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College of Engineering
Department of Chemical and Materials Engineering

Sodium Penetration Through Solid-State NaSICON Electrolytes Under High Current

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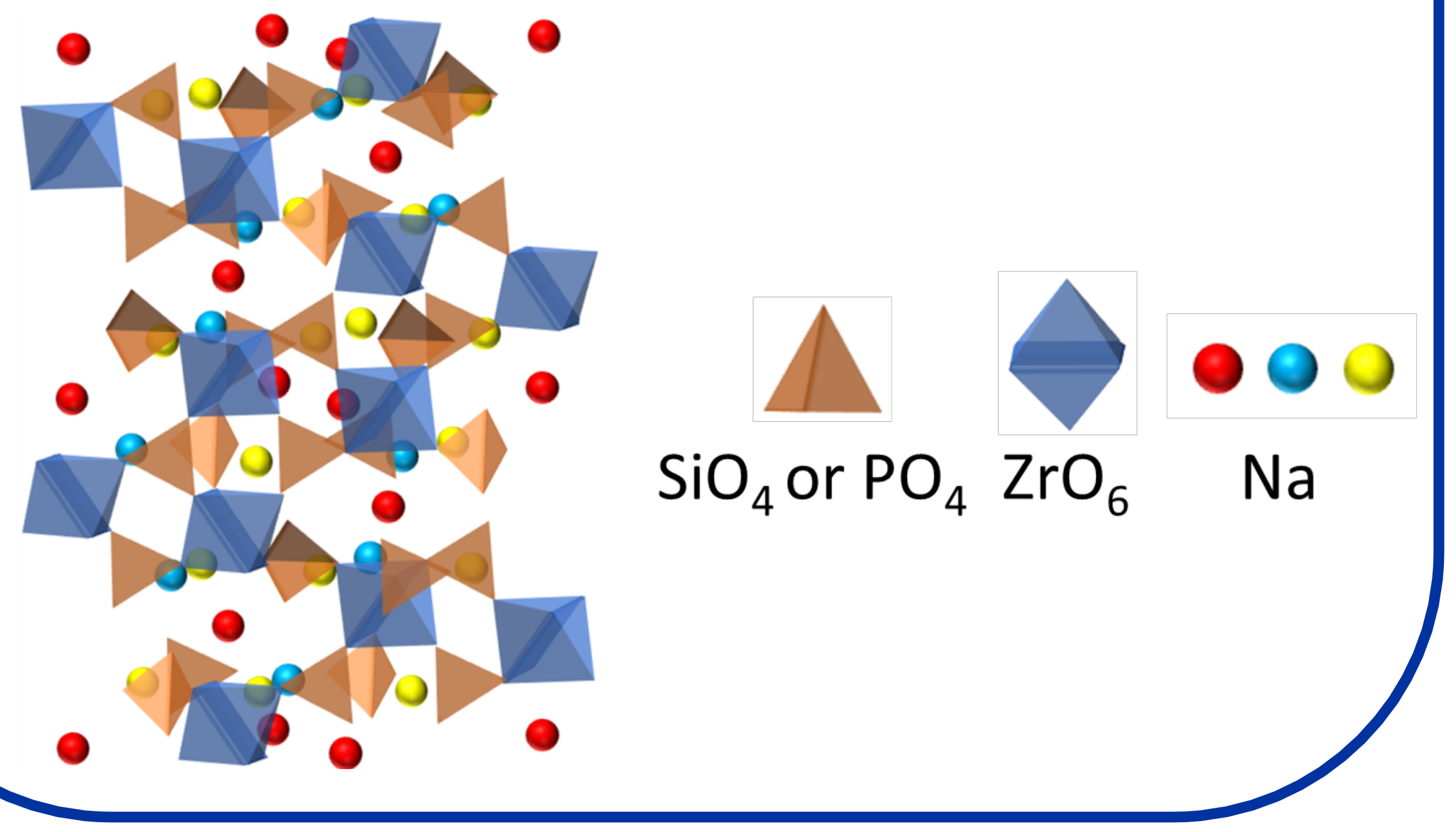
Motivation

