**Introduction**

Recent experimental studies\(^1\) have shown that forms of Li\(_{2}\)OHCl are fast ion conductors and promising candidates for solid-state electrolyte technology. Li\(_{2}\)OHCl is experimentally observed to exist in two phases, having an orthorhombic structure at low temperature and a cubic structure at temperatures above 35 °C. The cubic phase is a fast Li-ion conductor. In this work, both the orthorhombic and cubic phases are examined experimentally and computationally in order to understand the behavior of its Li-ion mobility.

**Search for a Low Temperature Structure**

Density functional optimization\(^4\) found two candidate structures:
- tetragonal (P4mm; #99)
- orthorhombic (Pmc2\(_1\); #26)

The tetragonal structure has been observed in experiment. The static lattice computed orthorhombic structure has a higher energy by 0.02eV per formula unit and its lattice parameters are in slight disagreement with experiment. In order to improve the system, we estimated that the free energy of the system on a grid of lattice parameters in the quasi-harmonic approximation.\(^4,5\)

**Molecular Dynamics of Cubic Structure**

Initial configurations started from randomly placing lithium on the available sites and randomly orienting the OH groups in 3x3x3 supercells. Relaxed at lattice parameters of Scherrer scaled by 0.98.

**Insights from MD into Lithium Ion Conductivity**

For a fast ionic conductor, conductivity can be expressed in terms of the "tracer" or tracked particle diffusion constant:\(^6\)

$$\sigma = \frac{n(Q)D}{kTVH_L}$$

where \(n\) is the number of mobile ions, \(Q\) is the charge of the ions, \(e\) is the fundamental charge, \(k\) is the Boltzmann constant, \(T\) the temperature, \(V\) the volume, \(H_L\) the Haven ratio, and \(D\) given as:

$$D = \frac{1}{6t} \lim_{t \to \infty} \lim_{D \to 0} \left( \frac{R(t) - R(t_0)}{t} \right)^2 = \frac{1}{6t} \lim_{D \to 0} MSD(t)$$

**Monitoring Ergodicity**

Define a time averaged order parameter for each possible Li site:

$$\langle S_i(t) \rangle_{time} = \frac{1}{t} \int_0^t S_i(t') dt'$$

where \(S_i(t)\) is 1 if site \(i\) is occupied at time \(t\)

$$E_n(t) = \left( \langle S_i(t) \rangle_{time} \right)^2, \lim_{t \to \infty} E_n(t) = 0$$

The closer to zero the more ergodic.

**Arrhenius Plots (Calculated and Experiment)**

The Haven ratio is defined as \(H_L = \frac{\delta}{\delta_{exp}}\), where \(\delta_{exp}\) is the experimental conductivity and \(\delta\) is the theoretically calculated conductivity in the Nernst-Einstein relation. It gives an indication to the level of correlation in the ionic motion.

\[ \text{calculated } \log(\sigma_T) \text{ experiment (Hood)} \]

For this cubic system there are 3 equivalent lithium sites for every 2 lithium per unit cell; this means that \(\lim_{t \to \infty} \langle S_i(t) \rangle_{time} = \frac{3}{2}\) for all temperatures of initial configuration 1.

**Conclusions**

- For temperatures \(T < 310\) K, Li\(_2\)OHCl has been experimentally analyzed to have an orthorhombic structure which is well simulated using a quasi-harmonic approximation, and is characterized by the OH bonds along the b axis of the lattice.
- For temperatures \(T > 310\) K, Li\(_2\)OHCl has a cubic structure generated by the random ordering of the OH bonds, allowing the 2 Li ions to migrate among 3 equivalent sites. In order to make better comparison with simulations, samples in this study were prepared using the slow cooled method and have been cooled down to 100K.

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