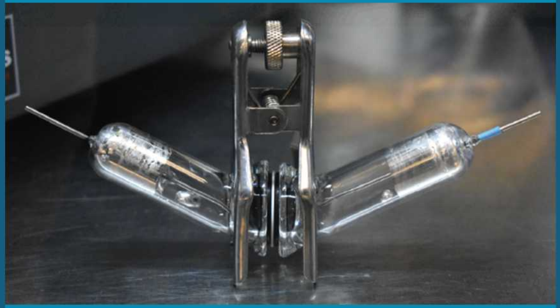
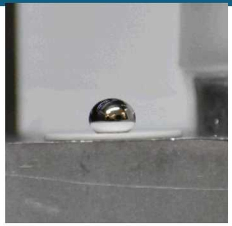
SAND2020-0577C

Interfacial Engineering of Ceramic Separators in Sodium Batteries





Martha M. Gross

Amanda S. Peretti, Stephen J. Percival, Leo J. Small, Mark A. Rodriguez, and Erik D. Spoerke

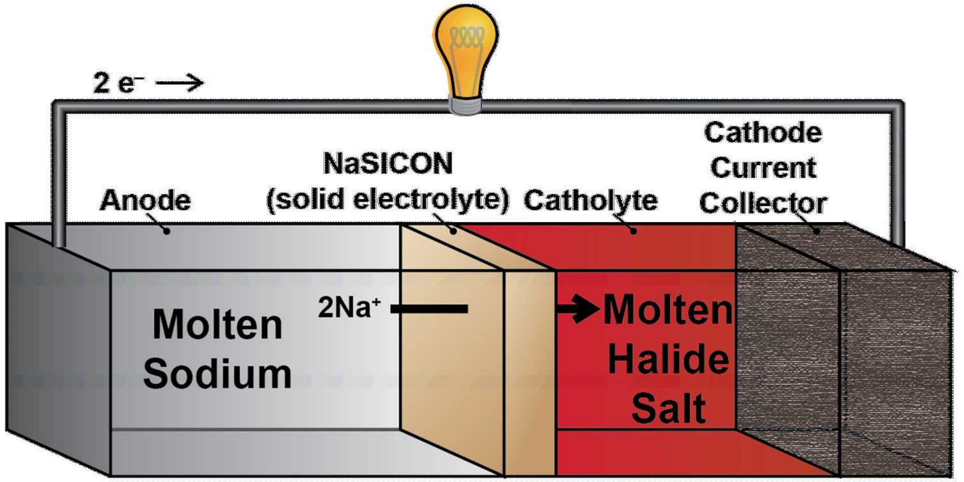
Electronic Materials and Applications 2020
S9: Ion Conducting Ceramics
January 23, 2020
Orlando, FL

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.

margros@sandia.gov

Molten Na Batteries for Grid Scale Energy Storage: **New Approaches for an Old Technology**

- Traditional Chemistries Operate at High Temperature (~300 °C)
  - High Materials Cost
  - Increased Operational Cost
  - Shortened Lifetimes
  - Safety (Na-S)
- Substantially Lowering Operating Temperature Requires Novel Chemistry
  - **Anode**: Molten Na
  - **Separator**: NaSICON
  - **Cathode**: 25 mol% NaI in $AlBr_3$ liquid catholyte



OCV: ~3.24 V

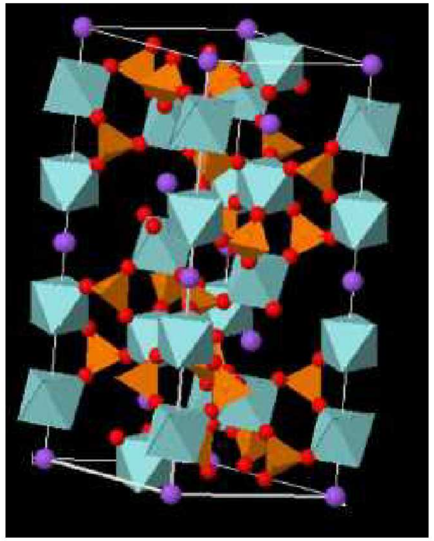
Anode: $Na \rightarrow Na^{+} + e^{-}$

Cathode: $I_3^{-} + 2e^{-} \rightarrow 3I^{-}$

Overall: $2Na + I_3^{-} \rightarrow 2Na^{+} + 3I^{-}$

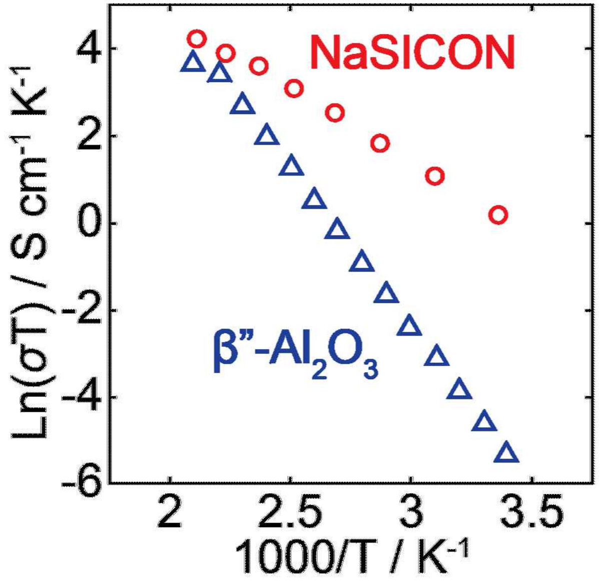
NaSICON Promotes Low Temperature Operation

- Sodium (**Na**) **S**uper **I**onic **CON**ductor
  - $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$
- "Skeleton structure" of ZrO_6 octahedra and PO_4, SiO_4 tetrahedra enable fast Na^+ transport



Advantages:

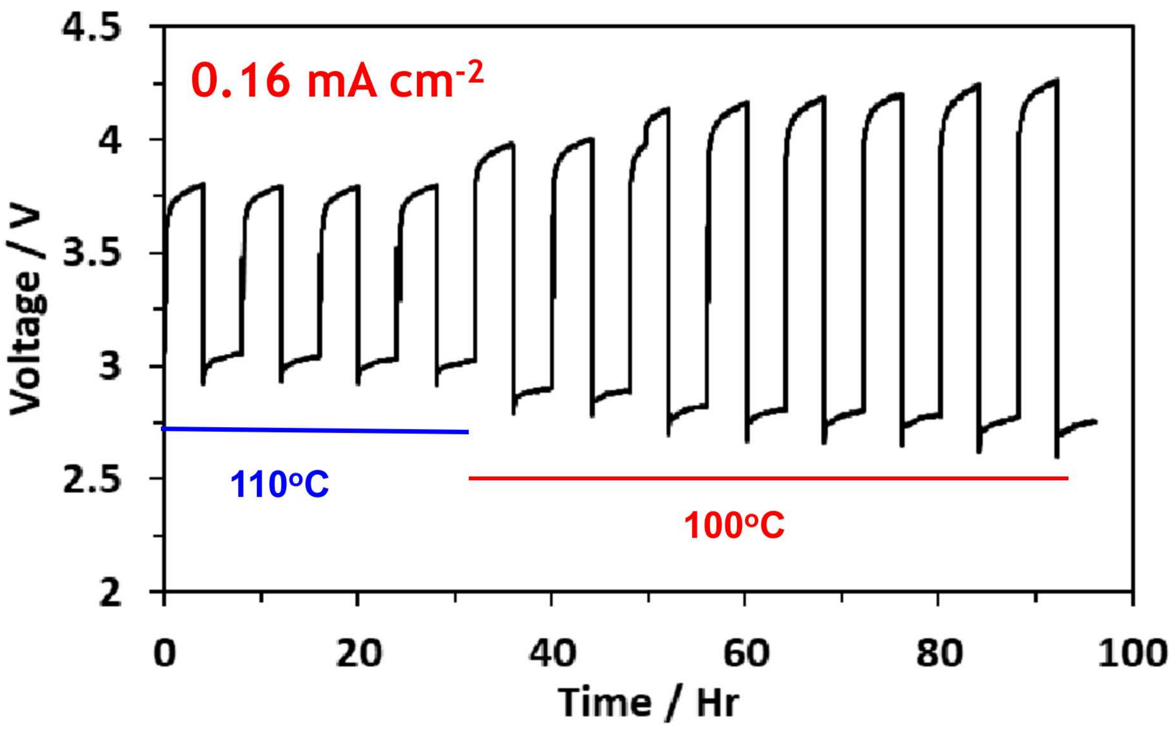
- Tunable crystal structure
- High conductivity at low temperature
- Chemical stability with molten sodium 100 – 150 °C
- Flexibility in end design
  - Sheets, discs, tubes, & thin films can be synthesized

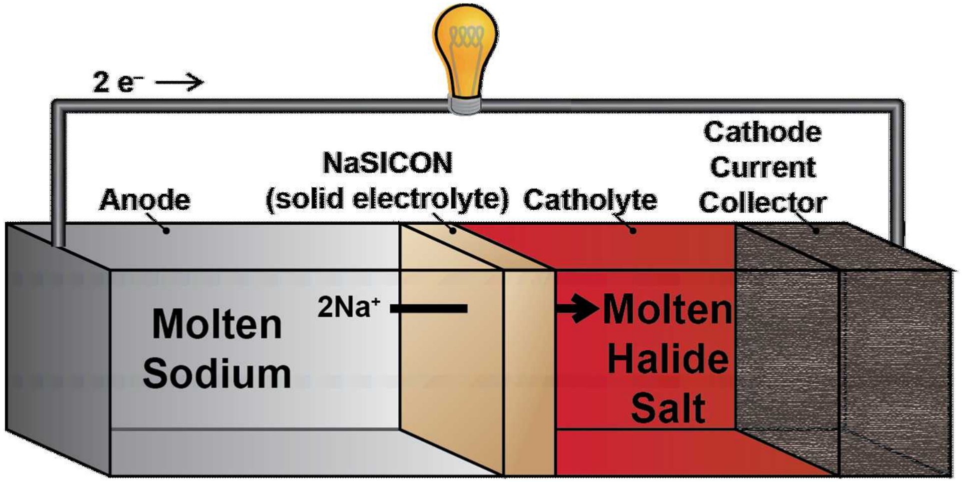


Synthesized by Amanda S. Peretti

L.J. Small, E.D. Spoerke et al., *J. Power Sources*, 360 (2017) 569-574.

