Shorting in NaSICON Solid Electrolytes for Long Duration Storage

Authors: **Ryan Hill***, Amanda Peretti**, Adam Maraschky**, Leo Small**, Erik Spoerke**, Yang-Tse Cheng*

*University of Kentucky and **Sandia National Laboratories

College of Engineering
Department of Chemical and Materials Engineering

Sandia National Laboratories

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

DOE OE Energy Storage Peer Review

October 24-26, 2023

SAND2023-10935C

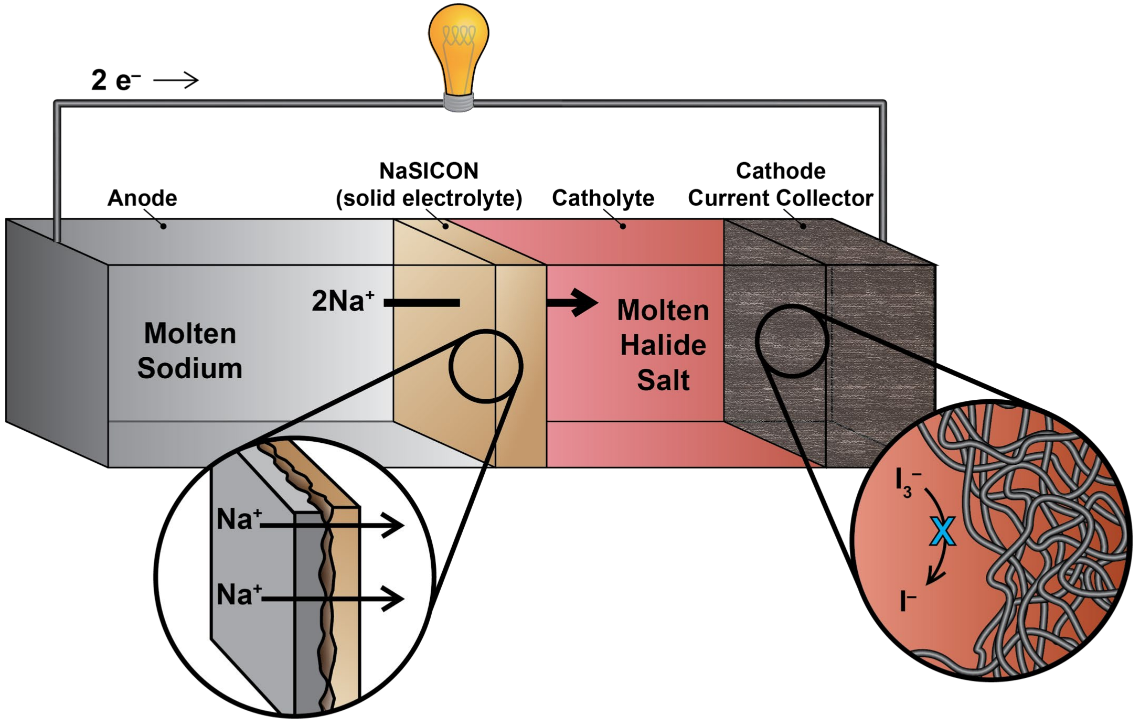
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

"Low" (110 °C) Temperature Molten Sodium (Na-NaI) Batteries

*Realizing a new, low temperature molten sodium battery requires new battery materials and chemistries – particularly in **solid-state sodium ion conductors***

Important electro-chemo-mechanical properties

- Highly Na^+-conductive
- Physical barrier between molten anode and catholyte
- ❑ (Electro)chemical compatibility with Na and halide salts
- ❑ Mechanical integrity and "dendrite" suppression
  - ✓ Important for large-scale, long-duration, long-life applications



<u>Na-NaI battery:</u>

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

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

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

$NaI\text{-}AlCl_3$: Small, L.J. et al. *J. Power Sources*. 2017, **2**, 100489

$NaI\text{-}AlBr_3$: Gross, M.M. et al. *ACS Appl. Energy Mater.* 2020, **3**, 11456

