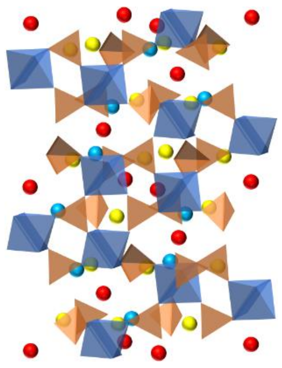
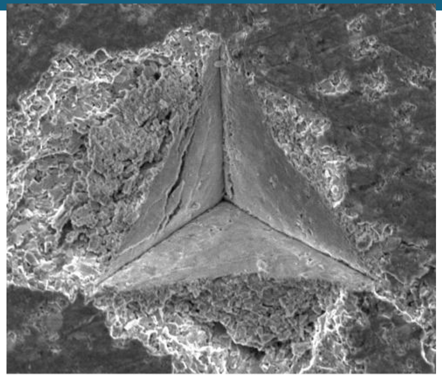
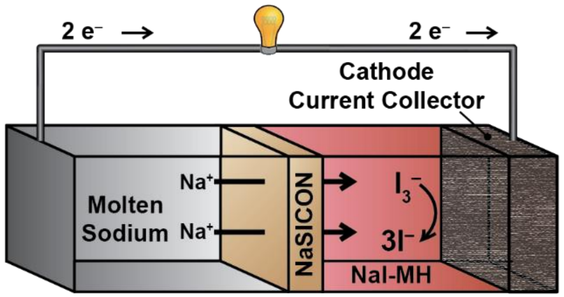
Mechanical, Microstructural, and Electrochemical Characterization of NaSICON Sodium Ion Conductors







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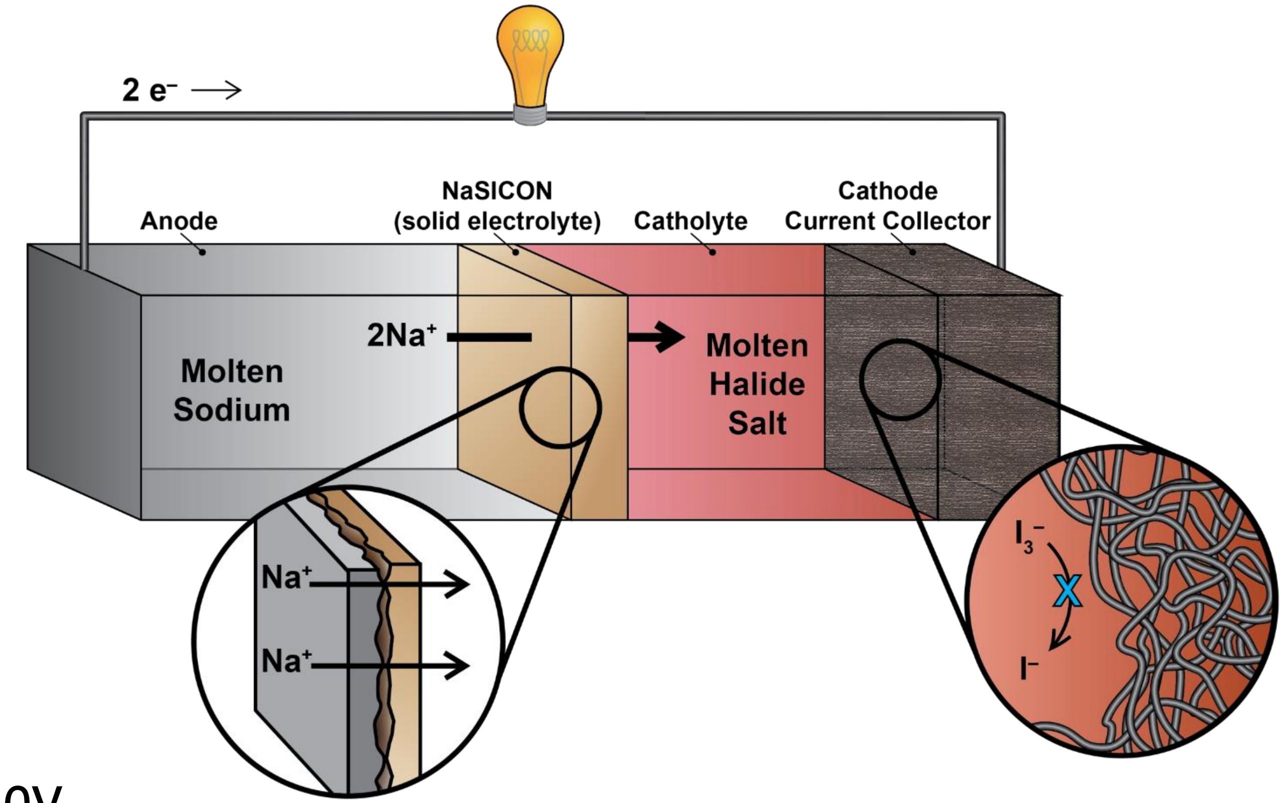
Background and Motivations: Low Temperature Molten Sodium (Na-NaI) Batteries

