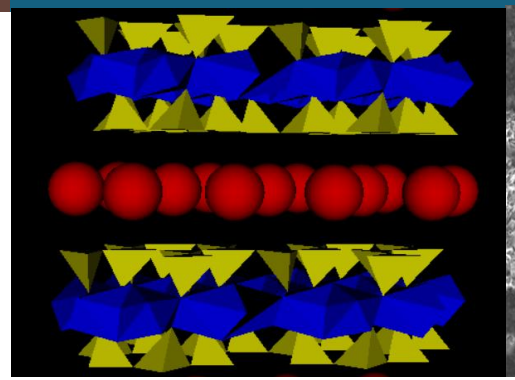
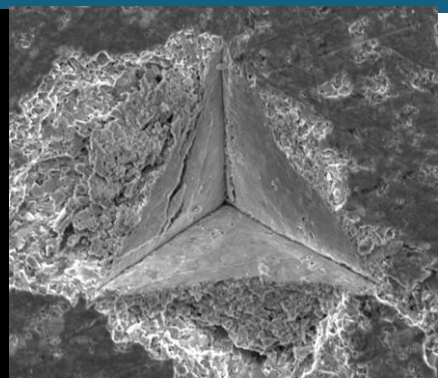
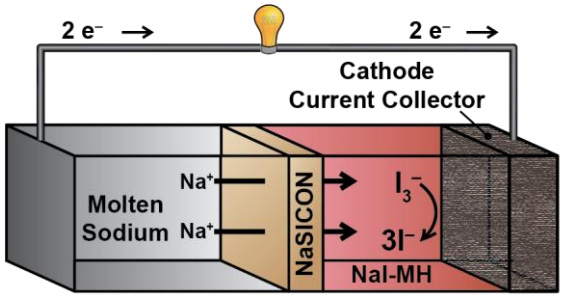
Multi-scale Characterization of the Structure and Mechanical Properties of Sodium Ion Conductors







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

*University of Kentucky and **Sandia National Laboratories

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

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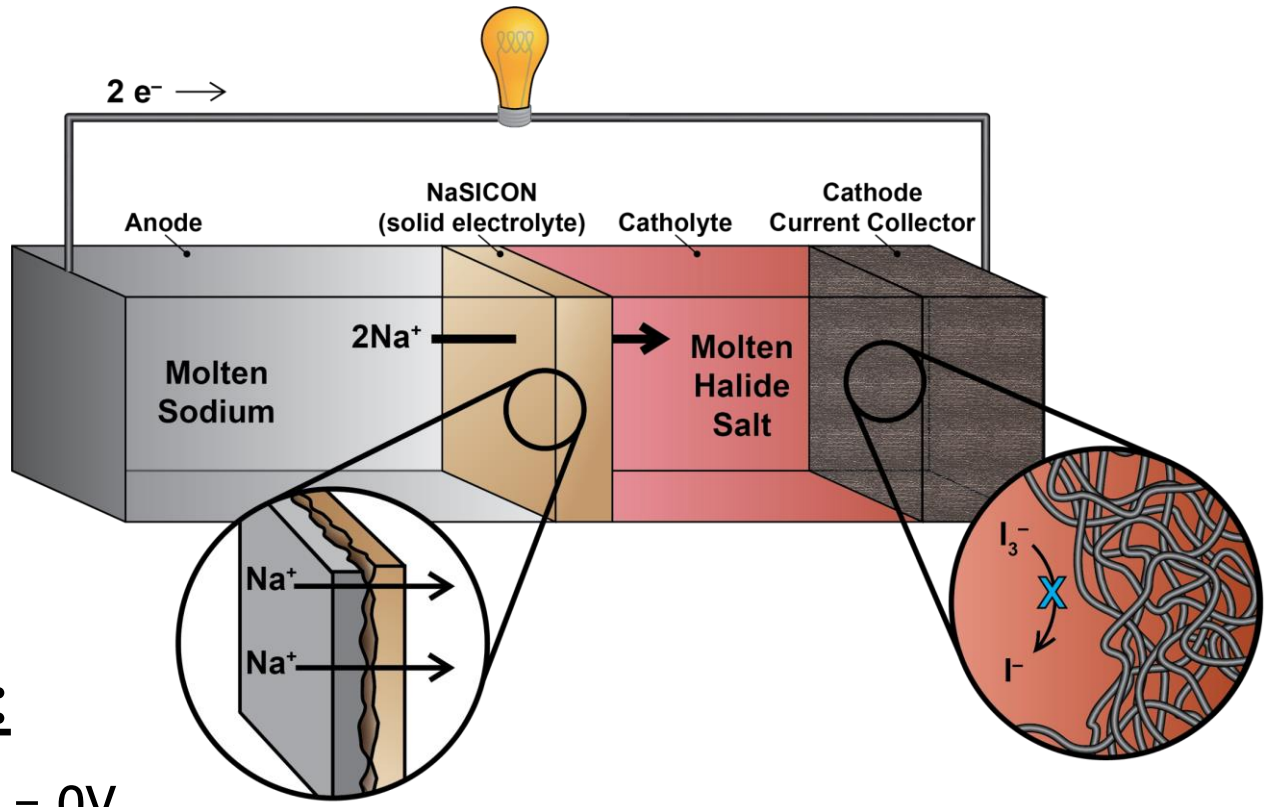
SAND No.: SAND2020-9616 C

