Designing 3D Interfaces and Enhancing Sodium Wettability for Next-Generation Sodium Ion Batteries

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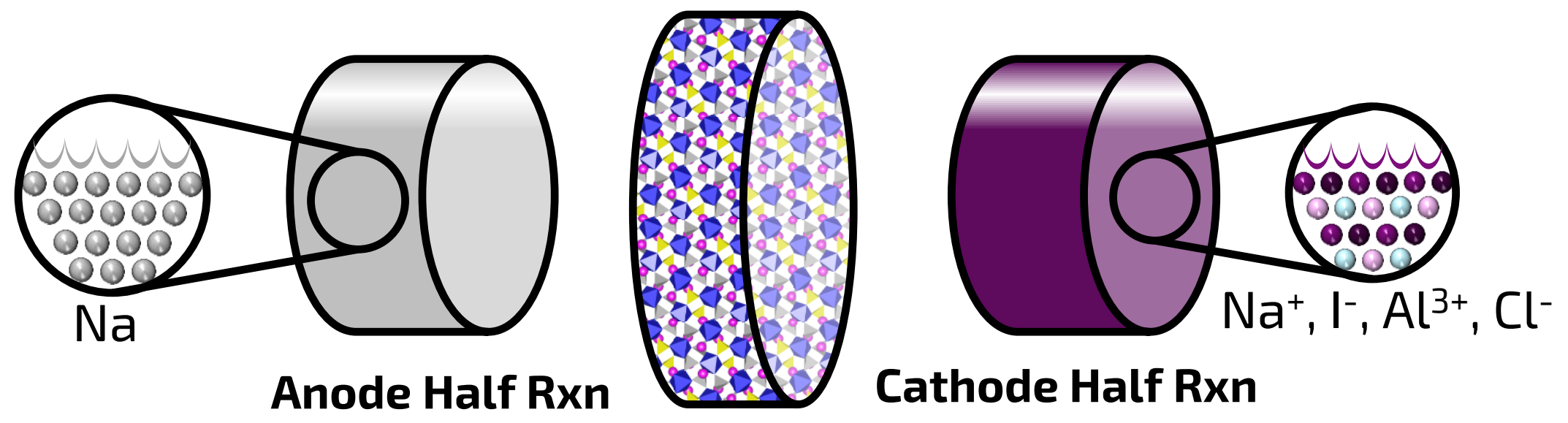
Motivation: Sodium-ion batteries are emerging as a cost-effective and sustainable alternative to lithium-ion batteries, driven by the abundance of geological sodium resources and avoiding critical minerals. While lithium-ion batteries dominate mobile energy storage applications due to their high energy density, sodium-ion batteries are increasingly recognized for their potential to stabilize the electric grid via applications such as long duration energy storage.

Our Approach

We focus on developing safe, low cost, sodium batteries.



Molten Sodium Anode

NaSICON Solid-state Electrolyte

Molten Salt Catholyte

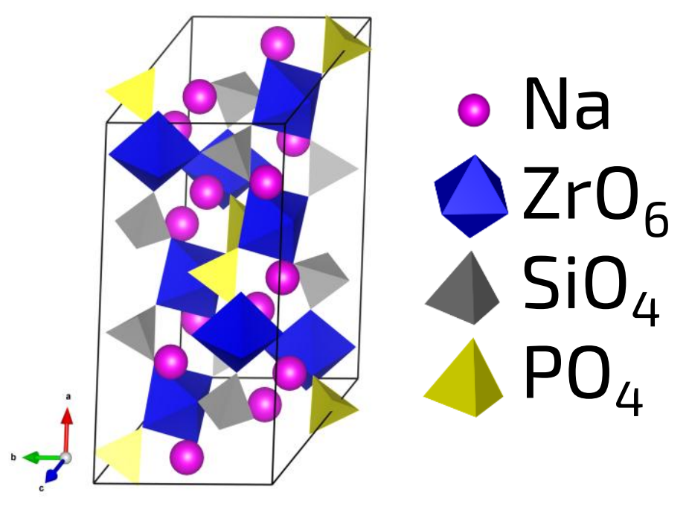
Anode Half Rxn
$Na \rightarrow Na^+ + e^-$