*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:

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

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

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

Martha Gross

“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

FY20: *In situ* exposure or environmental tests of basic materials and components identified in FY19

- **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)**

FY21: *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

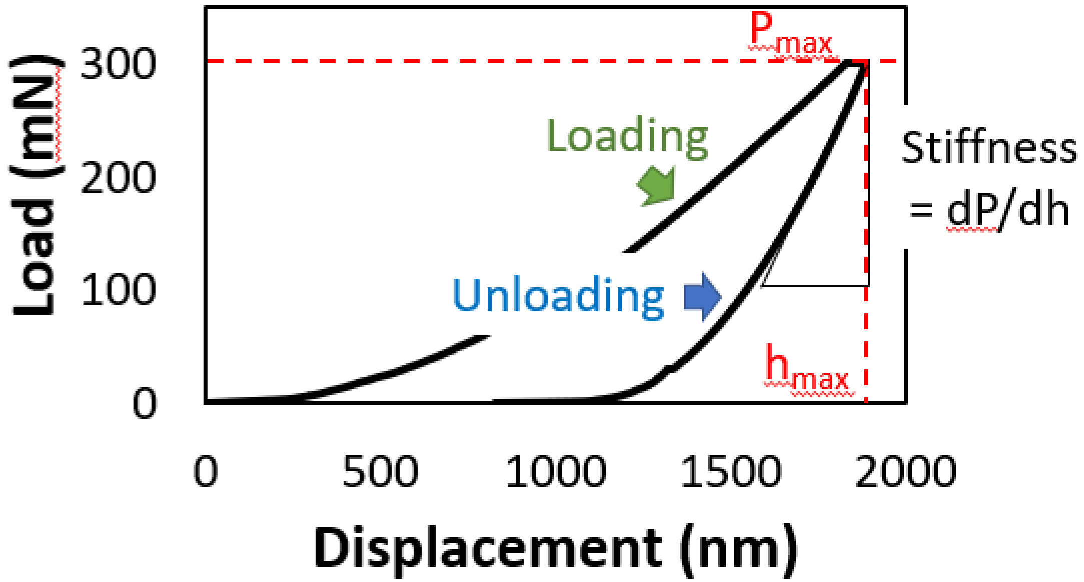
Methodology: Nanoindentation and Scanning Probe Microscopy inside a Glovebox

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: Micro- and Nano-indentation, Scratch, Impact tests up to 650^{o}C

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

Check for updates

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

Ryan Hill[1,*], Amanda S. Peretti[2], Leo J. Small[2], Erik D. Spoerke[2], and Yang-Tse Cheng[1]

