

Defect Chemistry and Li Transport in Antiperovskite Materials

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Abstract:

Solid-state electrolytes with fast lithium conduction are the core of the all-solid-state Li battery technology. By substituting the organic electrolyte with a piece of non-flammable ceramic material, we can achieve a better safety, a higher specific capacity and a higher energy density. To date, the major bottleneck for this technology is the slow bulk diffusion of solid-state electrolyte and the interfacial incompatibility between the electrolyte and electrodes. To resolve these issues, several families of fast ionic conductors have been developed. The understanding of Li diffusion in these materials is essential to the development of novel family fast ionic conductors. In this sense, atomistic modeling provides us with a unique tool to obtain comprehensive information on the atom motion, which is difficult to access with experimental techniques. In this work, we use density functional theory (DFT) calculations as well as large scale classical molecular dynamics (MD) simulations to simulate the Li diffusion in a novel family of superionic conductor, lithium-rich anti-perovskites and provide an understanding of the Li diffusion behavior.

Lithium-rich anti-perovskites (LiRAPs) are a promising family of solid electrolytes, which exhibit ionic conductivities above $10^{-3} \text{ S cm}^{-1}$ at room temperature, among the highest reported values to date. We investigate the defect chemistry and the associated lithium transport in Li_3OCl , a prototypical LiRAP, using DFT calculations and classical MD simulations. We studied three types of charge neutral defect pairs, namely the LiCl Schottky pair, the Li_2O Schottky pair, and the Li interstitial with a substitutional defect of O on the Cl site. Among them the LiCl Schottky pair has the lowest binding energy and is the most energetically favorable for diffusion as computed by DFT. This is confirmed by classical MD simulations, where the computed Li ion diffusion coefficients for LiCl Schottky systems are significantly higher than those for the other two defects considered and the activation energy in LiCl deficient Li_3OCl is comparable to experimental values. The high conductivities and low activation energies of LiCl Schottky systems are explained by the low energy pathways of Li between the Cl vacancies. We propose that Li vacancy hopping is the main diffusion mechanism in highly conductive Li_3OCl .

References:

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