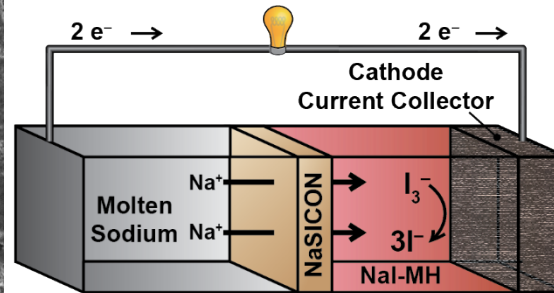
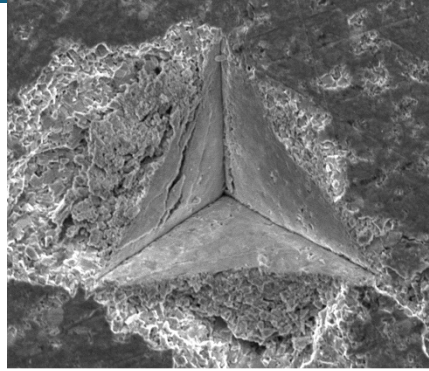
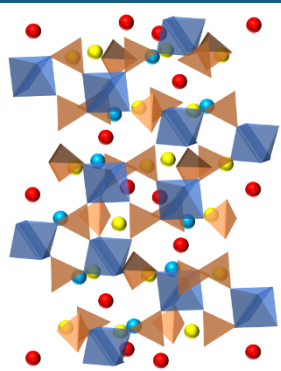




Mechanical, Microstructural, and Electrochemical Characterization of NaSICON Sodium Ion Conductors



Ryan Hill,* Jacob Hempel,* Yang-Tse Cheng*, Erik Spoerke,** Leo Small,**
Amanda Peretti**

*University of Kentucky and **Sandia National Laboratories

DOE Office of Electricity 2021 Virtual Peer Review Meeting
October 26-28, 2021

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



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SAND No.: SAND2021-xxxx

Background and Motivations: Low Temperature Molten Sodium (Na-NaI) Batteries

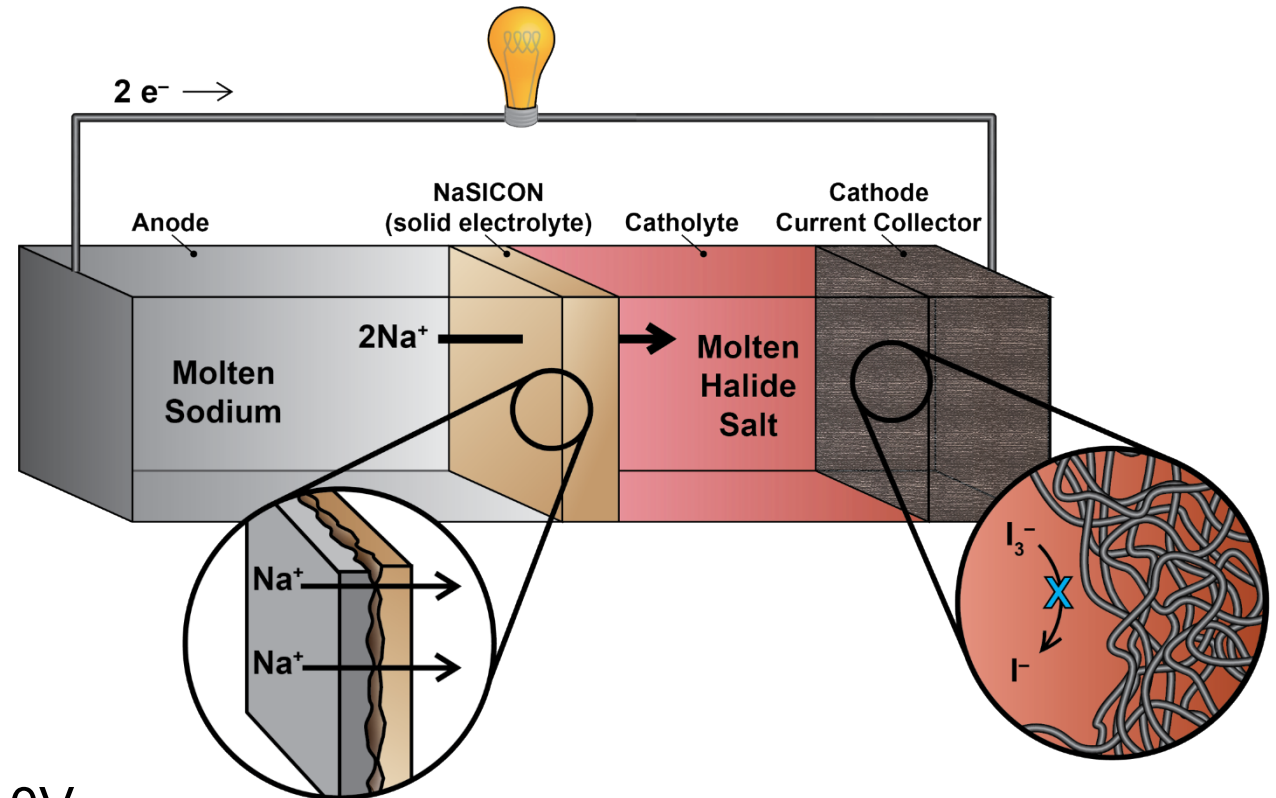
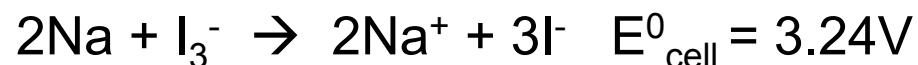
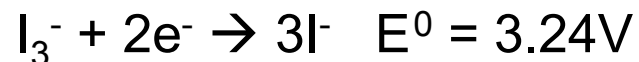
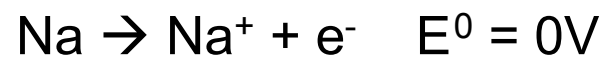


