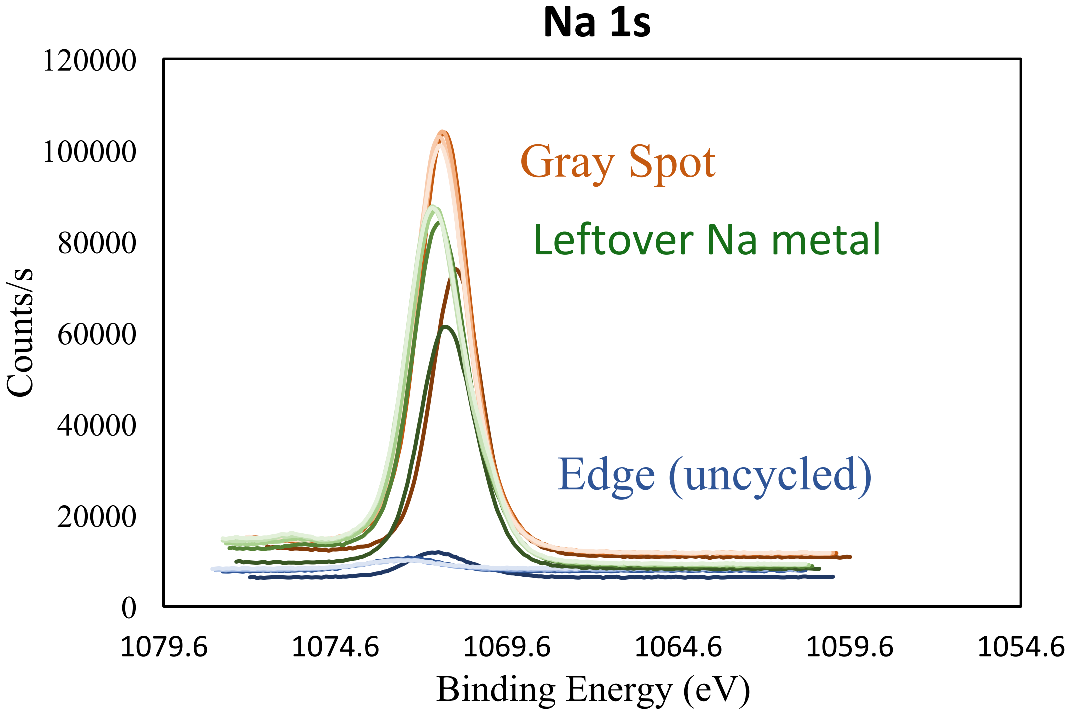


Chemical Changes in NaSICON

- XPS to determine composition in various areas
  - Gray spots have much higher Na1s signal than edge (uncycled) area - more similar to leftover "pure" Na metal
  - Gray spots still show expected Zr and Si signals