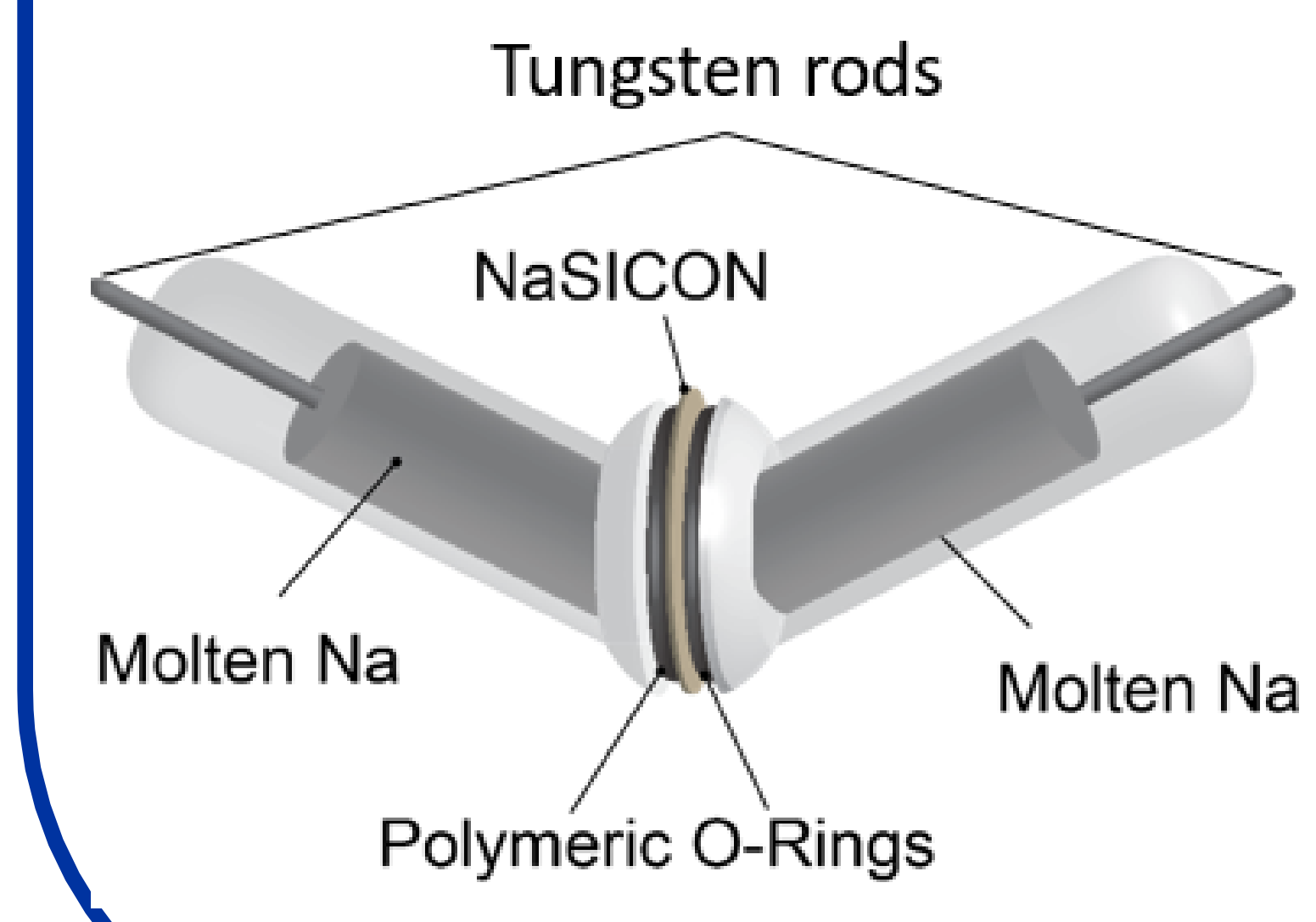
The DOE Office of Electricity views sodium batteries as a priority in pursuing a safe, resilient, and reliable grid. Improvements in solid-state electrolytes are key to realizing the potential of these large-scale batteries.