*Realizing a new, low temperature molten Na battery requires new battery materials and chemistries, in particular, **sodium ion conductors***

Sodium ion conductors -A Key Ingredient for Success

- Highly Na⁺-conductive
 - Chemical compatibility with molten Na and halide salts
 - Zero-crossover
 - Good mechanical integrity
- ✓ Important for large-scale, long-duration, long-lifetime applications

Na-NaI battery:



“Collaborative research to advance solid state ion conductors for emerging batteries”



Objectives: Multiscale mechanical characterization to evaluate the properties of newly developed bulk ceramic and ceramic/polymer composites for large-scale, long-duration, long-lifetime applications

FY21: *In situ* exposure or environmental tests of basic materials and components identified in FY20

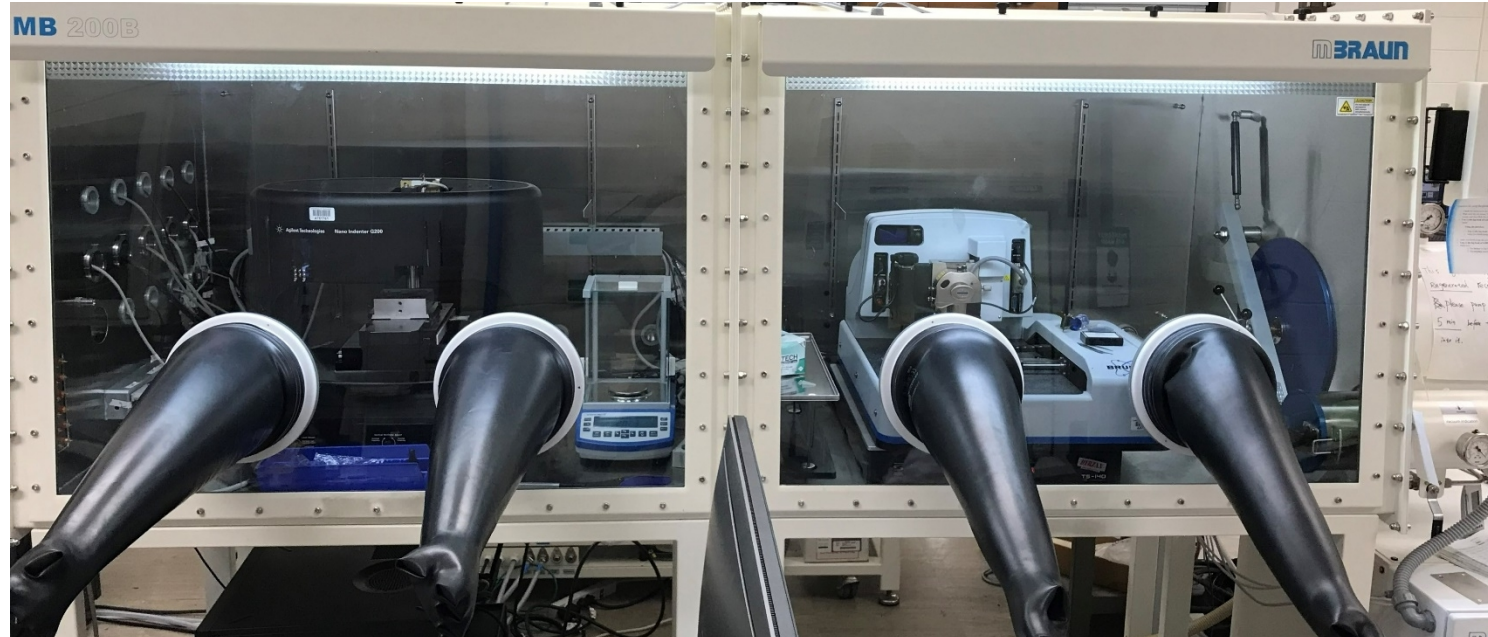
- Mechanical and Microstructural Characterization of Montmorillonite Sodium Ion Conductors (completed with one publication in press)
- Mechanical and Microstructural Characterization of NASICON (sodium (Na) Super Ionic CONductor)

FY22: *Continuation/completion of testing on previous materials, but aim to develop capability to do in situ testing of battery assemblies*

Support DOE OE's Core Mission

- Drives electric grid modernization and resiliency in the energy infrastructure
- Leads the DOE's efforts to ensure a resilient, reliable, and flexible electricity system
- Accomplishes this mission through research, partnerships, facilitation, modeling and analytics, and emergency preparedness

