Supplementary Information

The typical LGPS alloy $Li_{10}GeP_2S_{12}$ has a tetragonal lattice containing 50 atoms, with the $P4_2mc$ space group (lattice parameters a=8.758Å, c=12.626Å). CI-NEB searching for diffusional pathways results in highly different activation barriers along the a- and c-axis. **Fig. s1** summarizes the activation barriers along pathways labelled as A, B, C, D in **Fig. s2**. The former two pathways are along the c-axis, while the latter two are along the a-axis.

The most likely diffusional channel for Li^+ along the c-axis is made of alternating A and B pathways, with the controlling barrier being 0.217 eV. On the other hand, the channel to facilitate Li^+ migration along the a-axis is zigzag, consisting of C and D pathways. The dictating barrier along the a-axis is nearly three times of that along the c-axis, being 0.615 eV and thus making Li^+ transportation rather unlikely along the a-axis. The effective diffusion of Li^+ in LGPS is therefore one-dimensional only, along the long c-axis of the materials.

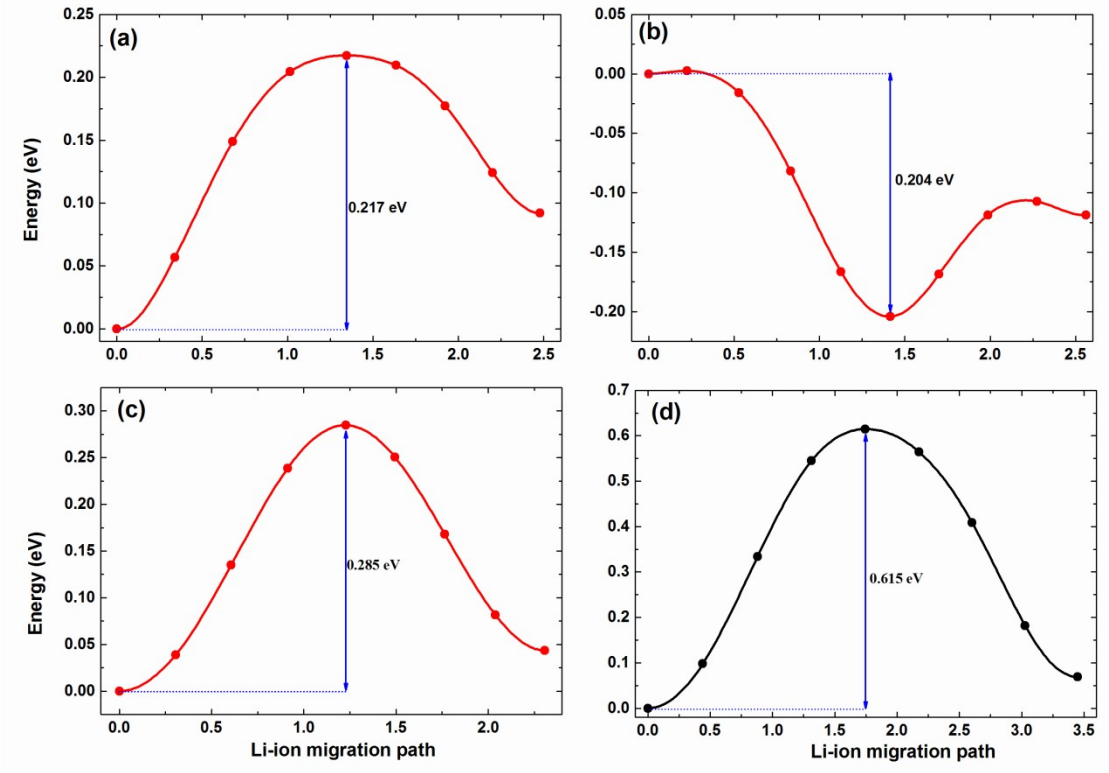

Fig. s1 Calculated energy barriers for the migration of Li^+ ions through pathways labelled as A, B, C and D in **Fig. s2**.

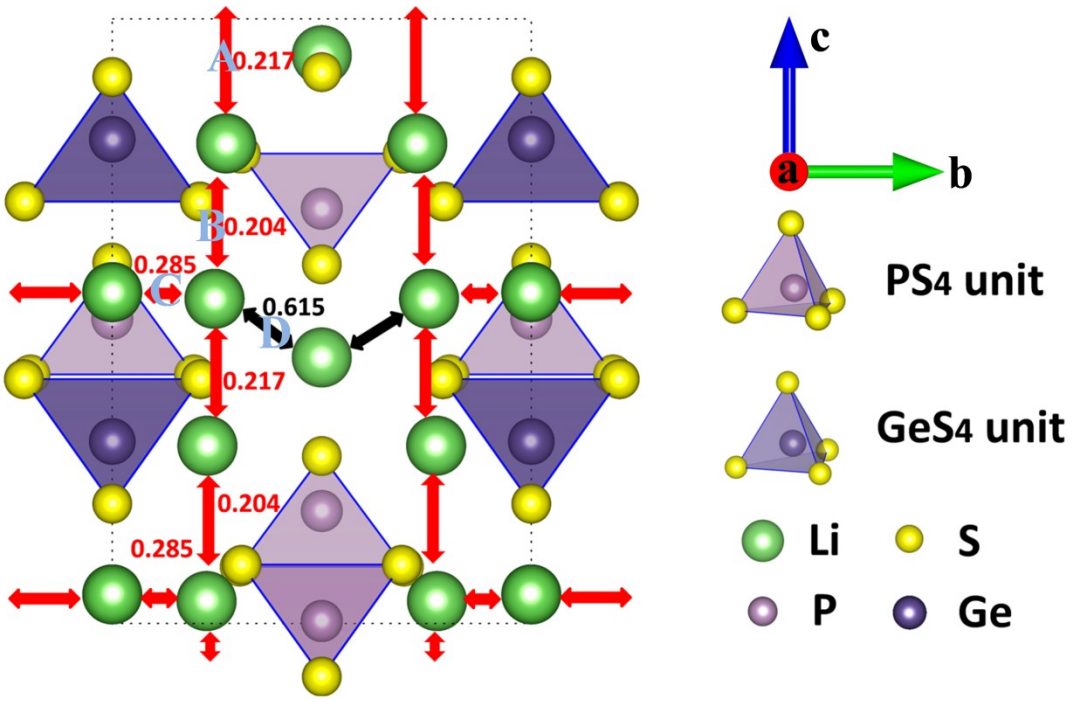

Fig. s2 Diffusion pathways in LGPS with labels A, B, C and D having activation barriers corresponding to (a), (b), (c) and (d) in **Fig. s1**. Values are associated activation barriers in electron volts.