

# High-Entropy Argyrodite Lithium Superionic Conductors

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*In a recent study published in ACS Materials Letters, Lin and colleagues reported a compositionally complex superionic conductor,  $\text{Li}_{6.5}[\text{P}_{0.25}\text{Si}_{0.25}\text{Ge}_{0.25}\text{Sb}_{0.25}]\text{S}_5\text{I}$ , for solid-state battery applications. This (multi-cation substituted) argyrodite-based electrolyte material has a configurational entropy greater than  $1.5 R$  and was found to exhibit high ionic conductivity at room temperature ( $\sim 13 \text{ mS/cm}$ ) and a low activation energy for lithium transport ( $\sim 0.2 \text{ eV}$ ).*

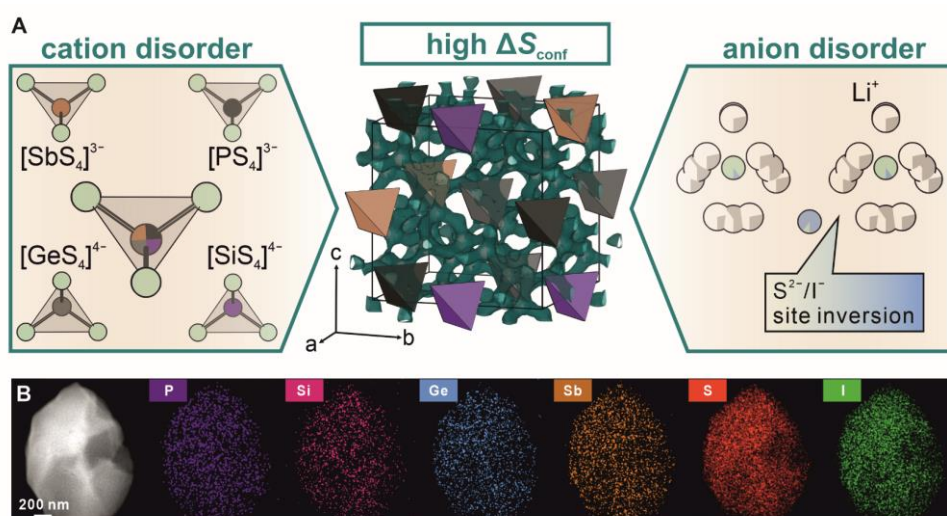
Developing next-generation solid electrolytes is paramount to the advancement of bulk-type solid-state batteries to compete with or outperform conventional Li-ion batteries.<sup>1</sup> Because the diffusion pathways of superionic conductors are strongly dependent on the cation and/or anion configuration, ion mobility can be modulated by altering the host structure via doping or substitution.<sup>2</sup> Apart from the ionic conductivity (ideally,  $\sigma_{\text{ion,rt}} \geq 10 \text{ mS/cm}$ ), (electro)chemical stability, stiffness and yield stress are factors that need to be taken into account in the design of high-performance solid electrolytes. A new strategy for modifying crystal structure, thereby potentially leading to improved or even unprecedented properties, is the high-entropy materials (HEMs) concept.

HEMs refer to materials having five or more elements occupying a single crystallographic site (typically with equimolar compositions) and are characterized by configurational entropies  $\Delta S_{\text{conf}} \geq 1.5 R$ , with  $R$  representing the ideal gas constant. In addition to manifold interactions, so-called “cocktail effects”, the introduction of various elements causes lattice distortions. Originally, this was shown for high-entropy alloys, while only recently the HEMs concept has been applied to ceramics with different crystal structures such as oxides, sulfides or carbides.<sup>3</sup>

In the field of solid electrolytes, only few examples have been reported so far, including rocksalt, garnet and NASICON (Na Superionic CONductor)-type HEMs. However, there were no major improvements in ionic conductivity over state-of-the-art, low-entropy counterparts.<sup>4,5</sup> Nevertheless, high cathodic stability (against Li metal) and stabilization of the desired cubic phase, along with a reduction in nucleation

temperature, have been demonstrated for high-entropy garnet solid electrolytes derived from  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ .<sup>5</sup>

