# Understanding Electronic Conduction in NaSICON to Improve Sodium Batteries

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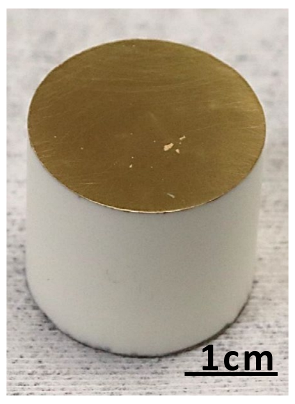
## Background

Improved, cost-effective sodium batteries are needed to increase the resiliency and reliability of the electric grid. We aim to understand the performance limitations of the Sodium (Na) Super Ionic Conductor (NaSICON) under high current density (50 mA cm-2) for long discharge times (>8 h) and low operating temperature (< 135 °C).

We aim to reach these goals through investigation of the electrical features, dendrite formation, and cycling limitation of these cells using electrical impedance spectroscopy, voltage profiles, and cross-sectional imaging.

### Why NaSICON?

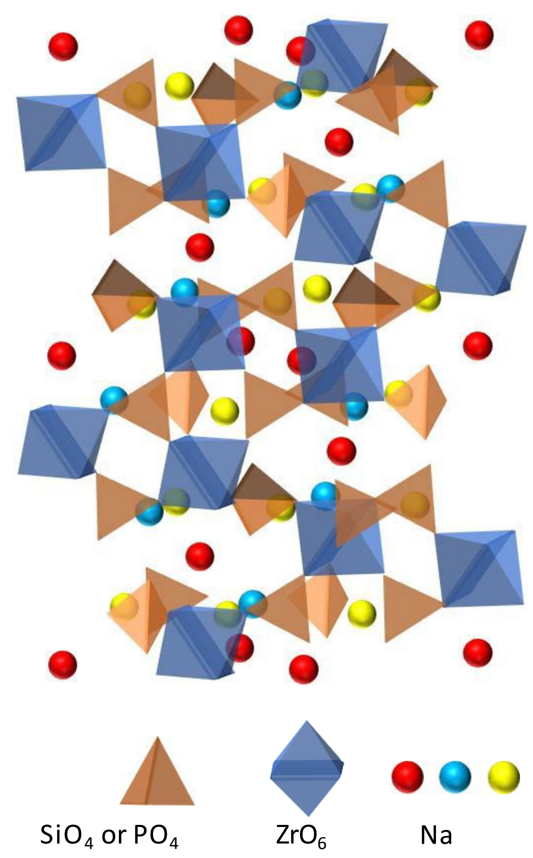
- High Ionic Conductivity
- Low e⁻ Conductivity
- Improved Thermal Stability
- Relatively Chemical Stable
- Sodium is in High Abundance




## Objectives

- Understand detrimental electrical features effects on the bulk system. Electron leakage current has been previously claimed as a form of dendrite formation, thus quantifying this property will bring better insight into the formation of dendrites.
- By lowering the operating temperature, we reduce the cost of large-scale operation yet encounter issues of lower conductive/accelerated dendrite formation. Herein we investigate the effects of external pressure and temperature on the symmetric system.

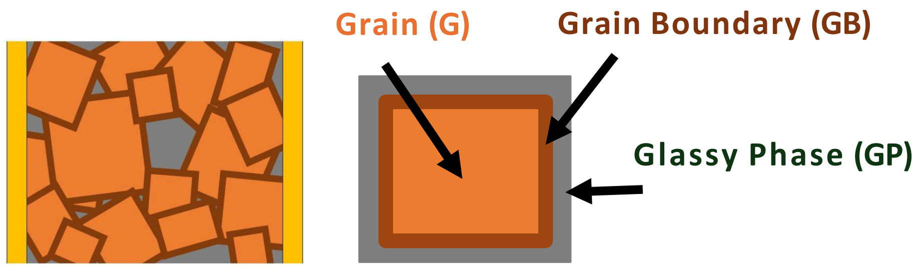
$Na_{3.4}Zr_{2.0}Si_{2.4}P_{0.6}O_{12}$ provides high ionic conductivity up to >3 mS cm$^{-1}$ at room temperature.