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



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

"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.

FY19: Focus on baseline mechanical testing of current materials including ceramics, composites, and polymers

- **Mechanical and Microstructural Characterization of Montmorillonite Sodium Ion Conductors**
- **Mechanical and Microstructural Characterization of NASICON (sodium (Na) Super Ionic CONductor)**

FY20: *In situ* exposure or environmental tests of basic materials and components identified in FY19. As appropriate, *ex situ* testing shall be performed on materials exposed to electrolytes (above) as well as materials used in electrochemical tests.

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

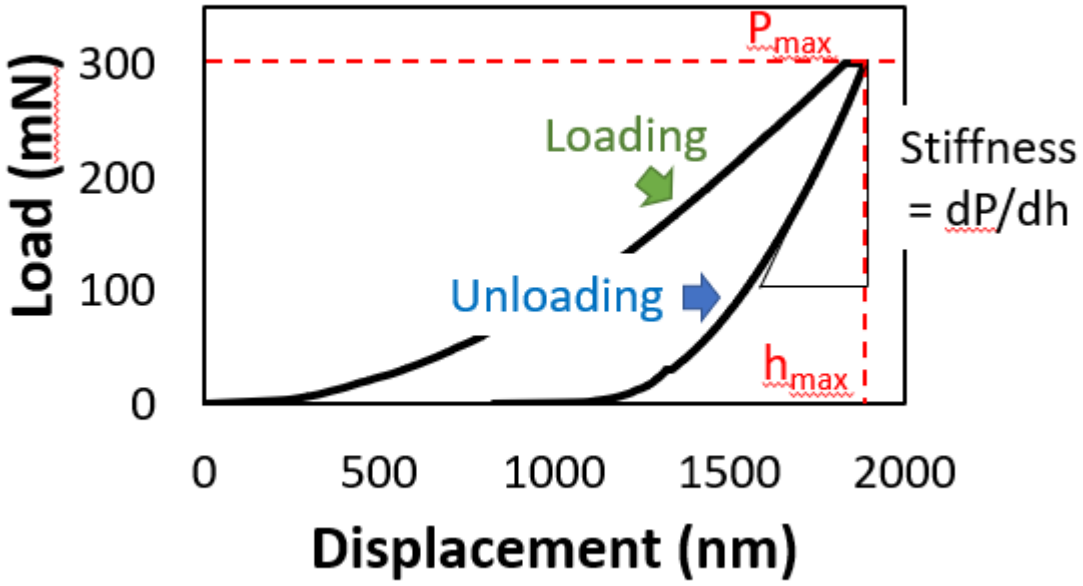
Methodology: Nanoindentation and Scanning Probe Microscopy inside a Glovebox

