

Ion Transport in Lithium-Argyrodites $\text{Li}_6\text{PS}_5\text{X}$ (X: Cl, Br, I): Activation Energies, Pre-Factors, Lattice Disorder and Polarizabilities

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The realization of solid-state-lithium-based batteries needs suitable solid electrolytes. Over the last couple of years, design strategies and structure principles, as well as attempts at generalization have been presented to explain the origins of ‘superionic’ conduction in solids. To identify one of the general rules of superionic conduction, and the physical principles underlying it, “very detailed studies of individual systems”, as Hayes pointed out as early as 1978 [1], are needed to advance in the field. A suitable model system is *conditio sine qua non* for this purpose.

In 2011, Deiseroth and co-workers have introduced lithium argyrodites [2], with the general formula $\text{Li}_6\text{PS}_5\text{X}$ (X: Cl, Br, I), as promising electrolytes. Although several studies already reported on ionic conductivities [3-6] and on test cells using argyrodites as solid electrolytes [5], we need a clearer picture of the relevant factors that promote its superionic behaviour. Ionic conductivity is governed by (i) the effective number of charge carriers and (ii) their mobility. Compounds with extensive lattice disorder and many unoccupied regular or interstitial sites often show rapid cation movements, as far as these sites are connected by low energy pathways. Other factors are (iii) the size of the mobile ions, (iv) the ionic charge, (v) the (local) bonding character, *i.e.*, the preferred co-ordination of the ions and whether ionic, covalent or mixed bonding is present, and (vi) the polarizability of the immobile ions. The latter, together with the crystal structure, directly affects the potential landscape the mobile ions are exposed to.

Partial replacement of the sulfur anions in $\text{Li}_6\text{PS}_5\text{X}$ with distinctly polarizable anions, such as Cl, Br, and I, is expected to influence local ion jump processes and macroscopic ion transport [4]. Here, we used broadband conductivity spectroscopy, carried out over a large frequency range, to study conductivities, activation energies and pre-factors of the underlying Arrhenius behaviour. Long-range ion transport in phase-pure $\text{Li}_6\text{PS}_5\text{Br}$, as seen by macroscopic conductivity measurements in the low frequency limit, is characterized by an activation energy E_a of 0.296 eV and a pre-factor of $A = \log(\sigma_0/(S \text{ cm}^{-1} \text{ K})) = 4.87$. The same pre-factor ($A = 4.60$), but a larger activation energy (0.470 eV), determines ion transport in $\text{Li}_6\text{PS}_5\text{I}$. Interestingly, although the Γ anion is highly polarizable, which allows the Li ions to ‘squeeze’ through eventually smaller voids, ionic conductivity is noticeably lower, see also Ref. [4]. $\text{Li}_6\text{PS}_5\text{Cl}$ shows an activation energy of 0.369 eV, which lies in between that of $\text{Li}_6\text{PS}_5\text{I}$ and $\text{Li}_6\text{PS}_5\text{Br}$. Despite the fact that Cl anions are polarizable to a lesser extent than Br anions, for $\text{Li}_6\text{PS}_5\text{Cl}$ similar conductivities as for $\text{Li}_6\text{PS}_5\text{Br}$ were found at ambient temperature and slightly below ($\sigma_{\text{bulk}} = 3.8 \text{ mS cm}^{-1}$). The larger activation energy of $\text{Li}_6\text{PS}_5\text{Cl}$ is compensated by an increase of the corresponding pre-factor by 2 orders of magnitude yielding $A = 6.81$. The pre-factor depends, besides other factors, on attempt frequencies and contributions from entropy. We will discuss how ionic transport is affected by these parameters.

References:

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