Investigation of New Phosphorous-free Thio-LISICON Phases as Solid State Electrolytes

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The development of solid lithium ion conductors is a crucial step towards all-solid lithium ion batteries. These could benefit from increased safety, improved compatibility to new anode and cathode materials and increased long-term stability. New thio-phosphate and thio-germanate based materials have recently emerged as the leading solid state electrolytes with exceptionally high conductivities and good mechanical properties.[1] Especially $Li_{10}GeP_2S_{12}$ and the Li-argyrodite Li_6PS_5X (X= Cl, Br, I) family stand out with RT conductivities of $1.2x10^{-2}$ S cm^{-1} and 10^{-4} S cm^{-1} respectively, which are comparable to commercial liquid-based electrolytes.[2, 3] Both materials comprise unusual anion-sublattices, the argyrodite phase is based on a tetrahedral close packing while $Li_{10}GeP_2S_{12}$ is related to a body-centred cubic packing. The $M^{4+/5+}$ cations are tetrahedrally coordinated while lithium ions can be coordinated octahedrally or tetrahedrally. Accordingly $Li_{10}GeP_2S_{12}$ is based on a framework of $[GeS_4]^{4-}$ and $[PS_4]^{3-}$ tetrahedra and mobile tetrahedral/octahedral lithium ions.

But those materials suffer inherently from poor stability towards the electrode materials. Computational and experimental studies of the Li/Li_6PS_5Cl and $Li/Li_{10}GeP_2S_{12}$ interface respectively show that especially thiophosphate is prone to reduction to LiP and Li_3P.[4, 5]

This research focuses on the discovery and characterization of new sulphide based phosphorous-free phases. Synchrotron PXRD, neutron scattering and NMR were employed to solve the crystal structures while ICP confirmed the proposed compositions. AC-impedance spectroscopy and ^7Li dynamic NMR showed high lithium mobility ~ $4x10^{-5}$ S/cm and chemical stability was tested against lithium metal. We compare the structures, stabilities and conductivities of the new phases with those of $Li_{10}GeP_2S_{12}$ and Li_6PS_5X to gain new insight into the search for workable electrolytes in this class of materials.

References:

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