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Polarizability-Enhanced Ionic Transport in Rare-Earth-Free Halide–Sulfide Electrolytes: $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$

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Abstract

Commercially viable all-solid-state batteries (ASSBs) rely on solid electrolytes (SEs) that combine high ionic conductivity, electrochemical stability, low cost, and scalable production. Here, we report a series of rare-earth-free solid electrolytes, $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ ($0 \leq x \leq 4$), synthesized via a rapid, energy-efficient mechanochemical route. The optimized composition, amorphous $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$, exhibits an ionic conductivity of $\sim 1.03 \text{ mS cm}^{-1}$, one order of magnitude higher than crystalline Li_2ZrCl_6 . Structural analyses (XRD, SEM/EDS, and ^6Li MAS NMR) reveal that progressive Br^- substitution drives amorphization, enhances anion polarizability, and yields dynamically disordered Li^+ environments conducive to rapid ion migration. Compared to the semi-crystalline $\text{Li}_2\text{ZrSCl}_4$ and fully brominated $\text{Li}_2\text{ZrSBr}_4$ end members, $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ achieves an optimal balance between structural disorder and diffusion-pathway connectivity, increasing the effective population of mobile Li^+ ions and promoting percolative transport, resulting in enhanced ionic conductivity. When used as a catholyte in an ASSB with TiS_2 as the cathode active material, $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ exhibits good rate capability and stable long-term cycling performance. This work highlights the viability of $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ as a high-performance and inexpensive solid electrolyte, combining fast Li-ion transport, electrochemical stability, and scalable synthesis, making it a promising candidate for commercial ASSBs.

Keywords: Solid Electrolyte, Mixed-Anion Chemistry, Solid-state NMR, Chalcogenides, Battery



Introduction

The advancement of solid-state batteries (SSBs) hinges on developing solid electrolytes (SEs) that combine high ionic conductivity, broad electrochemical stability, and cost-effectiveness.^{1,2} Traditional liquid electrolytes face inherent drawbacks such as flammability, leakage, and limited electrochemical stability, which hinder the advancement of safer and more efficient batteries.^{3,4} Halides are a promising class of SEs for the next-generation ASSBs because of their compatibility with high-voltage cathode materials.^{5,6} Despite the advantages of halide SE, achieving high Li⁺ ion conductivities-up to $\sim 10^{-3}$ S cm⁻¹ - has largely relied on the use of expensive transition and rare-earth trivalent elements, such as in materials like Li₃YCl₆, Li₃ErCl₆, Li₃HoCl₆, and Li₃InCl₆.⁷⁻¹¹ More recently, pentavalent cations such as Ta⁵⁺ and Nb⁵⁺ have been introduced in compounds like LiTaOCl₄, LiNbOCl₄, NaTaOCl₄, further expanding the compositional landscape of high-performing but costly halide SEs.¹²⁻¹⁴ While these materials often exhibit favorable electrochemical properties, the use of rare-earth metals introduces challenges related to high cost, limited global supply, and supply-chain concentration, which can hinder large-scale manufacturing and long-term commercialization of solid-state batteries. Consequently, the development of rare-earth-free halide electrolytes based on earth-abundant elements is an important strategy for improving material sustainability and economic viability.¹⁵ In contrast, Li₂ZrCl₆, a rare-earth-free alternative, has garnered increasing attention owing to its lower cost and encouraging electrochemical properties.¹⁶⁻¹⁸ However, its room temperature ionic conductivity still falls short for practical solid-state batteries,^{19,20} highlighting the need for further enhancements.

Recent efforts to enhance the performance of Zr-based halide SEs have focused on compositional and structural modifications. These approaches include cationic substitutions at the Zr⁴⁺ site in Li₂ZrCl₆ - for example, Li_{2+x}Zr_{1-x}In_xCl₆,²¹ and Li_{2.4}Zr_{0.8}Zn_{0.2}Cl₆,²² - which have been shown to improve moisture stability. Similarly, anionic substitutions, such as replacing Cl⁻ with F⁻ in Li_{2.3}ZrCl_{6.1}F_{0.2},²³ have been employed to widen the electrochemical stability window. More recently, researchers have explored dual-anion systems that retain the beneficial features of halides, such as high polarizability and structural softness, while integrating anions like oxide or sulfide to tailor the local coordination environment and facilitate Li⁺ transport.²⁴⁻²⁶ Notably, superionic conductivities around $\sim 10^{-3}$ S cm⁻¹ have been observed for Li₃ZrCl₄O_{1.5},²⁷ Li_{3.1}ZrCl_{4.9}O_{1.1},²⁸ Li₃Zr_{0.75}OCl₄,²⁹ and ZrO₂-2LiCl-Li₂ZrCl₆.³⁰ Additionally, Xu and co-workers reported a Li⁺ conductivity of 0.86 mS cm⁻¹ for Li_{2.2}ZrCl_{5.8}S_{0.2}.³¹ However, these materials require



long milling durations, LiCl precursor, and/or secondary heat treatments, posing challenges for industrial scalability. Motivated by these advancements and limitations, we sought to further expand the compositional space by developing a new series of rare-earth-free solid electrolytes, $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ ($0 \leq x \leq 4$). This system leverages a diversified anion framework and mixed halide composition, leading to improvements in ionic conductivity from scalable synthesis.

In this work, we report the synthesis of the $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ composition by directly combining Li_2S and ZrX_4 ($X = \text{Cl}$ or Br), avoiding the commonly used LiCl precursor. This approach shortens the milling time, as pre-formed LiCl is highly crystalline and less reactive. The resulting $\text{Li}_2\text{ZrSCl}_4$ (LZSC), similar to recently reported S^{2-} doped Li_2ZrCl_6 (LZC),³² exhibits glassy crystalline characteristics, with observed $P-3m1$ and $C2/m$ phases, showing a modest conductivity improvement from ~ 0.1 in LZC to $\sim 0.45 \text{ mS cm}^{-1}$ in LZSC, accompanied by a substantial reduction in activation energy from ~ 0.41 to ~ 0.37 eV, highlighting sulfur's role in softening the anion framework and lowering the Li^+ migration barriers. Further Br^- substitution promotes amorphization and increases lattice softness through enhanced anion polarizability, yielding the optimized composition $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ (LZSCB), which reaches $\sim 1.03 \text{ mS cm}^{-1}$ at room temperature. While the activation energy remains nearly constant across the series (~ 0.36 - 0.37 eV), the conductivity enhancement arises from an increased pre-exponential factor associated with a larger population of mobile Li^+ ions and improved percolative transport pathways, whereas the fully Br-substituted end member, $\text{Li}_2\text{ZrSBr}_4$ (LZSB), shows reduced conductivity due to excessive disorder. Importantly, the amorphous $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ material can be synthesized through a single-step 2-hour mechanochemical process, offering a practical and scalable route for industrial production. To gain deeper insight into the structure, composition, and surface morphology, a suite of characterization techniques - including NMR, XRD, SEM, EDS, and Raman spectroscopy - was utilized. As a catholyte in an ASSB comprising TiS_2 as cathode active material, $\text{Li}_6\text{PS}_5\text{Cl}$ separator, and Li/In alloy anode, LZSCB demonstrates a good RT cycling performance with 94% capacity retention (248 mAh g^{-1}) over 70 cycles at 0.2 C. Our findings highlight LZSCB with remarkable conductivity, stability, and ease of production with low cost, positioning it for applications in commercially viable ASSB technologies.



