

Amorphous Oxyhalide Matters for Achieving Lithium Superionic Conduction

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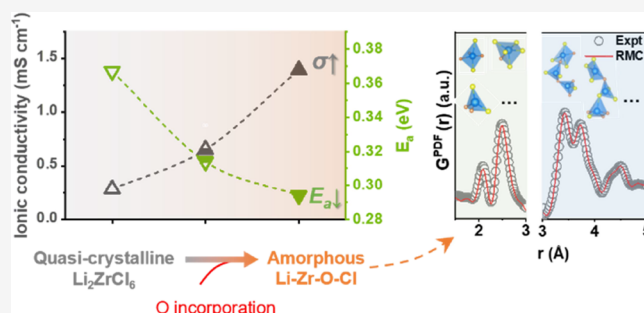


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ABSTRACT: The recently surged halide-based solid electrolytes (SEs) are great candidates for high-performance all-solid-state batteries (ASSBs), due to their decent ionic conductivity, wide electrochemical stability window, and good compatibility with high-voltage oxide cathodes. In contrast to the crystalline phases in halide SEs, amorphous components are rarely understood but play an important role in Li-ion conduction. Here, we reveal that the presence of an amorphous component is common in halide-based SEs that are prepared via mechanochemical synthesis. The fast Li-ion migration is found to be associated with the local chemistry of the amorphous proportion. Taking Zr-based halide SEs as an example, the amorphization process can be regulated by incorporating O, resulting in the formation of corner-sharing Zr–O/Cl polyhedrons. This structural configuration has been confirmed through X-ray absorption spectroscopy, pair distribution function analyses, and Reverse Monte Carlo modeling. The unique structure significantly reduces the energy barriers for Li-ion transport. As a result, an enhanced ionic conductivity of $(1.35 \pm 0.07) \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C can be achieved for amorphous $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$. In addition to the improved ionic conductivity, amorphization of Zr-based halide SEs via incorporation of O leads to good mechanical deformability and promising electrochemical performance. These findings provide deep insights into the rational design of desirable halide SEs for high-performance ASSBs.



1. INTRODUCTION

Green mobility plays a crucial role in achieving the objectives of the clean energy revolution. The transition to electric vehicles heavily depends on the development of advanced battery technologies and efficient production capabilities.^{1–3} All-solid-state batteries (ASSBs) with solid electrolytes (SEs) and potentially employing alkaline metal anodes and high-voltage cathodes are believed to provide an opportunity for achieving excellent safety and high-energy density.^{4–6} In ASSBs, SEs are in direct contact with electrode materials, replacing the flammable organic liquid electrolytes and inert separators. The advancement of SEs governs the development of ASSBs.^{7–10} Among different categories of SEs (e.g., oxides, sulfides, hydrides, polymers, hybrids, etc.), halide-based SEs have drawn increasing attention due to their high ionic conductivities (up to $10^{-2} \text{ S cm}^{-1}$), good antioxidation stability (over 4 V vs Li^+/Li), and decent mechanical deformability.^{11–14} Since Panasonic reported Li_3YCl_6 and Li_3YBr_6 in 2018,¹⁵ the ternary halides (Li-M-X , M = metal cation, X = halogen anion) have been widely reported.^{16–20} Most ternary halide-based SEs are in crystalline phases, which show either hexagonal-close-packed (*hcp*) or cubic-close-packed (*ccp*) anion sublattices.¹⁰

High crystallinity is generally pursued to ensure good ionic conductivity of *ccp* structured SEs, such as representative Li_3YBr_6 ,¹⁵ Li_3InCl_6 ,^{16,21} Li-Sc-Cl ,^{17,22} etc. A ball milling (BM) plus post-annealing or co-melting process contributes to form high-crystalline (*hc*) phases with the optimized ionic conductivity. However, for some halides, such as Li_3YCl_6 ,¹⁵ Li_3ErCl_6 ,²³ and Li_2ZrCl_6 ,^{24,25} their low-crystalline (*lc*) phases from a mechanochemical (e.g., high-energy BM) process possess decent ionic conductivities in the order of $10^{-4} \text{ S cm}^{-1}$, while a post-annealing treatment reduces the ionic conductivity (under the circumstance of maintaining the same crystalline phase). Possible explanations, such as cation sites disorder^{23,26} and stacking faults²⁷ have been proposed. Nevertheless, these understandings based on crystallography knowledge are inadequate to cover all the behaviors of halide SEs synthesized by the one-step mechanochemical method. Discussions about

