2017 DOE Vehicle Technologies Office Review

“Solid electrolytes for solid-state and lithium-sulfur batteries”

Project ID: ES277 DE-EE-00006821

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C. Monroe (University of Oxford, UK)

J. Wolfenstine and Jan Allen (Army Research Laboratory)

J. Nanda and M. Naguib (Oak Ridge National Laboratory)

June 8, 2017

Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

Overview

Timeline
- Project start date, Jan 1, 2015
- Project end date, Dec 31, 2017
- 83% complete

Budget
- $1,220K (total)
- Project end date, Dec 31, 2017
- 83% complete

Technical Barriers
- Prevent Li dendrites to enable metallic Li anodes
- Integrated solid-electrolyte into advanced solid-state batteries
- Achieve high current densities approaching 1 mA/cm^2

Partners
- Oxford University, UK (C. Monroe)
- Army Research Lab (J. Wolfenstine and J. Allen)
- Oak Ridge National Lab (J. Nanda, M. Naguib, and N.J. Dudney)

Relevance

Objectives

- Achieve a step increase in performance compared to Li-ion, by enabling the use of metallic Li anodes.
- Understand the role that defects play in governing the stability and kinetics of the Li-solid electrolyte interface.
- Quantify the effect of each defect type on the maximum tolerable Li plating/stripping rate.

Impact

- Fundamental knowledge can be used to develop approaches to increase tolerance to defects that control the maximum Li plating/stripping rate.
- Facilitate efforts to develop commercially-viable ceramic membrane technology to protect Li anodes.
- Maps the Li-solid electrolyte interface performance characteristics to determine relevance to vehicle electrification

DE-EE-00006821
Beyond Li-Ion
Sakamoto

RELEVANCE

Solid electrolytes for solid-state and lithium-sulfur batteries

J. Sakamoto, C. Monroe, J. Nanda, D. Siegel, and J.Wolfenstine

University of Michigan (UM), Oak Ridge National Laboratory (ORNL), Army Research Laboratory (ARL)

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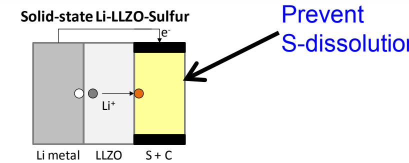
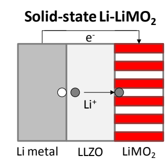
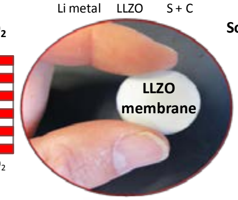
Area of Interest: Area 3, Beyond Li-ion Technologies
Estimated Total Cost: $1.22 M
Period of Performance: 3 years

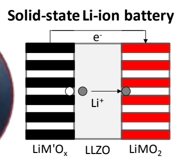
Solid electrolytes: a unifying technology for Beyond Li-ion batteries



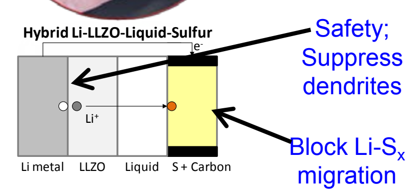
Our focus: LLZO garnet electrolyte







LLZO advantages:
- σ = 1 mS/cm at 298K
- Stable against Li & in air
- Adequate shear modulus

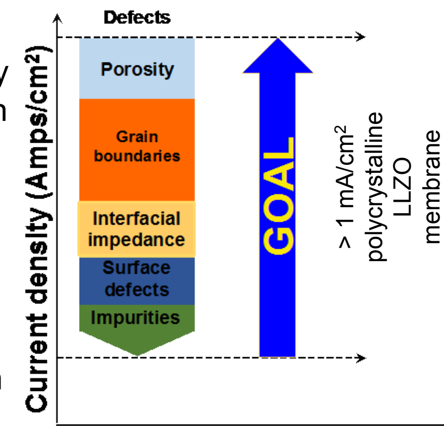


Gap: Various defects are expected to control current density, but little understanding of mechanisms and their relative importance

Defect Type	Effect or Plausible Consequence
Porosity	Discontinuities in transport → hot spots?
Grain Boundaries	Higher resistance than bulk → alters Li-ion migration pathway?
Interfacial Impedance	Localized polarization; amplified by incomplete wetting and roughness?
Surface Impurities	Increased interfacial resistance; formation of passivation barriers?
Bulk Impurities/Dopants	Slower Li transport if non-Li species occupy Li sites?

Goal: Demonstrate polycrystalline LLZO membranes in Li-metal & Li-S batteries that support current densities approaching that of defect-free crystals (> 1 mA/cm²)

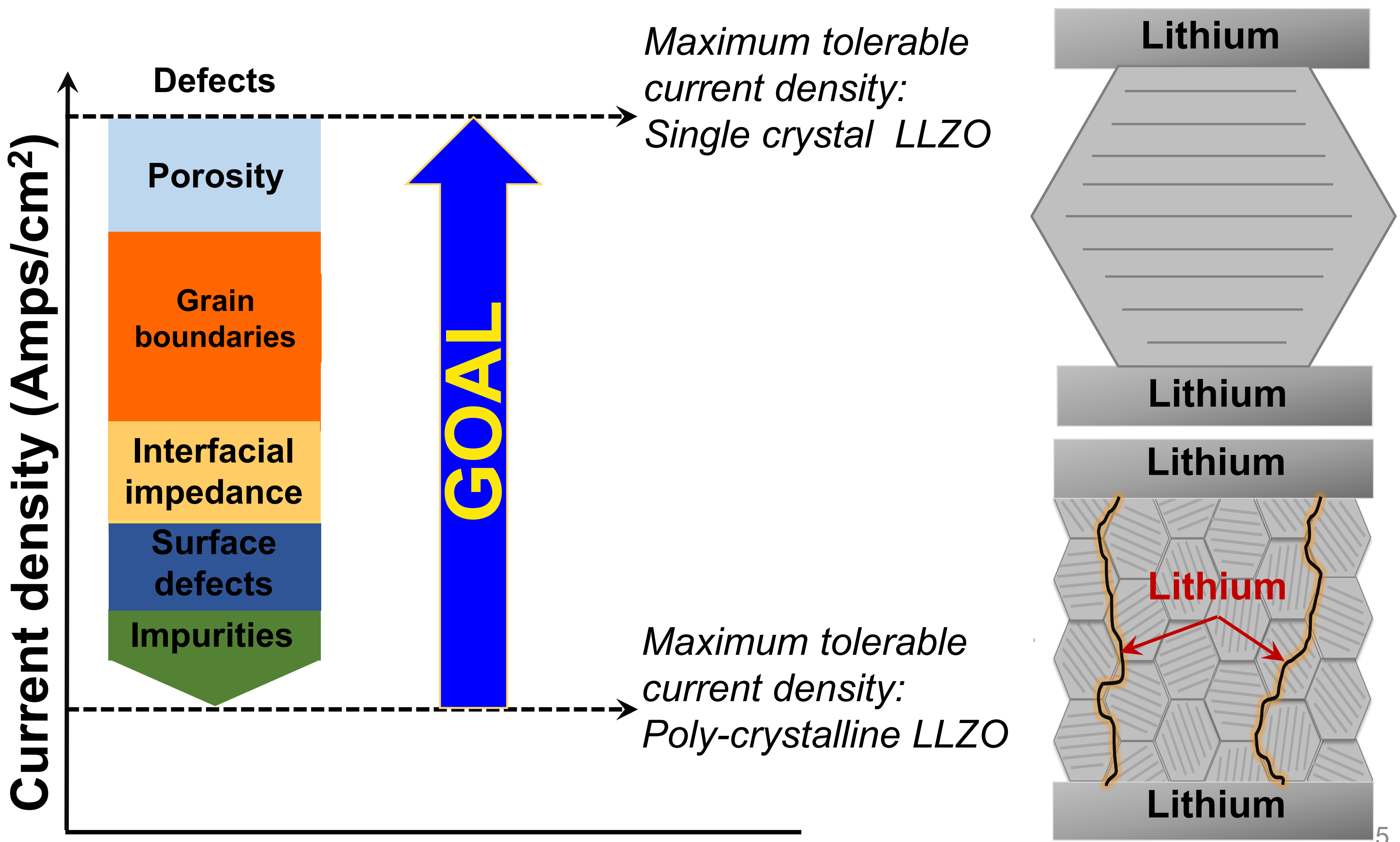
Approach: Quantify the role of defects in determining LLZO stability and maximum current density using a combination of experiments and atomistic/continuum modeling



Objective

Hypothesis: defects govern the maximum tolerable current density

Approach: study and quantify the effects of each defect type to enable solutions to suppress Li metal propagation in polycrystalline LLZO



Milestones (June 2016 – 2017, Project Q6-Q10)

M1.4 Milestone (Q6): Through theory and experiment, demonstrate a correlation between CCD, surface contamination and surface roughness.	✓ CCD increases with decreasing porosity, but not due to porosity; likely due to decreasing grain boundary resistance with decreasing porosity.
M1.5 Milestone (Q6): Through theory and experiment, evaluate and compare the effect of microstructural defects (grain boundaries vs porosity) on CCD.	✓ Clearly identified grain boundaries are the dominant defects that controll CCD.
Go/no-Go (Q6): Isolate the primary atomic and primary microstructural defects that are most likely to limit the CCD in Budget Periods 2 and 3.	✓ Down selected protons and grain boundaries as the primary atomistic and microstructural defects that govern CCD, respectively.
M1.6 Milestone (Q8): Demonstrate the ability to control the microstructural defect that has the most significant effect on CCD to achieve a CCD of $\geq$ 1 mA/cm^2.	✓ Demonstrated the ability vary the grain size (between 2-30 μm).
M1.7 Milestone (Q8): Demonstrate the ability to control the atomic-scale defect that has the most significant effect on CCD to achieve a CCD of $\geq$ 1 mA/cm^2.	✓ Demonstrated the ability to reduce the effect of proton contamination to achieve 2 $Ohm\text{-}cm^2$ interface resistance; diminished the impact of interface resistance on CCD.
M 2.1 Milestone (Q9): Characterize the beginning of life stability of Li-LLZO-liquid-S+carbon cells.	✓ Demonstrated viable cycling behavior or Li-LLZO-liquid+S+carbon cells. 99% coulombic efficiency over 25 cycles.
M2.2 Milestone (Q10): Characterize the beginning of life stability of Li-LLZO-liquid-SOA Li-ion cathode cells.	TBD.

