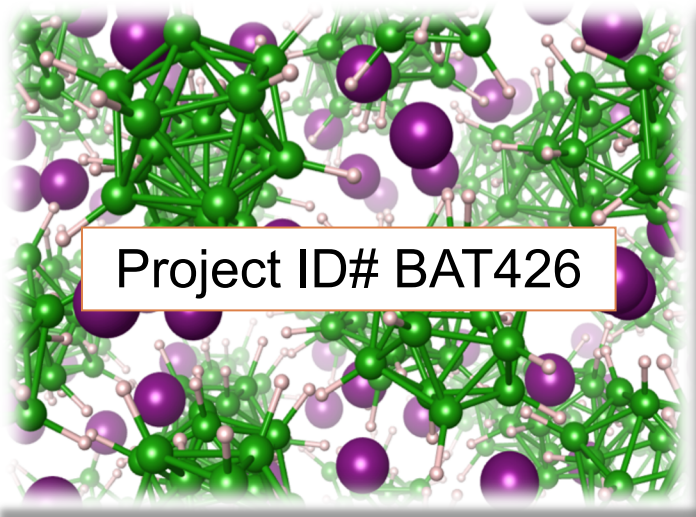
Integrated multiscale model for design of robust 3-D solid-state lithium batteries

2021 Vehicle Technologies Office Annual Merit Review

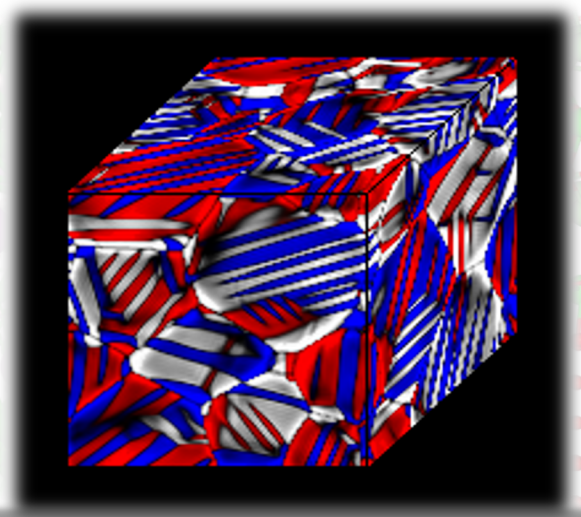
June 21-25, 2021

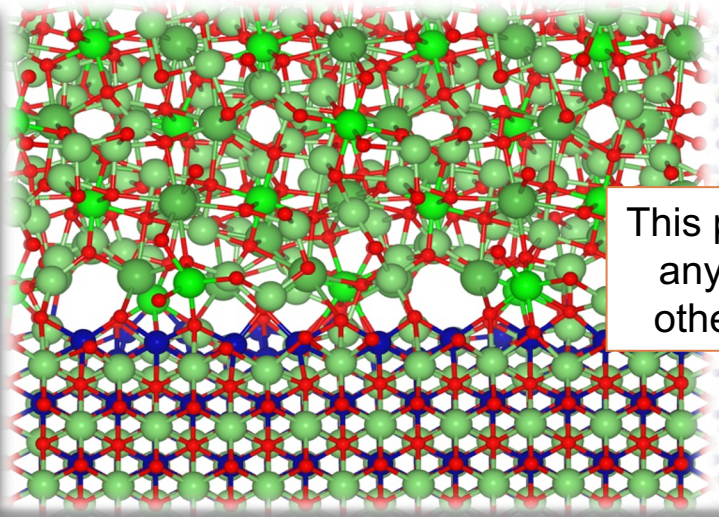
PI: Brandon C. Wood, LLNL

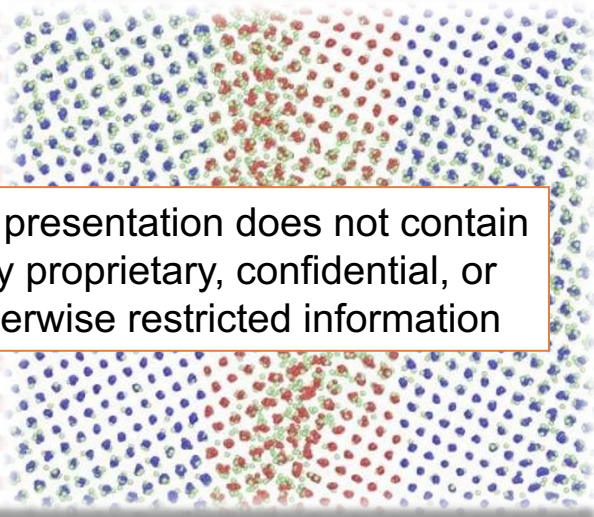
Team: Tae Wook Heo, Liwen Wan, Aniruddha Jana, Aniruddha Dive, Kwangnam Kim, Kyoung Kweon (LLNL)



Project ID# BAT426







This presentation does not contain any proprietary, confidential, or otherwise restricted information