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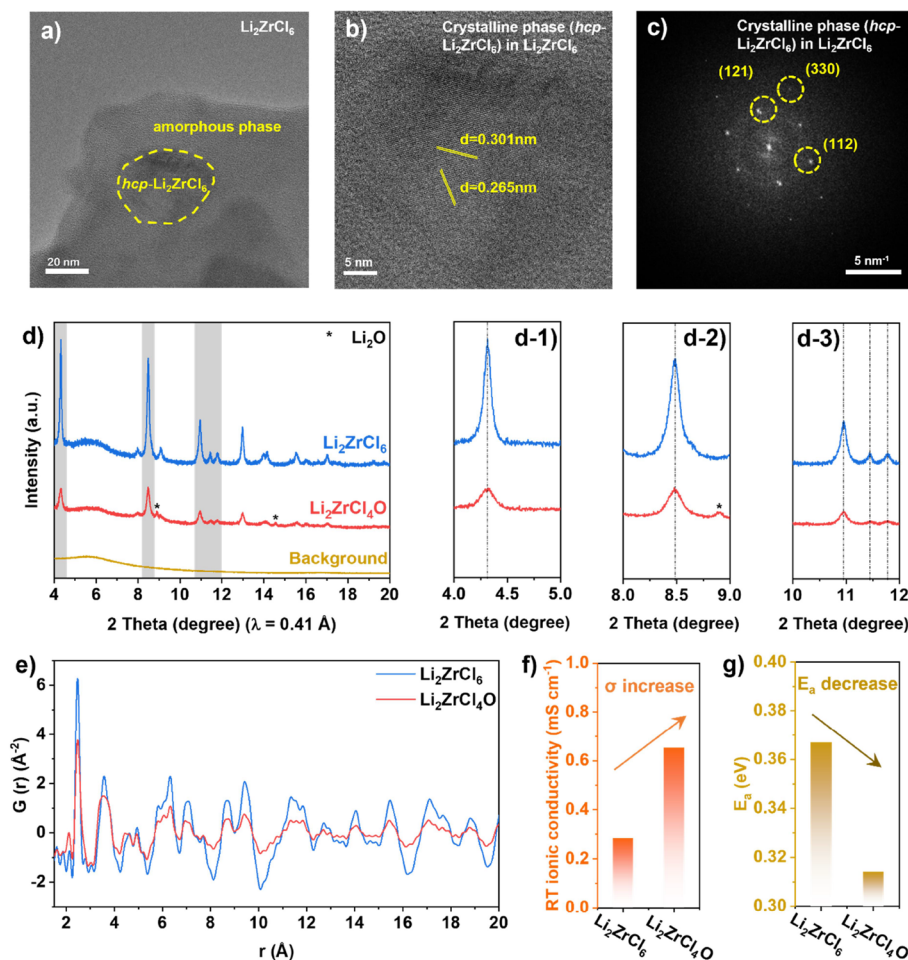


Figure 1. (a) Representative cryo-TEM images of the Li_2ZrCl_6 with (b, c) its crystalline component ($\text{hcp-Li}_2\text{ZrCl}_6$). (d) SXRDP patterns of the Li_2ZrCl_6 and $\text{Li}_2\text{ZrCl}_4\text{O}$ powders with magnified regions of (d-1) $4-5^\circ$, (d-2) $8-9^\circ$, and (d-3) $10-12^\circ$. Background signal comes from the quartz capillary that we used during the test. (e) Comparison of PDF ($\lambda \approx 0.23 \text{ \AA}$) patterns for Li_2ZrCl_6 and $\text{Li}_2\text{ZrCl}_4\text{O}$ materials. Comparisons of (f) ionic conductivities (RT is 25°C) and (g) activation energies for Li_2ZrCl_6 and $\text{Li}_2\text{ZrCl}_4\text{O}$ SEs.

the non-negligible amorphous proportion in the obtained halide SEs²⁸ are usually omitted. Wang et al. found the existence of a significant amount of nonperiodic components in Li_2ZrCl_6 halide SEs and speculated that the decent ionic conductivity of Li_2ZrCl_6 was originated from this nonperiodic structure rather than the specific crystalline phase(s).²⁵

Indeed, very recently, amorphous halide SEs have gradually attracted attention. Ishiguro et al. reported an amorphous LiTaCl_6 SE by using a long-duration ($>120 \text{ h}$) BM process,²⁹ which shows excellent ionic conductivity of over $10^{-2} \text{ S cm}^{-1}$. Our group reported a series of amorphous Li-M-O-Cl ($\text{M} = \text{Ta, Hf}$) oxychloride SEs via constructing mixed-anion (Cl and O) frameworks.³⁰ The highly disordered M-O/Cl arrangements with corner-sharing of the O and rich terminal Cl are regarded as the main reasons for the fast Li-ion transport (up to $6.6 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C). Although these reported amorphous halide SEs appear promising, either careful regulation of crystalline-to-amorphous transition, or the relevance between the structure and ionic conduction was rarely established. Nevertheless, solving these issues is essential to realize controllable synthesis of desirable halide SEs.

In this work, taking the cost-effective Zr-based halide SEs as an example, we first reveal the quasi-amorphous nature of the Li_2ZrCl_6 synthesized from a typical BM method. Through O incorporation, we further manipulate the amorphization of the

Zr-based halide SEs (amorphous content: 69.1–89.5%),⁸⁷ understanding the correlation between the enhanced ionic conduction and amorphous component. As a result, an optimized $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ amorphous SE shows a high ionic conductivity of $(1.35 \pm 0.07) \times 10^{-3} \text{ S cm}^{-1}$ at 25°C , which is an order of magnitude increase compared to the quasi-amorphous Li_2ZrCl_6 ($10^{-4} \text{ S cm}^{-1}$ level). The structure of $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ amorphous SE is investigated in depth. Particularly, the combined synchrotron-based spectroscopy and Reverse Monte Carlo (RMC) modeling analyses contribute to disclose the amorphous local structure and its close correlation to the high ionic conductivity. Finally, the practicality of the regulated amorphous Zr-based halide SEs is demonstrated in high-performance ASSBs with conventional layered oxide cathode materials.

