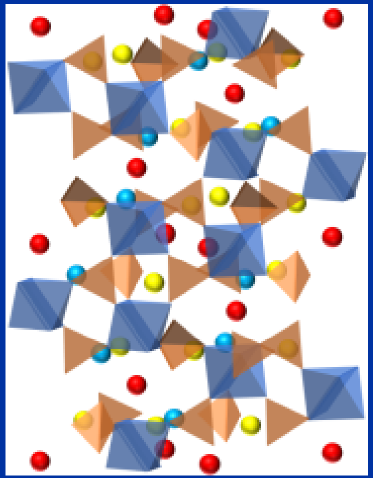
SAND2021-14642C

# Structural and Mechanical Characterization of NaSICON Solid Electrolytes Upon Cycling in Molten Sodium




**Ryan Hill***, Jacob Hempel*, Yang-Tse Cheng*,

Amanda Peretti**, Martha Gross**, Leo Small**, Erik Spoerke**

*University of Kentucky and **Sandia National Laboratories

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

Nov. 29–Dec. 2, 2021



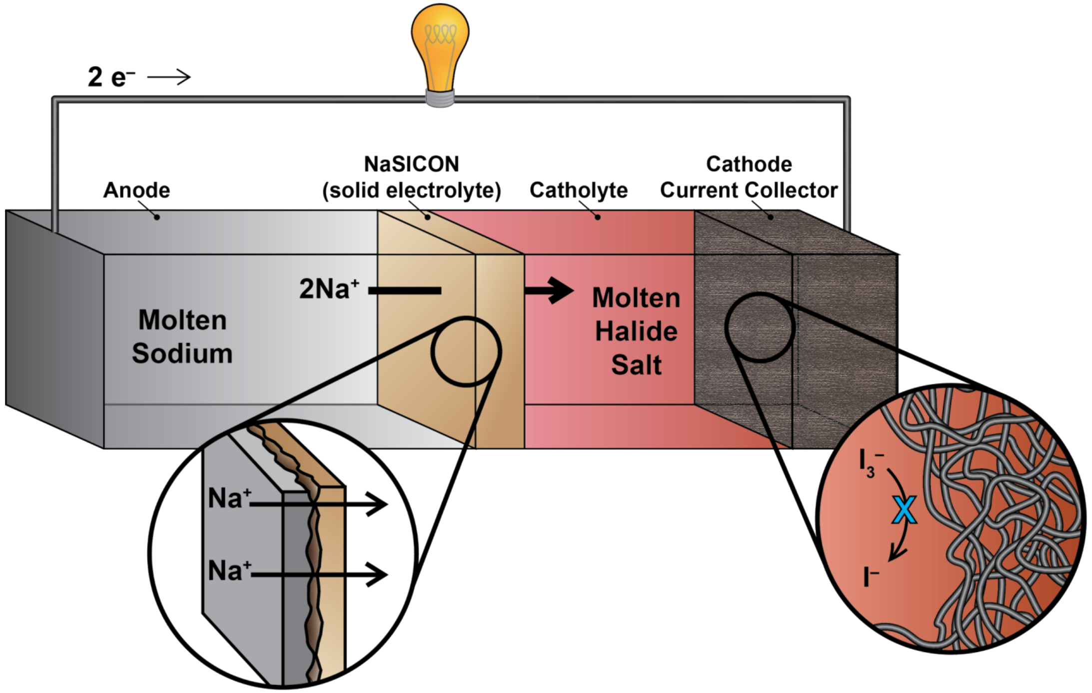
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

# 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***

**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




Martha Gross

**Na-NaI battery:**

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

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

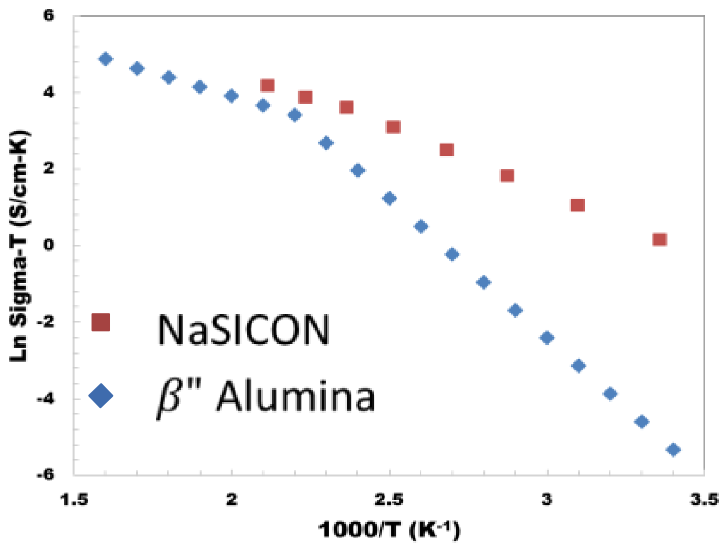
$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0_{cell} = 3.24$ V

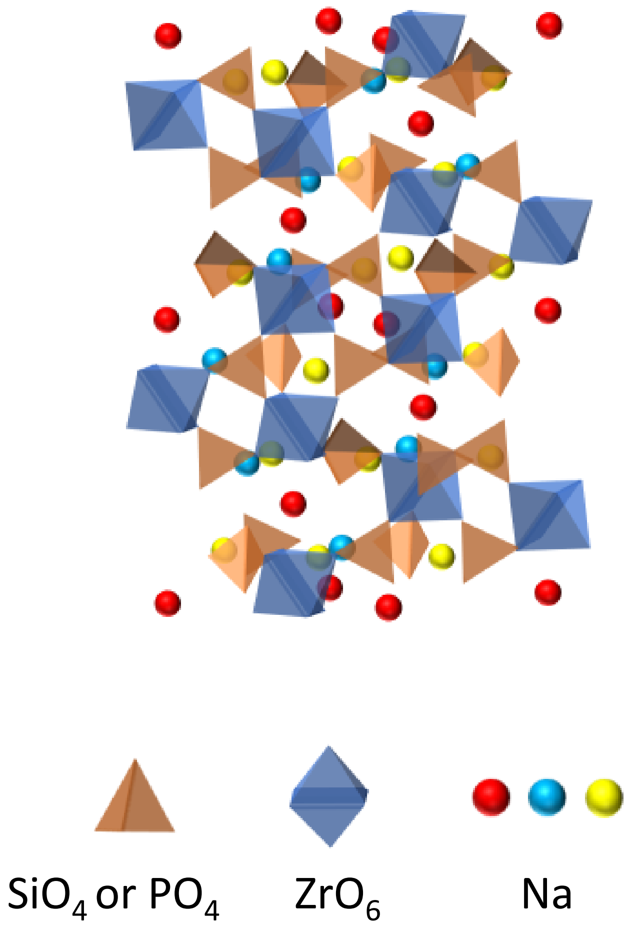
University of Kentucky Sandia National Laboratories