LLNL-PRES-XXXXXX

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

Lawrence Livermore National Laboratory

Overview

Timeline

Project start date: 11/1/2018

Project end date: 10/30/2021

Barriers addressed

- **Performance (Barrier B):** Capacity and ion transport within solid electrolyte and across cathode-electrolyte interface
- **Life (Barrier C):** Poor battery cyclability due to interfacial chemical reactions

Budget

Total project funding: $1,125K (DOE share)

New FY21 funding: $375K

Partners

Collaboration with Project # BAT421:
"3D Printing of Solid-state Li Batteries" (PI: Jianchao Ye, LLNL)

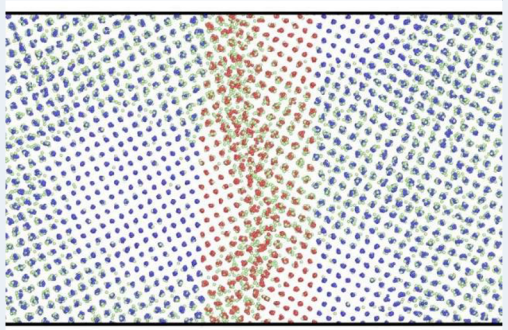
Collaboration with U.S.-Germany partnership on solid-state batteries: Cathode/electrolyte interface

Relevance: Decreasing interfacial impedance in 3D batteries

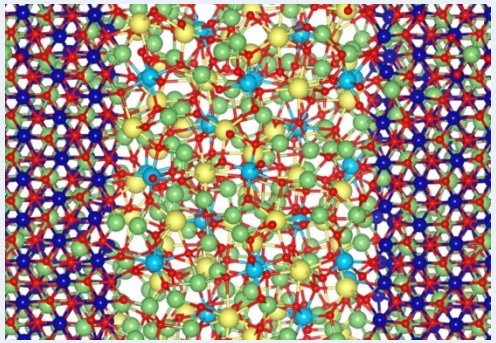
Poor ion transport at internal interfaces limits performance of ceramic solid-state batteries, but origins are not well understood and challenging to measure