2. RESULTS AND DISCUSSION

The base material, Li_2ZrCl_6 , was synthesized via a BM process (see experimental section for details). As shown in Figure S1, the synchrotron-based X-ray diffraction (SXRDP) pattern of the as-prepared Li_2ZrCl_6 can be indexed to a trigonal phase with an hcp anionic sublattice. Broad diffraction peaks were observed. This phenomenon also occurs to some other halide SEs prepared by the one-step BM method, such as Li_3YCl_6 and Li_3ErCl_6 .^{15,23} Figure 1a–c shows the cryogenic transition

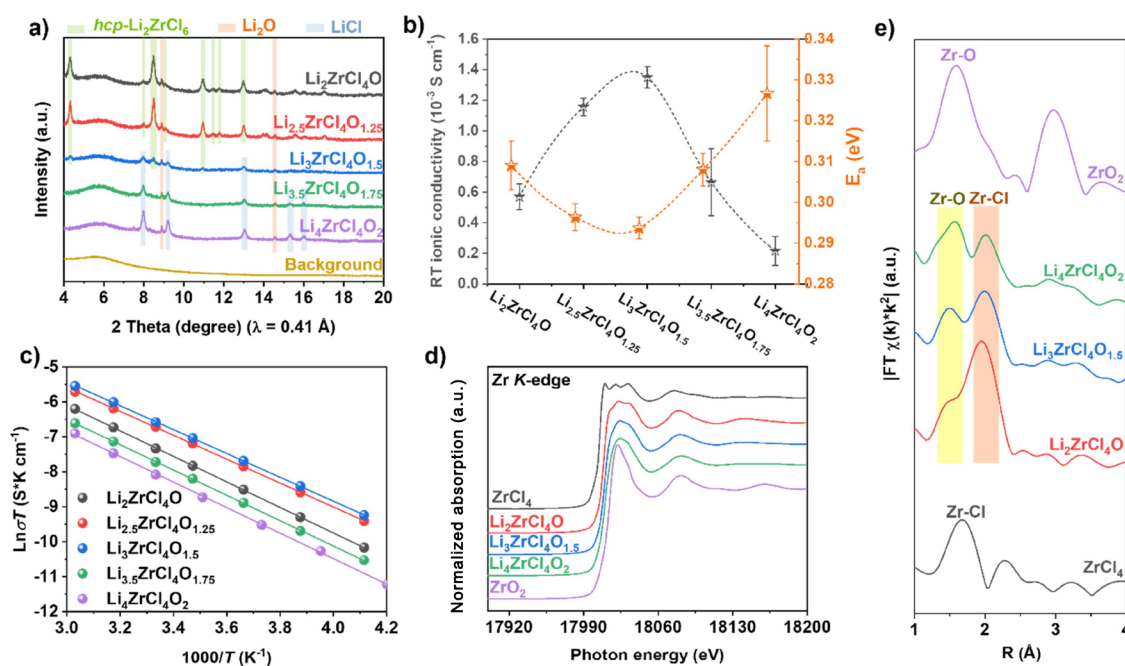


Figure 2. (a) SXR patterns of the $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ SEs ($x = 0, 0.25, 0.5, 0.75$, and 1). (b) Comparison of ionic conductivities and activation energies of the $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ SEs. (c) Arrhenius plots of the $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ SEs. (d) XANES and (e) FT-EXAFS spectra of the $\text{Li}_2\text{ZrCl}_4\text{O}$, $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$, and $\text{Li}_4\text{ZrCl}_4\text{O}_2$ SEs at the Zr K-edge, respectively. ZrCl_4 and ZrO_2 are reference samples.

electron microscopy (cryo-TEM) characterizations of the Li_2ZrCl_6 powder. Crystalline $\text{hcp-Li}_2\text{ZrCl}_6$ grains were embedded in highly disordered regions. The amorphous proportion may be originated from the mechanochemical synthesis method, in which mechanical energy is transformed into pulverization chemical energy to “thermal quench” the powder samples locally and rapidly with the formation of amorphous regions.³¹ In the present study, we used the internal standard method to figure out that the amorphous content in the Li_2ZrCl_6 SE was 46.0% (Figure S2), which was similar to the previous report (~48%).³² As we previously reported superionic amorphous Li-M-O-Cl ($\text{M} = \text{Ta}, \text{Hf}$) halide SEs,³⁰ here we further utilize the mixed-anion strategy with systematic O introduction to regulate the amorphization degree of the Zr-based halide SEs and to study the relationship with their ionic conduction. For a base formula of Li_2ZrCl_6 , partial substitution of Cl by O was achieved by using Li_2O in place of the LiCl starting material while maintaining the Li/Zr molar ratio of 2:1. The resultant $\text{Li}_2\text{ZrCl}_4\text{O}$ exhibited a similar diffraction pattern to that of Li_2ZrCl_6 except for a small amount of residual Li_2O (Figure 1d). Comparing $\text{Li}_2\text{ZrCl}_4\text{O}$ to Li_2ZrCl_6 , theoretically, a considerable amount of the Cl was replaced by O (33.3%), which showed a higher O substitution percentage compared to previous reports about doping O (8–21%) in the Li_2ZrCl_6 SEs,^{32–34} demonstrating a robust inclusive capability of our synthesis route. Nevertheless, although there is a big difference in radius between Cl^- (181 pm) and O^{2-} (140 pm), a nonobservable peak shift appeared in the $\text{Li}_2\text{ZrCl}_4\text{O}$ SE (see the magnified regions from Figure 1d-1–d-3). This indicated that O was not doped into the structure of crystalline $\text{hcp-Li}_2\text{ZrCl}_6$ but altered the properties of the amorphous phase that increased to 69.1% in $\text{Li}_2\text{ZrCl}_4\text{O}$ SE. The incorporation of the O into the amorphous portion of the $\text{Li}_2\text{ZrCl}_4\text{O}$ SE was further verified by conducting electron energy loss spectroscopy (EELS) element mapping as displayed in Figure S3.