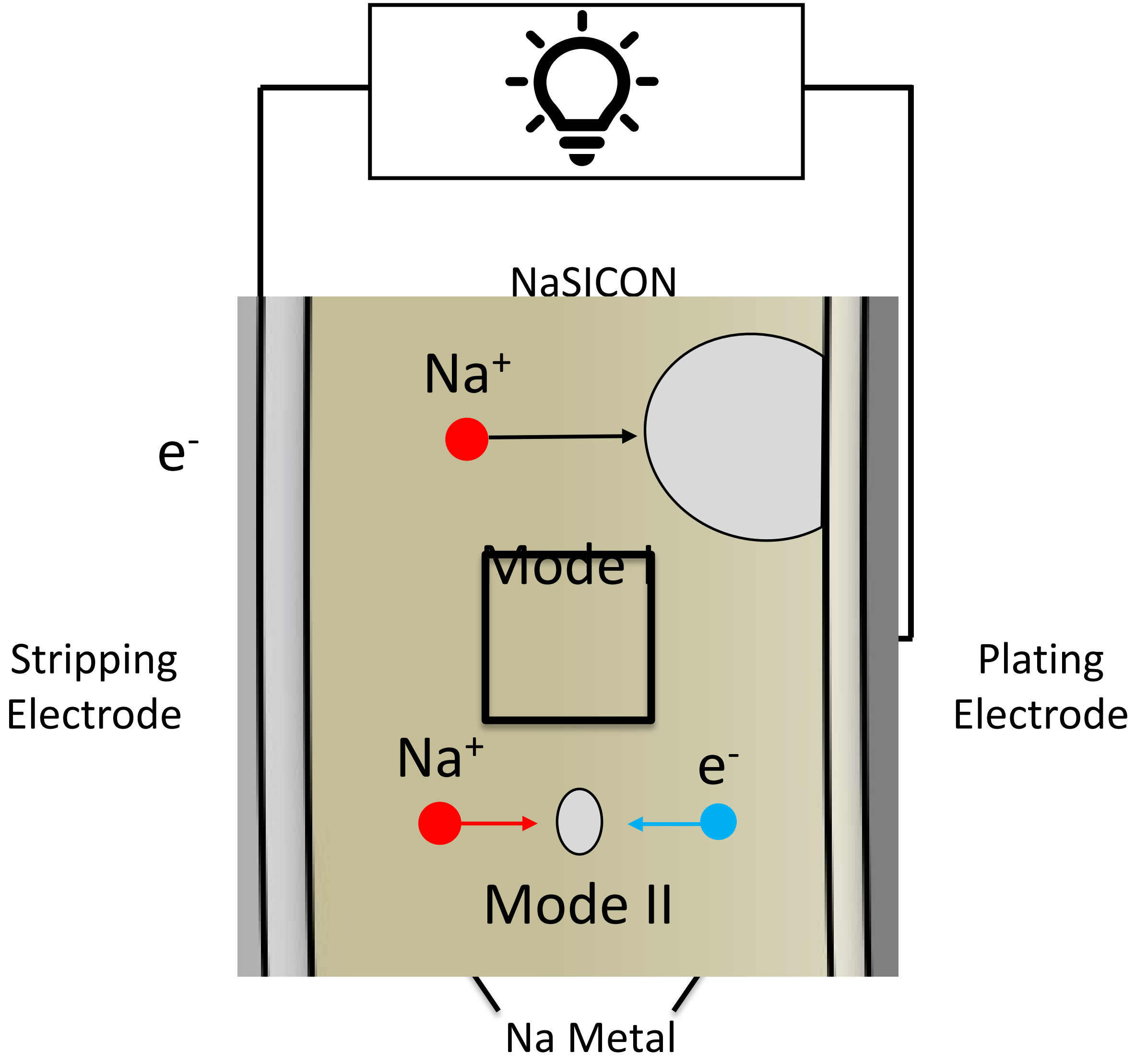
$NaI\text{-}GaCl_3$: Gross, M.M. et al. *Cell Rep. Phys. Sci.* 2021, **360**, 569

$NaI\text{-}AlCl_3$: Maraschky, A. et al. *J. Phys. Chem. C*. 2023, **127**, 1293

Na-NaI/MH battery diagram from Martha Gross

How Does NaSICON "Fail" in a Molten Sodium Battery?

- **Mode I**
  - Current concentration at "hotspots"
  - Poiseuille pressure buildup leads to cracking and sodium penetration
  - Initiates at <u>**plating interface**</u>
- **Mode II**
  - Caused by recombination of ions and electrons within electrolyte
  - Can occur anywhere within interior
- Mode I typically viewed as predominant mechanism



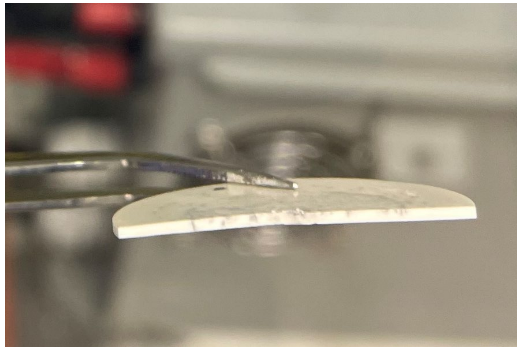
De Jonghe, et al. *Solid State Ionics* **1981**, *5*, 267-269.
<u>Hill, R.</u>, et al. *ACS Applied Energy Materials* **2023**, *6* (4), 2515-2523.

Unidirectional Current Testing in NaSICON

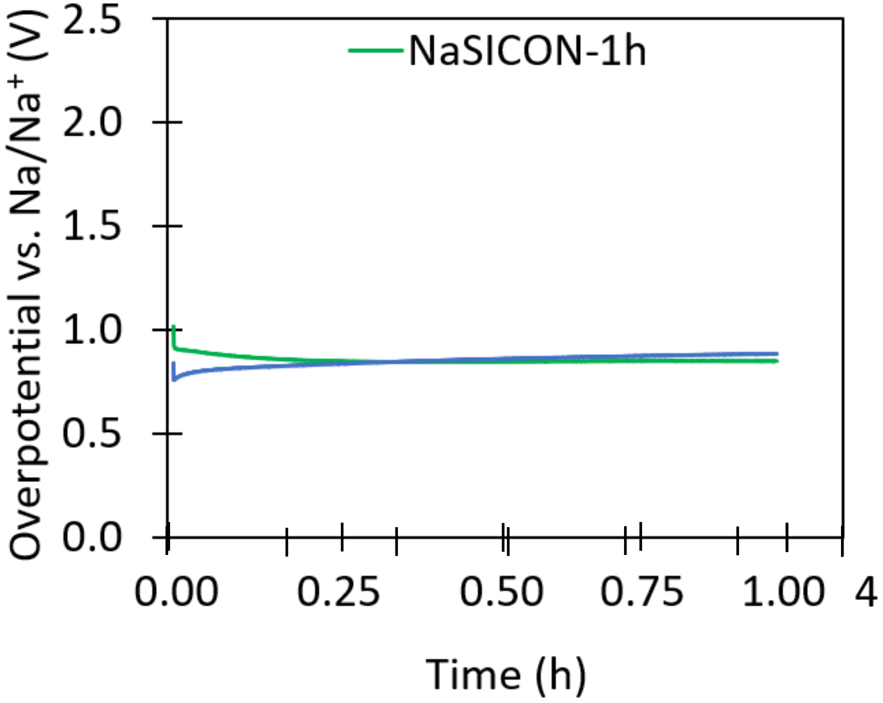
- Apply unidirectional current at 100 mA cm^{-2} in intervals
- Monitor overpotential and resistance during testing
- Visualize sodium "dendrite" progression as a function of time

