MS14-1-9 A Polycationic Substituted Lithium Argyrodite Superionic Solid Electrolyte
#MS14-1-9

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Abstract
Solid-state batteries are attracting great attention because of potentially higher energy and power densities than conventional Li-ion batteries based on liquid electrolytes.[1] Yet, they are plagued by the development of advanced solid electrolytes, mainly lacking in ionic conductivity and electrochemical stability; thus, the ongoing quest for exploration of new materials and compositions.[2-3] Despite increasing research interests in high-entropy materials, the effect that configurational entropy has on the charge transport properties remains largely elusive.[4] Recently, we have shown that high-entropy argyrodites can be achieved via polyanionic/cationic substitution, showing a low activation energy (E_A = 0.22 eV) and moderate r.t. ionic conductivity (~1 mS/cm).[5] However, the possibility of polycationic substitution and the resulting structure-property relationships have not been explored yet.
Within this context, we herein report about the influence of polycationic substitution on the Li-ion conductivity in argyrodite superionic conductors. Using electrochemical impedance spectroscopy and 7Li pulsed field gradient nuclear magnetic resonance (NMR) spectroscopy, it is found that polycationic substitution leads to a very low activation energy (E_A = 0.19 eV) for Li-ion conduction and a high r.t. ionic conductivity of ~13 mS/cm. These findings are rationalized via neutron powder diffraction (at 298 K and 10 K) in combination with magic angle spinning NMR spectroscopy. A high S^{2-}/I^- anion site disorder (up to ~10 %) and redistribution of Li lead to shortened jump distances and therefore facilitated long-range ion diffusion. Overall, our results show the possibility of polycationic substitution in lithium argyrodites, thereby opening up large compositional space for the development of novel superionic conductors with improved properties.

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