Figure 1e shows the pair distribution function (PDF) profiles of Li_2ZrCl_6 and $\text{Li}_2\text{ZrCl}_4\text{O}$ materials. Compared with Li_2ZrCl_6 , the reduced peak intensity and widened peak width for $\text{Li}_2\text{ZrCl}_4\text{O}$ suggested a higher amorphous content with disordered structures inside. Furthermore, combined with wavelet-transformed (WT) extended x-ray absorption fine structure (EXAFS) and Fourier-transformed (FT) EXAFS fitting results (Figure S4 and Table S1), an emerged peak at 2.09 Å in the $\text{Li}_2\text{ZrCl}_4\text{O}$ PDF profile can be attributed by Zr–O bonding. An asymmetric peak between 3 and 4 Å corresponds to connection diversity between Zr-centered polyhedrons. More importantly, the dominance of the amorphous content in the $\text{Li}_2\text{ZrCl}_4\text{O}$ sample can be verified by measuring the ionic conductivity and activation energy (Figure S5). As displayed in Figure 1f,g, after tuning and increasing the amorphous content via O participation with the formation of $\text{Li}_2\text{ZrCl}_4\text{O}$, there was a double increase in the ionic conductivity (at 25 °C), accompanied with a decreased activation energy.

We then tuned the composition of the Zr-base halide SEs to further elaborate the relation between amorphization and ionic conduction. A series of $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ SEs ($x = 0, 0.25, 0.5, 0.75$, and 1) was synthesized from various stoichiometric ratios of ZrCl_4 and Li_2O . Figure 2a shows the SXR patterns. The detailed quantification of the phase compositions for each $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ SE was obtained by refinement (Figure S6), and the results are summarized in Figure S7. Increasing the ratio of Li_2O reduced the formation probability of crystalline $\text{hcp-Li}_2\text{ZrCl}_6$. Minimal impurities of $\text{hcp-Li}_2\text{ZrCl}_6$, Li_2O , and LiCl were achieved for $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ when $x = 0.5$, showing the highest degree of amorphization (89.5%) with a further improved O substitution of 42.9% comparing to $\text{Li}_2\text{ZrCl}_4\text{O}$ (33.3% of O substitution). EELS mapping for the highly amorphous $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ sample suggested that the homogeneous dispersion of Zr, Cl, O, and Li elements constitutes the amorphous component (Figure S8). It is noted that such weak