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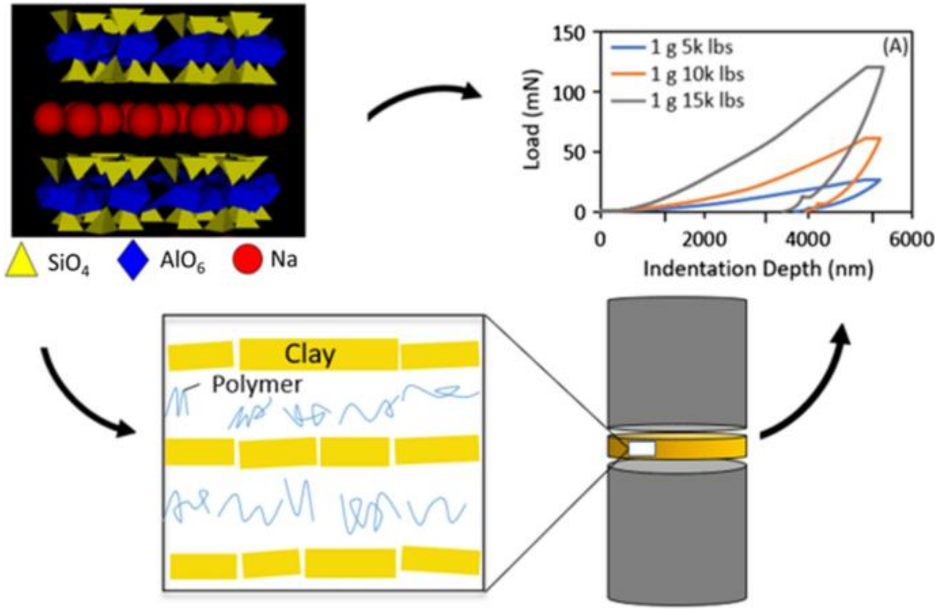
[2] *Sandia National Laboratories, Albuquerque, NM 87123, USA*



- 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.

https://doi.org/10.1007/s10853-021-06562-1

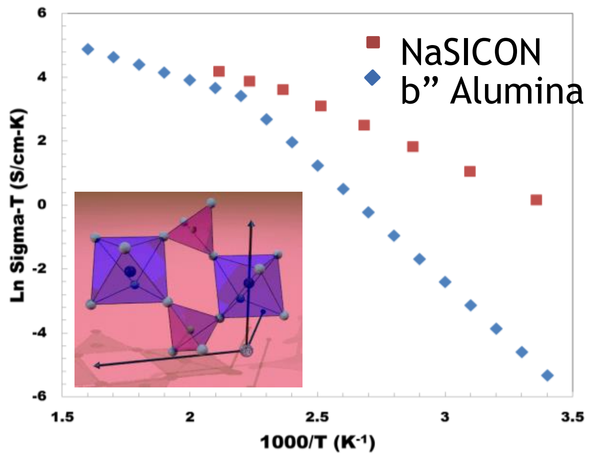
Springer

Published online: 04 October 2021

NaSICON Separator

Key Qualities of NaSICON Ceramic Ion Conductors

- $Na_3Zr_2PSi_2O_{12}$
- High Na-ion conductivity (>10^{-3} S/cm at 25^{o}C)
- Chemical Compatibility with Molten Na and Halide salts
- Zero-crossover
- Mechanical integrity???



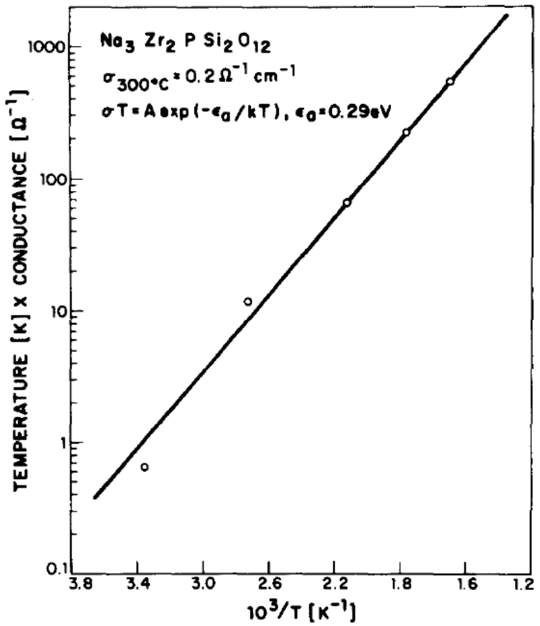
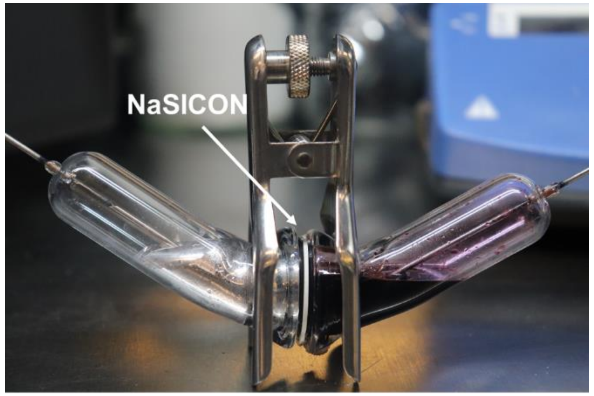