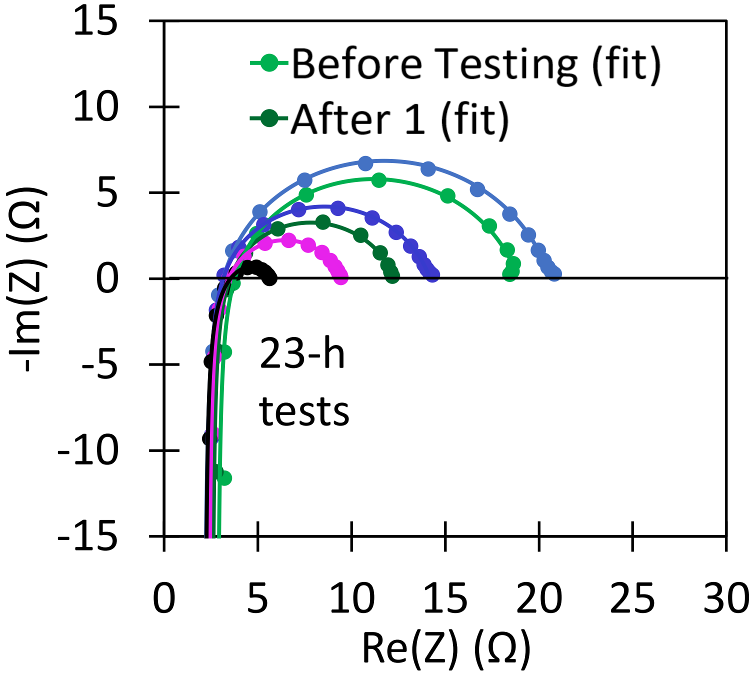
✓ **Mode II is just as prevalent as Mode I**

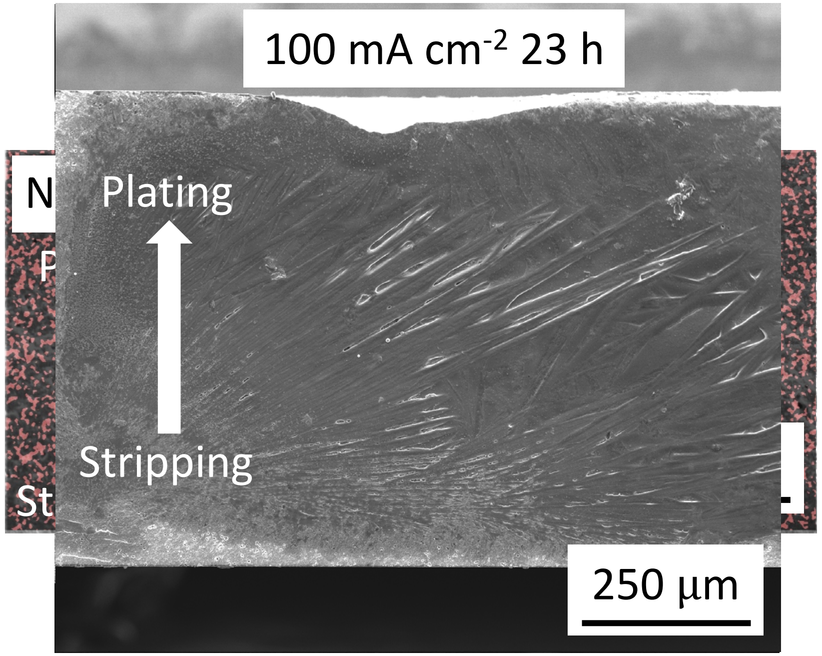
✓ **Critical Discharge Capacity (Current Density x Time)**