Challenges in Lowering the Operating Temperature

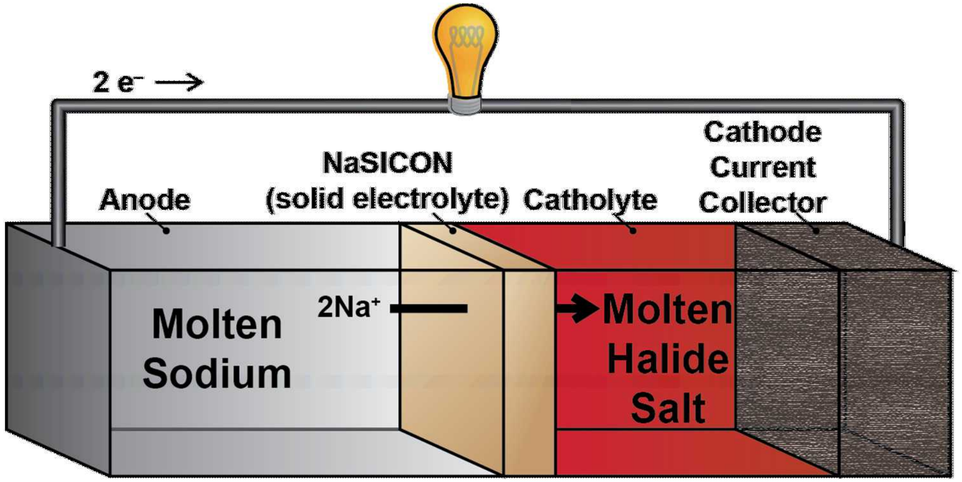




- High overpotential at low current density
  - > 1 V at 0.16 mA cm^{-2}
- Post Mortem: **Na wet very poorly to NaSICON**

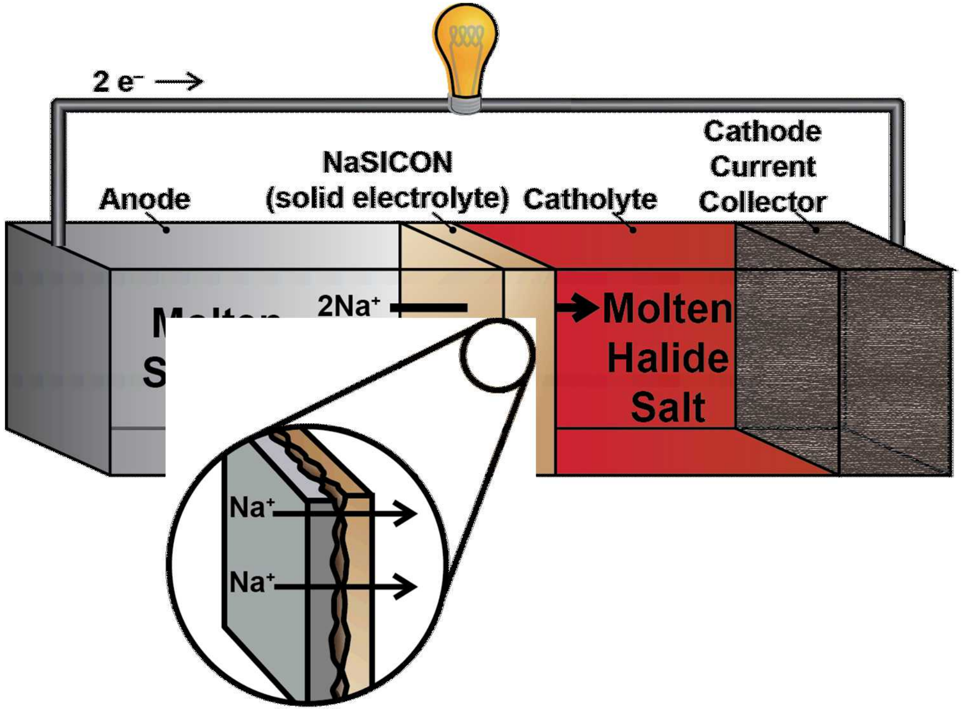
Data collected by Stephen J. Percival

Challenges in Lowering the Operating Temperature



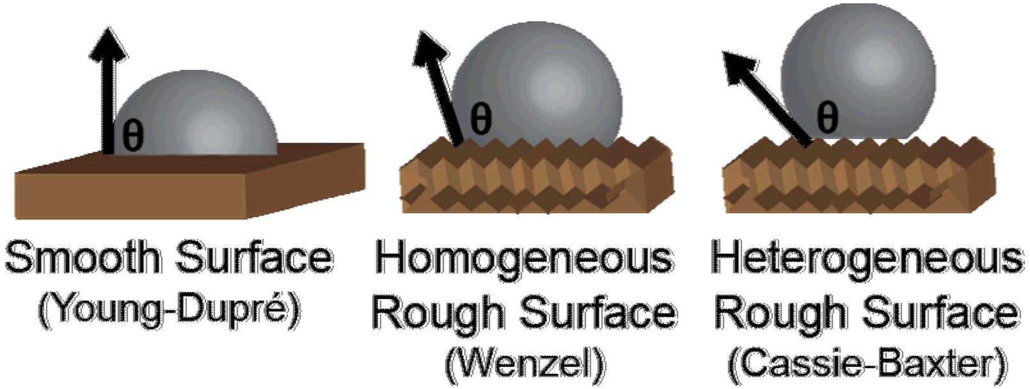
- Post Mortem: **Na wet very poorly to NaSICON**

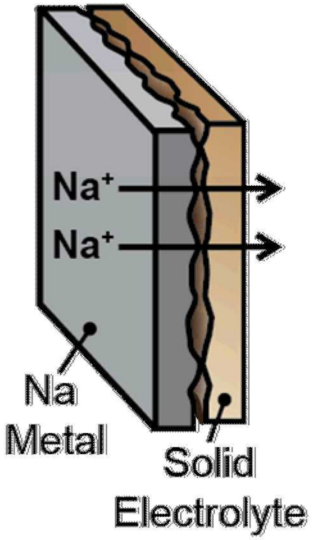
Challenges in Lowering the Operating Temperature

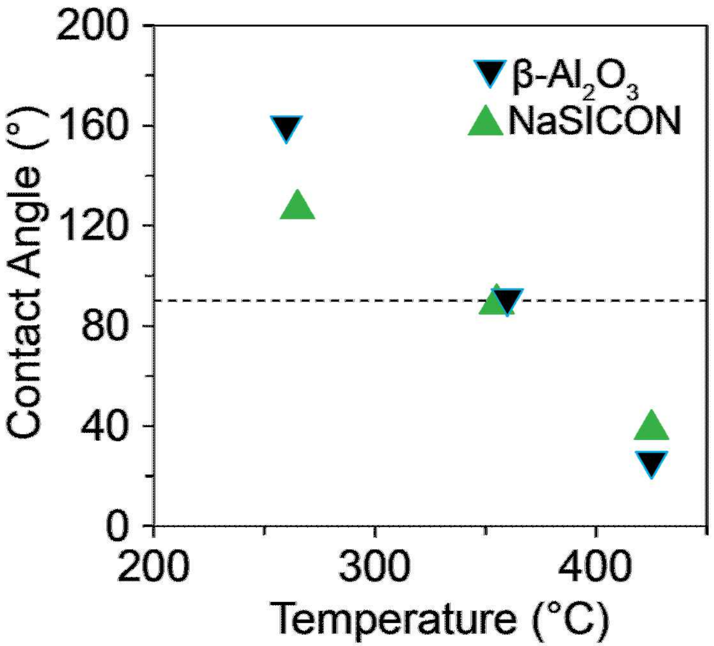


- Post Mortem: **Na wet very poorly to NaSICON**

Contact Angle Measures Wettability of Na on NaSICON



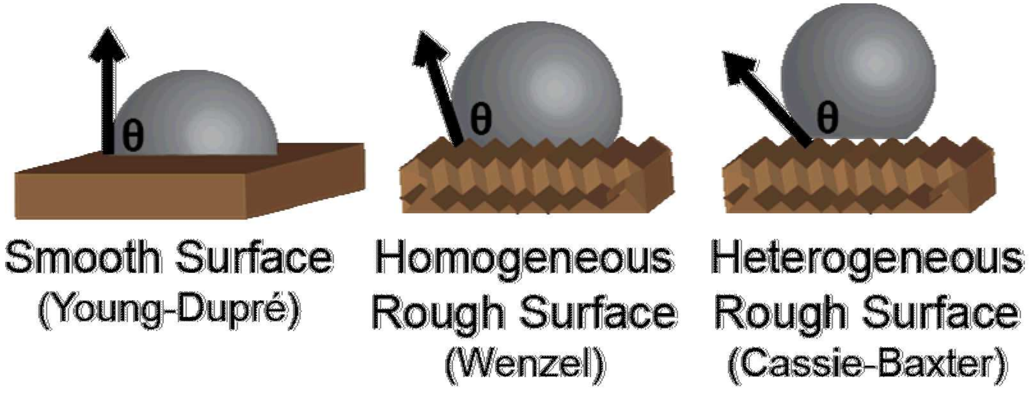


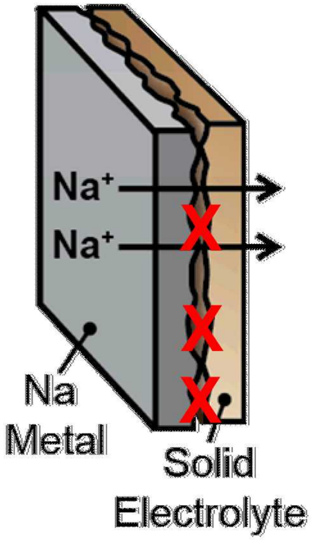


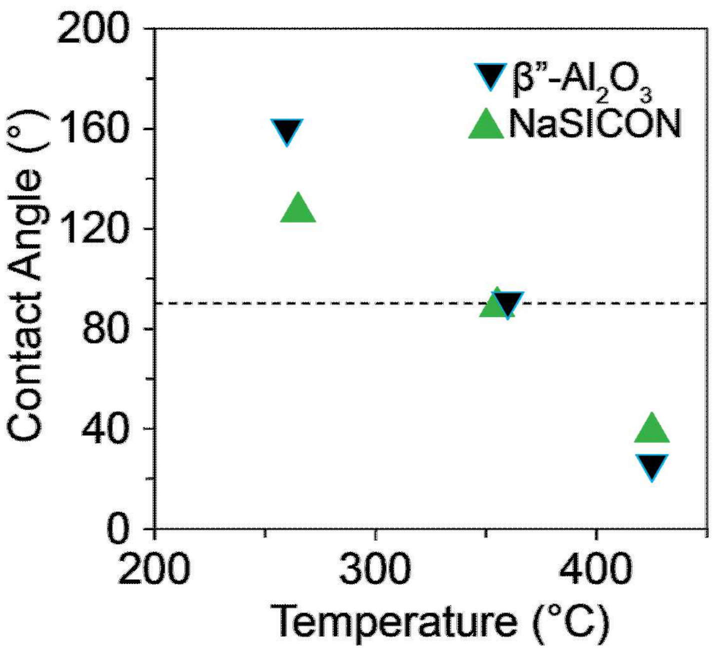
L. Viswanathan, A. V. Virkar, *J. Mater. Sci., (*1982) 17, 753.

