Theoretical Study of Solid/Solid Interfaces in All-solid-state Batteries

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All-solid-state batteries (ASSBs) are promising candidates to replace conventional Li-ion batteries with liquid electrolytes due to their high safety and design flexibility. In spite of several experimental investigations on interfaces between $Li_7La_3Zr_2O_{12}$ and $LiCoO_2$, which are among the most promising electrolyte and electrode materials, respectively, no theoretical simulation has been performed so far on these interfaces. In the proposed project, we aim to find the reason of reported low conductivity at these electrode/electrolyte interfaces using quantum mechanics calculations. Moreover, we aim to find a way to suppress this problem. In the first year of the project, we investigated for the first time electronic and atomic structure of complex $Li_7La_3Zr_2O_{12}/LiCoO_2$ interfaces. Based on our initial model, we found that cation interchange to be energetically favorable which was in agreement with an experimental study in 2016. For this reason, we proposed that the low conductivity of $Li_7La_3Zr_2O_{12}/LiCoO_2$ interface is due to the substitution of Zr and La in electrolyte by Co cation from the cathode side. To prove this statement, in the second year of the project, we proposed to compute ionic conductivity of Co-doped LLZO. However, recent experimental investigations in 2017 have found that ion interchange is unlikely and the reason of low ionic conductivity is due to the formation of a passive new phase at the interface due to the chemical reaction between $Li_7La_3Zr_2O_{12}$ and $LiCoO_2$ during cosintering. We therefore had to first find why our initial model and that experimental study in 2016 found ion interchange is energetically favorable. By considering a variety of possible models for the interface we found that the ion interchange can occur only when there is a large stress along the normal interface contact plane. This condition arises only under special experimental condition. Moreover, in 2017, we worked together with experimental groups to improve the stability of cathode materials by doping with transition metals which can be used in the future together with $Li_7La_3Zr_2O_{12}$ in all-solid-state batteries. In this proposed project, we aim to extend our work to Li ion transport in the new phase which is formed at the $Li_7La_3Zr_2O_{12}/LiCoO_2$ interface to determine whether this new phase is the reason of low conductivity in the interface. Moreover, we aim to continue our work on enhancement of stability of cathode materials through doping by different transition metals.