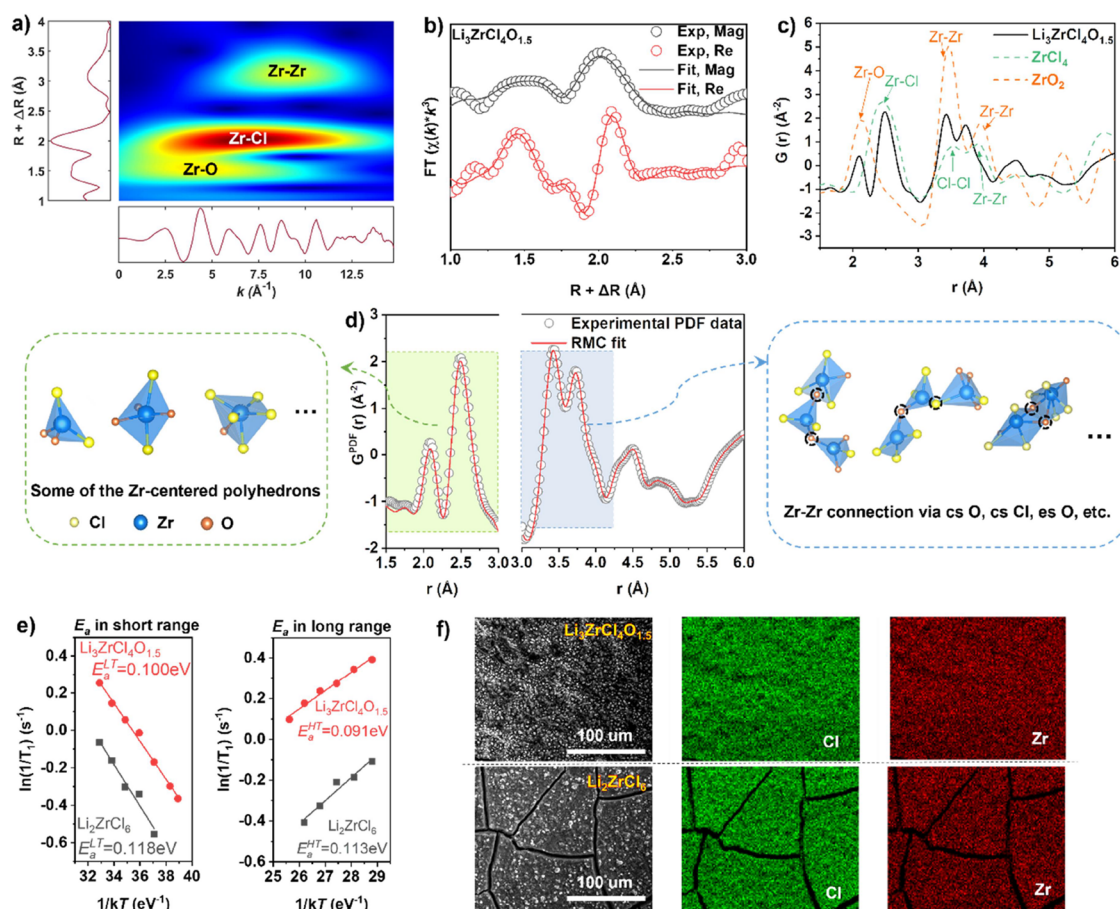


Figure 3. (a) WT spectrum of $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ at the Zr K -edge. A k^3 weighting was used. (b) FT-EXAFS fitting results for the Zr K -edge spectrum of the $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ showing the experimental data (gray circle) and Feff modeling (gray line) in terms of magnitude of FT and the real part of FT experimental data (red circle) and Feff modeling (red line) traces. (c) Comparison of the PDFs of $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$, ZrCl_4 , and ZrO_2 . (d) RMC fit (red line) to the experimental $G(r)$ (gray circle) of $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$. Several possible basic building blocks in $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ are shown on the left side. On the right side, the schemes show the connectivity that leads to the edge-sharing and corner-sharing Zr-centered polyhedra in $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$, respectively. (e) Temperature-dependent ^7Li SLR NMR rates for $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ and Li_2ZrCl_6 measured in the laboratory frame of the reference. (f) Backscattered electron (BSE) images and the corresponding energy dispersive X-ray spectroscopy (EDS) elemental mapping for the surface of cold-pressed $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ and Li_2ZrCl_6 pellets, respectively.

182 crystalline impurity signals in $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SEs were even
183 undetectable by lab-based XRD measurements. Further
184 increasing the amount of Li_2O ($x = 0.75$ and 1) led to
185 considerable impurities of LiCl and Li_2O in addition to the
186 amorphous main phases. At the Li/Zr molar ratio of $3:1$, and
187 improving the content of Cl or O , neither Cl -rich nor O -rich
188 attempts could show similarly high amorphization as the
189 $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ (Figure S9).

190 Ionic conductivities of the $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ SEs ($x = 0, 0.25,$
191 $0.5, 0.75$, and 1) were evaluated via electrochemical impedance
192 spectroscopy measurements. The temperature-dependent
193 Nyquist plots are displayed in Figure S10, and the extracted
194 ionic conductivity values at 25°C are shown in Figure 2b. The
195 $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE with the highest amorphization showed the
196 highest ionic conductivity of $(1.35 \pm 0.07) \times 10^{-3} \text{ S cm}^{-1}$ (at
197 25°C). Arrhenius plots of $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ samples were
198 compared in Figure 2c. $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ showed the lowest
199 activation energy (E_a) of $0.294 \pm 0.003 \text{ eV}$. The trend of the
200 activation energies implied that the structures of amorphous
201 proportion showed a flattened energy landscape for Li -ion
202 migration. Additionally, the electronic conductivity of the
203 representative $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE was determined as low as 7.10
204 $\times 10^{-10} \text{ S cm}^{-1}$ through direct current (DC) polarization

205 measurement (Figure S11). The value was 7 orders of
206 magnitude lower than that of the ionic conductivity, satisfying
207 the essential requirement of electron insulation for a qualified
208 SE. In addition, compared to the Li_2ZrCl_6 SE ($5.61 \times 10^{-9} \text{ S cm}^{-1}$),
209 the highly amorphous $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE shows a lower
210 electronic conductivity, which was also reported previously for
211 the sulfide glass ceramic SE comparing to its highly crystalline
212 one.³⁵

213 To describe the local structure of the amorphous Zr-based
214 halide SEs, we employed X-ray absorption near edge structure
215 (XANES) spectroscopy. Zr K -edge XANES spectra of the
216 SEs were obtained to correlate the average local chemistry
217 with Li -ion migration in the amorphous proportion because
218 the line shape of the K -edge of a transition metal is
219 influenced by the nearest interatomic distances of neighboring
220 atoms.³⁶ Figure S12 compares the spectral features of Li_2ZrCl_6
221 and $\text{Li}_2\text{ZrCl}_4\text{O}$ along with reference spectra of ZrCl_4 and ZrO_2
222 with known structures. The whiteline of Li_2ZrCl_6 showed three
223 obvious splits, which were almost identical with the whiteline
224 shape for ZrCl_4 . Therefore, the noncrystalline structure in
225 Li_2ZrCl_6 could be regarded as the fragmented $\text{hcp-Li}_2\text{ZrCl}_6$
226 with three kinds of distinct bond lengths ($>0.18 \text{ \AA}$ between
227 each other). In contrast, the whiteline shape of $\text{Li}_2\text{ZrCl}_4\text{O}$ was

