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Integrated Multiscale Model for Design of Robust 3D Solid-state Lithium Batteries

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Disclaimer

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Abstract

In FY23, we successfully established the multiscale modeling framework for probing the effects of materials microstructure on cell performance of 3D solid-state batteries. The framework covers physicochemical processes co-evolving at the atomistic and microstructure scales. Our simulations revealed the mechanism of initial interfacial degradation, formation of secondary phases, and the structure-property relationship for ion transport and mechanical stability at the interface. In addition, we also established the microstructure-performance relationships by performing sensitivity tests of various microstructure features and extracting their impact on cell performance during charge-discharge cycles. We have successfully applied our multiscale, multiphysics modeling capability to common electrode and electrolyte materials that are of interests to VTO and the experimental teams within the US-Germany collaboration. The insights we obtained from these simulations provide valuable design principles to optimize materials properties for advanced 3D solid-state batteries.

Impact of Research

Ion transport and chemo-mechanical stability at complex interfaces strongly dictates the performance of energy storage devices. It is important to understand how ion transport can be enhanced in bulk materials as well as at their dynamically evolving interfaces and how the chemical and microstructural evolutions of the interface impact the mechanical robustness of the electrochemical cell. Leveraging the computational support from NREL HPC and sponsorship from the Vehicle Technologies Office through the Battery Materials Research Program, we developed a multiscale modeling framework that integrates atomistic and mesoscale modeling capability at LLNL and couples multiphysics features, such as electro-chemo-mechanical effects and nonequilibrium kinetic processes, to (1) model composite architectures of $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolyte (SE) and $LiCoO_2$ (LCO) cathode material, (2) to extract Li-ion diffusivity in Li_4PS_4I (LPSI) SE, and (3) to predict degradation products at the cathode-electrolyte interface (CEI).

At the atomic-scale, we employed a combination of computational methods, including density functional theory (DFT), ab-initio molecular dynamics (AIMD), and large-scale molecular dynamics (MD) driven by machine-learning (ML) interatomic potentials. For LPSI SE, we performed AIMD simulations to investigate the role of Li sublattice disordering for promoting fast Li-ion transport in bulk material. Our results elucidate that aliovalent substitution of P with Si leads to a flat energy landscape between all Li accessible sites for efficient Li-ion transport. This demonstrates that the introducing a disordered mobile carrier to the sublattice can be a promising strategy to develop new, fast Li-ion conductors. For the study of CEI formation at the interface between Gen2 electrolyte and high-voltage cathode, such as $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NMC811) and $LiNiO_2$ (LNO), we performed DFT evaluation of the bulk and surface properties of NMC811 and LNO and the propensities for molecular decompositions of electrolyte species on the NMC811 and LNO surfaces.

For the LLZO|LCO interfaces, we performed AIMD, DFT, and large-scale MD simulations to investigate the structure-property relationship including chemical degradation and ion transport at complex interfaces. Our AIMD simulations reveal extensive La and Co interdiffusion across the interfaces and pinpoint distinct local chemical environments of Co and La ions as they cross the interface. Follow-up DFT simulations predict stable $LaCoO_3$ phase formation and factors that dictate its nucleation kinetics, including (i) volume of the initial chemical percussor, (ii) local coordination environment of La and Co, and (iii) respective transition states through which nucleation proceeds. Our results reveal the atomic pathways for forming $LaCoO_3$ at the LLZO|LCO interface and suggest strategies to kinetically prevent the formation of such undesired phases. We also performed large-scale MD simulations to probe non-equilibrium phase evolution at complex interface directly from atomistic scale, which is enabled by our recently developed ML potentials for large-scale atomistic simulations with quantum-level accuracy. Our simulation results revealed a strong relation between initial interfacial chemistry and the propensities for degradation, for example Li deficient interface shows more severe disordering and interdiffusion that can accelerate the degradation of interface and lead to secondary phase formation. It is also observed that Co initially interdiffused from the LLZO|LCO interface can continue to penetrate through the LLZO grain and accumulate at the LLZO grain boundaries. These results elaborate the fundamental understanding of experimental observations and suggest guidelines for interface design that can minimize interfacial degradation and improve the cycling performance of SSBs.