# NaSICON Solid Electrolyte

## Key Qualities of NaSICON Ceramic Ion Conductors

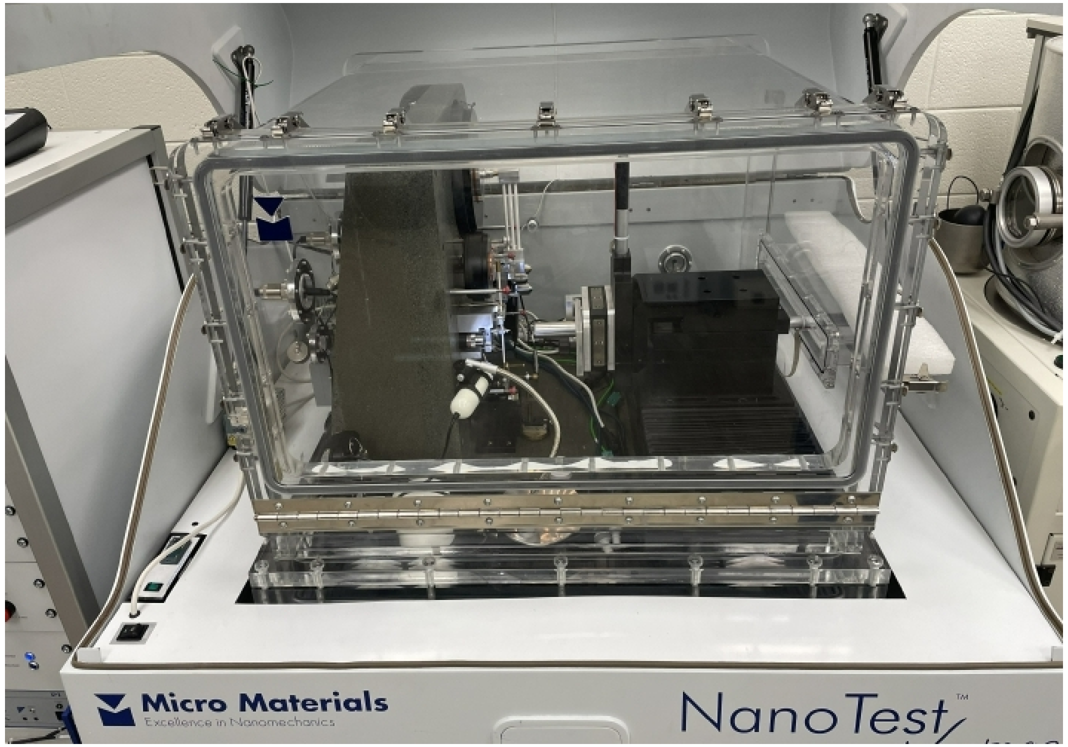
- $Na_3Zr_2PSi_2O_{12}$
- High Na-ion conductivity (>$10^{-3}$ S/cm at 25°C)
- Chemical compatibility with molten Na and halide salts
- Zero-crossover
- Mechanical integrity???




University of Kentucky
Sandia National Laboratories

# Methodology: Environmental Indentation and Atomic Force Microscopy

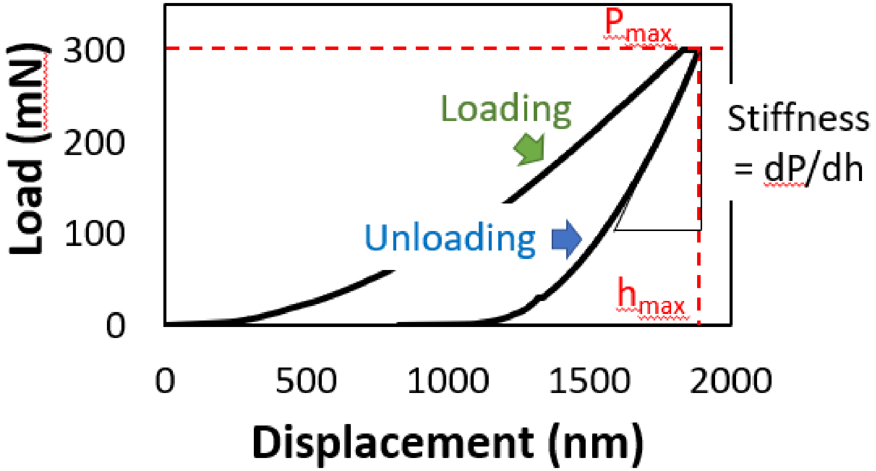




Left: G200 Nanoindenter and Bruker Dimension Icon AFM in glovebox

Right: Micromaterials NanoTest Vantage Micro/Nanoindenter with environmental chamber

# Nanoindentation Methodology: Mechanical Properties

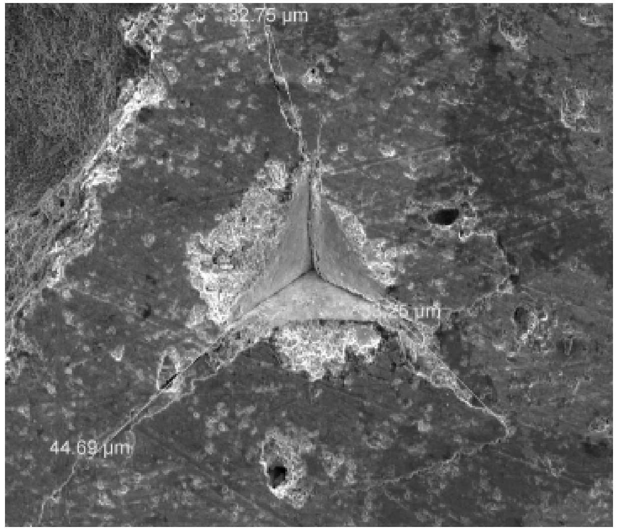
## Oliver-Pharr Analysis for modulus (E) and hardness (H)




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

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

## Crack length and energy-based methods for fracture toughness ($K_{ic}$)



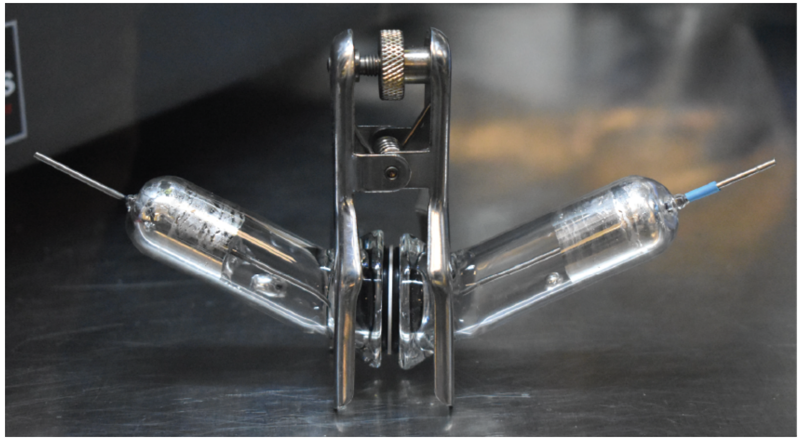

$$W_{crack} = W_{irrev} - W_{pp}$$

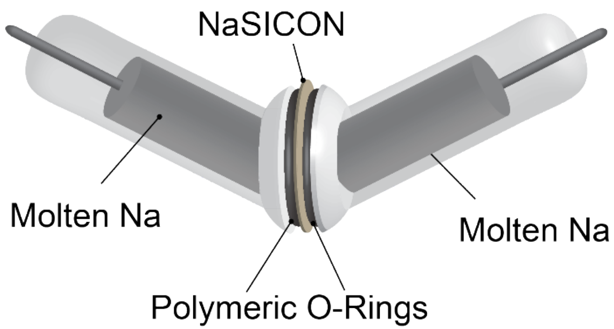
$$K_{ic} = \sqrt{\frac{E_r W_{crack}}{A_m}}$$