Types of interfaces

Grain boundaries

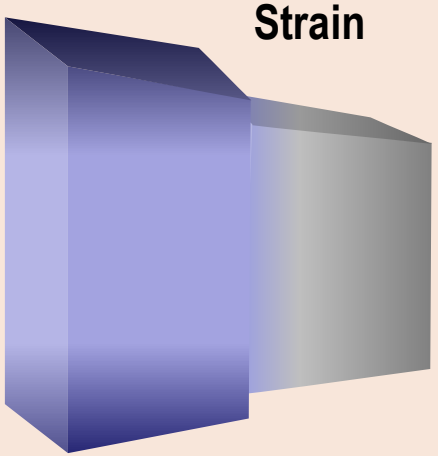


Cathode-electrolyte interfaces

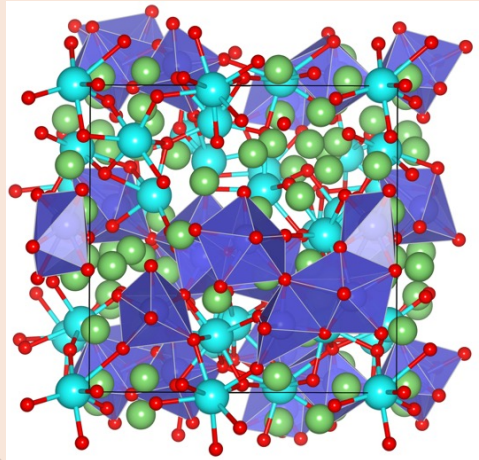


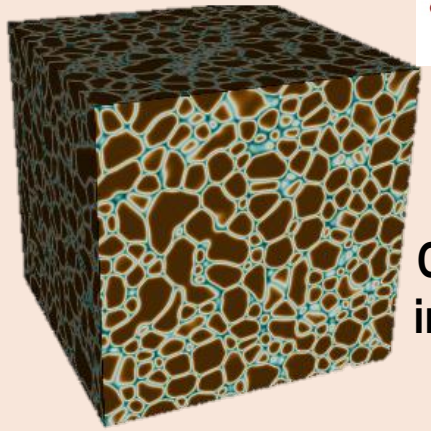
Potential physical factors

Strain



Structural disorder

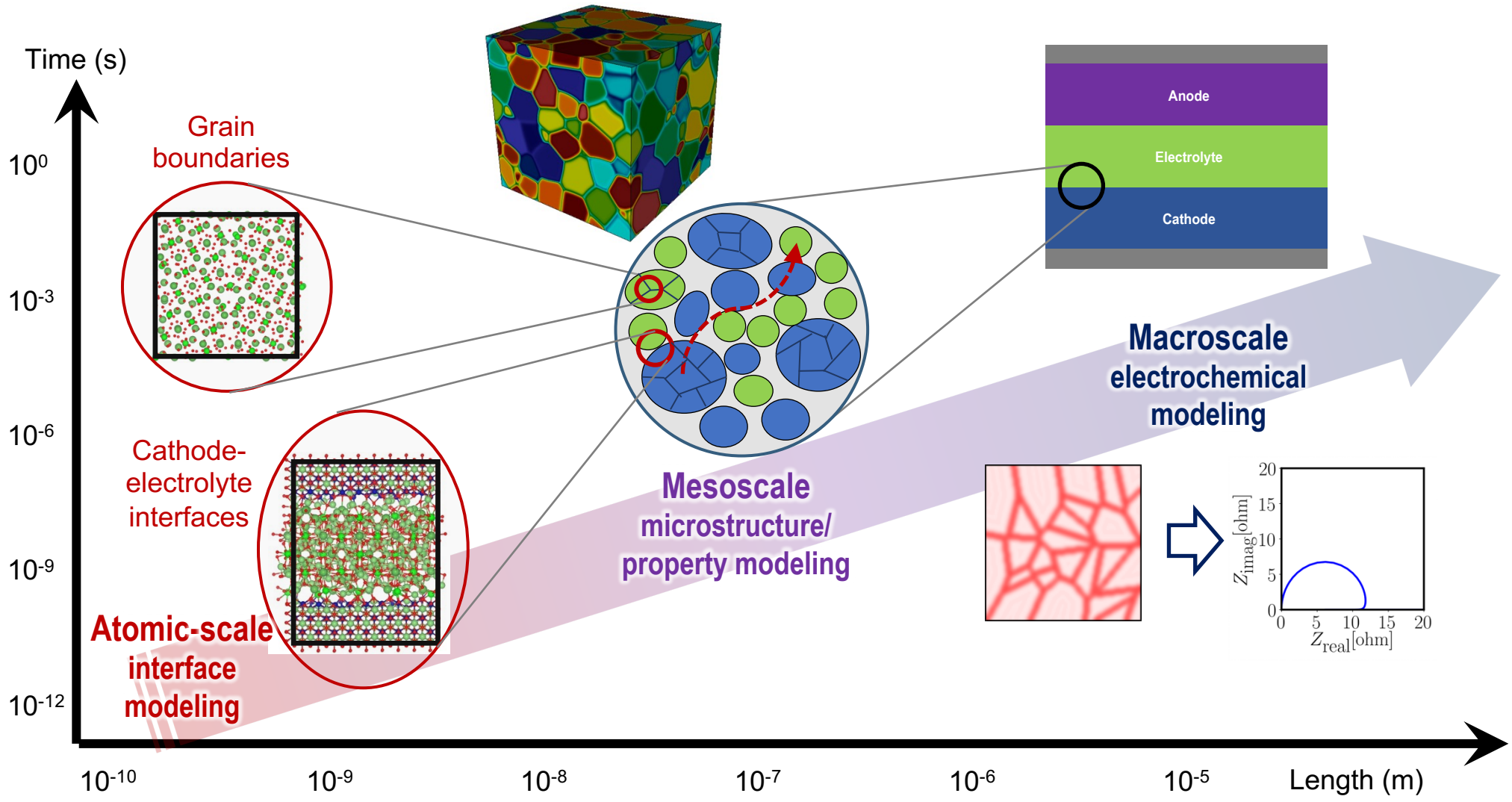




Compositional inhomogeneity

Focus on $Li_7La_3Zr_2O_{12}$ (LLZO) and Li_xCoO_2 (LCO) model materials

Approach: Multiscale modeling of ion transport across interfaces



Ab initio quantum simulations of chemistry	*Molecular dynamics of diffusion*	*Phase-field & effective-medium simulations of transport*	*Continuum simulations of impedance*

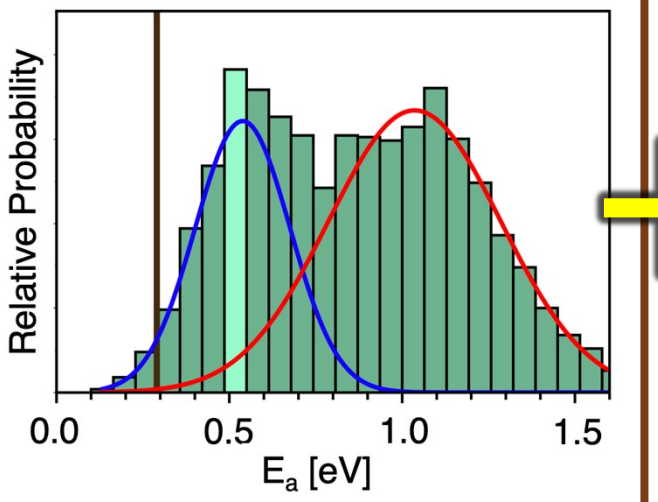
Progress towards project milestones

Month/Year	Description of Milestone	Status
January 2021	Demonstrate microstructural model of stress effect on ion transport	80 % complete
May 2021	Compute barriers for ion transport across LLZO/LCO interface	100% complete
July 2021	Integrate polycrystalline diffusion model with electrochemical impedance spectroscopy simulations	100 % complete
October 2021	Demonstrate full multiscale electrochemical impedance spectroscopy simulations of cathode/electrolyte interfaces	65 % complete

Accomplishment: Statistical approach for connecting atomistic-mesoscale predictions