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°C

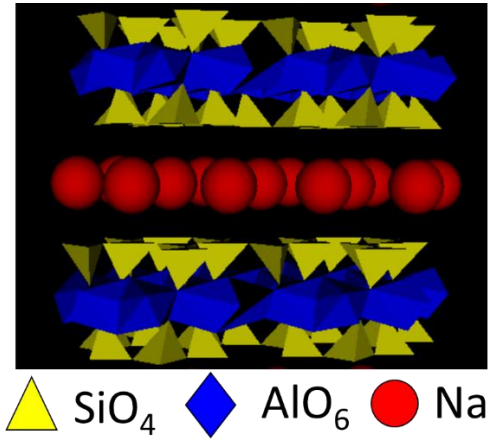
Methodology: Mechanical and Microstructural Characterization of Montmorillonite Sodium Ion Conductors (see Ryan Hill's poster presentation (ID#174) for details)



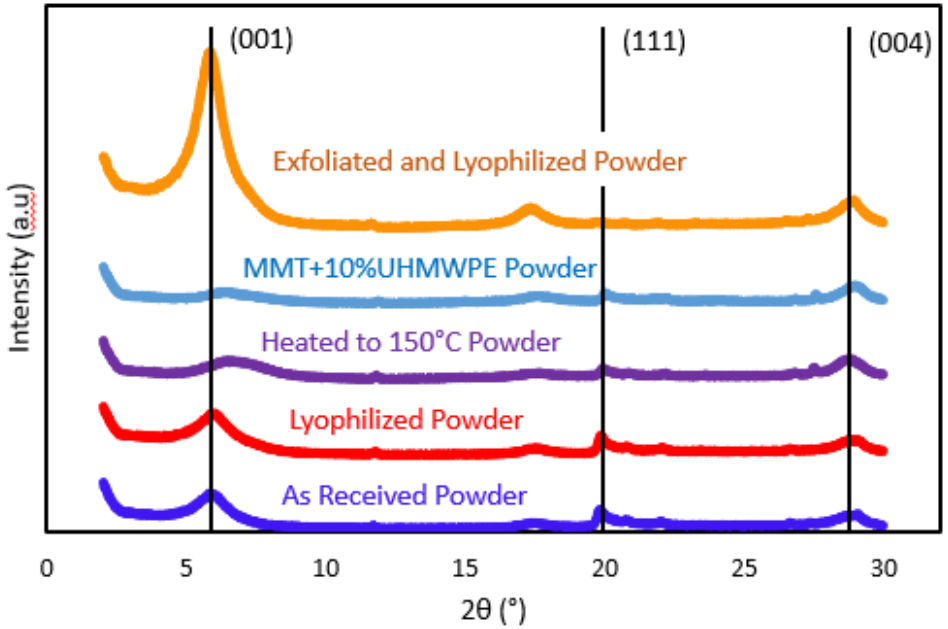
$$\frac{1}{E^*} = \frac{1-\nu^2}{E} + \frac{1-\nu^2}{E'}$$

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

Results: Mechanical and Microstructural Characterization of Montmorillonite Sodium Ion Conductors (see Ryan Hill's poster presentation (ID#174) for details)

