Tuning collective anion motion enables superionic conductivity in solid-state halide electrolytes

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Abstract

Halides of the family Li_3MX_6 (M=Y, In and Sc, etc., X=halogen) are emerging solid electrolyte materials for all-solid-state Li-ion batteries. They show higher chemical stability and wider electrochemical stability windows than existing sulfide solid electrolytes, but have lower room temperature ionic conductivities. Here, we report the discovery of the superionic transition in Li_3YCl_6 to be triggered by the collective motion of anions, evidenced by synchrotron X-ray and neutron scattering characterizations, and ab initio molecular dynamics simulation. From these findings, we employ a rational design strategy to lower the transition temperature and thus to improve the room temperature ionic conductivity of this family of compounds. We accordingly synthesize $Li_3YCl_xBr_{6-x}$ and $Li_3GdCl_3Br_3$ compounds and achieve very high room temperature conductivities of 6.1 mS cm^{-1} and 11 mS cm^{-1} for $Li_3YCl_{4.5}Br_{1.5}$ and $Li_3GdCl_3Br_3$, respectively. These results open new routes to design room-temperature superionic conductors for high-performance solid batteries.

Introduction

All-solid-state lithium-ion batteries (ALSOLIBs) are a promising next-generation energy storage technology owing to good safety, high energy density, and versatility of applications[1,2]. As the key component of ALSOLIBs, solid electrolyte (SE) was extensively explored in recent years and a variety of materials have been reported, including garnet-type ($Li_7La_3Zr_2O_{12}$ or LLZO)[3,4], NASITON-type ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ or LATP)[5,6], argyrodite-type ($Li_{6-x}PS_{5-x}X_x$, X=Cl, Br[7]), $Li_7P_3S_{11}$[8,9] and $Li_{10}GeP_2S_{12}$ (LGPS)[2,10], etc. However, the ideal SE with all properties desired for large scale commercialization of ALSOLIBs, including high room temperature (RT) ionic conductivity, wide electrochemical window, good chemical stability, good mechanical property and low cost, is yet to be discovered[11]. Li_3MX_6 (M=Y, Sc, and In, etc., X=halogens)[12-14] and $Li_2M'X_6$ (M' = Zr and Hf, X = halogen)[15-19] family halide materials recently attracted great attention due to their outstanding advantages in cathode stability over sulfides and in ionic conductivity over oxides. But the RT conductivities of these halides are still commonly one order of magnitude lower than those of sulfides, which is limiting their application and calling for improvement.

Asano et al. reported high RT conductivity (σ_{rt}) in Li_3YCl_6 (hereafter noted as LYC) with experimentally measured value of 0.51 $mS \cdot cm^{-1}$ and an activation energy (E_a) of 0.40 eV, and a higher σ_{rt} of 1.7 $mS \cdot cm^{-1}$ in Li_3YBr_6 (hereafter noted as LYB)[12]. However, later *ab* initio molecular dynamics (AIMD) simulations by Mo et al. suggested that in theory much higher σ_{rt} (14 $mS \cdot cm^{-1}$) and much lower E_a (0.19 eV) are possible for LYC with $P\bar{3}m1$ structure[20]. In a recent study on $Li_3YCl_3Br_3$[21], which is isostructural to LYB, higher σ_{rt} (7.2 $mS \cdot cm^{-1}$) and low E_a (0.25 eV) were achieved, which motivated us to explore if higher (> 0.51 mS/cm) σ_{rt} can be experimentally achieved in compounds with LYC structure.

Here, we systematically conducted synchrotron *in situ* X-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS) and *in situ* neutron diffraction (ND) at different temperatures for LYC samples. A type II superionic transition (SIT) with significantly lower E_a values above the transition temperature (T_c) was observed, which was revealed to be related to changes of the diffusion pathways of Li triggered by the collective motion of the anions. Guided by this finding, two series of compounds $Li_3YCl_{6-x}Br_x$ and $Li_3GdCl_{6-x}Br_x$ were designed to achieve lower T_c and higher RT conductivity. The compounds were successfully synthesized, electrochemically evaluated and characterized. The T_c was lowered to 70 °C with $Li_3YCl_{4.5}Br_{1.5}$ and ionic conductivity of 100 mS/cm at 80 °C and 6.1 mS/cm at RT were achieved. Even lower T_c of -10 °C and higher RT conductivity of 11 mS/cm was achieved in $Li_3GdCl_3Br_3$.