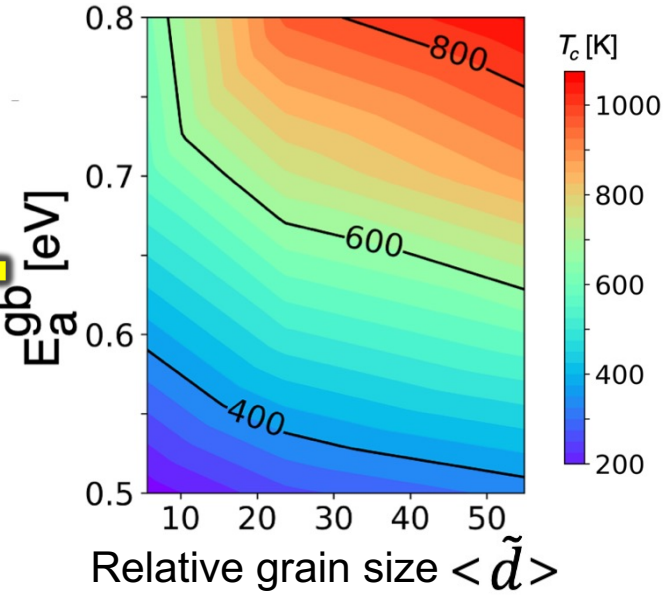
We applied a new statistical approach to connect atomistic and mesoscale models and predict likelihood of observing grain boundary effects in ion transport within an operation temperature range

