Machine-Learning Interatomic Potentials for the Investigation of Solid Electrolyte Interphase Formation

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The solid electrolyte interphase (SEI) is a critical component of rechargeable batteries. This thin passivation layer, formed at the interface between an electrolyte and an anode, directly impacts battery Coulombic efficiency, safety, and cycle life. In particular, a central challenge in the development of next-generation, high-energy-density batteries is the poor interfacial compatibility between solid electrolytes and Li-metal anodes.[1] Uncontrolled interfacial reactions can lead to continuous electrolyte degradation, impedance growth, and eventual battery failure. Therefore, the rational design and optimization of the SEI are essential for advancing battery technologies.[2] Achieving this goal requires a detailed understanding of the mechanisms of SEI formation and evolution during battery operation.

While experimental techniques (e.g., XPS, NMR, and TEM) provide valuable insight into SEI composition, thickness, morphology, and local structure, its nanoscale size, heterogeneity, and air sensitivity hinder direct access to the mechanisms of formation and the global atomic structure.[3]

Atomistic simulations, particularly *ab initio* molecular dynamics (AIMD), offer a powerful complementary approach that enables in silico observation of chemical reactions.[4] Despite its accuracy, AIMD is a computationally demanding method that is constrained to system sizes of up to thousands of atoms and timescales on the order of hundreds of picoseconds. As a result, AIMD can capture only the early stages of interfacial reactions, rather than long-term SEI evolution. Moreover, even in rare cases where final reaction products form within hundreds of picoseconds, the limited size of the periodic box (tens of angstroms) leads to unrealistic SEI microstructures.

These limitations may be overcome by employing machine-learning interatomic potentials (MLIPs), which combine near *ab initio* accuracy with computational efficiencies approaching those of classical force fields.[5] This is achieved by approximating the *ab initio* derived potential energy surface with flexible, high-dimensional models such as neural networks, Gaussian processes, and kernel methods. As a result, MLIPs can capture complex many-body interactions, bond breaking and formation, charge transfer, and anharmonic effects that are inaccessible to traditional force fields with fixed functional forms.

Nevertheless, the successful application of MLIPs to a complex, heterogeneous, multicomponent system such as the SEI presents its own set of challenges. In particular, SEI formation is a nonequilibrium process involving rare events, complex reaction dynamics, and significant structural evolution that occur over nanosecond timescales. Thus, the training datasets must sample a wide range of atomic configurations, including initial reagents, metastable intermediates, transition states, and final reaction products.

Generating such datasets at the *ab initio* level is nontrivial and requires robust training strategies, including active learning to iteratively refine the potential as new regions of configurational space are explored. Without such approaches, MLIPs may suffer from extrapolation errors that compromise their predictive reliability.

Utilizing MLIPs, we show how AIMD simulations of SEI formation can be upscaled to tens of thousands of atoms per simulation box and extended to nanosecond timescales without significant loss of accuracy. The methodology is illustrated for the interface between a lithium-metal anode and the halide Li_3InCl_6 solid electrolyte.[6] The system is modeled using a neural network potential (NNP) implemented within the DeepMD framework.[7]

The NNP was trained on an extensive dataset of density functional theory (DFT) derived energies, forces, and stress tensors from more than 100,000 AIMD trajectory frames generated in NVT simulations of the Li/Li_3InCl_6 interface model at 300 K. Additionally, we include in the training set data from 1 ps (1000 frames) NVT AIMD simulations, at 300 and 600 K, of bulk structures corresponding to the initial reactants (metallic Li and Li_3InCl_6) and thermodynamically expected products (metallic In and LiCl).

The resulting potential is further refined using an active learning procedure implemented in the GeNNIP4MD framework.[8] The validation is performed against an independent set of energies, forces, and stress tensors from 20,000 frames AIMD trajectory of the Li/Li_3InCl_6 model.

All DFT calculations are carried out using the Vienna Ab initio Simulation Package (VASP)[9–11], while the NNP-based molecular dynamics (MD) simulations are performed using the LAMMPS program.[12]

The interface models are constructed from bulk Li and Li_3InCl_6 structures obtained from the Materials Project database[13], using a lattice-matching algorithm[14] implemented in pymatgen.

The validation shows that the NNP accurately reproduces the results of DFT calculations. The root-mean-square errors (RMSEs) of energies, forces, and stress tensors are 1.6 meV/atom, 46.2 meV/Å, and 33.6 MPa, respectively. These errors are comparable to the numerical accuracy of typical DFT based MD calculations. In addition, radial distribution functions (RDFs) obtained from NNP MD closely match those computed from AIMD (Figure 1). Importantly, NNP MD fully reproduces the reaction mechanism observed during AIMD simulations.

According to the results of AIMD simulations, the interfacial reaction proceeds via reduction of In cations by Li metal. As the reaction front propagates into the bulk electrolyte, the reduced In atoms aggregate to form metallic clusters, which are encapsulated within an amorphous LiCl matrix. The same SEI structure is observed at the 100 ps frame of the NNP MD simulation (Figure 2).

The upscaled 10 ns NNP MD simulation of the Li/Li_3InCl_6 interface model, containing a 12,000 atoms metal Li slab and 2000 formula units of the electrolyte slab, reveals that the reaction leads to the formation of an unstable interface. The chemical reaction between the Li anode and the electrolyte results in the formation of an electronically conducting SEI due to the presence of a percolating metallic In phase distributed between LiCl grains. As a result, the SEI fails to effectively passivate the interface, leading to ongoing electrolyte decomposition and progressive degradation of the interfacial region. Thus, stabilizing the Li/Li_3InCl_6 interface requires the introduction of an appropriate coating to prevent electrolyte degradation.