Materials & Methods

Synthesis. Lithium sulfide (99.5%, Alfa Aesar), ZrCl_4 (99.9%, Alfa Aesar), and ZrBr_4 (99.9%, Alfa Aesar) were stored in an argon-filled glovebox (VTI) with moisture and O_2 levels below 0.1 ppm. Subsequently, a stoichiometric amount of the starting precursors was manually ground for 15 min to achieve a homogeneous powder. The ground powder was subsequently loaded into a 20 mL zirconia milling jar with three 10 mm-sized zirconia balls, and vacuum sealed within the argon-filled glovebox. The sealed jar was placed in a High-Energy Ball Mill (8000M Mixer/Mill®) and milled for 2 hrs. The processed sample was thereafter stored in the argon-filled glovebox for further characterization.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). The samples were mounted on aluminum stubs using carbon tape to ensure electrical conductivity during SEM analysis. SEM imaging was conducted using a JEOL JSM-7000F microscope operated at an accelerating voltage of 15 kV. Prior to imaging, samples were sputter-coated with a thin layer of iridium to minimize charging effects. EDS analysis was performed in conjunction with SEM to determine the elemental composition of the samples. EDS spectra were collected and analyzed using an Oxford Instruments X-Max detector and Aztec software to quantify the elemental distribution across different regions of the samples. The working distance was maintained at 10 mm to optimize both imaging resolution and EDS signal detection.

Solid-State NMR. ^6Li and ^7Li solid-state NMR spectra were acquired using a Bruker Avance III system equipped with a 500 MHz (11.74 T) Ultrashield wide-bore magnet (89 mm). The Larmor frequencies were 73.6 MHz for ^6Li and 194.4 MHz for ^7Li . Samples were sealed in 2.5 mm zirconia rotors under an argon atmosphere and measured under magic angle spinning at 24 kHz. Single pulse ^6Li and ^7Li NMR experiments were performed with a $\pi/2$ pulse length of 3.3 μs and recycle delays of 200 s and 20 s, respectively. To study the ion dynamics in $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$, the inversion-recovery approach was employed to measure ^7Li T_1 NMR relaxation times at variable temperatures. The T_1 experiments were performed on a 300 MHz spectrometer operating at the ^7Li Larmor frequency of ~ 116 MHz, with chemical shift calibration against $\text{LiCl}_{(\text{s})}$ at -1.1 ppm. ^{35}Cl and ^{79}Br NMR experiments were performed using an 800-MHz Bruker spectrometer with a field strength of 19.6 T. The Larmor frequencies for ^{35}Cl and ^{79}Br were 208.3 MHz and 40 MHz,



respectively. A single-pulse sequence was used for both ^{35}Cl and ^{79}Br experiments with a $\pi/2$ pulse length of 5.6 μs and 2.2 μs each and a recycle delay of 10 s and 5 s, respectively. Sample powders were packed under argon into 3.2 mm ZrO_2 pencil rotors and spun at 16 or 17 kHz. ^{35}Cl experiments were calibrated to a 0.1 M NaCl in D_2O solution at 0 ppm. ^{79}Br NMR experiments were calibrated to solid KBr at 54.5 ppm.

Raman Spectroscopy. Raman spectra were collected on a Horiba JY LabRam HR Evolution spectrometer using a 532 nm excitation laser and a 600 g mm^{-1} grating. Spectra were acquired over the 100 -1000 cm^{-1} range with a laser power of 20 mW and an integration time of 4 seconds. The resulting data were processed using LabSpec 6 software.

Electrochemical Impedance Spectroscopy (EIS). The processed sample was hand-ground and pressed, 300 MPa, in an 8 mm diameter PEEK mold to make a ~ 0.8 mm thick pellet for AC impedance measurements. The pellet was assembled in a split cell with steel as the blocking electrode. The electrochemical impedance measurements were carried out using a Gamry electrochemical analyzer, spanning frequencies from 5 MHz to 1 Hz, with an applied voltage of 10 mV. Ionic conductivities were calculated from the impedance values extracted from the Nyquist plots and pellet dimensions. A CSZ Microclimate chamber was used to perform impedance measurements across a range of temperatures from -20 to 60 $^\circ\text{C}$. Electronic conductivity was evaluated using DC polarization in a symmetric steel || $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ || steel configuration. Steady-state currents were recorded at applied voltages of 100, 200, 300, and 400 mV.

Lab X-ray Diffraction. The sample was sealed on a zero-background holder using Kapton film and analyzed using a Rigaku SmartLab X-ray diffractometer equipped with a Cu $\text{K}\alpha$ radiation source ($\lambda = 0.154$ nm) in Bragg–Brentano geometry. Diffraction data were collected over a 2θ range of 10° to 70° , with a step size of 0.03° and a scan rate of $1.5^\circ/\text{min}$.

Linear Sweep Voltammetry (LSV) measurements. Approximately 150 mg of $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ was weighed into a 10 mm diameter polyether ether ketone (PEEK) cylinder and pressed at 250 MPa for 1 min. A composite with a mass ratio of 9:1 of $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ to carbon nanofiber was hand-ground in an agate mortar for 15 minutes. An 8 mg portion of this composite was spread over one side of the $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ pellet, contained in the PEEK cylinder, to serve as the working electrode, and pressed at 350 MPa for 1 minute. Indium foil (~ 7.9 mm diameter) and lithium foil (~ 4.8 mm diameter), both with a thickness of 0.1 mm, were hand-pressed onto the opposite side of the pellet.



The cell was then placed into a stainless-steel casing with a constant pressure of 250 MPa. The LSV measurement was performed with a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$ using a BioLogic SP-300.

Assembly of the All-Solid-State Battery. All-solid-state battery (ASSB) half-cells were assembled in custom-made 10 mm diameter stainless-steel cells, using stainless-steel plungers as current collectors. All cell preparation and handling were performed in an Ar-filled glovebox with H_2O and O_2 levels below 0.1 ppm. The composite catholyte was prepared by ball milling TiS_2 powder (Sigma-Aldrich, 99.9%) with the synthesized $\text{Li}_2\text{ZrSCL}_{4-x}\text{Br}_x$ electrolyte in a 1:2 weight ratio (TiS_2 :SE) for 30 min. Approximately 12 mg of the catholyte mixture was uniformly distributed onto one side of the separator pellet, corresponding to an areal capacity of approximately 1.22 mAh cm^{-2} , and compacted at 300 MPa for 10 s to ensure intimate interfacial contact. The separator consisted of a $\sim 100 \text{ mg}$ $\text{Li}_6\text{PS}_5\text{Cl}$ pellet, prepared following previously reported procedures,³³ and pressed at 300 MPa for 10 s. On the opposite side of the separator, a 7.9-mm-diameter indium foil was placed directly in contact with the pellet, followed by a 4.8-mm-diameter lithium foil ($\sim 1 \text{ mg}$) to form the Li–In alloy anode in situ. The assembled cell was sealed with vacuum grease to prevent air exposure. Electrochemical testing was conducted at room temperature under a constant stack pressure of $\sim 35 \text{ MPa}$. Galvanostatic charge–discharge measurements were performed over a voltage window of 1.0–2.5 V vs. Li–In at various C-rates, where 1C was defined based on the theoretical capacity of TiS_2 (239 mAh g^{-1}).

Results & Discussions

Average Structure and Morphology

The X-ray diffraction patterns for the as-milled $\text{Li}_2\text{ZrSCL}_{4-x}\text{Br}_x$ ($x = 0, 2.0, 2.7,$ and 4.0) and Li_2ZrCl_6 reveal a clear structural evolution with increasing Br content, shown in Figure 1a. For $x = 0$ (LZSC), the pattern indexes to a two-phase mixture comprising a trigonal $P-3m1$ polymorph and a monoclinic $C2/m$ polymorph. A transition from Li_2ZrCl_6 , which typically crystallizes in the trigonal phase.^{15,30} The corresponding Rietveld refinement plot, in Figure 1b and Tables S1 and S2, confirms the coexistence of these two phases, with good agreement between the observed and calculated patterns.