Approach/Strategy

APPROACH

Develop solid-electrolyte technology

- Enabling metallic Li anodes could increase the energy density (>1000 Wh/l) at the cell and battery pack level.
- The parameters that control the stability and kinetics of the Li metal-SE interface are not well understood.
- This project focuses on understanding the role that defects play in controlling the highest tolerable current density (critical current density - CCD).
- To achieve relevance to EVs, our goal is to demonstrate a CCD of > 1 mA/cm^2 in prototypical half cells.
- This project involves close collaboration with ORNL (Dr. N. J. Dudney, BMR; “Mechanical Properties at the Protected Lithium Interface”).
- Go/No-Go Decision: Down-selected which microstructural defect had the most profound effect on CCD in Q6.

APPROACH

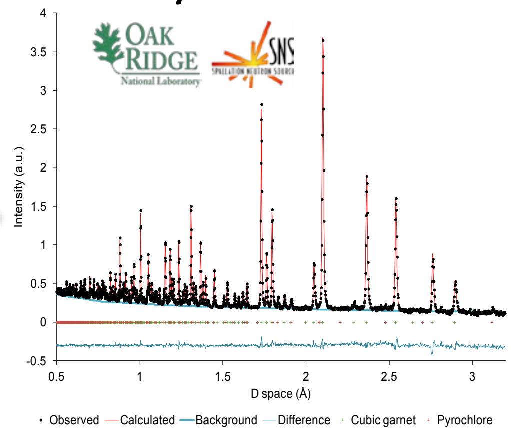
Materials approach

Powder synthesis

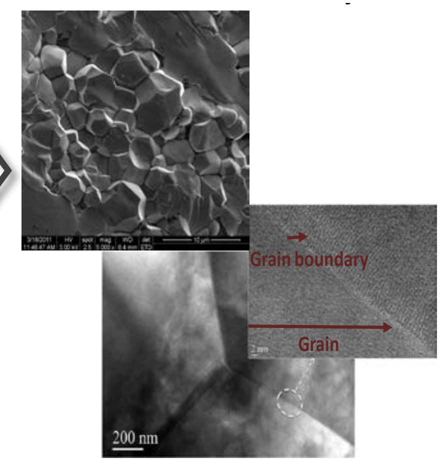
Induction hot pressing

$\geq$ 98% relative density

Neutron + Synchrotron Diffraction



Microstructural analysis

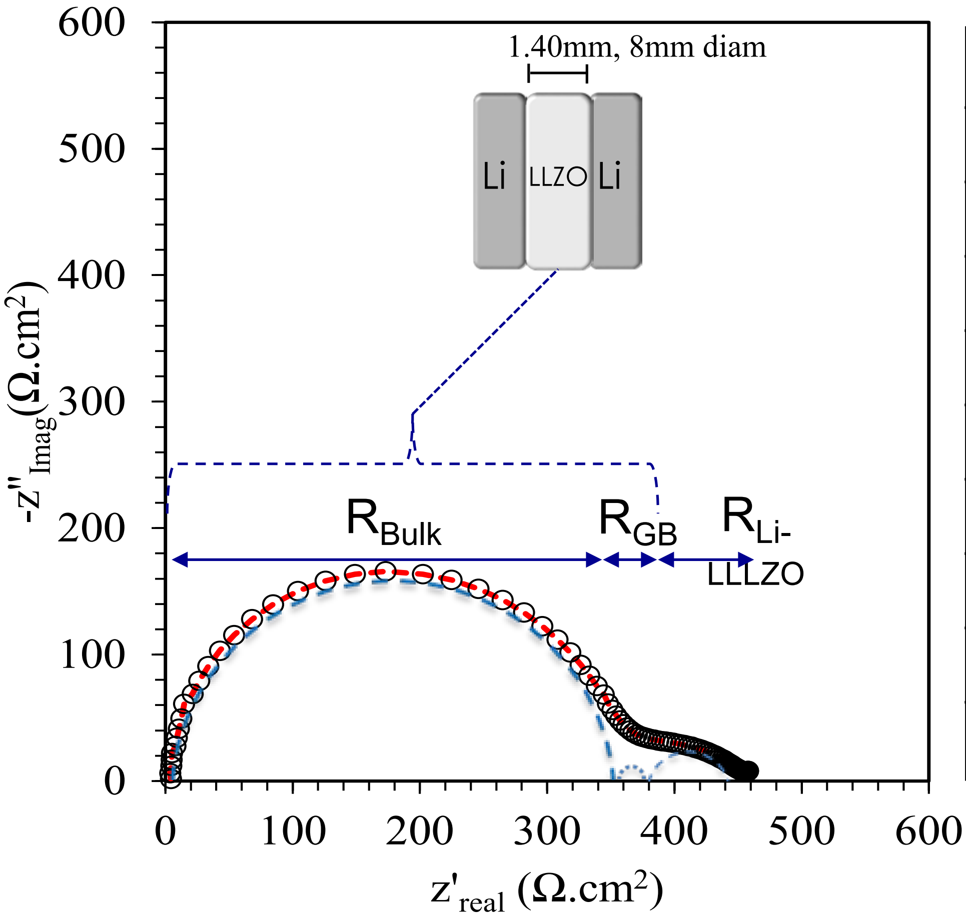


❖ Goal: make LLZO under highly controlled conditions to control defects

❖ Philosophy: if it doesn't work in the idealized form, it won't work at all

Electrochemical characterization

Simplified complex impedance

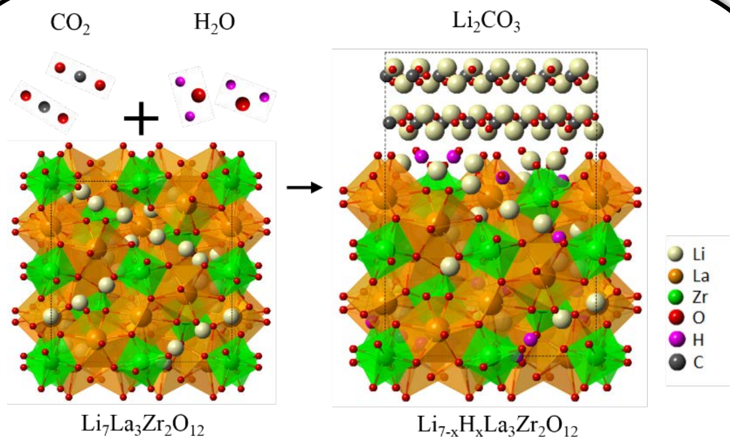


R_{bulk} $(\Omega.cm^2)$	333.2
Q_1 $(F.cm^2)$	2.0 e^{-12}
α	1
$R_{GB}(\Omega.cm^2)$	21
Q_2 $(F.cm^2)$	$0.99e^{-8}$
α	1
$R_{li-LLZO}(\Omega.cm^2)$	116 (2X)
Q_3 $(F.cm^2)$	$5.5e^{-6}$
α	0.8
$R_{Li-LLZO}(\Omega.cm^2)$	58

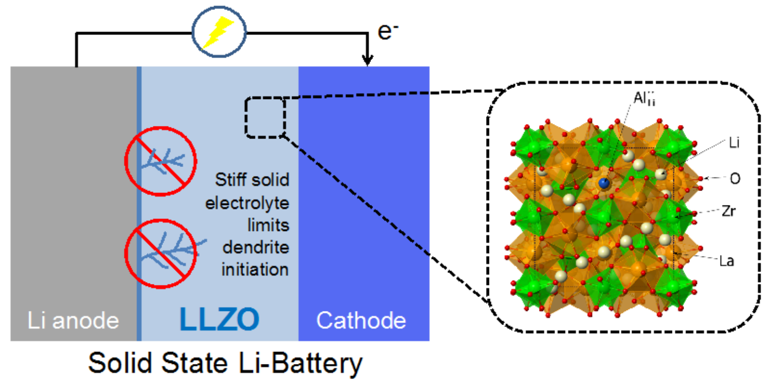
❖ Complex impedance isolates and quantifies transport phenomena

❖ Lack of side reactions simplifies interpretation

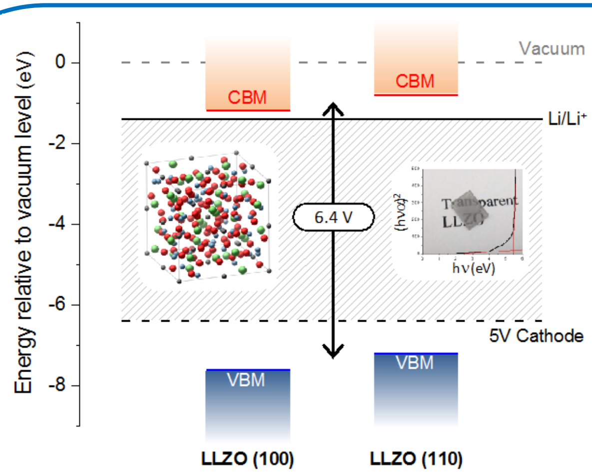
Computation



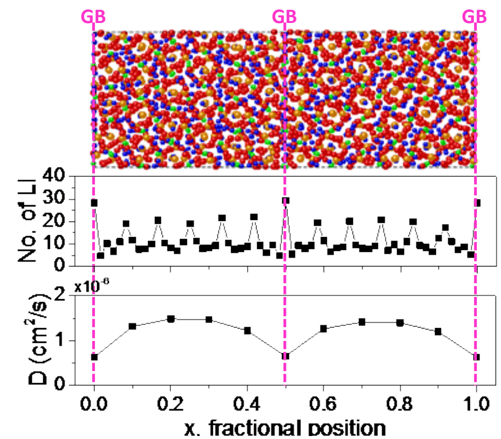
First-principles calculations of surface reactivity