- Contact angle is a measure of Na wetting
- Traditional thinking:
  - High Contact Angle = Poor Charge Transfer
- > 90° nonwetting, < 90° wetting
- Contact angle increases as temperature decreases
- **Na metal wets poorly to NaSICON at low temperature**

Contact Angle Measures Wettability of Na on NaSICON



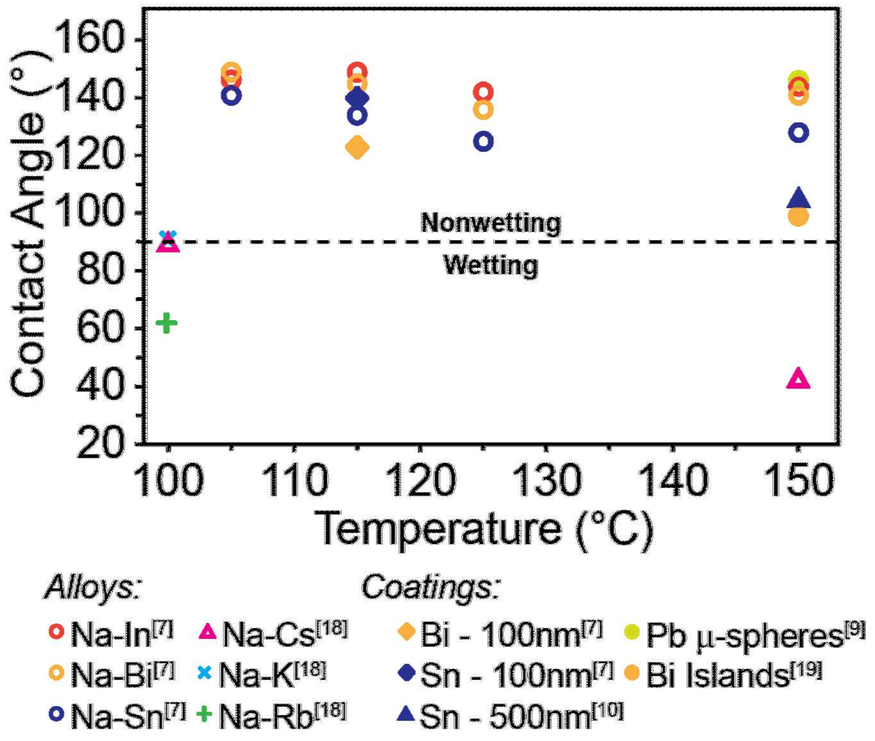


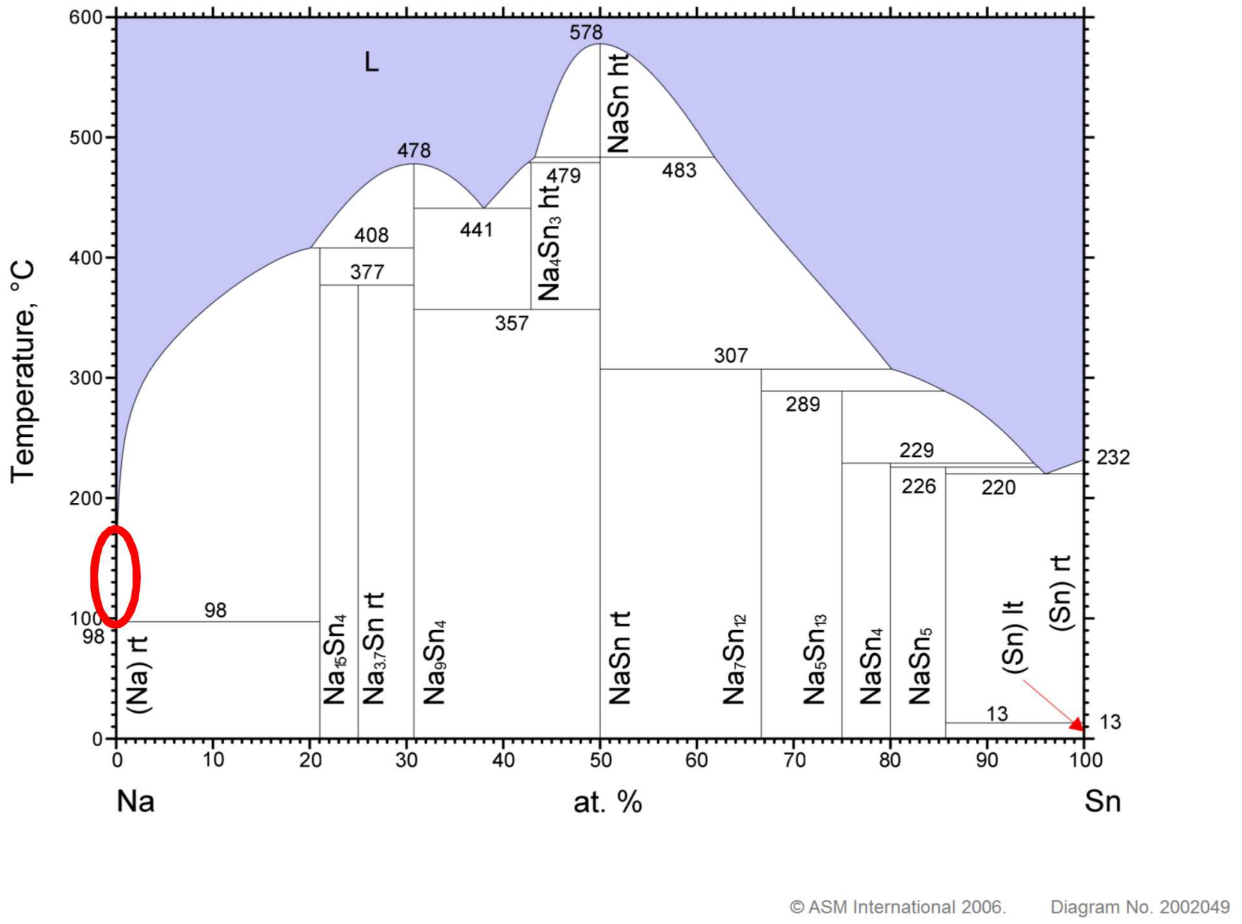


L. Viswanathan, A. V. Virkar, *J. Mater. Sci., (*1982) 17, 753.

- Contact angle is a measure of Na wetting
- Traditional thinking:
  - High Contact Angle = Poor Charge Transfer
- > 90° nonwetting, < 90° wetting
- Contact angle increases as temperature decreases
- **Na metal wets poorly to NaSICON at low temperature**

Sn Coating on NaSICON a Promising Candidate to Improve Battery Performance



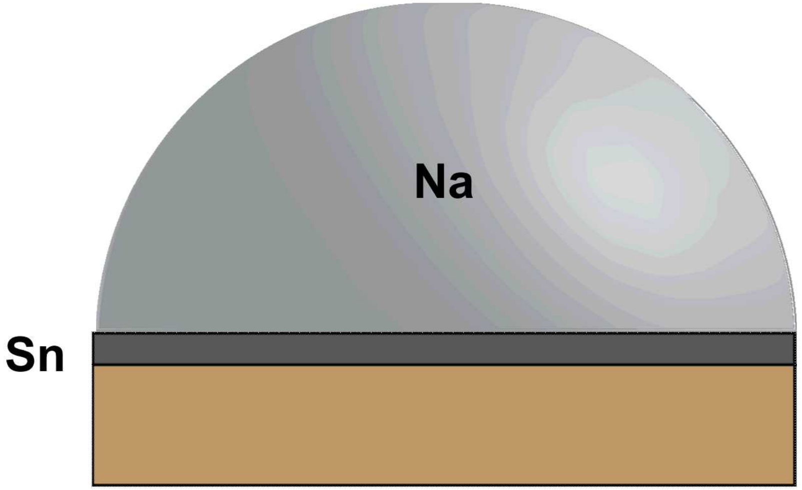


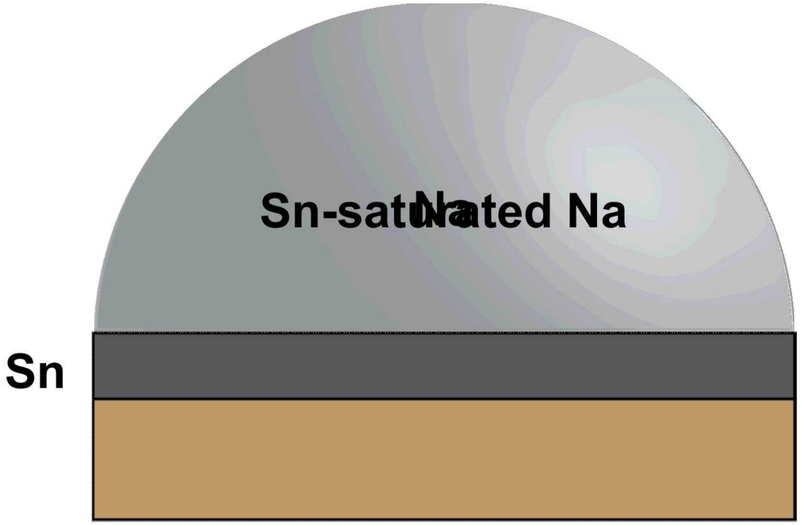
- Previous work at low temperatures entirely on β''–Al_2O_3
- Sn shows promise as a coating material
  - Alloys with Na
  - High Na^+ conductivity based on Na^+-ion anode work

- Sn is sparingly soluble in Na
- Solubility: ~ 6.7 x 10^{-3} wt% at 110 °C

M.M. Gross, E.D. Spoerke et al., *submitted* (2020)

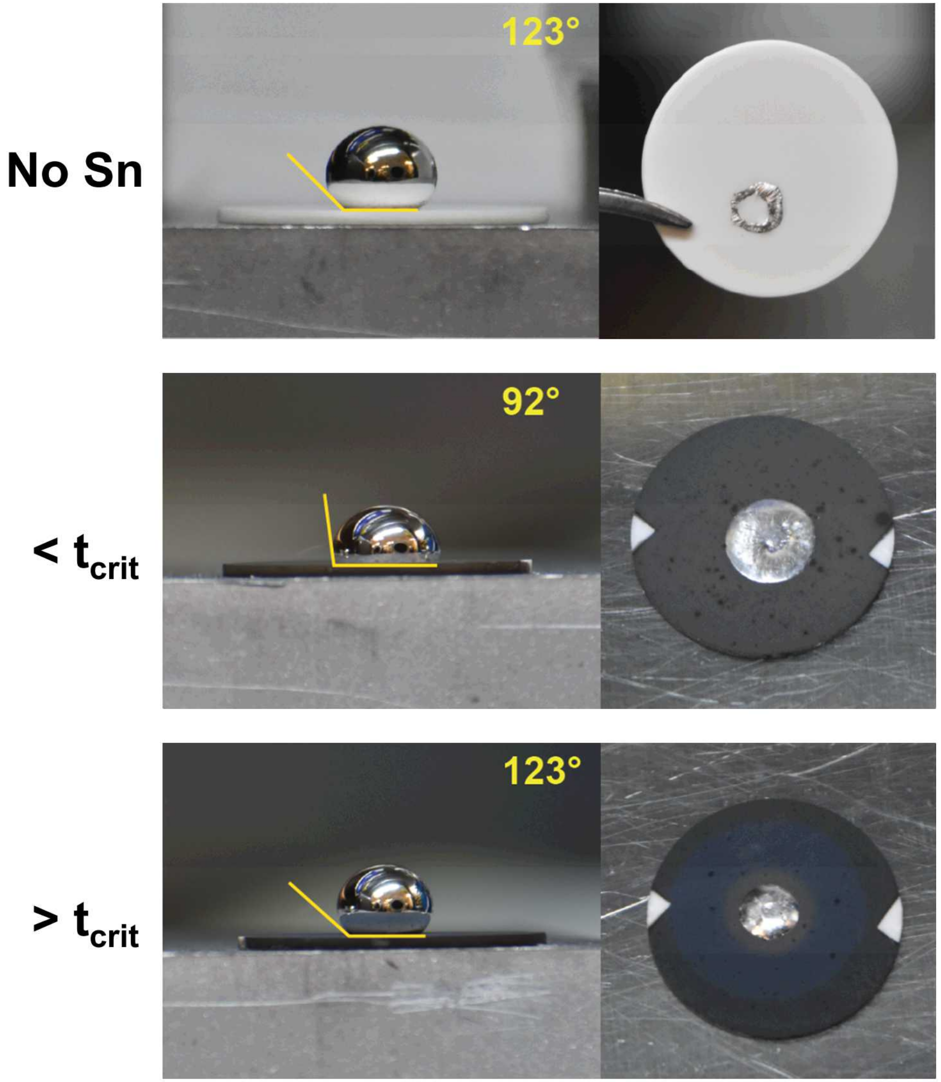
Sn Coating Behavior Differs Based on Thickness