Fractured NaSICON Electrolyte



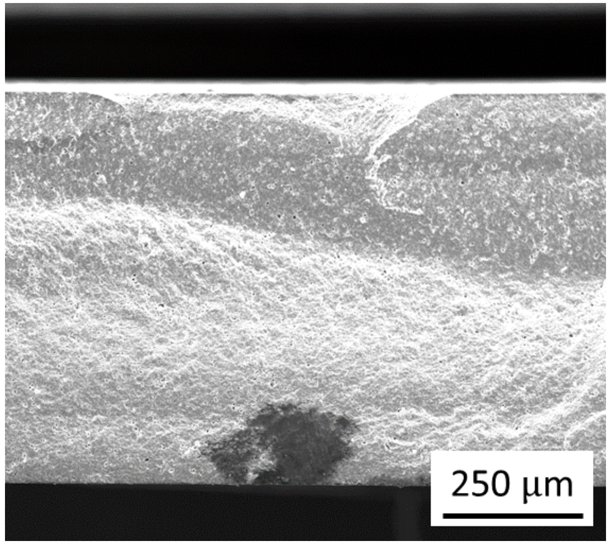




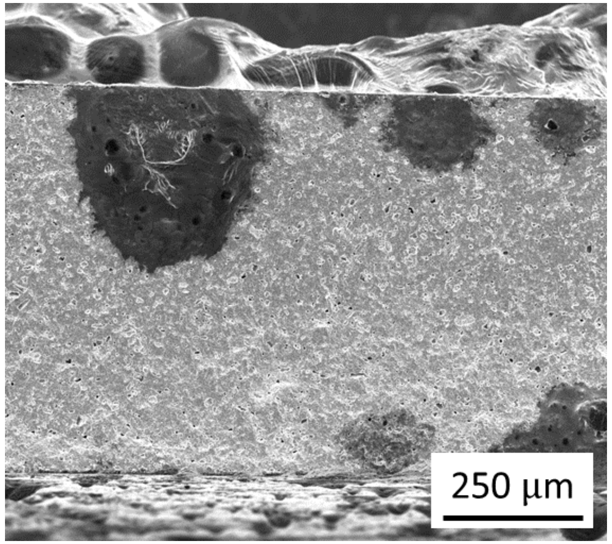
Hill, R., et al. *ACS Applied Energy Materials* **2023**, *6* (4), 2515-2523.