First-principles calculations of elastic moduli

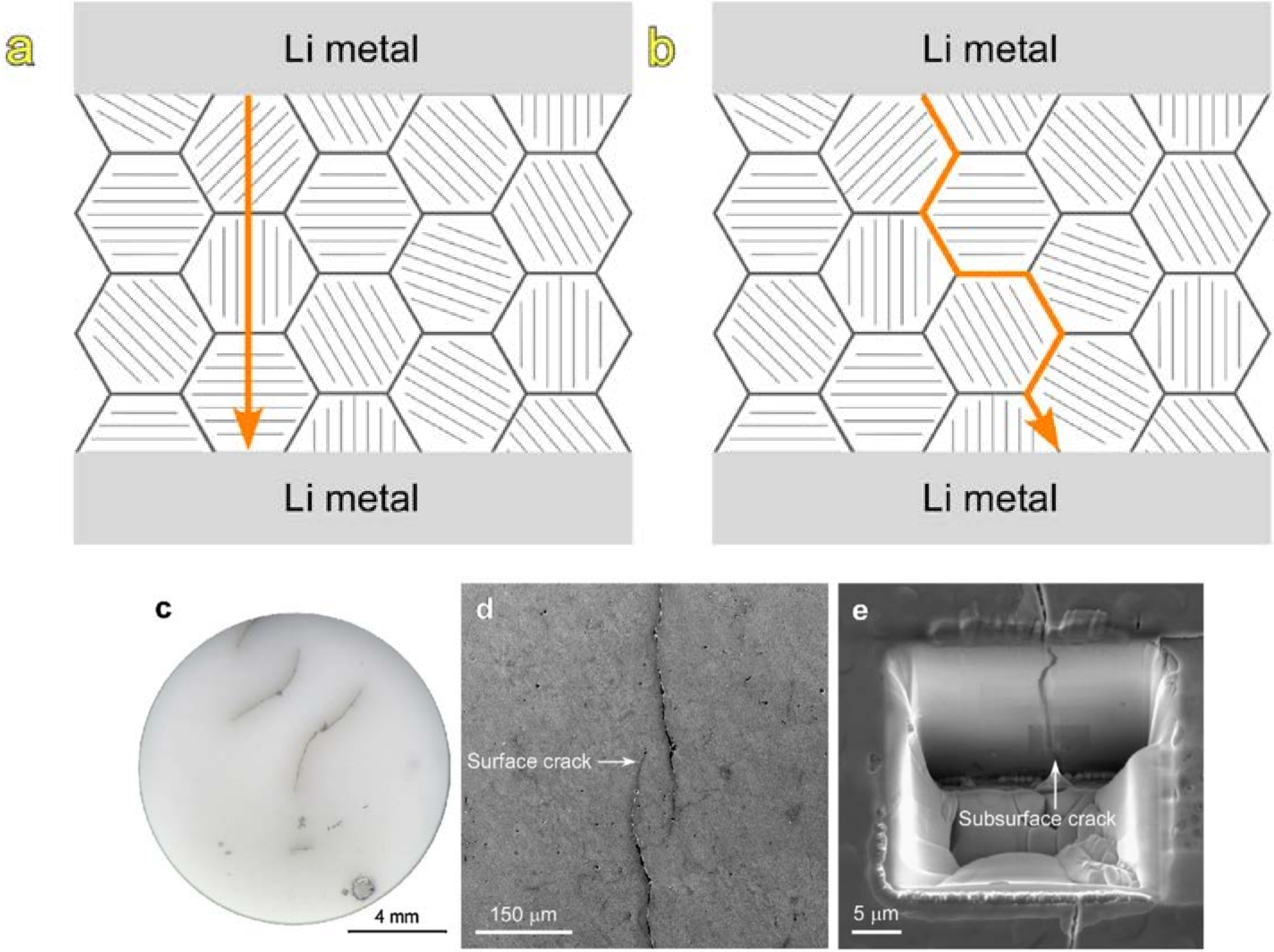


Electrochemical window evaluated using many-body perturbation theory (GW method)



MD &Monte Carlo simulations of segregation and transport at grain boundaries

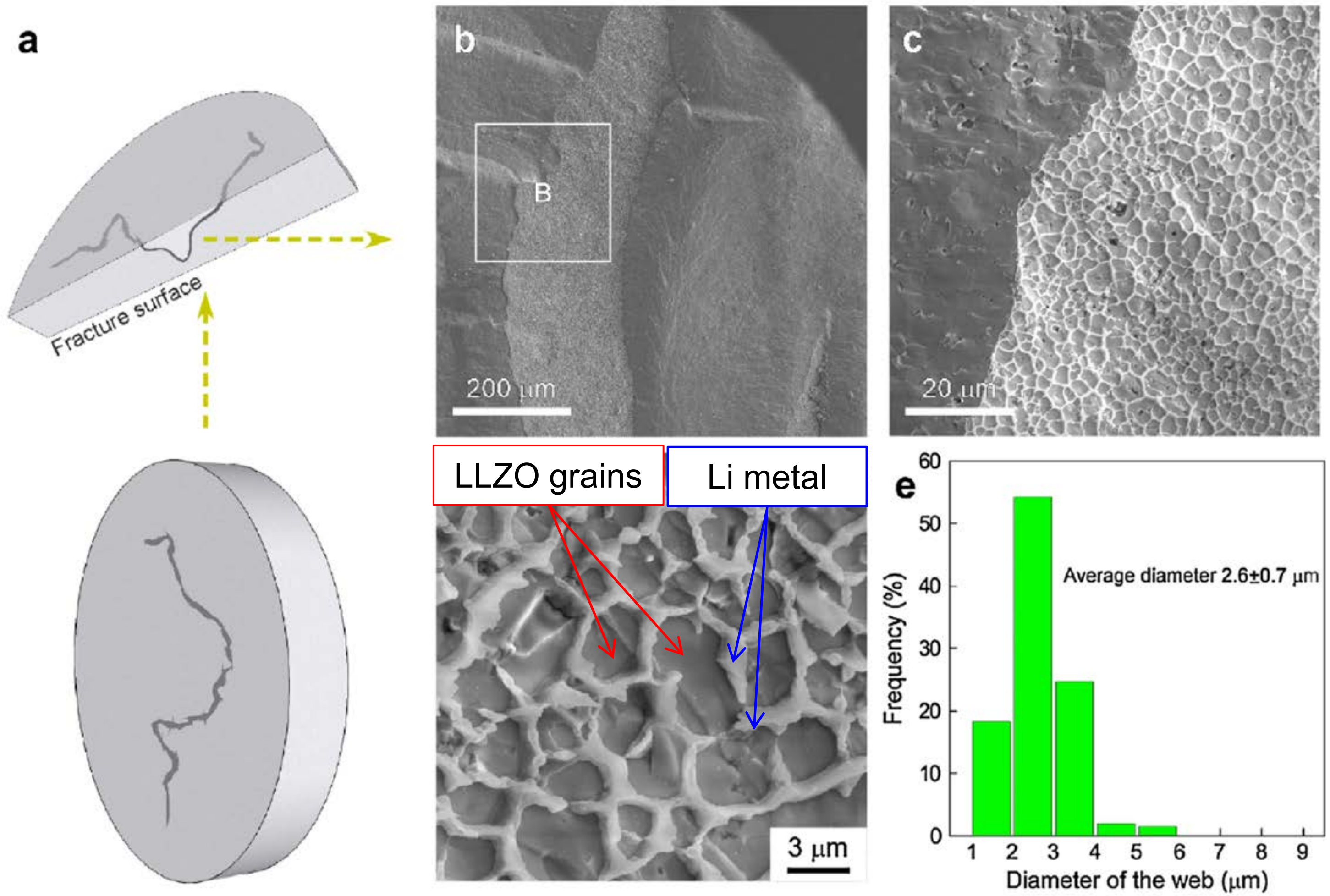
Effect of grain boundaries



Cheng E. J., Sharafi A. and Sakamoto *J.*, *Electrochimica Acta* (2016).

❖ How does soft Li penetrate a hard ceramic?