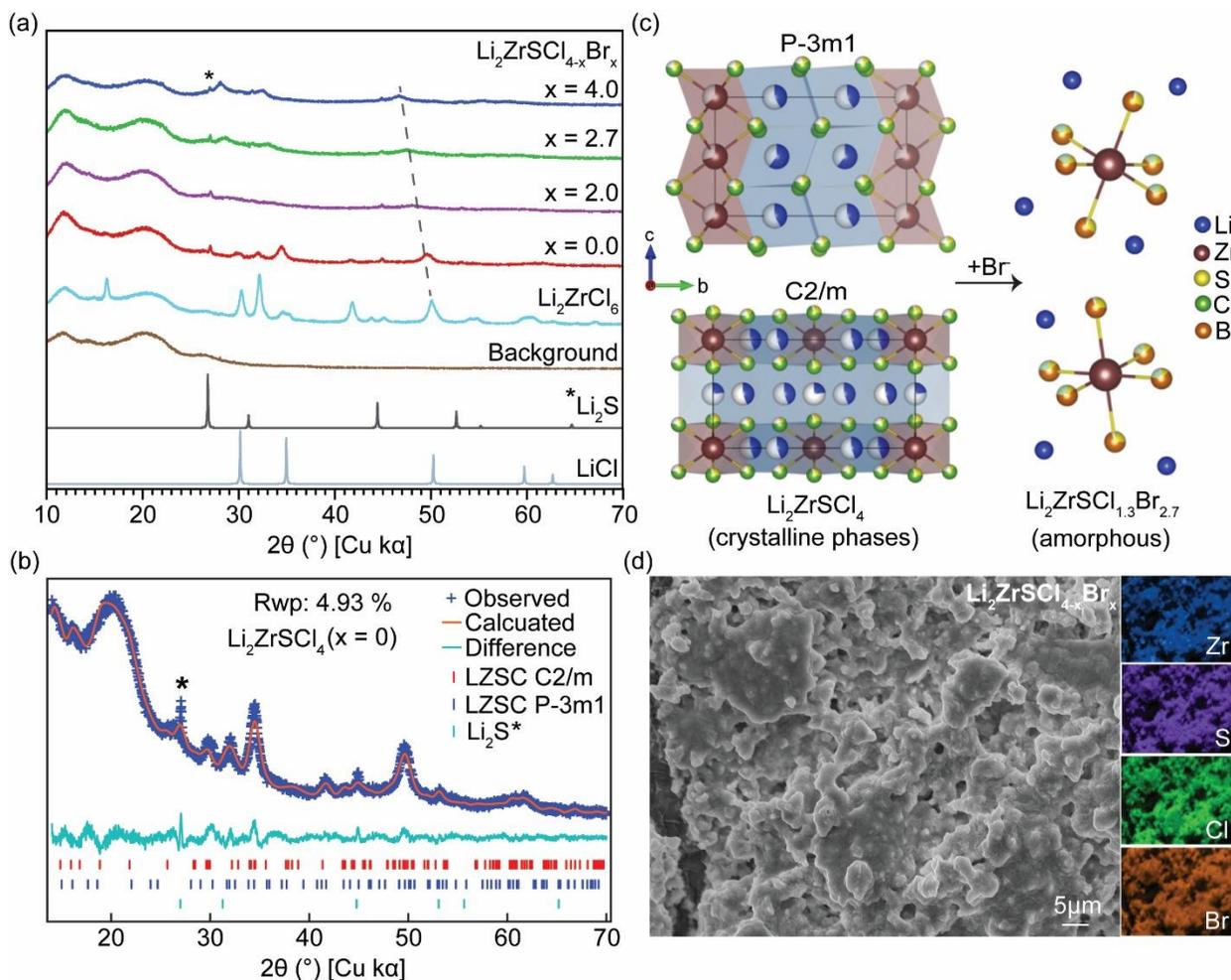


Figure 1: Structural evolution and morphology of $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ ($0 \leq x \leq 4$) (a) Powder X-ray diffraction of $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ showing progressive peak shifts (dashed line), peak broadening, and intensity loss with increasing Br^- content. (b) Rietveld refinement of $\text{Li}_2\text{ZrSCl}_4$ ($x = 0$), confirming a biphasic structure comprising trigonal $P\bar{3}m1$ and monoclinic $C2/m$ phases. (c) Crystal structure models of the $P\bar{3}m1$ and $C2/m$ polymorphs of $\text{Li}_2\text{ZrSCl}_4$ and schematic representation of the structural evolution upon Br^- substitution, leading to an amorphous $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ network (d) SEM micrograph and corresponding EDS elemental maps showing uniform distribution of Zr, S, Cl, and Br in $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$.

The refined structural models for both polymorphs are illustrated in Figure 1c, featuring the layered trigonal and monoclinic frameworks of LZSC and the transition toward an amorphous configuration upon partial substitution of Cl^- by the larger Br^- anion. This transition is evident in



the diffraction patterns in Figure 1a, where the Bragg peaks broaden, diminish in intensity, and shift toward lower 2θ ($\sim 35^\circ$, 50°), consistent with lattice expansion induced by Br⁻ addition. At higher substitution levels ($x = 2.0, 2.7, 4.0$), as in $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$, the diffraction pattern becomes increasingly featureless, with broad humps replacing sharp Bragg peaks. This behavior indicates extensive amorphization and collapse of the long-range crystalline order, Figure 1c, while short-range structural motifs are retained. The low-intensity peak at $\sim 27^\circ$ is likely associated with the Li_2S secondary phases.

Figure 1d shows a scanning electron microscopy (SEM) image of the LZSCB sample (see Figure S1 for LZSC), revealing uniform particle agglomeration and a smooth surface texture, features characteristic of an amorphous material. No evidence of crystalline domains or phase separation was observed, indicating structural homogeneity. Energy dispersive X-ray spectroscopy (EDS) mapping (also in Figure 1d) confirmed the even distribution of constituent elements - Zr, S, Cl, and Br - throughout the sample. As expected, lithium was not detected due to EDS limitations in detecting low-atomic-number elements. To address this, nuclear magnetic resonance (NMR) was employed, offering better sensitivity for detecting and quantifying light elements such as lithium.

Local Structural Analysis

A comparison of the ^6Li MAS NMR spectra of LZSC and LZSCB is shown in Figure 2a. The ^6Li MAS NMR spectrum of LZSC shows two resonances at -0.68 and -0.54 ppm, consistent with the coexistence of trigonal and monoclinic phases identified by XRD (Figure 1). The signal at -0.68 ppm (blue) likely corresponds to the more ordered trigonal phase, while the downfield resonance, -0.54 ppm, arises from Li environments in the less symmetric monoclinic lattice.

