Exploring Surface Stability of Li-argyrodite Solid Electrolytes Using First-principles Calculations Combined with Machine-learning Interatomic Potentials

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Li-argyrodite solid electrolytes, such as Li_6PS_5Cl (LPSC), are promising candidates for all-solid-state lithium batteries (ASSLBs) due to their high ionic conductivity, low cost, and favorable mechanical properties. However, their commercial application is hindered by poor air stability and lithium incompatibility, leading to surface degradation and byproduct formation, such as hydrogen sulfide (H_2S). To address this challenge, we employ density functional theory (DFT) to investigate the atomic-scale hydrolysis mechanism through Gibbs free energy calculations and electron transfer analysis. We evaluate the electron energy levels of the valence band maximum (VBM) and conduction band minimum (CBM) for surface structures, as well as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for adsorbates like water and oxygen. Our results reveal that the hydrolysis of LPSC involves both water and oxygen molecules simultaneously, with the surface donating electrons to oxygen molecules. To further explore adsorption behavior, we construct all possible adsorption configurations by considering different adsorbate orientations and adsorption sites. Given the high computational cost of traditional DFT methods, we integrate the Crystal Hamiltonian Graph Neural Network (CHGNet), a machine-learning potential pre-trained on 1.6 million datasets from the Materials Project. By fine-tuning CHGNet with additional DFT data, we efficiently simulate adsorption configurations, significantly reducing computational costs while maintaining consistency with experimental observations. Finally, we employ ab initio molecular dynamics (AIMD) combined with CHGNet interatomic potentials to comprehensively elucidate the hydrolysis reaction mechanism. This approach provides crucial insights into enhancing the air stability of argyrodite solid electrolytes, further advancing their potential for next-generation energy storage applications.