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

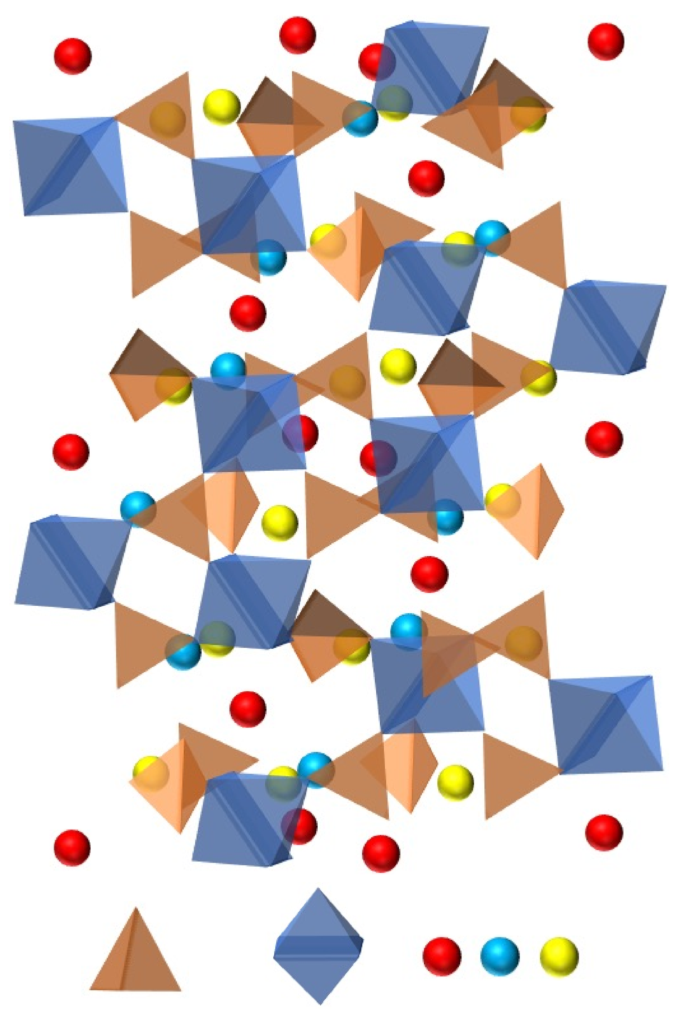
College of Engineering
Department of Chemical and Materials Engineering

Ryan Hill (Ryan.C.Hill@uky.edu)*, Jacob Hempel*, Yang-Tse Cheng*, Erik D. Spoerke**, Leo J. Small**, Martha Gross**, and Amanda Peretti**
*University of Kentucky, Lexington, KY, USA and **Sandia National Laboratories, Albuquerque, NM, USA

Motivation

The DOE Office of Electricity views sodium batteries as a priority in pursuing a safe, resilient, and reliable grid. Improvements in solid-state electrolytes are key to realizing the potential of these large-scale batteries

- NaSICON structure consists of SiO_4 or PO_4 tetrahedra sharing common corners with ZrO_6 octahedra
- Structure forms "tunnels" in three dimensions that can transport interstitial sodium ion
- 3D structure provides higher ionic conductivity than other conductors (β″-alumina), particularly at low temperature
- Lower temperature (cheaper) processing compared to β″-alumina



Objective

Identify fundamental structure-processing-property relationships in NaSICON solid electrolytes to inform design for use in sodium batteries

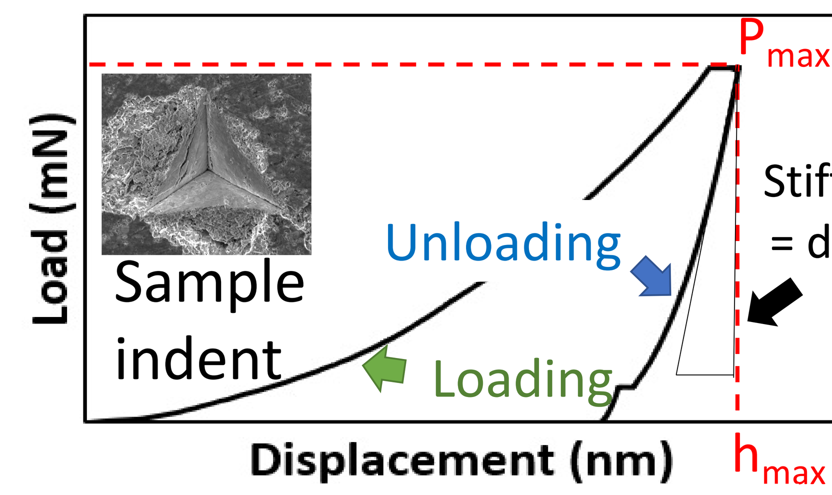
Characterization Methodology

- **Nanoindentation** –small deformation to measure modulus, hardness, and fracture toughness

