Aliovalent doping of tetra lithium ortho-sulfidostannate Li_4SnS_4 as air stable solid electrolyte with high ionic conductivity

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Solid electrolytes with fast lithium ion conduction are a key requisite for enabling high-energy and safer all-solid-state lithium-sulfur (Li-S) batteries.[1-4] Achieving high ionic conductivity along with impressive chemical stability and easier battery processability in solid electrolytes remain a challenge for their synthesis. Here, we present a lithium ion conductor, $Li_{3.833}Sn_{0.833}As_{0.166}S_4$ that showed a high lithium ionic conductivity of $9.94*10^{-4}$ Scm^{-1} at room temperature and superior chemical stability when processed in air and/or moisture conditions. Various compositions of $Li_{4-x}Sn_{1-x}As_xS_4$ (where, x= 0 to 0.250) were systematically investigated through solid state synthesis. Obtained results were compared with the parent undoped chalcogenidotetrelate Li_4SnS_4.[5] The ionic conductivity, σ of aliovalent-doped Li_4SnS_4 increases in a trend with decreasing dopant concentration. σ reaches a maximum at a dopant concentration of As = 0.166 mol%. Further decreased concentration of dopant leads to inferior conductivity. Furthermore, the chemical stability of the compound was demonstrated by exposing the sample to ambient air and moisture conditions (64°F temp. and 80% humidity) for 48 hours. The air exposed sample showed no change in crystallinity and ionic conductivity as compared to the non-exposed sample. The As doped Li_4SnS_4 solid electrolyte represents high ionic conductivity that is an order of magnitude higher than the parent undoped compound Li_4SnS_4 and possess extraordinary chemical stability. This enhanced performance could be attributed to the speculations that accommodate two vital effects. (1) The aliovalent doping of As^{5+} leads to controlled atomic disorder and creates lithium vacancies or interstitial lithium ions. The solid solution $Li_{3.833}Sn_{0.833}As_{0.166}S_4$ shows one of the highest found conductivities in the LISICON family. (2) Presence of As, a soft acid satisfies the hard soft acid base (HSAB) theory and promotes desired high chemical stability of the doped compound. The synthesis, concept of aliovalent doping effect, air stability studies, and their ionic conductivities will be presented.

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