“Progressive” Failure in NaSICON

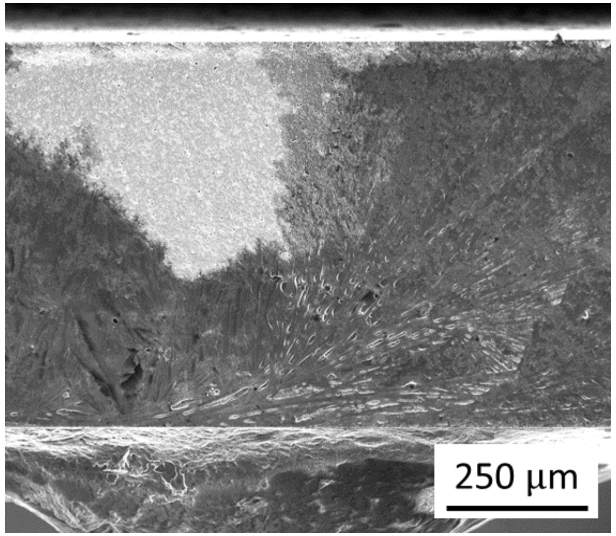
1 hour



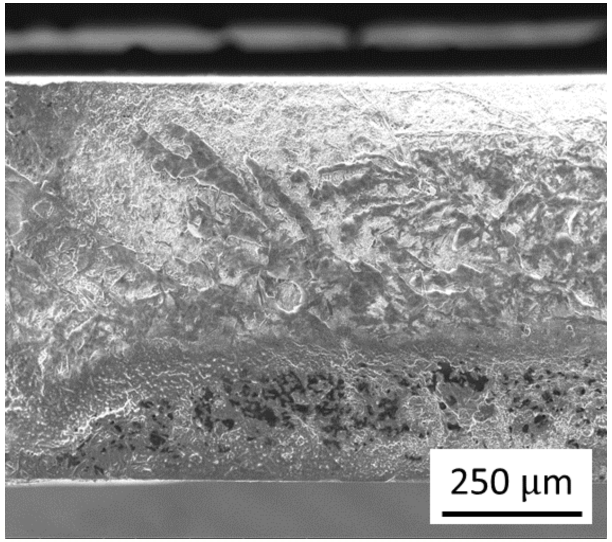
4 hours



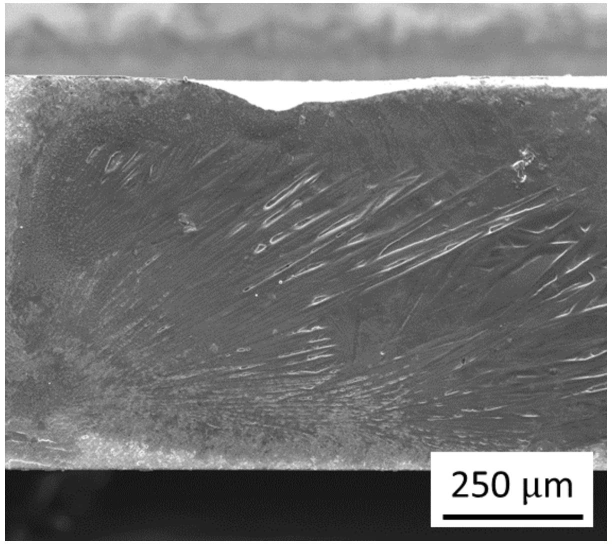
6 hours

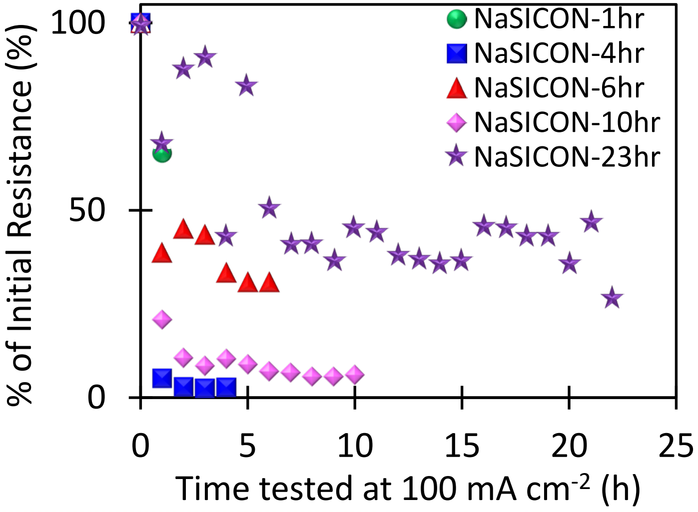


10 hours



23 hours

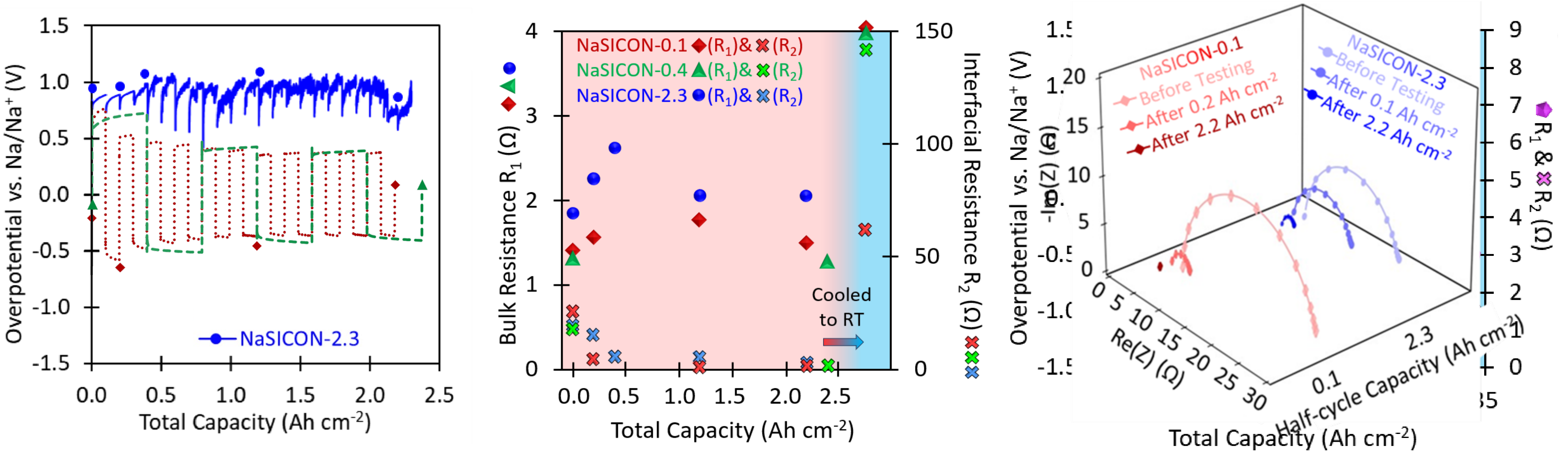




Hill, R., et al. *ACS Applied Energy Materials* **2023**, *6* (4), 2515-2523.

"Critical" Half-cycle Capacity in NaSICON

- Half-cycles up to 4 h showed stable overpotentials at 2.3 Ah cm^{-2} total capacity
- Interfacial resistance decreased, but cells did not "completely" short



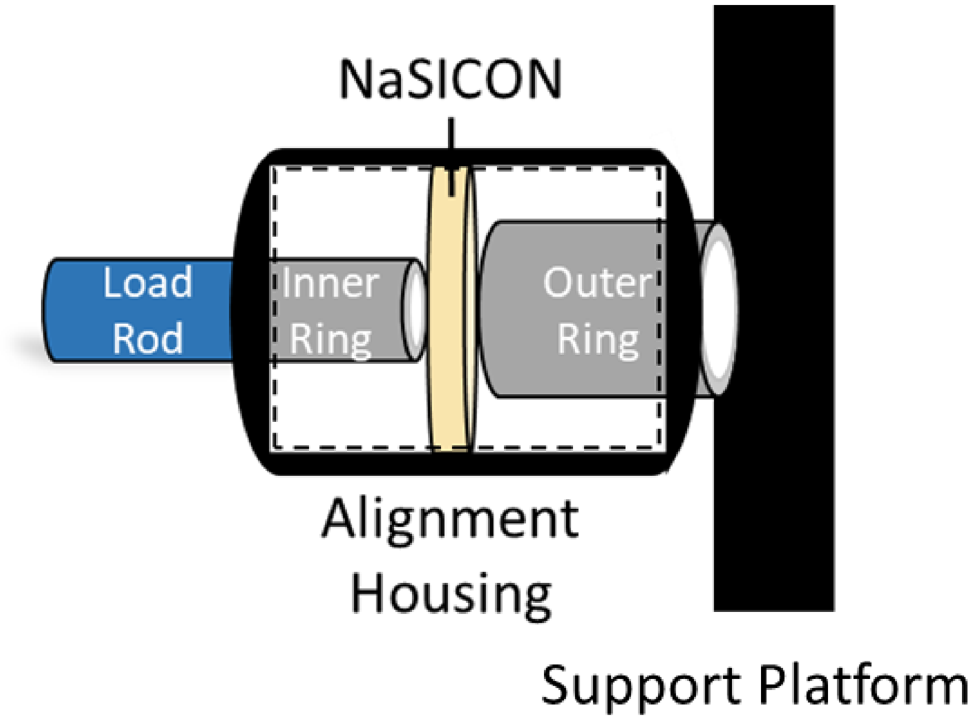
✓ **Promising for high-current, high-capacity applications**

