Sandia National Laboratories

Charge Transfer Kinetics of the Sodium | NaSICON Interface

Isaac D. Dyer, Amanda S. Peretti, Stephen J. Percival, Corey R. Carlos, Robert L. Craig, Michael E. Ureña, and Leo J. Small
Sandia National Laboratories, Albuquerque, NM USA 87185

PROJECT PROFILE

Topic: Sodium Batteries
Vertical: Materials & Systems Innovation
Strategic Pathway: Grow
Project start and finish: FY25-26

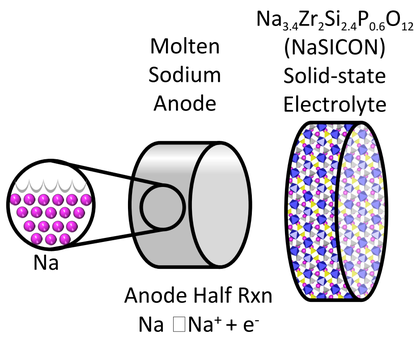
PROBLEM

Why Sodium Batteries?

- Grid Scale Stationary Storage
- Low cost & Abundant Elements
- AI Data Center Deployment
- High Peak Load Variability

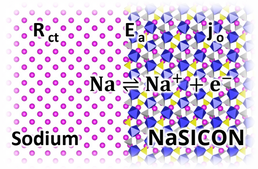
Despite Progress

The anodic interface in NaSICON sodium systems remains inadequately understood

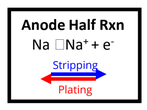


Kinetic Parameters

Few reported values limit our understanding and ability to predict performance of new interface architectures

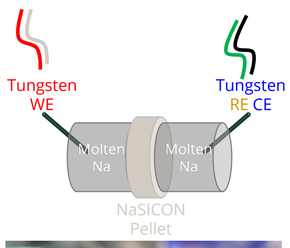


R_{ct} - Charge Transfer Impedance
E_a - Activation Energy
j_o - Exchange Current Density



APPROACH

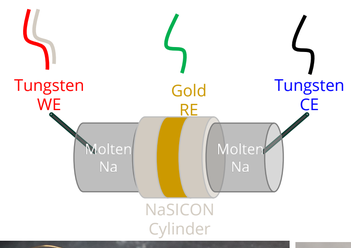
Two Electrode Cell

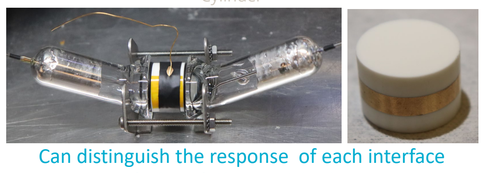


The response is measured through both interfaces simultaneously

Two Electrode: Simpler but ambiguous

Three Electrode Cell





Can distinguish the response of each interface during plating or stripping

Three-electrode: more complex but yields isolated interface information

RESULTS

Two Electrode Cell

Charge Transfer Impedance & Activation Energy

- Solid and liquid sodium follow the same Arrhenius trendline
- Interfacial charge-transfer is kinetically limited by a NaSICON-dominated process
- The physical state of sodium (solid vs. molten) does not influence the activation barrier

Figure 1. Charge transfer impedance of the NaSICON | Na metal interface from 70 °C to 135 °C. (a) 3D Nyquist plot showing the impedance as a function of temperature (data collected from 1 MHz to 1 Hz). (b) Temperature dependence of the fitted interfacial charge transfer resistance extracted from equivalent circuit modeling. The inset shows the equivalent circuit used. The melting point of sodium (~98.7 °C) separates the molten (orange) and solid (blue) sodium regimes. (c) Arrhenius plot of ln(T / R_interface) versus 1000/T (in K^{-1}), with data points (red/orange circles for molten sodium, blue circles for solid sodium) fitted to a linear regression (black line). The slope yields an activation energy for interfacial charge transfer of E_a = 0.788 eV, with R^2 = 0.996.

RESULTS (Cont.)

