DFT simulations of Li-ion conductor Li2(OH)Cl

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Outline

• Motivation

• Background of material

• Low temperature phase structure search

• Molecular dynamics simulations of high temperature phase
Motivation

• Solid state, fast lithium ion conductor

• Finding structure for low temperature phase is stepping stone for understanding the phase transition.

  related materials \( Li_{2+x}OH_{1-x}Cl \), \( Li_2(OH)_{1-x}F_xCl \), \( Li_2(OH)Br \)

• Understanding the structure of the low temperature phase can help to understand the differences in the phase transitions or lack thereof for the related materials

• Understanding the properties of diffusion on a disordered lattice is of general interest

• In principle the combination of calculated tracer diffusion coefficients and experimentally measured conductivity can allow for a calculation of the Haven ratio.
Background of Li$_2$OHCl

- Two phases orthorhombic -> cubic (disordered) at 312K
- Low temperature phase poor Li-ion conductor
- Disordered cubic phase is a good Li-ion conductor


- Has been cycled with a lithium anode with the apparent creation of stabilizing SEI layer
Methods

• Quantum Espresso  

  QUANTUM ESPRESSO. (Giannozzi et al. JPCM 21, 394402 (2009))

• PAW formalism with LDA, data sets generated with ATOMPAW

  (Holzwarth et al. CPC 135, 329 (2001)) http://pwpaw.wfu.edu
Low Temperature structure

- Orthorhombic, diffraction peaks available but no cif file as of yet
- Rapid change in conductivity orthorhombic -> cubic indicates order-> disorder transition of lithium sites
- Schwering et. al. has experimentally predicted lattice parameters
  Schwering, Georg CHEMPHYSCHM 2003, 4, 343 - 348
- My DFT studies predict a tetragonal ground state, a Orthorhombic structure slightly higher in energy is also predicted

Yutao Li et al
International Edition: DOI: 10.1002/anie.201604554
Lattice parameters and XRD

• Orthorhombic phase lattice parameters reported by Schwering et al. In angstrom

  \[ a = 3.82 \quad b = 7.998 \quad c = 7.74, \quad (b/2 = 3.999, \quad c/2 = 3.87) \]

  Schwering, Georg CEMPHYSCHM 2003, 4, 343 - 348

• Tetragonal lattice parameters (DFT)  Orthorhombic lattice parameters (DFT)

  \[ a = 3.89 \quad b = 3.89 \quad c = 3.66 \quad a = 3.83 \quad b = 7.97 \quad c = 3.6 \quad (\text{if scaled by } 1.08 \quad c = 3.81) \]

Candidate DFT orthorhombic with a-axis and b-axis scaled by 1.02 and c-axis scaled by 1.08

Azuma et al. report an underestimation of up to 8% in the axis along the OH bond in

\[ Mg(OH)_2, \quad Ca(OH)_2, \quad LiOH, \quad \text{and NaOH} \]

Azuma et al., *Computational and Theoretical Chemistry* 963 (2011) 215–220
Molecular Dynamics of disordered cubic phase

• Started from randomly placing lithium on available sites

• Used the micro-canonical ensemble, 1 shifted Kpoint, Ecut 45ryd, 1fm second t-step

“Scatter” plots of Lithium and hydrogen positions
Goals of MD simulations

- Calculate tracer diffusion coefficients from slopes of mean square displacement vs time plots

\[ \text{MSD}(t) = \frac{1}{\#Li} \times (R(Li)_t - R(Li)_{t_0})^2 \]

\[ \langle \text{MSD}(t) \rangle_{t_0} \text{ vs } t \]

- Tracer diffusion coefficients are related to the ionic conductivity by the equation

\[ \sigma(T) = \frac{D^*(T) \rho e^2}{kT H_r} \]

where \( D^*(T) \) - tracer diffusion coefficient


\( \rho \) - density of mobile ions per unit volume, \( e \) - fundamental charge, \( k \) – Boltzmann constant

\( T \) – temperature, \( H_r \) - the Haven ratio
MSD continued

\[ \frac{1}{6} \langle MSD(t) \rangle_{t_0,L_i} = D^* (t - t_0) - c \]

\[ \sigma(T) = \frac{D^*(T) \rho e^2}{kTH_r} \]

\[ \log(\sigma \ast T) \text{ vs } \frac{1}{T} \]

\[ 2.5 \log \left( \frac{S}{cm \ast K} \right) \]

\[ 0.5 \log \left( \frac{S}{cm \ast K} \right) \]

Initial #1

Initial #2
Conclusions

• $T = 0K$ ground state predicated to be tetragonal

• A candidate structure is found for the low temperature Orthorhombic structure

• MD simulations show Lithium hopping that corresponds to the proposed model for lithium jumps

• Hydrogen positions qualitatively correlated with Li vacancies

• Measurable diffusion occurring $\sim 350K-650K$ but results are not converged enough to produce accurate Arrhenius plots
Internal energy, kinetic energy, total energy and temperature
In Micro Canonical Ensemble

\[ MSD(t) = \frac{1}{\#Li} \cdot (R(Li)_t - R(Li)_{t_0})^2 \]

Temperature

Kinetic (green) and internal (red)

kinetic + internal
time avg kinetic and internal

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19ps

time avg temperature

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19ps
Order parameter analysis

- Need a parameter that can gauge if the simulation is long enough

- Define $\langle SO_i \rangle_t = \frac{1}{t} \int_0^t SO_i(t) dt$ where $SO_i(t) = 1$ if a lithium is occupying the site $i$ at time $t$
  $SO_i(t) = 0$ if a lithium is not occupying the site $i$ at time $t$

- Because each site should be equally occupied and there are 3 sites for every 2 lithium's
  $\langle SO_i \rangle_t \rightarrow \frac{2}{3}$ at long $t$

- For a supercell this leads to $\left| 1 - \langle SO_i \rangle_t \right| \rightarrow 0$ for long $t$. The index $i$ is for the possible Li sites in simulation cell

\[
\text{MSD}(t) = \frac{1}{\# \text{Li}} \left( R(\text{Li})_t - R(\text{Li})_{t_0} \right)^2
\]

\[
\left| \frac{2}{3} - \langle SO_i \rangle_t \right| (t)
\]
Effective temperature in the Micro canonical ensemble

- Temperature fluctuates in MD simulation in small (not in Thermodynamic limit) supercell

- Calculated diffusion constants are an average over a range of temperatures

\[
\langle D(T) \rangle_T = \int_{T_{min}}^{T_{max}} \rho(T) D_0 e^{-\frac{E_a}{kT}} dT = D_0 e^{-\frac{E_a}{kT_{eff}}} = D(T_{eff})
\]

Where \( \rho(T) \) probability of the Temperature T during the run.

\( T_{eff} \) is an effective temperature for the run