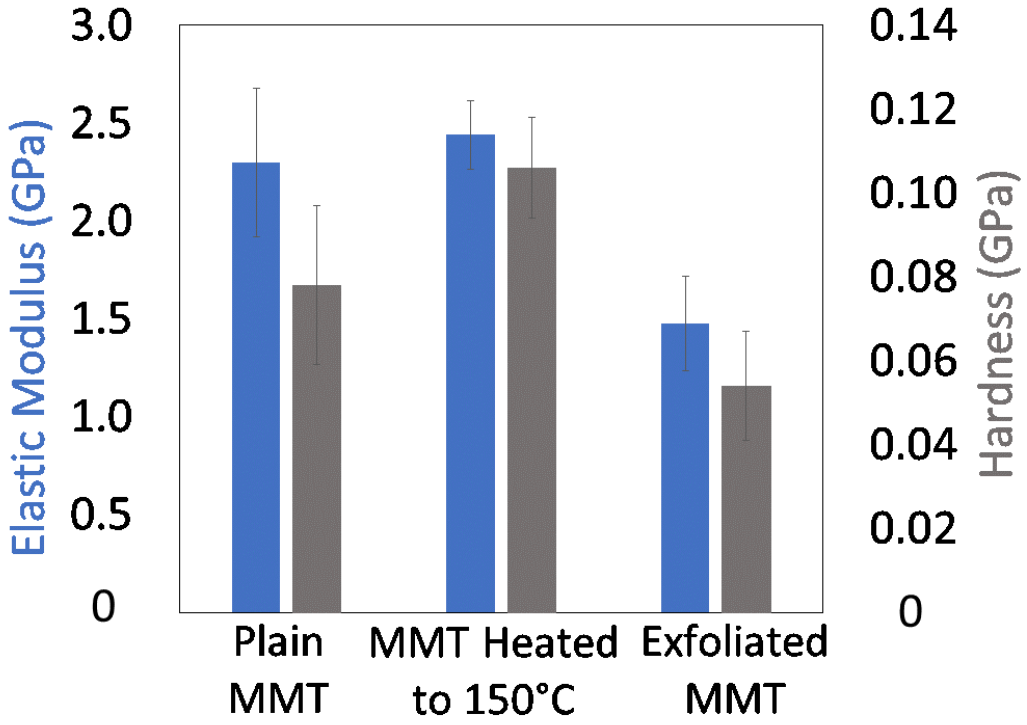


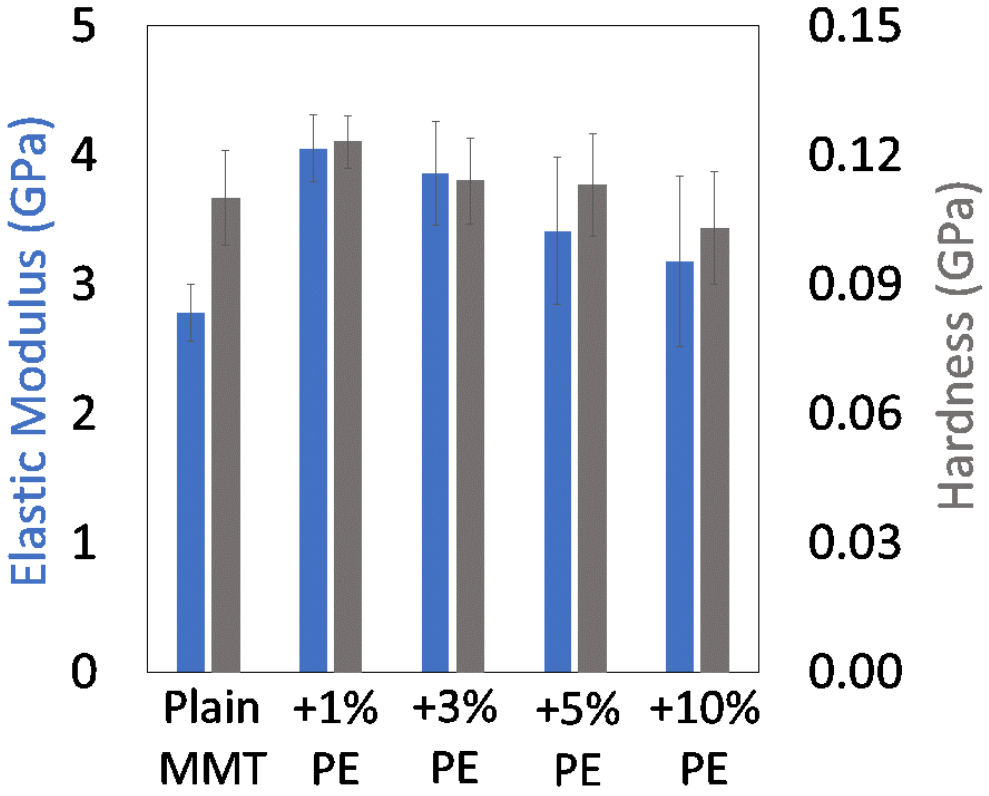
X-ray diffraction



Hypothesis: Clay structure can affect the mechanical properties of clay-based sodium ion conductors

Results: Mechanical and Microstructural Characterization of Montmorillonite Sodium Ion Conductors (see Ryan Hill's poster presentation (ID#174) for details)





Layered structure of MMT clay contributes strongly to mechanical stability

Addition of polymer synergistically enhances modulus and hardness of composites!