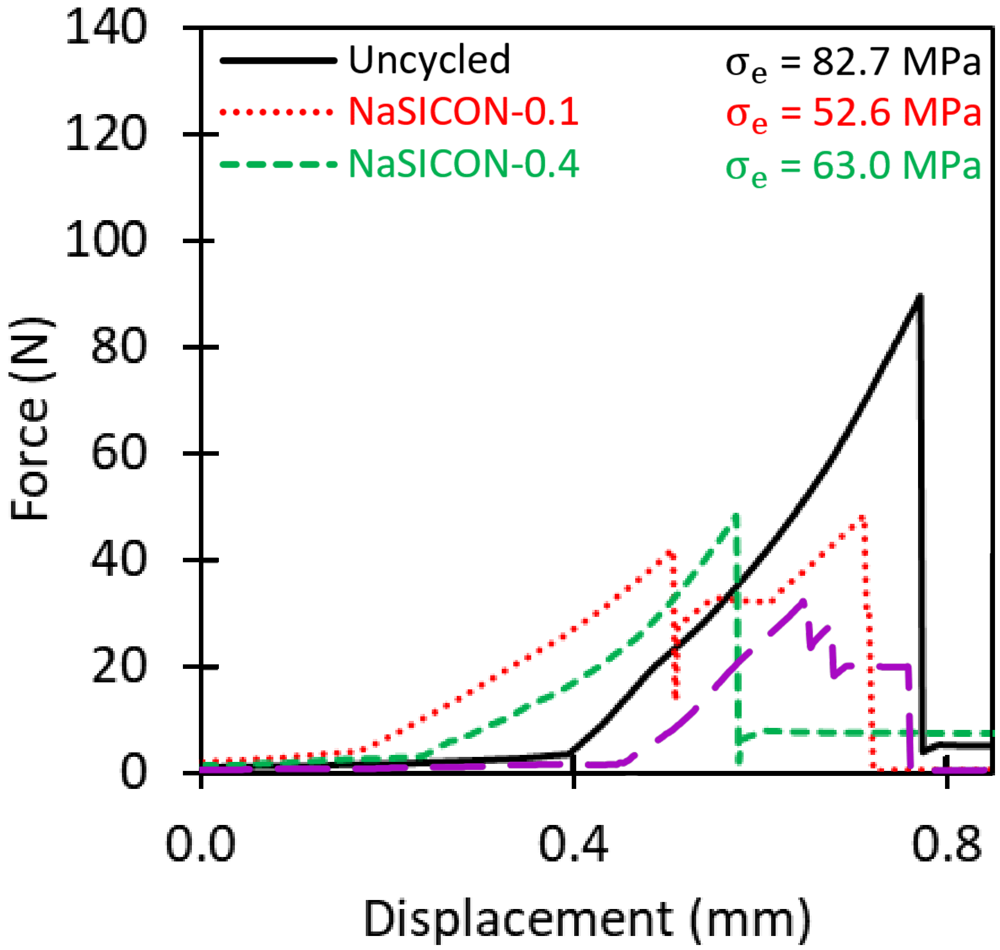
Hill, R., et al. *In Preparation*

Sandia National Laboratories
College of Engineering

“Critical” Half-cycle Capacity in NaSICON

- Even low-capacity half-cycles led to significant NaSICON weakening
- Long duration testing led to most severe weakening

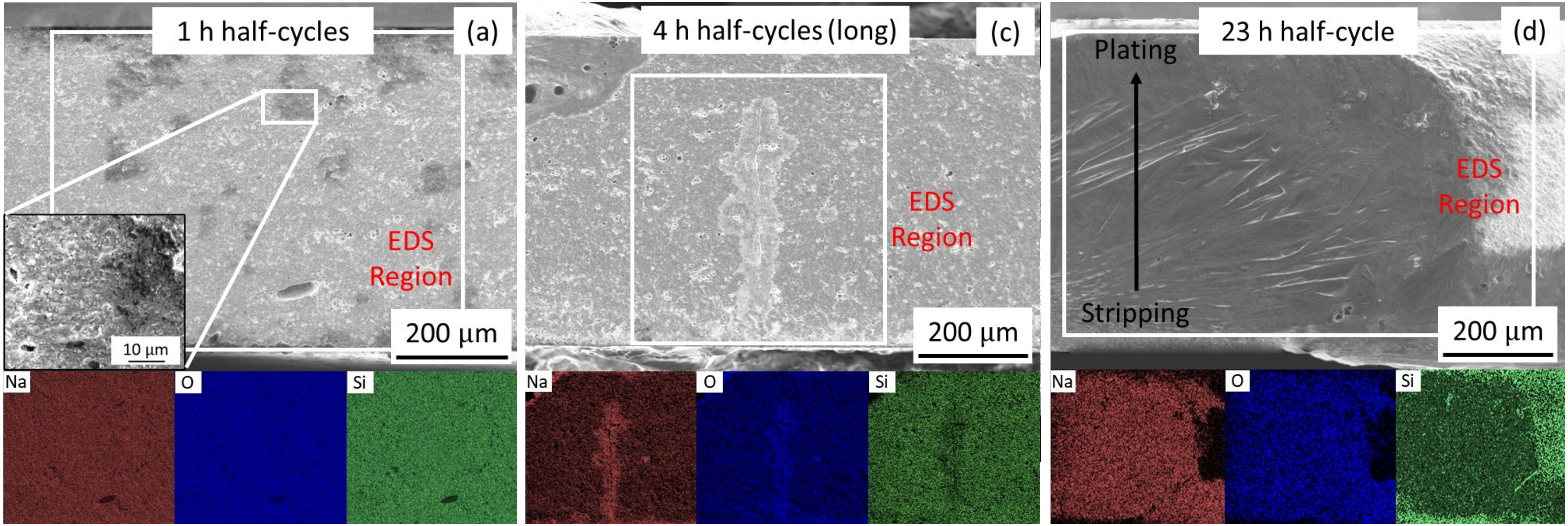




Hill, R., et al. *In Preparation*

Na Penetration and Half-cycle Capacity

- ✓ At low-capacity half-cycles, Na penetration is minimal/reversible
- ✓ At higher capacities, Na penetration becomes irreversible/catastrophic