Probability of GB diffusion across different models

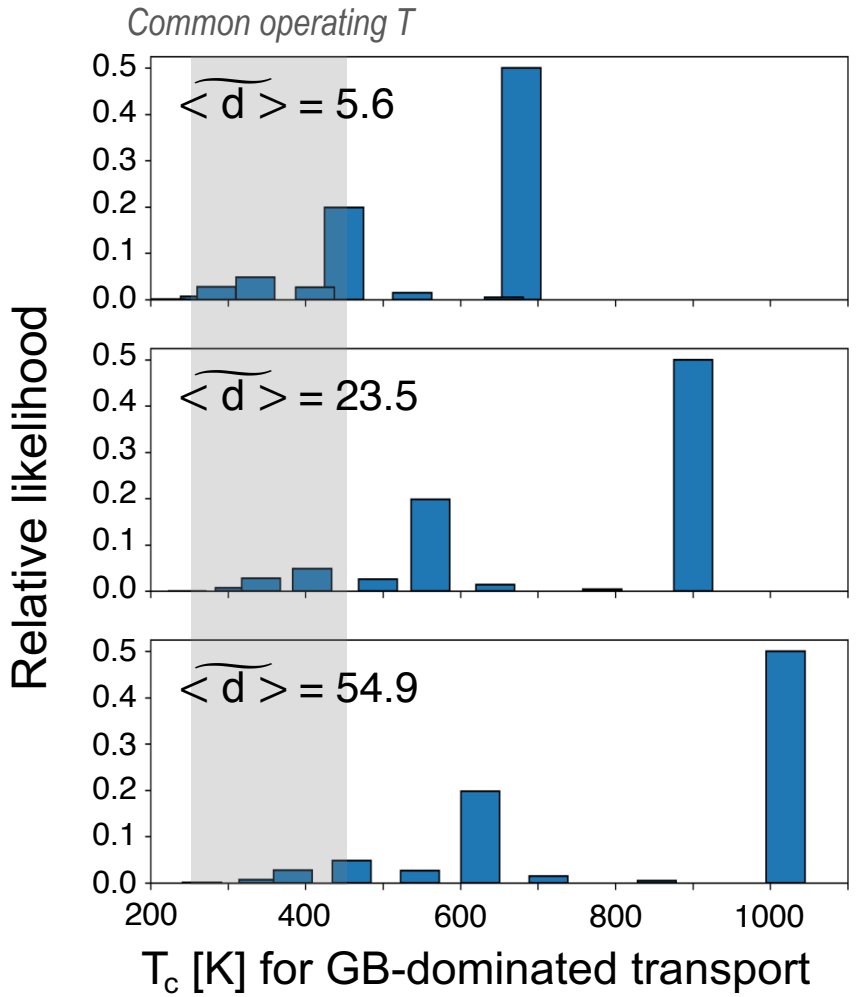


Atomistic simulations

"Microstructure-aware" temperature for GB-dominated transport



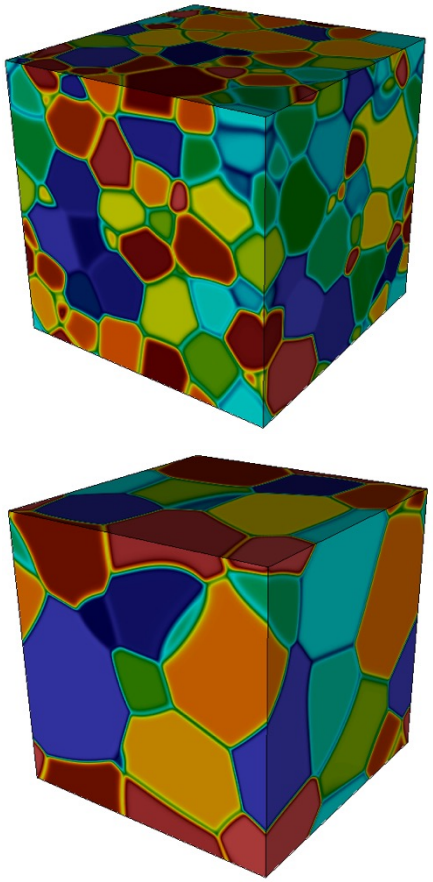
Mesoscopic modeling

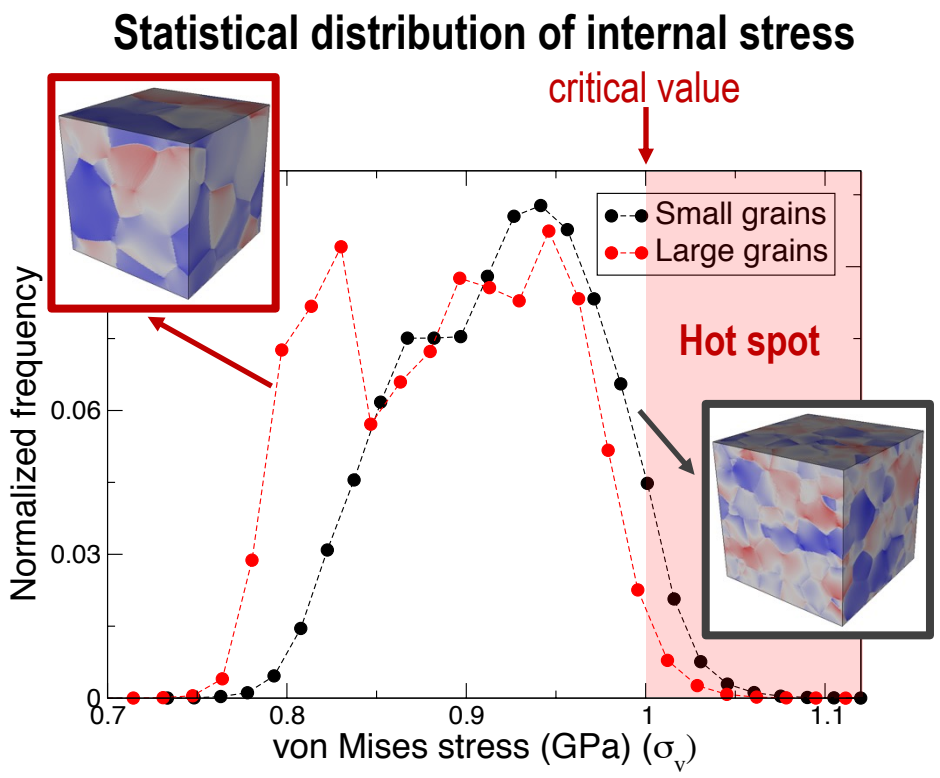


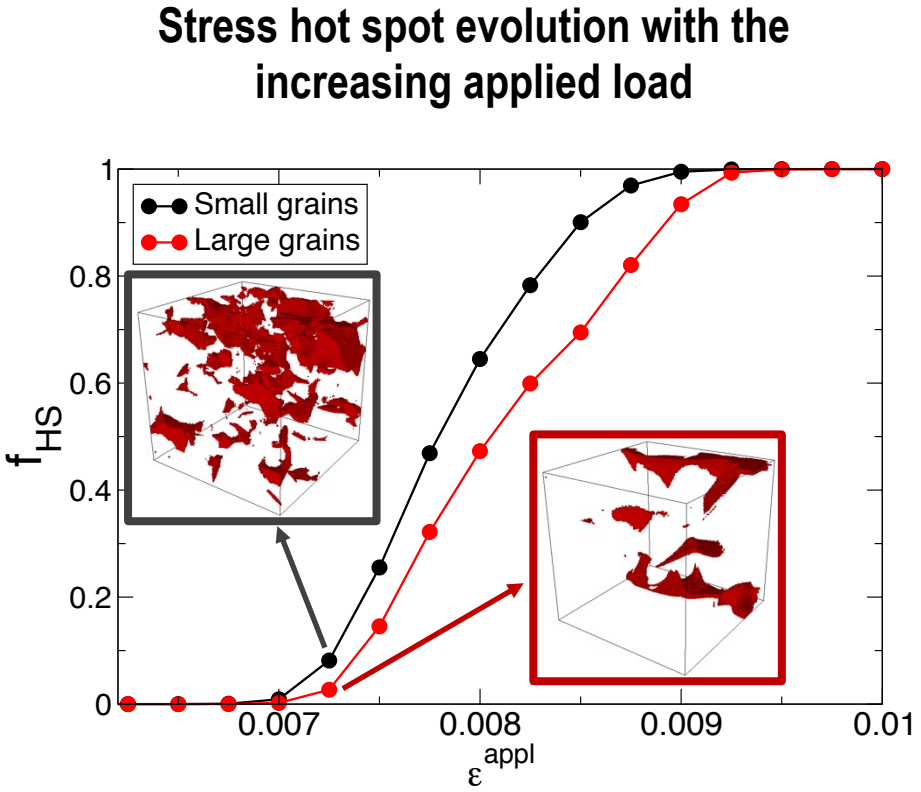
Analysis provides practical guidance for controlling grain size to leverage or avoid grain boundary conduction

