Li migration and charge transfer through $Li/Li_7La_3Zr_2O_{12}$ interfaces under constant-charge conditions

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Lithium-ion batteries with solid-state electrolyte have a number of superior properties over batteries with liquid electrolyte. Among the advantages of solid-state electrolytes are a wide electrochemical window and better thermal stability. Solid-state electrolytes are potentially compatible with metallic lithium, allowing to increase energy density significantly [1]. If in batteries with a liquid electrolyte, the contact between the electrodes and the electrolyte is excellent due to the filling of all voids with liquid electrolyte, in solid-state batteries, it is difficult to ensure a tight contact between the two solid phases.

At the moment, there are methods to manufacture Li/LLZO interfaces with low resistance, which show small capacity retention over 10–100 cycles. However, all these methods involve modification of LLZO and introduction of an additional phase at the phase boundary [2]. Meanwhile, it is not completely clear why the capacities of batteries with unmodified LLZO electrolyte decline fast, and how the interfaces evolve with cycling. Modeling of interfaces between lithium metal and LLZO with the consecutive study of structure's transformation during cycling can fill this gap.

Electrochemical experiments together with diffraction and microscopy studies provide data on the electrical conductivity of interfaces and, perhaps, regions where conductivity deteriorates. In addition, using the maximum entropy method [3], it is possible to find migration pathways of Li-ions. Yet, such experiments require extensive time and financial expenses, without providing information on the magnitude of migration barriers. In order to investigate and qualitatively characterize the Li-ion migration at the atomic scale with reasonable time and financial expenses, computational modeling is required. At the same time, we study this process on idealized structures with their intrinsic properties, avoiding imperfections that are always present in a real experiment.

In this study, we investigate the migration of Li-ions at the interfaces between $Li_7La_3Zr_2O_{12}$ (LLZO) and lithium metal using density functional theory calculations. We have considered all terminations for the tetragonal phase of LLZO with space group 230. The results of surface energies are consistent with other computational works [4]. Next, we used surfaces with the lowest surface energies to construct interfaces with lithium metal (Li/LLZO). Having selected interfaces with the lowest interface energy and adhesion energy, we investigated migration pathways and barriers in these structures under the constant-charge conditions, as shown in Figure 1. In addition, we studied the influence of uncompensated electric charge at the surface on the shape of the transfer energy profile.

Our results show that charge transfer barriers are moderately larger compared with migration barriers in bulk LLZO. The difference is of the order of 0.2 eV, showing the origin of interfacial resistance observed in the experimental studies [1]. Also, we demonstrate that Li vacancy formation is favored at the interface region, pointing out a possible reason for voids' formation and interface structure degradation.

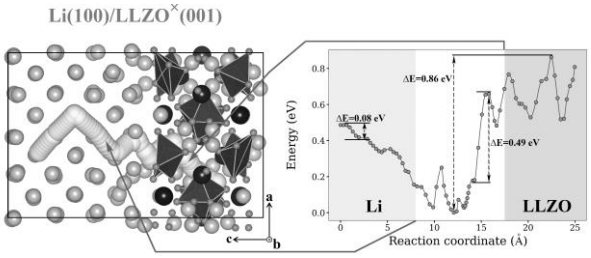

Figure 1. Pathway and energetics of Li-ion migration at Li/LLZO interface under the constant-charge conditions.

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