At the larger scale, we used our in-house developed microstructure-aware mesoscale modeling tools to generate realistic cathode-electrolyte composite structure and predicted effective mechanical and transport properties. The input parameters of materials properties were directly calculated from atomic simulations to ensure key atomistic features and processes are incorporated into mesoscale models. We further developed phase-field grain growth simulator to generate representative 3D digital microstructures including interfaces and grain boundary features of each material. Our approach considers bi-continuous morphology of LLZO and LCO by combing physics-based spinodal microstructure simulator, image analysis toolkits, and the stochastic microstructure generation method. Notably, the two-phase configurations, phase fractions, and thicknesses of all interfaces can be independently and deterministically controlled in our modeling workflow, which allows to study their individual effect on the effective properties. This flexibility is also useful for reproducing experimental imaging of microstructures with high accuracy and fidelity.

With the generated microstructures, we used LLNL's *MesoMicro* code framework to simulate micromechanical responses and predict the effective elastic properties in dense polycrystalline LLZO. We found that the microstructure-aware effective elastic moduli deviate from those obtained by simple analytical models, indicating the importance of local microstructural features in integrated modeling of 3D electrochemical devices. Specifically, the mechanical hotspot in LLZO microstructure can be alleviated by disordered GBs with less-stiffness than grain interiors. Also, we simulated chemo-mechanical stress evolution during the lithiation/delithiation process in an isolated LCO particle and revealed different hotspot modes during cycling: the stress hotspots develop at the LCO GBs where delithiation occurs inside the particle at the earlier stage of delithiation, whereas the hotspots tend to concentrate at the interface between LCO and LLZO near the end of delithiated stage. Our model can also predict the overall transport characteristics in the microstructures with different diffusion characteristics between grain interiors and

boundaries in various phases. The predicted effective Li diffusivities implies that LLZO|LCO interfaces present stronger Li blocking effect than GBs, thus interfacial impedance would critically define the overall Li transport performance in the cathode composite. In summary, we developed a mesoscale modeling capability that enables the prediction of ion transport and chemo-mechanical behavior in complex SSB architectures. It will be extremely useful to diagnose the transport bottleneck and mechanical failure mechanisms under operating conditions and suggest design strategies of electrochemical devices with improved cycling performance.