NaSICON Separator

Key Qualities of NaSICON Ceramic Ion Conductors

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

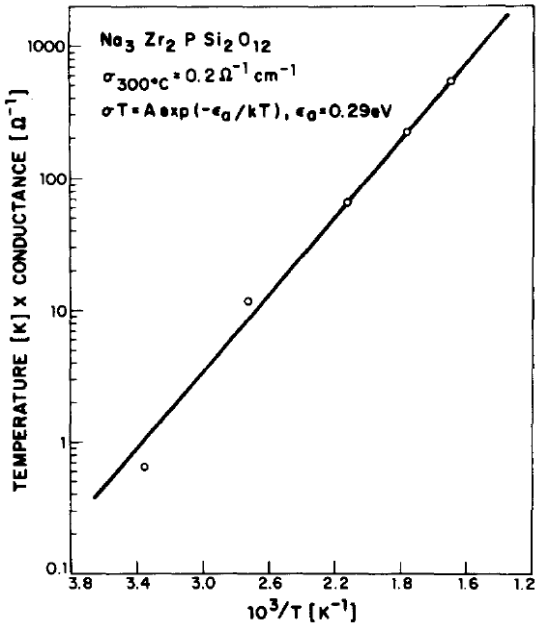
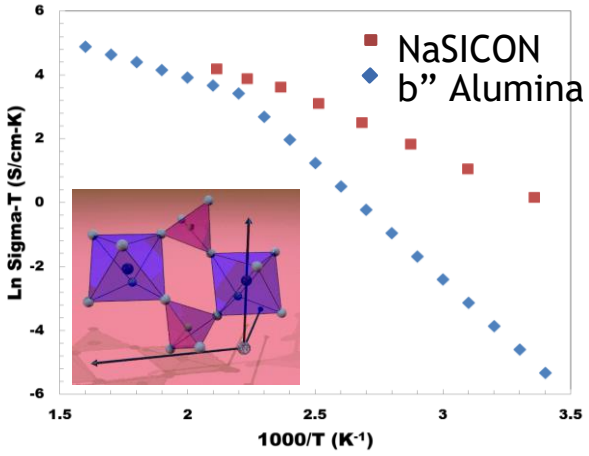
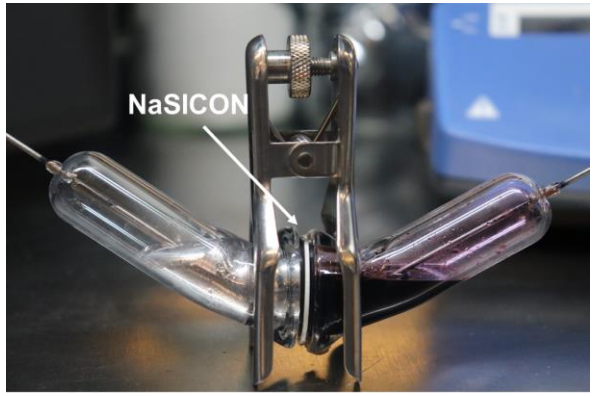


FIG. 8
Temperature - conductance product T/R vs 1/T for a typical ceramic specimen of $Na_3Zr_3PSi_2O_{12}$ with graphite electrodes at 500 kHz.