Methodology: Nanoindentation and Scanning Probe Microscopy inside a Glovebox

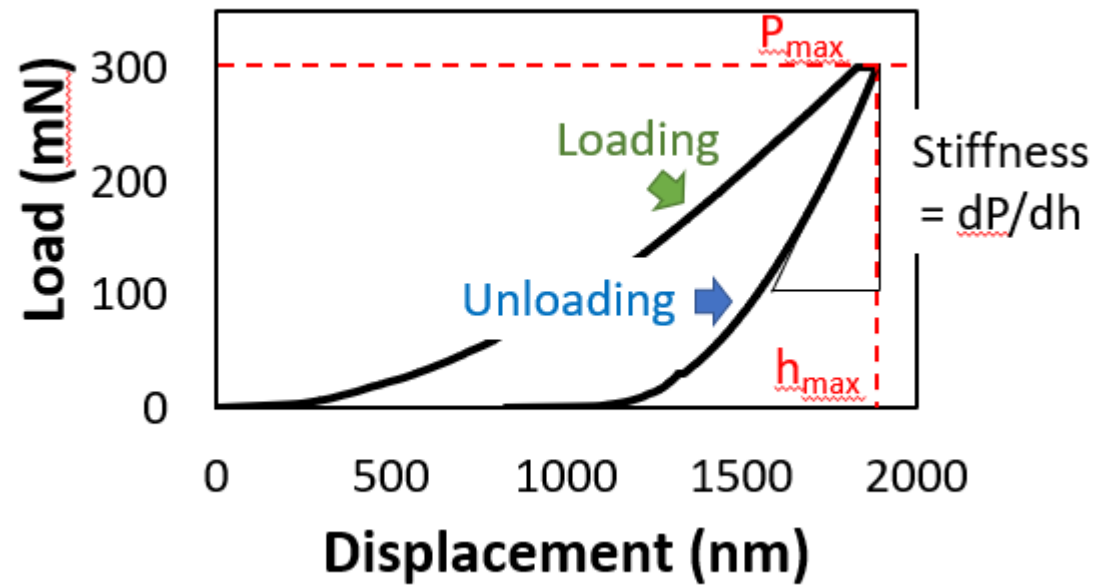


Left: The Nano Indenter G200 system (now KLA-Tencor)

Right: Bruker Dimension ICON system: Atomic Force Microscopy (contact, tapping, lateral force modes), conducting tip, Scanning Electro-Chemical Microscopy, and Scanning Kelvin Probe



Methodology: Mechanical Characterization of Sodium Ion Conductors: Modulus and Hardness



$$\frac{1}{E^*} = \frac{1 - \nu^2}{E} + \frac{1 - \nu'^2}{E'}$$

$$H = \frac{P_{max}}{24.5h_p^2}$$

Results: Mechanical and Microstructural Characterization of Clay-based Solid State Sodium Ion Conductors



J Mater Sci

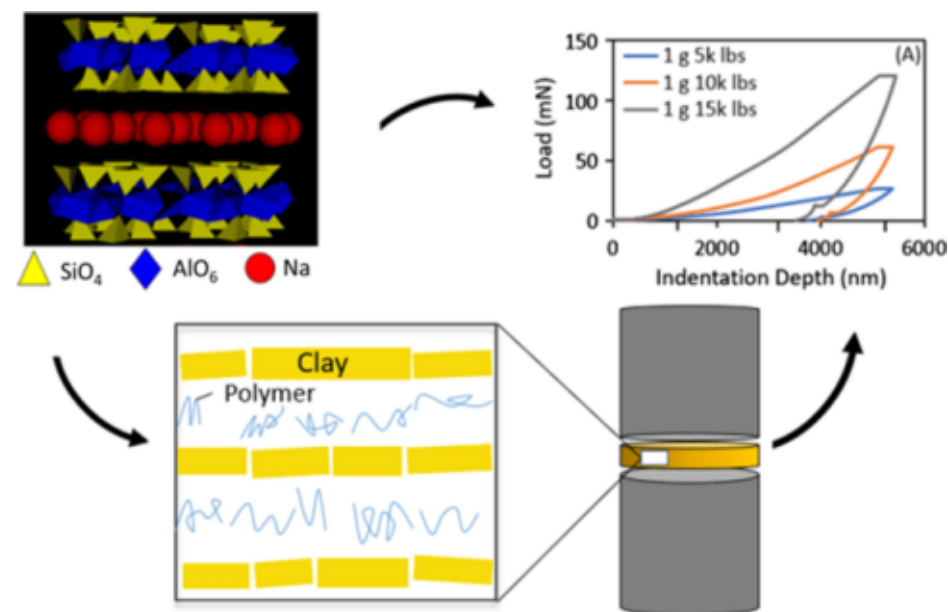
Composites and nanocomposites

Characterizing mechanical and microstructural properties of novel montmorillonite-rich polyethylene composites

Ryan Hill^{1,*}, Amanda S. Peretti², Leo J. Small², Erik D. Spoerke², and Yang-Tse Cheng¹

¹Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506-0046, USA

²Sandia National Laboratories, Albuquerque, NM 87123, USA



- Increased pressing force during pellet fabrication increases elastic modulus and hardness.
- A critical pressing force (10,000 lbs here) is required to achieve maximum MMT pellet density for a given set of processing conditions. Beyond this pressure no increase in density is observed.
- Pellets can be made thinner by decreasing mass without compromising the elastic modulus or hardness.
- The addition of 1 wt% PE to form MMT/PE composites significantly increases the modulus and hardness of the pellets.

Key Qualities of NaSICON Ceramic Ion Conductors

- $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$
- High Na-ion conductivity ($>10^{-3}$ S/cm at 25°C)
- Chemical Compatibility with Molten Na and Halide salts
- Zero-crossover
- Mechanical integrity???

