

## Li-ion diffusion mechanisms in $\gamma$ -Li<sub>3</sub>PO<sub>4</sub> electrolytes

Yaojun Du, N. A. W. Holzwarth, and Xiao Xu

*Department of Physics, Wake Forest University  
Winston Salem, NC, USA*

Recently, there has been interest in Li<sub>3</sub>PO<sub>4</sub> 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  $\gamma$ -Li<sub>3</sub>PO<sub>4</sub>, 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<sup>+</sup> vacancy or an interstitial Li<sup>+</sup>. The supercell charge is adjusted to maintain the insulating phase. The nudged elastic band method<sup>1</sup> 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.<sup>2</sup> Using the experience of previous cluster simulations,<sup>3</sup> 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<sup>+</sup> 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<sup>+</sup> to be 1.3 eV, which happens to be close to the experimentally measured activation energies.<sup>2</sup>

---

<sup>1</sup>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.

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

<sup>3</sup>Hassen Rabaâ *et al.*, *J. Solid State Chem.* **161**, 73 (2001).