

All-solid-state batteries (ASSBs) represent a promising advancement in electrochemical energy storage, with solid electrolytes (SEs) playing a crucial role. Sulfide and halide SEs have garnered substantial interest due to their distinct characteristics; sulfide SEs offer high ionic conductivity and stability with Li metal anodes, while halide SEs have better compatibility with high-voltage cathodes. This dissertation explores the structure-property relationship of mixed-anion frameworks in both sulfide- and halide-based SEs, aiming to fine-tune material structures and properties for enhanced battery performance.

Firstly, we delve into the transformation of  $\text{Li}_3\text{PS}_4$  via the introduction of  $\text{LiBr}$ .  $^{31}\text{P}$  NMR unveils the emergence of a glassy  $\text{PS}_4^{3-}$  network interspersed with  $\text{Br}^-$ . Solid-state NMR corroborates fast  $\text{Li}^+$  migration between  $\text{PS}_4^{3-}$  and  $\text{Br}^-$ , with increased  $\text{Li}^+$  mobility. A more than four-fold enhancement in ionic conductivity is observed upon  $\text{LiBr}$  incorporation ( $1.06 \text{ mS cm}^{-1}$ ) into  $\text{Li}_3\text{PS}_4$  ( $0.23 \text{ mS cm}^{-1}$ ) resulting from the reduction of the energy barrier and transitioning  $\text{Li}^+$  transport dimensionality from 2D to 3D. The compatibility of  $\text{Li}_3\text{PS}_4$  with Li metal is improved alongside an increase in critical current density (CCD) from  $0.34 \text{ mA cm}^{-2}$  to  $0.50 \text{ mA cm}^{-2}$  while preserving the electrochemical stability window. ASSB cells with  $3\text{Li}_3\text{PS}_4:\text{LiBr}$  as the SE and  $\text{TiS}_2$  as the cathode active material (CAM) show robust high-rate and long-term cycling performance.

Secondly, we incorporated  $\text{LiBr}$  and  $\text{LiI}$  simultaneously in  $\text{Li}_3\text{PS}_4$  as a mixed-halide strategy. We achieve a two-fold increase in conductivity using a one-step ball milling technique. Subsequent low-temperature sintering further enhances conductivity to  $4.43 \text{ mS/cm}$  with a low activation energy of  $0.29 \text{ eV}$ . Furthermore, we engineered a cell configuration with stable milled SE layers toward Li metal and a high-conductive sintered SE separator in the symmetric cell with which CCD further increases compared to individual separators.

In addition to sulfide-based SEs, Li-deficient lithium yttrium bromide,  $\text{Li}_{3-x}\text{YBr}_{6-x}$ , was prepared using the co-melting method. High-resolution X-ray diffraction and Rietveld refinement confirm the formation of the monoclinic structure with the  $C2/m$  space group with increased cation site disorder and polyhedral volume. Bond valence site energy calculations show the  $\text{Li}^+$  migration energy barrier from Li-deficiency. Ab-initio molecular dynamics simulations show the emergence of 3D- $\text{Li}^+$  conduction. Solid-state NMR spectroscopy confirms the elimination of  $\text{LiBr}$  impurities and reveals increased Li-ion dynamics. An ionic conductivity of  $4.49 \text{ mS cm}^{-1}$  and activation energy of  $0.28 \text{ eV}$  were achieved.

Furthermore, we synthesized a series of  $\text{Li}_{2.73}\text{Ho}_{1.09}\text{Cl}_{6-x}\text{Br}_x$  compounds using a solid-state co-melting approach. Crystal structure analysis revealed the presence of Li-ions in 2d octahedral sites of the  $C2/m$  space group for  $x \geq 2$ . Analysis shows highly disordered cation sites with mixed occupancy of Li/Ho.  $^6\text{Li}$  solid-state NMR revealed a highly disordered local Li environment, which increases with Br/Cl substitution. The significant improvement in room-temperature ionic conductivity from  $0.45 \text{ mS cm}^{-1}$  for  $\text{Li}_{2.73}\text{Ho}_{1.09}\text{Cl}_6$  to  $3.79 \text{ mS cm}^{-1}$  for  $\text{Li}_{2.73}\text{Ho}_{1.09}\text{Cl}_{3.27}\text{Br}_{2.73}$  is achieved with a significant decrease in activation energy from  $0.38 \text{ eV}$  to  $0.32 \text{ eV}$ , respectively.

Further mixing anions and cations within a SE significantly enhances ionic conductivity by introducing controlled disorder at both cation and anion sites. This increases the system's configurational entropy and allows for the overlap of energy bands. Incorporating  $\text{Mg}^{2+}$  and  $\text{Hf}^{4+}$  into a  $\text{Li}_3\text{ClBrI}$  mixed-rock-salt structure results in a substantial increase in ionic conductivity, reaching  $0.88 \text{ mS cm}^{-1}$  for  $\text{Li}_{1.54}\text{Mg}_{0.23}\text{Hf}_{0.17}\text{Cl}_{0.68}\text{BrI}$ . The enhanced conductivity is attributed to a nanoscale solid solution between the disordered rock-salt and spinel structure.

Moreover, introducing a mixed anion sublattice into cost-effective  $\text{LiAlCl}_4$  through a simple one-step mechanochemical milling process led to a 22-fold increase in ionic conductivity – from  $0.0083 \text{ mS cm}^{-1}$  to  $0.18 \text{ mS cm}^{-1}$  for  $\text{Li}_2\text{AlCl}_3\text{S}$ . This improvement can be attributed to the formation of new Li sites, enabling efficient 3D  $\text{Li}^+$  transport. The strategy leverages the inherent disorder to modify the Li-sublattice locally, leading to broader lithium-ion site occupancies and enhanced ion dynamics through polyhedral edge sharing.

Mechanochemical milling of thiophosphate-based SEs combined with  $\text{TiS}_2$  CAM produces a composite material that leverages both cationic ( $\text{Ti}^{3+/4+}$ ) and anionic ( $\text{S}^{2-/n-}$ , where  $n < 2$ ) redox processes – resulting in  $\sim 2\times$  enhancement in specific capacity. Catholytes containing mixed-anion SEs, especially with  $3\text{Li}_3\text{PS}_4:\text{LiBr}$ , demonstrate better cycling performance compared to their mono-anion counterparts due to the improved ionic conductivity and thermodynamical stability.

In summary, this dissertation explores innovative compositional design, optimal synthesis environment, and characterization of mixed-anion SEs, in addition to the utilization of these SEs in ASSBs. Overall, this research provides valuable insights into the development and application of high-performance ASSBs, addressing challenges associated with SEs in energy storage.