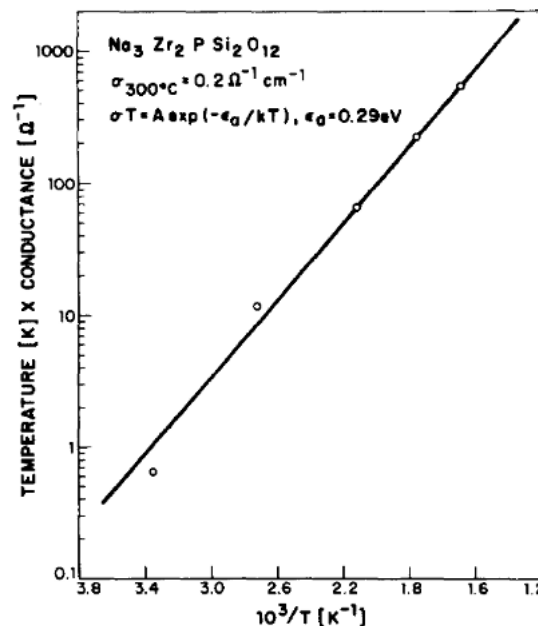
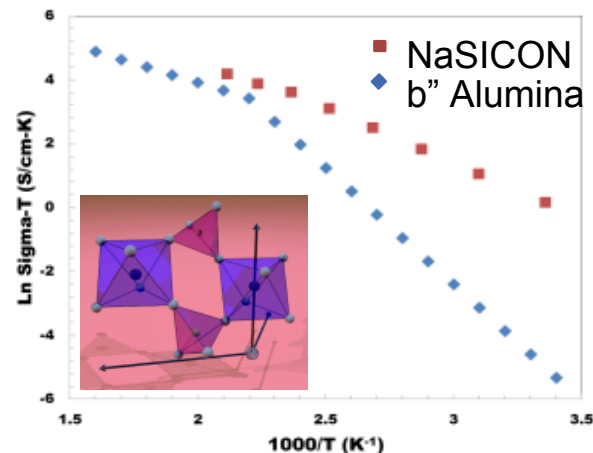
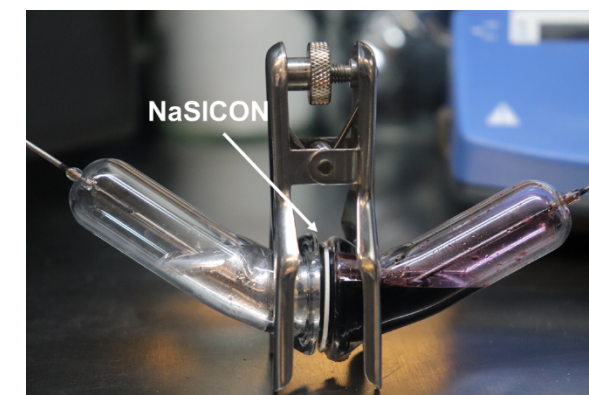


FIG. 8

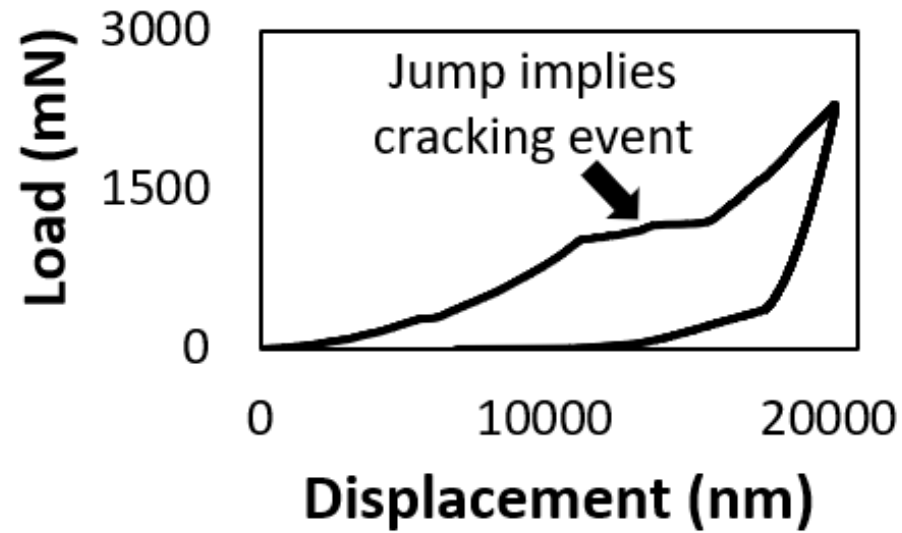
Temperature - conductance product T/R vs $1/T$ for a typical ceramic specimen of $\text{Na}_3\text{Zr}_3\text{PSi}_2\text{O}_{12}$ with graphite electrodes at 500 kHz.



