

## Introduction

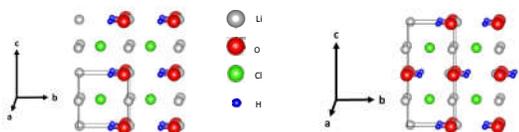
Recent experimental studies<sup>1,2,3</sup> have shown that forms of Li<sub>2</sub>OHCl are fast ion conductors and promising candidates for solid-state electrolyte technology. Li<sub>2</sub>OHCl is experimentally observed to exist in two phases, having an orthorhombic structure at low temperature and 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 details of its structures and mechanisms of its Li-ion mobility.

## Search for a Low Temperature Structure

Density functional optimization<sup>4</sup> found two candidate structures:

tetragonal (*P4mm*; #99)

orthorhombic (*Pmc2<sub>1</sub>*; #26)



The tetragonal structure has not 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 simulation, we estimated the free energy of the system on a grid of lattice parameters in the quasi-harmonic approximation.<sup>4,5</sup>

Quasi-harmonic free energy:

$$F_{QH}(T, a, b, c) = U_{SL}(a, b, c) + F_{vib}(T, a, b, c)$$

Vibrational contribution:

$$F_{vib}(T, a, b, c, T) = kT \int_0^\infty \ln \left( 2 \sinh \left( \frac{\hbar\omega}{2kT} \right) \right) g(\omega, a, b, c) d\omega$$

Optimal lattice parameters at each  $T$ :

$$F_{min}(T) = \min_{(a,b,c)} F_{QH}(T, a, b, c)$$

$g(\omega, a, b, c)$  is the harmonic phonon density of states at fixed lattice parameters  $(a, b, c)$ ,  $k$  is the Boltzmann constant,  $T$  the temperature. In practice,  $F_{QH}(T, a, b, c)$  is calculated on a grid of lattice constants and interpolated to find the free energy minimum at each  $T$ .  $U_{SL}(a, b, c)$  is the static lattice internal energy.

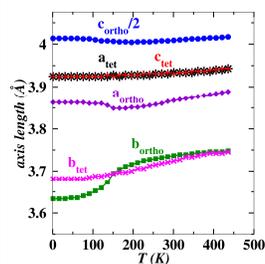


Fig. 1 Simulated parameters  $a(T)$ ,  $b(T)$ ,  $c(T)$ , as functions of temperature

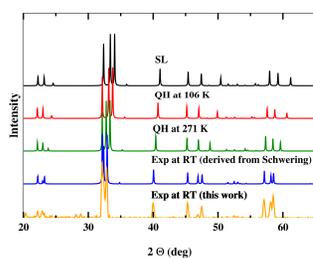
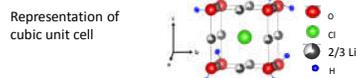


Fig. 2 Comparison of simulated X-ray pattern for orthorhombic structure with experiment

## Molecular Dynamics of Cubic Structure

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



Two starting configurations were initialized for target temperatures 300-600K

Time super imposed structural diagram of lithium and hydrogen positions

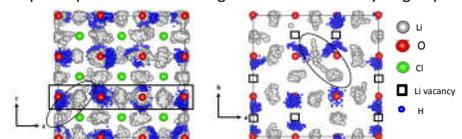


Fig. 3 Snap shots of Li and H approximately every 10 fs for a 2 ps run at ~550 K. The ideal locations of Cl and O are displayed.

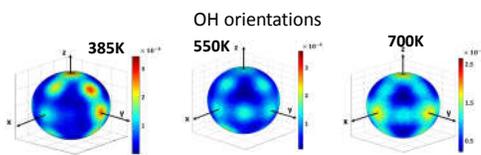


Fig. 4 Histograms of theta and phi angles for OH groups.