For LZSCB, only one broad isotropic resonance is observed, centered around -0.54 ppm. The line width increases from ~ 19.7 Hz in LZSC to 26.9 Hz in LZSCB, reflecting a more homogeneous distribution of local Li environments. The increased chemical shift dispersion with Br⁻ incorporation indicates increased structural disorder introduced by Br⁻ substitution, which broadens the range of Li-anion coordination environments and results in the wider ^6Li peak observed for LZSCB. This is also consistent with the extensive amorphization observed in the XRD patterns. Li_2S impurity phases are observed in both samples at ~ 2.4 ppm, these could result from unreacted precursors. This residual Li_2S is also detected as a secondary impurity by XRD, evidenced by weak diffraction features. Owing to the highly disordered or partially amorphous



nature of the $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ framework, quantitative phase analysis based on XRD is inherently uncertain, as peak broadening and overlap can influence refined weight fractions. ^6Li MAS NMR directly probes Li speciation and provides a more reliable estimate of the Li_2S content in this system. Using a long recycle delay (200 s), the integrated ^6Li NMR signal indicates that $\sim 17\%$ of Li environments in LZSCB correspond to Li_2S , a molar ratio of $\text{Li}_2\text{S}/\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ of $\sim 1/5$, which converts to an estimated ~ 2.3 wt% Li_2S due to the large molar-mass difference between Li_2S and the main phase,¹⁴ indicating that Li_2S is present as only a minor impurity. Similarly, a ~ 3.6 wt % Li_2S is observed for LZSC. A summary of the NMR-based phase quantifications is provided in the Supporting Information (Table S3).

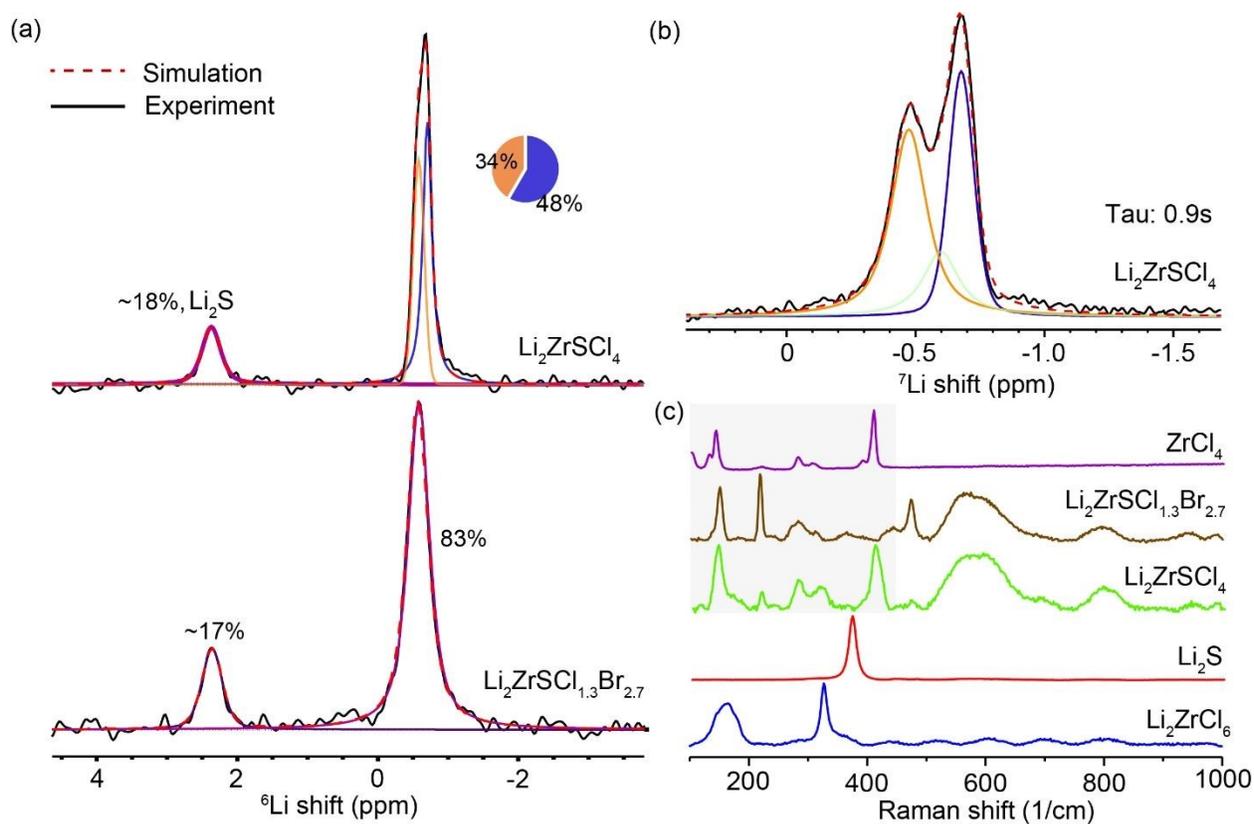


Figure 2. Local structural environment analysis of Li^+ ions (a) ^6Li MAS NMR spectra of $\text{Li}_2\text{ZrSCl}_4$ and $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$. (b) Select ^7Li MAS NMR spectrum obtained from inversion recovery experiments showing the different relaxation behavior of the Li sites; the full series of inversion-recovery spectra is shown in the Supporting Information, Figure S2. (c) Raman Spectra of $\text{Li}_2\text{ZrSCl}_4$ and $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ compared to related structures.



To better resolve different Li sites observed in LZSC, the T_1 -edited ^7Li MAS NMR spectrum is shown in Figure 2b and S2, which is obtained from spin-lattice inversion recovery experiments at a recovery time of 0.9 s after inversion. Li^+ sites with varied ion dynamics will exhibit different T_1 relaxation behavior and thus show different recovery rates to their equilibrium states. At an intermediate relaxation time shorter than 20 s, e.g., 0.9 s, the enlarged difference in intensity can help better resolve different components in the ^7Li NMR spectrum. Figure 2b reveals three Li^+ sites in LZSC with slightly different T_1 relaxation times, indicating a heterogeneous local environment of Li^+ and slow exchange among these lithium sites. Whereas LZSCB shows a symmetric NMR peak, well described by a single-component fit, suggesting a more homogeneous distribution of Li sites or fast chemical exchange among different Li sites, characteristic of fast ion conductors.³⁴

The Raman spectra of the $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ series, presented in Figure 2c, confirm the presence of distorted ZrX_6 ($X = \text{Cl}, \text{Br}, \text{S}$) octahedra as the base structural motifs,³⁵ with broad, overlapping bands indicating an amorphous, disordered lattice. Compared to sharp peaks in reference compounds (ZrCl_4 , Li_2S , Li_2ZrCl_6), the LZSC and LZSCB spectra show more peaks from the Zr-Cl/Br/S bending and stretching modes and significant broadening of these peaks due to variations in bond lengths and angles contributing to complex vibrational dynamics. The broad peaks at $> 500 \text{ cm}^{-1}$ are likely to originate from Zr-S stretching vibrations in distorted or mixed-ligand octahedra such as $\text{ZrSCl}_{4-x}\text{Br}_x$. Additionally, the absence of the Li_2S peak at $\sim 370 \text{ cm}^{-1}$ confirms sulfur incorporation into the framework.³¹

Anion substructure

Anionic local structures in $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ were directly probed using ^{35}Cl (spin-3/2) and ^{79}Br (spin-3/2) MAS NMR spectroscopy (Figure 3). ^{35}Cl is a spin-3/2 quadrupolar nucleus, which makes its NMR behavior highly sensitive to local symmetry and electric field gradients (EFGs) around Cl^- ions. The ^{35}Cl MAS NMR of LZSC shows a sharp resonance at 9.6 ppm, suggesting a relatively symmetric local environment. The slight asymmetry is from 2nd-order quadrupolar effects. The ^{35}Cl NMR spectrum of LZSCB (Figure 3a) exhibits an upfield shift (isotropic peak at 2.5 ppm) along with a broad (610 Hz), asymmetric lineshape, indicating increased site asymmetry and disorder from Br^- substitution in the LZSCB structure.



