

High lithium ion diffusion in Al doped lithium phosphidosilicate Li_2SiP_2 : a solid Li electrolyte material

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The lithium phosphidosilicates¹⁻³ are an interesting new class of potential solid Li electrolyte materials. These systems are made up of a complex framework comprised of $(\text{Si}_4\text{P}_{10}^{14-})$ corner-sharing “super-tetrahedra”, between which the lithium cations are accommodated. The high anionic charge on the super-tetrahedral framework allows for a large number of charge compensating lithium ions to be present in the system. Experimentally, this results in very low energy barriers to lithium diffusion, within the region of 0.1 eV or below, with ionic conductivities of approximately $6 \times 10^{-6} \text{ Scm}^{-1}$.^{1,2} As a result, the lithium phosphidosilicates are a promising new class of materials for solid state lithium ion batteries.

In this work, we have focused on the system Li_2SiP_2 (LSP)^{1,2} and studied both the lithium diffusion and doping properties using density functional theory (DFT). We find that trivalent cation dopants prefer to occupy the silicon site rather than the lithium site. The most favourable being Al doping. This is similar to observations in oxide zeolite materials.⁴

Ab initio molecular dynamics (AIMD) calculations on both pure and 10% Al doped LSP, imply increased lithium ion diffusion at temperatures below 700 K in the doped LSP system. The nudged elastic band (NEB) calculations elucidate a lithium interstitial mechanism as the most favourable low energy barrier pathway. The use of dopants primes these pathways and enables improved lithium conductivity at lower temperatures.

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