Effect of grain boundaries

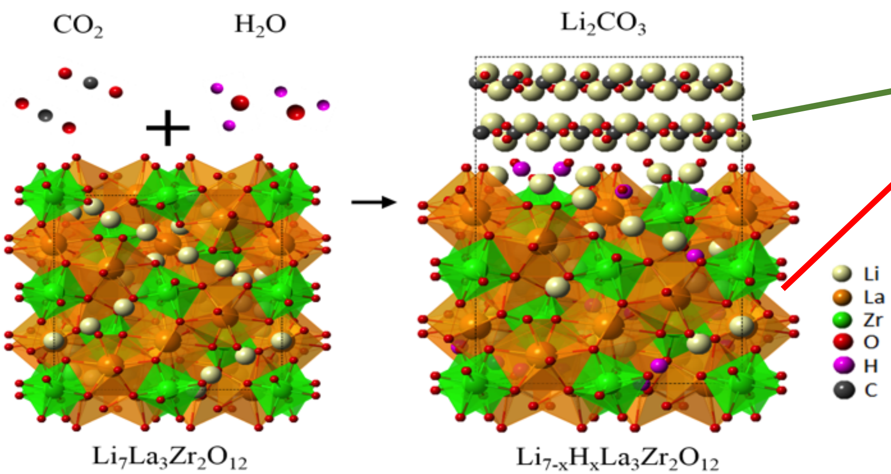


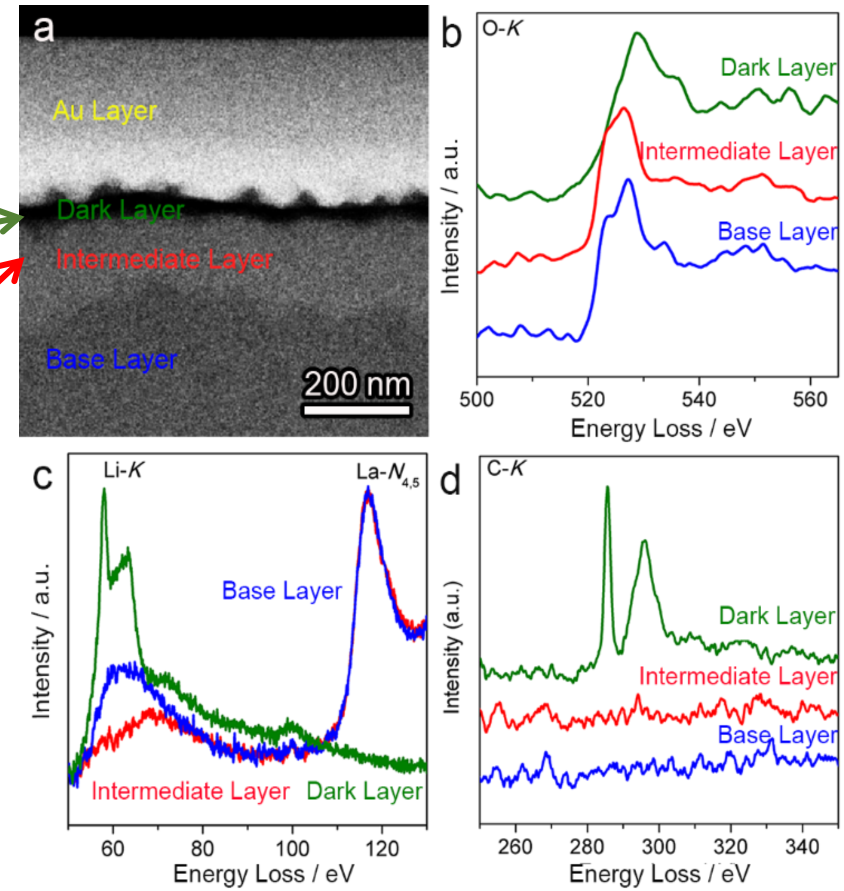
Cheng E. J., Sharafi A. and Sakamoto J., *Electrochimica Acta* (2016).

❖ Clearly identified grain boundaries as the primary defect that governs CCD.

Effect of surface contamination

Reducing $R_{Li\text{-}LLZO}$





Li^+/H^+ ion exchange: $Li_7La_3Zr_2O_{12} + x\,H_2O \rightarrow Li_{7-x}H_xLa_3Zr_2O_{12} + x\,LiOH$

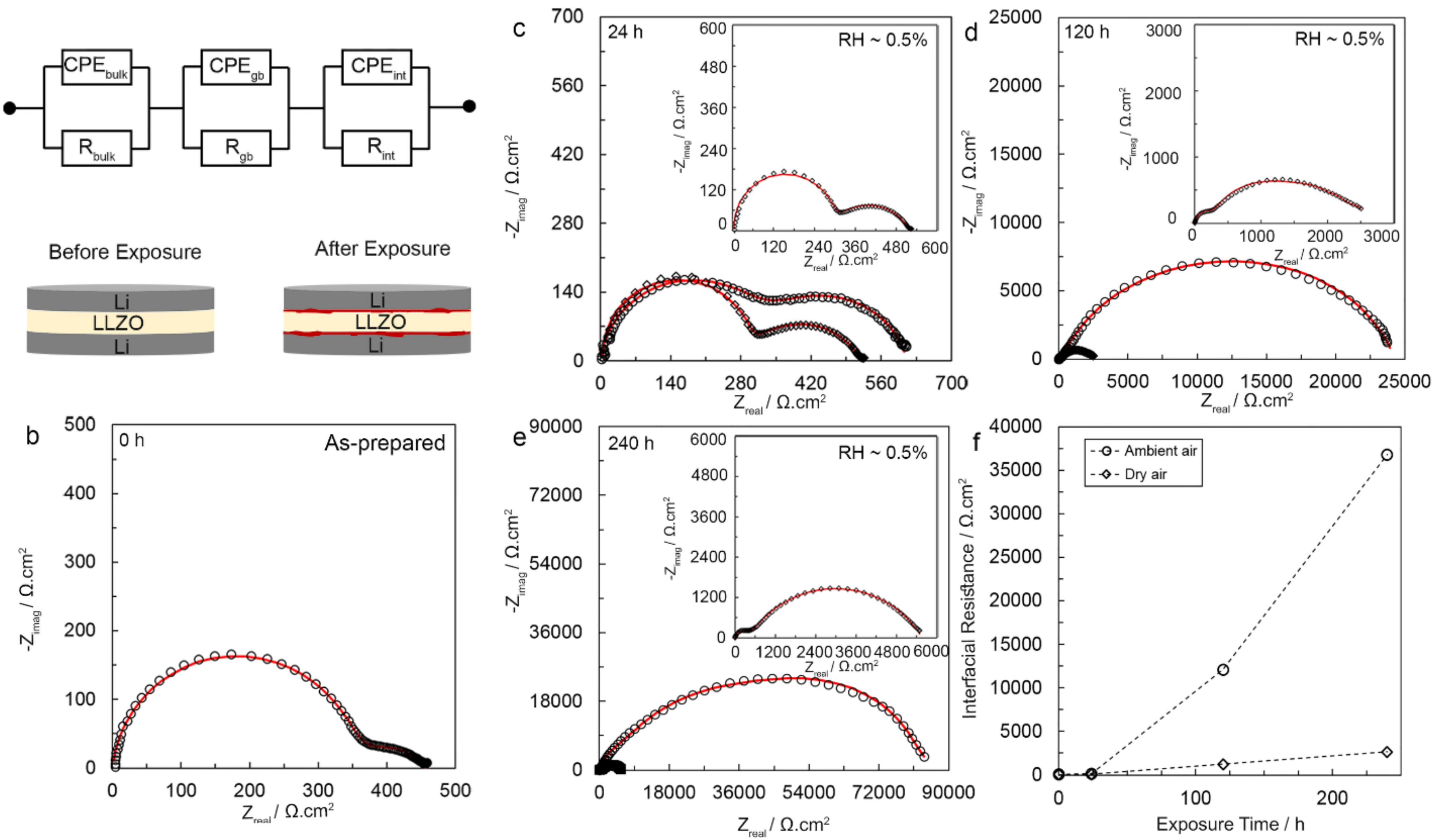
Carbonation of LiOH: $LiOH + \frac{1}{2}\,CO_2 \rightarrow \frac{1}{2}Li_2CO_3 + \frac{1}{2}\,H_2O$

A. Sharafi, et al., Impact of air exposure and surface chemistry on the Li-$Li_7La_3Zr_2O_{12}$ interfacial resistance, In Peer Review

❖ Analyzed the reaction pathways between air and LLZO.