Results and Discussion

The superionic transition of Li_3YCl_6

LYC samples were synthesized by hot-pressing ball-milled LYC powder at 200 °C and characterized with XRD and ND. LYC was reported to crystalize in different polymorphs[12,22-24] and the trigonal $P\bar{3}m1$ structure is most commonly observed during solid state syntheses. Fig. 1a shows the ND pattern of obtained LYC and it can be well-described by $P\bar{3}m1$ structure with hexagonal close packed (*hcp*) anion sublattice with stacking sequences of ABAB…. The average structure of the $P\bar{3}m1$ phase can be regarded as stacking of two types of layers alternatively (Fig. 1b). Both layers contain $LiCl_6$, YCl_6 and $\dot{V}Cl_6$ ($\dot{V}$: vacancy) octahedra. Y^{3+} occupies three different octahedral sites: one $1a$ site (M1) and two $2d$ sites (M2 and M3)[25]. As shown in Fig. 1c and 1d, the $1a$ site and one of the $2d$ sites (M3) are within the same layer (hereafter noted as Y layer). It is worth noting that the distances between the centers of the face shared YCl_6 octahedra (between

M2 and M3 site) is only ~ 3 Å, which induces large electrostatic repulsion and energetically unfavorable states if M2 and M3 sites are simultaneously occupied. Therefore, it is likely that the partial Y occupancies refined at both sites are due to the difference in *ab*-plane arrangements of Y-vacancy ordering instead of the stacking disorder along *c*-axis direction. This has further been confirmed by the neutron pair distribution function (nPDF) data (Supplementary Fig. 1), where no observable positive peak is found around 3 Å. The detailed in plane Y-vacancy ordering patterns is out of the scope of the current report and will be reported elsewhere. The other 2*d* site that Y locates in the adjacent layer, which is Li-rich (hereafter noted as Li layer). Li^+ occupies two octahedral sites: 6*h* Li sites in the Li layer, fully occupied by Li^+, and 6*g* sites in the Y layer, partially occupied by Li^+ at RT. The 6*g* and 6*h* sites are connected by face shared $LiCl_6$ octahedra, forming a long-range diffusion channel for Li^+ along *c*-axis. Meanwhile, they are also broadly proposed to connect via two tetrahedral sites to form a 2D diffusion pathways (O-T-O pathway) along the *ab*-plane[20].

We then measured the conductivity of LYC pellets in a broader temperature range than previously reported[12]. The Arrhenius plot of the conductivity of LYC is shown in Fig. 2a. LYC shows an ionic conductivity of 1.4×10^{-4} $S \cdot cm^{-1}$ at 25 °C, with an E_a of 0.70 eV below 130 °C. However, the slope becomes much flatter at higher temperatures with a greatly reduced E_a of 0.22 eV, showing a type II superionic transition (SIT) and indicating a significantly facilitated diffusion via a different mechanism above the transition temperature T_c. Such SIT in halides is also computationally presented by Ong et al.[26]. This low E_a is close to AIMD simulation results obtained by Mo et al.[20]. If we extrapolate the Arrhenius curve from T_c to RT, the expected σ_{rt} is 29 $mS \cdot cm^{-1}$, which also agrees with the AIMD simulation result[20]. Apparently, the steep slope below T_c is the major reason for the discrepancy between previous experimentally measured ionic conductivity and theoretical prediction.

To understand the origin of the SIT, we investigated the structural change of LYC with *in situ* synchrotron XRD from 20 to 200 °C. As shown in Supplementary Fig. 2, the broad diffuse scattering peaks around 5 Å and 3.8 Å remain in the XRD patterns through the whole temperature range, in good agreement with the previous report[27]. However, no significant phase transition is observed during both heating and cooling processes. This indicates that the SIT seen in the EIS test is not caused by the specific arrangements of the Y^{3+}-vacancy ordering pattern or any long-range symmetry breaking.

We further investigated the structural changes using variable temperature (VT) neutron diffraction (ND). As shown in Fig. 2b, the diffraction patterns of LYC maintain similar Bragg reflections despite the obvious peak position shift due to the thermal expansion. Fourier difference maps (FDM, F_{calc}-F_{obs}) were generated from the refined structure (S.G. $P\overline{3}m1$) using the 100 K and 500 K ND data and shown in Fig. 2 and Supplementary Figs. 3-4. At 100 K, very clear residual Li scattering length density can be found on the two major lithium sites 6*g* and 6*h* (Fig. 2c and Supplementary Fig. 3), while no noticeable densities can be seen between these two sites, neither within the *ab*-plane nor along the *c*-axis direction (with a cut-off of -0.035 fm/Å^3). Further lowering the residual density cut-off to -0.02 fm/Å^3 shows the connection along c-axis direction, but still without obvious connection along *ab*-plane (Fig. 2d). This indicates that Li^+ diffusion is likely one dimensional (along *c*-axis) with relatively high energy barrier, which is consistent with the high E_a value measured from EIS (0.70 eV). In clear contrast to the 100 K data, at 500 K (Fig. 2e), the residual Li^+ densities are clearly connected among 6*g* sites to form hexagonal rings around the M1 Y site within the *ab*-plane at a threshold of -0.03 fm/Å^3. These rings are further connected to form 2D diffusion pathways at a threshold of -0.02 fm/Å^3 (Fig. 2f), indicating facilitated 2D diffusion channels within the *ab*-plane.