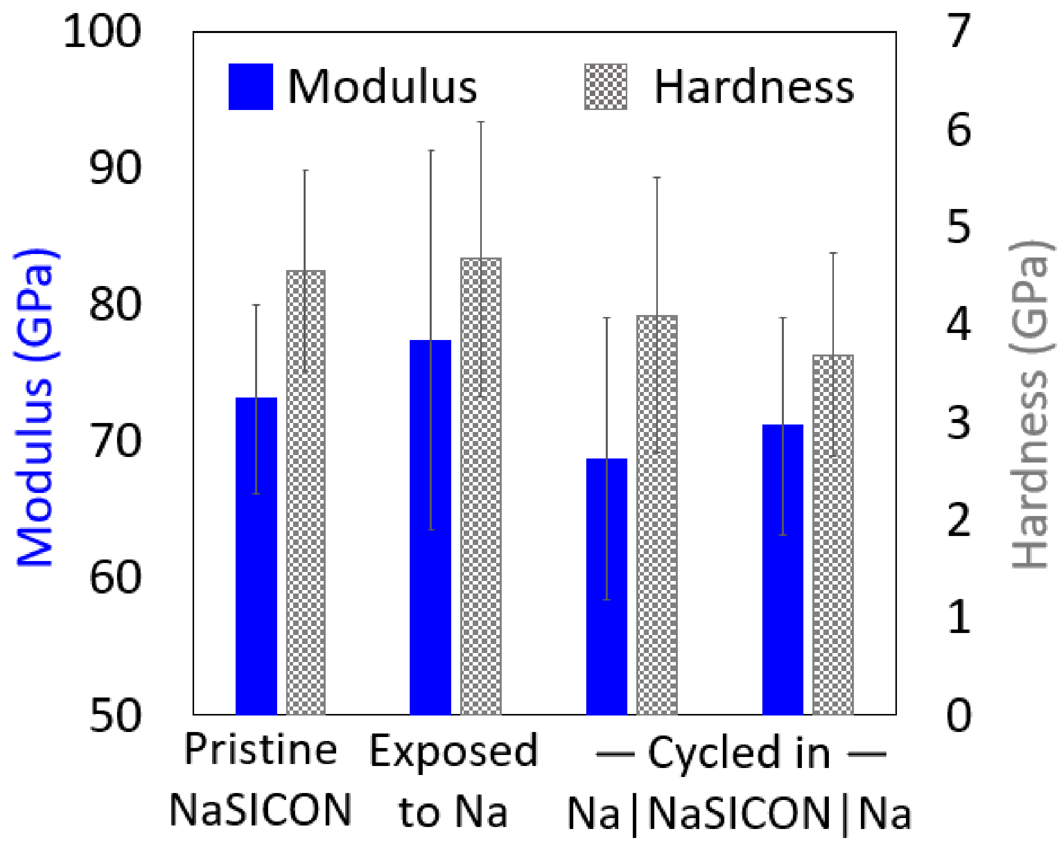
University of Kentucky
Sandia National Laboratories