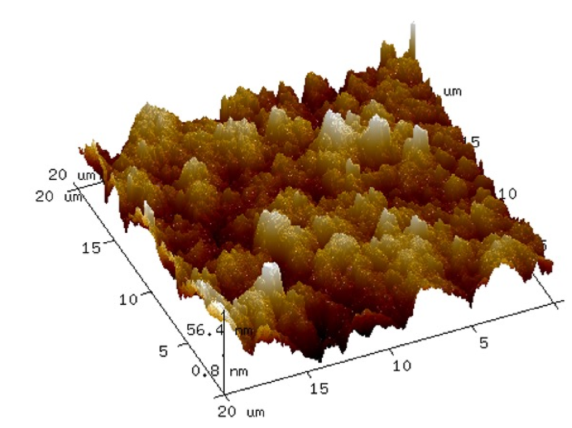
$$\frac{1}{E^*} = \frac{1-\nu^2}{E} + \frac{1-\nu^2}{E'}$$

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

Oliver-Pharr Nanoindentation Equations

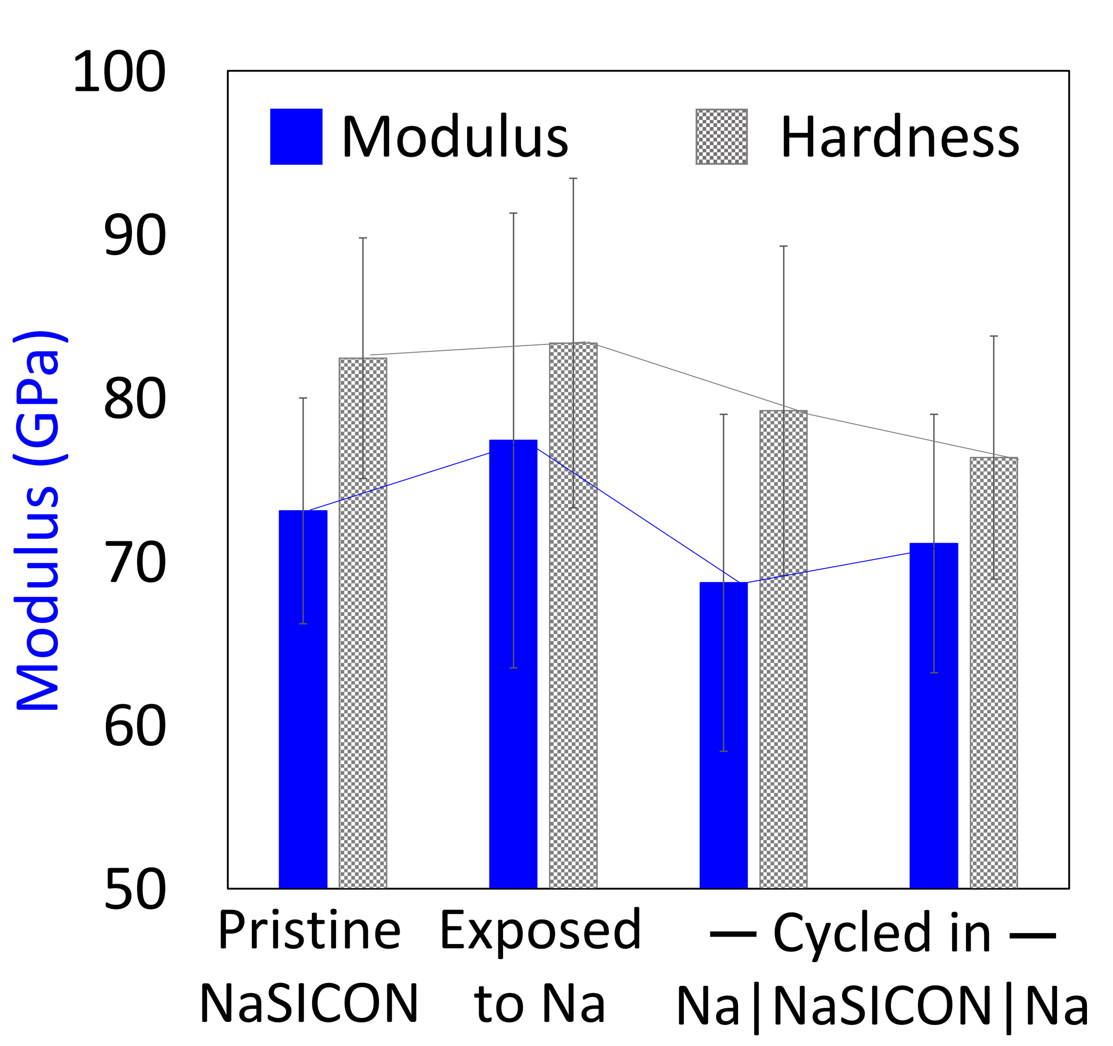


