Tailoring the Disorder Landscape to Increase Conductivity in Thiophosphate Electrolytes

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In a recent study published in Angewandte Chemie, Li and colleagues reported that introducing disorder into $Li_{5.5}PS_{4.5}Cl_xBr_{1.5−x}$ solid electrolytes via $Cl^−/Br^−/S^{2−}$ mixing affects charge transport, leading to a room-temperature ionic conductivity beyond 20 mS/cm. This entails the possibility of improving ion mobility by tailoring the occupational disorder in lithium argyrodites.

Designing advanced solid electrolytes is an important step towards bulk-type solid-state batteries that are capable of competing or even outperforming conventional Li-ion batteries.[1] In ceramic solid electrolytes, ion mobility is usually strongly dependent upon the cation and/or anion arrangement in the lattice. Ionic conductivity can be increased by altering the host structure via doping or substitution.[2] In addition to ionic conductivity (with $\sigma_{ion,rt}$ ideally being ≥10 mS/cm), both the (electro)chemical stability and the mechanical properties need to be considered in the development of next-generation solid electrolytes. The high-entropy materials (HEMs) concept deviates from common doping or substitution approaches for improving properties and increasing stability of the crystal structure. In general, the concept relies on complex substitution patterns, with HEMs typically referring to materials having five or more principal elements occupying a single crystallographic site. However, this criterion has originally been proposed for high-entropy alloys with a single sublattice. In the case of more complex structures, mixed occupancies (occupational disorder) over multiple sublattices contribute to the overall configurational entropy, ΔS_{conf}. As per definition, HEMs are characterized by a $\Delta S_{conf} \geq 1.5R$.[3] Aside from complex interactions among the constituent elements, so-called cocktail effects, the introduction of ions of differing sizes causes local lattice distortions and defect formation, which in turn may lead to unprecedented properties and functionalities.

The HEMs concept has only recently been applied to ceramics, such as oxides, sulfides, and carbides.[4] Controlled introduction of anion and/or cation (occupational) disorder into the crystal lattice of solid electrolytes is receiving much attention lately due to potential improvements in the charge-transport and/or (electro)chemical properties. Regardless, only a few high-entropy solid electrolytes, including rock-salt, garnet, and NASICON-type materials, have been reported up until now, with compositional complexity being added through cation substitution.[5,6] However, no major advances in ionic conductivity (for the most part) have been achieved. Recently, the choice of high-entropy solid electrolytes has been expanded to include lithium argyrodites, where anion and cation substitutions can be performed.[7] This promising class of superionic solid electrolytes is represented by the general formula Li_6PS_5X (X = Cl, Br, I) and adopts a cubic crystal structure ($F{-}43m$ space group, see **Figure 1A**). Substitution on the P site with semimetal species, such as germanium, antimony, or silicon, and altering the S^{2-}/X^- ratio have been shown to increase $\sigma_{ion,rt}$ beyond 10 mS/cm in some cases.

Now, Li *et al.* reported that anion substitution in the lithium argyrodite solid-solution system of $Li_{5.5}PS_{4.5}Cl_xBr_{1.5-x}$ ($0 \leq x \leq 1.5$) can be exploited to tailor configurational entropy towards superionic conductivity. In this case, ΔS_{conf} is determined by the number of possibilities for distributing sulfur, chlorine, and bromine in the zinc blende-type anion sublattice within the argyrodite structure. The $S^{2-}/Cl^-/Br^-$ occupation over the respective $4a$ and $4d$ Wyckoff sites (**Figure 1B**) was quantitatively probed using neutron powder diffraction and solid-state nuclear magnetic resonance (NMR) spectroscopy. For $Li_{5.5}PS_{4.5}Cl_{0.8}Br_{0.7}$, a configurational entropy of $\Delta S_{conf} = 1.98R$ was achieved, accompanied by a high ionic conductivity of $\sigma_{ion,rt} = 22.7$ mS/cm (from NMR spectroscopy; 9.6 mS/cm for cold-pressed pellets, as determined by electrochemical impedance spectroscopy). Furthermore, what's even more interesting is that this work shows that a direct correlation exists between the ionic conductivity and the configurational entropy (**Figure 1C**).