The Rietveld refinement results of the ND data are shown in Fig. 3 and Supplementary Table 1-5. Fig. 3a shows the lattice parameters. The increase of $2c/a$ ratio confirms the anisotropic thermal expansion. In previous reports, Li sites in Li layer (6*g*) were often assumed to be fully occupied in $P\bar{3}m1$ structure[28]. However, our refinement results (Fig. 3b) show a partial occupancy at 6*g* site and a full occupancy of 6*h* site below 400 K. A detailed inspection of the refined structure reveals that Li^+ coordination environment is strongly correlated with the collective motion of Cl^-. From 100 K to 400 K, there is only limited change of Li^+ occupancy and minor volume change of the YCl_6 octahedra (Fig. 3c). The deformation of YCl_6 octahedra can be evaluated by the Cl-Y-Cl angles: φ11 in $M1Cl_6$, φ22 and φ33 in $M3Cl_6$ (Fig. 3d); φ22' and φ33' in $M2Cl_6$ (Fig. 3e). The slight increase of the φ11 angle (Cl-M1-Cl) suggests that the $M1Cl_6$ octahedra were slightly compressed along the *c*-axis (Fig. 3f). The neighboring face shared $M2Cl_6$-$M3Cl_6$ chains are found to rock toward the opposite direction (movie 1). This correlated anion motion leads to only slight increase of the intralayer Cl-Cl distances (the edge between two neighboring $LiCl_6$ octahedra within *ab*-plane, noted as S12, S33 in Fig. 3d). At 500 K, an abrupt elongation of $M1Cl_6$ and $M3Cl_6$ octahedra along *c*-axis emerges (Fig. 3f). A drastic shrinkage of the φ22 and φ33 (Cl-Y3-Cl) angles (Fig. 3f) and a drastic increase of S12 and S33 (intralayer Cl-Cl) distances (Fig. 3g) are identified, which together indicates a "breathing" type of correlated motion of the $M1Cl_6$ and $M3Cl_6$ octahedra and in turns means a drastic expansion of the bottle neck of the diffusion channels within the *ab*-plane among the 6g Li^+ sites (in the z=0 plane, i.e., the Y layer). The facilitation effect of the mode shift can also be seen from the change in the area of the diffusion bottleneck windows

(BN1 and BN3, as shown in Supplementary Fig. 5). In contrast, as shown in Supplementary Fig. 6a, the $M2Cl_6$ octahedra became compressed at 500 K (relative to the 400 K structure) and the in-plane diffusion channel bottle neck does not change much or even shrinks slightly (S12' and S33' in Supplementary Fig. 6b) for the Li^+ on the 6*h* sites (in the z =0.5 plane, i.e., the Li layer). This finding suggests that the 2D Li^+ diffusion channels with low energy barrier likely only open up for Li^+ on the 6g sites (or z = 0 plane) when temperature increases from 400 K to 500 K. While the in-plane Li^+ hopping is still difficult within the z =0.5 plane. This is fully consistent with the results of the Fourier difference maps (Fig. 2e and 2f). Taken together, the observed SIT above 130 °C in LYC is very likely due to the opening up of the 2D Li^+ diffusion channel, which is rooted in the switch from "rocking" to "breathing" mode of motion of the MCl_6 units. This transition has been further confirmed by the in situ nPDF investigation (Supplementary Fig. 1). The Y-Cl bond is very stiff, as evidenced by the nearly unchanged Y-Cl bond lengths. However, the correlation between neighboring Cl-Cl and the second shell Y-Cl pairs become much weaker or even become entirely uncorrelated above 400 K, suggesting that anion motions are likely to induce much wider diffusion channels for Li^+ hoping.

This transition is also confirmed by the AIMD simulations results presented as follows in Fig. 4a, where a leap of the average S12 and S33 distances is captured between 350 K and 400 K. The ionic diffusion within the *ab*-plane is inactive at the low temperature of 350 K (Fig. 4b), which agrees well with the ND results. The Li^+ diffusion in the *ab*-plane would not be activated until at high temperature, such as 600 K (Fig. 4c). In addition to the leap of the averaging S12 and S33 distances, a broader distribution of S12 and S33 distances and an asymmetric tail toward larger S12 and S33 values are also captured, which also indicates that in a high fraction of time the bottleneck of the diffusion channel is opened up at higher temperature (Fig. 4d and e).