Cathode Half Rxn
$I_3^- + 2e^- \rightarrow 3I^-$

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

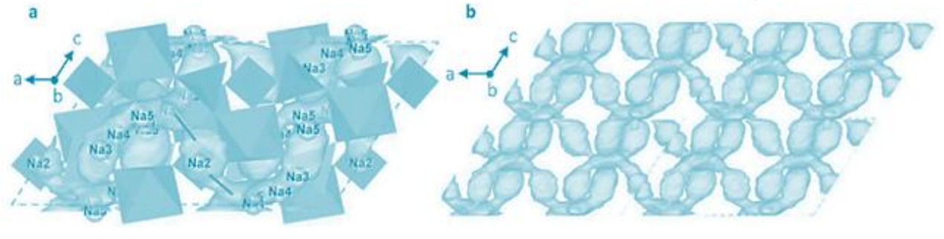
NaSICON Solid-state Electrolyte

- Sodium (**Na**) **S**uper **I**on **Con**ductor (**NaSICON**).
- $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (0 < x < 3).
- High Na⁺ ionic conductivity (~10^{-3} S/cm) at room temperature.
- Good stability against sodium metal.



$Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$
Monoclinic
Unit Cell

Sodium Conduction Pathways



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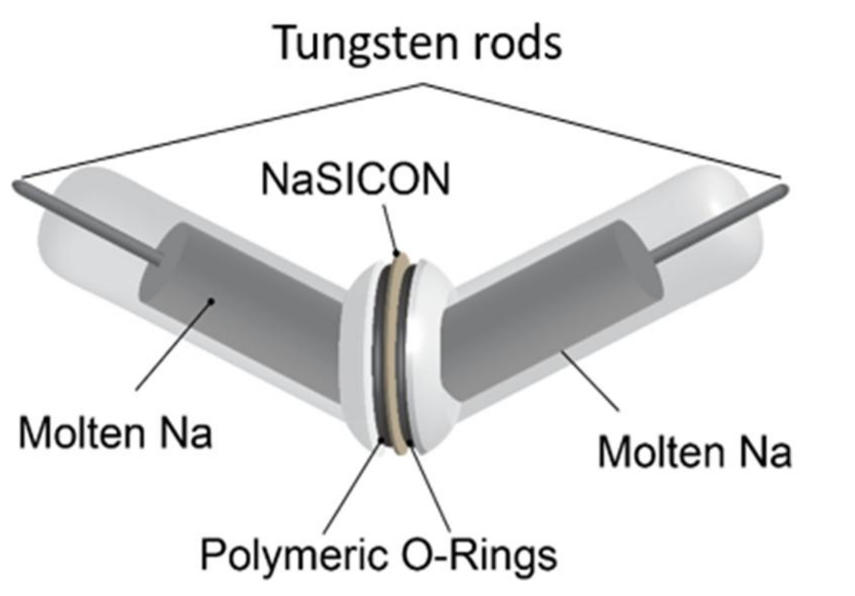
Rigid network of corner sharing SiO_4/ZrO_4 tetrahedron and ZrO_6 Octahedron enabling high Na⁺ conductivity

Molten Sodium Cell Design

Symmetric cell enables isolation and evaluation of the sodium-NaSICON interface.

Symmetric cell Characterization:
- NaSICON/Sodium interface wetting tests
- Rate capability
- NaSICON/Na interfacial impedance evolution
- Dendritic failure

Symmetric Cell



Project Goal

Study the effects of NaSICON surface topography on interfacial charge transport at the sodium-NaSICON interface,

Ultimately, we want 50 mA/cm² at 75 °C for a Na-NaSICON-Na system.

Current Practice

Our electrochemical cells currently operate at 50 mA/cm² at 135°C. Lower temperature would increase attractiveness for widespread commercialization.

Why SNL?

SNL leverages over a decade of expertise in NaSICON based cells. Experienced in material synthesis & electrochemical characterization of fully assembled devices.

Innovation

High-surface-area electrode-electrolyte interfaces engineered for enhanced sodiophilicity. By optimizing sodium wetting properties and maximizing interfacial contact area, we hope to enable elevated current densities at lower temps.