Beyond interfacial reaction mechanisms, MLIPs can also be applied for the evaluation of ion transport properties of SEI. Access to nanosecond timescales and a large simulation box enables statistically meaningful calculations of Li-ion diffusivity, migration pathways, and activation barriers within chemically heterogeneous SEI structures, which are difficult to probe experimentally. In addition, MLIP can be used for the evaluation of mechanical properties such as elastic modulus and stress arising from volume changes and phase transformations during SEI growth. Thus, MLIPs open a new horizon for comprehensive investigation of interfacial processes, bridging atomistic and mesoscale descriptions to enable the rational design of stable SEIs for advanced battery technology.

References

[1] Bouguern M. D., M R A. K., Zaghib K. J. Power Sources, (2024), 235457.

[2] Li B., Chao Y., Li M., Xiao Y., Li R., Yang K., Cui X., Xu G., Li L., Yang C., Yu Y., Wilkinson D. P., Zhang J. Electrochemical Energy Reviews, (2023) 7.

[3] Wu J., Ihsan-Ul-Haq M., Chen Y., Kim J. K. Nano Energy, (2021) 106489.

[4] Golov A., Carrasco J. ACS Applied Materials & Interfaces, (2021), 35.

[5] Wang G., Wang C., Zhang X., Li Z., Zhou J., Sun Z. iScience, 5, (2024), 109673.

[6] Li X., Liang J., Luo J., Norouzi Banis M., Wang C., Li W., Deng S., Yu C., Zhao F., Hu Y., Sham T. K., Zhang L., Zhao S., Lu S., Huang H., Li R., Adair K. R., Sun X. Energy and Environmental Science, 9, (2019), 2665.

[7] Zeng J., *et all*. Journal of Chemical Theory and Computation, 9, (2025), 4375.

[8] Matsumura N., Yoshimoto Y., Yamazaki T., Amano T., Noda T., Ebata N., Kasano T., Sakai Y. Journal of Chemical Theory and Computation, 8, (2025), 3832.

[9] Kresse G., Hafner J. Physical Review B, (1993), 558.

[10] Kresse G., Furthmüller J. Computational Materials Science, 6, (1996), 15.

[11] Kresse G., Furthmüller J. Physical Review B, (1996), 11169.

[12] Thompson A. P., *et all.* Computer Physics Communications, (2022), 108171.

[13] Jain A., Ong S. P., Hautier G., Chen W., Richards W. D., Dacek S., Cholia, S. Gunter D., Skinner D., Ceder G., Persson K. A. APL Materials, 1, (2013), 1.

[14] Zur A., McGill T. C. Journal of Applied Physics, 2, (1984), 378.

[15] Ong S. P., Richards W. D., Jain A., Hautier G., Kocher M., Cholia S., Gunter D., Chevrier V. L., Persson K. A., Ceder G. Computational Materials Science, (2013), 314.

Figures

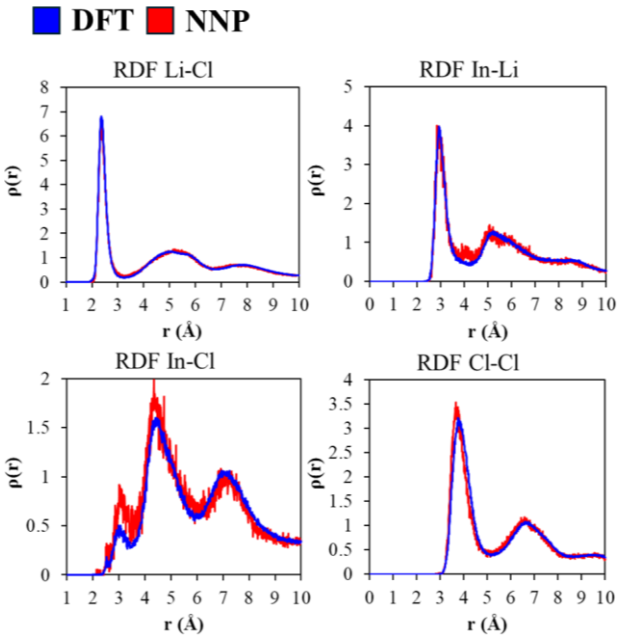

Figure 1. Comparison of RDFs calculated for the 100 ps NVT NNP MD and AIMD simulations of the Li/Li_3InCl_6 interface at 300 K.

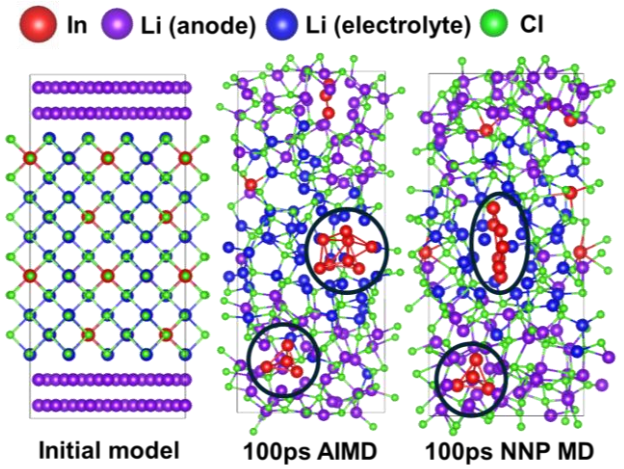

Figure 2. Comparison of 100 ps AIMD and NNP MD frames of NVT simulation for Li/Li_3InCl_6 interface at 300 K. Metallic In clusters are highlighted by circles.