- **Critical Thickness (t_{crit}):**
  - **Thickness above which the solubility limit is reached**
  - Dependent on surface area of coating and mass of Na used
- t_{crit} of our cells: **~220 nm**
- Coatings of thicknesses below and above the critical thickness were tested
  - 40 nm
  - 170 nm
    ] $< t_{crit}$
  - 500 nm
  - 700 nm
    ] $> t_{crit}$

Sn Coating Promotes Na Wetting on NaSICON



M.M. Gross, E.D. Spoerke et al., *submitted* (2020)

SURFACE TEMP: 110°C

- Poor contact angle and ‘sticking’ of Na on bare NaSICON
- Best contact angle achieved on Sn-coated NaSICON with thickness < t_{crit}
- Contact angle not improved when Sn thickness > t_{crit}
- Better adherence of Na to NaSICON surface with Sn coating

Sn Coating Promotes Na Wetting on NaSICON

Sn-coated

SURFACE TEMP: 110°C

- Poor contact angle and 'sticking' of Na on bare NaSICON
- Best contact angle achieved on Sn-coated NaSICON with thickness < t_{crit}
- Contact angle not improved when Sn thickness > t_{crit}
- Better adherence of Na to NaSICON surface with Sn coating

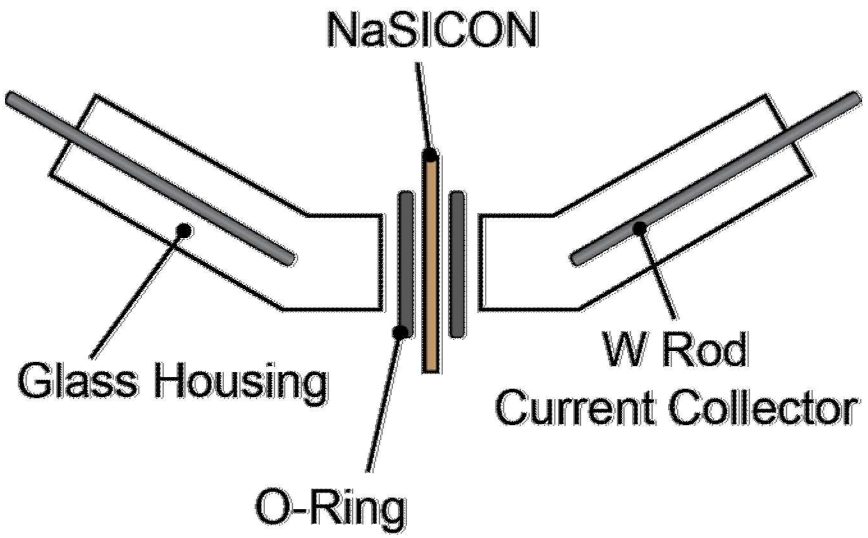
Sn Coating Promotes Na Wetting on NaSICON

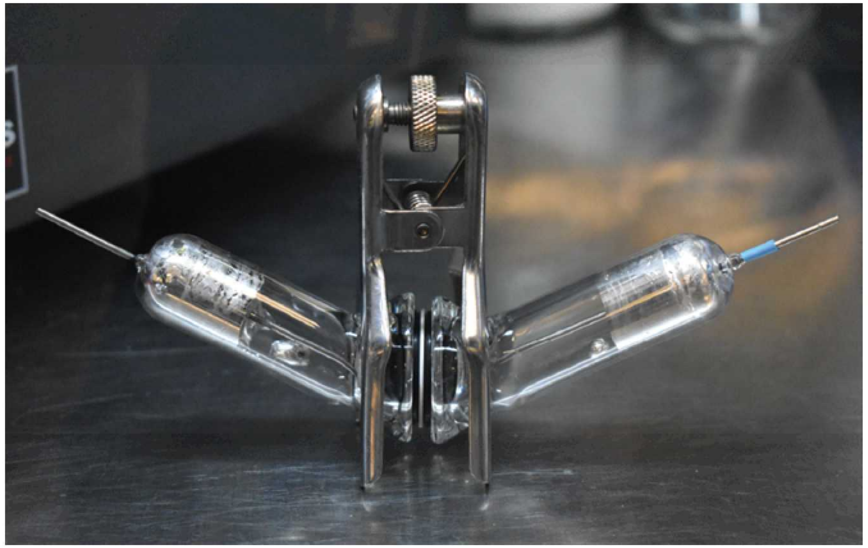
Sn-coated

SURFACE TEMP: 110°C

- Poor contact angle and 'sticking' of Na on bare NaSICON
- Best contact angle achieved on Sn-coated NaSICON with thickness < t_{crit}
- Contact angle not improved when Sn thickness > t_{crit}
- Better adherence of Na to NaSICON surface with Sn coating

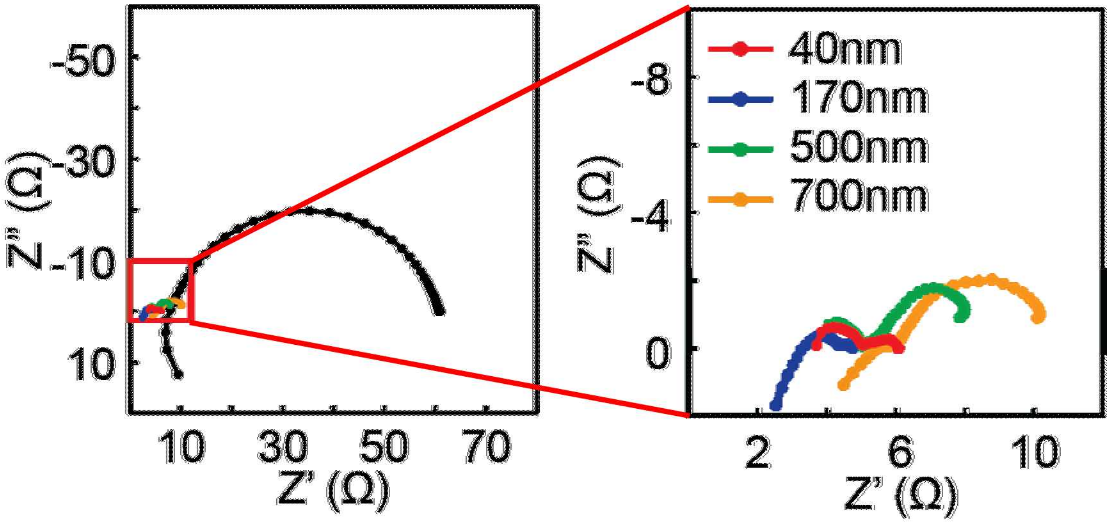
Sn Coating on NaSICON Lowers Symmetric Cell Resistances





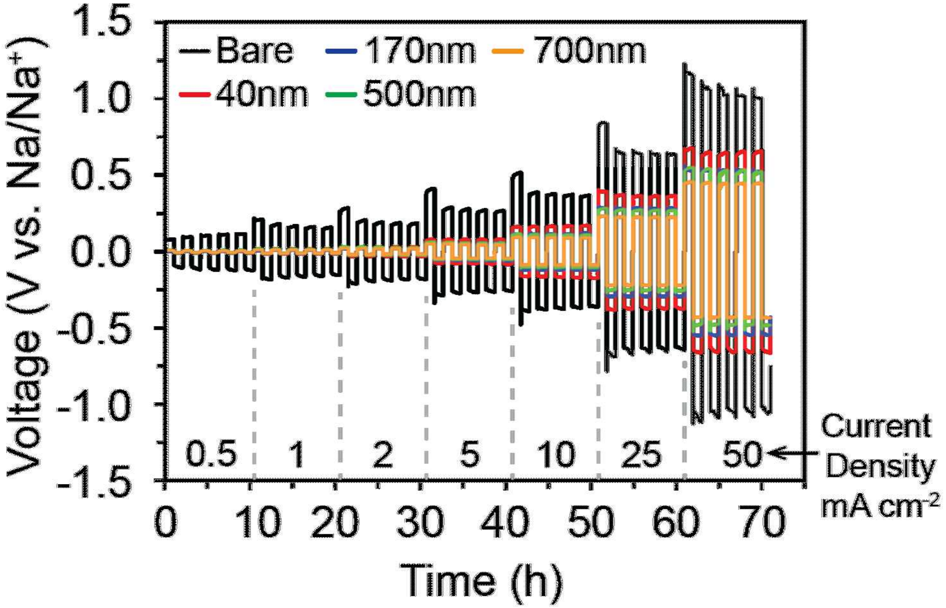
- Symmetric cells assembled and heated to **110 °C**
- Substantially lower resistance in assembled symmetric cell with Sn-coated NaSICON
  - Regardless of Sn thickness

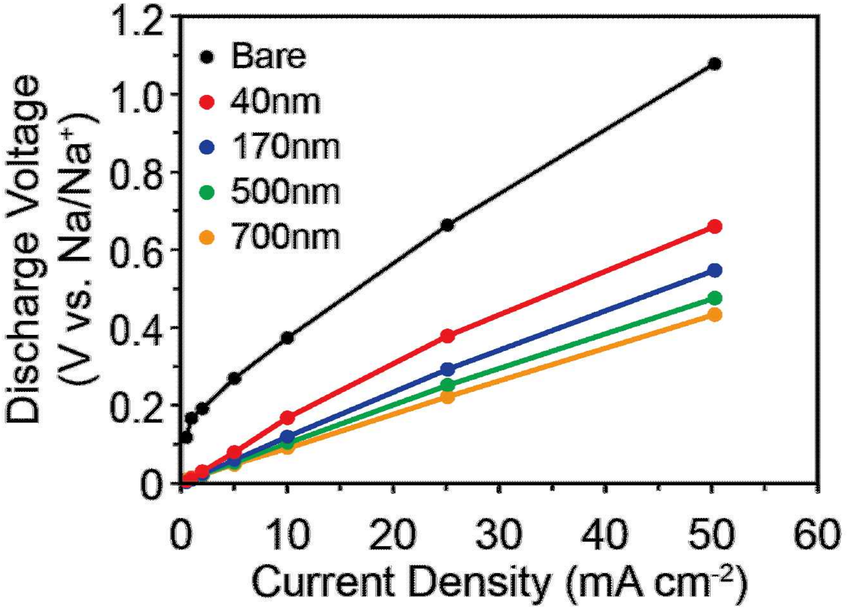
Electrichemical Impedance Spectroscopy (EIS)