- 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 ions
- Higher ionic conductivity (at lower temperature) and cheaper to produce than β''-alumina

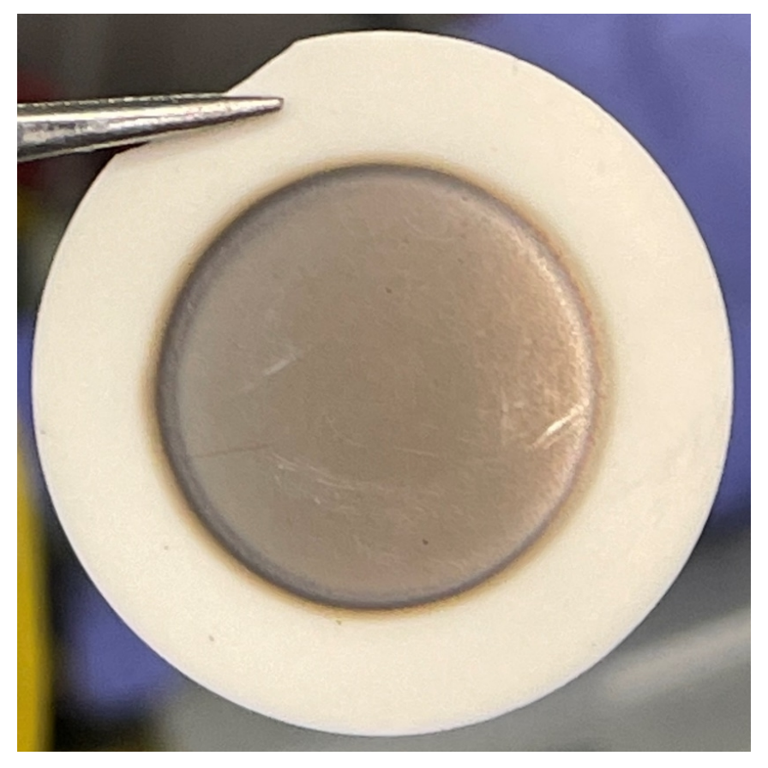


Objectives

- Identify mechanisms of dendrite initiation and propagation from molten Na electrodes using high-current (100 mA/cm²), one-directional testing.
- Use classical electrochemical methods, such as electrochemical impedance spectroscopy (EIS), to further understand Na|NaSICON interface and detect initial dendrite formation.
- Use interfacial coating to eliminate dendrite formation and identify key properties for effective coatings.

