Simulations of Li ion diffusion in the electrolyte material – Li$_3$PO$_4$[1]

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Solid-state lithium ion electrolytes are becoming increasingly important in batteries and in related technologies. We have used first-principles modeling techniques based on density functional theory and the nudged elastic band method to examine possible Li ion diffusion mechanisms in terms of their migration energies E_m. Simulations were performed in idealized crystals of the electrolyte material Li$_3$PO$_4$, considering both vacancy and interstitial processes. We find that an "interstitialcy" mechanism, involving the concerted motion of an interstitial Li ion and a neighboring lattice Li ion, is likely to provide the most efficient ion transport in Li$_3$PO$_4$. Ion transport in pure crystals involves the formation of vacancy-interstitial pairs requiring an additional energy E_f, resulting in a thermal activation energy of $E_A = E_m + E_f/2$. Calculated values of E_A are in excellent agreement with single crystal experiments on γ-Li$_3$PO$_4$. Our simulations examine similarities and differences between diffusion processes in the γ and β crystal structures. In addition, we analyze zone center phonon modes in order to further validate our calculations with available experimental measurements and to determine the range of vibrational frequencies associated with Li ion motion.