

Ab-Initio Study on Buffer Layer, Li Depletion, Ion Mixing at Interfaces between LiCoO₂ and Sulfide Electrolyte in All-Solid-State Battery

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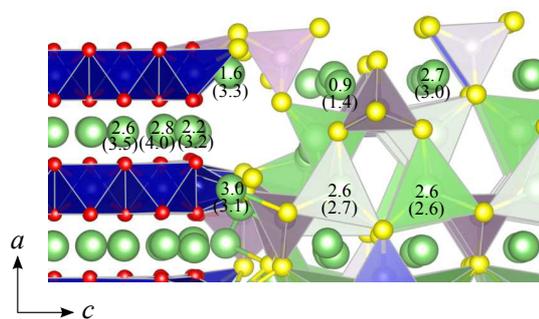
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All-solid-state Lithium-ion batteries (ASS-LIBs) have been regarded as promising next-generation batteries. Recently, sulfide-based electrolytes have attracted considerable attention because of the high Li-ion conductivities comparable to those of the ordinary organic-liquid electrolytes. However, large interfacial resistance is usually observed if we combine sulfide electrolytes and oxide cathodes [1]. On the other hand, it has been also observed that the interfacial resistance is reduced dramatically by interposing an insulating buffer layer to the interfaces [1]. Compared to these observations, little is known about the atomistic aspects of the solid-solid interfaces in the ASS-LIBs. Therefore, we investigated those properties such as potential origins of the interfacial resistance (e.g. space-charge layer model, reaction layer model) as well as the buffer layer effect by using first-principles DFT+U calculations [2,3].

As a representative model system, LiCoO₂ (LCO), β -Li₃PS₄ (LPS), and LiNbO₃ (LNO) were selected for cathode, sulfide electrolyte, and buffer layer, respectively. We carried out first-principles calculations of the several possible interface configurations and obtained the stable structures and the electronic states. Besides, we calculated the site-dependent Li chemical potentials with respect to Li metal. The results indicate that the Li depletion can proceed at the beginning of the charge process, which may correspond to the space-charge layer scenario, and the interposition of buffer layer can suppress the depletion. [2] Moreover, we evaluated the interfacial ion diffusion by examining possible exchange of cations between the cathode and the electrolyte. The results show that the Co and P mixing is preferred at the LCO/LPS interface, and the LNO interposition can suppress these mixings. Interestingly, the Li-depletion tendency still exists under these circumstances [3]. Thus, the Li-depletion is likely to be a major factor of the interfacial resistance. These aspects would be useful for future improvement of the interfacial resistance of ASS-LIBs.

Fig. Chemical potentials of Li at the sites around the LCO/LPS interface with (without) the Co-P exchange.



References:

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