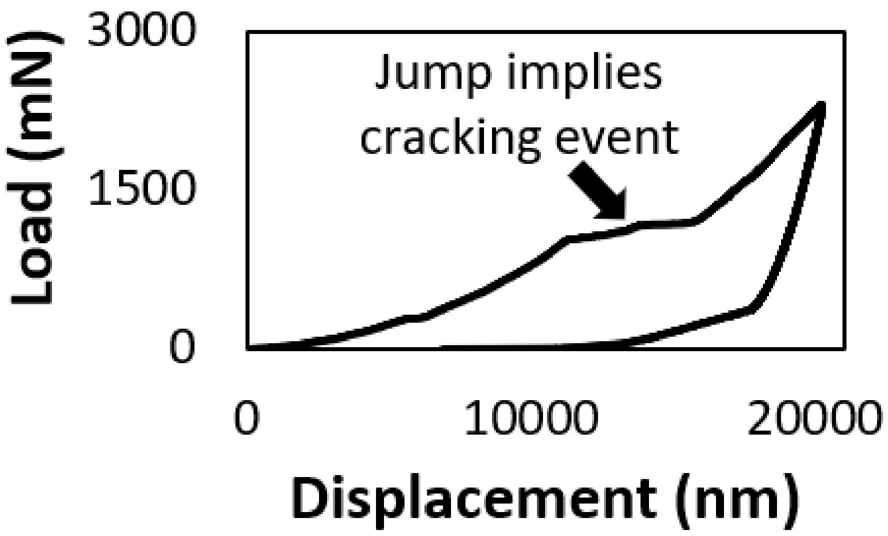
FIG. 8
Temperature - conductance product T/R vs 1/T for a typical ceramic specimen of $Na_3Zr_3PSi_2O_{12}$ with graphite electrodes at 500 kHz.

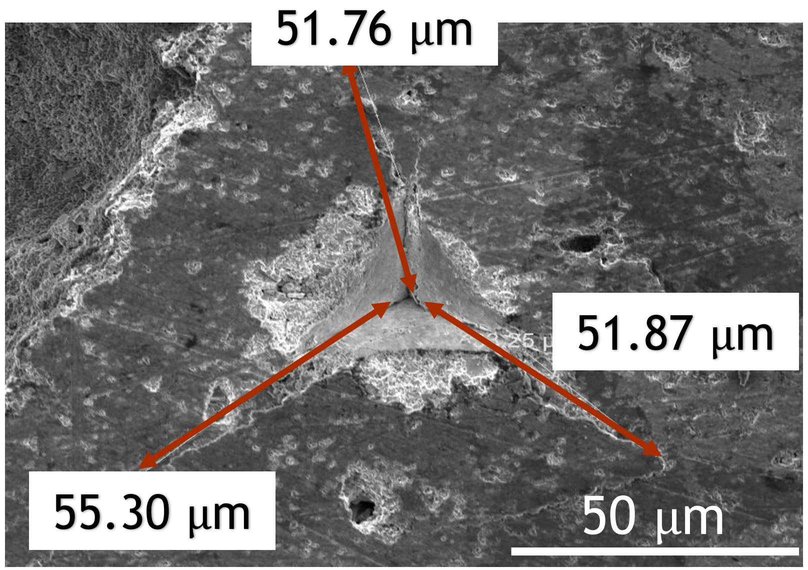
Goodenough, J. B., et al. (1976). "Fast Na+-ion transport in skeleton structures." Materials Research Bulletin **11(2):**



Molten Na Battery Cell Set-Up

Methodology: Mechanical Characterization of Sodium Ion Conductors: Fracture toughness





