

Abstract Submitted
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Li-ion diffusion mechanisms in crystalline Li_3PO_4 electrolytes¹

YAOJUN A. DU, N.A.W. HOLZWARTH, Wake Forest University — Using first principles electronic structure methods and “nudged elastic band” optimization techniques,² we examine ideal Li-ion diffusion in crystalline Li_3PO_4 electrolytes, considering both vacancy and interstitial mechanisms. The simulations are performed in supercells containing 16 Li_3PO_4 units. We determine the activation barriers for several plausible diffusion paths, considering the effects of the exchange-correlation functional forms, of the crystalline form in the β - and γ - structures, and also the effects of substitutional N. Using the generalized gradient approximation, results for γ - Li_3PO_4 show diffusion barriers of 0.6-0.7 eV for the vacancy mechanism with a small dependence on the crystallographic direction. For the interstitial mechanism, the diffusion barriers are 0.8 eV and 1.3 eV along the **b**- and **c**-axes, respectively. The larger activation barriers of the interstitial mechanism are closer to experimental measurements on polycrystalline and single crystal samples³ which find $E_a \approx 1.1 - 1.3$ eV.

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²Using the Quantum ESPRESSO package <http://www.pwscf.org/>.

³J. Solid St. Chem. **115**, 313 (1995), Cryst. Rep. **46**, 864 (2001)

Yaojun A. Du
Wake Forest University

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