# Indentation Results: Cycled NaSICON

## Exposed and cycled in symmetric sodium test cell

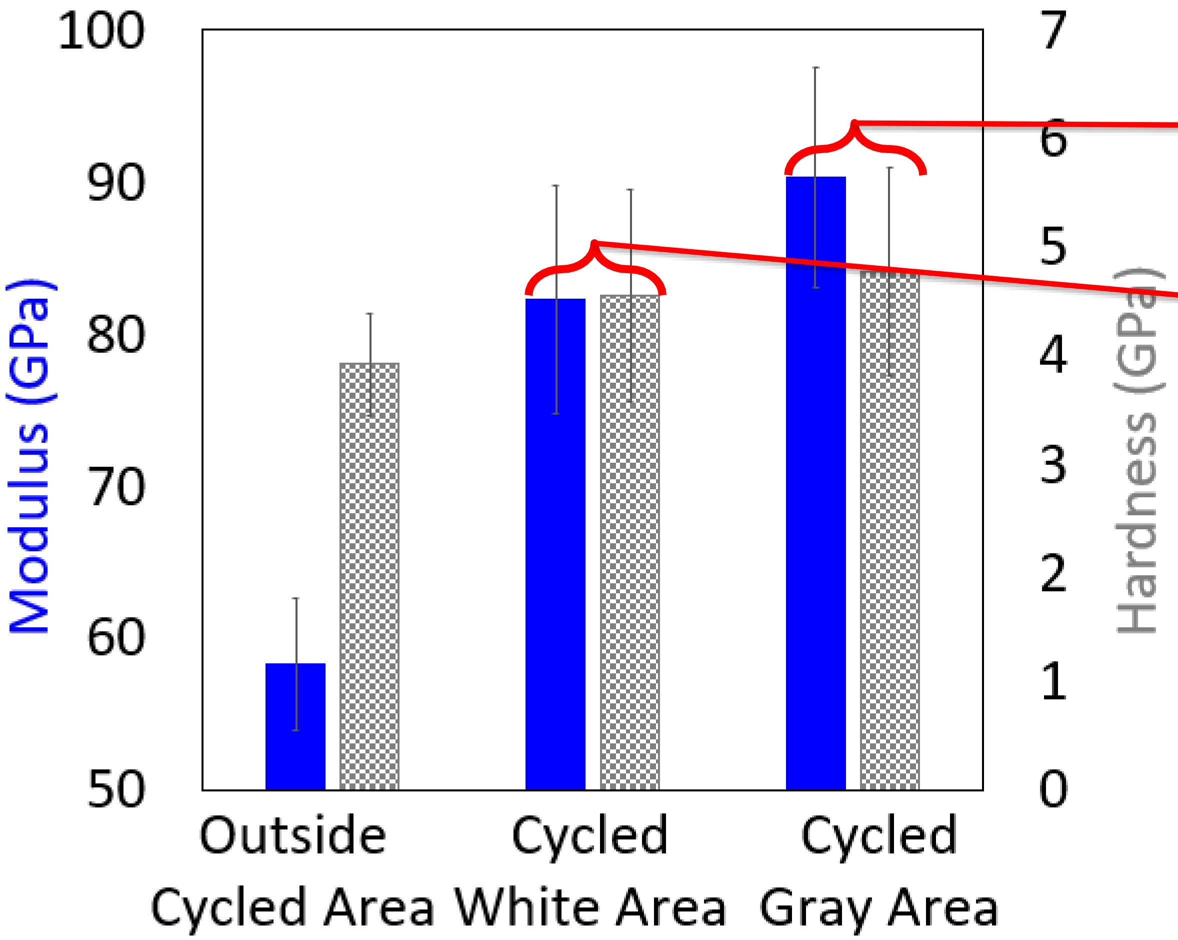


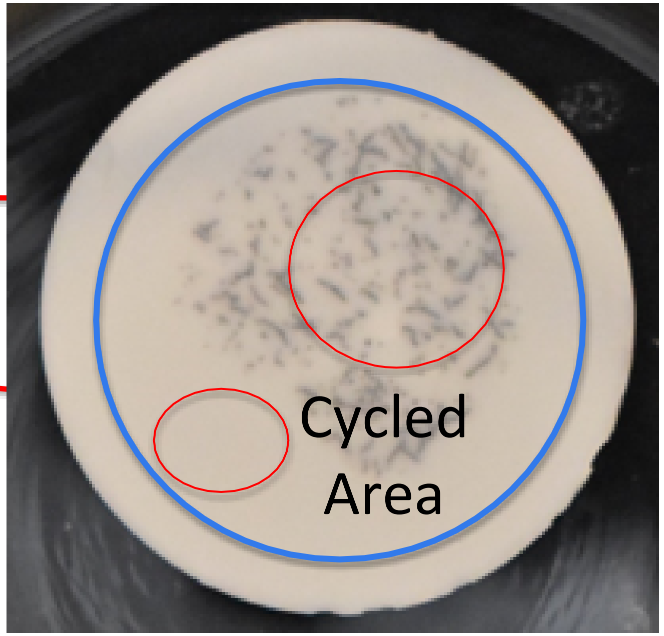


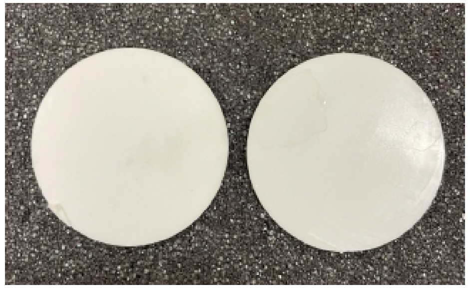

***Sodium conduction causes mechanical changes in NaSICON***

# Indentation Results: Cycled NaSICON (cont.)




Uncycled NaSICON



***New features appear during cycling at high current density; these regions have higher modulus and hardness***

University of Kentucky | Sandia National Laboratories

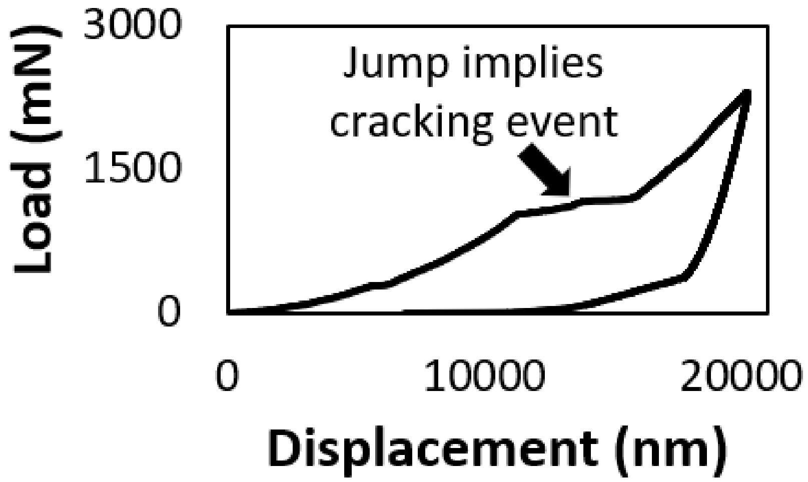
# Indentation Results: NaSICON Fracture Toughness

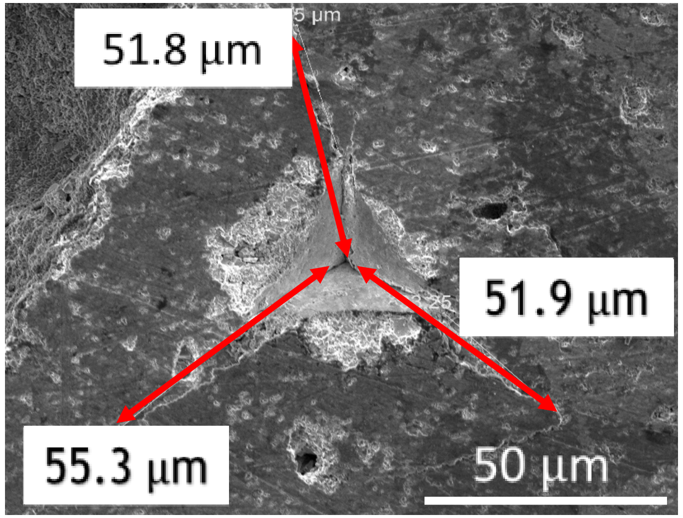
**Fracture toughness is closely related to critical current density in solid electrolytes**

Fracture toughness can be measured by observing indentation cracks:

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

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

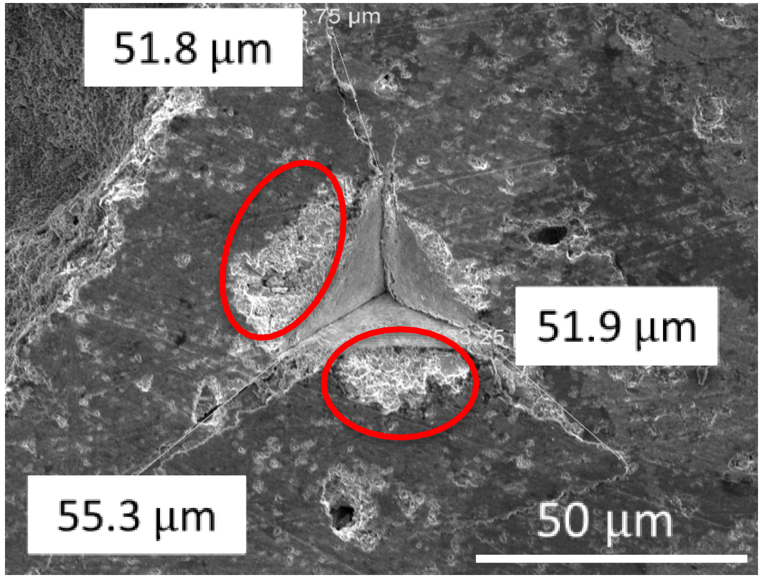


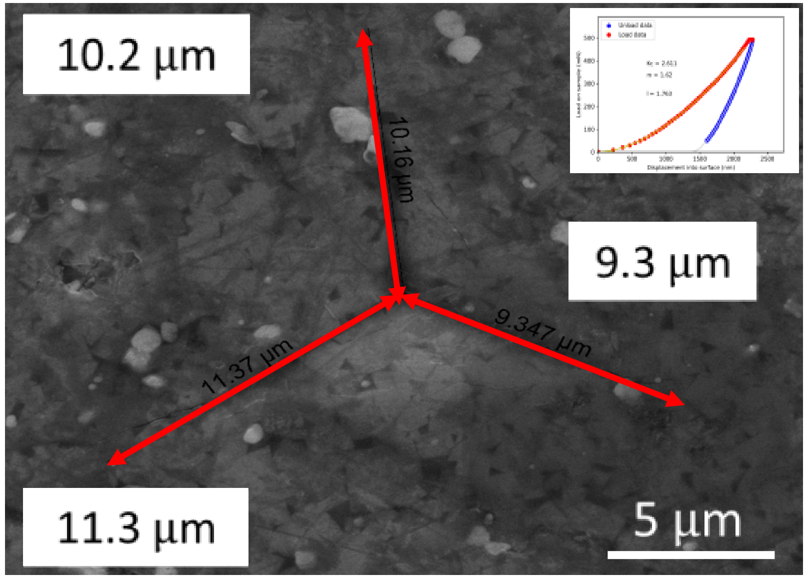



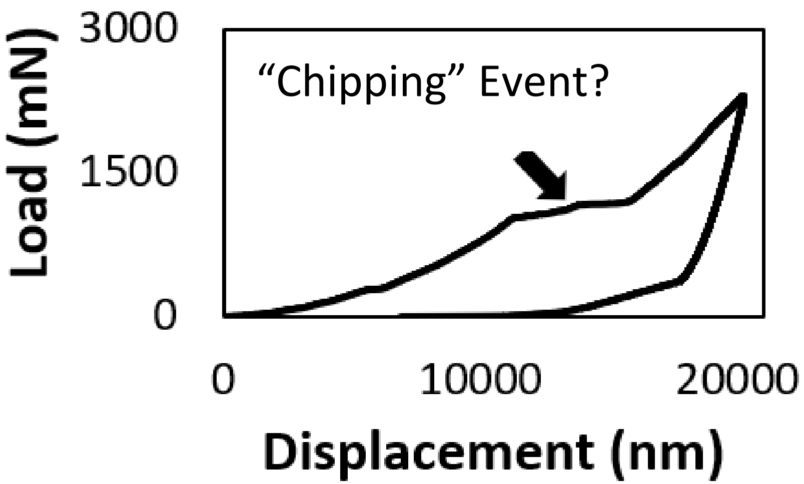

| Material | $K_{Ic}$ (MPa√m) |
|---|---|
| SiC | 3.00-6.00 |
| MgO | 2.50 |
| Fused Silica | 0.80 |
| WC | 6.00-20.00 |
| NaSICON (crack length method) | 1.90 ± 0.60 |

University of Kentucky
Sandia National Laboratories

# Indentation Results: Fracture Toughness by Small Cracks



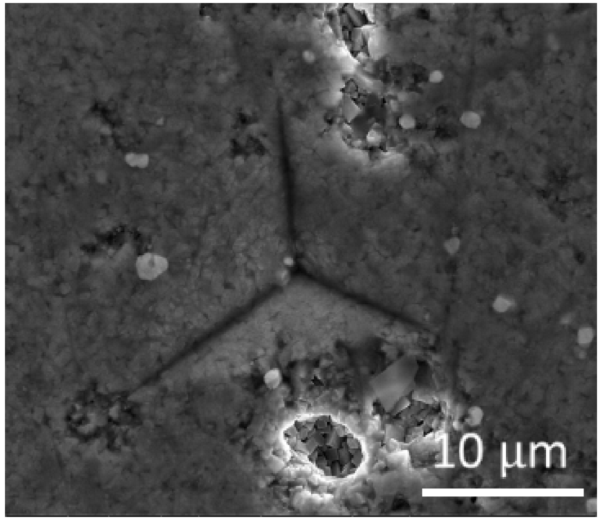

| Material | $K_{Ic}$ (MPa√m) |
|---|---|
| NaSICON (large crack length method) | 1.90 ± 0.60 |
| NaSICON (small crack length method) | 5.18 ± 0.77 |

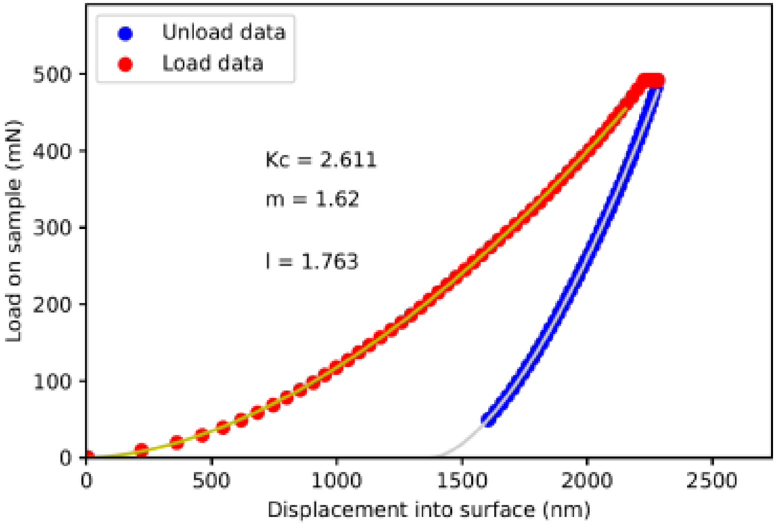
**Smaller cracks may not be long enough to give "accurate" fracture toughness values**