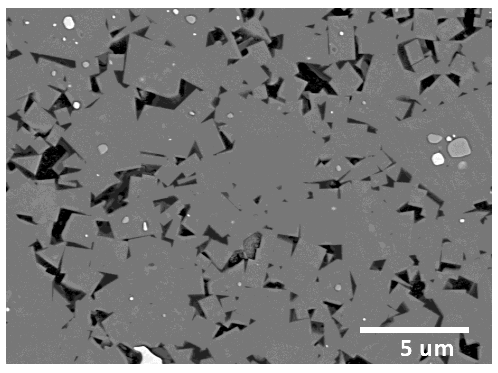



## Electrical Features of NaSICON

### 1. Feature Analysis

- An additional feature is observed in EIS Nyquist data.
- $ZrO_2$ defects cause formation **excess NaSiPO** resulting in the glassy phase.
- The **glassy phase** is known to be slightly ionic yet may contribute to the electronic conductivity of the sample.
- Previous works indicate the glassy phase with an activation energy of around 0.6 eV, similar to our results.



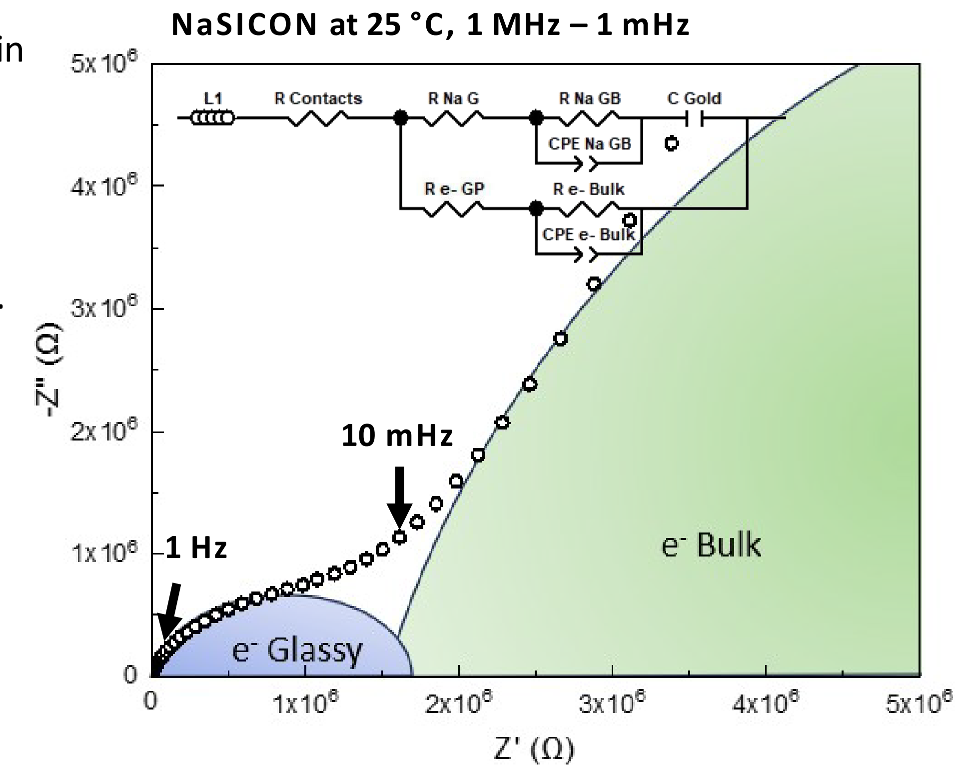




SEM image of NaSICON crystal grains.

