

A Molecular Dynamics Study of Anion Disorder Effects on Lithium Transport Mechanisms in Argyrodite Solid Electrolytes

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Halide-substituted lithium-argyrodites, $\text{Li}_6\text{PS}_5\text{X}$ ($X=\text{Cl, Br, I}$) are a promising family of lithium-ion solid electrolytes, with potential applications in all-solid-state lithium-ion batteries. Changing X from I to Cl produces a strong increase in lithium-ion conductivity, which has been attributed to increased crystallographic disorder for X and S ions across 4a and 4c sites. A previous molecular dynamics study [1] has predicted that efficient long-ranged Li-ion transport is only achieved for such X/S disordered systems, with this attributed to changes in the rates of lithium-ion jumps between lattice sites. A microscopic explanation for this change in lithium-ion dynamics, however, is lacking.

To study this behaviour, we have performed a series of *ab initio* molecular dynamics simulations of ordered and disordered $\text{Li}_6\text{PS}_5\text{X}$. In contrast to previous computational studies, we have analysed the lithium-ion dynamics in terms of transitions between local potential minima (inherent structures) in lithium-ion configuration space, which allows us to resolve non-trivial lithium motion [3].

We find that in fully ordered $\text{Li}_6\text{PS}_5\text{X}$, the lithium ions form six-coordinate coordination octahedra around the (4a/4c) S anions. Interestingly, this is the case for X ordered over the 4a sites and over the 4c sites, indicating a strong preference for separated (4a/4c) S ions to be octahedrally coordinated by Li. Lithium motion consists of highly correlated processes within individual octahedra; octahedral rotations, and reorganisations via trigonal prismatic configurations; neither of which give long ranged lithium diffusion.

For anion-disordered $\text{Li}_6\text{PS}_5\text{X}$, this preferred octahedral coordination is disrupted. We observe a number of Li_xS coordination environments with $x \neq 6$, and 6-fold coordination environments increasingly deviate from ideal octahedral symmetry. This increased Li-coordination disorder facilitates long-ranged Li-ion diffusion between Li_xS polyhedra. We note that for pairs of S ions in adjacent 4a / 4c sites, it is not possible for both S ions to simultaneously achieve ideal octahedral coordination. We propose, therefore, that the capacity for long-ranged lithium transport in anion-disordered $\text{Li}_6\text{PS}_5\text{X}$ arises from geometric frustration of preferred octahedral lithium configurations, which produces a highly disordered network of lithium-ion polyhedra, with fast lithium-ion diffusion.

References:

- [1] Rao et al. Sol. Stat. Ionics (2013), 230, 72.
- [2] de Klerk et al. Chem. Mater. (2016), 28, 7955.
- [3] Stillinger and Weber, Science (1984), 225, 983.