Molten Na Battery Cell Set-Up

Goodenough, J. B., et al. (1976). "Fast Na⁺-ion transport in skeleton structures." Materials Research Bulletin **11(2)**:

Methodology: Mechanical Characterization of Sodium Ion Conductors: Fracture toughness



Fracture toughness then calculated by:

$$K_c = A \left(\frac{E}{H} \right)^{\frac{1}{2}} \left(\frac{P}{c^{\frac{3}{2}}} \right)$$

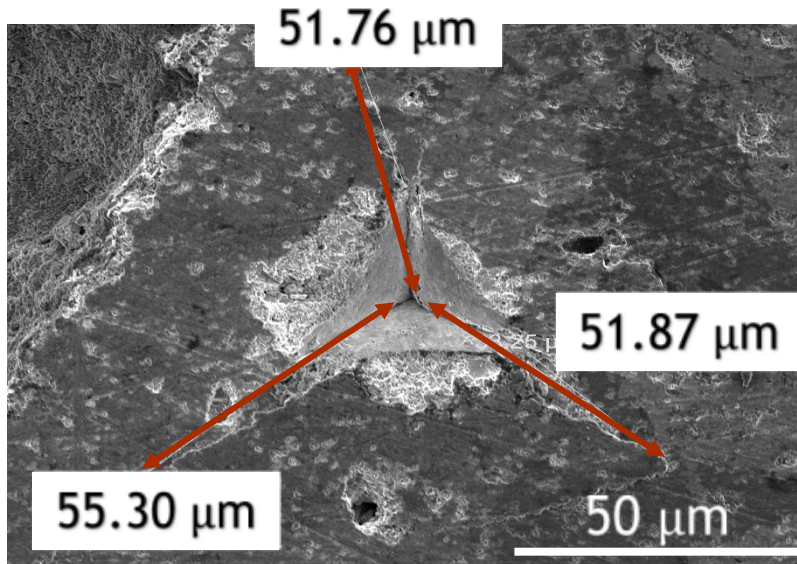
A: Material independent constant = 0.040 ± 0.004

E: Young's Modulus

H: Hardness

P: Maximum load during indentation

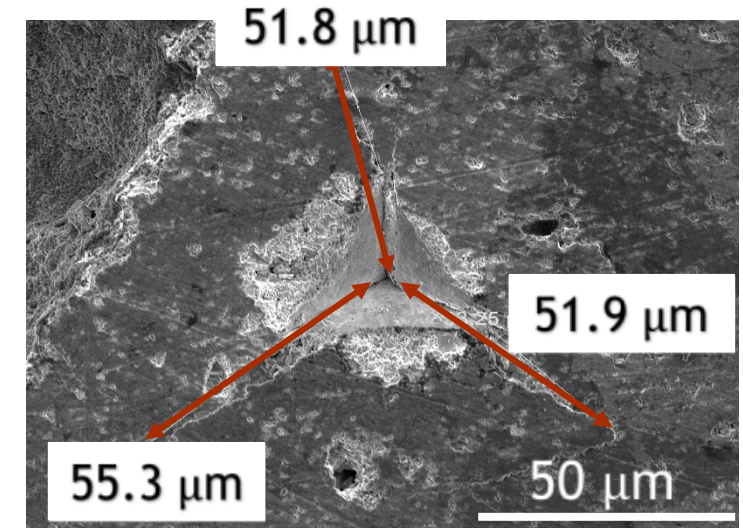
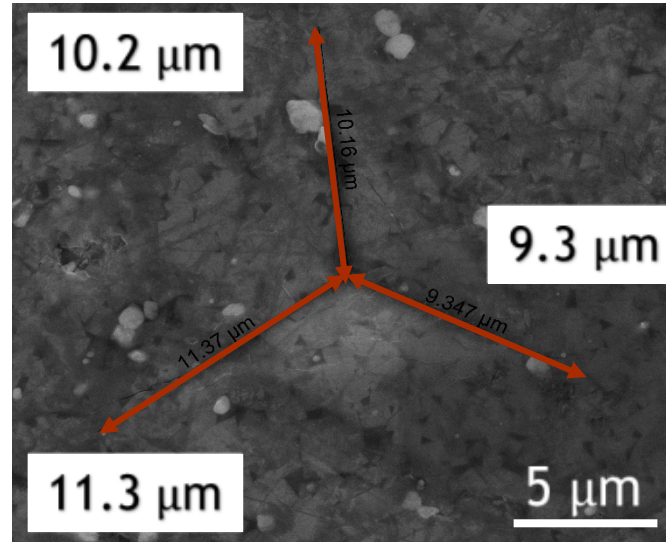
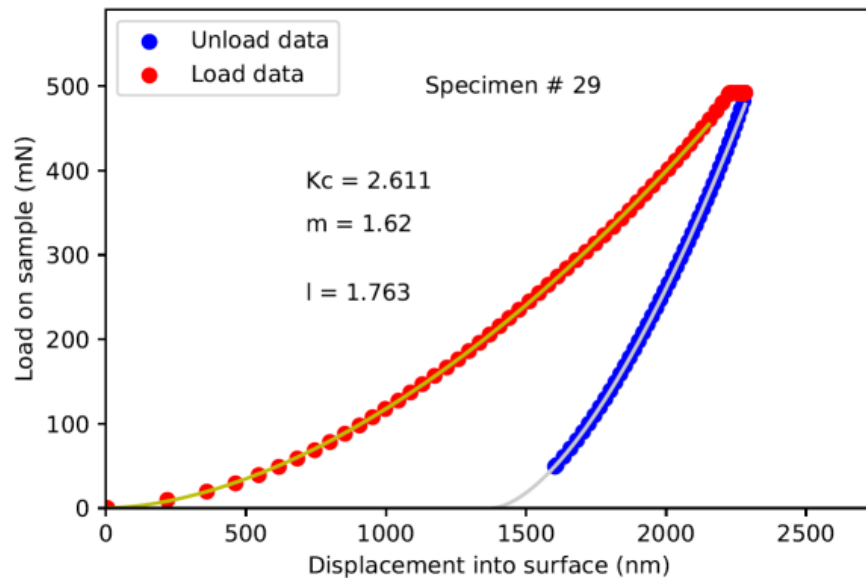
c: Length of crack measured by SEM