Impact

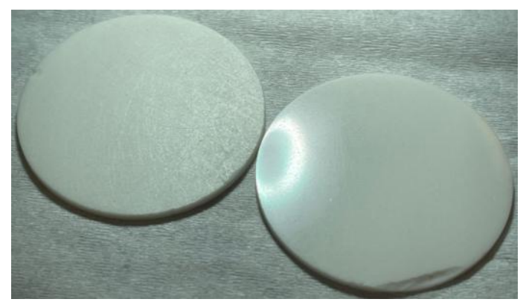
Achieving 50 mA/cm² at 75 °C will enable commercially attractive energy storage systems capable of addressing peak load demands, thereby bolstering energy storage grid reliability.

Alignment with DOE

By advancing long-duration energy storage technologies, the work enhances grid resilience and facilitates the seamless integration of diverse energy sources—ranging from nuclear to natural gas energy generation.

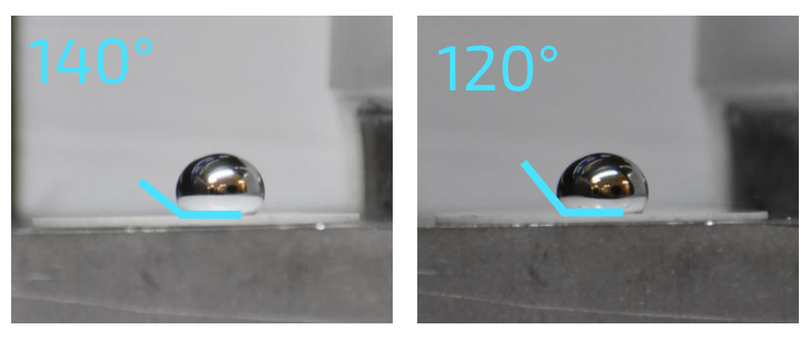
Sodium NaSICON Wettability

Rough vs. Smooth
1" NaSICON Pellets



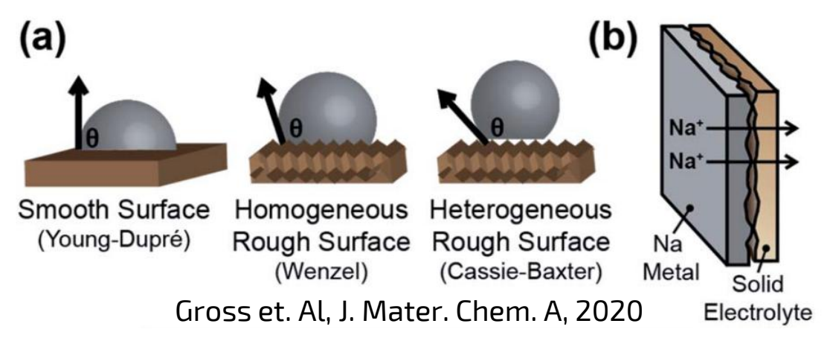
80 grit (Rough)	Vs.	1200 grit (smooth)
~R_a = 20 µm		~R_a = 0.1 µm

Contact Angle Measurement
Na on NaSICON



Unpolished

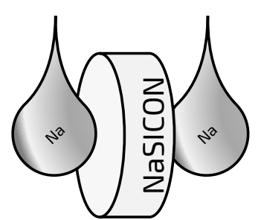
Polished



Gross et. Al, J. Mater. Chem. A, 2020

- Unpolished surface has poor sodium wettability
- Polished NaSICON has improved sodiophilicity
- Sn coating NaSICON has the best wettability due to Sn-Na alloying
- Zn doping the NaSICON enables good wetting without coating