Effect of surface contamination

Reducing $R_{Li\text{-}LLZO}$

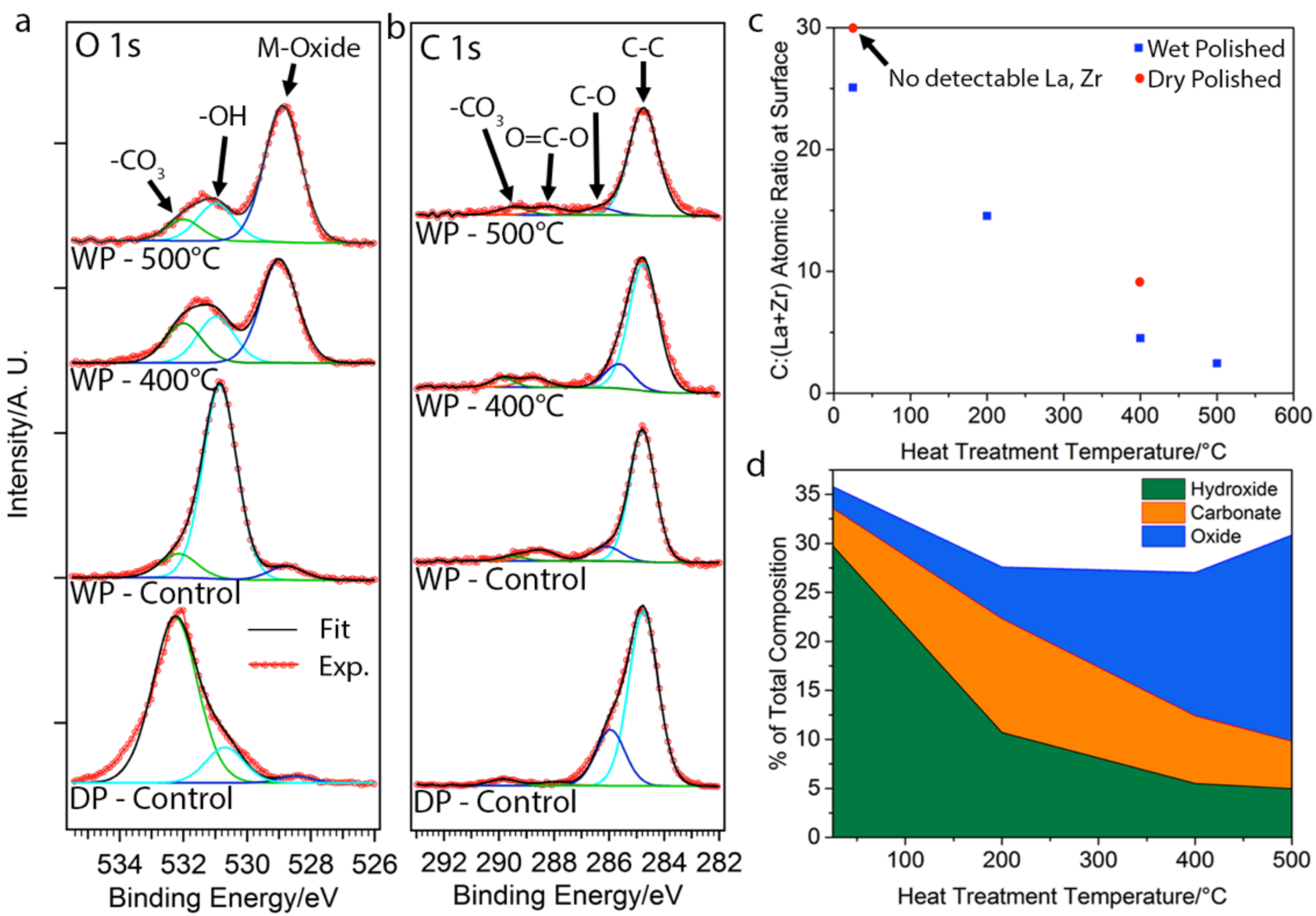


A. Sharafi, et al., In Peer Review

❖ Correlated the interfacial resistance to surface chemistry

Effect of surface contamination

Reducing $R_{Li\text{-}LLZO}$

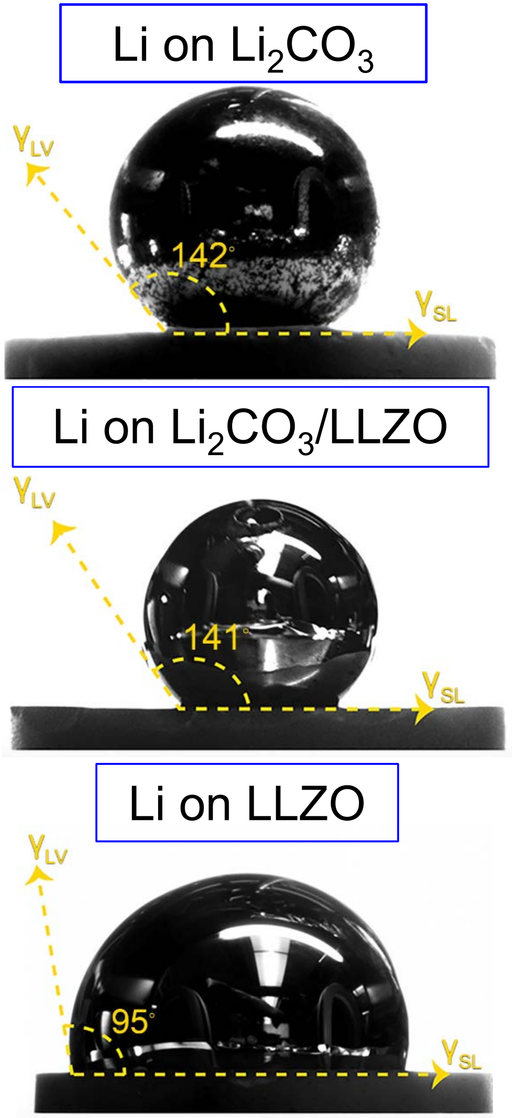


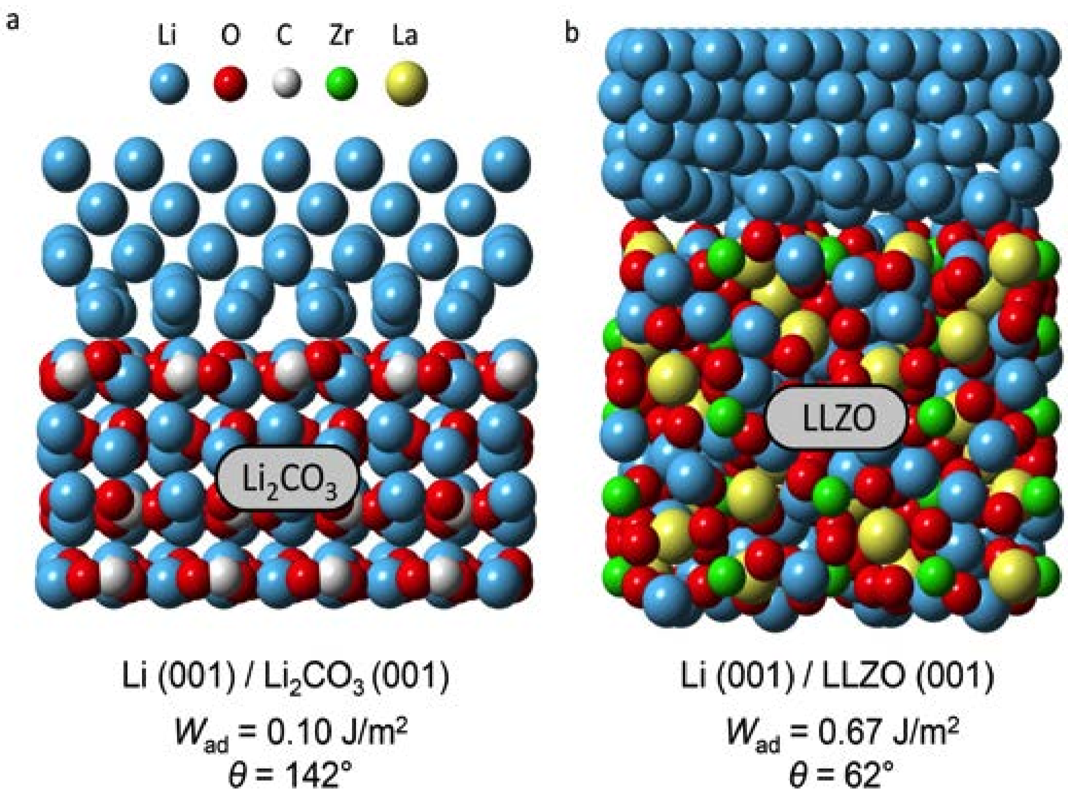
A. Sharafi, et al. submitted, patent application

❖ Developed a simple method to clean LLZO.

Effect of surface contamination

Reducing $R_{Li\text{-}LLZO}$





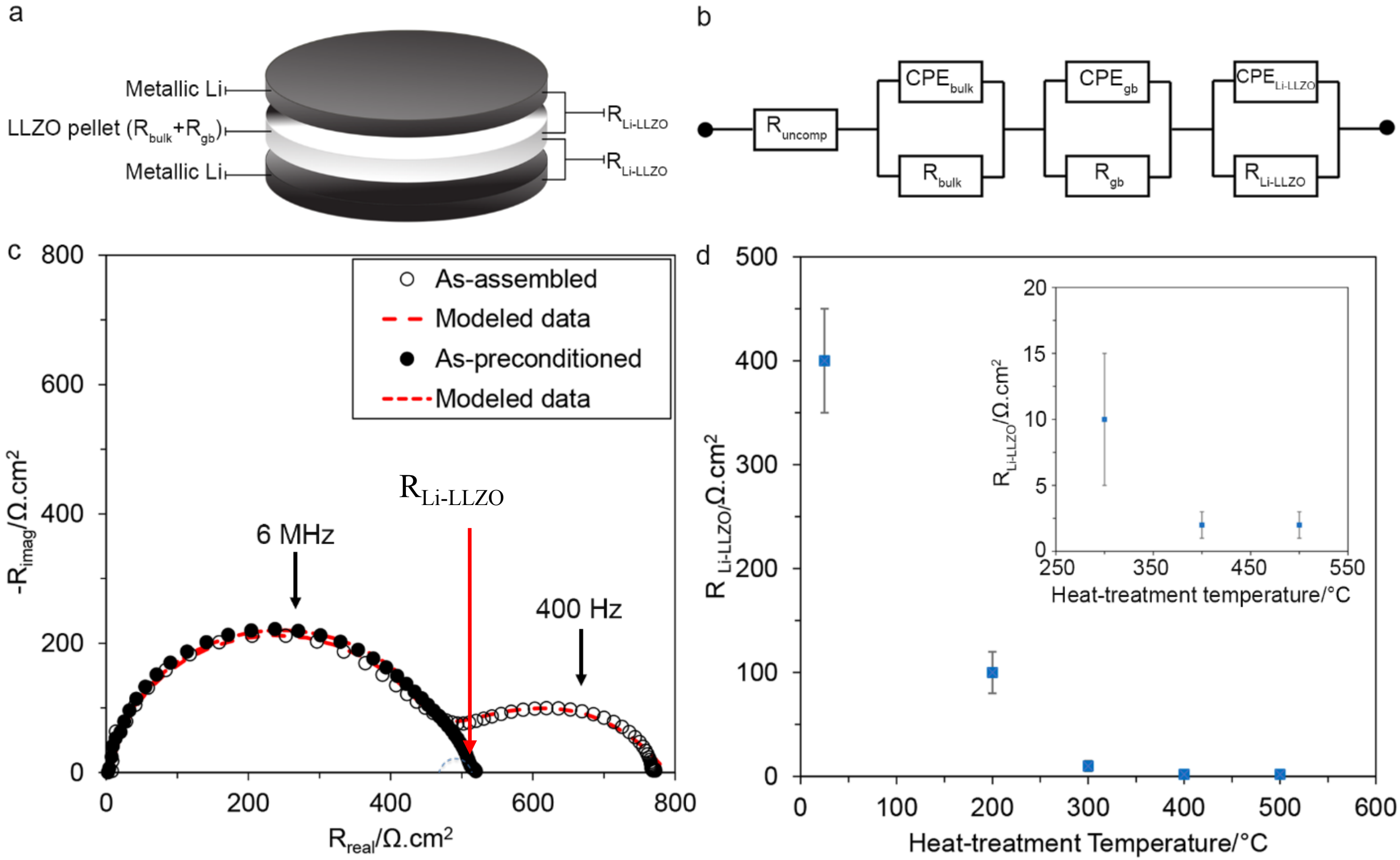
A. Sharafi, et al. submitted, patent application

❖ Correlated and quantified the effect of surface chemistry and Li wetting.