Cracks can be measured by SEM

Material	K_{Ic} (MPa√m)
SiC	3.00-6.00
MgO	2.50
Fused Silica	0.80
WC	6.00-20.00
NaSICON (measured)	1.90 ± 0.60

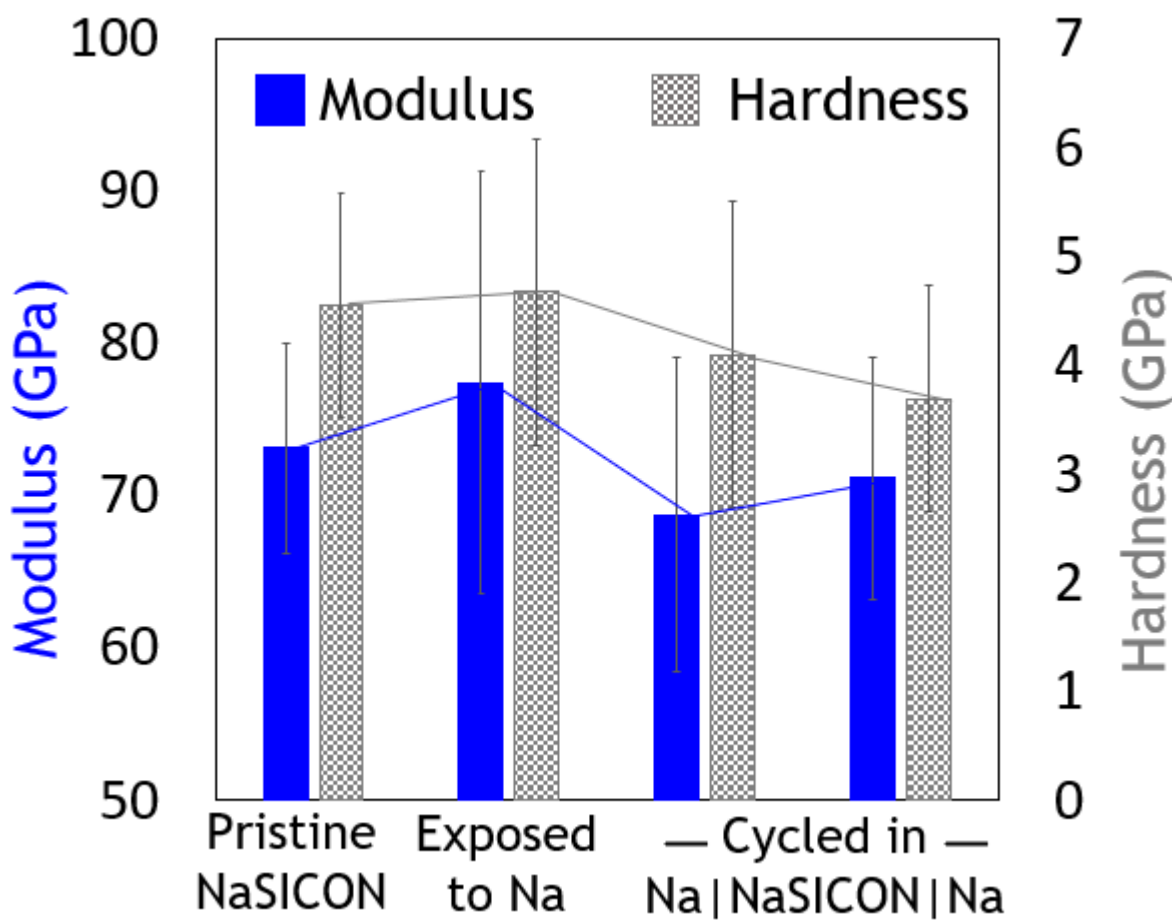
Methodology: Mechanical Characterization of Sodium Ion Conductors: Fracture toughness using crack length and a new energy-based method



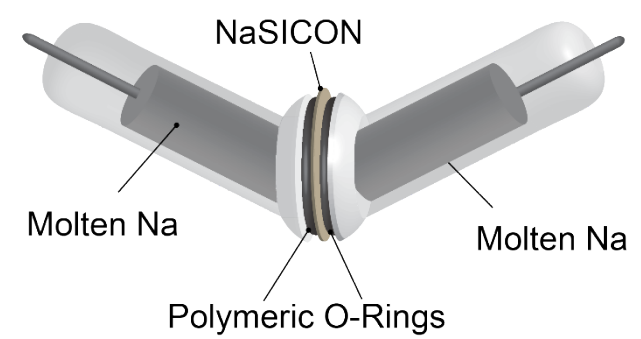
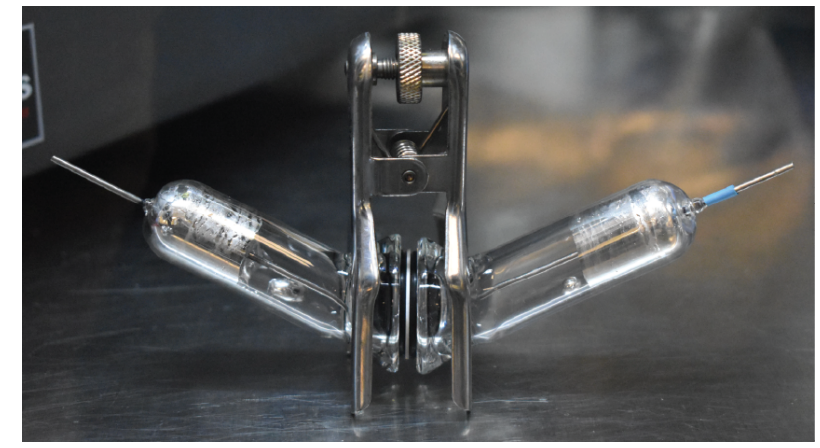
Energy-based method allows for situations where:

- Crack lengths are small relative to the size of the indents
- Cracks are subsurface
- Ease of measurement

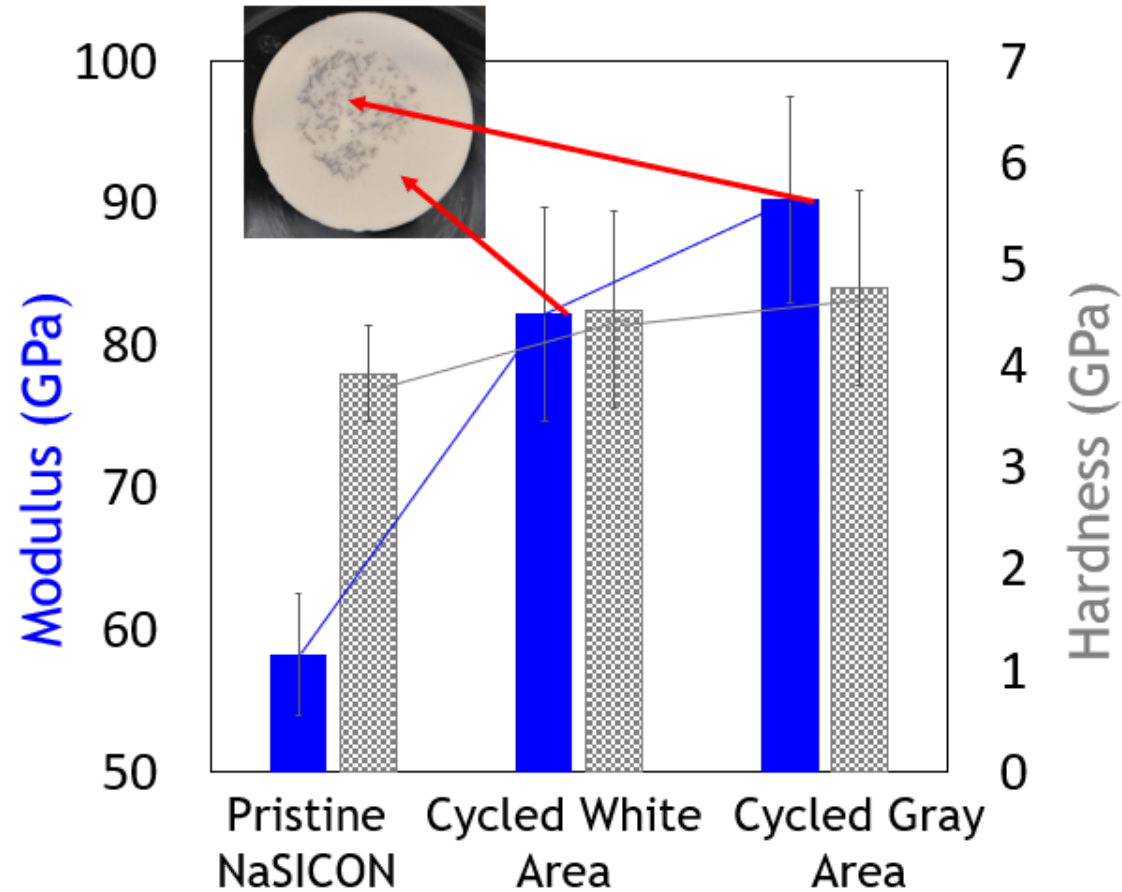
Material	K_{Ic} (MPa $\sqrt{\text{m}}$)
SiC	3.00-6.00
MgO	2.50
Fused Silica	0.80
WC	6.00-20.00
NaSICON (crack length)	1.90 ± 0.60
NaSICON (energy-based)	3.30 ± 0.40