- **Atomic force microscopy** – topography, nanomechanical mapping, electrochemical strain microscopy

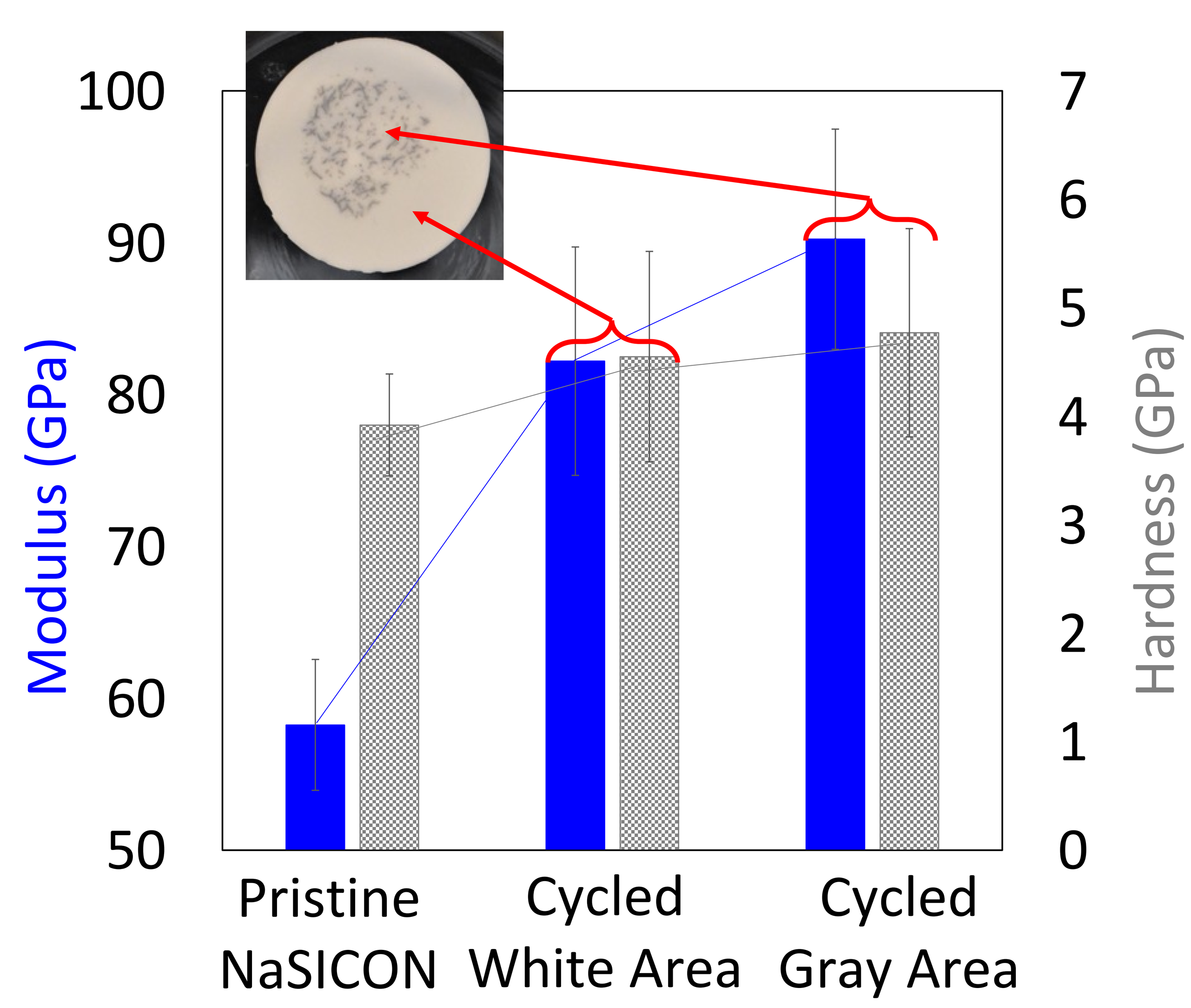


Mechanical properties are affected significantly by:

Electrochemical cycling – exposure to molten sodium symmetric cells

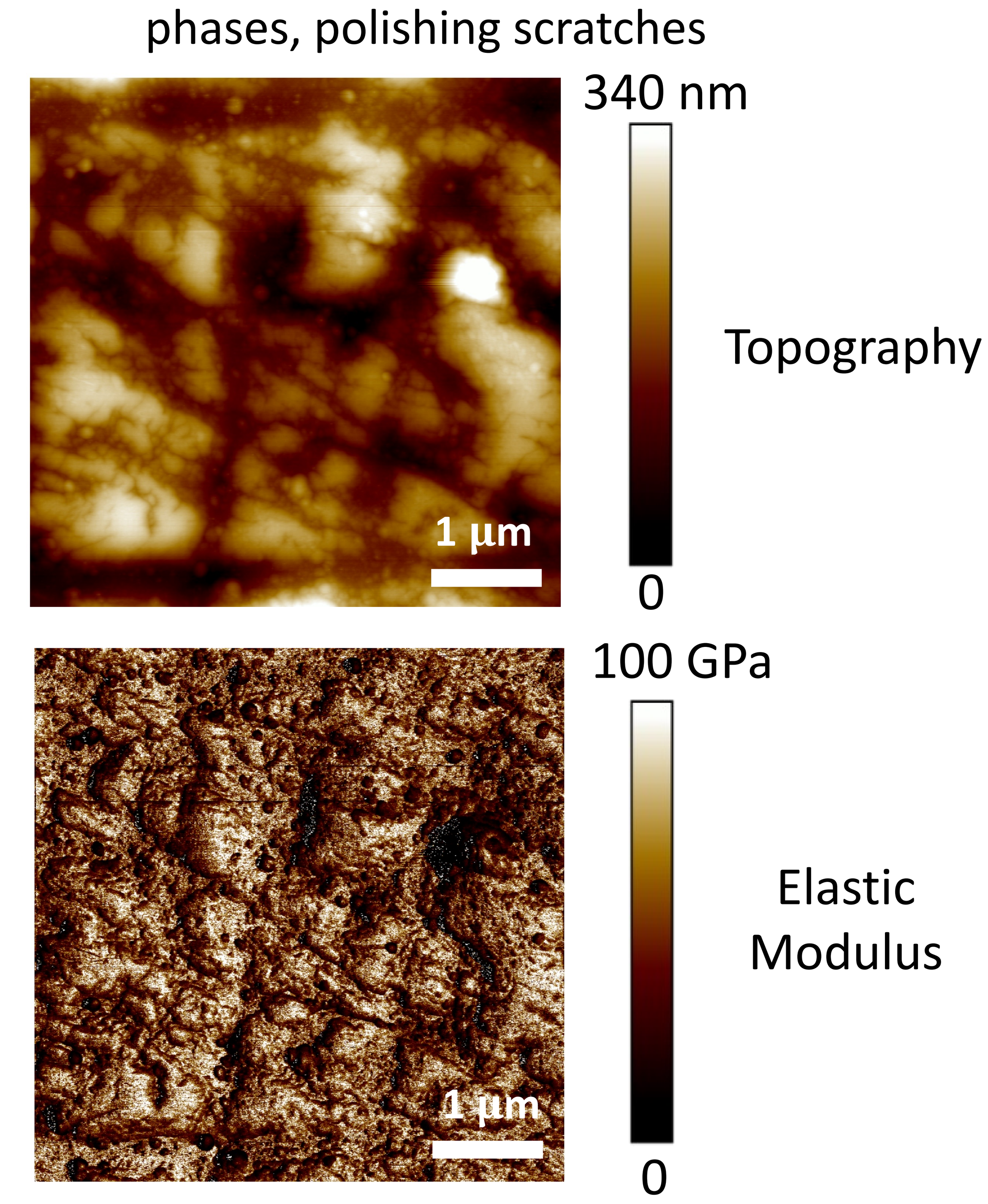


Sodium conduction causes mechanical changes in NaSICON.