University of Kentucky | Sandia National Laboratories

# Indentation Results: Energy-based Fracture Toughness

## What if there are no cracks?




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

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

$K_{ic}$: 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

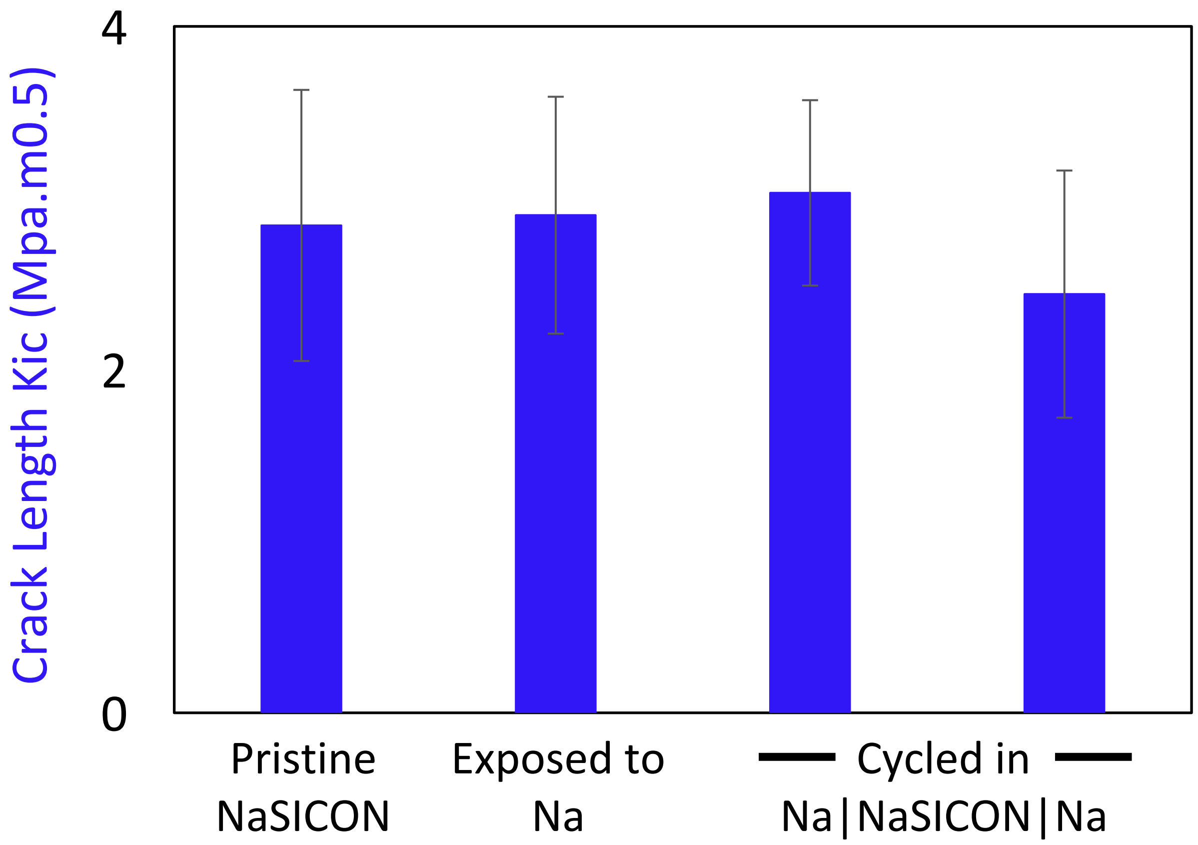
| Material | $K_{Ic}$ (MPa$\sqrt{m}$) |
|---|---|
| NaSICON (large crack length method) | 1.90 ± 0.60 |
| NaSICON (small crack length method) | 5.18 ± 0.77 |
| NaSICON (energy-based method) | 2.84 ± 0.79 |

**Energy-based method provides:**

- More consistent cracking behavior
- Simplified measurement (no imaging)
- Reduced damage to samples
- **Agrees with traditional crack length method**

University of Kentucky | Sandia National Laboratories

# Cycled NaSICON Fracture Toughness: Energy-based Method




***Fracture toughness not significantly impacted by $Na^+$ conduction***

***Cycling NaSICON should not affect ability to handle higher current densities***

# Conclusions and Future Work

- **Characterized the mechanical performance of NaSICON solid electrolytes before and after electrochemical cycling in molten sodium cells**
  - Mechanical properties change during electrochemical cycling and may depend on current density and new phases
- **Employed an energy-based method to measure the fracture toughness of NaSICON solid electrolytes**
  - Allows for simplified measurement
  - Agrees well with traditional fracture toughness measurement
- **Will explore failure behavior of NaSICON at high current densities**
  - How dendrites may affect solid electrolyte even in molten environment
- **Characterization of coatings for NaSICON interfaces and NaSICON/polymer composite electrolytes**

University of Kentucky
Sandia National Laboratories

# 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.

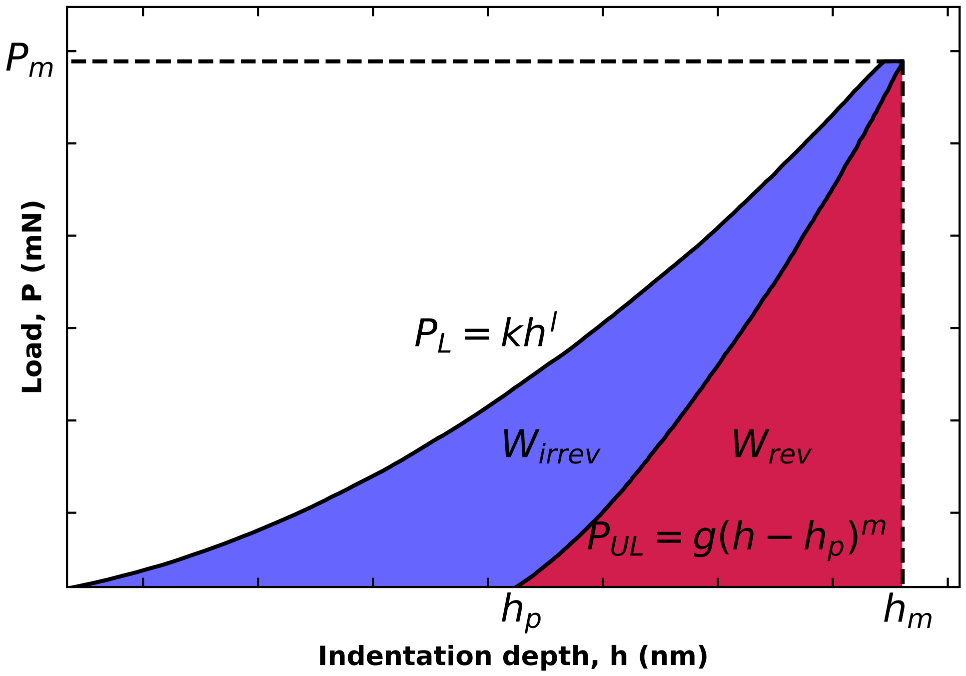
**Ryan Hill**

Ryan.C.Hill@uky.edu

Thank you!