**Testing Conditions**

- Thick Sample
- Gold electrodes in Air
- Low Frequency
  - **1 MHz - 1 mHz**
- Range of Temperatures
  - **25 – 150 ° C**

### 2. Electrochemical Impedance Spectroscopy

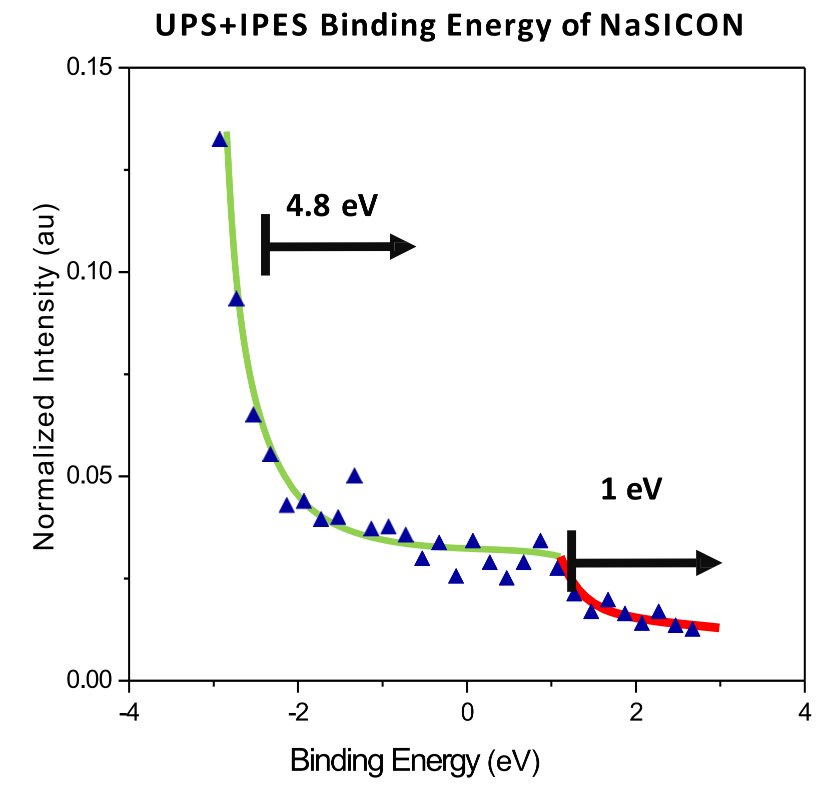



**Activation Energy**

| Sample | Na G+GB (eV) | e- Glassy Phase (eV) | e- Bulk (eV) |
|---|---|---|---|
| #1 | 0.227 +/- 0.009 | 0.614 +/- 0.036 | - |
| #2 | 0.267 +/- 0.008 | 0.750 +/- 0.052 | 1.21 +/- 0.157 |
| #3 | 0.251 +/- 0.008 | 0.565 +/- 0.034 | 0.98 +/- 0.108 |

### 3. UPS and IPES

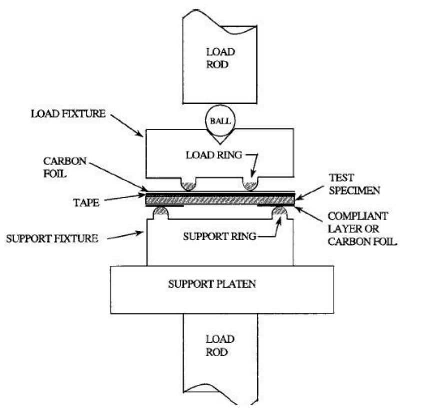
Using Ultraviolet Photoelectron Spectroscopy (UPS) and Inverse PhotoEmission Spectroscopy (IPES) we see the presence of an **additional phase**.