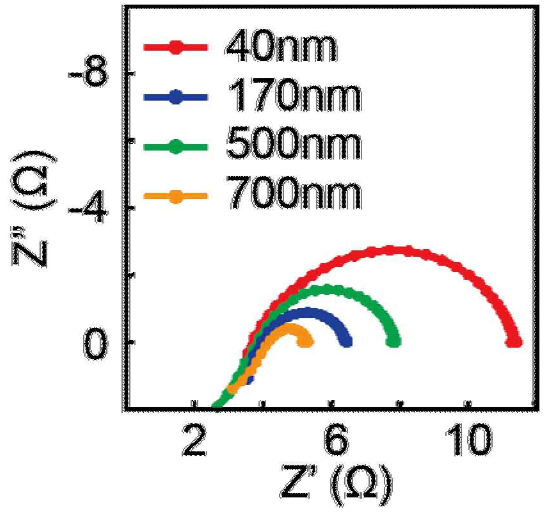
M.M. Gross, E.D. Spoerke et al., *submitted* (2020)

Sn Coating on NaSICON Lowers Symmetric Cell Overpotential





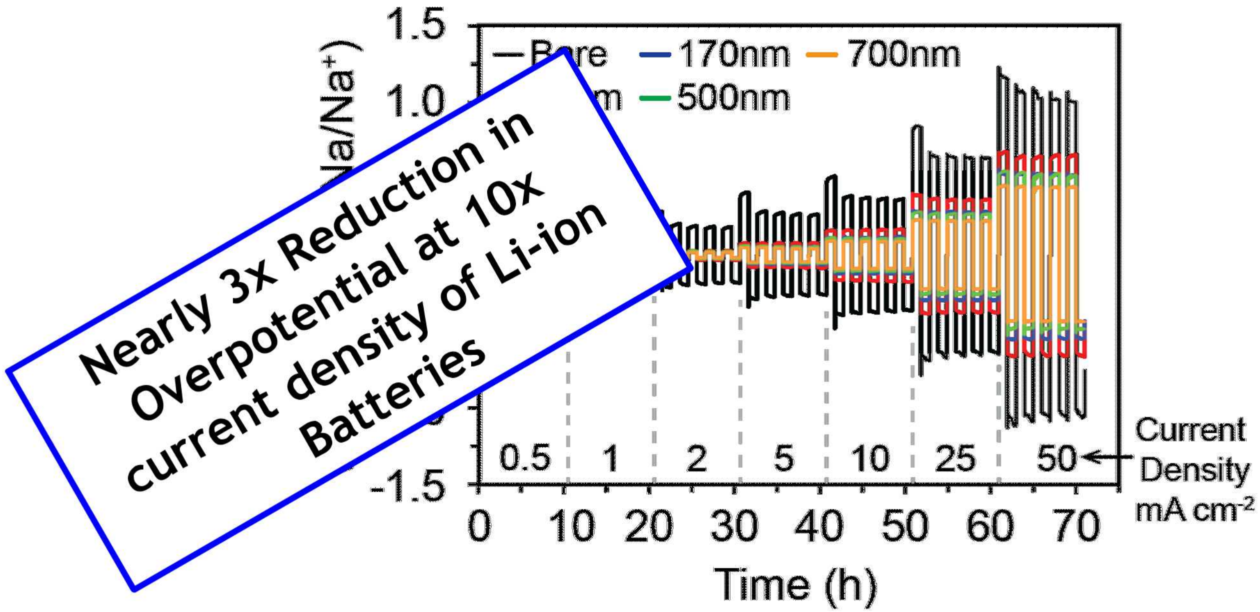
- Cells with Sn-coated NaSICON demonstrated lower overpotential at all current densities, regardless of Sn coating thickness
- **Sn coatings > t_{crit} performed better than coatings < t_{crit}**
  - **Contradicts results expected from contact angle testing**

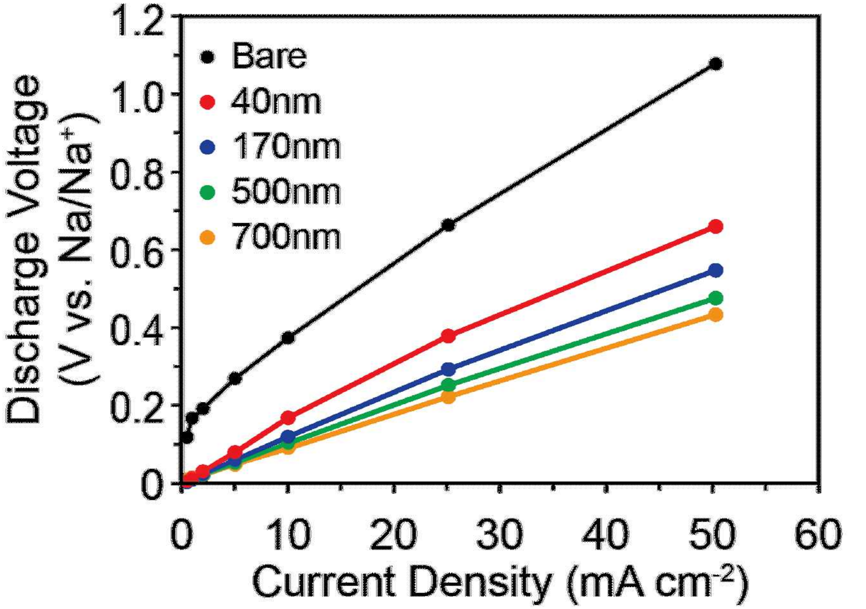


EIS of symmetric cells with Sn-coated NaSICON

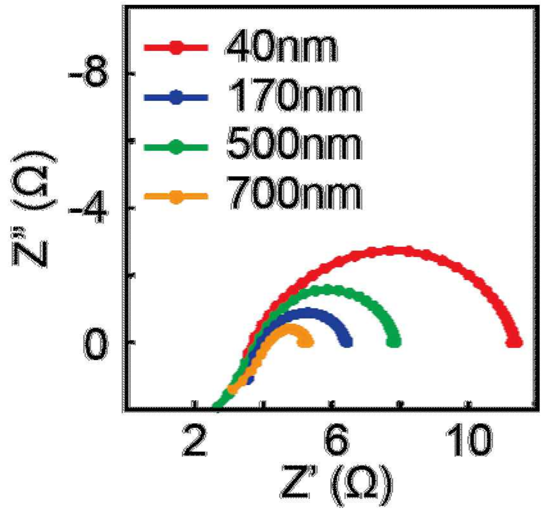
M.M. Gross, E.D. Spoerke et al., *submitted* (2020)

Sn Coating on NaSICON Lowers Symmetric Cell Overpotential





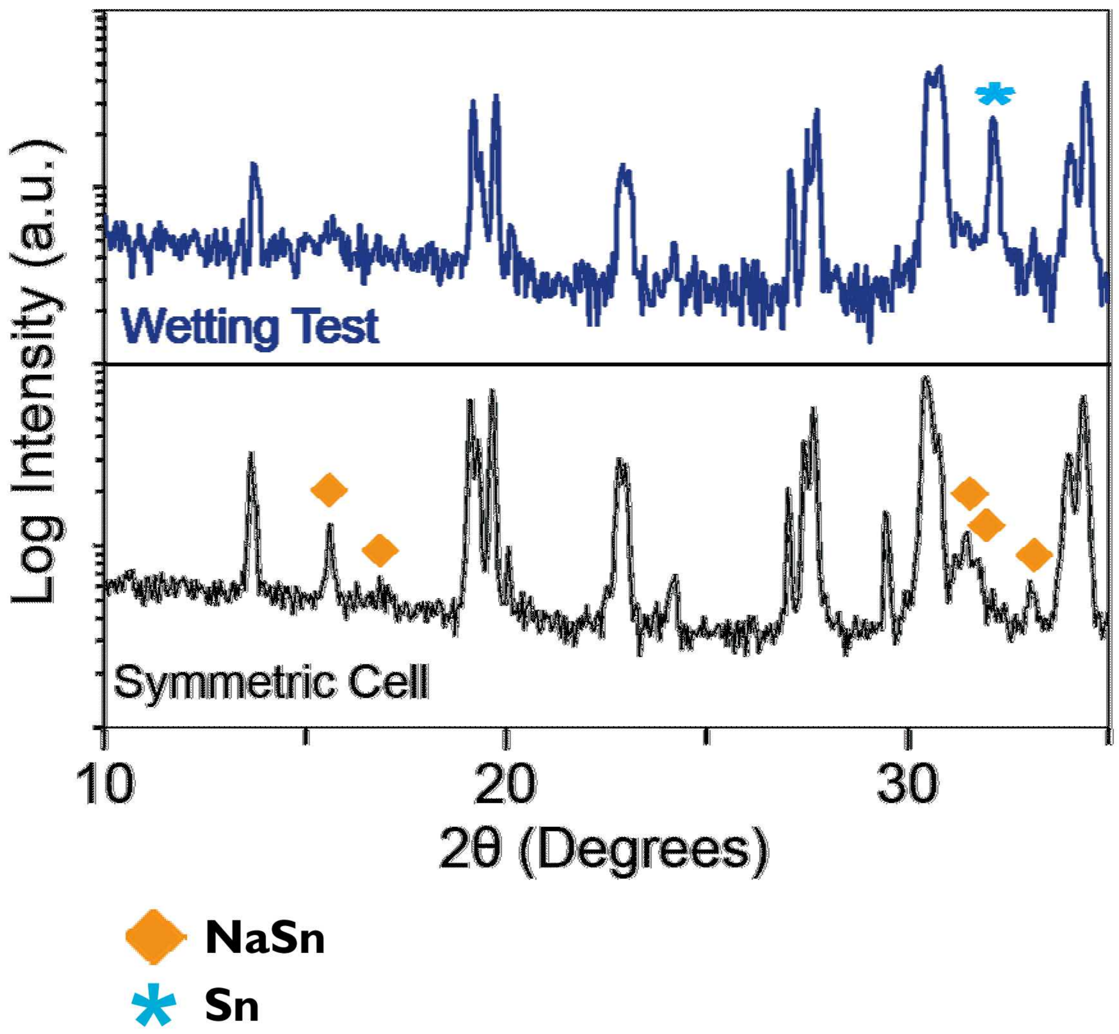
- Cells with Sn-coated NaSICON demonstrated lower overpotential at all current densities, regardless of Sn coating thickness
- **Sn coatings > t_{crit} performed better than coatings < t_{crit}**
  - **Contradicts results expected from contact angle testing**