Recently, Lin and colleagues extended the choice of high-entropy electrolyte materials with a multi-cationic substituted argyrodite lithium superionic conductor,  $\text{Li}_{6.5}[\text{P}_{0.25}\text{Si}_{0.25}\text{Ge}_{0.25}\text{Sb}_{0.25}]\text{S}_5\text{I}$ .<sup>6</sup> Lithium argyrodites with the general formula  $\text{Li}_6\text{PS}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) are a promising class of fast solid electrolytes and have been heavily investigated in the past.<sup>7</sup> Increased conductivity was primarily achieved by substitution on the P site with semimetal species such as Ge, Sb or Si, or by altering the sulfur/halide ratio. Indeed, in some cases, materials with very high ionic conductivities were realized in this way.<sup>8,9</sup> Lin *et al.* showed in their work that it is possible to combine P, Si, Ge and Sb in equimolar amounts on the 4b Wyckoff position (P site). X-ray and neutron powder diffraction as well as  $^{31}\text{P}/^{29}\text{Si}$  magic-angle spinning nuclear magnetic resonance spectroscopy measurements indicated the material adopts a cubic structure ( $F\bar{4}3m$  space group) with a local tetrahedral environment of the aforementioned elements. Both the cation disorder ( $[\text{P}_{0.25}\text{Si}_{0.25}\text{Ge}_{0.25}\text{Sb}_{0.25}\text{S}_4]^{3.5-}$  representing a combination of  $[\text{PS}_4]^{3-}$ ,  $[\text{SiS}_4]^{4-}$ ,  $[\text{GeS}_4]^{4-}$  and  $[\text{SbS}_4]^{3-}$  units) and a  $\sim 11\%$   $\text{S}^{2-}/\text{I}^-$  site inversion (**Figure 1A**) led to a  $\Delta S_{\text{conf}}$  of 2.03  $R$ . This means, according to definition,  $\text{Li}_{6.5}[\text{P}_{0.25}\text{Si}_{0.25}\text{Ge}_{0.25}\text{Sb}_{0.25}]\text{S}_5\text{I}$  is a true HEM. Electron microscopy studies further confirmed uniform elemental distribution on the micrometer level (**Figure 1B**).



**Figure 1. High-entropy argyrodite lithium superionic conductors for solid-state batteries: Results from structural characterization and electron microscopy.**

(A) Different tetrahedral motifs in the crystal structure result in cation disorder, while  $\text{S}^{2-}/\text{I}^-$  site inversion induces anion disorder, leading to a high-configurational-entropy electrolyte material.

(B) Uniform elemental distribution on the micrometer length scale as shown by energy-dispersive X-ray spectroscopy mapping.

(A) and (B) are reprinted and/or adapted from Lin *et al.*<sup>6</sup>

Investigations into the transport properties by temperature-dependent electrochemical impedance spectroscopy and  $^7\text{Li}$  pulsed field gradient nuclear magnetic resonance spectroscopy revealed a high lithium diffusivity of  $\sim 7 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$  at  $30 \text{ }^\circ\text{C}$  ( $\sigma_{\text{ion,rt}} \approx 13 \text{ mS/cm}$ ) and low activation energy ( $E_{\text{A}}$ ) for lithium transport of  $\sim 0.2 \text{ eV}$ . These results suggest that introducing compositional disorder into the argyrodite structure or, in other words, achieving high configurational entropy may help in increasing ion mobility. Of note, it has been shown that anion disorder alone has no profound effect on the  $\sigma_{\text{ion}}$ , however lowers the  $E_{\text{A}}$ .<sup>10</sup> Overall, it appears that low activation energy for conduction is a key feature of  $\text{Li}_6\text{PS}_5\text{X}$ -based high-entropy solid electrolytes, presumably originating in part from lattice softening with increasing complexity.

The material was also tested in solid-state batteries with a Ni-rich layered oxide cathode ( $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$ ). Using X-ray photoelectron spectroscopy, the authors identified elemental constituents that are detrimental to the electrochemical stability. In particular, antimony and sulfur were found to undergo (irreversible) redox reactions during cycling, while silicon and germanium showed some susceptibility to oxygenation.

Taken together, Lin *et al.* showed that high-entropy versions of superionic lithium argyrodites can be readily produced by mechanical milling and post annealing, allowing the exploration of a large chemical parameter space and the tailoring of properties through compositional design. This is important for practical applications and may further provide insight into how configurational entropy affects ion mobility. Apart from the  $\Delta S_{\text{conf}}$ , lattice distortions and chemical environment effects are known to directly affect the lattice dynamics and therefore the vibrational entropy ( $\Delta S_{\text{vib}}$ ). The resulting energy landscape for ion transport may ultimately lead to increased conductivity and decreased activation energy. However, whether or not compositional complexity offers real benefits over conventional doping/substitution and defect engineering strategies and high-entropy solid electrolytes can compete with the best existing materials remains to be seen. Nevertheless, the vast chemical space available for discovery of novel solid electrolytes with enhanced conductivity and stability makes the HEMs concept very appealing from a broader perspective.

## Declaration of Interests

The authors declare the following competing interest(s): A patent was filed for this work through BASF SE and the Karlsruher Institut für Technologie (KIT).

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