Tuning T_c with Br doping in Li_3YCl_6

The impact of anion motion on fast ionic conduction was also discussed previously[29,30], which implies that this may be an important factor to tune the ionic kinetics. The finding of superionic transition of Li_3YCl_6 inspired us to raise a design strategy: a much-improved RT ionic conductivity can be achieved by tuning T_c down to RT or lower temperatures, which may be realized by elementary position and bond tuning. The "breathing" mode is likely related to the properties of the metal-halogen bond. We hypothesize that with the lower electronegativity and higher polarizability of Br than Cl, partly replacing Cl with Br may promote the "breathing" mode than the "rocking" mode and thus can lower the T_c. A previous study in halide SEs with $C2/m$ space group (LYB structure) also suggested that anion mixing may lower the migration barrier[21]. We then designed a series of $Li_3YCl_{6-x}Br_x$ compounds and successfully synthesized them via ball-milling and subsequent hot-pressing. Their XRD patterns are shown in Fig. 5a $0 \leqslant x \leqslant 1.5$. With $x \leq 1.5$, pure phase isostructural to LYC can be obtained. The peak broadening at ~5.3 Å is greatly suppressed in XRD patterns of Li_3YCl_5Br and $Li_3YCl_{4.5}Br_{1.5}$ and the Rietveld refinement results of these compounds are shown in Supplementary Fig. 7. Further increasing x to 2 leads to a noticeable impurity, which can be indexed as a LYB phase (Supplementary Fig. 8). Because of the larger size of Br^- (1.96 pm) relative to that of the Cl^- (1.81 pm)[31], the lattice parameters of $Li_3YCl_{6-x}Br_x$ increase linearly with increased Br doping amount (Supplementary Fig. 9a). Also, the peaks at ~3.9 and 5 Å become narrower and more symmetric with more Br doped, indicating the gradual increase of coherent lengths of the in-plane ordering of Y^{3+}-vacancies. Supplementary Fig. 9b compares the $2c/a$ value of $Li_3YCl_{6-x}Br_x$. With increased Br content, the unit cell of $Li_3YCl_{6-x}Br_x$ elongates along c-axis. The Young's modulus and hardness of $Li_3YCl_{4.5}Br_{1.5}$ were measured via nanoindentation and compared with those of LYC. The results (Supplementary Table 11) show that both the modulus and hardness of $Li_3YCl_{4.5}Br_{1.5}$ are lower than those of LYC, which is likely due to the higher polarizability of Br^- anions than Cl^- anions. Fig. 5b shows the ionic conductivity of $Li_3YCl_{6-x}Br_x$ extracted from EIS tests of pellets hot-pressed at 200 °C. Corresponding Nyquist plots are shown in Supplementary Figs. 10-13. For samples with $x = 0.5$, 1 and =1.5, the Arrhenius plots of the conductivity are almost identical at high temperatures (>130 °C), showing an E_a of ~0.22 eV. All samples show the SIT at different temperatures. With more Br doped, T_c is effectively lowered: 130 °C for LYC, 100 °C for $Li_3YCl_{5.5}Br_{0.5}$, 90 °C for Li_3YCl_5Br and 70 °C for $Li_3YCl_{4.5}Br_{1.5}$. As a result, $Li_3YCl_{4.5}Br_{1.5}$ shows an ionic conductivity over 100 mS cm^{-1} at 80 °C and a σ_{rt} of 6.1 mS cm^{-1} (magenta curve in Fig. 5b). The same EIS measurements were also conducted for LYC and $Li_3YC_{4.5}Br_{1.5}$ samples with high crystallinity, which were synthesized at 500 °C, 5h before hot-pressed at 200 °C to form pellets. The same Tc values of 130 °C and 70 °C were also observed for LYC and $Li_3YC_{4.5}Br_{1.5}$, respectively, as shown in Supplementary Figs. 14 and 15, despite that the RT conductivity of the 500 °C synthesized LYC sample is lower than that of the 200 °C hot-pressed LYC sample, which is likely caused by the difference in crystallinity and Y distribution at M2 and M3 sites[24,25,27] due to different synthesis protocols. We also collected the synchrotron diffraction data of highly crystalline LYC at varied temperatures and the Rietveld refinement results are shown in Supplementary Table 11-15. The "rocking to breathing" transition is also confirmed in highly crystalline LYC, demonstrated by the leaps of interlayer Cl-Cl distances (S12 and S33) and bottleneck area size (SN1 and SN3), as shown in Supplementary Fig. 16. If T_c can be further tuned down to RT, the resulting ionic conductivity would be above 20 mS/cm. However, further increasing Br doping makes LYB phase become the thermodynamic stable phase instead of LYC and this change in long-range structure lowers the diffusivity and results in a lower conductivity in the samples tested.