Exchange Current Density

- Molten Sodium | Solid ceramic interface follows Butler-Volmer relationship
- Fitting Galvanostatic cycling data with Butler Volmer Equation, can obtain j_o
- Linear region (low η) fit is a more accurate representation of j_o
- Exchange current Density follows an exponential trendline with temperature, useful for extrapolation

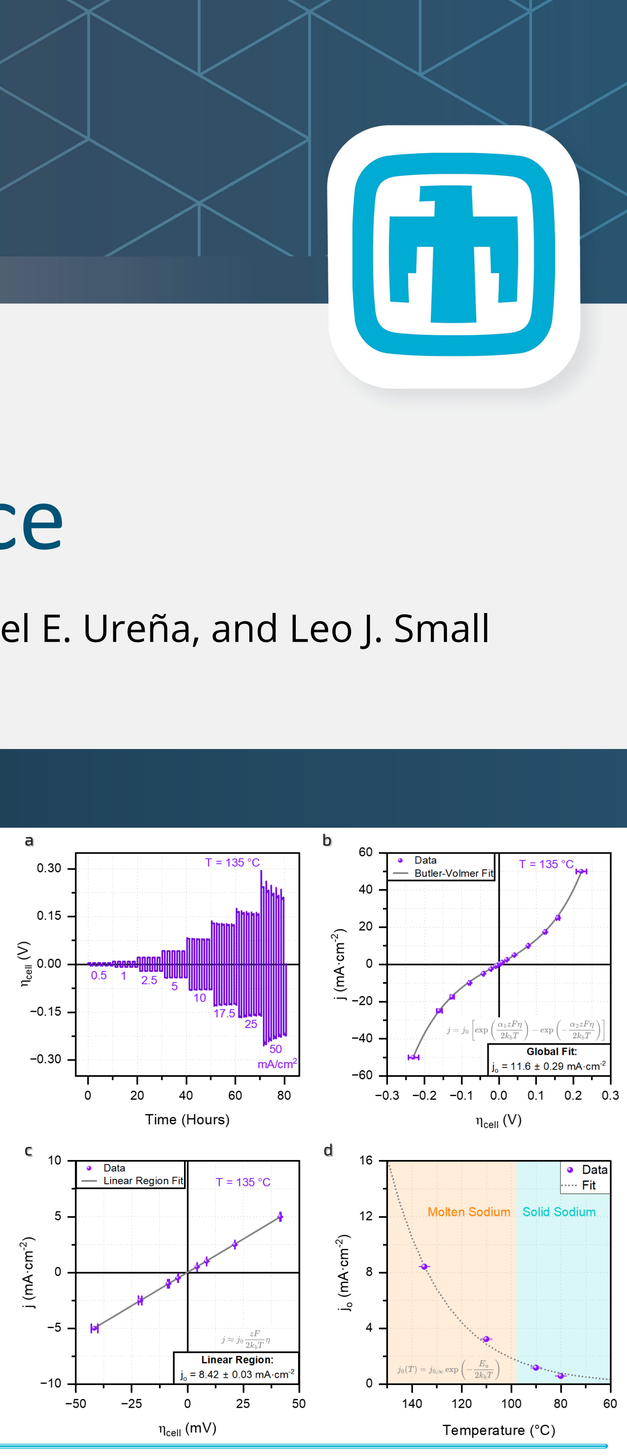


Figure 2: Galvanostatic cycling and exchange current density (j_0) analysis of the Na | NaSICON interface at 135 °C. **(a)** Galvanostatic cycling of Na | NaSICON symmetric cell **(b)** Polarization curve of symmetric cell current density (j) versus overpotential (η), The Butler-Volmer fit (grey line) is overlaid on the experimental data (purple circles). **(c)** Linear regression fit to the low-overpotential region (±50 mV) of the same polarization data, where the Butler-Volmer equation approximates linear behavior. **(d)** Exchange Current density (j_o) values of the same cell with T = 80, 90, 110, and 135 °C. Extrapolated exponential fit of the j_o data (grey dashed Line). Solid Sodium (teal) and Molten sodium (orange) regimes are colored.