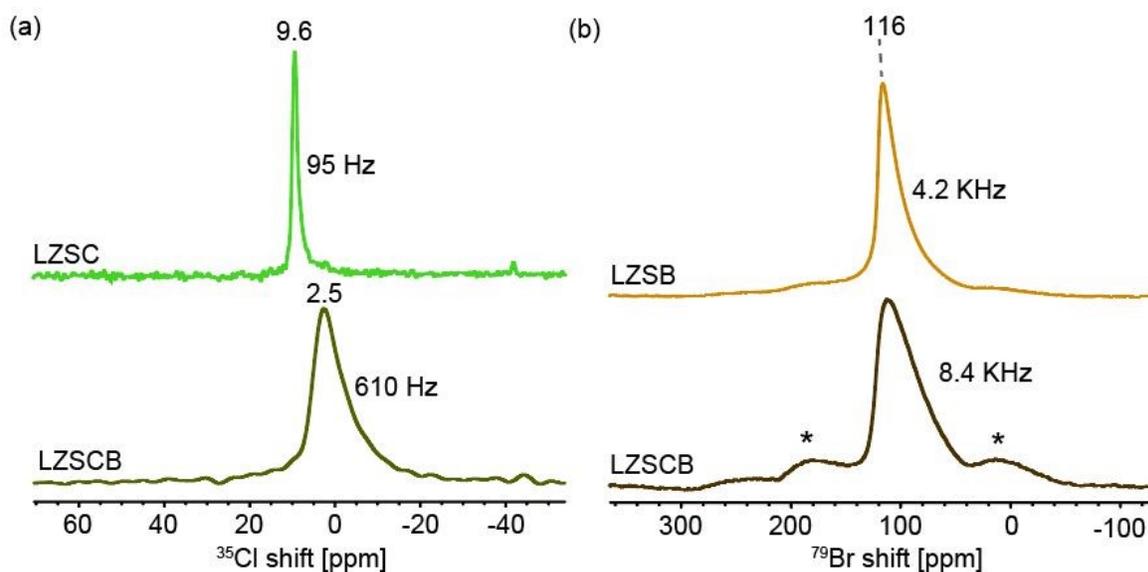


Figure 3: Halide local environments in $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ probed with NMR (a) ^{35}Cl MAS NMR spectra of $\text{Li}_2\text{ZrSCl}_4$ and $\text{Li}_2\text{ZrSCl}_{1.3}\text{B}_{2.7}$ (b) ^{79}Br MAS NMR spectra of $\text{Li}_2\text{ZrSBr}_4$ and $\text{Li}_2\text{ZrSCl}_{1.3}\text{B}_{2.7}$.

^{79}Br is a quadrupolar nucleus with spin $3/2$, much like ^{35}Cl , but with a larger quadrupolar moment, thus more sensitive to local structural distortion and symmetry. The ^{79}Br MAS NMR spectra of $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ further reveal the impact of halide substitution on the local structure (Figure 3b). Both LZSB and LZSCB display broad resonances in the order of several kHz, characteristic of moderate quadrupolar interactions. In LZSB, a relatively broad (4.2 kHz) isotropic peak is observed at 116 ppm, while in LZSCB, the resonance becomes even broader (8.4 kHz), suggesting a higher degree of local structural disorder and the presence of mixed halide environments.

Ion Dynamics probed with T_1 NMR relaxation time measurements

To probe Li^+ dynamics in $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$, ^7Li T_1 NMR relaxation times were measured across a temperature range of 25 to 85°C using the inversion recovery method under static conditions, as shown in Figure 4a. LZSC shows a relatively large T_1 across the temperature range, 1.35 s at 25°C, indicating slower Li^+ dynamics. LZSCB, on the other hand, shows shorter T_1 values (starting at ~0.37 s at 25 °C, decreasing to ~0.15 s at 85 °C), suggesting faster Li^+ motion in the Br substituted material.



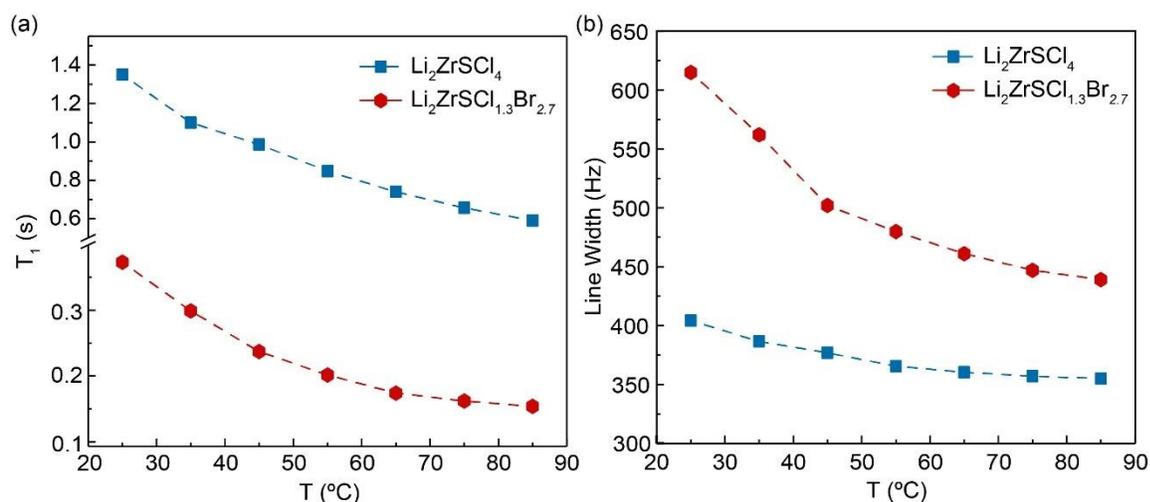


Figure 4: (a) Variable-temperature ${}^7\text{Li}$ static T_1 relaxation times for $\text{Li}_2\text{ZrSCl}_4$ and $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ (b) Linewidth narrowing of the ${}^7\text{Li}$ static NMR spectra with increasing temperature, due to increased motion.

According to the Bloembergen-Purcell-Pound (BPP) theory³⁶ presented in equation (1), T_1 is dependent on the correlation time τ_c of ionic motion.

$$\frac{1}{T_1} = \frac{3\mu_0^2\gamma^4\hbar^2}{10r_0^6} \left[\frac{\tau_c}{1 + (\omega_0\tau_c)^2} + \frac{4\tau_c}{1 + 4(\omega_0\tau_c)^2} \right] \quad (1)$$

Where τ_c denotes the average residence time between consecutive Li^+ ions hops, ω_0 is the Larmor frequency, γ is the magnetogyric ratio, μ_0 is the magnetic permeability of free space, \hbar is the reduced Planck constant, and r_0 is the interatomic distance.

In the slow-motion regime, wherein $\omega_0\tau_c \gg 1$, increasing temperature leads to faster motion and shorter T_1 time due to the correlation time (τ_c) of the molecular motions approaching the Larmor frequency (ω_0). Both systems operate in the slow or intermediate motion regime, but LZSCB exhibits faster ion dynamics than LZSC, as indicated by the consistently lower T_1 values across the temperature window. Linewidth decreases with temperature in both samples (Figure 4b), indicating dynamic averaging of dipolar interactions as lithium mobility increases. LZSCB generally shows broader lines (~ 620 Hz at RT) compared to LZSC (~ 400 Hz), in agreement with increased structural or anionic disorder. However, the steeper line width decrease with temperature in LZSCB suggests greater Li^+ mobility, consistent with the conclusion drawn from ${}^7\text{Li}$ T_1 NMR relaxation time measurements.