To testify whether the SIT at lower T_c seen in $Li_3YCl_{6-x}Br_x$ is indeed due to the "rocking" to "breathing" transition, synchrotron *in situ* XRD and *ex situ* VT ND were conducted. XRD data of $Li_3YCl_{4.5}Br_{1.5}$ collected in the same temperature range for EIS test is shown in Supplementary Fig. 17a. Similar to LYC, no obvious phase transition is identified during the entire heating and cooling cycle, other than the anisotropic thermal expansion and shrinkage of the unit cell (Supplementary Fig. 17b and 17c). FDMs of 100 K and 500 K are shown in Fig. 5c and 5d. Clear residual Li scattering length density can be found on the two major lithium sites (6*g* and 6*h*) at both temperatures. No noticeable densities can be seen connecting these sites within the *ab*-plane (both at z = 0 and z = 0.5 planes) at 100 K at a cut-off of -0.03 fm/Å^3 (Supplementary Fig. 18a). Further decreasing the residual density to the cut-off threshold of -0.02 fm/Å^3 shows the connection of residual densities along *c*-axis direction and some residual densities can also be seen on the tetrahedral sites (Supplementary Fig. 18b). This implies that $Li_3YCl_{4.5}Br_{1.5}$ is a one-dimensional (along *c*-axis direction) Li^+ conductor at low temperature. In clear contrast, connected residual Li densities around $M1(Cl/Br)_6$ octahedra (z=0 plane) can be seen even at a large cut-off threshold (-0.02 fm/Å^3) for the 500 K data (Supplementary Fig. 19). These findings indicate that in *ab*-plane Li^+ diffusion pathways are opened up at 500 K. Similar to LYC, the 2D diffusion channels are still not available at z = 0.5 plane, as evidenced by the isolated residual Li densities even using very low threshold (Supplementary Fig. 19b). To further understand why the 2D Li^+ diffusion channels open up at much lower temperature in $Li_3YCl_{4.5}Br_{1.5}$ relative to that of LYC, Rietveld refinements were carried out using both VT ND and synchrotron XRD data. Refinement results are shown in Figs. 5e-5f and Supplementary Table 6-10 for ND data and in Supplementary Fig. 20 for XRD data. Clear transition from the "rocking" to "breathing" type collective motion of anions can be seen above ~340 K, as evidenced by the switch from the compression mode of $M1(Cl/Br)_6$ and

M3(Cl/Br)$_6$ octahedra to the expansion (along *c*-axis) mode (φ11 and φ33 angles in Fig. 5e and Supplementary Fig. 20a and 20b). This transition drastically increases the S12 and S33 distances (intralayer Cl/Br-Cl/Br, Fig. 5f and Supplementary Fig. 12c), resulting in the open-up of the diffusion bottleneck windows BN1 and BN3, as shown in Supplementary Fig. 21. The electrochemical performance of all-solid-state cells employing NMC811 cathode, $Li_3YCl_{4.5}Br_{1.5}$ electrolyte and InLi alloy anode is shown in Supplementary Fig. 22. The cells show reasonably good capacity and rate performance, despite that a relatively low stack pressure of ~20 MPa is used, benefiting from the high conductivity of $Li_3YCl_{4.5}Br_{1.5}$. Yet, more substantial engineering and optimization in the configuration and fabrication of the cells (e.g., stack pressure, particle size of the solid electrolyte, type and morphology of the cathode, etc.) are necessary to further improve the cycling and rate performances.

Extending Br doping limit in $P\bar{3}m1$ structure

From the above results, it is confirmed that substituting of Br at Cl site can better trigger the transition from the rocking mode to the breathing mode in LYC structures, which resulted in a lower T_c of 70 °C. However, in $Li_3YCl_{6-x}Br_x$ system, the solid solubility limit of Br is at $x = 1.5$. To further lower T_c to RT, it is then necessary to push the Br doping limit higher. We then designed $Li_3GdCl_{6-x}Br_x$ series with the expectation that the greater size of Gd^{3+} (0.938 pm)[31] than Y^{3+} (0.9 pm) can promote the tolerance of Br mixing in LYC structure. A series of $Li_3GdCl_{6-x}Br_x$ samples were synthesized and tested. Their XRD patterns and Arrhenius plots of the conductivity are shown in Supplementary Figs. 23a and 23b, respectively. Due to the larger size of Gd^{3+} than Y^{3+}, only with x = 3, LYC phase is obtained with minor LYB phase impurity. The Rietveld refinement result is shown in Fig. 6a. The Nyquist plots of $Li_3GdCl_3Br_3$ collected at varied temperatures are shown in Supplementary Fig. 24. Fig. 6b shows the Arrhenius plot of the conductivity of $Li_3GdCl_3Br_3$. It shows an σ_{rt} of 11 mS cm^{-1}, which is to date the highest among reported halide-based lithium ionic conductors. Unfortunately, as Gd is an extremely absorbing element for ND, ND was not conducted. However, $Li_3GdCl_3Br_3$ indeed shows a lowered T_c at -10 ^oC, evidenced by the very different E_a values above and below this temperature (Fig. 6b), which is similar to what was observed in $Li_3YCl_{6-x}Br_x$ series samples. This result clearly demonstrates the success of the design strategy to low T_c as an effective means to achieve very high conductivity at RT. In situ synchrotron XRD were collected for $Li_3GdCl_3Br_3$ from 420 K down to 220 K. The diffraction patterns are shown in Supplementary Fig. 25 and refinement results are shown in Fig. 6c-6e. φ22 clearly shows the transition from the "rocking" to "breathing" type collective motion of anions at ~260 K (Fig. 6c), which is consistent with the EIS results. As a result, the bottlenecks (S12 and S33) for the 2D diffusion channels within *ab*-plane open up (Fig. 6d and 6e).

