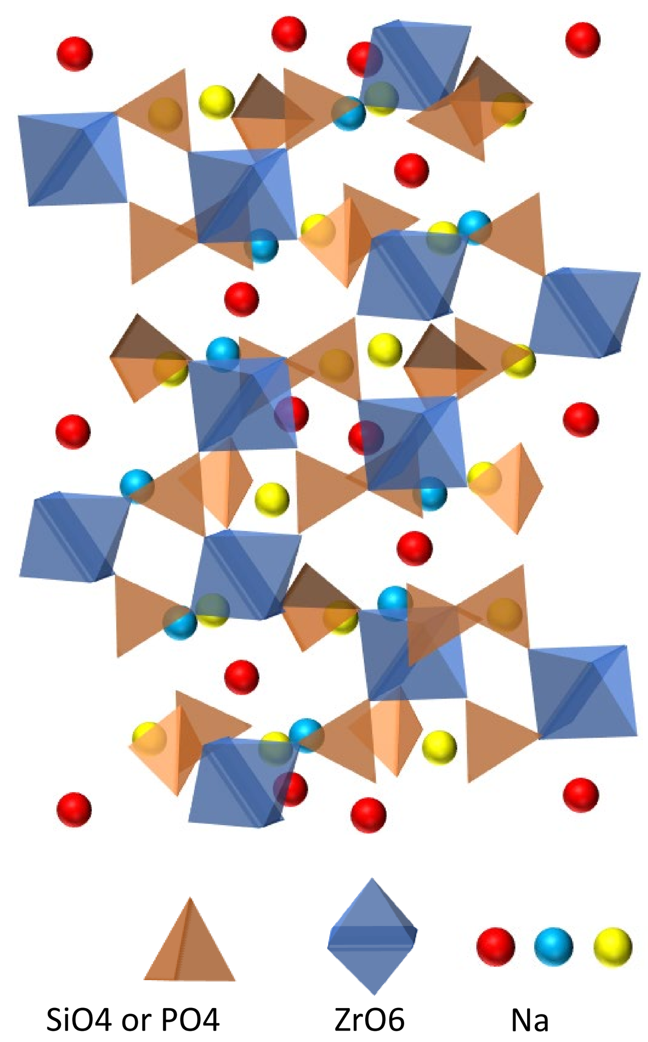
Investigating the Electronic Conductivity of NaSICON Solid Electrolyte

Ethan J. Lauricella(ethan.lauricella@uky.edu)*, Amanda S. Peretti**, Yang-Tse Cheng*, and Leo J. Small**
*University of Kentucky, Lexington, KY, USA and **Sandia National Laboratories, Albuquerque, NM, USA

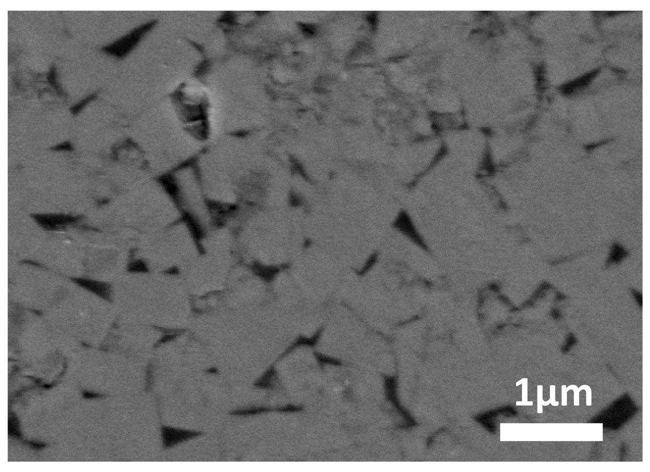
Motivations

- NaSICON, $Na_{3.4}Zr_{2.0}Si_{2.4}P_{0.6}O_{12}$, structure consists of SiO_4 or PO_4 tetrahedra sharing common corners with ZrO_6 octahedra.
- Dendrite formation mechanisms have previously been proposed: Mode I (pressure-induced cracking) and Mode II (ion-electron recombination)
- Desirable high ionic conductivity while limiting electronic conductivity for solid electrolytes to avoid cell shorting from dendrite penetration.
- Better understand ion-electron recombination by measuring the electronic conductivity.