Accomplishment: Microstructure-level mechanical responses in polycrystalline LLZO

We assessed stress concentrations in polycrystalline LLZO under applied loads by employing a micromechanical modeling approach



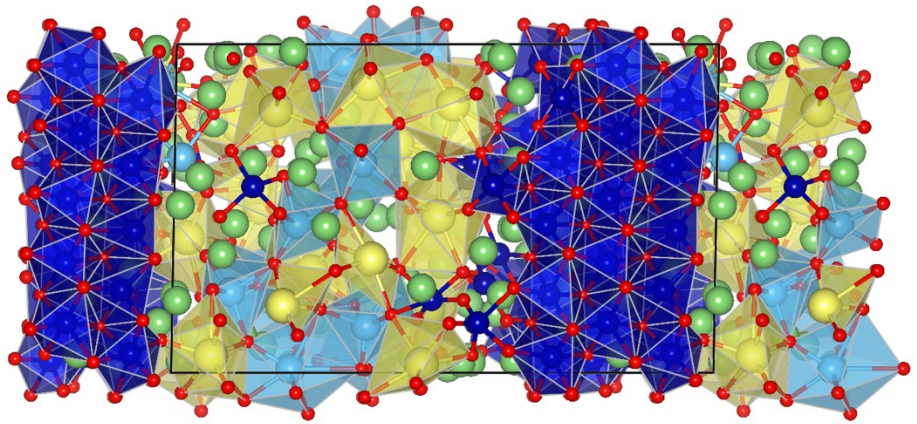


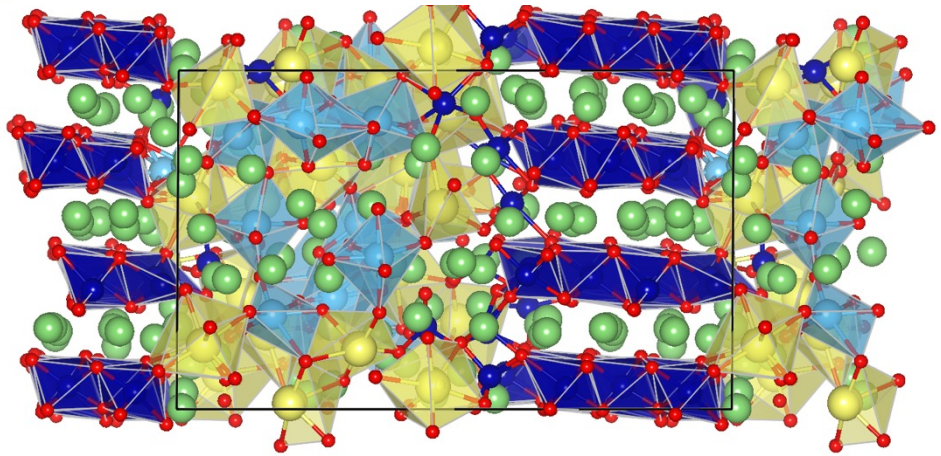


- **Stress distributions depend on grain size, changing expression of "hot spots" and leading to different fracture likelihoods with increased loading**
- **Completed implementation of the stress effect on ion transport and simulations are underway**

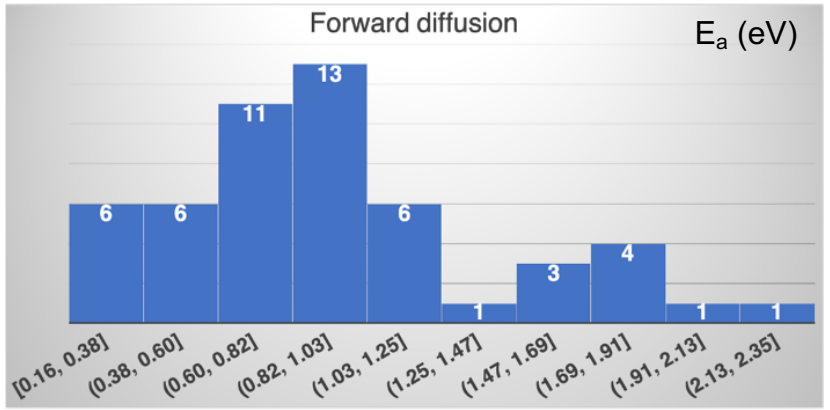
Accomplishment: Atomic-scale simulations of energy barriers for Li-ion diffusion across the LLZO/LCO interface

We performed high-temperature ab initio molecular dynamics simulations to probe the structural and chemical evolution of the LLZO/LCO interface and impacts on activation energies for Li diffusion