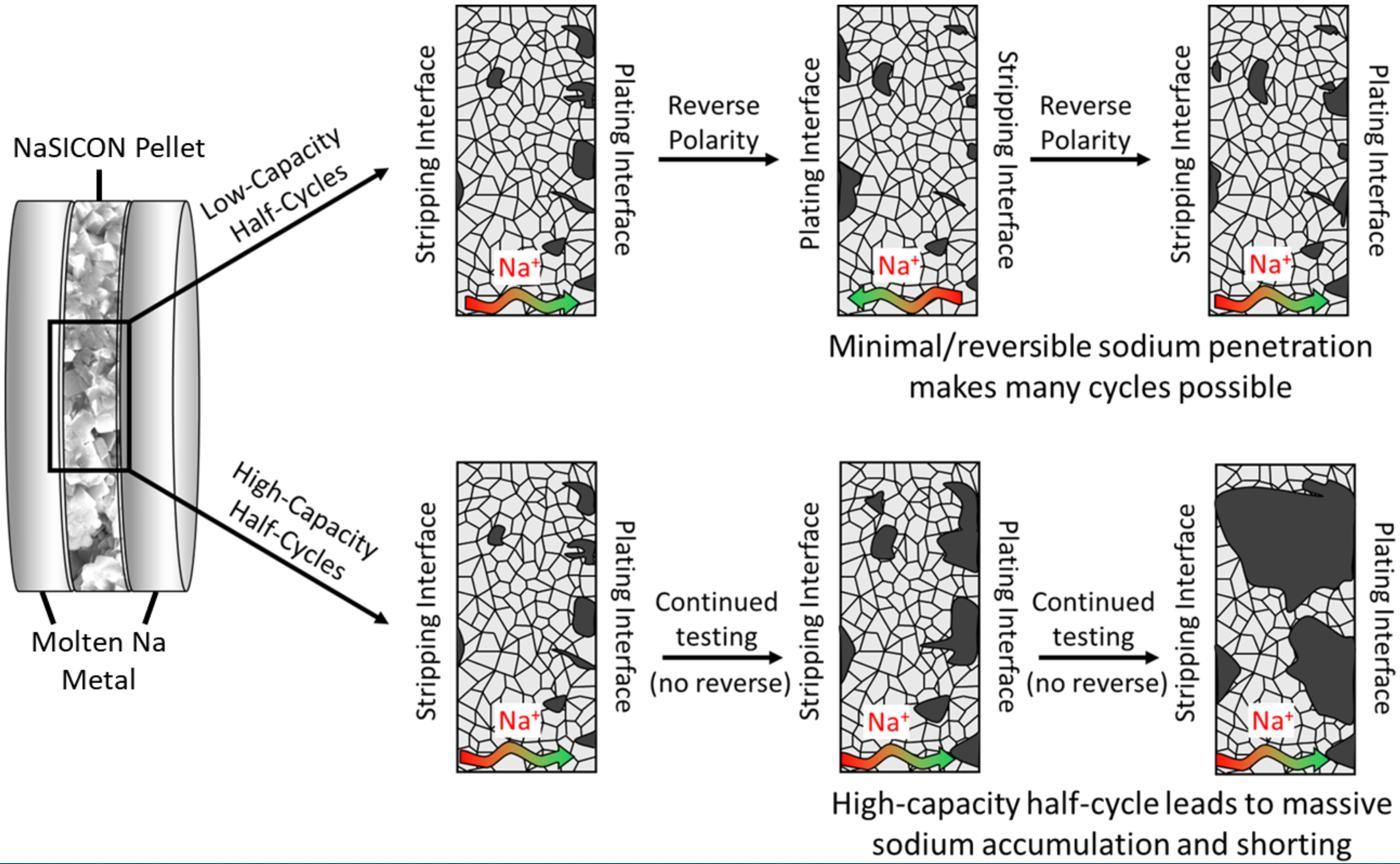


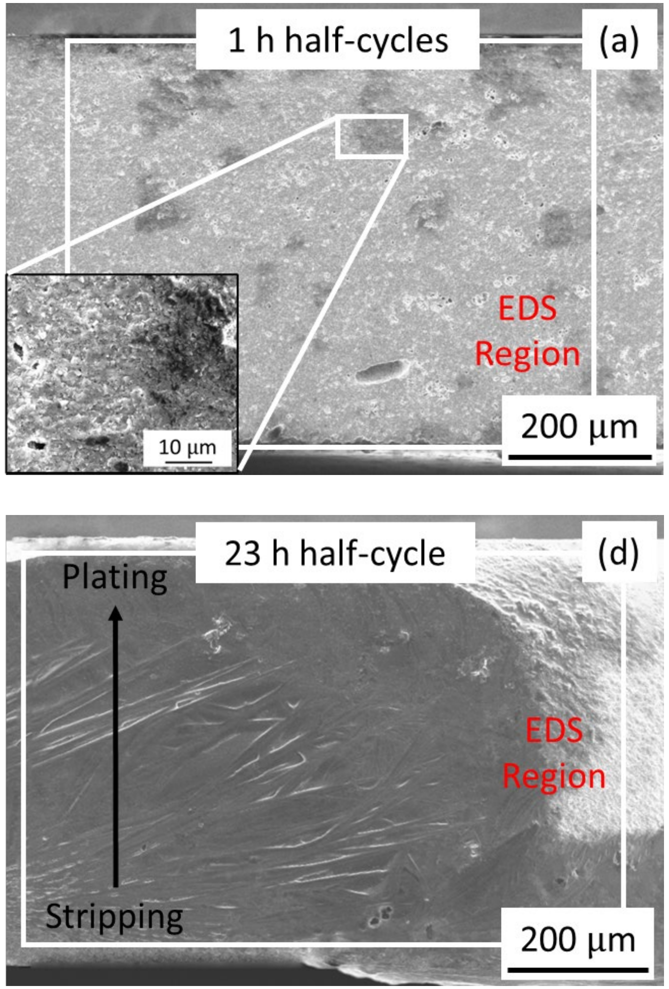
Hill, R., et al. *In Preparation*

Sandia National Laboratories
College of Engineering

Na Penetration and Half-cycle Capacity

- ✓ At low-capacity half-cycles, Na penetration is minimal/reversible
- ✓ At higher capacities, Na penetration becomes irreversible/catastrophic