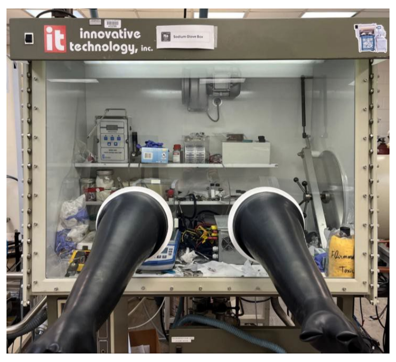

**Glassy Phase contributes to the electronic conductivity which is a main source of dendrite formation.**

## Observing Dendrite Growth in Sodium Cells

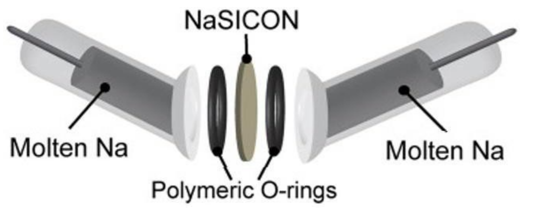
NaSICON symmetric cells are all assembled within an argon glove box. Cells are kept to a specific temperature and cycled until reaching a desired capacity or failure. **Unidirectional currents** are used to accelerate the failure of the cells to determine the limits of dendrite formation.



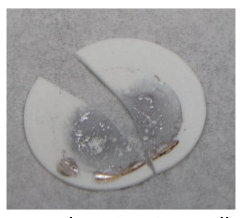

NaSICON Preparation
- 1 mm thick
- Polished to 1200 grit
- Molten 110 °C
- Solid State 90 °C



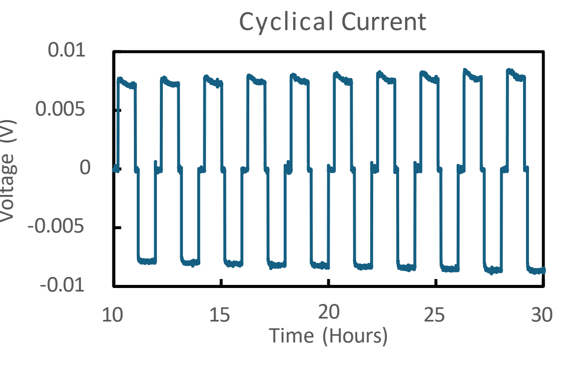
Fracturing the pellets using ASTM equiaxial flexural strength provides **uniform stress** breaking the pellet at the **weakest location**.

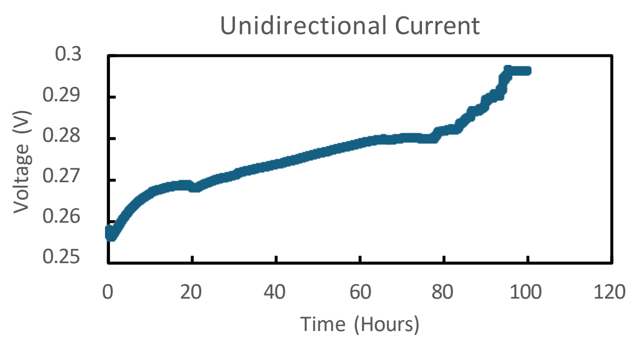


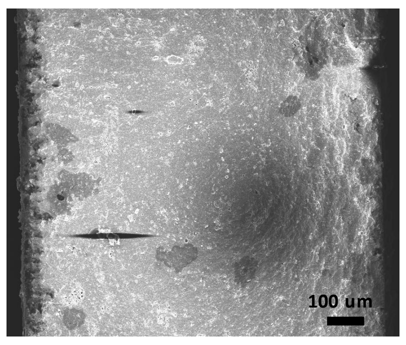

- Constant current up to 100 mA cm$^{-2}$
- EIS 1 MHz to 10 Hz
- 1 Hour half cycles
- **Cycling or Unidirectional** current



Fractured NaSICON Pellet




Cross section of molten cell dendrite formation.

## Conclusions and Future Work

**Additional electrical glassy phase contributes to the electronic leakage current associated with dendrite formations.**

- SEM imaging and circuit element construction provide adequate fitting to EIS data collected, with resulted fitting activation energies agreeing with previous works values for ionic conductivity.
- EIS measurements show an additional high impedance feature for all temperatures tested along with multiple samples.
- UPS + IPES confirm the existence of a secondary phase present.

**Future Work**

- Unidirectional capacity limitation at varying currents. This will help accelerate failure and determine the longevity of cells at different current densities.
- Pressure and temperature effects on NaSICON symmetric cell. Lowering the temperature allowing for lower operating costs yet leads to issues of interfacial contact and reduction in conductivity.

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