ACCOMPLISHMENT

Effect of surface contamination

Reducing $R_{Li\text{-}LLZO}$

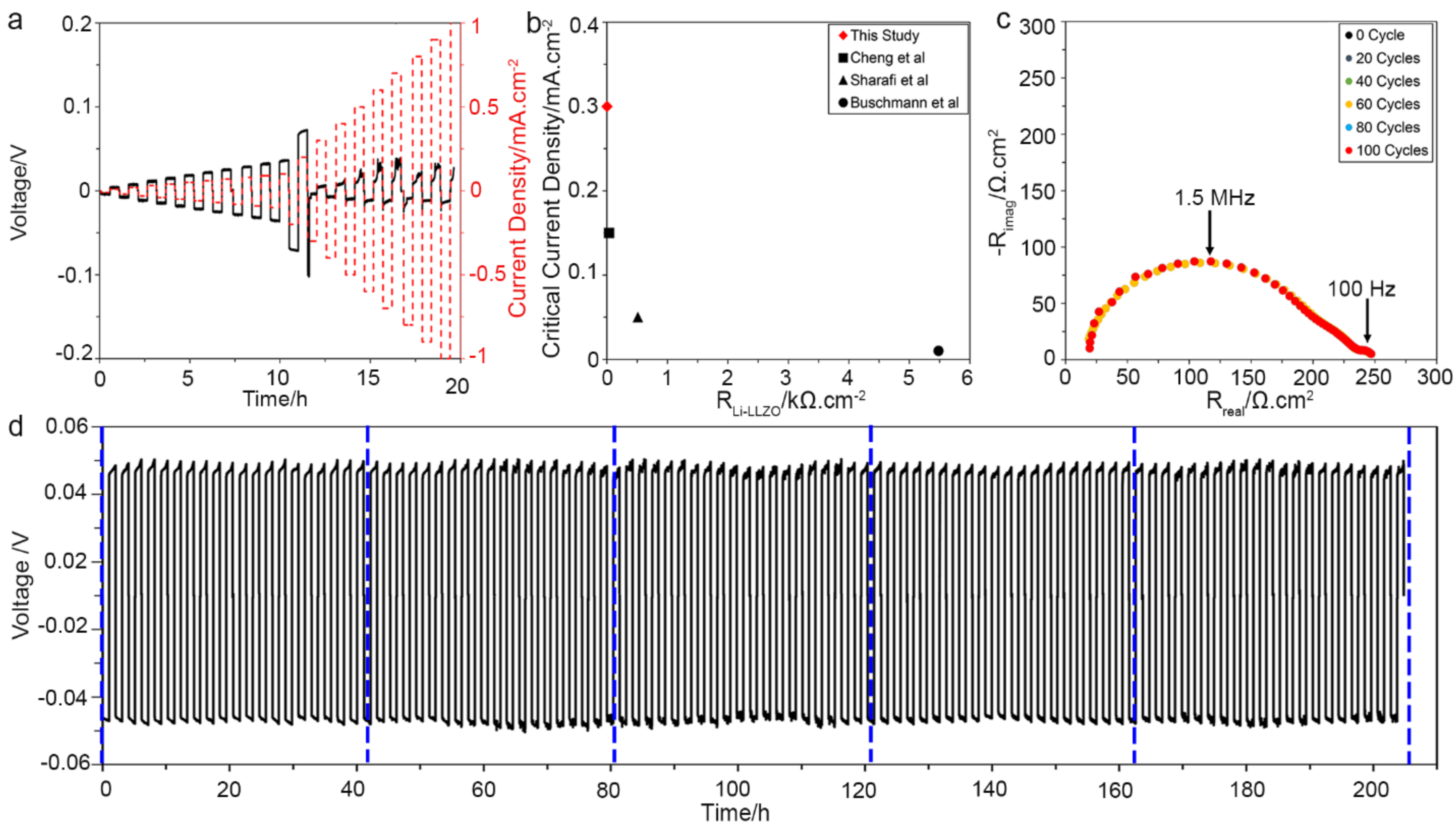


A. Sharafi, et al. submitted, patent application

- ❖ Achieved ultra-low $R_{Li\text{-}LLZO}$ interface resistance.
- ❖ Validated/reproduced by National labs and industrial partners.

Effect of surface contamination

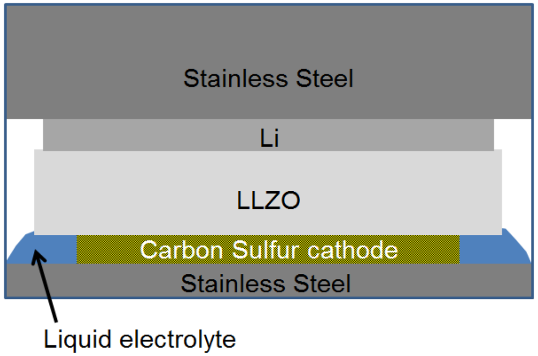
Reducing $R_{Li\text{-}LLZO}$

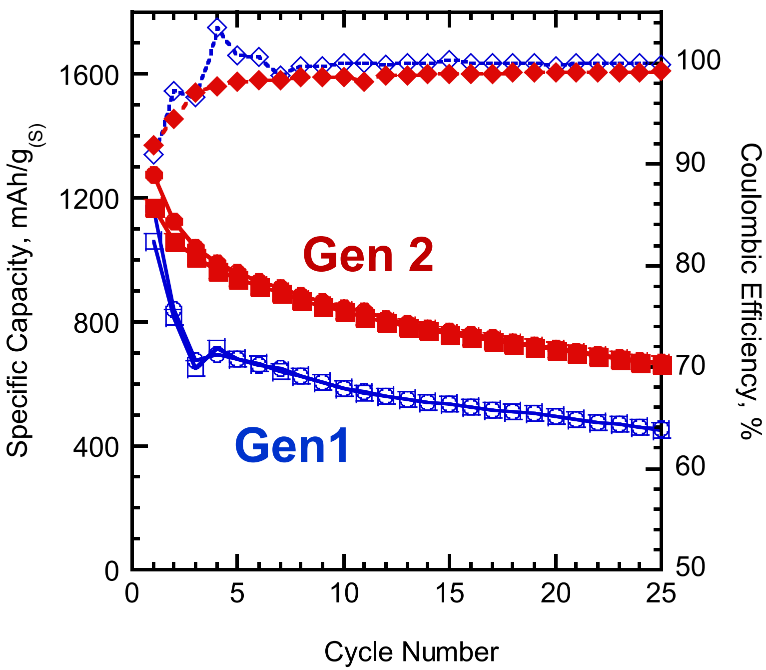


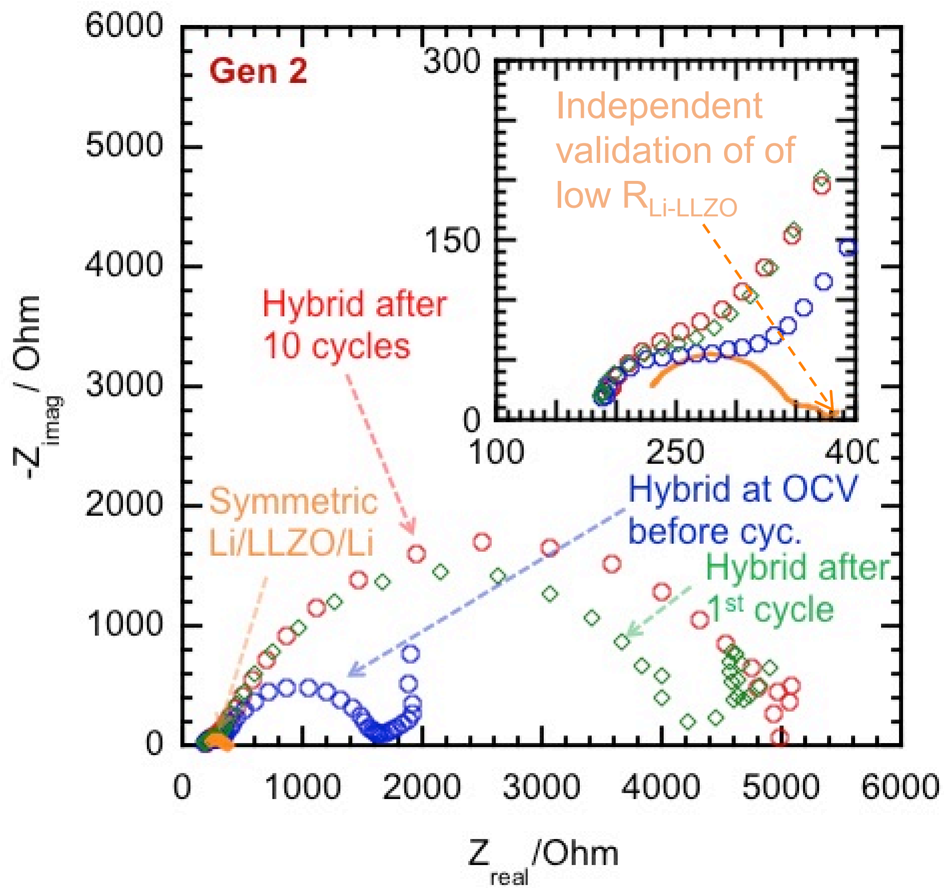
A. Sharafi, et al. submitted, patent application