Ion transport properties determined with EIS

Figure 5a displays the Nyquist plot and the corresponding equivalent circuit fit (inset) for the SEs at room temperature. The data were modeled using an equivalent circuit composed of two resistor–constant phase element (R||CPE) pairs in series with an additional CPE, accounting for total ionic transport and electrode interface contributions. Attempts to deconvolute bulk and grain boundary resistances, even at low temperatures (-20 °C; Figure S3), were unsuccessful; thus, the extracted values represent total ionic conductivity.³⁷ Among the compositions studied, the LZSCB exhibits the highest ionic conductivity of $\sim 1.03 \text{ mS cm}^{-1}$, a nearly tenfold increase compared to LZC, which shows a conductivity of 0.1 mS cm^{-1} . The intermediate composition $\text{Li}_2\text{ZrSCl}_2\text{Br}_2$ (LZSCB2) shows an intermediate ionic conductivity of $\sim 0.57 \text{ mS cm}^{-1}$, while the end members LZSC and LZSB exhibit lower conductivities of 0.45 and 0.43 mS cm^{-1} , respectively (Figure 5c, Table S4). To further investigate the transport behavior, variable-temperature (VT) impedance spectroscopy was performed (Figure S3). The resulting Arrhenius plots (Figures 5b and S4) show a linear dependence of conductivity on inverse temperature across the entire range, indicating the absence of phase transitions or thermal degradation. Activation energies extracted from the slopes of the Arrhenius plots were 0.41 eV (LZC), 0.37 eV (LZSC), 0.36 eV (LZSCB), 0.36 eV (LZSCB2), and 0.37 eV (LZSB).

LZC exhibits a relatively high activation energy ($\sim 0.41 \text{ eV}$) and low ionic conductivity ($\sim 0.1 \text{ mS cm}^{-1}$), indicating strongly hindered Li^+ migration. Upon sulfur incorporation, the activation energy decreases to $\sim 0.36\text{--}0.37 \text{ eV}$ across the $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ series, confirming that sulfur introduces a softer, more polarized anion lattice that fundamentally lowers the intrinsic migration barrier. In comparison, Br^- substitution has little effect on the activation energy but further enhances lattice softness and promotes increased amorphization and dynamic disorder, strongly influencing ionic conductivity through changes in the pre-exponential factor, which increases systematically and reaches a maximum for LZSCB (Table S4).³⁸ This trend indicates that the conductivity enhancement is driven primarily by an increased fraction of mobile Li^+ ions, and improved percolative transport connectivity rather than further barrier lowering. This correlates with the enhanced Li^+ dynamics observed in the $^7\text{Li T}_1$ NMR measurements.

The superior performance of LZSCB relative to LZSC and LZSB arises from an optimal balance between structural disorder, anion polarizability, and lattice dynamics.³⁹ Although LZSCB is largely amorphous, Li^+ transport is governed by short-range interactions rather than long-range



order. In the more crystalline LZSC, Li^+ migration is partially hindered by the residual crystalline domains and stronger Li-Cl interactions, which create deeper potential wells and limited site connectivity. Partial substitution of Cl^- with the larger, more polarizable Br^- in LZSCB further softens the anion framework, introduces intrinsic structural frustration within the disordered matrix, and increases the local free volume, as evidenced by lattice expansion and increased disorder in XRD (Figure 1a). These effects enhance Li^+ site accessibility, weaken electrostatic interactions, and likely couple to low-frequency anion motions that promote dynamic Li^+ hopping.^{24,40–44}

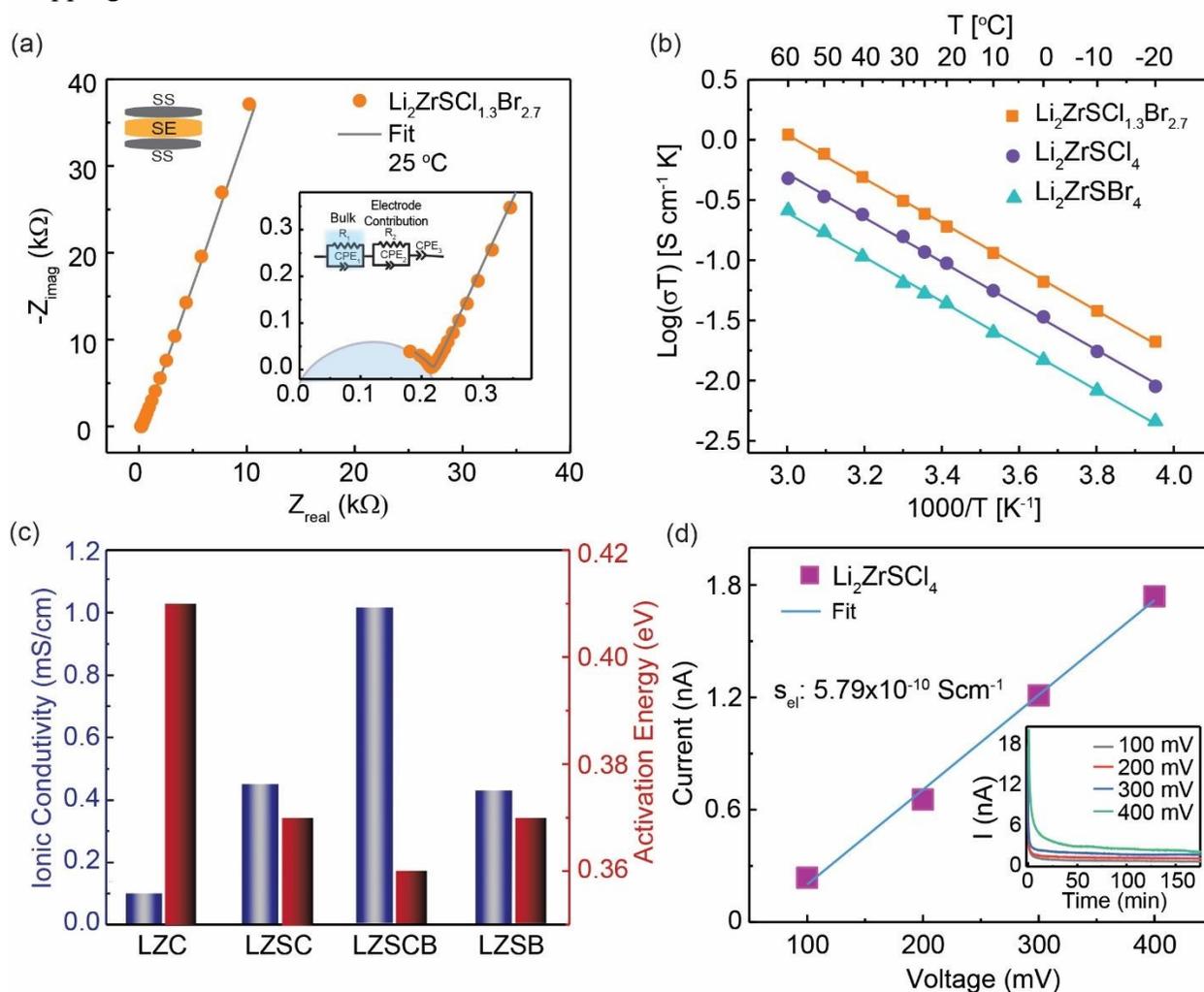


Figure 5: Charge transport properties of $\text{Li}_2\text{ZrSCL}_{4-x}\text{Br}_x$ ($0 \leq x \leq 4$) determined with AC electrochemical impedance spectroscopy and DC polarizations. (a) Representative Nyquist plot and corresponding equivalent circuit fitting at 25 °C for $\text{Li}_2\text{ZrSCL}_{1.3}\text{Br}_{2.7}$ (b) Arrhenius-type plot for the series (c) Chart showing the comparative ionic conductivity and activation energy for Li_2ZrCl_6



and $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ (d) Plots from DC polarization measurements to determine the electronic conductivity.