smooth and merged, indicating that the differences of bond lengths in Zr–Cl/O polyhedrons became subtle for the O-substituted sample. Figure 2d compares the Zr *K*-edge spectra of $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ SEs ($x = 0, 0.5$, and 1). With x increasing, the whiteline shape of the spectra changes to be more concentrated without any obvious splits. This further indicates that the nearest Zr-related bond lengths in amorphous $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ materials are regular and uniform. Zr *K*-edge FT-EXAFS spectroscopy was then adopted to quantitatively understand the coordination environment around the central Zr in $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ SEs ($x = 0, 0.5$, and 1) (Figure 2e). Based on the single scattering information from ZrO_2 and ZrCl_4 (Figure S4), the peaks resulting from the O and Cl scatters around Zr can be roughly determined, which showed an intensity growth in Zr–O while a decrease in Zr–Cl. This suggests that increasing the x value in $\text{Li}_{2+2x}\text{ZrCl}_4\text{O}_{1+x}$ materials led to the replacement of more Cl anions nearest Zr cations by O anions. Consequently, there is a high possibility that displaced Cl anions combine with Li cations to form LiCl impurity, which is consistent with the SXRD results.

In-depth structural analysis was further conducted on the representative $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE. As shown in Figure 3a, phase-uncorrected WT-EXAFS^{37,38} confirmed that Zr was successfully coordinated by O, Cl, and Zr at ~ 1.5 , 2 , and 3 Å, respectively. EXAFS fitting (Figure 3b) provides average coordination information nearest to Zr in $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$. A centered-Zr is surrounded by 2.5 oxygens at 2.07 Å and 5.6 chlorines at 2.49 Å (Table S2). RMC modeling for total scattering data was utilized to understand the structure configurations in the most amorphous $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE. As suggested in the PDF profiles in Figure 3c, the first two peaks correspond to Zr–O and Zr–Cl pairs, while the next two peaks within 3.0 – 4.1 Å are attributed to Zr–Zr bonding. We carried out RMC modeling on both the normalized $F(Q)$ and $G^{\text{PDF}}(r)$ of $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ to produce a statistical ensemble reconciling configurations (Figure S13a). The fitted data were in good agreement with the experimental data in both long-range orders and local structures (Figure S13b,c). As illustrated in Figure 3d, extracted statistical information around Zr atoms reveals basic building blocks, including $[\text{ZrO}_a\text{Cl}_b]^{(2a+b-4)-}$ ($0 \leq b/a < 6$) and $[\text{ZrCl}_6]^{2-}$ polyhedrons (Figure S13d). These Zr-centered polyhedrons are predominantly connected via corner-sharing (cs) Cl ($\sim 55\%$) and cs O ($\sim 37\%$), with the rest exhibiting edge-sharing and a few face-sharing configurations (Figure S13e). Over 90% of Cl anions are closely surrounded by Li ions (53%) or served as terminal Cl (38%) (Figure S13f). We further performed 50 repeated RMC runs on $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ total scattering data, each with distinctive randomness. The small uncertainty for each of the relevant results guarantees the reliability of the RMC resulted conclusion.

The E_a for Li-ion transport in the determined local structures in $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ was evaluated by temperature-dependent ^7Li spin–lattice relaxation (SLR) nuclear magnetic resonance (NMR) measurements. According to the “Bloembergen, Purcell and Pound” model,³⁹ slopes of two-flank divisional points below the highest value of $1/T_1$ can be used to depict the E_a of Li-ion migrations in short-range (low-temperature flank, E_a^{LT}) and long-range (high-temperature flank, E_a^{HT}), respectively.⁴⁰ As shown in Figure 3e, E_a^{LT} for $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ was 0.100 eV, which was around 20% lower than that of Li_2ZrCl_6 (0.118 eV) with the crystalline phase dominating. The O/Cl corner-sharing Zr-based polyhedral

networks also led to a low E_a for long-range Li-ion transport ($E_a^{\text{HT}} = 0.091$ eV) in $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$.