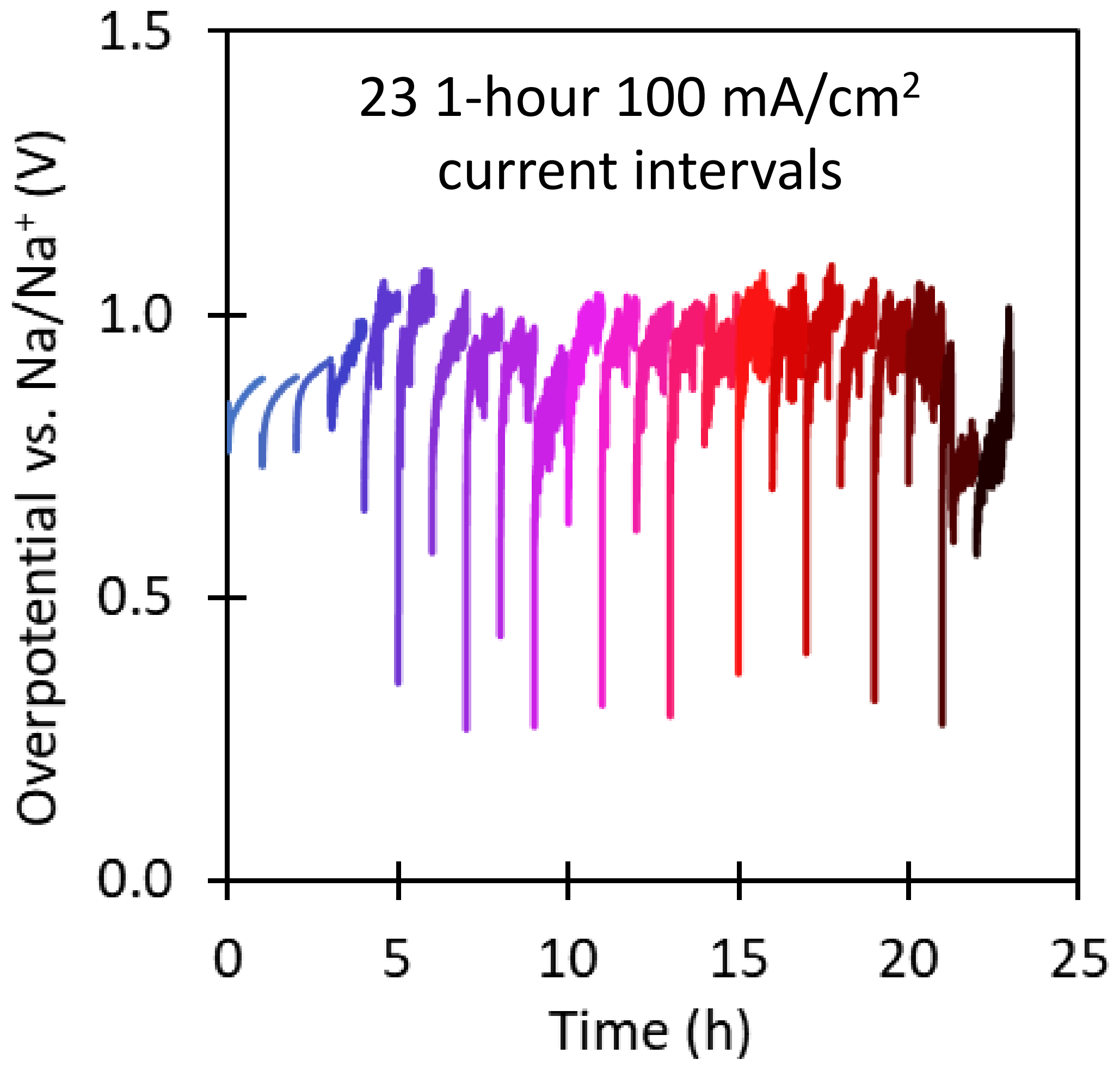


Tin-coated NaSICON



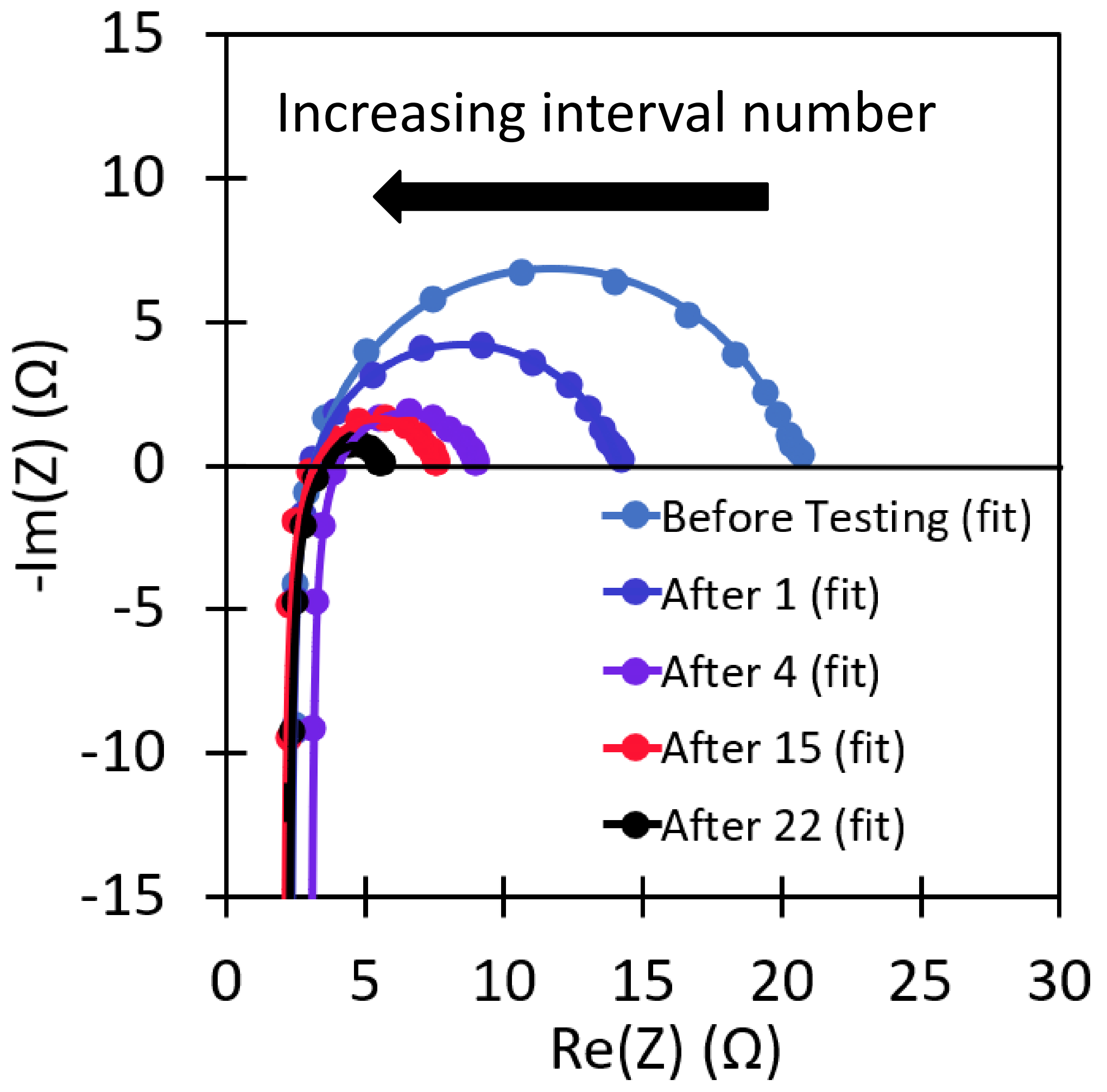
One-direction Current Symmetric Cell Testing of Bare NaSICON

Initially, a stable voltage can be achieved at high current density (100 mA/cm²)