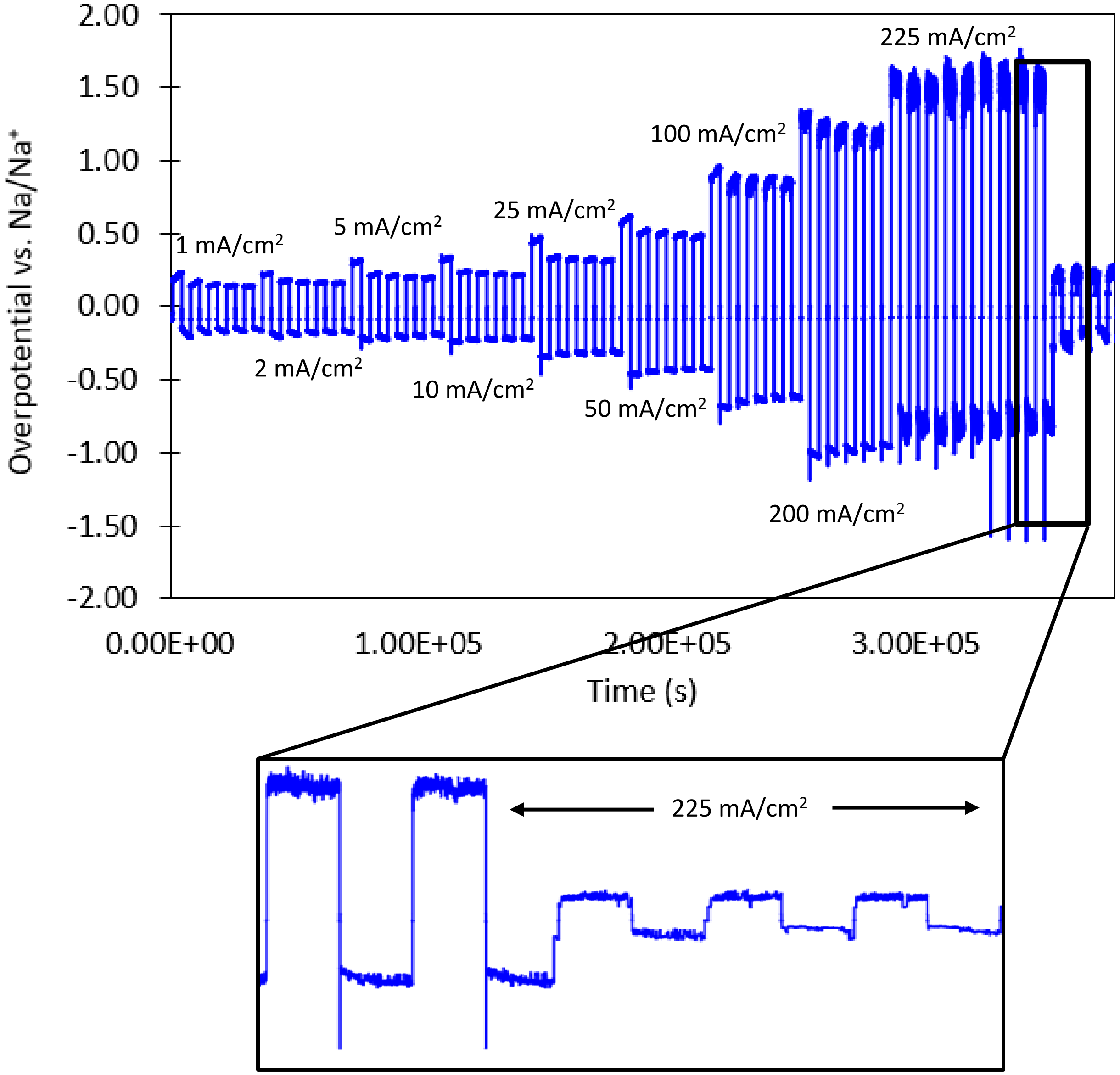


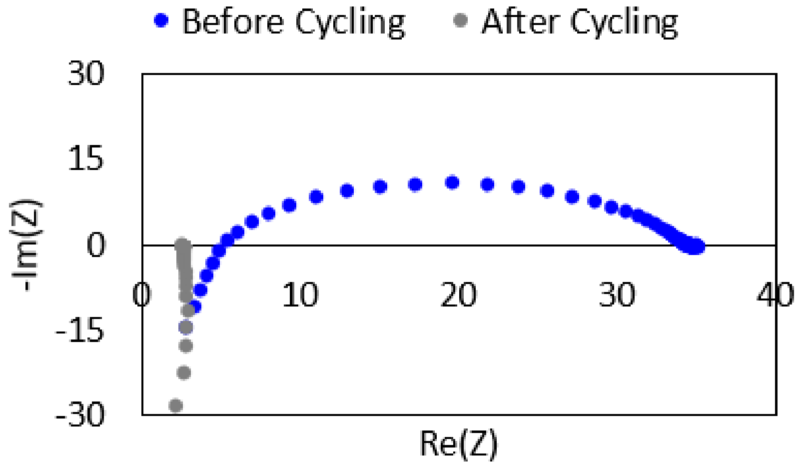


"Dendrites"?