Based on the above structural analyses for the Zr-based halide SEs and corresponding ionic conduction properties, we can claim several important conclusions. First, the amorphous component in the Zr-based halides (synthesized via the one-step BM method) shows a close correlation with the Li-ion conduction behaviors. Second, enhancing the amorphization (or reducing the crystalline impurities) by changing the local structure in the Zr-based halide SEs can improve the ionic conductivity. Third, we demonstrate that the O substitution is effective to facilitate the amorphization of Zr-based halide SEs. Specifically, compared to Li_2ZrCl_6 , $\text{Li}_2\text{ZrCl}_4\text{O}$ shows disordered and distorted Zr–O/Cl polyhedrons, in which the bond length of Zr–X ($X = \text{Cl}, \text{O}$) is averaged to flatten the energy landscape for Li-ion migration. Furthermore, optimizing the amorphization of Zr-based halide SEs with a higher O content ($\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$) leads to the formation of corner-shared connections within Zr–Zr polyhedrons. These are predominant to induce a wide range of distortions of Li sites and lower the energy barriers for Li-ion migration.⁴¹ So far, we have revealed several important factors to cause an improved ionic conduction in amorphous O-substituted Zr-based halide SEs. Among these scenarios, the elongation of the average bond length of Zr–Cl was also theoretically explored by Kwak et al. as one of the main reasons for the high interfacial Li-ion conduction in the crystalline O-substituted Zr-based materials.³³ Importantly, the amorphization of Zr-based halide SEs with incorporation of O and the resulting improvement in ionic conductivity can extend to other halides based on Ta, Nb, or Hf as the central element adjacent to Zr in the periodic table, as depicted in Figure S14. While for typical halide SEs with a formula of Li_3MCl_6 (where $M = \text{Y}, \text{Er}$), the simple introduction of O by replacing LiCl with Li_2O reactant proves ineffective in achieving amorphization and enhancing ionic conductivity (Figure S15). This limitation may be associated with the intrinsic glass-formation capability of the central metal element.

In addition to the favorable Li-ion conduction property of the highly amorphous $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE, good mechanical deformability is an extra highlight. As displayed in Figure 3f, at low magnification (in the scale of hundreds of micrometers), the cold-pressed Li_2ZrCl_6 pellet with low amorphization shows evident cracks on the surface. In sharp contrast, the surface of the $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ pellet was compact and continuous, indicating the high deformability of highly amorphous materials, which was also reported before for Li–Zr–O–Cl SE by Hu et al.³² and other amorphous SEs.⁴² One important benefit derived from the good deformability of amorphous materials is the potential to minimize grain boundaries (GBs).⁴³ However, the influence of GBs on the delivered ionic conductivity is still elusive for halide-based SEs, because theoretically the GB effect on the ionic conduction in Li_3InCl_6 was regarded negligible.⁴⁴ Detailed studies about the mechanical properties and GBs are unfortunately beyond the scope of this work and will be investigated in our following research.

The application potential of the amorphous $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE was evaluated in ASSBs. The electrochemical stability window (ESW) of the $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE was determined via linear cyclic voltammetry (LSV) measurements, as shown in Figure S16. The high oxidation limit of 4.1 V and reduction limit of 2 V made it possible to integrate different 4 V class cathode materials. The ESW and electrochemical stability of