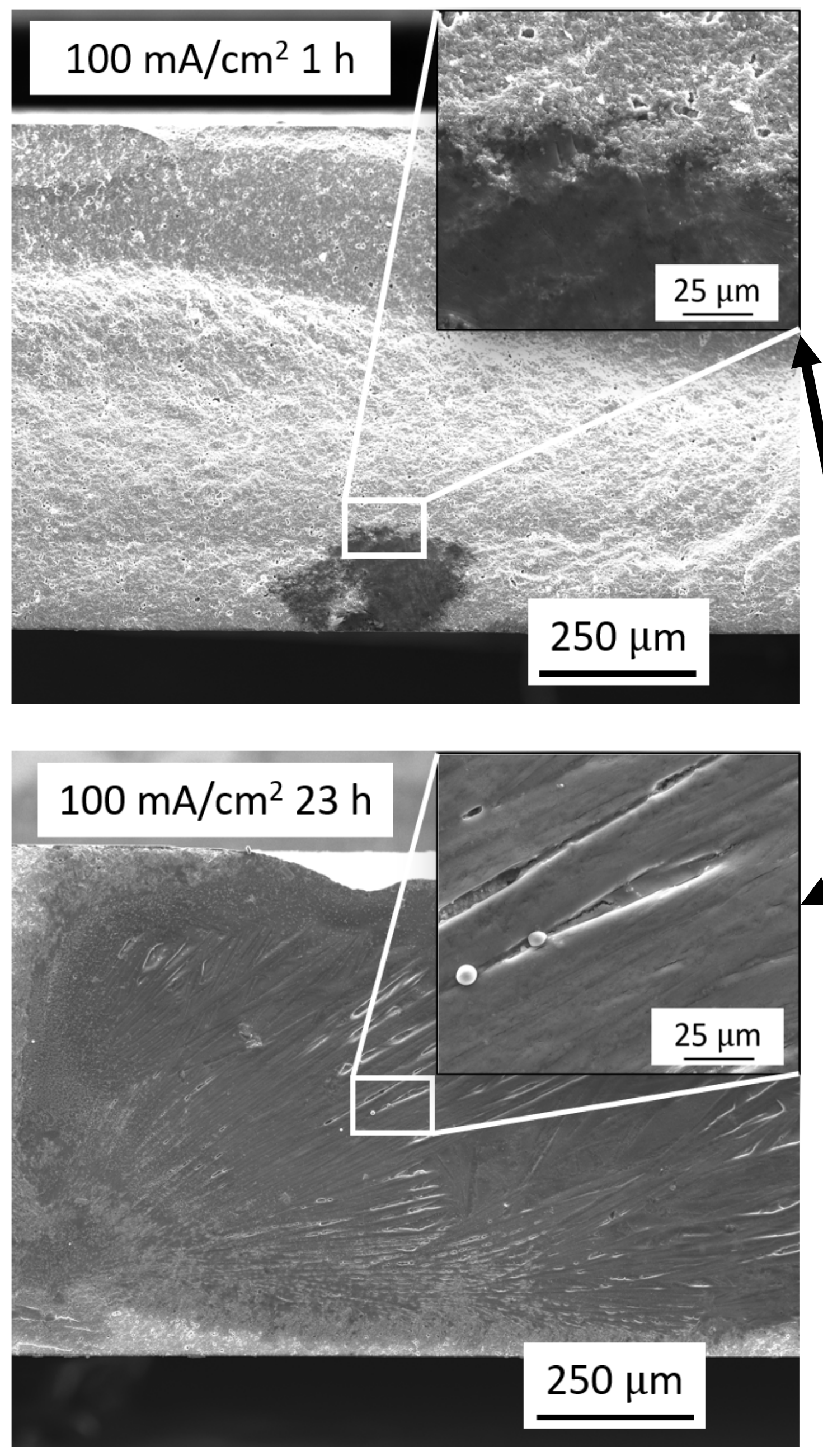


Symmetric Cell Overpotential Profile

EIS shows a resistance decrease after each current interval – a visible decrease occurs when voltage becomes noisy