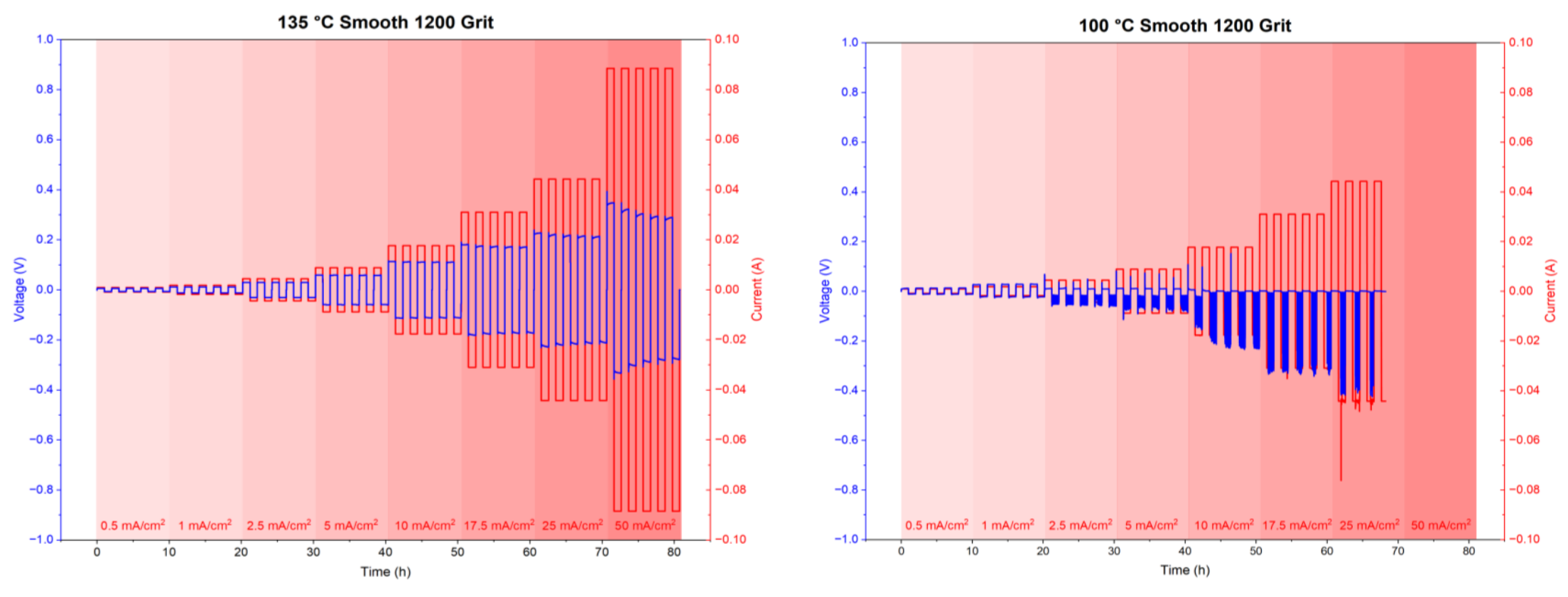
Surface Roughness Cycling Stability



Polished Unmodified NaSICON Rate Test

135 °C Molten Sodium

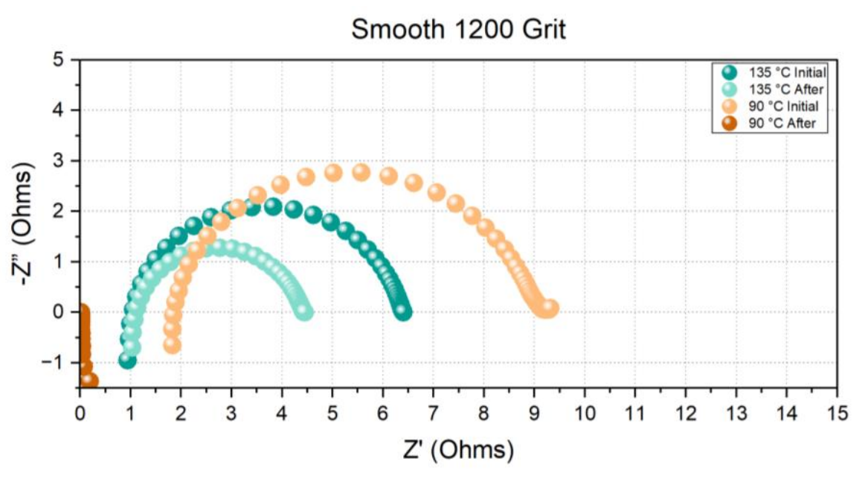
90 °C Solid Sodium

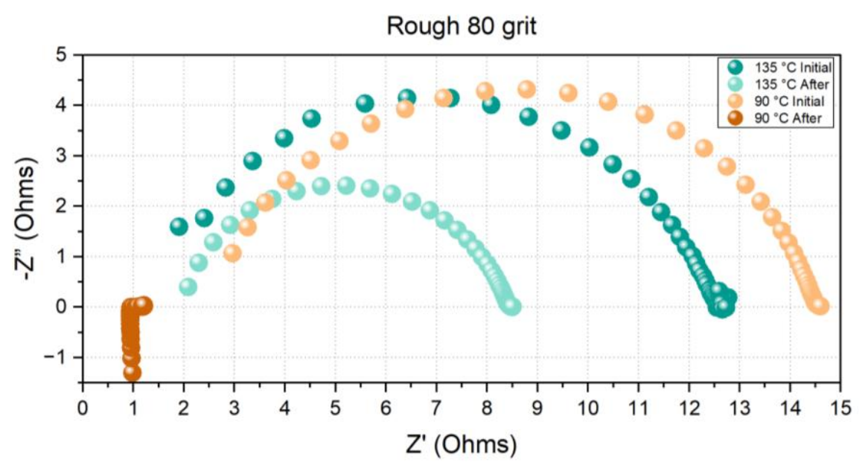


- Molten sodium can achieve >50 mA/cm² with no dendritic failure
- Solid sodium, the cells short at currents above 1 mA/cm²