University of Kentucky Sandia National Laboratories

# Energy-based Fracture Toughness




$$\frac{W_{PP}}{W_{total}} = \frac{l+1}{m+1}\frac{h_p}{h_m} - \frac{l-m}{m+1}$$

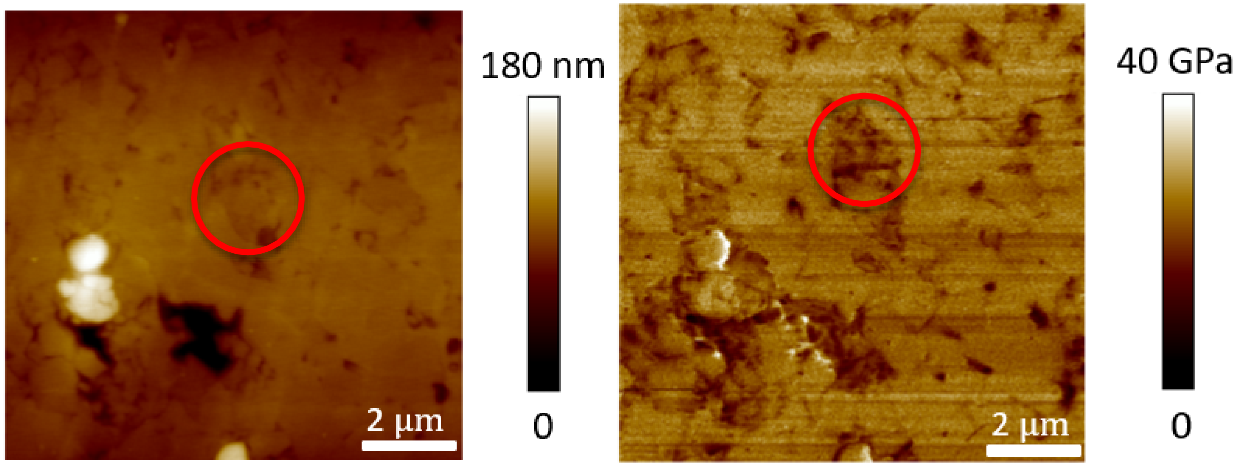
$$W_{crack} = W_{irrev} - W_{pp}$$

$$K_c = \sqrt{\frac{E_r W_{crack}}{A_m}}$$

$K_{ic}$: 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
l: Exponent fit for loading curve
m: Exponent fit for unloading curve
$h_p$: Residual indentation depth
$h_m$: Maximum indentation depth