Symmetric Cell EIS Spectra



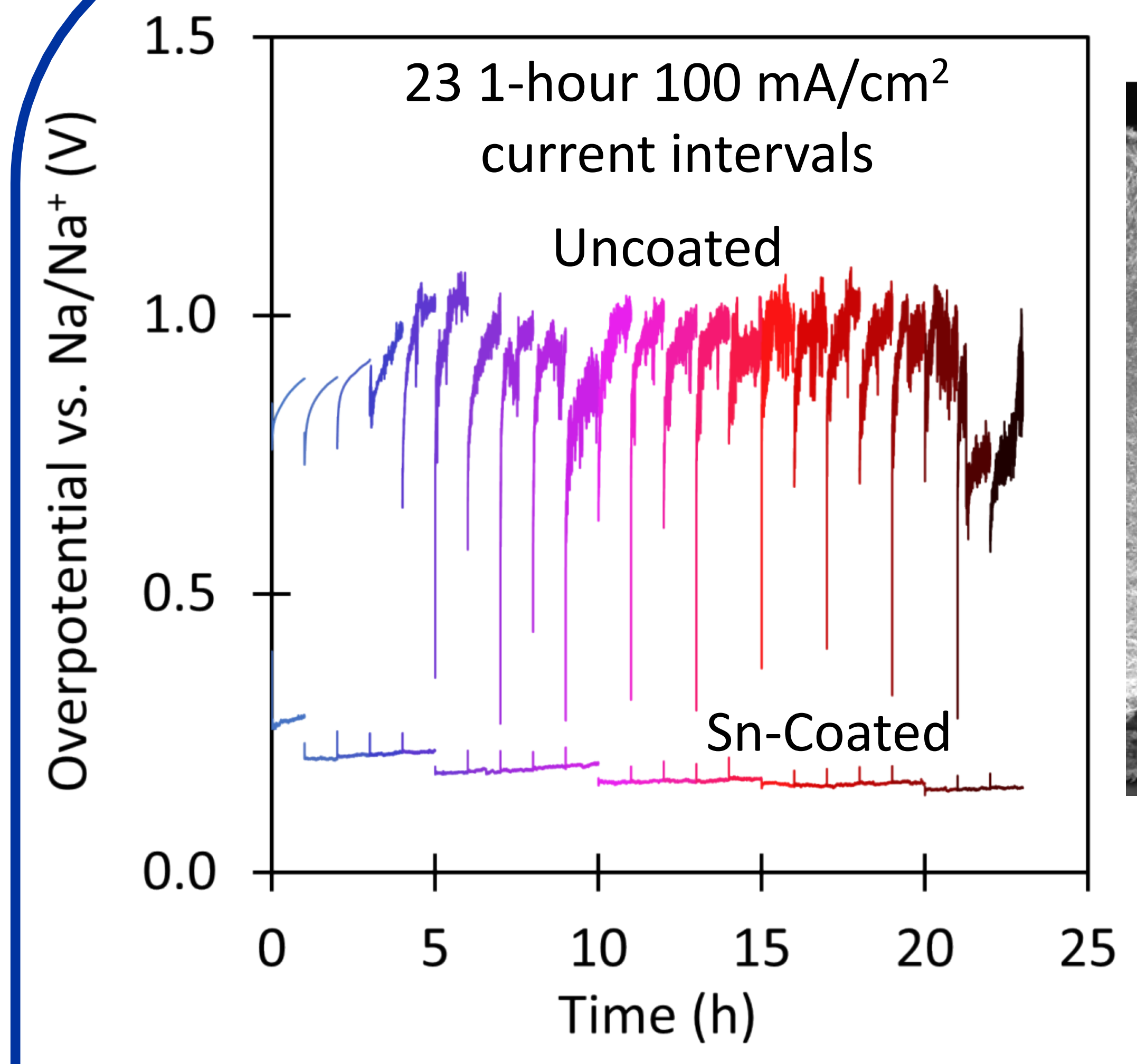
Mode II Degradation

Sodium-rich Regions (dendrites)

