Li-ion diffusion mechanisms in γ-Li_3PO_4 electrolytes

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Recently, there has been interest in Li_3PO_4 as a solid-state electrolyte material for batteries and sensor technologies. In this poster, we report on simulations of ideal Li-ion diffusion in crystalline γ-Li_3PO_4, considering both vacancy and interstitial mechanisms. The simulations are performed in the framework of density functional theory using the plane-wave pseudopotential code *PWscf* – http://www.pwscf.org, and supercells containing either a Li^+ vacancy or an interstitial Li^+. The supercell charge is adjusted to maintain the insulating phase. The nudged elastic band method[1] computes the activation barriers for diffusion.

We find two meta-stable vacancy sites which differ in energy by 0.1 eV. Diffusion barriers for vacancy vary slightly with crystallographic direction. The computed diffusion barriers of 0.4 $\pm$ 0.1 eV are considerably smaller than the experimentally measured activation energies for conductivity in this crystal.[2] Using the experience of previous cluster simulations,[3] we also consider the effects of N substituting for O, finding N-doping to lower the diffusion barrier for vacancy by less 0.1 eV.

We currently find three meta-stable interstitial Li^+ sites. The two lowest-energy sites differ by 0.1 eV, and the third site has an energy of 0.8 eV above the lowest one. We estimate the diffusion barrier for interstitial Li^+ to be 1.3 eV, which happens to be close to the experimentally measured activation energies.[2]

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[1] H. Jónsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998), p. 385.

[2] A. K. Ivanov-Shitz *et al.*, *Crystallography Reports* **46**, 864 (2001), B. Wang *et al.*, *J. Solid State Chem.* **115**, 313 (1995).

[3] Hassen Rabaâ *et al.*, *J. Solid State Chem.* **161**, 73 (2001).