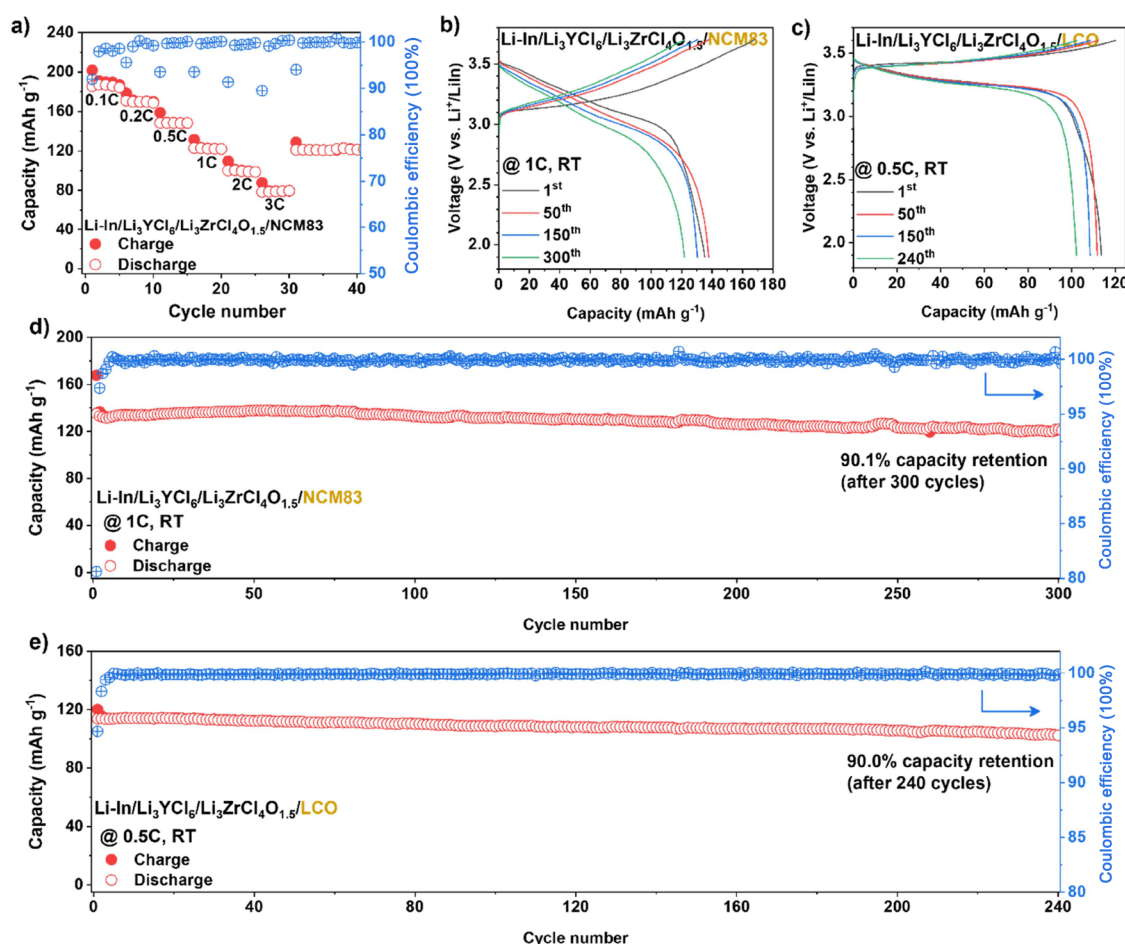


Figure 4. (a) Rate performance of ASSB with the NCM83 cathode at RT. (b) Cycling performance of ASSB with NCM83 cathode and (d) charge–discharge curves at 1 C. (c) Cycling performance of ASSB with LCO cathode and (e) charge–discharge curves at 0.5 C.

amorphous $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ was examined as superior to that of the relatively crystalline Li_2ZrCl_6 SE. The reason is not only attributed to the benefits of incorporating O³⁴ and reduced electronic conductivity³⁵ but also is possibly related to the mechanically constrained effect of the amorphous component in SEs.^{45,46} However, considering the high reduction limit of the $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE (2 V), an anode interlayer SE of Li_3YCl_6 was used to prevent direct contact between Li–In anode and $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SEs.^{15,18} The electrochemical performance of the constructed ASSBs with high-voltage $\text{LiNi}_{0.83}\text{Co}_{0.11}\text{Mn}_{0.06}\text{O}_2$ (NCM83) was demonstrated. As displayed in Figures 4a and S17a, an excellent rate performance was achieved. The reversible capacities of 185.7, 170.9, 148.4, 123.0, 100.1, and 78.5 mAh g^{-1} were achieved at 0.1, 0.2, 0.5, 1, 2, and 3 C (1 C = 200 mA g^{-1}), respectively. The cycling performance of the NCM83 ASSBs at large current densities was also desirable. As shown in Figure 4b,d, ASSBs could stably operate for over 300 cycles with a capacity retention of 90.1% at 1 C. Moreover, a reversible capacity of 96.6 mAh g^{-1} could be maintained after ASSB cycling over 600 times at 2 C (Figure S17b). The excellent interfacial compatibility between $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ and NCM83 was proved by a close observation on the interfacial composition via cryo-TEM characterizations as displayed in Figure S18, which was in contrast to the interface decomposition between Li_2ZrCl_6 and NCM83 revealed by Janek and Nazar.²⁸ That is to say, the incorporation of the O into the Zr-based SEs can prevent the formation of ZrO_2 as the

interfacial reaction product when pairing up with Ni-rich 380 cathode materials (e.g., NCM83). Besides the NCM83 381 cathode, the LiCoO_2 (LCO) cathode was also used for the 382 $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE-based ASSBs. As exhibited in Figure 4c, the 383 initial Coulombic efficiency of LCO ASSB evaluated at 0.5 C 384 (1 C = 140 mA g^{-1}) reached 94.7, and 90.0% of the initially 385 reversible capacity could be sustained after 240 consecutive 386 cycles (Figure 4e). 387

3. CONCLUSIONS

In summary, taking the Zr-based halide SEs as an example, we 388 successfully illustrated how the amorphous content correlates 389 with the ionic conductivity of some lithium metal (IV or V) 390 (oxy)halide SEs. The amorphization of Zr-based halides (SEs) 391 can be elaborately tuned by incorporating oxygen, resulting in 392 a content change from 46.0 to 89.5%. As an optimized 393 composition, $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ was highly amorphous and with a 394 high ionic conductivity of $(1.35 \pm 0.07) \times 10^{-3} \text{ S cm}^{-1}$ at 25 395 °C. Combining synchrotron-based X-ray absorption spectroscopy 396 analysis and RMC fitting, we reveal the local structure of the 397 amorphous $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$ SE. The distorted Zr–O/Cl 398 polyhedrons with averaged Zr–X (X = O, Cl) bond length 399 constitute the anion framework via a desirable O/Cl corner-sharing 400 manner. This is regarded as the intrinsic reason for the 401 promising ionic conductivity. In addition to the improved ionic 402 conductivity, amorphization brings about an enhanced 403 mechanical property. Consequently, the representative 404

Li₃ZrCl₄O_{1.5} SEs enable ASSBs operating with outstanding performance at 25 °C. This study shall provide new understandings and design principles of high-performance halide SEs, leading to a key advancement for halide-based ASSBs.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c07343>.

Experimental section; SXRD ($\lambda = 0.41 \text{ \AA}$) pattern of the Li₂ZrCl₆ prepared; quantification of the amorphous content; cryo-TEM characterizations on the Li₂ZrCl₄O sample; Zr K-edge wavelet transformed (WT) extended X-ray absorption fine structure (EXAFS) contour plots; Nyquist plots and Arrhenius plots; refinement for the SXRD data; summary of the quantification of the phase composition; cryo-TEM characterizations on the most amorphous Li₃ZrCl₄O_{1.5} sample; lab-based XRD patterns; normalized Nyquist plots; DC polarization curves; Zr K-edge XANES spectra; RMC modeling results; extended studies; LSV results; charge-discharge curves; HRTEM image; and structural parameters; references (PDF)

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Notes

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