- ❖ Demonstrated the Li-LLZO interface is stable upon during and after DC cycling.
- ❖ Validated/reproduced by National labs and industrial partners

Enabling Li-S



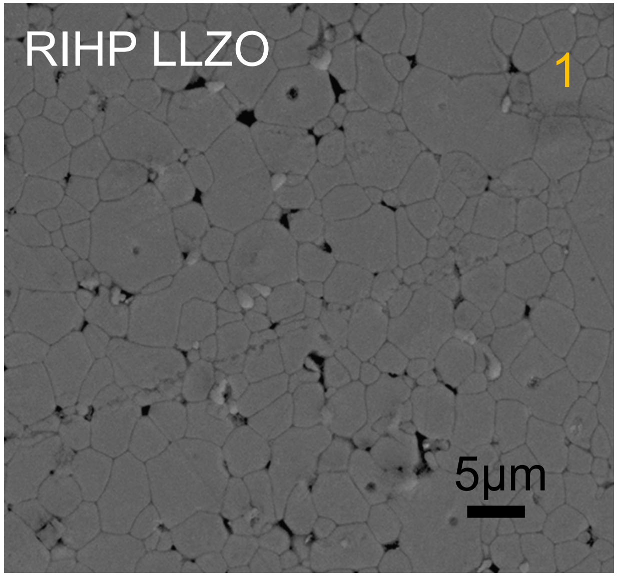


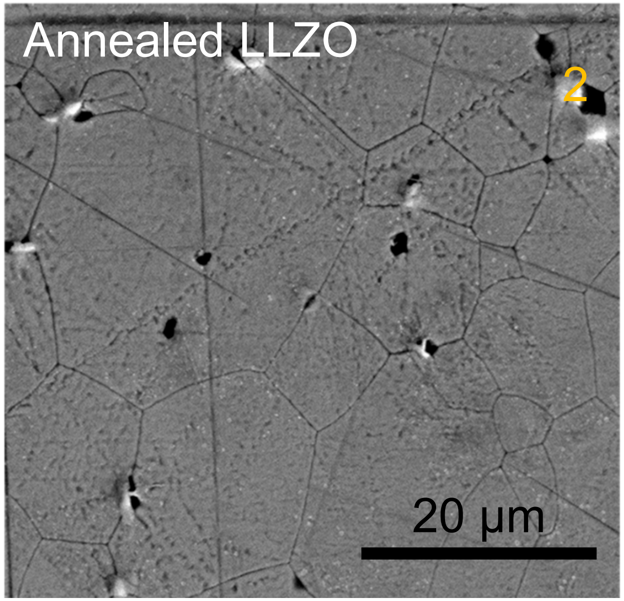


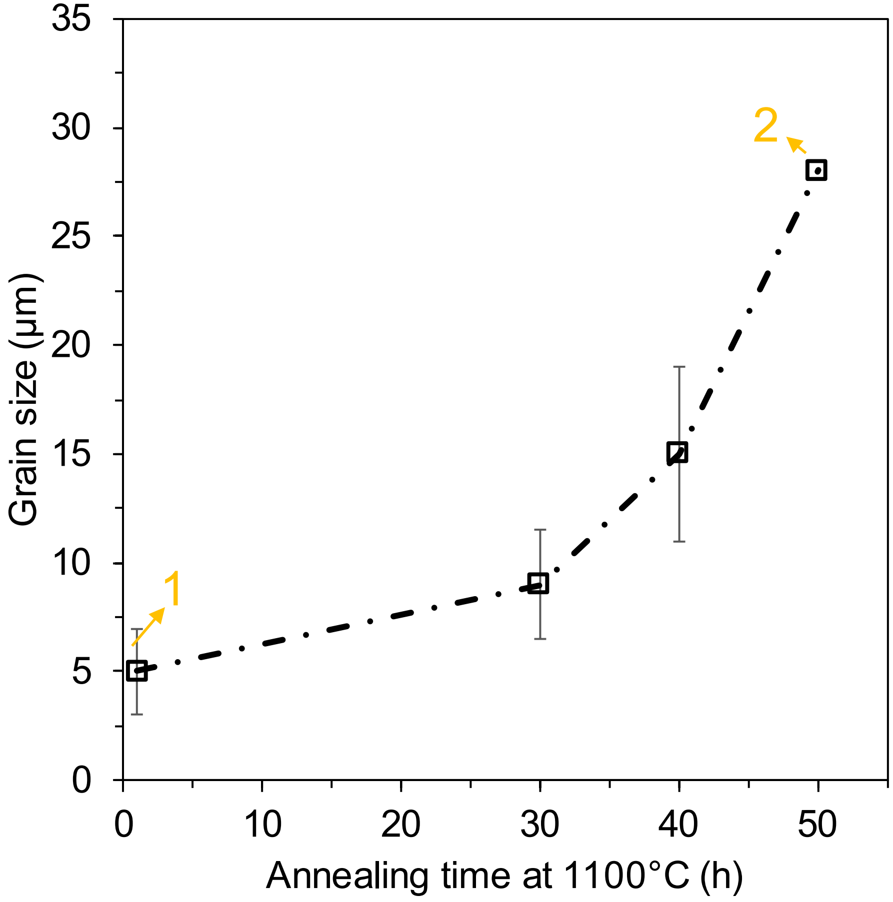
❖ Completed initial assessment of hybrid Li-LLZO-Sulfur cell performance.

Varying grain size

ACCOMPLISHMENT

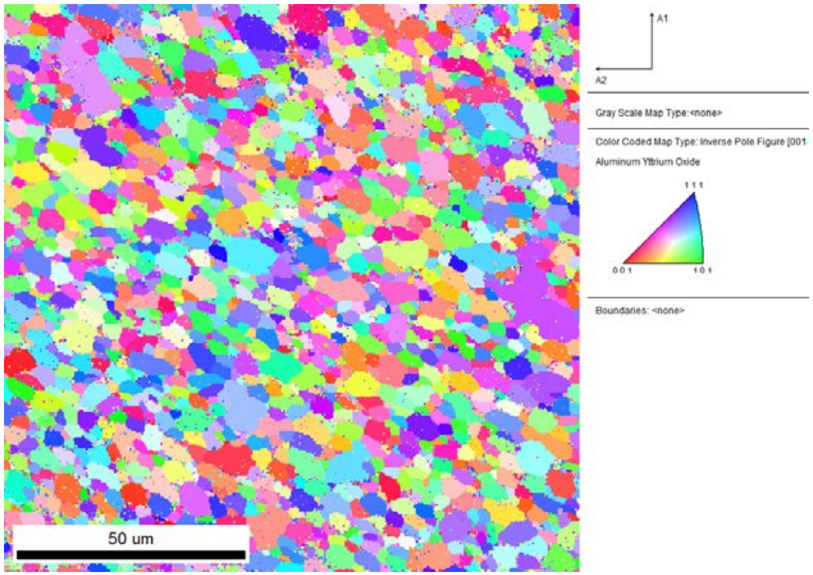






❖ Can vary the grain size and grain boundary morphology/curvature.