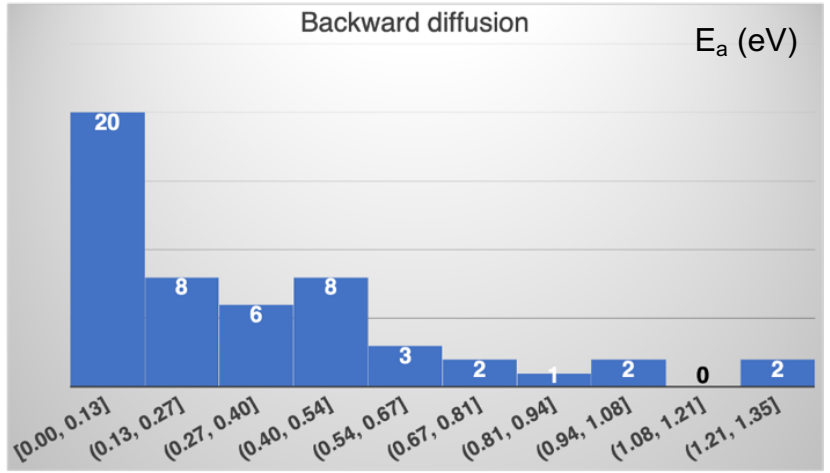




Li
O
Zr
La
Co



Li diffusion across the interface into a vacancy site

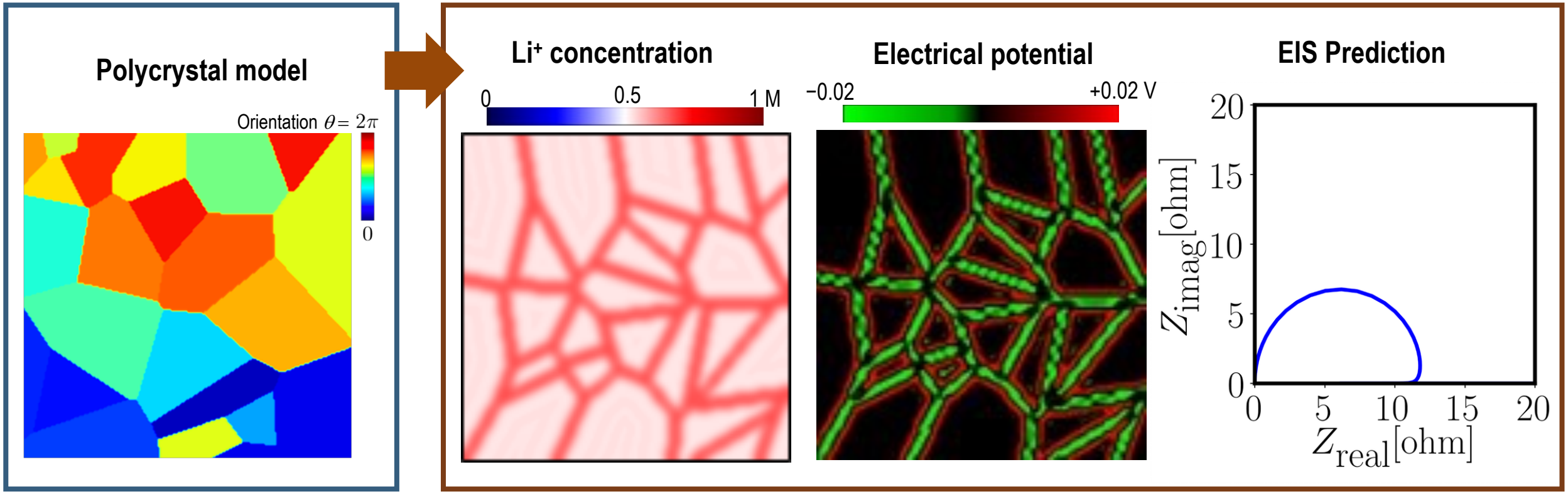


Li back-diffusion from the vacancy site to its original position

Simulations reveal cation interdiffusion and predict high activation energies and anisotropy for Li diffusion across the LLZO/LCO interface

Accomplishment: Direct simulation of electrochemical impedance spectroscopy (EIS) to connect microstructural properties to performance

We are directly simulating EIS based on our microstructural models for polycrystalline LLZO and LLZO/LCO interfaces (collaboration with DLR under U.S.-Germany partnership)



Simulations reveal grain boundary segregation and space charge effects on ion transport as first step towards connecting microstructural impacts to macroscopic experimental observables

Collaborations

Dr. Jianchao Ye, LLNL (Project # BAT421: "3D printing of solid-state batteries")

- *Analysis of 3D printed/sintered structures for informing microstructure models*
- *Interpreting effects of processing on microstructure and diffusivity*

Prof. Nicole Adelstein, San Francisco State University

- *Methods for simulating diffusion of Li^+ in disordered LLZO*
- *Benchmarking classical and machine learning interatomic potentials for LLZO*

U.S.-Germany collaboration on solid-state battery research

- *Timo Danner, Arnulf Latz, Katharina Becker-Steinberger, Jan Dippel, DLR: Modeling microstructure effects of LLZO ionic conductivity*
- *Ellen Ivers-Tiffee, KIT: Electrochemical impedance spectroscopy of polygranular LLZO*
- *Eric Wachsman, U. Maryland; Dina Fattakhova, Jülich; Jeff Sakamoto, U. Michigan: Synthesis and characterization of polygranular LLZO*