Cracks can be measured by SEM

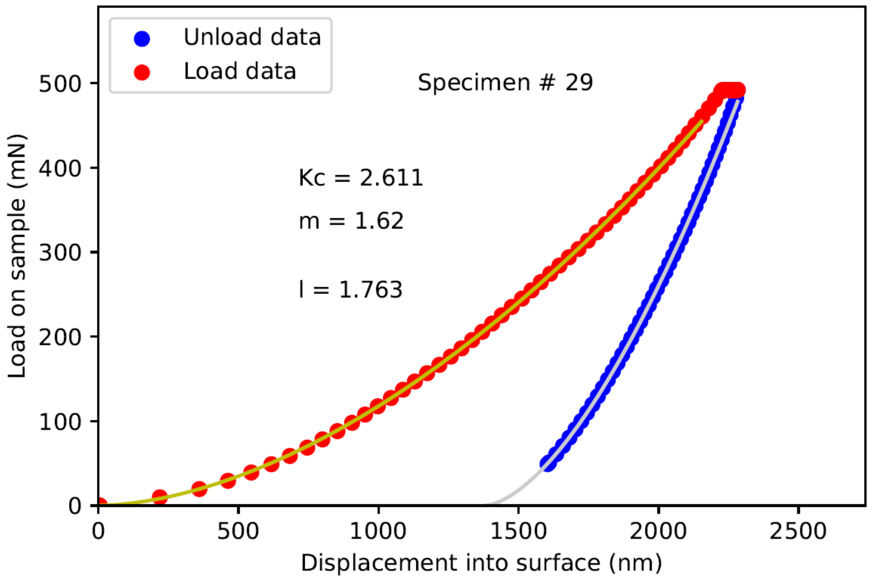
Fracture toughness then calculated by:

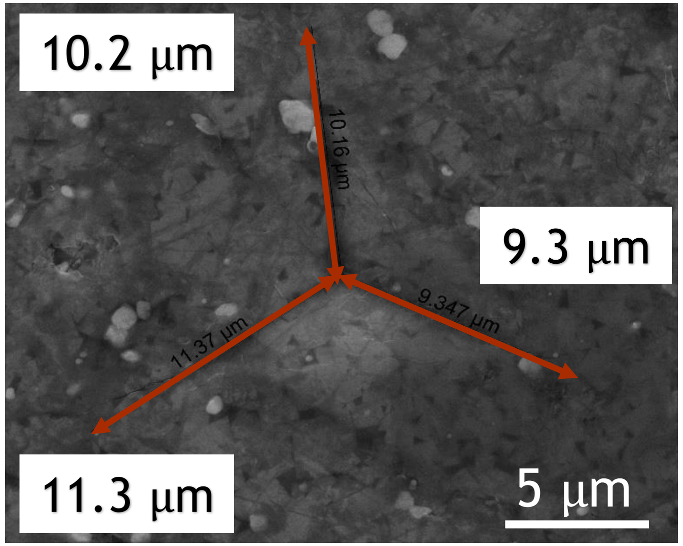
$$K_c = A\left(\frac{E}{H}\right)^{\frac{1}{2}}\left(\frac{P}{c^{\frac{3}{2}}}\right)$$

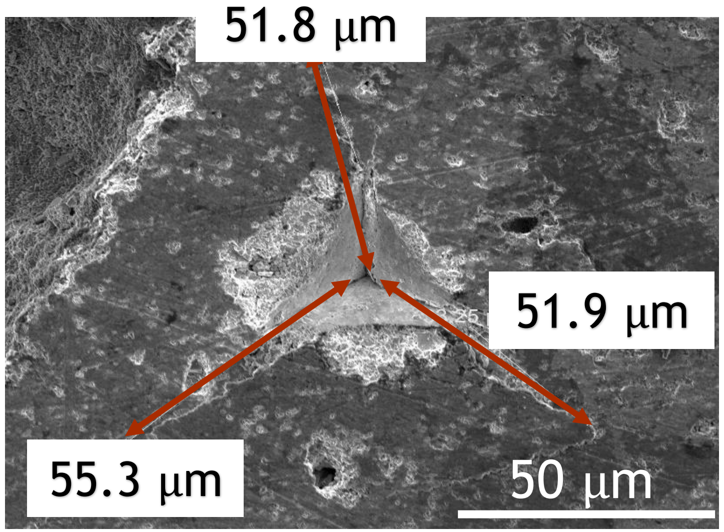
A: Material independent constant = 0.040 ± 0.004
E: Young's Modulus
H: Hardness
P: Maximum load during indentation
c: Length of crack measured by SEM