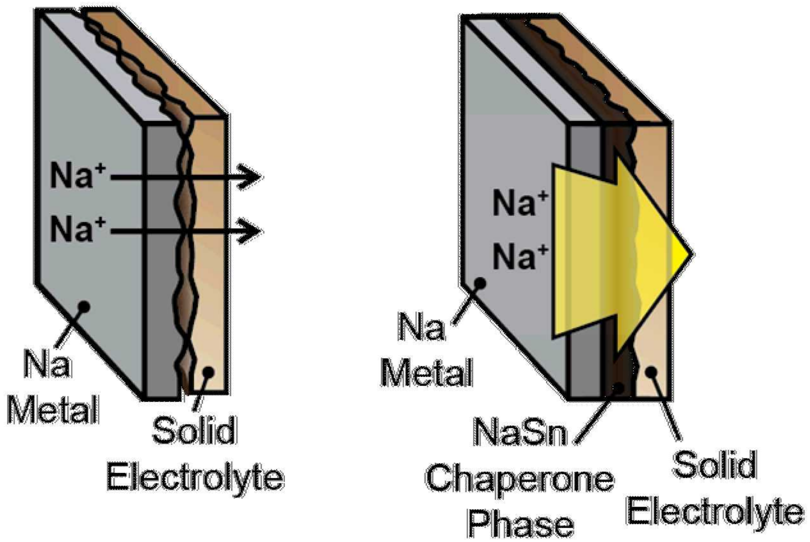
EIS of symmetric cells with Sn-coated NaSICON

M.M. Gross, E.D. Spoerke et al., *submitted* (2020)

In-situ Formation of Na^+-Conducting "Chaperone Phase" Improves Charge Transfer

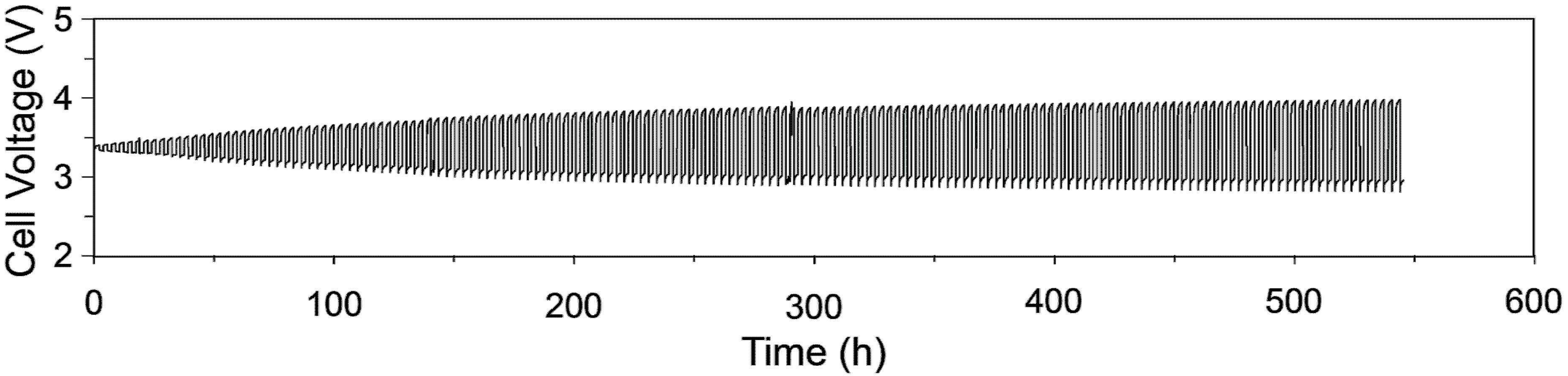


- XRD analysis of uncycled & cycled Sn-coated NaSICON
- Intermetallic NaSn phase identified in cycled samples
  - Not identified in samples from static contact angle measurements
- **Na^+-ion conducting NaSn "chaperone phase" formed during cycling produces enhanced battery performance**



M.M. Gross, E.D. Spoerke et al., *submitted* (2020)

Sn Coating on NaSICON Enables Long Battery Lifetime!



Over 500 hours of cycling achieved!

Take Home Messages

- Lowering the operating temperature of a molten Na battery increases interfacial resistance due to poor Na wetting on the NaSICON separator
  - Results in high battery overpotentials
- Application of a Sn coating on NaSICON lowers interfacial resistance in a Na symmetric cell at low temperature (110 °C)
  - ***Best battery performance is achieved with Sn coatings where $t > t_{crit}$***
- Dynamic formation of a NaSn "chaperone phase" enhances charge transfer, lowering interfacial resistance and improving battery performance

High Na^+-conductivity intermetallic-forming coatings offer a path towards advancing the performance of low temperature molten sodium batteries

Synthetic Designs for Improved NaSICON Sodium Ion Conductors **Erik Spoerke**
8:30a Friday 1/24 Citrus A

ACKNOWLEDGEMENTS

Sandia National Labs

- Dr. Leo J. Small
- Amanda S. Peretti
- Dr. Stephen J. Percival
- Dr. Mark A. Rodriguez
- Dr. Erik D. Spoerke
- Sara Dickens
- Luis Jauregui
- Dr. Babu Chalamala

Program Sponsor

- Dr. Imre Gyuk – Program Manager, DOE – OE
- DOE – 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.

Questions?

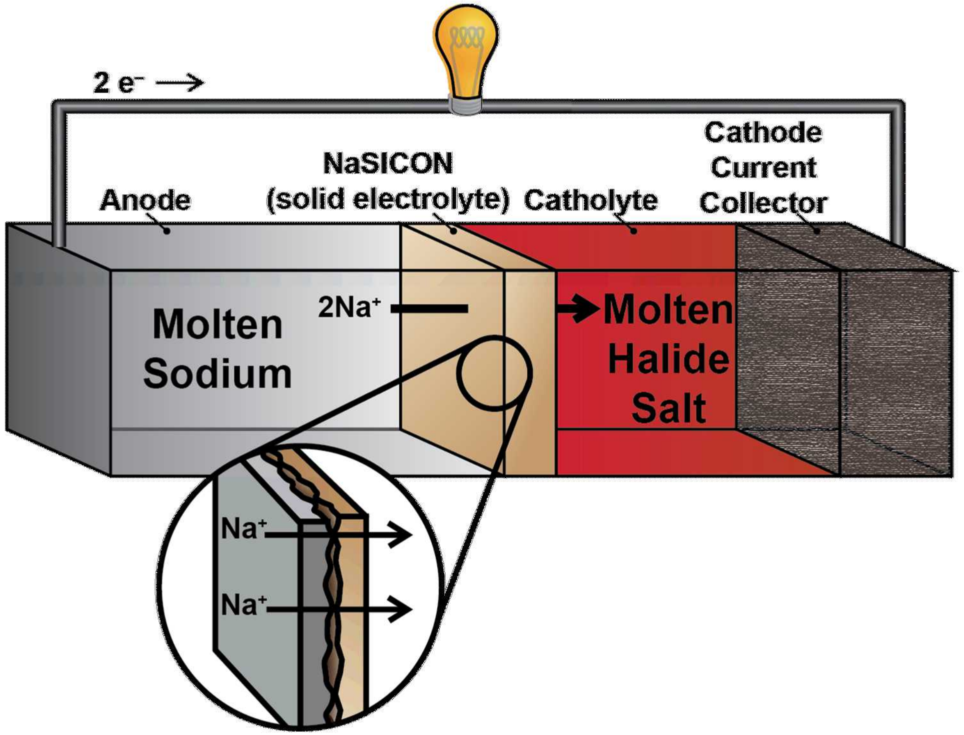
Martha M. Gross
Sandia National Laboratories
margros@sandia.gov

Backup Slides

Molten Na Batteries for Grid Scale Energy Storage: **New Approaches for an Old Technology**

Challenges in Low Temperature Molten Na Batteries

- Temperature > 100°C to maintain Na in molten state
- Low separator ionic conductivity
- Unknown interactions between ceramic & catholyte
- Catholyte materials selection – molten at low temperatures
- Materials compatibility with molten salt catholyte
- Poor charge transfer at cathode current collector
- **Poor Na wetting on ceramic separator**

