

Princeton University 29th Annual Workshop on Recent
Developments in Electronic Structure MethodsAb-initio study of Li-ion electrolyte $\text{Li}_2(\text{OH})\text{Cl}$

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The material $\text{Li}_2(\text{OH})\text{Cl}$ is experimentally found to exist in two phases, a poor Li-ion conducting orthorhombic phase ($T \lesssim 312\text{K}$) and a fast Li-ion conducting disordered cubic phase ($T \gtrsim 312\text{K}$). Recently experiments report the high temperature phase can be cycled in a symmetric cell with lithium electrodes with the apparent creation of a stabilizing solid electrolyte interphase layer[1]. $\text{Li}_2(\text{OH})\text{Cl}$ is related to a variety of other materials that have been studied for their Li-ion electrolyte properties; $\text{Li}_{2+x}(\text{OH}_{1-x})\text{Cl}$, $\text{Li}_2(\text{OH})\text{Br}$, and $\text{Li}_2(\text{OH}_{1-x})\text{F}_x\text{Cl}$ [2][3].

A structural analysis using ab-initio calculations is performed to search for the structure of the low temperature phase, with experimental X-ray diffraction and lattice constants from the literature for comparison[1][2]. The calculations find possible phases having tetragonal and orthorhombic symmetries. Within the quasi harmonic approximation, the Helmholtz free energy and temperature dependent lattice constants are calculated for the orthorhombic and tetragonal structures.

Additionally, using ab-initio molecular dynamics, the Li-ion tracer diffusion, total ionic charge density diffusion, and several order parameters are analyzed in the temperature range of 350-650K, for the disordered cubic phase.

[1] Hood Z. , et al. J. Am. Chem. Soc 2016, 138 1768-1771

[2] Schwering G. , et al CHEMPHYSICHEM 2003 , 4, 343-348

[3] Yuato Li , et al. Angew. Chem. Int. Ed. 2016 55 , 1-6

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