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





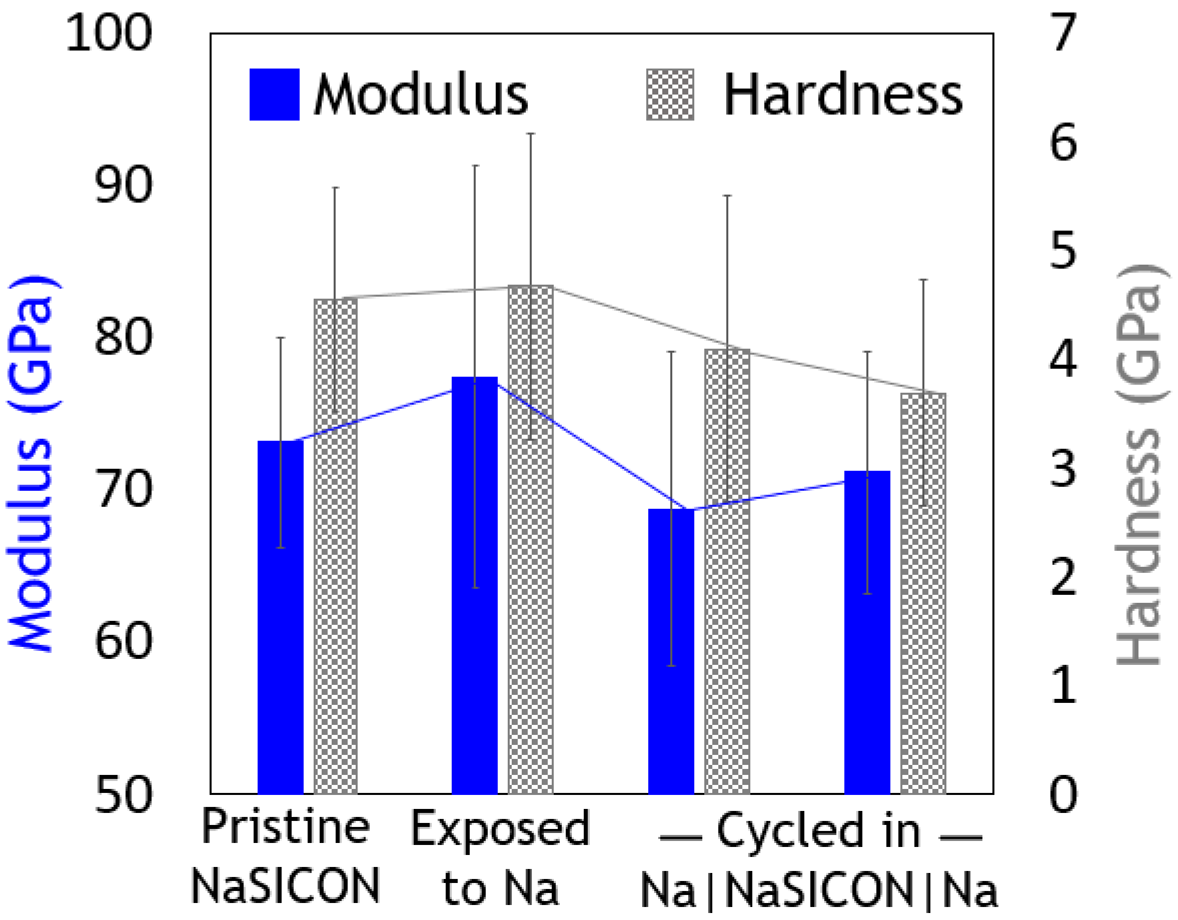


Material	K_{Ic} (MPa√m)
SiC	3.00-6.00
MgO	2.50
Fused Silica	0.80
WC	6.00-20.00
NaSICON (crack length)	1.90 ± 0.60
NaSICON (energy-based)	3.30 ± 0.40

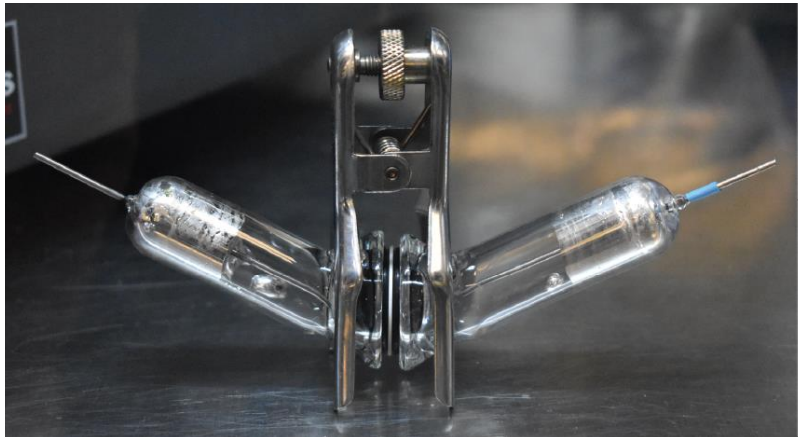
Energy-based method allows for situations where:

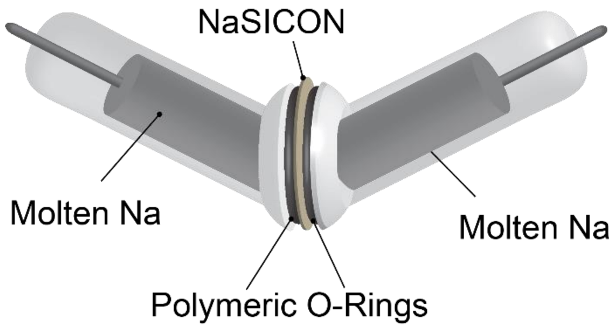
- Crack lengths are small relative to the size of the indents
- Cracks are subsurface
- Ease of measurement

Results: Mechanical and Microstructural Characterization of NaSICON



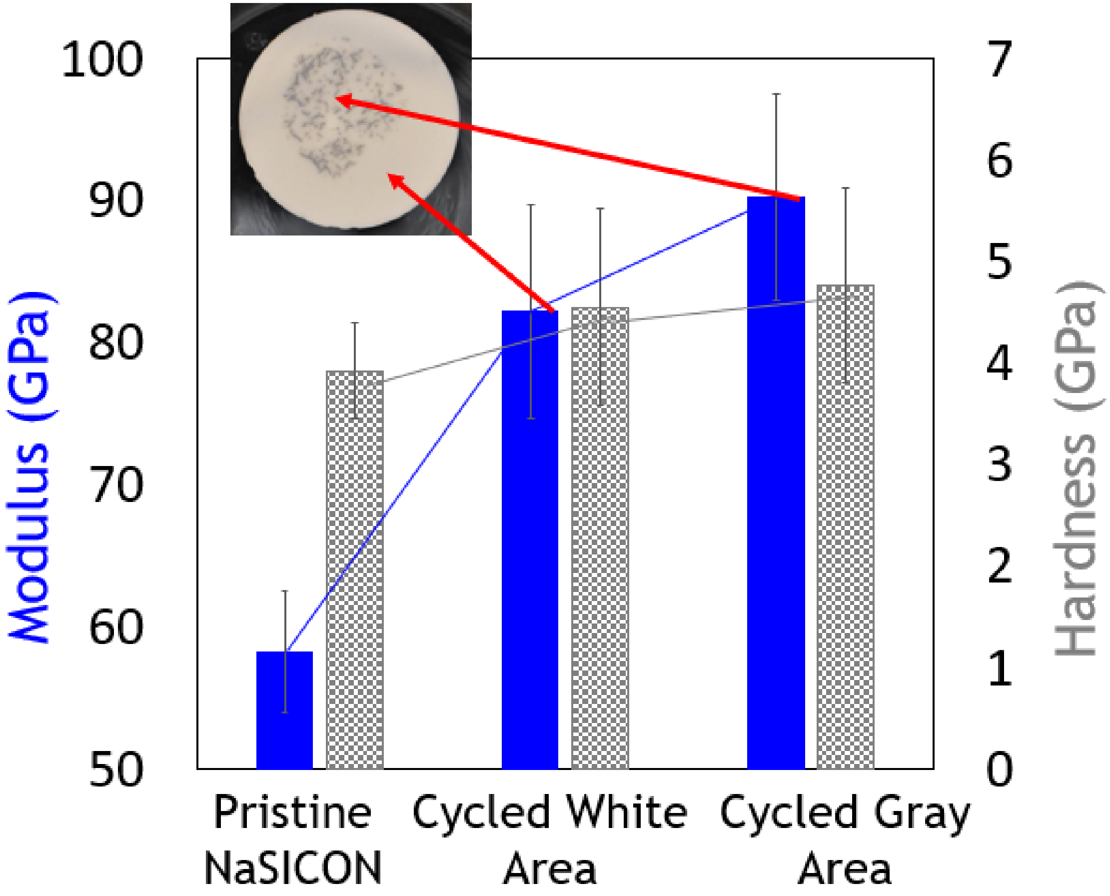
Exposed and cycled in symmetric sodium test cell