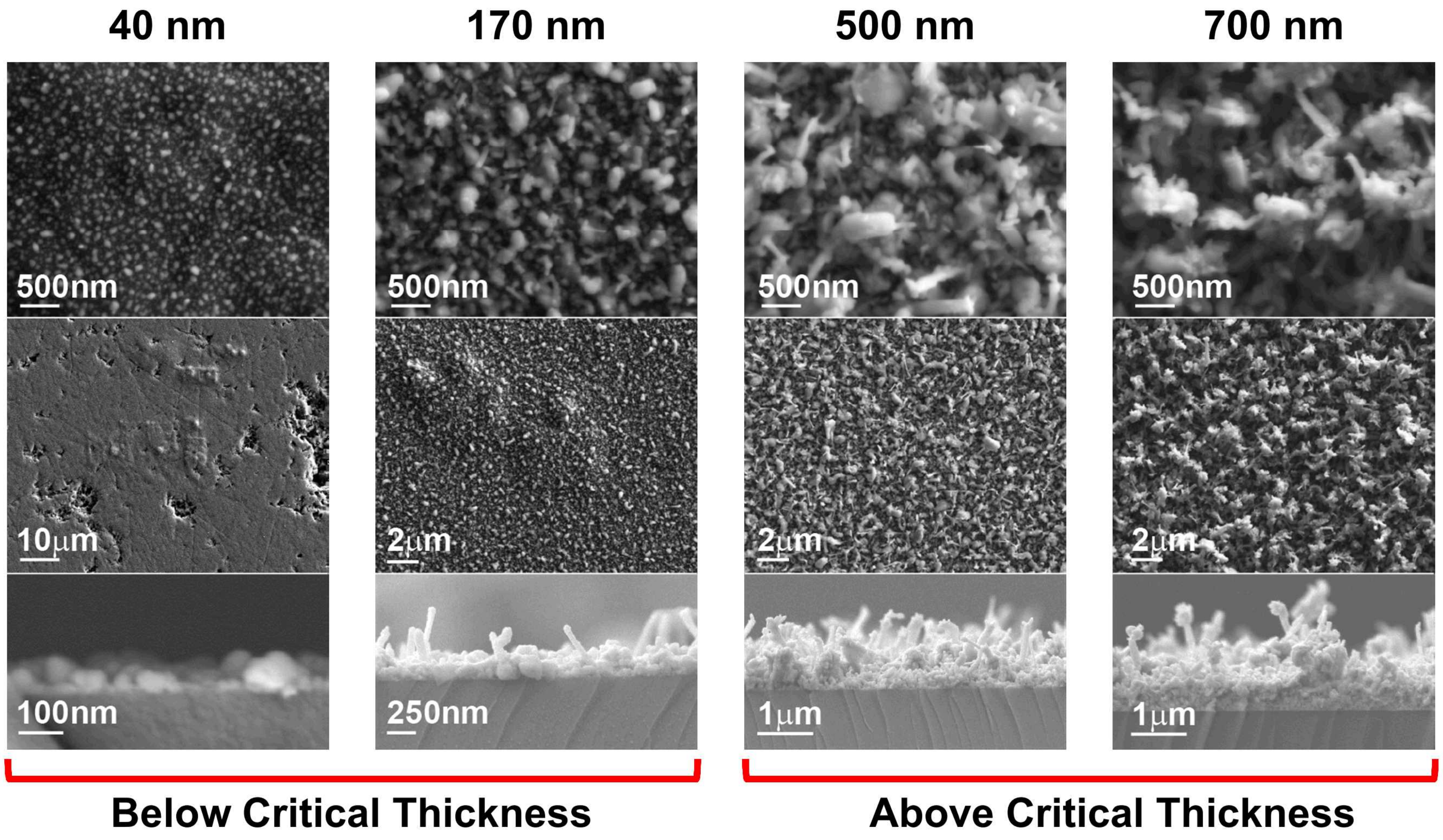


Anode: $Na \rightarrow Na^{+} + e^{-}$

Cathode: $I_3^{-} + 2e^{-} \rightarrow 3I^{-}$

Overall: $2Na + I_3^{-} \rightarrow 2Na^{+} + 3I^{-}$

Sn Coating Surface Morphology & Thickness Determination



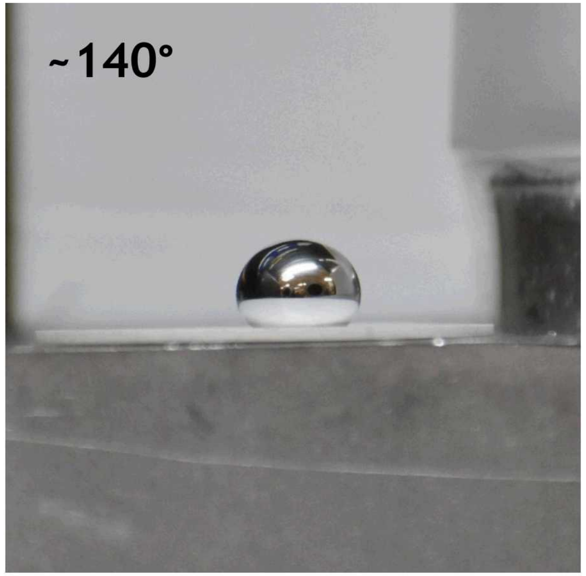
- Increased surface roughness with increased coating thickness
  - Thinnest (40nm) coating non-conformal
- 4 thicknesses tested:
  - 2 coatings < t_{crit}
  - 2 coatings > t_{crit}

M.M. Gross, E.D. Spoerke et al., *submitted* (2020)

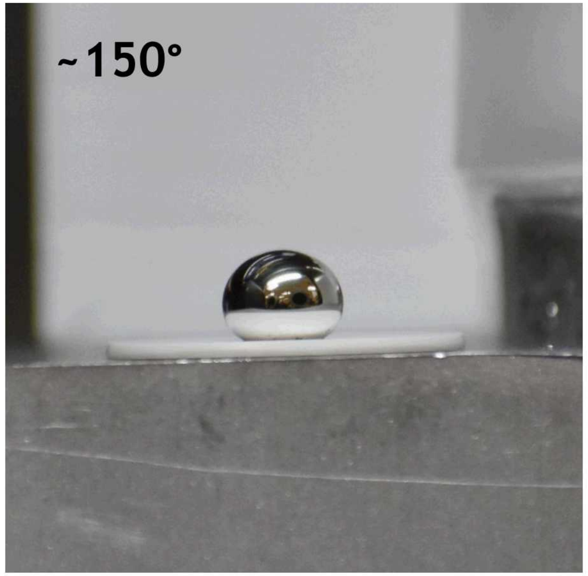
Surface Roughness & Composition

110°C

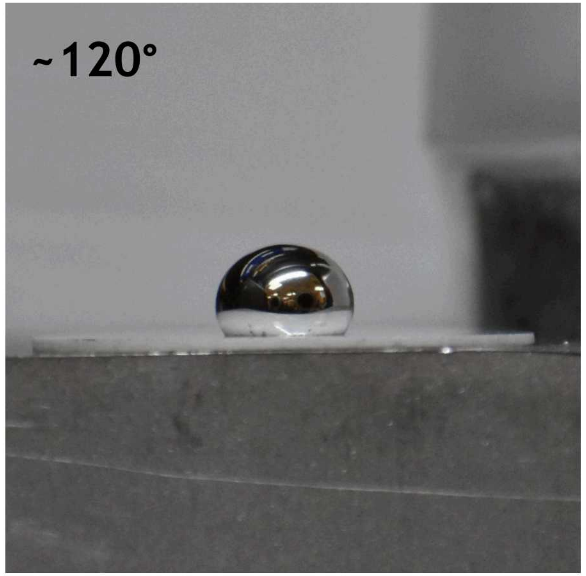
In-House NaSICON, Unpolished



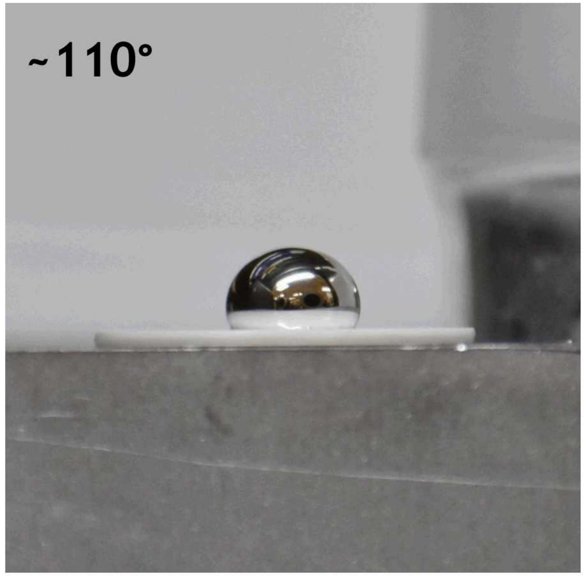
UNIST NaSICON, Unpolished



In-House NaSICON, Polished



UNIST NaSICON, Polished



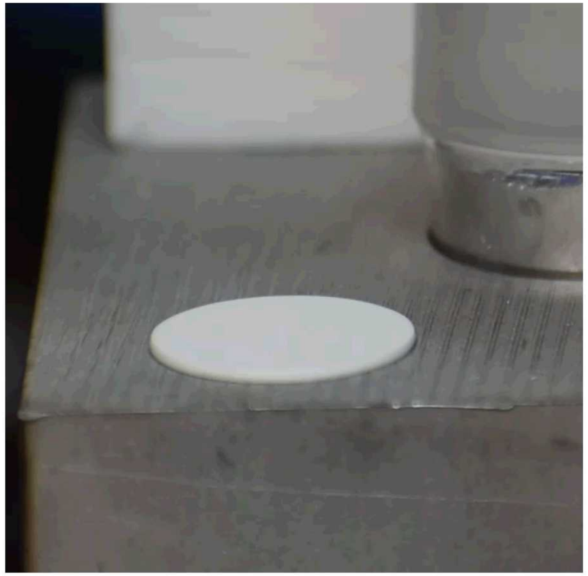
- Surface roughness & ceramic composition have profound effect on contact angle
- Surface prep, impurity composition, ceramic porosity, and surface roughness often underreported

UNIST NaSICON received from Professor Youngsik Kim

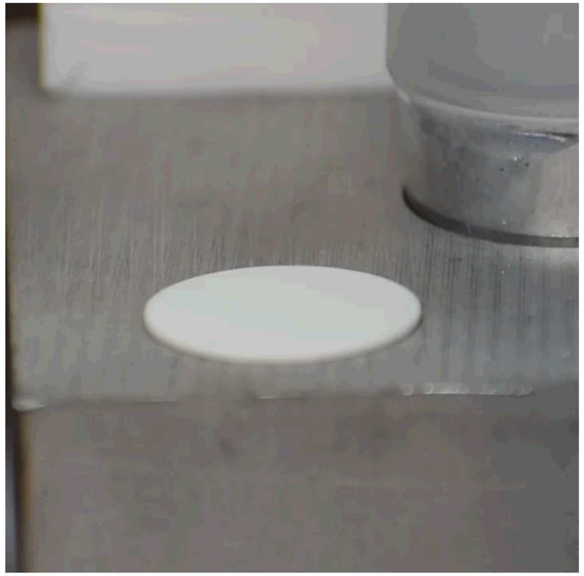
Surface Roughness & Composition

110°C
VIDEOS

UNIST NaSICON, Unpolished



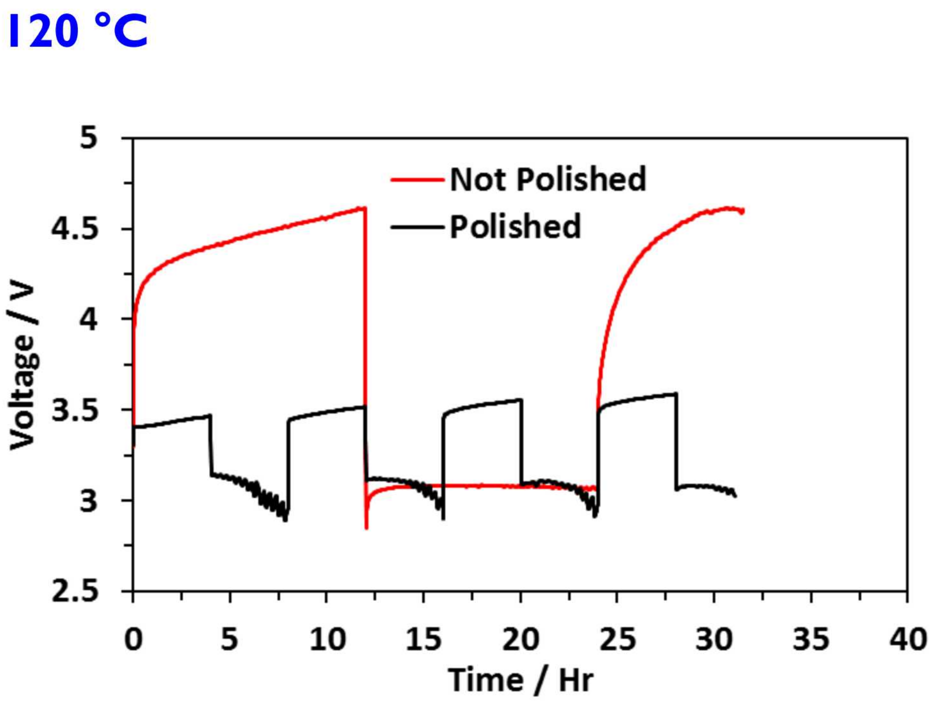
UNIST NaSICON, Polished



- Surface roughness & ceramic composition have profound effect on contact angle
- Surface prep, impurity composition, ceramic porosity, and surface roughness often underreported

