Li ion diffusion mechanisms in Li_3PO_4 electrolytes[1]

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Solid-state lithium ion electrolytes are becoming increasingly important in batteries and related technologies. We have used first-principles modeling techniques[2] based on density functional theory and the nudged elastic band method to examine possible Li ion diffusion mechanisms in idealized crystals of the electrolyte material Li_3PO_4.[3] In general, LDA and GGA exchange-correlation functionals give similar results, however, LDA results for the phonon frequencies of the perfect crystals are in better agreement with experiment. For both the $\beta-$ and $\gamma-$crystalline forms, we consider interstitialcy and vacancy mechanisms. In modeling Li ion vacancy diffusion, we find direct hopping between neighboring meta-stable vacancy configurations to have a minimal migration barrier of $E_m = 0.7$ eV and $E_m = 0.6$ eV for the $\gamma-$ and $\beta-$phases, respectively. In modeling Li ion interstitial diffusion, we find an interstitialcy mechanism, involving the concerted motion of an interstitial Li ion and a neighboring Li ion of the host lattice, that can result in a migration barrier as low as $E_m = 0.3$ eV ($\gamma-$form) and $E_m = 0.4$ eV ($\beta-$form). The minimal formation energy of a Li ion vacancy-interstitial pair is determined to be $E_f = 1.7$ eV ($\gamma-$form) and $E_f = 2.1$ eV ($\beta-$form). Assuming the activation energy for intrinsic defects to be given by $E_A = E_m + E_f/2$, the calculations find $E_A = 1.1$ eV for $\gamma-Li_3PO_4$, in good agreement with reported experimental values of 1.1-1.3 eV,[4] while for $\beta-Li_3PO_4$, the calculations find $E_A = 1.4 - 1.6$ eV, slightly depending on crystallographic directions.

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[2] *PWscf* – http://www.pwscf.org.

[3] Y. A. Du and N. A. W. Holzwarth, Submitted to *J. Electrochem. Soc.* Preprint: http://www.wfu.edu/∼natalie/papers/Li3PO41/

[4] A. K. Ivanov-Shitz *et al.*, *Crystallography Reports* **46**, 864 (2001).