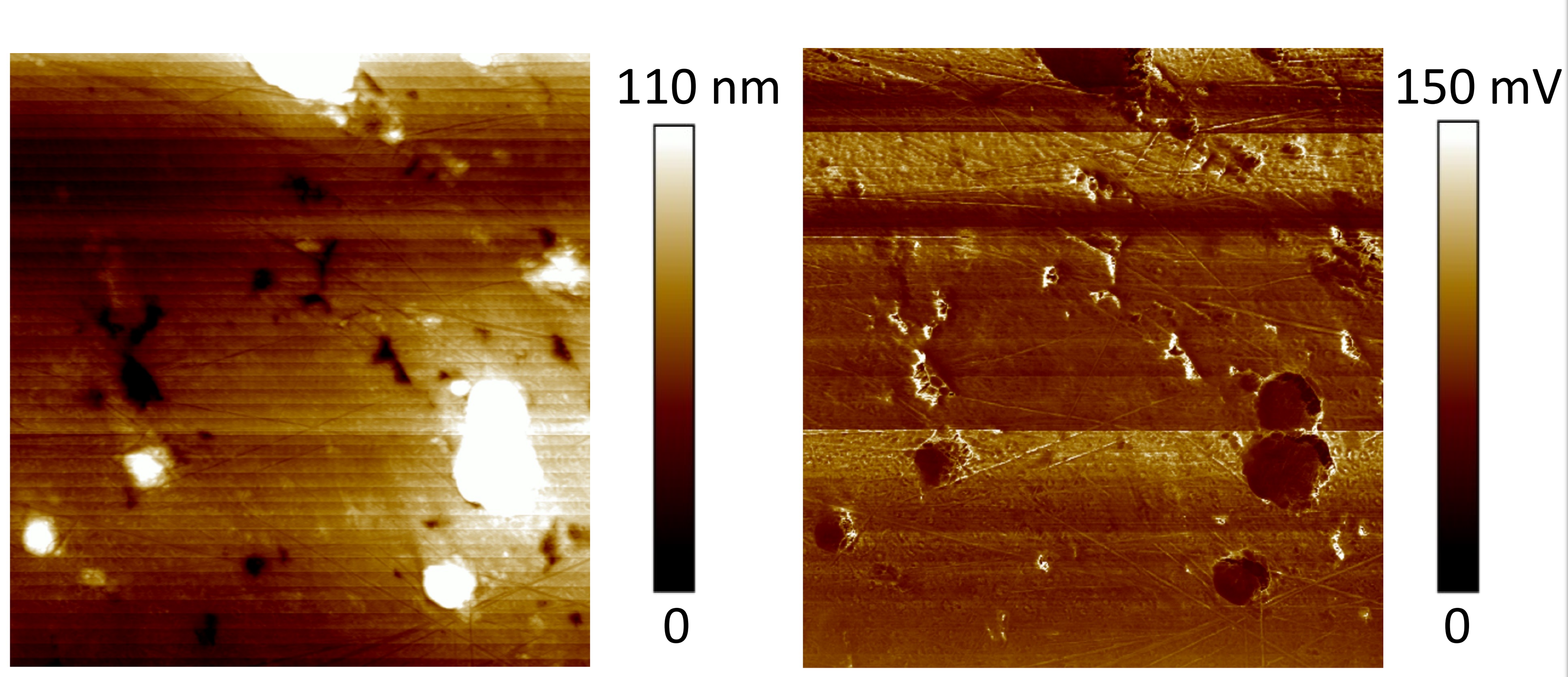


Excessive cycling can precipitate new phases that increase modulus and hardness

Microstructure– grains & boundaries, secondary phases, polishing scratches



Electrochemical Strain Microscopy



Topography

Electrochemical strain amplitude

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

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

Conclusions and Future Work

Conclusions:

- 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 and/or dendrite formation that change mechanical properties in NaSICON.
- Mechanical and electrochemical properties can be correlated with topographical features to further inform design decisions

Future Considerations:

- What microstructural changes drive mechanical changes during cycling?
- Are NaSICON pellets' mechanical performance also affected by interactions with cathode materials?
- For details regarding battery performance see "Low-Temperature Molten Sodium Batteries" presentation and poster by Leo Small and Martha Gross

Acknowledgments

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