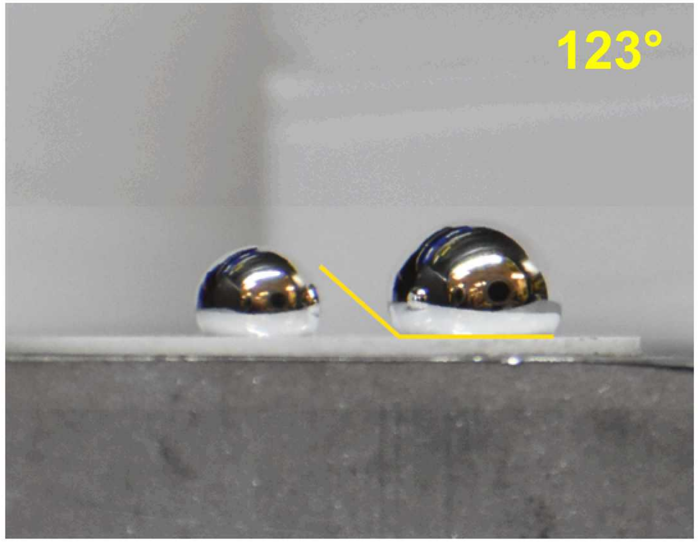
UNIST NaSICON received from Professor Youngsik Kim

Effect of Polishing NaSICON on Full Battery performance



- Cell with unpolished NaSICON cycled at C/12
- Cell with polished NaSICON cycled at C/4

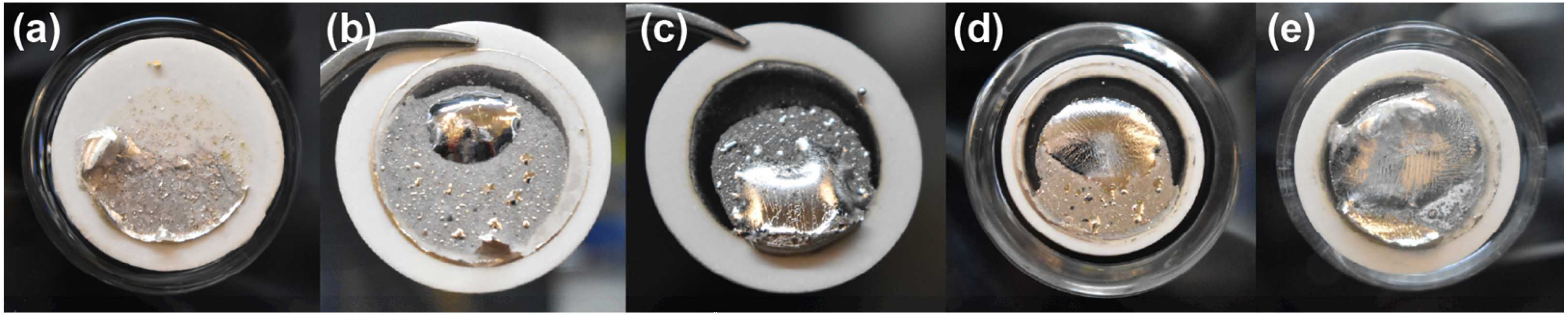
Sn-Saturated Na on Bare NaSICON



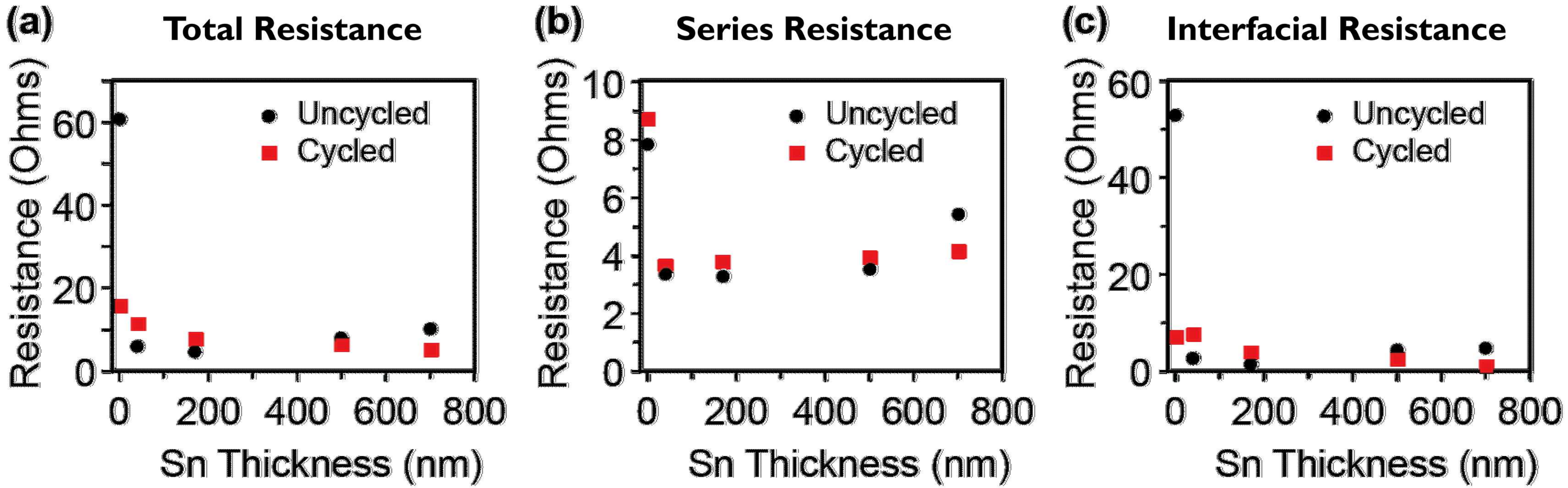
- No improvement over pure Na on Bare NaSICON

Wetting of Na in Cycled NaSICON

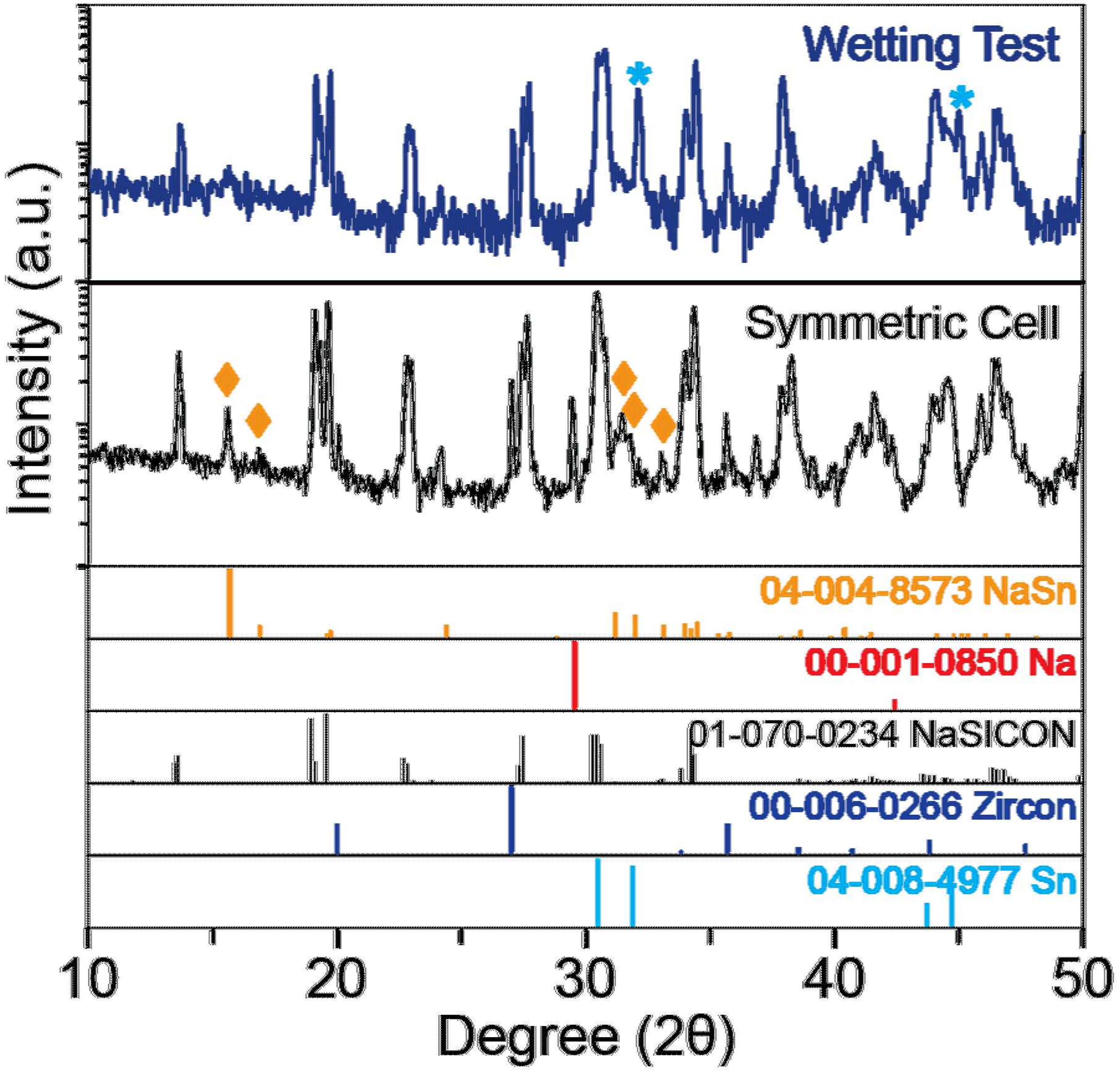
Increasing Sn thickness



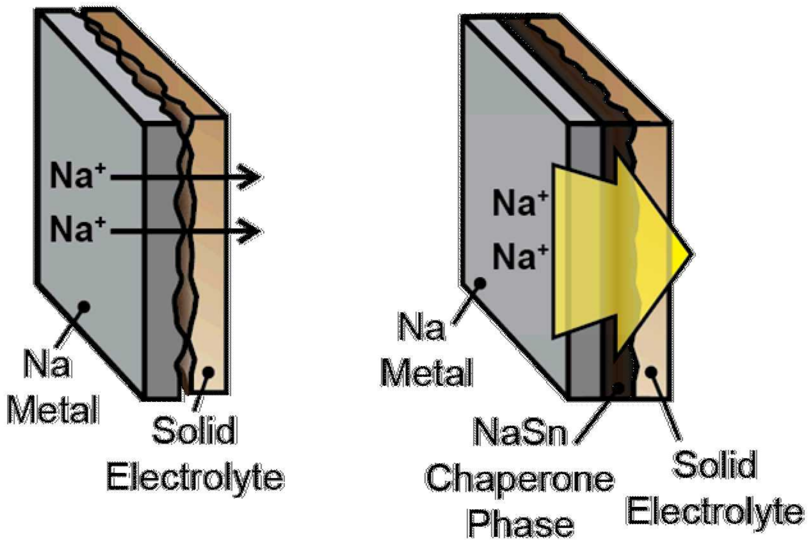
Summary of Symmetric Cell Resistance



In-situ Formation of Na^+-Conducting "Chaperone Phase" Improves Charge Transfer



- XRD analysis of uncycled & cycled Sn-coated NaSICON
- Intermetallic NaSn phase identified in cycled samples
  - Not identified in samples from static contact angle measurements
- **Na^+-ion conducting NaSn "chaperone phase" formed during cycling produces enhanced battery performance**



M.M. Gross, E.D. Spoerke et al., *submitted* (2020)