In contrast, the fully Br-substituted LZSB, though highly polarizable, becomes excessively disordered, disrupting the percolation of Li^+ pathways and leading to a saturation of conductivity. While partial Br substitution enhances ionic transport relative to the Cl-rich end member, the $x = 2$ composition (LZSCB2) does not reach the conductivity of the optimized electrolyte, demonstrating that compositional tuning beyond simple Br addition is required to achieve optimal transport behavior. Accordingly, LZSCB ($x = 2.7$) achieves superior Li^+ transport by maintaining sufficient amorphization and optimal anion softness^{39,45,46} while preserving a connected diffusion network, representing the “sweet spot” between order and disorder.

The pressure dependence of ionic conductivity was evaluated under varying stack pressures, as shown in Figure S5. Ionic conductivity increases with applied pressure due to improved particle-particle contact and reduced interfacial resistance,⁴⁷ and then plateaus at $\sim 1.02 \text{ mS cm}^{-1}$ between 35 and 40 MPa, with no further enhancement at higher pressures. Furthermore, electronic conductivity measurements (Figure 5d, S6, and S7) show very low values ($\sim 10^{-9} - 10^{-10} \text{ S cm}^{-1}$) across the $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ series, confirming that the total measured conductivity is dominated by ionic transport. Notably, Li_2S is a poor Li^+ conductor at room temperature⁴⁸ and, given its low volume fraction, has a negligible influence on ionic conductivity, which is dominated by the $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ framework.

Electrochemical Stability and Half-Cell Cycling

The electrochemical stability window (ESW) of the compounds was assessed using linear sweep voltammetry (LSV), shown in Figure S8. In the Li-In|SE|SE-C setup used for this measurement, the solid electrolyte ($\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$) was positioned between a Li-In alloy anode and a composite cathode consisting of carbon and the SE. Li-In alloy was used as the working electrode in the LSV measurements to minimize interfacial instability and enable a reliable assessment of the electrolyte's intrinsic electrochemical stability. Compared to pure Li metal, Li-In forms a less reactive interface with solid electrolytes, suppressing parasitic reactions and interphase growth that can otherwise dominate the LSV response.⁴⁹ The LSV results reveal that $\text{Li}_2\text{ZrSCl}_4$ exhibits the widest electrochemical stability window ($\sim 0.7\text{-}2.6 \text{ V}$), due to the high oxidative stability of Cl^- .



Partial Br substitution in $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ slightly narrows the window to $\sim 1\text{-}2.6$ V, with oxidative decomposition onset occurring near 2.6 V. Fully substituted $\text{Li}_2\text{ZrSBr}_4$ displays the narrowest range ($\sim 1.3\text{-}2.0$ V), with both earlier oxidation and reduction, indicating it is the least electrochemically stable. Figure S8d summarizes this trend, where the broader voltage window of the all-Cl compound aligns with the fact that Br^- is more readily oxidized than Cl^- .⁵⁰

When integrated into composite cathodes to facilitate ion transport, $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ SEs demonstrated excellent cycling performance in ASSB half-cells. These cells were assembled using a $\text{TiS}_2:2\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ composite cathode, a Li-In alloy anode, and a $\text{Li}_6\text{PS}_5\text{Cl}$ separator. Prior to full-cell testing, the compatibility between LZSCB and a Li metal anode was evaluated using time-resolved impedance spectroscopy on a $\text{Li}|\text{LZSCB}|\text{Li}$ symmetric cell (see Figure S9). The continuous increase in interfacial impedance observed in the $\text{Li}|\text{LZSCB}|\text{Li}$ symmetric cell indicates the non-self-limiting formation of a resistive interphase at the Li/electrolyte interface, consistent with reductive decomposition of the halide framework under direct contact with Li metal. Similar behavior has been reported for a broad range of halide solid electrolytes and reflects their limited intrinsic stability against Li.⁵¹ In this work, $\text{Li}_6\text{PS}_5\text{Cl}$ was intentionally used as a separator to decouple cathode performance from known interfacial challenges arising from direct contact between halide electrolytes and Li metal. This cell configuration allows LZSCB to be evaluated specifically as a catholyte, focusing on its ionic transport and compatibility within composite cathodes. Also, preliminary cycling experiments with NMC and LiFePO_4 (LFP) composite cathodes resulted in rapid cell failure (see Figure S10) due to electrolyte instability at higher voltages, further supporting the selection of TiS_2 as an appropriate cathode active material for evaluating the LZSCB electrolyte system.

As shown in the voltage profiles (Figures 6a-b, S11), at a current rate of 0.1C, initial discharge capacities reached 415 mAh g^{-1} for LZSC, 382 mAh g^{-1} for LZSCB, and 330 mAh g^{-1} for LZSB. These discharge capacities at low current densities exceed the theoretical capacity of TiS_2 (239 mAh g^{-1}), a behavior commonly reported for TiS_2 -sulfide-electrolyte composite cathodes when capacities are normalized to the TiS_2 mass. This excess capacity arises from interfacial and electrolyte-derived electrochemical contributions, enabled by intimate contact between TiS_2 and the solid electrolyte.⁵²⁻⁵⁵ In the present work, using ball-milled TiS_2 together with a ball-milled halide catholyte ($\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$) increases the interfacial area and thus the capacity contributions from interfacial reactions, which are often kinetically limited. These contributions are most



pronounced at low C-rates and early cycles and are progressively suppressed at higher rates, where the electrochemical response becomes increasingly dominated by TiS_2 intercalation. The capacity stabilized after the second cycle, suggesting the formation of a passivating interphase that supports reversible cycling. Rate performance tests further showcased the superior behavior of LZSCB, which delivered 322, 289, 248, 200, and 133 mAh g^{-1} at 0.1, 0.2, 0.5, 1, and 2 C, respectively. In comparison, LZSC delivered 323, 263, 200, 141, and 62 mAh g^{-1} , while LZSB realized 330, 304, 235, 160, 109, and 48 mAh g^{-1} , across the same C-rates. The higher capacities observed for the LZSCB cell are linked to its enhanced ionic conductivity and the improved utilization of the active cathode CAM material. Notably, LZSCB retained 81% of its initial capacity after 80 cycles at 0.2 C (Figure 6c), underscoring its long-term cycling stability. These improvements are likely a result of its high ionic conductivity and enhanced compatibility at the cathode-electrolyte interface. Li_2S , present as a minor impurity, is electrochemically stable within the relevant voltage window and does not adversely affect electrolyte stability.⁵⁶ Even at a high current rate of 2C, LZSCB maintained a significantly higher specific capacity (133 mAh g^{-1}) compared to LZSC (62 mAh g^{-1}) and LZSB (48 mAh g^{-1}), highlighting its potential for application in high-performance ASSBs.

To directly probe interfacial stability during long-term cycling, we measured the EIS before and after cycling (see Figure S12 and Table S5). EIS data reveal increased bulk and interfacial resistances after cycling (R_{bulk} : 107.8 to 146.6 Ω ; Interface 1: 14.9 to 24.7 Ω ; Interface 2: 35.5 to 685.5 Ω). Owing to depressed arcs and overlapping time constants, assignments are made based on frequency position and literature precedent.^{57–59} The mid-frequency response (Interface 1) is attributed to the $\text{TiS}_2/\text{catholyte}|\text{Li}_6\text{PS}_5\text{Cl}$ interface and the low-frequency response (Interface 2) to the $\text{Li-In}|\text{Li}_6\text{PS}_5\text{Cl}$ interface. The pronounced growth of the low-frequency resistance is consistent with progressive anode-side interphase formation, where sulfide electrolytes are known to form Li_2S -, Li_3P -, and LiCl -rich reduction products,⁶⁰ whereas cathode-side interphases typically involve sulfur- and phosphorus-rich species like S, polysulfides,^{55,61} or in our case Li-Ti-P-S-Br-Cl phases. Despite this interfacial evolution, the cell maintains high Coulombic efficiency and good capacity retention, indicating that the formed interphases are largely passivating rather than performance-limiting.