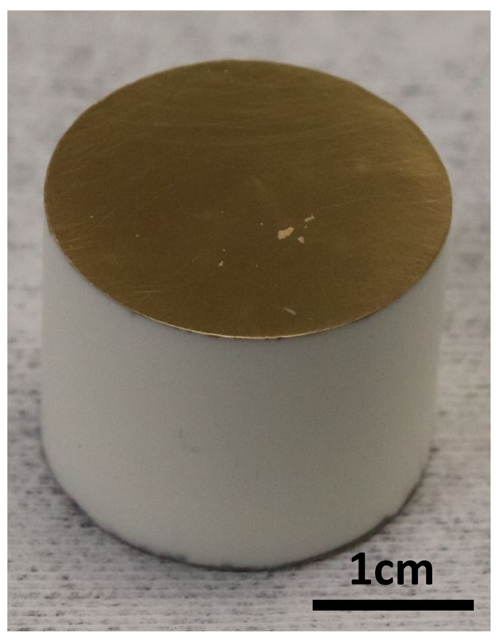


Objectives

- Investigate the electronic conductivity of a NaSICON cylinder using gold as blocking electrodes over a range of temperatures from 0 °C to 150 °C.
- Use methods, such as electrochemical impedance spectroscopy and DC polarization, to compare and validate results.
- From these techniques, extract the activation energy, conductivities, and further investigate NaSICON mode II process.

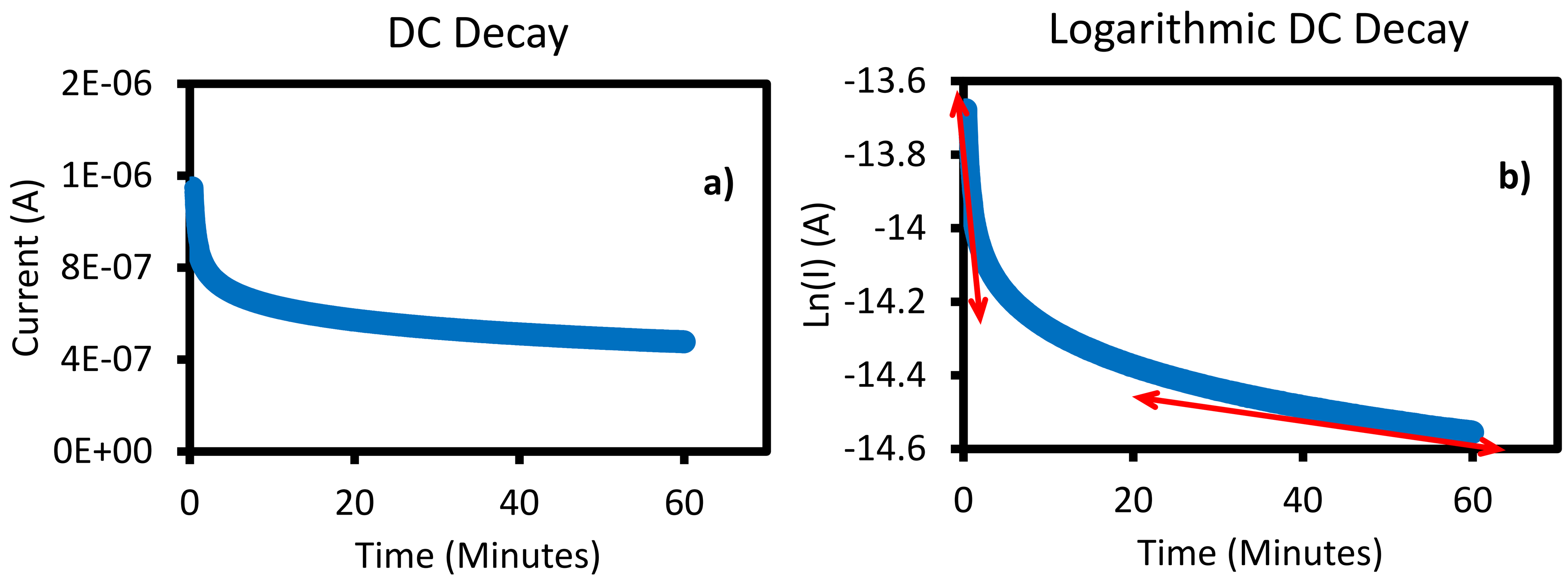


SEM image of NaSICON crystal grains.