## 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:<sup>6</sup>

$$\sigma = \frac{n(Qe)^2 D^*}{kTVH_r}$$

where  $n$  is the number of mobile ions,  $Q$  is the charge of the ions,  $e$  is the fundamental charge,  $k$  is Boltzmann’s constant,  $T$  the temperature,  $V$  the volume,  $H_r$  the Haven ratio, and  $D^*$  given as:

$$D^* = \frac{1}{6nt} \lim_{t \rightarrow \infty} \left\langle \sum_{i=1}^n (R_i(t) - R_i(t_0))^2 \right\rangle_{t_0} = \frac{1}{6t} \lim_{t \rightarrow \infty} MSD(t)$$

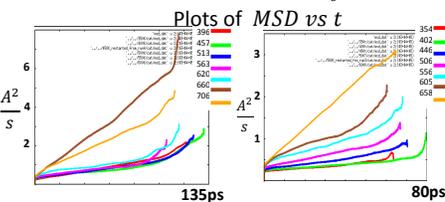


Fig. 5. Initial configuration 1. Fig. 6 Initial configuration 2.

## References

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## Monitoring Ergodicity

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

$$\langle S_i(t) \rangle_{time} = \frac{1}{t} \int_0^t S_i(t') dt' \quad \text{where } S_i(t) = \begin{cases} 1 & \text{if site } i \text{ occupied at time } t \\ 0 & \text{if site } i \text{ is not occupied at time } t \end{cases}$$

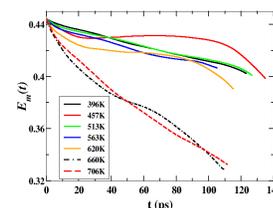


Fig. 7  $E_m(t)$  for all temperatures of initial configuration 1.

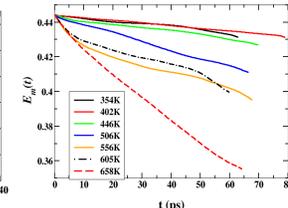


Fig. 8  $E_m(t)$  for all temperatures of initial configuration 2.

For this cubic system there are 3 equivalent lithium sites for every 2 lithium per unit cell; this means that  $\lim_{t \rightarrow \infty} \langle S_i(t) \rangle_{time} = \frac{2}{3}$

To monitor the Ergodicity of the lithium hopping across all sites define:

$$E_m(t) = \left\langle \left[ \frac{2}{3} - \langle S_i(t) \rangle_{time} \right]_{sites}^2 \right\rangle, \quad \lim_{t \rightarrow \infty} E_m(t) = 0$$

The closer to zero the more ergodic

## Arrhenius Plots (Calculated and Experiment)

In tracer picture:  $\log(\sigma T) = \log \left( \frac{n(Qe)^2 D^*}{kV} \right) - \log(H_r)$

The Haven ratio is defined as  $H_r \equiv \frac{D^*}{D_{eff}}$ . Where  $D_{eff} \equiv \frac{\sigma kTV}{n(Qe)^2}$ . In principle the Haven ratio is a measure of the discrepancy of the measured conductivity and one calculated using  $D^*$  in the Nernst-Einstein relation. It gives an indication to the level of correlation in the ionic motion.

■ calculated  $\log(\sigma T)$  assuming  $H_r = 1$     ●  $\log(\sigma T)$  experiment (Hood)

Assuming the Arrhenius

$$\text{form } \sigma = \frac{\sigma_0}{T} e^{-\frac{E_a}{kT}}$$

The theoretical  $E_a$ , assuming  $H_r = 1$ , is 0.12 eV and the experimental  $E_a$  for the cubic phase is 0.7 eV.

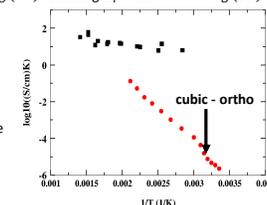


Fig. 9 Arrhenius plots (calculated and experimental)

Results predict large Haven ratio that ranges from ~2e5 to 1e2 over the experimental temperature range 310K – 470K

## Conclusions

- For temperatures  $T < 310$  K, Li<sub>2</sub>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<sub>2</sub>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 smaller conductivity than previous work.<sup>1</sup> Comparison of the measured conductivity  $\sigma$  with the computed tracer diffusion  $D^*$  suggest that this material has a very large Haven ratio due to Li ion correlations.

## Acknowledgements

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