Conclusion

In conclusion, this work systematically revealed that the SIT in halide compounds with LYC structures is triggered by the change of the collective motion of the anions, which not only explains the discrepancies between previous experimental and computational results, but also offers an effective rational design strategy. $Li_3YCl_xBr_{6-x}$ and $Li_3GdCl_3Br_3$ compounds are designed following the strategy of lowing T_c. Lower T_c of 70 ℃ and -10 ℃ were realized and high room temperature conductivities of 6.1 mS cm^{-1} and 11 mS cm^{-1} are achieved in $Li_3YCl_{4.5}Br_{1.5}$ and $Li_3GdCl_3Br_3$, respectively. This is a successful example of rational materials design guided by the structure-property relationship revealed by in-depth crystal structure characterization with synchrotron and neutron scattering techniques. The discovery of the highly conductive halide SEs offers new options for the development of ALSOLIBs and the design of ionic conductors.

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Author contributions

Z.L. and H.C. conceived the ideas and designed the experiments. Z.L conducted synthesis, electrochemical testing, and part of the characterizations. P.C. and J.L. performed ND characterizations and analyses. S.W. performed computer simulations under the supervision of

Y.M.. S.S. and S.C. contributed to the processing of the materials. M.L., Z.L. and S.X. performed mechanical property measurements and analyses. Z.L., H.C., J. L., and W.S. wrote the manuscript. All authors reviewed and revised the manuscript.

Competing interests

The authors declare no competing interests.

Figure Legends/Captions

Fig. 1: Crystal structure of Li_3YCl_6. a, Rietveld refinement against ND data (Bank 2, center 2θ = 31°). Experiment data are shown in back dots, calculated data in red curve and difference in blue. Bragg reflection positions are shown in magenta markers. **b,** Crystal structure of LYC viewed from [110] direction. **c,** Crystal structure viewed from [001] direction showing the Y layer. **d,** Crystal structure viewed from [001] direction showing the Li layer. Y at 1a site is in dark cyan. Li^+ at 6h site (fully occupied) is in orange. Partially occupied 2d sites of Y in Y layer and Li layer are in blue and magenta, respectively.

Fig. 2: Ionic conductivity and Li diffusion paths of LYC visualized by Fourier difference map (FDM) generated from ND patterns at varied temperatures. a, Arrhenius plot of the conductivity of LYC. **b**, Neutron diffraction pattern of LYC collected at different temperature. FDM generated from ND pattern of YCl_6 at 100 K with a cut-off of **c,** -0.035 fm/Å^3 and **d,** -0.02 fm/ Å^3. FDM generated from ND pattern of YCl_6 at 500 K with a cut-off of **e,** -0.03 fm/Å^3 and **f,** -0.02 fm/ Å^3. The projections along c-axis are shown in Supplementary Figs. 3-4.

Fig. 3: Collective motion of anion ligands and its influence on Li ion diffusion behavior. a, Lattice parameter extracted from Rietveld refinement against ND patterns of LYC at varied temperature. **b,** Li occupancy at 6g and 6h sites at varied temperature. 6h sites are fully occupied below 400 K and turn to be partially occupied at 500 K. **c,** Volume change of $M1Cl_6$, $M2Cl_6$ and $M3Cl_6$ at varied temperature. **d,** Schematic of Li ions diffusion bottleneck in Y layer in LYC. **e,** Schematic of Li ions diffusion bottleneck in Li layer in LYC. **f,** Evolution of Cl-Y-Cl angle in $M1Cl_6$ and $M3Cl_6$ octahedra at varied temperature. **g,** Evolution of Li ions diffusion bottleneck S12 and S33 in Y layer at varied temperature. The error bars in these plots are the "estimated standard deviations" of the corresponding refined parameters, which is a measure of the irreducible minimum in the uncertainty of refined parameters during Rietveld refinement.

Fig. 4: AIMD simulations of LYC at different temperatures. a, Average intralayer Cl-Cl distances (S12 and S13) evolution against temperature. **b,** Mean square displacement (MSD) of Li^+ in each direction at 350 K. **c,** Mean square displacement (MSD) of Li^+ in each direction at 600 K. **d,** Intralayer Cl-Cl distances (S12) distribution at different temperatures. **e,** Intralayer Cl-Cl distances (S33) distribution at different temperatures.