Electrochemical Behavior of NaSICON

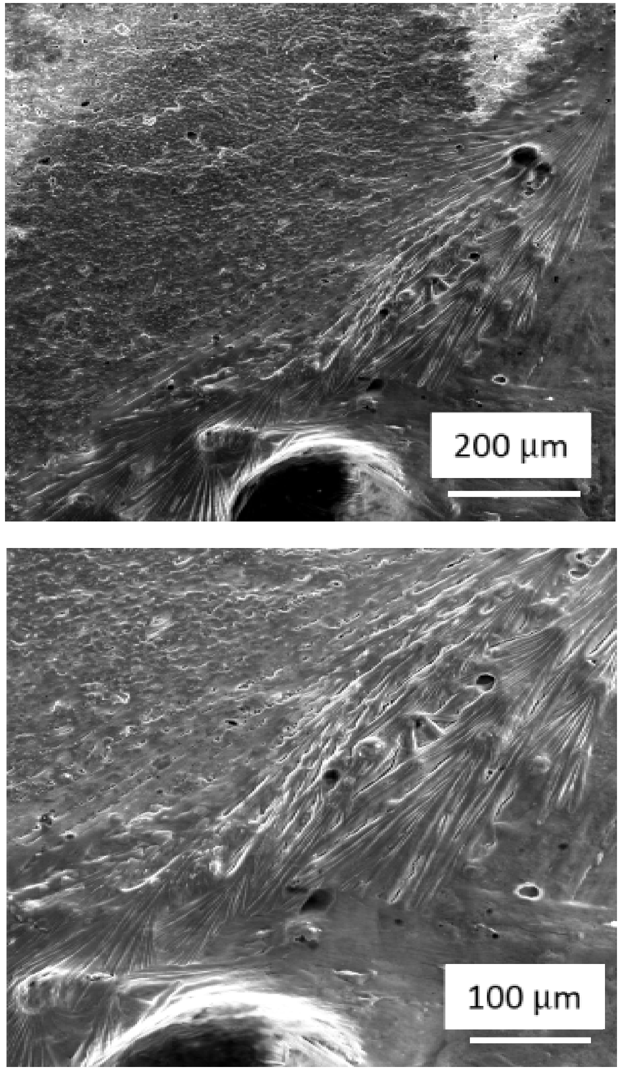
- Cycling above 100 mA/cm^2 led to unstable voltage plateaus
- Continued cycling at 225 mA/cm^2 led to eventual voltage drop
  - Very small impedance measured by impedance spectroscopy
  - Consistent with electronic short



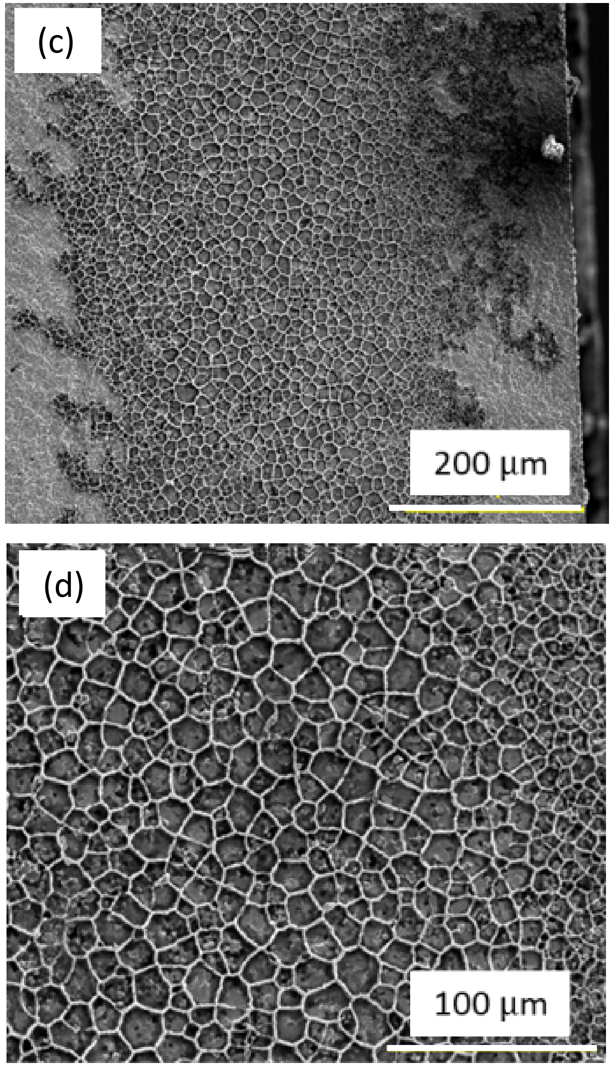


Electrochemical Behavior of NaSICON

- Na can propagate through NaSICON causing an electronic short
- Morphology of Na within NaSICON is vastly different than Li within LLZO
  - Needle-like vs. grain boundary accumulation



Na propagation in NaSICON



Li propagation in LLZO

Meyer, A.; An Electrochemical-mechanical Investigation of Next Generation Lithium Metal Electrode and Solid Electrolyte (PhD thesis 2022)

In Short

- NaSICON solid electrolytes will play an integral role in next -generation energy storage technology
- NaSICON SEs exhibit changes in their mechanical, chemical, and electrochemical behavior during cycling
  - These all contribute to NaSICON failure in Na batteries
- Failure of NaSICON at high-temperature is significantly different than in RT batteries
  - A fundamental understanding of this failure will guide improved electrolyte fabrication

Acknowledgments

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