Grain size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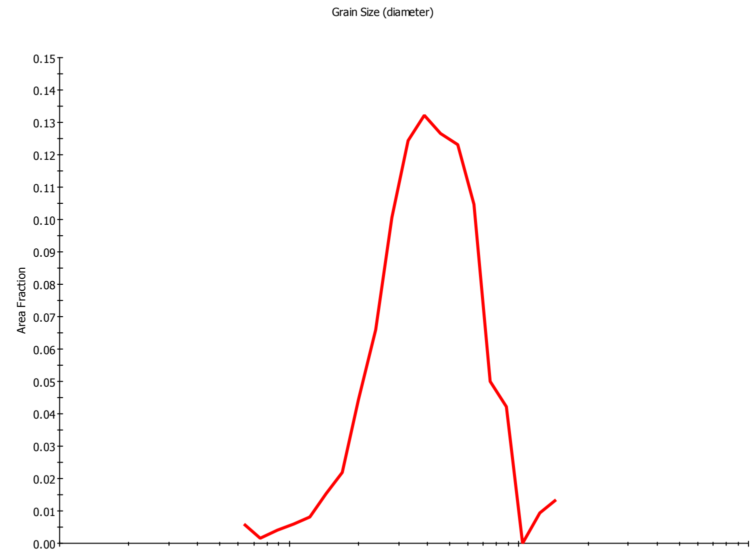
Grain Size (diameter)
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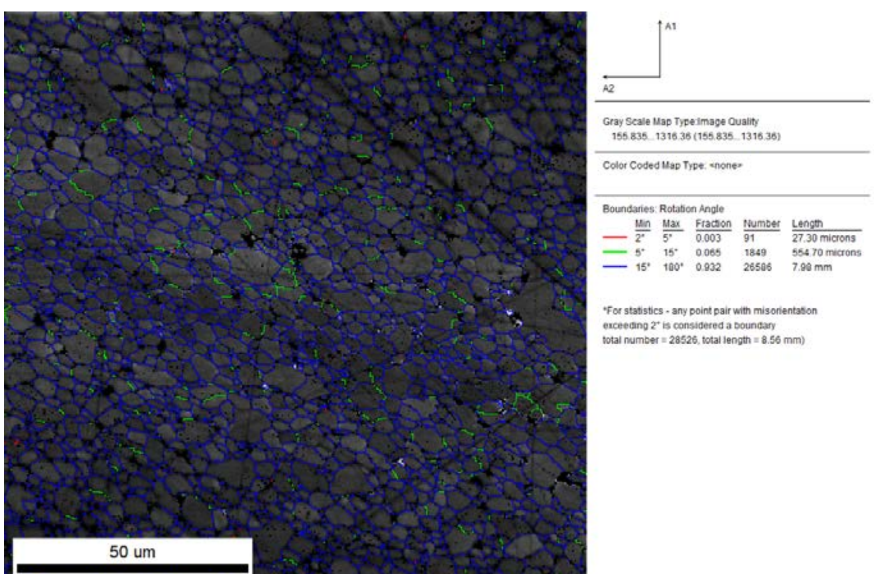
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Boundaries: Rotation Angle
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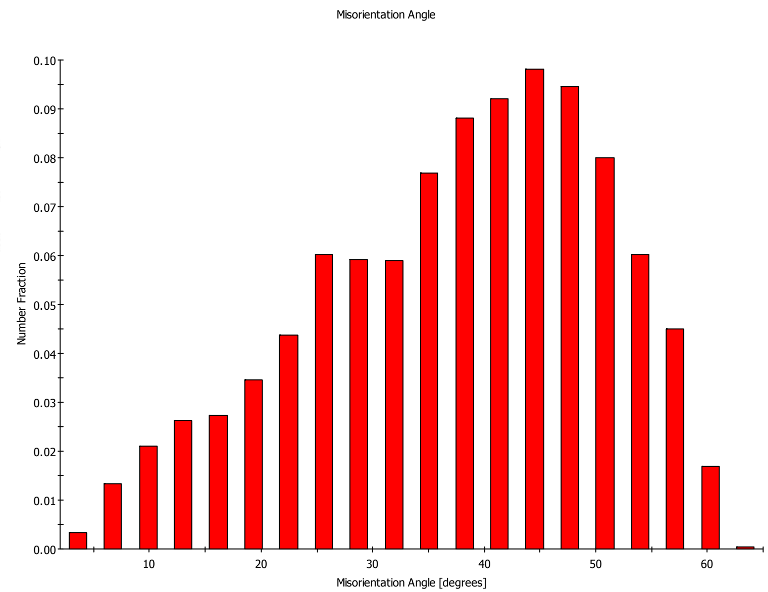
2° 5° 0.003 91 27.30 microns
5° 15° 0.065 1849 554.70 microns
15° 180° 0.932 26586 7.98 mm
*For statistics - any point pair with misorientation
exceeding 2° is considered a boundary
total number = 28526, total length = 8.56 mm)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Responses to Preview Years Comments

- None, new project.

Partners and Collaborators

Prof. Don Siegel

- Lead the atomistic computational modeling component of the project

Dr. Jagjit Nanda

- Perform in-situ/in-operando spectroelectrochemical analysis

Drs. Jeff Wolfenstine and Jan Allen

- Atomic force microscopy in a state-of-the-art battery dry room to enable testing of cycling LLZO interfaces

Dr. Andy Drews

- Contribute in an advisory role through quarterly or bi-annual interaction

Prof. Chuck Monroe

- Lead the continuum-scale computational modeling

Remaining Challenges and Barriers

FUTURE WORK

Need to learn more about grain boundaries

- What is unique about certain grain boundaries that triggers Li metal propagation?
- What are the transport properties of grain boundaries?
- What techniques are available to help elucidate instabilities at the Li-SE interface?
- At the end of this project, transition to characterizing the interface stability in thin films (~10 μm) to assure relevance; defects will be different in bulk monoliths vs. thin films.

Future work

FUTURE WORK

FY 2018 (Q1)

- Map the effect of stack pressure and temperature on optimized Li-SE interfaces. Milestone 1.8 (FY 2017 Q4)

- Through experiment and computation, establish a theory to correlate the critical current density with defects in bulk processed LLZO. Milestone 1.8 (FY 2018 Q1)

- Characterize the stability and kinetics of the LLZO-liquid electrolyte interface in hybrid Li-S cells.

- Demonstrate, through independent validation, stable cycling of metallic Li anodes in hybrid solid-liquid cells operating at $\geq$ 1mA/cm^2. Milestone 3.1 (FY 2018 Q1)

Any future work is subject to change based on funding levels

Summary

Develop solid-electrolyte technology

- Enabling metallic Li anodes could increase energy density (>1000 Wh/l) at the battery cell and pack level.
- Because solid-electrolyte membrane technology is new, there is a need to understand the phenomena that govern performance in prototypes.
- Specifically, this project seeks to understand how material processing affects the microstructure, which affects highest tolerable current density (mA/cm^2). <u>To achieve relevance to EVs, our goal is to achieve > 1 mA/cm^2.</u>
- This project involves close collaboration with ORNL (Dr. N. Dudney, “Mechanical Properties at the Protected Lithium Interface”).
- Go/No-Go Decision: Determine which aspect has the most profound effect on the maximum tolerable current density (critical current density – CCD).

Publications and Patents

ACCOMPLISHMENTS

Publications

- Y. Kim,, H. Jo, J. L. Allen, H. Choe, J. Wolfenstine, and J. Sakamoto, "The Effect of Relative Density on the Mechanical Properties of Hot-Pressed Cubic $Li_7La_3Zr_2O_{12}$" *J. Am. Ceram. Soc.,* 99 [4] 1367–1374 (2016).
- C. Ma, Y. Cheng, K. Yin, J. Luo, A. Sharafi, J. Sakamoto, J. Li, K. L. More, L., N. J. Dudney, and M. Chi, "Interfacial Stability of Li Metal–Solid Electrolyte Elucidated via in Situ Electron Microscopy: *Nano Letters*, 16(11), 7030-7036 (2016).
- T. Thompson, S. Yu, L. Williams, R. D. Schmidt, R. Garcia-Mendez, J. Wolfenstine, J. A. Allen, E. Kioupakis, D. J. Siegel, and J. Sakamoto, "Electrochemical Window of the Li-Ion Solid Electrolyte $Li_7La_3Zr_2O_{12}$" *ACS Energy Letters*, 2(2), 462-468 (2017).
- E. J. Cheng, A. Sharafi, and J. Sakamoto, "Intergranular Li metal propagation through polycrystalline $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ceramic electrolyte" *Electrochim. Acta* 223, 85-91 (2017).
- A. Sharafi, S. Yu, M. Naguib, M. Lee, C. Ma, H. Meyer, J. Nanda, M. Chi, D. J. Siegel, and J. Sakamoto, "Impact of Air Exposure and Surface Chemistry on the Li-$Li_7La_3Zr_2O_{12}$ Interfacial Resistance" *J. Mater. Chem. A.,* under review.
- A. Sharafi, E. Kazyak, A. L. Davis, S. Yu, T. Thompson, D. J. Siegel, N. P. Dasgupta, and J. Sakamoto, "Achieving low resistance all-solid-state Li-LLZO interfaces through surface chemistry control" *Energy Envir. Sci.*, under review.

Patent

- J. Sakamoto, A. Sharafi, and T. Thompson, "System and Method for Treating the Surface of Solid Electrolytes" US Utility Patent Application Serial No. 62/480,080 (2017).

Presentations and Posters

Oral Presentations

- Invited: J. Sakamoto et al. “Mechano-electrochemical aspects in solid-state batteries” MRS, Phoenix (2017)
- Invited: D. J. Siegel et al. “Atomic Scale Simulations of Solid Electrolytes—Mechanical Properties and Beyond” MRS Phoenix (2017).
- A. Sharafi, “ Controlling the Microstructure of Polycrystalline $Li_7La_3Zr_2O_{12}$ Solid State Electrolyte to Mitigate Li Dendrite Propagation ”, MRS, Phoenix (2017)
- J. Wolfenstine et al. “Mech. Properties of Oxide Based Li-ion Conducting Solid Electrolytes” MRS Phoenix (2017).
- Invited: J. Sakamoto, “Ceramic electrolytes enabling all solid-state batteries”, Int. Battery Seminar, Ft. Lauderdale, FL (2017).
- Invited: J. Sakamoto, “Solid Electrolytes: An Enabling Technology for Vehicle Electrification”, Batt. Cong., MI (2016).
- Invited : A. Sharafi, “ Stability of $Li_7La_3Zr_2O_{12}$ Garnet Solid-State Electrolyte Against Lithium”, Plug Volt, (2016)
- Invited: J. Sakamoto, “Solid-state electrolytes enabling beyond Li-ion cell chemistries”, Beyond Li-ion, Pacific Northwest National Laboratory, Richland, WA (2016).
- Invited: J. Sakamoto, “Solid Electrolytes: An Enabling Technology for Vehicle Electrification”, American Automotive Battery Conference, Detroit, MI, (2016).
- Invited: J. Sakamoto, “Mechanical Stability of Solid Electrolyte Interfaces in Solid-State Batteries”, Electrochemical Society, San Diego, CA (2016).
- A. Sharafi, “Chemical stability of garnet solid-state electrolyte”, Electrochemical Society, San Diego, CA (2016)
- Invited: J. Sakamoto, “Solid State Batteries”, The Battery Show, Novi, MI (2016).
- Invited: J. Sakamoto, “Fast ion conducting ceramic electrolyte based on $Li_7La_3Zr_2O_{12}$ garnet”, American Chemical Society, Philadelphia, PA (2016).

Poster Presentations

- Correlating the effects of air exposure with surface chemistry and the impedance of the Li-$Li_7La_3Zr_2O_{12}$, *Beyond Lithium Ion IX*, 2016 (*Poster)*