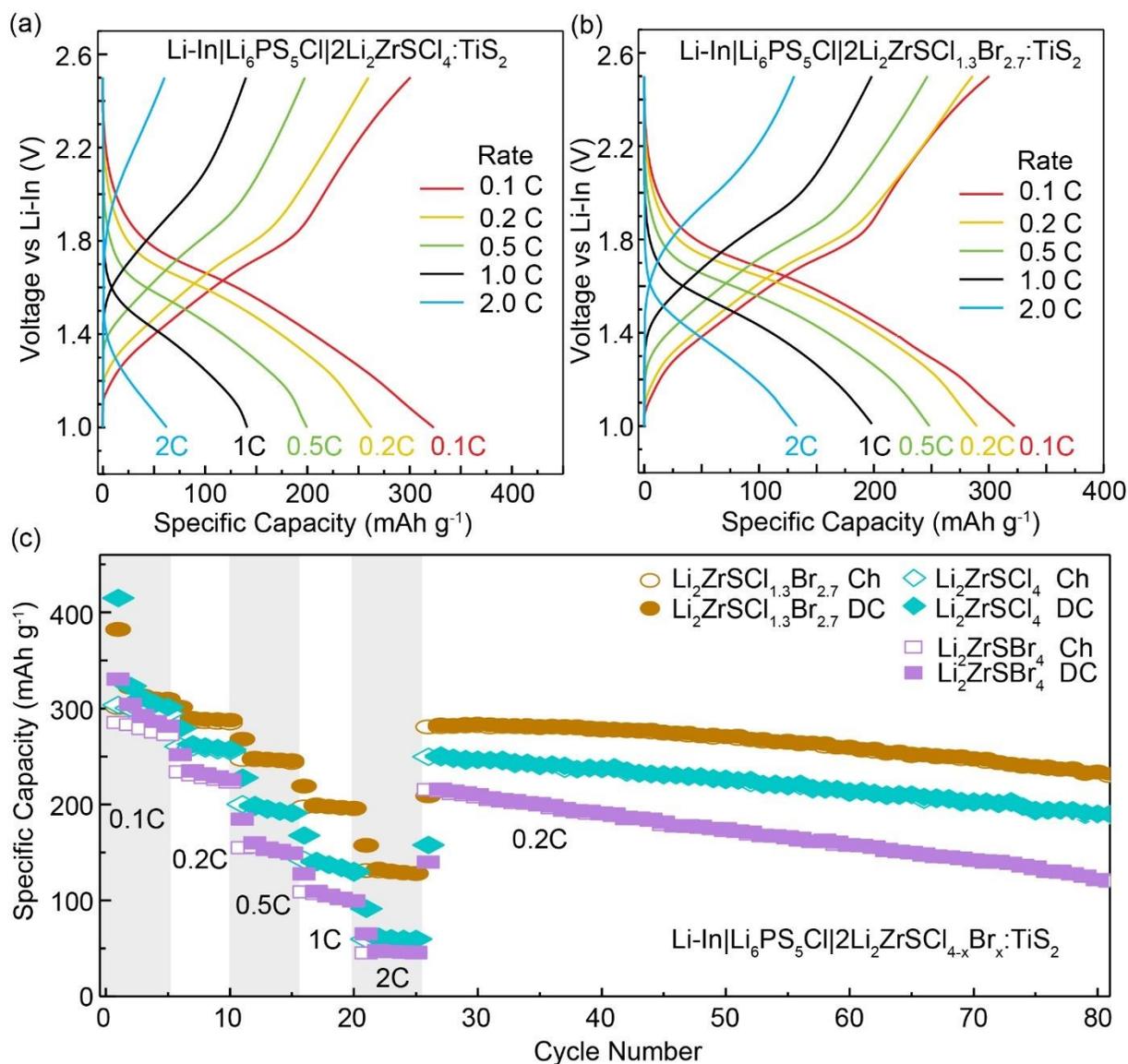


Figure 6: Electrochemical profiles of half cells using (a) $\text{Li}_2\text{ZrSCl}_4$ and (b) $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$ in the composite cathodes at 0.1C, 0.2C, 0.5C, 1C, and 2C, respectively. (c) The corresponding rate performance and long-term cycling stability cycled at 0.2C, where $C = 239 \text{ mAh/g}$ referenced to the theoretical capacity of TiS_2 . $\text{Li}_2\text{ZrSBr}_4$ is included for comparison.

Conclusion

In this study, we developed a family of rare-earth-free halide-sulfide solid electrolytes, $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$ ($0 \leq x \leq 4$), synthesized via a rapid, energy-efficient, two-hour mechanochemical method using a mixed-anion design strategy. Structural analysis from XRD and NMR data reveals that



partial Br^- substitution in $\text{Li}_2\text{ZrSCl}_4$ induces progressive amorphization, enhanced anion polarizability, and dynamic local disorder, leading to significantly improved Li^+ transport. The optimized composition, amorphous $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$, exhibited a high ionic conductivity of 1.03 mS cm^{-1} , outperforming its end members and an order of magnitude higher than that of crystalline Li_2ZrCl_6 compound. Sulfur incorporation introduces a softer, more polarizable anion lattice that fundamentally lowers the intrinsic Li^+ migration barrier from $\sim 0.41 \text{ eV}$ in Li_2ZrCl_6 to $\sim 0.36\text{-}0.37 \text{ eV}$ in $\text{Li}_2\text{ZrSCl}_{4-x}\text{Br}_x$. Whereas Br^- substitution further enhances lattice softness and promotes increased amorphization and dynamic disorder, the resulting conductivity enhancement is governed primarily by an increased pre-exponential factor, which peaks for $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$, indicating optimal lattice softening that increases the mobile Li^+ population, improves site accessibility, and promotes percolative migration pathways. When applied as a catholyte in all-solid-state battery half-cells, LZSCB enabled high capacities, excellent rate capability, and stable long-term cycling, retaining 81% capacity after 80 cycles at 0.2 C. The good performance of the solid-state battery cells employing $\text{Li}_2\text{ZrSCl}_{1.3}\text{Br}_{2.7}$, especially at high rates, is attributed to improved ionic conductivity and favorable interfacial compatibility between cathode and solid electrolyte. These findings demonstrate that compositional tuning via mixed halides is an effective strategy to develop scalable, high-performance chalcogenide electrolytes for next-generation solid-state batteries.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author Contributions

Thilina N.D.D. Gamaralalag: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – review & editing Pawan K. Ojha: Data curation, Formal analysis, Investigation, Validation, Visualization



Bright O. Ogbolu: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing

Md Mahinur Islam: Investigation, Validation

Tehreem Toheed: Investigation, Validation

Sean C. Wilkerson: Investigation

Yan-Yan Hu: Funding acquisition, Project administration, Resources, Software, Supervision, Validation, Writing – review & editing

Acknowledgement

The authors gratefully acknowledge support from the National Science Foundation under Grant No. DMR-1847038. Solid-state NMR measurements were conducted at the National High Magnetic Field Laboratory, supported by NSF Cooperative Agreement Nos. DMR-1644779 and DMR-2128556 and the State of Florida. Raman spectroscopy was carried out at the Materials Characterization Laboratory, Department of Chemistry and Biochemistry, Florida State University (FSU075000MAC), with technical assistance from Dr. J. S. Raaj Vellore Winfred.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

