Li ion diffusion mechanisms in Li₃PO₄ electrolytes

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Introduction

- Solid-state lithium ion electrolytes such as Li₃PO₄-based materials are becoming increasingly important in batteries and related technologies.
- Li ion diffusion in crystalline Li₃PO₄ has been measured to be slightly anisotropic with activation energies of 1.1–1.3 eV. The activation energies can be reduced to 0.97 eV by N doping and to 0.5 eV by admixture with Li₂SO₃.
- In this work, first-principles calculations have been performed to model the migration energies for both vacancy and interstitial mechanisms of Li ions in γ-Li₃PO₄ and β-Li₃PO₄. For extrinsic defects, activation energy $E_A$ is the same as the migration energy of the defects, $E_m$. However, for intrinsic defects, using quasi-equilibrium statistical mechanics arguments, it follows that $E_A = E_m + E_f/2$, where $E_f$ is the formation energy of the vacancy-interstitial pair.

Vacancy mechanism

γ-Li₃PO₄

Interstitial mechanism

γ-Li₃PO₄

Crystal structures

γ-Li₃PO₄: Space group Pmna; metastable at room temperature, experimentally measured. The Li ions are located on two crystallographically different sites indicated with different shadings (gray and dark balls in the figure). Using the Wyckoff labels, the f site accounts for 2 equivalent atomic sites and the e site accounts for 4 equivalent atomic sites per unit cell. Our calculations verify that the f form is energetically more stable: $E_f = E_e = 0.03(0.01)$ eV/LiPO₄ for LDA (GGA) calculations.

β-Li₃PO₄: Space group Pnnm; low-temperature phase and energetically more stable than γ-phase. Two crystallographically distinct Li sites are also indicated with different shadings in the figure. Using the Wyckoff labels, the f site accounts for 4 equivalent atomic sites and the e site accounts for 2 equivalent atomic sites per unit cell. Our calculations show that the β form is energetically more stable: $E_f = E_e = 0.00(0.01)$ eV/LiPO₄ for LDA (GGA) calculations.

Raman spectra

LDA calculations show better agreement with experimental spectra than GGA; simulation results in this poster are presented for the LDA functional unless otherwise specified.

Raman active modes of γ-Li₃PO₄, comparing experimental results with LDA and GGA calculations. Experiment A (from Ref. 6) was measured at room temperature (RT). Experiment B and C (from Ref. 7) were measured at RT and liquid nitrogen temperature (LNT), respectively. Experiment D (from Ref. 8) was measured at LNT.

Raman active modes of β-Li₃PO₄, comparing experimental results with LDA and GGA calculations. Experimental data (from Ref. 8) were measured at LNT.

Energy path diagrams for various vacancy migration paths in crystalline Li₃PO₄, showing minimal barriers of 0.62 eV along the a-axis path for the γ form and 0.55 eV along the b-axis path for the β form. These barriers are 0.3 eV lower than the measured activation energy for vacancy-rich Li₃PO₄/β-Li₃PO₄ where oxygen-vacancies may affect the migration barrier.

The formation energies of interstitial-vacancy pairs are found to be $E_f(γ) = 1.7$ eV and $E_f(β) = 2.1$ eV. Estimating the intrinsic activation energy as $E_A = E_m(\text{interstitial}) + E_f/2$, we obtain good agreement with experiment.

Intrinsic defects

<table>
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<th>Crystal</th>
<th>Net direction</th>
<th>Experiment (eV)</th>
<th>This work (eV)</th>
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<td>c</td>
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<tr>
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Reference