Fig. 5. Activating 2D in *ab*-plane Li^+ diffusion path in $Li_3YCl_{6-x}Br_x$. a, Synchrotron XRD patterns (λ = 0.24083 Å) of LYC, $Li_3YCl_{5.5}Br_{0.5}$, Li_3YCl_5Br and $Li_3YCl_{4.5}Br_{1.5}$. They all crystallized in $P\bar{3}m1$ structure with minor LiCl impurity. **b,** Comparison of Arrhenius plot of the

conductivity of $Li_3YCl_{6-x}Br_x$. **c,** FDM generated from ND data of $YCl_{4.5}Br_{1.5}$ at 100 K with a threshold of -0.02 fm/Å^3. **d,** FDM generated from ND data of $YCl_{4.5}Br_{1.5}$ at 500 K with a threshold of -0.015 fm/Å^3. **e,** Evolution of Cl-Y-Cl angle in $M1Cl_6$ and $M3Cl_6$ octahedra at varied temperature. **f,** Evolution of intralayer Cl-Cl distances S12 and S33 at varied temperature. The error bars in these plots are the "estimated standard deviations" of the corresponding refined parameters, which is a measure of the irreducible minimum in the uncertainty of refined parameters during Rietveld refinement.

Fig. 6. Design of $Li_3GdCl_3Br_3$ as solid-state electrolyte. a, Rietveld refinement of $Li_3GdCl_3Br_3$ against synchrotron X-ray diffraction data. The refinement result shows $Li_3GdCl_3Br_3$ mainly crystallize in LYC structure (85 wt.%). **b,** Arrhenius plot of the conductivity of $Li_3GdCl_3Br_3$ at extended low temperature range. T_c appears at -10 ºC. **c,** Evolution of Cl/Br-Gd-Cl/Br angle φ22 in $M3Cl_6$ octahedra at varied temperature. **d,** Evolution of Li ions diffusion bottleneck S12 Gd layer at varied temperatures. **e,** Evolution of Li ions diffusion bottleneck S33 Gd layer at varied temperatures. The error bars in these plots are the "estimated standard deviations" of the corresponding refined parameters, which is a measure of the irreducible minimum in the uncertainty of refined parameters during Rietveld refinement.

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Methods

Material Synthesis. $Li_3YCl_{6-x}Br_x$ (x = 0, 0.5, 1, 1.5) were synthesized via high energy ball-milling and subsequent heat treatment. Anhydrous LiCl (>99%, Sigma-Aldrich), LiBr (>99%, Sigma-Aldrich) and anhydrous YCl_3 (99.99%, Sigma-Aldrich) as starting materials were weighed in desired molar ratio and ball-milled with using zirconia jars (50 mL) and balls in a planetary ball mill (PM 200, Retsch) at 500 rpm for 5h. The hot-pressed Li_3YCl_6, $Li_3YCl_{5.5}Br_{0.5}$, Li_3YCl_5Br and $Li_3YCl_{4.5}Br_{1.5}$ were prepared by pressing the as-ball-milled powder into pellets, heated under 1.5 ton to 200 ^{o}C and held for 10 minutes. All the processes were carried under Ar atmosphere. $Li_3GdCl_{6-x}Br_x$ were synthesized through a similar protocol. Anhydrous LiCl (> 99%, Sigma-Aldrich), LiBr (> 99%, Sigma-Aldrich), anhydrous $GdCl_3$ (≥ 99%, Strem) and anhydrous $GdBr_3$ (≥ 99%, Strem) were weighed in desired molar ratio and ball-milled at 500 rpm for 5h followed by hot-pressing.

Material Characterization.

Lab X-ray diffraction (XRD) patterns data were collected with using a D8 Advance X-ray diffractometer (Bruker AXS) with Mo radiation ($\lambda_{K\alpha 1}$ = 0.7093 Å). High resolution synchrotron XRD spectra were collected at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL) at beam line 17-BM and at 28ID-2 XPD beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory (BNL).

Neutron diffraction and PDF

Data collection: Neutron total scattering data were collected at Spallation Neutron Source (SNS) NOMAD beamline[32]. About ~ 0.3 g powder samples were loaded into 3 mm thin-walled quartz capillaries for the measurements. The collected scattering data were background subtracted from the measurements of empty 3mm quartz capillary, and then normalized by the scattering from a 6 mm vanadium rod to correct for incident beam profile and detector efficiency. The Bragg diffraction data were reduced in bank-by-bank manner (data from detector banks centered at 31°, 67°, 122° and 154° were used for Rietveld refinement). For the PDF data reduction, the obtained one-frame structure function S(Q) were Fourier transformed into the reduced pair distribution function using the following equation with a Q_{max} of 35 $Å^{-1}$:

$$G(r) = \left(1 - g(r)\right)r = \frac{1}{2\pi^2\rho_0}\int_{Qmin}^{Qmax} Q(S(Q)-1)sin(Qr)dQ$$

Structure refinement:

Neutron: structure refinements using neutron Bragg diffraction were carried out using TOPAS v6 software[33]. Time-of-flight (TOF) were converted to d-spacing using the conventional second order polynomial TOF = ZERO + DIFC*d + DIFA*d^2, where ZERO is a constant, DIFC is the diffractometer constant and DIFA is an empirical term to correct for sample displacements and absorption induced peak shifts. DIFC were determined from the refinement of a standard NIST Si-640e data set and held fixed, while Zero and DIFA were refined to account for the sample displacements and wavelength dependent effects. The moderator induced line profile was modeled using a modified Ikeda-Carpenter-David function[34,35]. Lorentz factor is corrected by multiplying d^4.[36] The absorption correction was carried out using the empirical Lobanov formula (assuming each detector bank has an average scattering angle)[37].