The mixing of anions over the aforementioned crystallographic sites is typically referred to as X^-/S^{2-} site inversion or disorder.[8] However, if more than one halide species is introduced, this descriptor is not accurate anymore. To express the degree of disorder more precisely, Li *et al.* introduced the ΔS_{conf}, which also considers partial occupancies of the elemental constituents (not only mixing over two crystallographic sites) and thus represents an overall better descriptor. Frankly speaking, configurational entropy is a measure of anion disorder in the $Li_{5.5}PS_{4.5}Cl_xBr_{1.5-x}$ solid electrolytes, and the number of anion conformations is high for a high ΔS_{conf}. Accordingly, the more equally the S^{2-} and halide ions are distributed over the available crystallographic sites, the higher the ΔS_{conf} is. This leads to severe structural distortions on the unit-cell level, which in turn affects the Li-site energy distribution and facilitates ion motion through the structure. Ultimately, this means that ionic conductivity scales with the degree of disorder in the anion sublattice (**Figure 1C**).
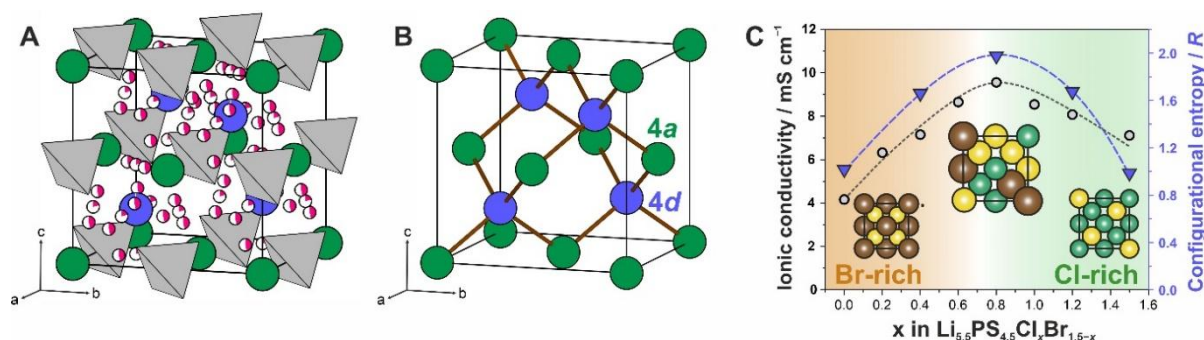
Figure 1. Crystal structure of the anion-substituted lithium argyrodite solid electrolytes $Li_{5.5}PS_{4.5}Cl_xBr_{1.5-x}$ and relationship between configurational entropy and ionic conductivity.

(A) Schematic view of the crystal structure. Gray tetrahedra indicate the $[PS_4]^{3-}$ units, lithium is shown as pink spheres, and the green and blue spheres denote the $4a$ and $4d$ Wyckoff sites, respectively.

(B) Zinc blende-type anion sublattice. Both the $4a$ and $4d$ positions can be occupied by sulfur and halide ions.

(C) Experimentally observed correlation between configurational entropy (anion disorder) and room-temperature ionic conductivity of cold-pressed pellets. Adapted from Li *et al*.[9]

The material exhibiting the highest ionic conductivity was also tested in solid-state battery cells using a single-crystal NCM ($LiNi_{0.90}Co_{0.06}Mn_{0.04}O_2$) cathode and found to enable stable performance over hundreds of cycles. This result demonstrates the practicality of using halogen-rich lithium argyrodite solid electrolytes devoid of costly elements for electrochemical energy-storage applications.

Taken together, Li *et al*. have shown that introducing disorder into the anion sublattice of lithium argyrodites has a profound effect on the charge-transport properties. Notably, ionic conductivity was found to increase with increasing configurational entropy. It should be noted that an article published in Science reported recently on a cation- and anion-substituted $Li_{10}GeP_2S_{12}$ (LGPS)-type solid electrolyte.[10] The authors also showed that anion disorder induced by oxygen and bromine substitution on the sulfur sites, along with silicon substitution on the germanium site, increases the ionic conductivity up to 32 mS/cm for sintered pellets of $Li_{9.54}[Si_{0.6}Ge_{0.4}]_{1.74}P_{1.44}S_{11.1}Br_{0.3}O_{0.6}$. However, in this case, anion disorder relates to the polyanionic $[MS_4]^{x-}$ units (M = P, Si, Ge), in which sulfur is covalently bonded to the central atom. Regardless, the studies on high-entropy argyrodite[9] and LGPS-type solid electrolytes[10] indicate that compositional complexity may be key to developing advanced ion conductors, with implications even beyond thiophosphate chemistry.

Declaration of Interests

The authors declare no competing interests.

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