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

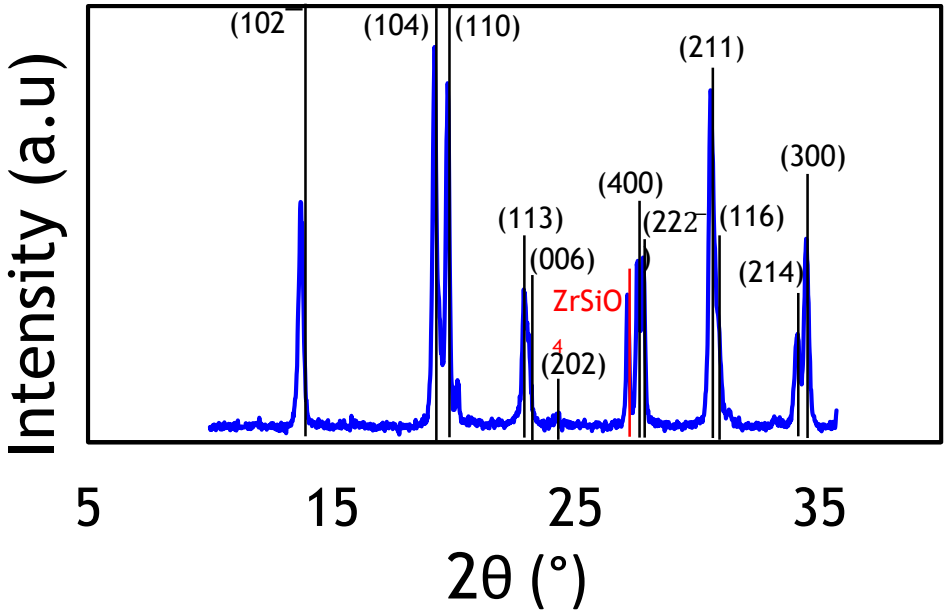




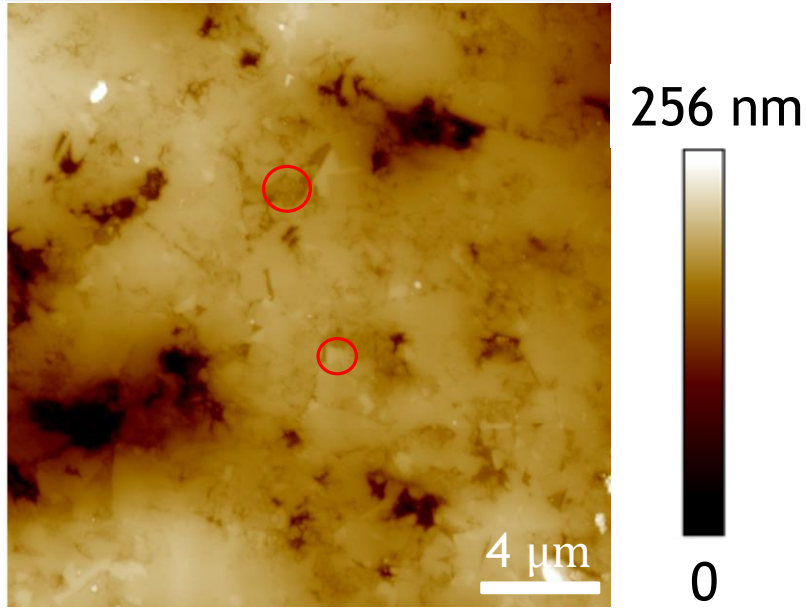
Molten Na Battery Cell Set-Up

Results: Mechanical and Microstructural Characterization of NaSICON

X-ray diffraction

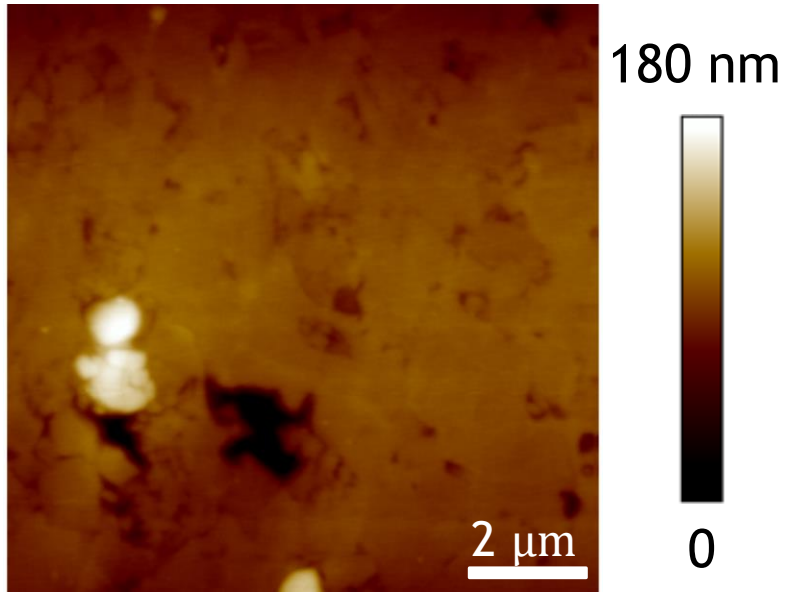


AFM

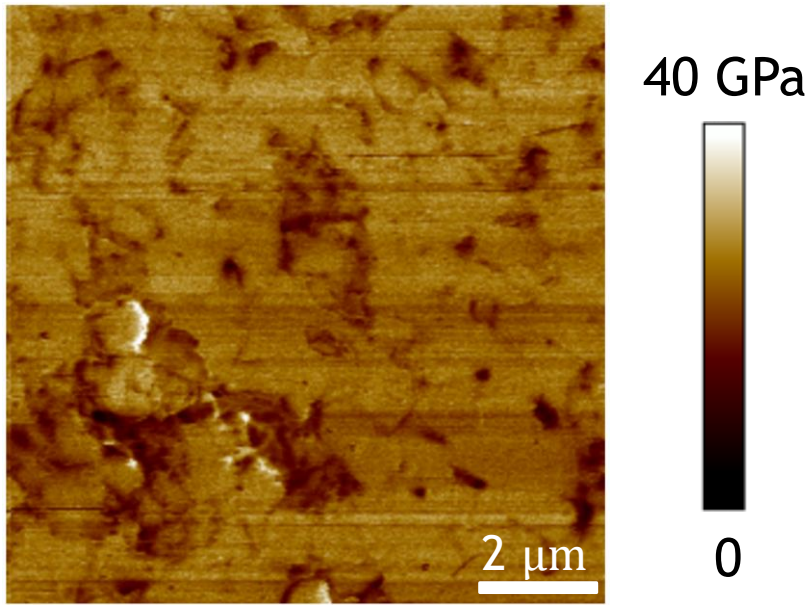