DC Polarization and Electrochemical Impedance Spectroscopy of NaSICON Cylinder

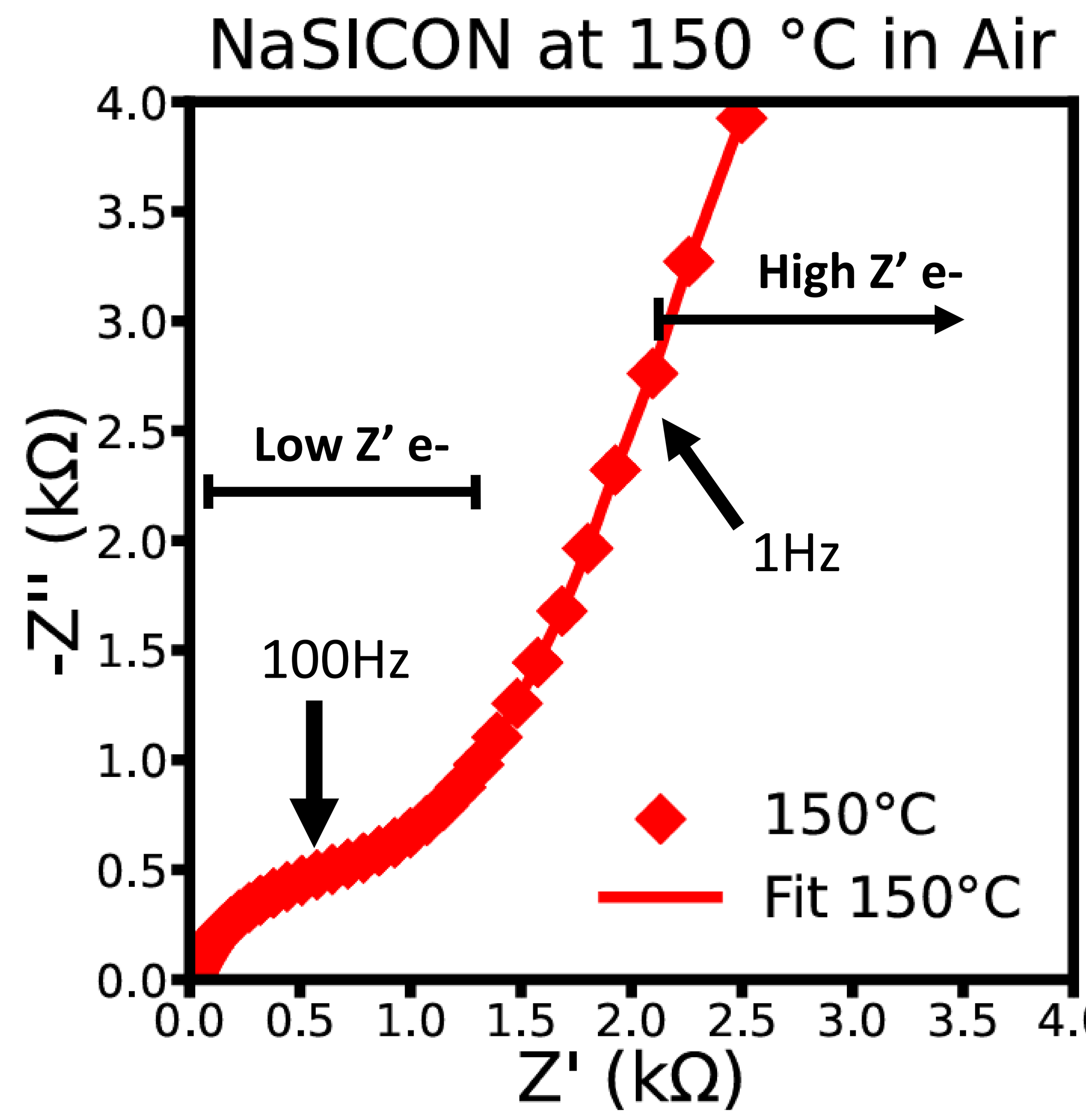
DC Polarization exhibited two decay features with different rates



a) DC Polarization of NaSICON cylinder with gold blocking electrodes at 1 V 150 °C in air. **b)** Logarithmic of data showing two linear decay regions.

DC Polarization using gold blocking electrodes was measured from 0 °C to 150 °C and using a range of .2 to 1 V.