Rietveld refinement using X-ray Bragg diffraction: fundamental peak profile approach was used to describe the instrument peak profile. The sample broadening from size and microstrain were also included during the refinement. Sequential structure refinements were carried out using TOPAS version 6.

Electrochemical Measurements. Ionic conductivity of samples was measured with electrochemical impedance spectroscopy (EIS) with using an electrochemical impedance analyzer (VMP3, Bio-Logic) and a custom-built electrochemical cell. Typically, ~1 g $Li_3YCl_{6-x}Br_x$ powder was pressed into a pellet with a diameter of ½ inch at a pressure of 100 bars. Two stainless steel rods were used as the ion-blocking electrodes. EIS data were collected in the temperature range of 25 °C to 200 °C in a frequency range of 1 MHz to 1 Hz and with AC amplitude of 50 mV.

For the all-solid-state battery assembly, a battery configuration similar to previously reports was employed[12]: NMC811, LYC and super P were mixed in a weight ratio of 65: 30 :5 as the cathode composites. 120 mg $Li_3YCl_{4.5}Br_{1.5}$ was pressed into a pellet (d = ½ inch) in a PMMA sleeve at 294 MPa as the separator. ~10 mg cathode composites were spread on one side of the pellet and pressed at 294 MPa. InLi alloy was attached on the other side of the pellet to serve as the anode. Stainless steel rods were used as current collectors. The cycling tests were performed on solid cells in galvanostatic mode between 2.52 and 4.3 V vs. Li^+/Li at room temperature.

Computation Methods.

First-Principles Computation: All density functional theory (DFT) calculations were carried out using Vienna Ab initio Simulation Package[38] (VASP) within projector augmentedwave[39] (PAW) approach. Generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional[40] was used for most energy calculations. The plane-wave energy cutoff and k-points density used in the calculations were consistent with that of Materials Project[41] (MP).

Structural ordering: Both LYC and $Li_3YCl_{6-x}Br_x$ samples are indexed well with hexagonal close-packed structure with space group $P\bar{3}m1$, where Li partially occupies the octahedral 6h, 6g sites.

In $Li_3YCl_{6-x}Br_x$, the Br partially occupy the 6i sites with Cl. Based on experimentally refined structure, we enumerated all configurations in a unit cell of LYC and generated 50 symmetrically distinctive structures in a unit cell of LYBC by randomizing the disordered occupancies. Then we performed structural relaxation in the DFT calculations, the lowest-energy structure is identified as the ground-state structure for further calculations. It should be noted that the same uniform Y sublattice is used in all our structural ordering to reduce the coulombic repulsion.

Ab Initio Molecular Dynamics Simulation: We performed AIMD simulation in 1×1×2 supercell models with lattice parameters larger than 10 Å in each lattice direction using NVT ensemble with Nosé-Hoover thermostat [1]. Non-spin mode, a time step of 2 fs, and Γ-centered 1×1×1 k-point grid were used. In each simulation, structures were heated from 100K to the target temperatures (350–900 K) at a constant rate during a period of 2 ps. The lithium ionic conductivity was calculated following the Nernst− Einstein relation as:

$$\sigma = \frac{N}{V}\frac{q^2}{k_B T}D = \frac{q^2}{Vk_B T}\frac{\mathrm{TMSD}(\Delta t)}{2d\Delta t}$$

where N is the number of the mobile carriers and d is the diffusion dimensionality, which is 3 in our simulation, V is the volume of the model, q is the charge of the carrier, k_B is the Boltzmann constant, and T is the temperature, total mean square displacement (TMSD) represents the total diffusion of all lithium ions in the material. Arrhenius relation is used to get activation energy and to extrapolate ionic conductivity at the desired temperature:

$$\sigma T = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right)$$

where E_a is the activation energy, σ_0 is the pre-exponential factor. Given that ion hopping is a stochastic process, the statistical deviations of the conductivity were evaluated according to the number of hopping events in our previous report [2]. The total time duration of AIMD simulations was within the range of 100 to 400 ps until the ionic diffusivity converged with a relative standard deviation between 20% to 40%.

Data Availability

All data in this work are available in the text and Supplementary Information. The relevant raw data are listed in Excel documents and provided as source or supplementary data files. Source data are provided with this paper.