Publications & presentations

- T.W. Heo, A. Grieder, B. Wang, M. Wood, T. Hsu, S. Akhade, L.F. Wan, L.-Q. Chen, N. Adelstein, and B.C. Wood, "Microstructural impacts on the ionic conductivity of oxide-based solid electrolytes: A combined atomistic-mesoscale approach," submitted for publication (2021).
- K. Kim, D. Park, H.-G. Jung, K.Y. Chung, J.H. Shim, B.C. Wood, and S. Yu, "Materials design strategy for halide solid electrolytes for all-solid-state high-voltage Li-ion batteries," submitted for publication (2021).
- B.C. Wood, "Understanding kinetics of complex interfaces in solid-state batteries from multiscale simulations," Electrochemical Society PRiME Meeting, Virtual (October 2020) [invited].
- T.W. Heo, "Integrated modeling framework for investigating multiscale microstructural impacts on the ionic conductivity of garnet solid electrolytes", ECS PRiME Meeting, Virtual (October 2020).
- A. Jana, "Microstructural Effects on Electrochemical Impedance Spectroscopy," ACS Fall Meeting, Virtual (August 2020)
- L.F. Wan, "Probing structural and chemical evolutions of interfaces in all-solid-state batteries from first-principles simulations," Bay Area Battery Summit, Virtual (November 2020).
- L.F. Wan, "Elucidating interfacial instability in all-solid-state lithium batteries from first-principles simulations", MRS Spring Meeting, Virtual (April 2021).

Remaining challenges & barriers

Atomic-scale simulations are limited to short timescales

- *Interface chemistry is difficult to access during short ab initio molecular dynamics simulations, so only initial stages are captured*
- *Focus on understanding relationship between local chemistry/structure and transport rather than mimic realistic long-time evolution of interfacial chemistry*

Length scale integration may prove challenging

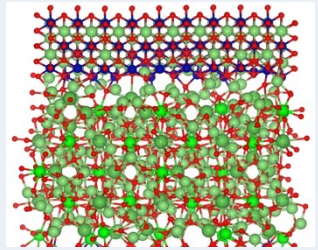
- *Electrochemical impedance spectroscopy models are a key focus in order to link with mesoscale effective permeability model; initial efforts are underway*

Need robust experimental validation scheme

- *In addition to LLNL partners, we are working with collaborators through the U.S.-Germany solid-state battery partnership to validate our models*

Proposed future work

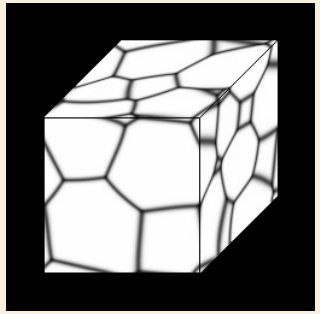
Atomistic



Cathode-electrolyte interface

- Complete analysis of variations in activation energies for Li-ion diffusion in relation to local environments across the LLZO/LCO interfaces and compare with collaborator experiments

Mesoscale



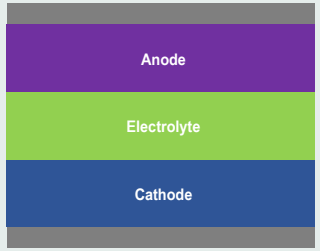
Mechanical stress effects on ion transport

- Complete simulations and quantitative analysis of the stress effect on Li ion transport through polycrystalline LLZO microstructures

Composite electrolyte microstructures (stretch)

- Apply mesoscale models to analyze composite polymer-ceramic microstructure effects on Li ion transport (collaboration with experimental project BAT421, J. Ye)

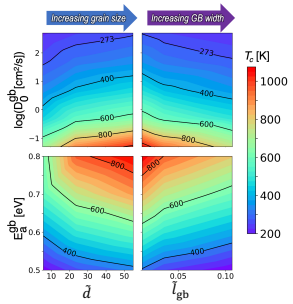
Macroscale



Impedance simulations

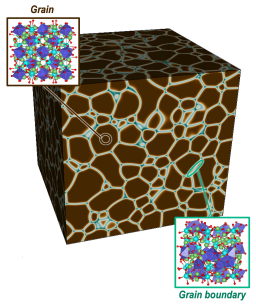
- Complete model development for electrochemical impedance spectroscopy (EIS) simulations
- Analyze effects of dopant segregation on EIS behavior to complete chemistry-to-performance mapping

Summary



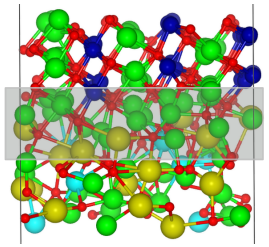
Simulated effects of realistic LLZO microstructures on transport

- Used new statistical approach to predict significance of grain boundary contributions to transport
- Similar approach was used to predict stress hot spots that can affect lithium diffusion rates



Developed impedance spectroscopy model to show effects of microstructure

- Model successfully captured lithium segregation effects and space-charge effects



Improved understanding of interfacial impedance at cathode-electrolyte interface

- *Ab initio* simulations show anisotropic limitations for ion transport across interface