EIS shows two different features corresponding to electronic conduction

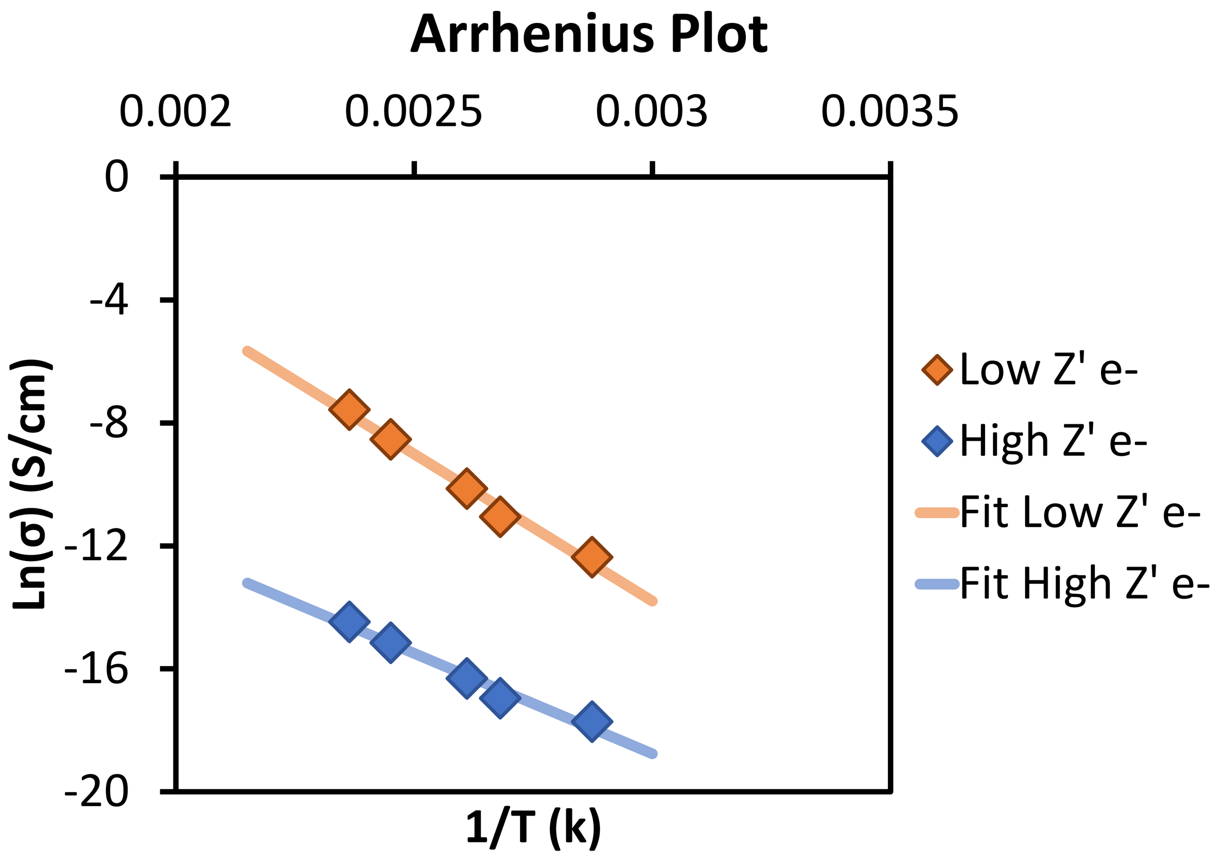


Conductivities 150 °C
Na G+GB: 89.37 mS/cm

Low Z' (100Hz) e⁻: 5.18E-01 mS/cm

High Z'(1Hz<) e⁻: 5.19E-04 mS/cm

Arrhenius behavior



Activation energy found after fitting EIS data to equivalent circuit

Activation Energy
Low e- Impedance: 0.825 eV
High e- Impedance: 0.563 eV

Temp (°C)	Low Z' e⁻ Conductivity (mS/cm)	High Z' e⁻ Conductivity (mS/cm)
75	4.26E-03 +/- 1.0E-04	2.01E-05 +/- 2.9E-06
100	1.59E-02 +/- 2.0E-04	4.33E-05 +/- 2.1E-06
110	3.98E-02 +/- 3.4E-04	8.24E-05 +/- 3.7E-06
135	1.97E-01 +/- 1.9E-03	2.63E-04 +/- 8.1E-06
150	5.18E-01 +/- 9.4E-03	5.19E-04 +/- 1.9E-05

Conclusions and Future Work

Conclusions:

- DC Polarization shows two differing decay functions, one within a short time frame of 5-10 minutes, while another over several hours.
- EIS data shows two differ high impedance features from the electronic impedance.
- These two features may be indicative of the electronic grain and grain boundary impedance and may help provide more insight into which feature is predominantly caused by Mode II dendrites.

Future Considerations:

- Will changes in grains/grain boundaries change the conductivity? Which feature in the EIS is the grains/grain boundaries?
- Would dopants within the grain boundaries reduce the electronic conduction?
- How will differences in fabrication process alter electronic conductivity?

Acknowledgments

This work was supported the Energy Storage Program in the U.S. Department of Energy's Office of Electricity. 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. SAND2024-09297C