Reporting and Recognition

#	Citation	Type of Publication
1	Kim, K., Dive, A., Grieder, A., Adelstein, N., Kang, S., Wood, B., and Wan, L. 2022. "Development of machine-learning force fields for simulating interfaces in solid-state batteries". *Materials Research Society (MRS) Fall Meeting*. Boston, MA.	Conference Presentation
2	Wood, B.C., 2022. "Paradigms of structural, chemical, and dynamical frustration in superionic conductors". *Royal Society Meeting on Understanding Fast-ion Conduction in Solid Electrolytes*. Lancaster, UK.	Conference Presentation
3	Adelstein, N., 2022. "Simulating Li-diffusion in amorphous and crystalline LLZO". *Royal Society Meeting on Understanding Fast-ion Conduction in Solid Electrolytes*. Lancaster, UK.	Conference Presentation
4	Oskar, G., Kim, K., Wan, L., and Adelstein, N. 2023. "Ionic Transport Across Disordered Interfaces with Atomic-Scale Simulations". *Materials Research Society (MRS) Spring Meeting*. San Francisco, CA.	Conference Presentation
5	Wang, B., Kim, K., Wan, L., Wood, M., Heo, T.W., and Wood, B. 2023. "Assessing Mesoscopic Chemo-mechanical Coupling Effects on Effective Transport Properties of Solid Electrolytes based on a Fourier Spectral Method". *Materials Research Society (MRS) Spring Meeting*. San Francisco, CA.	Conference Presentation
6	Jeong, W., Dive, A., Kim, K., Wood, B., and Wan, L. 2023. "Predicting Secondary Phase Formation at the Solid-Electrolyte/Cathode Interface Using Machine-Learning Interatomic Potential". *Materials Research Society (MRS) Spring Meeting*. San Francisco, CA.	Conference Presentation
7	Wan, L., Kim, K., Dive, A.M., Wang, B., Heo, T.W., and Wood, B.C. 2023. "Multiscale Modeling of Ion Transport Phenomena at Interfaces in All Solid-State Batteries" *Materials Research Society (MRS) Spring Meeting*. San Francisco, CA.	Conference Presentation
8	Kim, K., Dive, A., Kang, S-Y., Adelstein, N., Wood, B.C., and Wan, L. 2023. "Probing Interfacial Degradation at $Li_7La_3Zr_2O_{12}$|$LiCoO_2$ Interfaces in All Solid-state Batteries Using Machine Learning Interatomic Potential". *Materials Research Society (MRS) Spring Meeting*. San Francisco, CA.	Conference Presentation
9	Wan, L.F., Kim, K., Dive, A.M., Wang, B., Feng, L., Heo, T.W., Wood, B.C. 2023. "Multiscale modeling of ion transport phenomena at interfaces in all solid-state	Conference Presentation

	batteries", *243rd Electrochemical Society (ECS) Meeting*. Boston, MA.	
10	Wan, L., Kim. K., Jeong, W., Wang, Bo., Dive, A. M., Feng, L., Heo, T. W. and Wood, B. C. 2023. "Addressing ion transport and degradation at interfaces in all solid-state batteries". *American Chemical Society (ACS) Fall Meeting*. San Francisco, CA.	Conference Presentation
11	Ren, Y., Danner, T., Moy, A., Finsterbusch, M., Hamann, T., Dippell, J., Fuchs, T., Müller, M., Hoft, R., Weber, A., Curtiss, L.A., Zapol, P., Klenk, M., Ngo, A.T., Barai, P., Wood, B.C., Shi, R., Wan, L.F., Heo, T.W., Engels, M., Nanda, J., Richter, F.H., Latz, A., Srinivasan, V., Janek, J., Sakamoto, J., Wachsman, E.D., and Fattakhova-Rohlfing, D. 2023. "Oxide-based solid-state batteries: A perspective on composite cathode architecture." *Advanced Energy Materials* 13: 2201939.	Peer-Reviewed Journal Article
12	Ramos, E., Kim, N., Assoud, A., Kochetkov, I., Wan, L., and Nazar, L. 2023. "Triggering Fast Lithium Ion Conduction in Li_4PS_4I" *ACS Materials Letter* 5 (1): 144–154.	Peer-reviewed Journal Article
13	Scheld, W.S., Kim, K., Schwab, C., Moy, A.C., Jiang, S-K., Mann, M., Dellen, C., Sohn, Y.J., Lobe, S., Ihrig, M., Danner, M.G., Chang, C-Y., Uhlenbruck, S., Wachsman, E., Hwang, B.J., Sakamoto, J., Wan, L.F., Wood, B.C., Finsterbusch, M., and Fattakhova-Rohlfing, D. 2023. "The riddle of dark LLZO: Cobalt diffusion in garnet separators of solid-state lithium batteries." *Advanced Functional Materials*, 2302939.	Peer-reviewed Journal Article
14	Dive, A., Kim, K., Kang, S., Wan, L.F., and Wood, B.C. 2023. "First-principles evaluation of dopant impact on structural deformability and processability of $Li_7La_3Zr_2O_{12}$." *Physical Chemistry Chemical Physics*, Advanced Article.	Peer-reviewed Journal Article

Integration with other facilities

No integration with other facilities was made in FY23.