Three Electrode Cell

- During Sodium stripping progressive overpotential increase
- During Sodium plating initial Nucleation overpotential spike, then rapid relaxation
- Verified Kinetic Parameters from 2 electrode cell

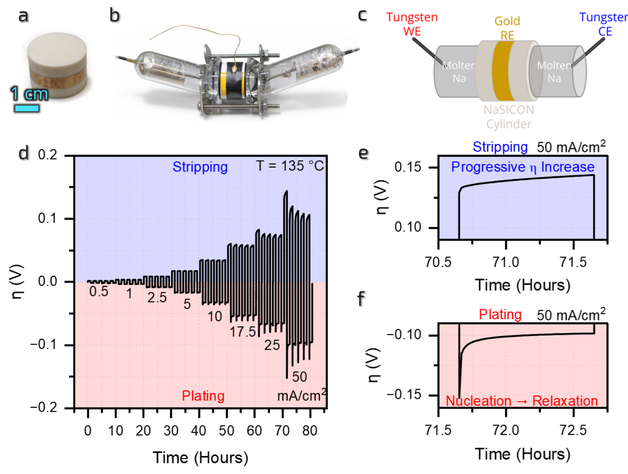


Figure 3. Three-electrode characterization of the Na | NaSICON | Na interface at 135 °C. Photograph of the **(a)** NaSICON cylinder **(b)** assembled into the three-electrode cell. **(c)** Schematic of the cell configuration: tungsten working electrode (WE, red) and counter electrode (CE, blue) in molten sodium, a gold thin film belt serving as the reference electrode (RE, gold) on the NaSICON cylinder. **(d)** Galvanostatic stepwise cycling. Blue-shaded region denotes Na stripping; red-shaded region denotes Na plating. **(e)** Zoomed stripping half-cycle at 50 mA cm^{-2}. **(f)** Zoomed plating half-cycle at 50 mA cm^{-2}

CONCLUSIONS & IMPACT

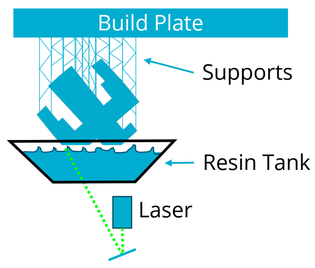
- Sodium | NaSICON interfacial kinetics show a consistent activation energy of 0.788 eV from 135–70 °C, The physical state of sodium (solid vs. molten) does not influence the activation barrier
- Exchange current density at 135 °C is 7.42 ± 0.94 mA cm^{-2}, extrapolating to about 72 µA cm^{-2} at 25 °C
- Three-electrode tests confirm asymmetric plating/stripping behavior
- Validated Two electrode symmetric cells as a reliable method to extract interfacial kinetics
- Methodology can be applied to other coatings or interlayers to compare (e.g. Tin coating, Hard Carbon, etc.) For Sn coated NaSICON 135°C j_o = 12.9 ± 0.03 mA·cm^{-2} and E_a = 0.74 eV

Presentations: **Isaac D. Dyer**; Urena, M. E.; Peretti, A. S.; Percival, S. J.; Small, L. J. Designing 3D Interfaces and Enhancing Sodium Wettability for Next-Generation Molten Sodium Batteries. *Presented at the Boston MRS Meeting,* Boston, MA, December 2025.

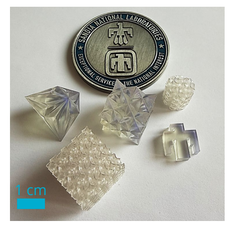
Papers: **Isaac D. Dyer**, Amanda S. Peretti, Stephen J. Percival, Corey R. Carlos, Robert L. Craig, Michael E. Ureña, and Leo J. Small Charge Transfer Kinetics of The Sodium | NaSICON Interface, *In Review at Sandia*

FUTURE DIRECTIONS

- The sodium batteries team at Sandia is working towards 3D printing NaSICON in hopes of achieving more intricate interfaces with substantially higher surface areas
- Utilizing a Photocurable Resin mixed with our NaSICON powder and a 25 µm SLA Laser Printer
- Utilize the kinetic parameters to inform improved interface architectures



SLA Printing Schematic



Resin Test Prints

iddyer@sandia.gov

SAND2026-23654C

This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.