Primary grains and secondary phases can be spatially resolved using AFM

Results: Mechanical and Microstructural Characterization of NaSICON



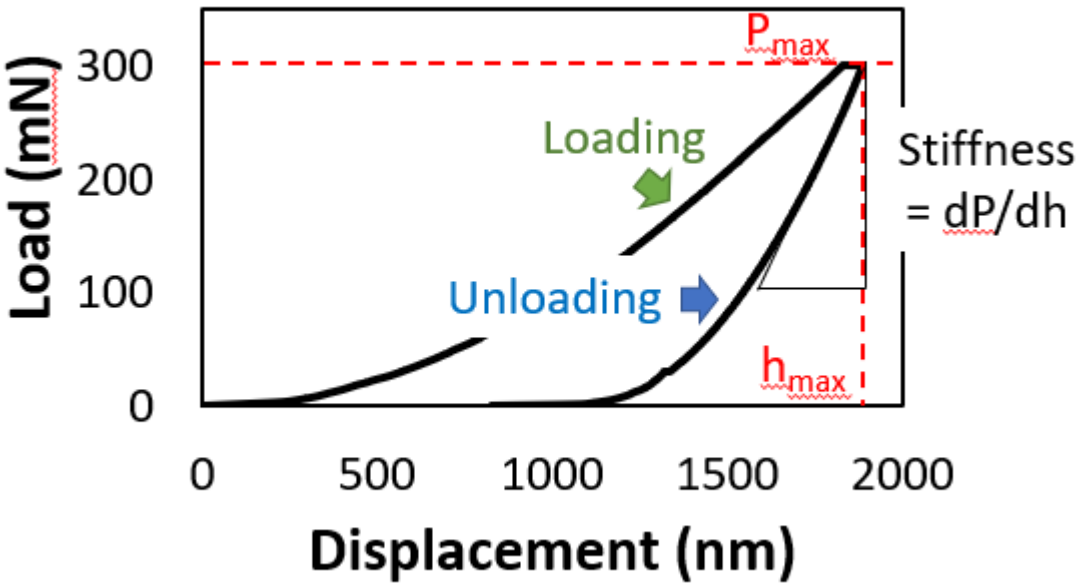
Surface Height



Elastic Modulus

Mechanically different regions can be visualized and reconciled with topographical features and phase differences