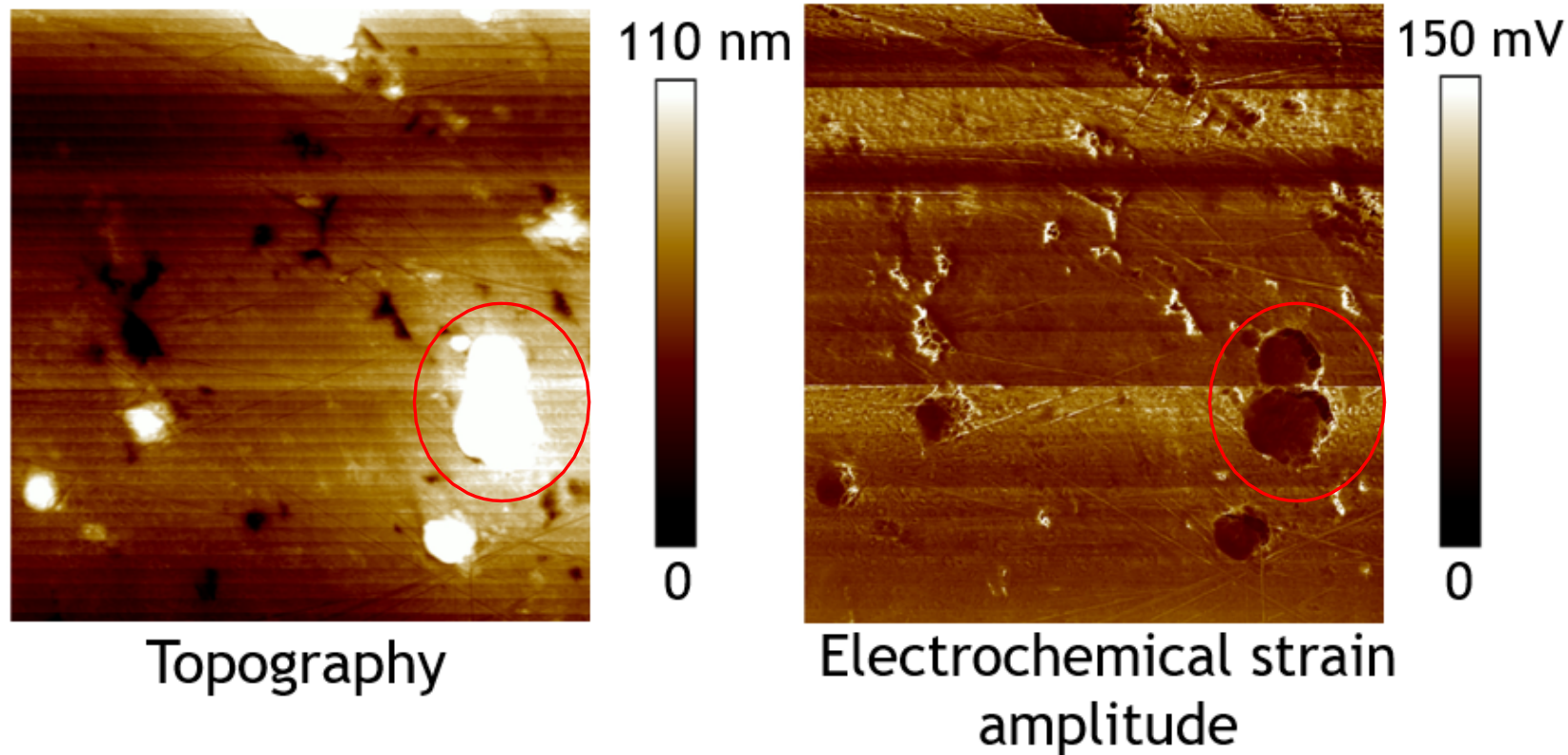
Exposed and cycled in symmetric sodium test cell



Sodium conduction causes mechanical changes in NaSICON



Discolored features form after excessive cycling; these features have high modulus and hardness



By applying an AC voltage at the surface-probe interface, local volume changes due to ionic movement can be detected

Ionic mobility of Na in NaSICON can be correlated with surface features (pores, secondary phases, grains, and boundaries)



Publications:

R. Hill, A.S. Peretti, L.J. Small, E.D. Spoerke, and Y.-T. Cheng. “Characterizing Mechanical and Microstructural Properties of Novel Montmorillonite-rich Polyethylene Composites.” *J. Mater. Sci.* (2021)

D. Arnot, M. Lim, N. Bell, N. Schorr, R. Hill, A. Meyer, Y.-T. Cheng, and T. Lambert. “High Depth-of-Discharge Zinc Rechargeability Enabled by a Self-Assembled Polymeric Coating.” *Adv. Energy Mater.* (2021)

E.D. Spoerke, A.S. Peretti, S.J. Percival, L.J. Small, R. Hill, and Y.-T. Cheng. “Clay based ion conductors: A dirt cheap separator?” In preparation for submission to *J. Mater. Chem. A.* (2021).

Presentations:

R. Hill, M.Gross, A. S. Peretti, L. J. Small, E. D. Spoerke, Y.-T. Cheng “Structural and Mechanical Characterization of NaSICON Solid Electrolytes Upon Cycling in Molten Sodium .” 2021 MRS Fall Meeting and Exhibit, Boston, MA, Nov. 2021.

E. D. Spoerke, A. S. Peretti, S. J. Percival, L. J. Small, M. M. Gross, E. Schindelholz, M. Melia, S. B. Rempe, D. Nelson, S. Russo, R. Hill, and Y.-T. Cheng, “Controlling Ion Transport in Multilayered Polymer Composites.” Layered Polymeric Systems (ACS Polymer Division) - 2020, Windsor, CA, Feb. 2020. (Invited)



- Characterized the structure and mechanical properties of freshly made and electrochemically cycled NaSICON
 - The mechanical properties of NaSICON sodium ion conductors are affected by sodium conduction.
 - Electrochemical cycling can alter modulus and hardness in NaSICON.
- Excessive cycling can lead to secondary phases, discolored features, and dendrite formation that change mechanical properties in NaSICON. Will map mechanical properties using grid indentation and AFM, along with FIB/SEM and EBSD, to help establish relationships between microstructure, mechanical properties, and electrochemical performance and durability.
 - Grain vs. grain boundary properties that may lead to preferential Na plating
- Temperature could affect electrochemical and mechanical properties of NaSICON
 - High-temperature indentation
 - Coupled thermal-mechanical-electrochemical effects



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Thank you