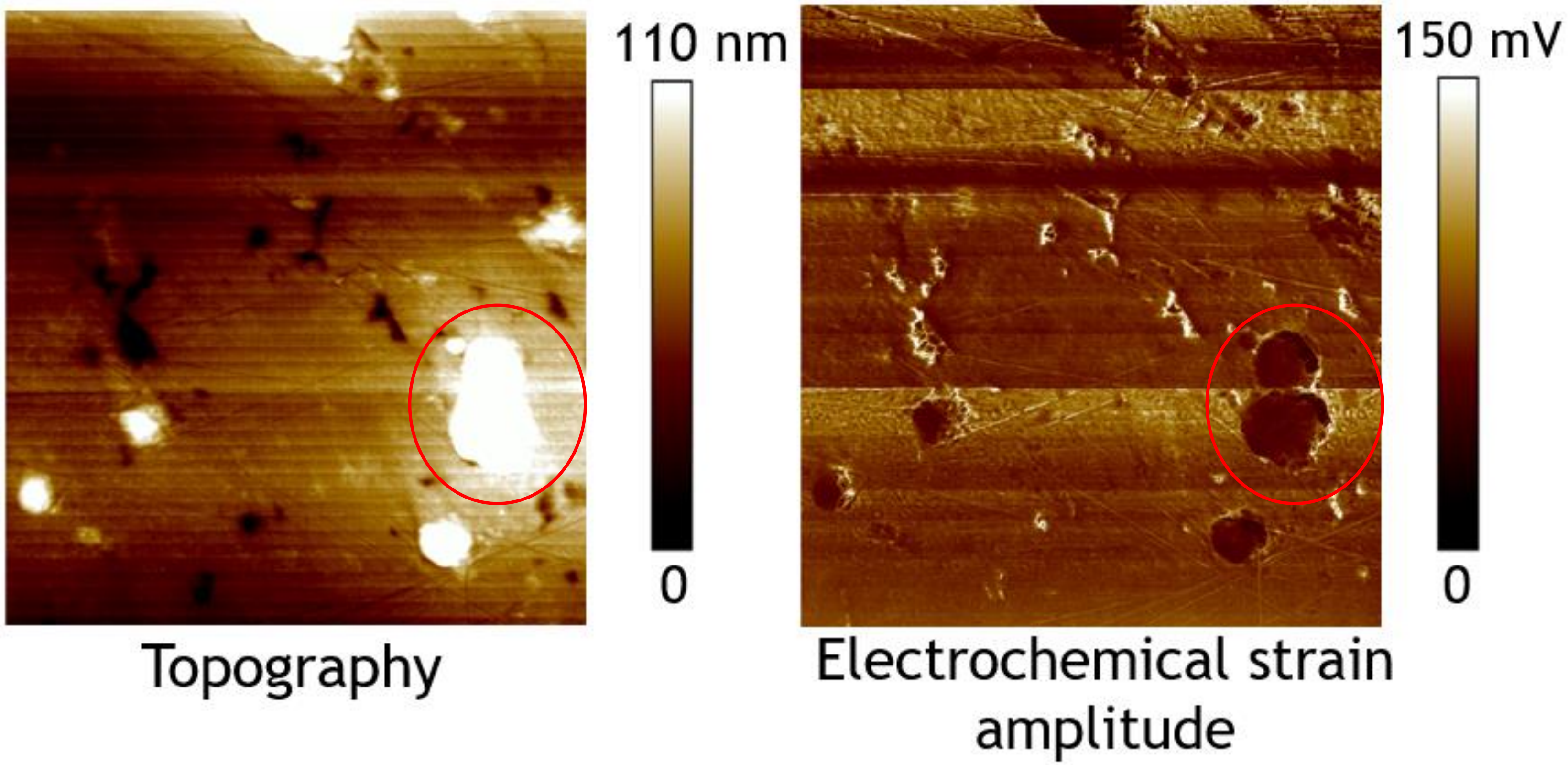
Sodium conduction causes mechanical changes in NaSICON

Results: Mechanical and Microstructural Characterization of NaSICON



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

Results: Mechanical and Microstructural Characterization of NaSICON



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)

Programmatic accomplishments

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)**

Conclusions and future work

- 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

Acknowledgments

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Thank you