Mode I + II Degradation

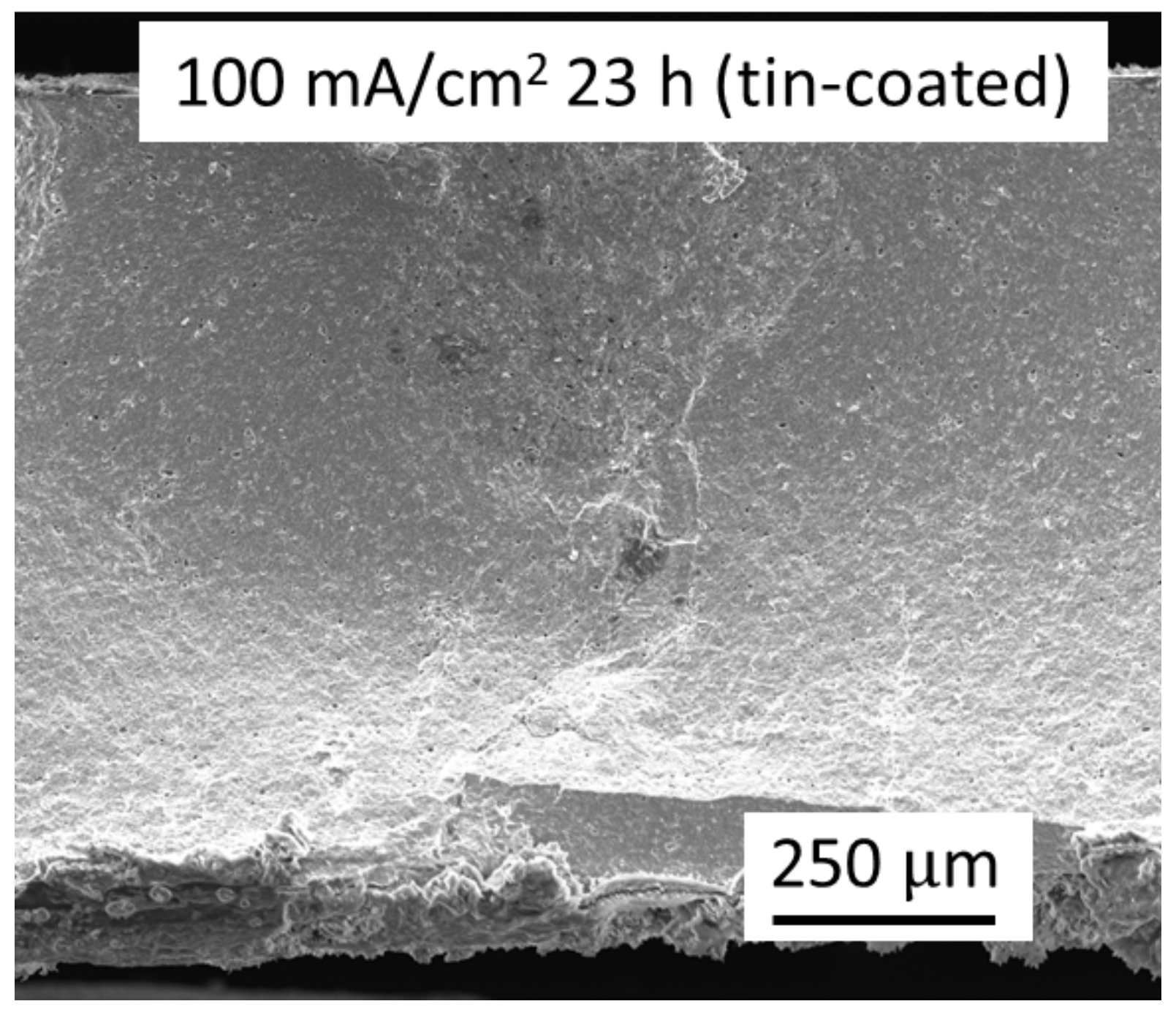
Cross-section SEM Images

Symmetric Cell Testing with Tin Coating



Overpotential Profiles

Tin coating eliminates interfacial resistance and allows for stable plating at high current density (100 mA/cm⁻²)



Cross-section of Sn-coated NaSICON

Tin coating also eliminates dendrite formation, even at high current density

Conclusions and Future Work

Conclusions:

- Initially, high current densities (100 mA/cm²) can be achieved in molten Na|NaSICON symmetric cells with a stable voltage profile
  - After some time, the voltage profile becomes noisy
- EIS can be used to measure the cell impedance and a decrease in impedance corresponds to the increasingly noisy voltage profile
- NaSICON degradation can occur by both Mode I (pressure-induced cracking) and Mode II (ion-electron recombination) mechanisms
- Tin coating eliminates reduces interfacial resistance, eliminates dendrite formation, and enables stable plating

Future Considerations:

- What features (porosity, etc.) cause early degradation?
- How are mechanical properties related to sodium penetration?

Acknowledgments

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