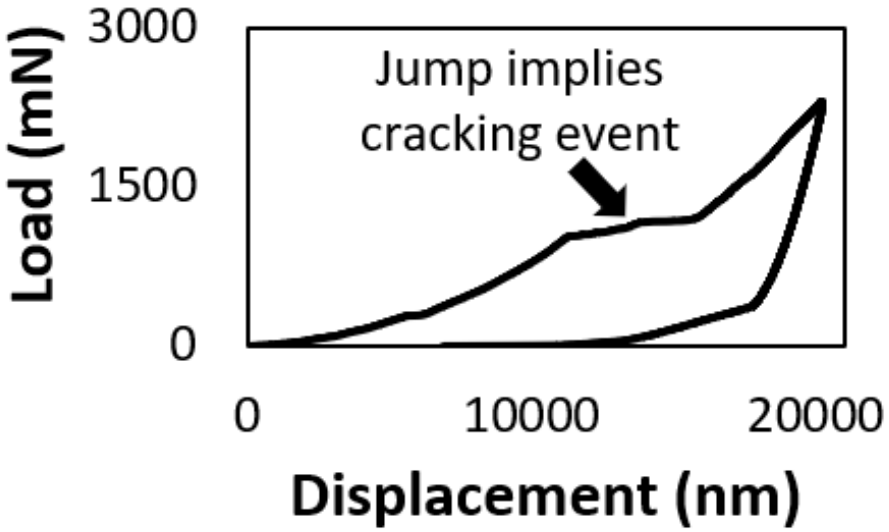
Results: Mechanical and Microstructural Characterization of NaSICON

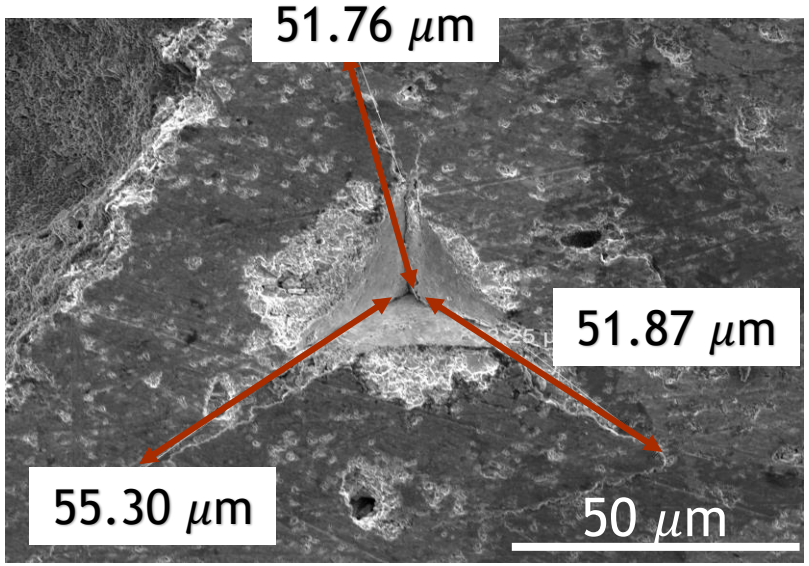


Elastic Modulus (GPa)	Hardness (GPa)
76.32 ± 5.80	4.57 ± 0.55

Baseline mechanical properties of NaSICON – which can be compared with electrochemically cycled ones in further measurements.

Results: Mechanical and Microstructural Characterization of NaSICON





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

Baseline mechanical properties of NaSICON – which can be compared with electrochemically cycled ones in further measurements.

Programmatic accomplishments

Publications:

R. Hill, Y.-T. Cheng, E.D. Spoerke, A.S. Peretti, S.J. Percival, L.J. Small. "Characterizing Mechanical and Microstructural Properties of Novel Montmorillonite-based Sodium Ion Conductors" In preparation for submission to *J. Mater. Chem. A.* (2020).

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.* (2020).

Presentations:

R. Hill, Y.-T. Cheng, E. D. Spoerke, A. S. Peretti, S. J. Percival, L. J. Small, "Characterizing Mechanical and Microstructural Properties of Novel Montmorillonite-Based Sodium-Ion Conductors." 2020 MRS Spring and Fall Meeting and Exhibit Presented Jointly, Online, Nov. 2020.

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 montmorillonite sodium ion conductors and NaSICON
- Help optimize synthesis conditions for dense and mechanically robust solid electrolytes
- Will characterize the montmorillonite sodium ion conductors and NaSICON after electrochemical cycling to help understand degradation mechanisms
- Will map mechanical properties using grit indentation and AFM, along with FIB/SEM and EBSD, to help establish relationships between microstructure, mechanical properties, and electrochemical performance and durability

Acknowledgments

We greatly appreciate the support from Dr. Babu Chalamala. This work was in collaboration with Sandia National Labs and was supported by the U.S. Department of Energy Office of Electricity's Energy Storage Program, managed by Dr. Imre Gyuk.

Thank you