- Rough pellet had 2× the overpotential and shorted at 0.5 mA/cm²

Failure Mechanisms

Symmetric Cell Electrochemical
Impedance Spectroscopy (EIS)



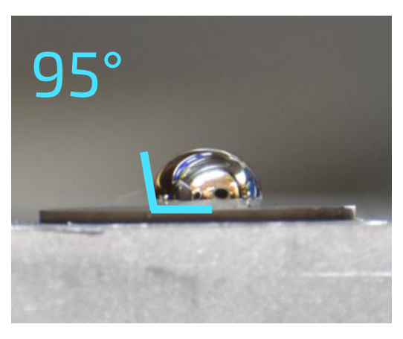


- Rough pellet had 2x the initial impedance
- Impedance decreased after 135 °C cycling
- Impedance increased with lower temp 90 °C
- Both cells shorted at 90 °C

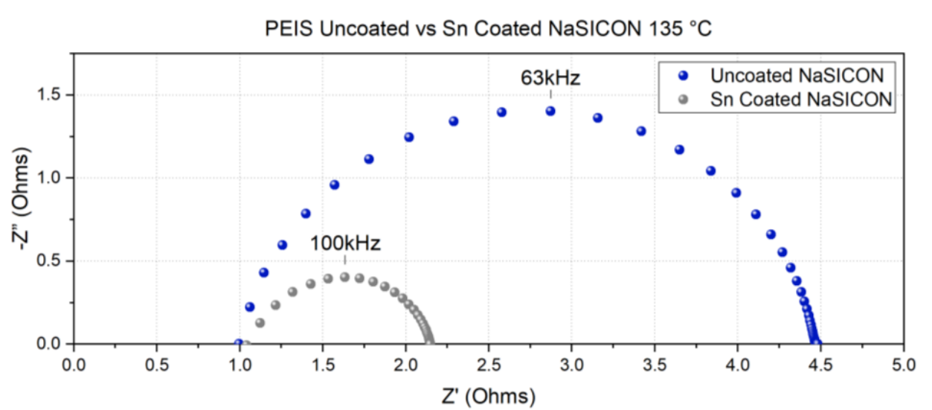
After Cycling:

Dendrites through NaSICON

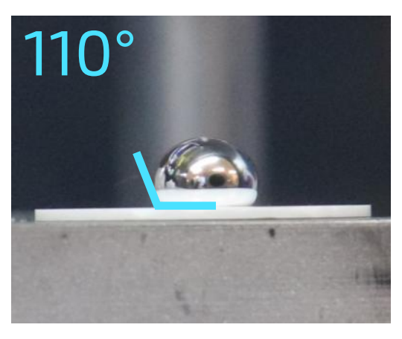
Chemical Modifications of Interface



Sn coated NaSICON



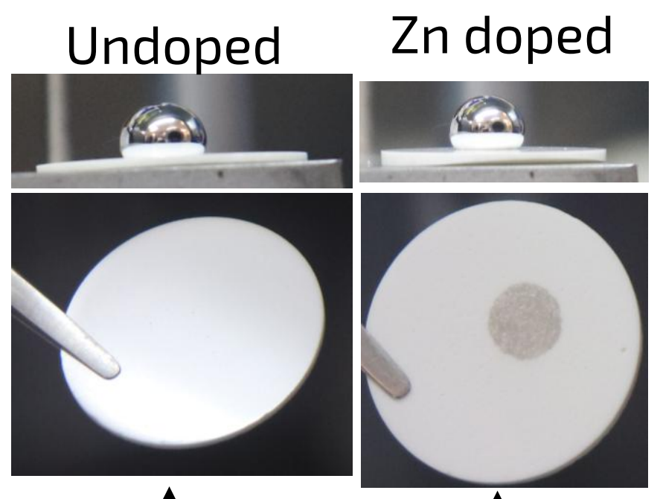
- Sn coating reduced interfacial impedance by ½
- Zn doping exhibits surface reaction grey spot
- Surface Chemistry and electrochemical analysis on going.



Zn doped NaSICON

Undoped

Zn doped



Na rolled off easily

Na stuck the most

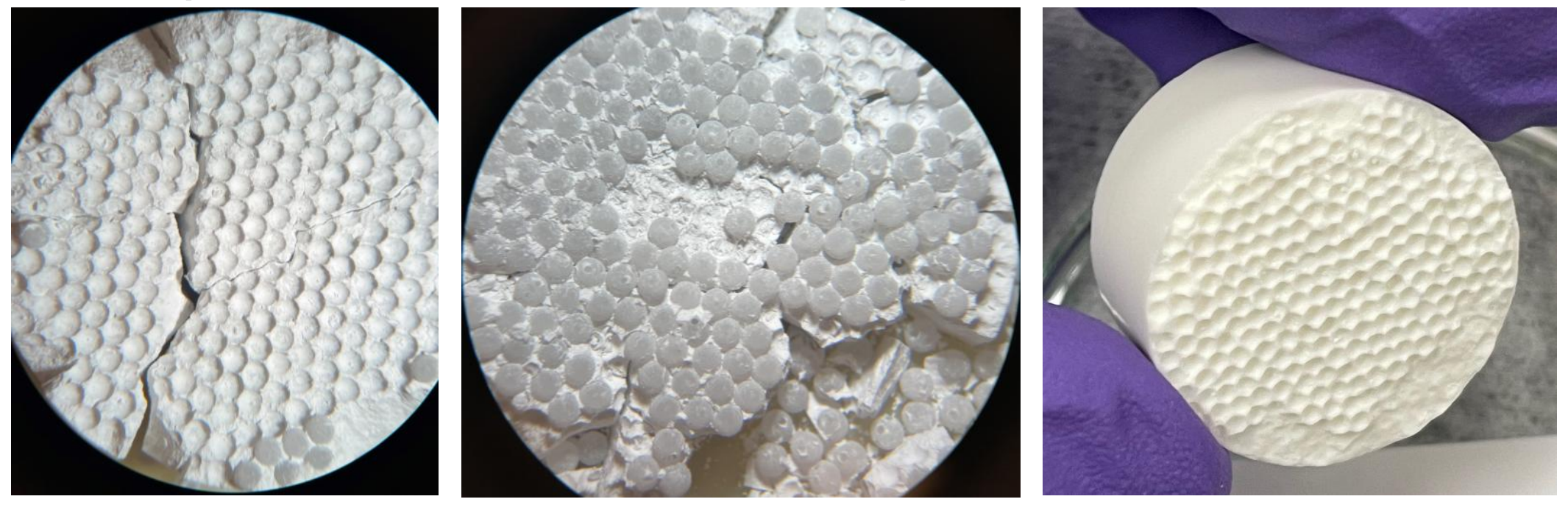
Residual Grey Spot

3D Interface Texturing

Top View

With PMMA Shperes

After sintering



- Developed a methodology to imprint NaSICON Ceramic pellets with textured surface
- PMMA burns out with negligible ash or residue
- Ceramic body ~92% dense, good enough for battery cycling
- Plan to incorporate this in symmetric cell to test performance

Future Work

Design 1" Puck

3D Resin Print

Imprint Ceramic

- Utilize rapid prototyping 3D Printing for exotic ceramic imprint dies
- Treat as feedback loop to iterate designs to find the ideal imprint technique
- Ideally, achieve a latticed thickness gradient for maximum surface area

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