# Local Mechanical and Electrochemical Behavior

## Quantitative Nanomechanical Mapping (QNM)



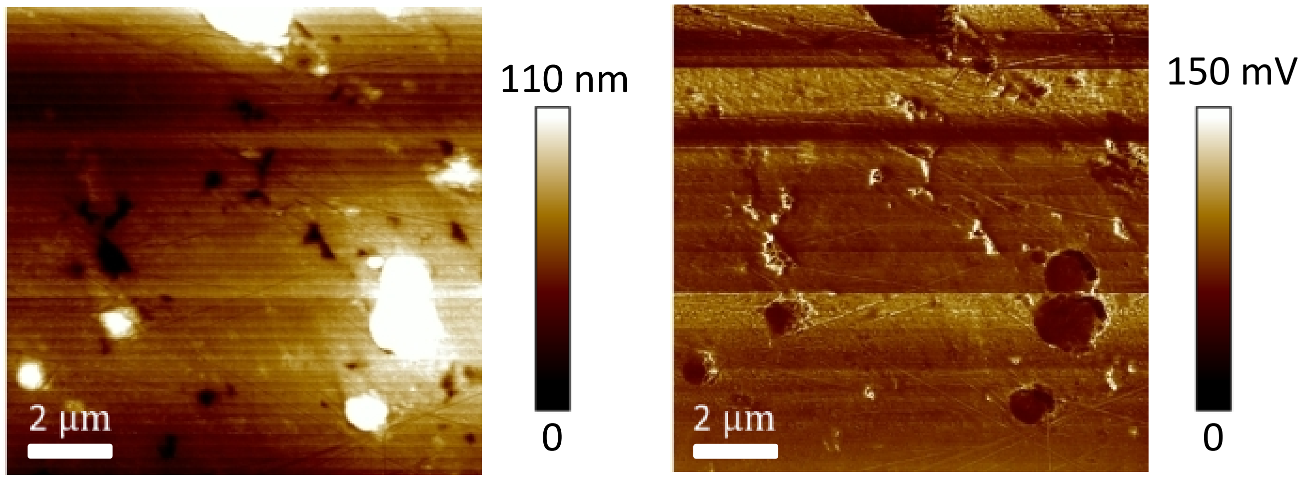

Surface Height

Elastic Modulus

***Grains/boundaries, secondary phases, porosity contribute to mechanical performance***

## Electrochemical Strain Mapping (ESM)

***Ionic mobility of $Na^+$ in NaSICON can be correlated with surface features***

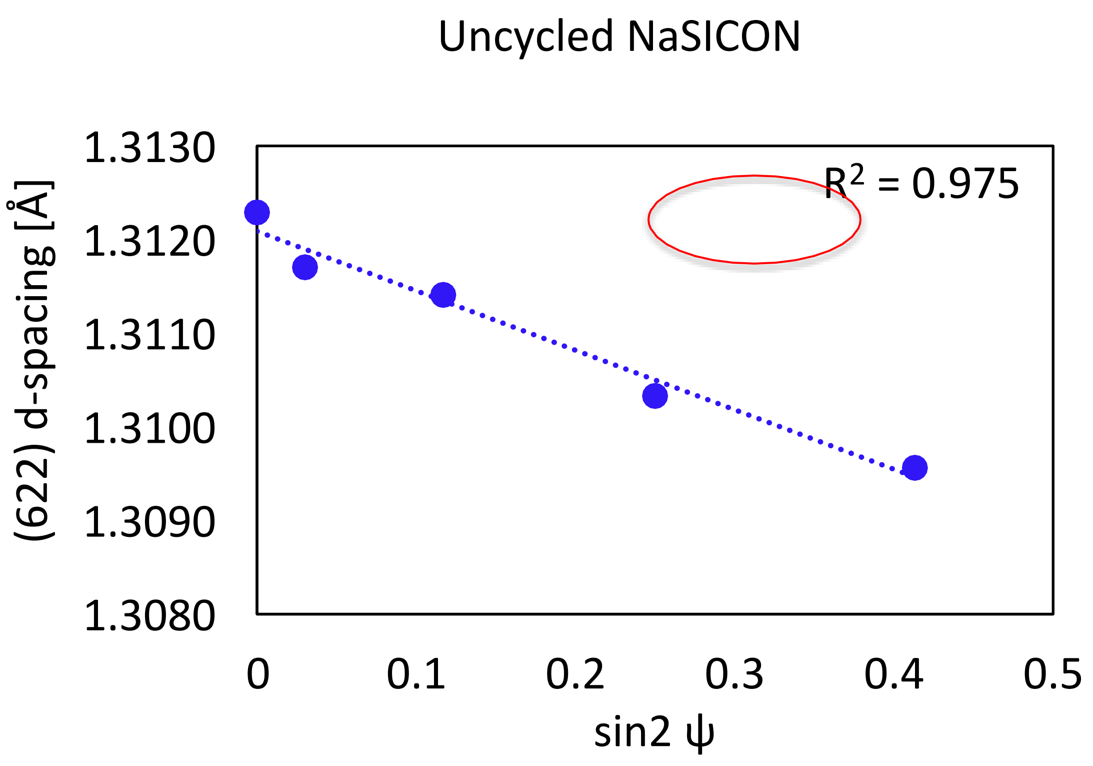


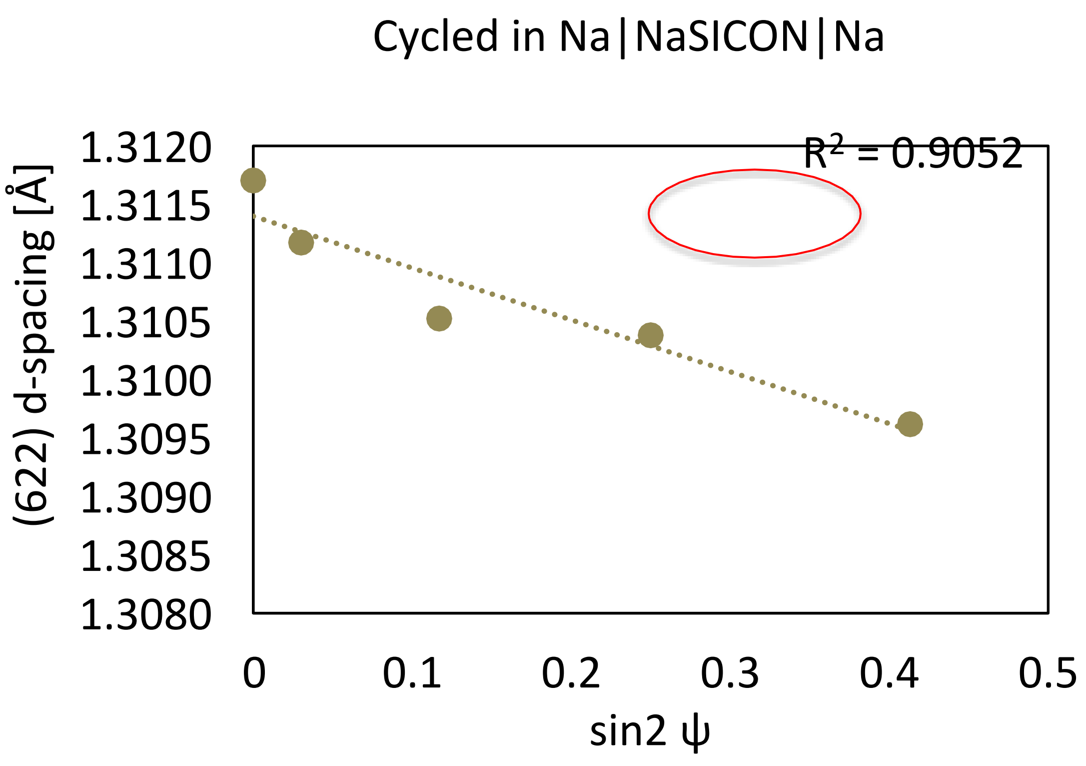

Surface Height

Electrochemical strain amplitude

University of Kentucky Sandia National Laboratories

# Residual Stress in NaSICON by XRD

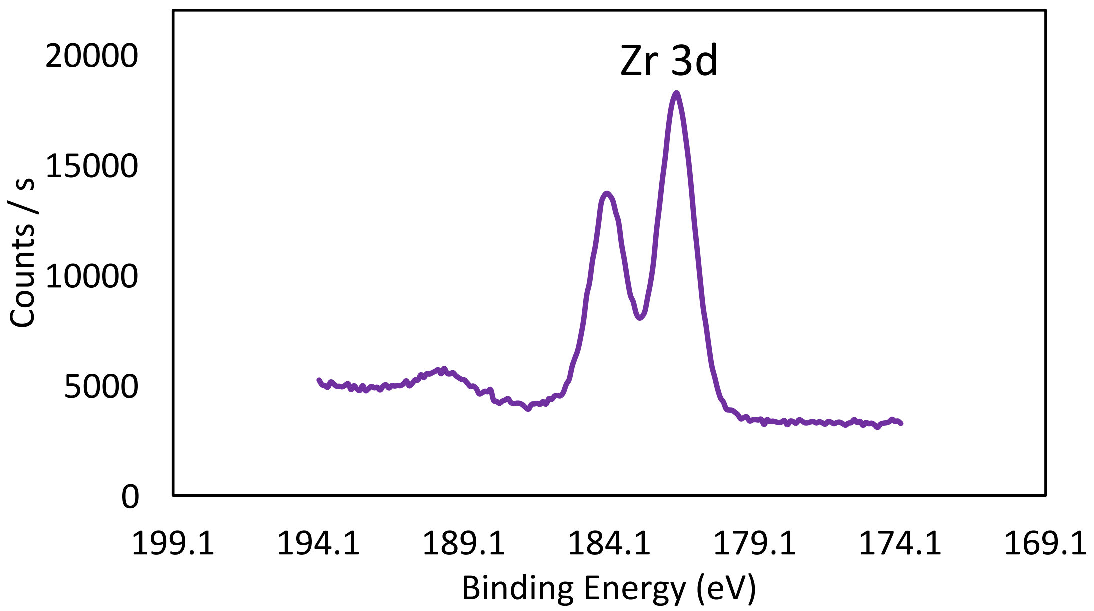


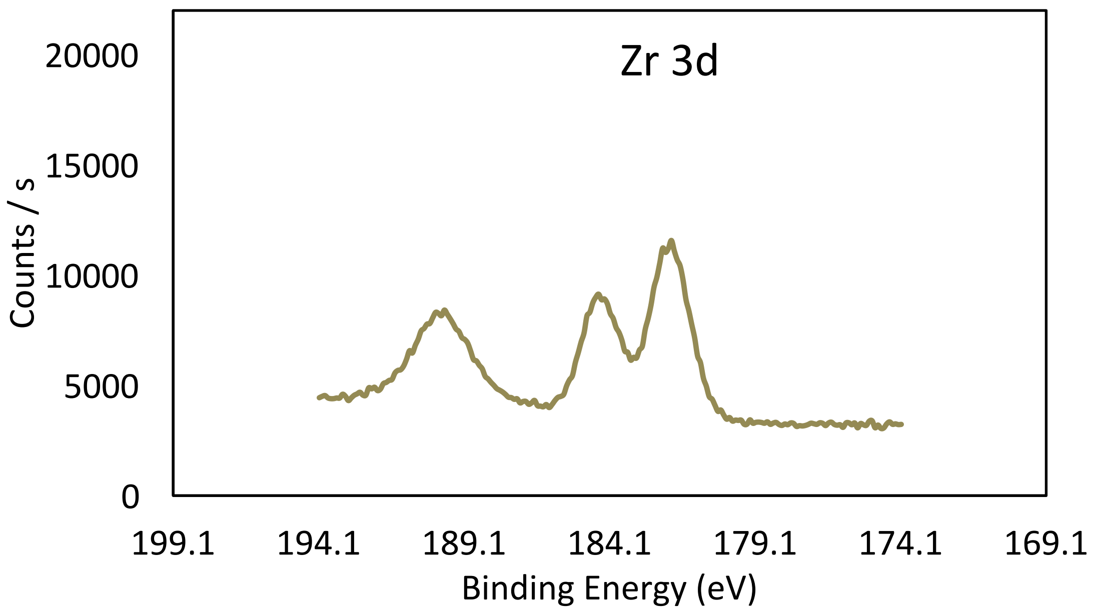

***Compressive stress in NaSICON pellet changes after cycling – may be responsible for different modulus/hardness***

# Surface Chemistry of NaSICON by XPS

Exposed to Na




Cycled in Na|NaSICON|Na




***Zr signal in cycled NaSICON is weaker than before cycling – possibly contributing to difference in mechanical performance***