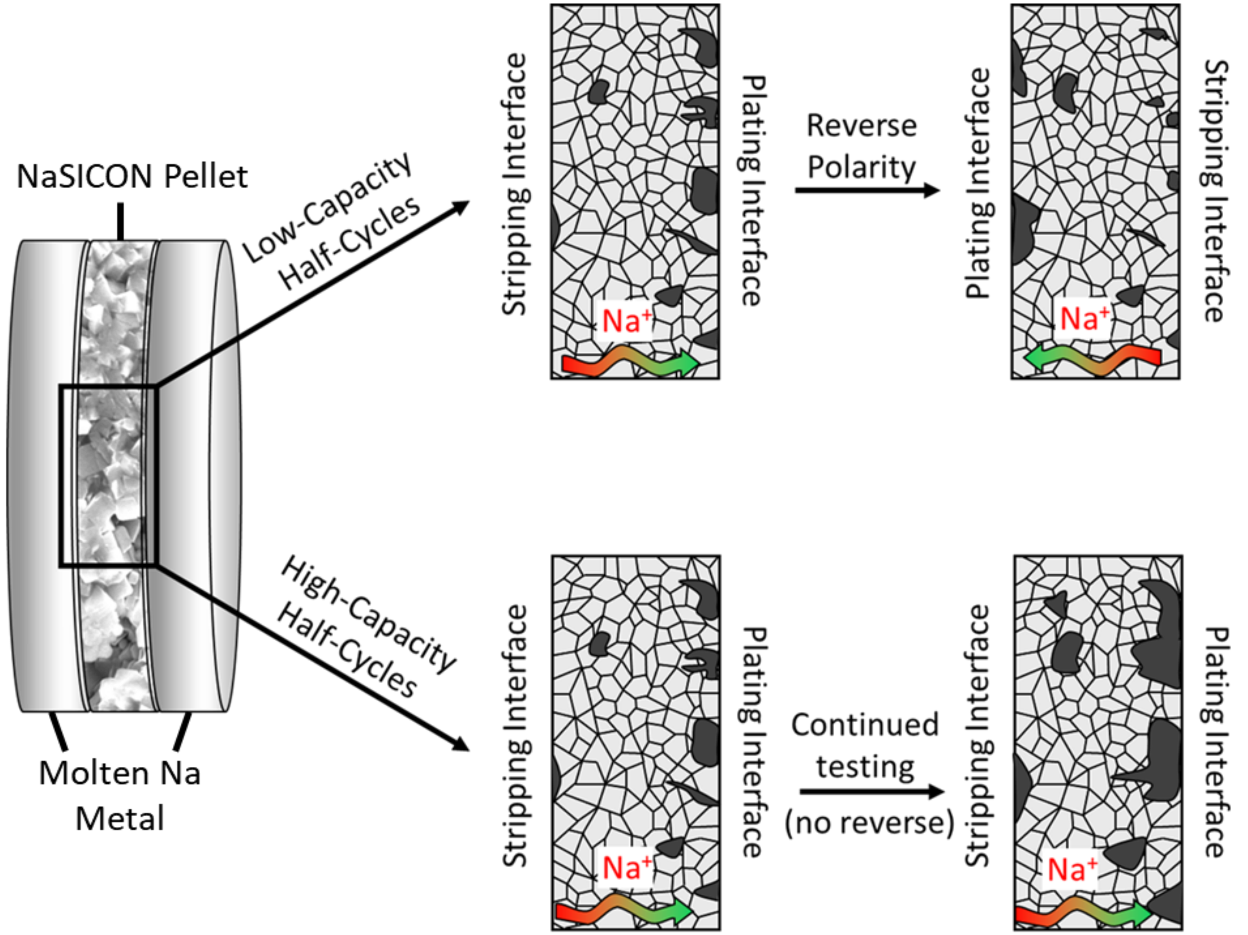
Hill, R., et al. *In Preparation*

In Short

- High current densities lead to both **Mode I and Mode II** failure in NaSICON
  - Can lead to catastrophic electrical or mechanical failure

- **Ring-on-ring bending** can gauge mechanical weakening from sodium penetration

- Critical cycling conditions for solid electrolytes depend strongly on **current density *and* half-cycle capacity**
  - Reversing polarity at low capacities can partially "heal" Na penetration



Sandia National Laboratories
College of Engineering

Acknowledgments

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.

Paper with details!

University of Kentucky
Yang-Tse Cheng
Bhamiti Sharma
Jacob Hempel
Kübra Uzun
Haidar Alolaywi
Santosh Thapa
Ethan Lauricella
Jiaxiang Cui
Luke Hentz
Dongcheng Liu

Sandia National Labs
Erik Spoerke
Leo Small
Adam Maraschky
Martha Gross
Amanda Peretti
Babu Chalamala

Ryan Hill

Ryan.C.Hill@uky.edu

Sandia National Laboratories
College of Engineering