

Probing Structural Attributes for Li-Argyrodite as a Fast Ion Conductor using Neutron Powder Diffraction

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Driven by technological importance, the development of all-solid-state lithium-ion batteries has awakened the pursuit of solid electrolytes with superior Li⁺ conductivity. Li-Argyrodite is a unique player in the field of solid electrolytes because this sulfide-based material was shown to achieve an ionic conductivity of 24 mS/cm at room temperature. This record, which even outperforms the liquid electrolyte (~ 10 mS/cm at r.t.), calls for an understanding of the origin of fast ion conduction in Li-Argyrodite. In this work, we employ variable-temperature neutron diffraction and impedance spectroscopy to investigate the structural attributes for Li⁺ transport properties in Li-Argyrodite, Li₆PS₅X (X = Cl, Br, and I). Structural analyses based on the Rietveld refinements, maximum entropy method (MEM) analysis, and bond valence site energy (BVSE) reveal that Li⁺ has the potential to take an interstitial site 16e, enabling a cage-to-cage three-dimensional Li⁺ conduction via 48h–16e–48h pathway. In addition, we find that the anion site disorder between S₂⁻ and X⁻, which is commonly perceived as the key factor to promote Li⁺ conductivity, is fundamentally correlated with the negative charge distribution over the anion 4a and 4c sites. Learned from this understanding, we further show that tuning the negative charge ratio of 4a and 4c to unity is an effective approach to realizing higher Li⁺ conductivity in Li_{5.7}PS_{4.7}ClBr_{0.3}.