A universal wet-chemistry synthesis of solid-state halide electrolytes for all-solid-state lithium-metal batteries

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Solid-state halide electrolytes have gained revived research interests owing to their high ionic conductivity and high-voltage stability. However, synthesizing halide electrolytes from a liquid phase is extremely challenging because of the vulnerability of metal halides to hydrolysis. In this work, ammonium-assisted wet chemistry is reported to synthesize various solid-state halide electrolytes with an exceptional ionic conductivity (>1 mS cm⁻¹). Microstrain-induced localized microstructure change is found to be beneficial to lithium ion transport in halide electrolytes. Furthermore, the interfacial incompatibility between halide electrolytes and lithium metal is alleviated by transforming the mixed electronic/ionic conductive interface into a lithium ion-conductive interface. Such all-solid-state lithium-metal batteries (ASSLMBs) demonstrate a high initial coulombic efficiency of 98.1% based on lithium cobalt oxide and a high discharge capacity of 166.9 microampere hours per gram based on single-crystal LiNiO.6MnO.2CoO.2O2. This work provides universal approaches in both material synthesis and interface design for developing halide-based ASSLMBs.

INTRODUCTION
All-solid-state lithium-metal batteries (ASSLMBs) are attracting tremendous attention because of their high theoretical energy density and much-improved safety (1, 2). To develop ASSLMBs, a solid-state electrolyte is an indispensable component to replace conventional organic separators and flammable organic liquid electrolytes. Meanwhile, lithium metal anodes are used to boost the energy density (3, 4). Over the past decades, various solid-state electrolytes have been developed, such as polymer electrolytes (5–7), oxide electrolytes (8, 9), sulfide electrolytes (10), borohydrides (11–15), and recently revived halide electrolytes (Li₃MX₆, M = Y and In; X = Cl, Br, and I) (16, 17). Among them, polymer electrolytes show excellent flexibility and viability for manufacturing but low room temperature (RT) ionic conductivity (5–7). Oxide electrolytes demonstrated high ionic conductivity and wide electrochemical windows but unfavorable mechanical stiffness for processing (8, 9). Sulfide electrolytes exhibit high ionic conductivity and soft mechanical properties but poor air stability, being prone to release toxic H₂S gas upon exposure to humid air (18). Recently, solid-state halide electrolytes (e.g., Li₃YCl₆ and Li₃YBr₆) have gained substantial research attention because of their high ionic conductivity (>1 mS cm⁻¹), high-voltage cathode compatibility, and favorable mechanical properties for directly cold-sintering for intimate solid-solid ionic contact (19). Compared to sulfide electrolytes, solid-state halide electrolytes do not release harmful H₂S gas when exposed to the ambient environment and have better high-voltage stability and wider electrochemical windows, making them attractive and feasible for ASSLMBs toward high safety and high energy density (16).

Inspired by these advantages, research into halide electrolytes has rapidly revived in recent years. For example, our group developed Li₃InCl₆ (20–23), Li₃ScCl₆ (24), and Li₃Y₁ₓInₓCl₆ (25); optimized Li₃YBr₆ (26); and provided comprehensive reviews about halide electrolytes (16, 17). Nazar and coworkers also synthesized LiₓM₀.₇ZrₓCl₆ (M = Y and Er) (27) and spinel Li₂Sc₂/₃Cl₄ (28) with a disordered spinel structure. Zeier and coworkers investigated LiₓYCl₆ (29), LiₓErCl₆ (29, 30), NaₓEr₁₋ₓZrₓCl₆ (31), and LiₓEr₁₋ₓZrₓCl₆ (32). Jung and coworkers (33) developed cost-effective Fe-doped LiₓZrCl₆. Besides, β-LiAlF₆ has also been synthesized with a low RT ionic conductivity (34), which could be useful as a surface coating material for the high-voltage cathodes (35). Along with the experimental progress, theoretical calculations were widely used to predict the electrochemical stability and ionic conductivity of halide electrolytes (36–39). Most of these halide electrolytes were synthesized by a mechanochemical approach. So far, only Li₃InCl₆ can be synthesized from an aqueous solution for easy scale-up, as demonstrated in our previous work with a hydrate intermediate (Li₃InCl₆·H₂O) (20). Other halide electrolytes cannot be synthesized from the solvent-assisted process because of the easy hydrolysis of MCl₃·nH₂O upon heating. Considering the wet-chemistry method with great advantages in controlling the morphology and size of solid electrolytes as well as fabricating sheet-type electrodes with intimate solid-solid ionic contact for practical pouch cell manufacturing (22, 40), it is of great importance to develop a general wet-chemistry route to synthesize halide electrolytes with a decent ionic conductivity.

On the other hand, using lithium metal as the anode to realize ASSLMBs is compulsory to realize the high energy density competitive with that of the prevailing lithium-ion batteries based on liquid electrolytes (3). However, the poor interfacial stability between halide electrolytes and lithium metal is another concern for the successful application of halide electrolytes in ASSLMBs (41). Therefore, a rational design of the anode interface between halide electrolytes and lithium metal is an urgent task for propelling ASSLMBs.

With the two motivations in mind, we report ammonium-assisted wet chemistry to synthesize solid-state halide electrolytes. Inspired
by the industrial “ammonium chloride route” to synthesize anhydrous MCl₃ (M = trivalent metals) (42, 43), the most common issue of the MCl₃ hydrolysis in water is inhibited by the formation of (NH₄)₃[MCl₆] intermediates. Therefore, the ammonium-assisted wet-chemistry synthesis is developed to be a universal approach to obtaining various solid-state halide electrolytes. Taking Li₃YCl₆ as an example, Li₃YCl₆ with an RT ionic conductivity of 0.345 mS cm⁻¹ was successfully achieved. To demonstrate the universality, Li₃ScCl₆, Li₃YBr₆, and Li₃ErCl₆ were obtained with high ionic conductivity of 1.25, 1.09, and 0.407 mS cm⁻¹, respectively. Localized microstrain-induced microstructural change is found to be beneficial for Li⁺ transport along the ab plane, thus improving the ionic conductivity. Moreover, the long-standing anode interface issue between halide electrolytes and lithium metal was resolved by changing the mixed Li⁺/Cl⁻ conductive interface into a Li⁺-conductive interface, effectively preventing the continuous reduction and degradation of halide electrolytes. As a result, halide-based ASSLMBS are successfully constructed with excellent electrochemical performance. It should be mentioned that this is the first time to report halide-based ASSLMBS with exceptional electrochemical performance, eliminating the considerable concern for their anode interface incompatibility. The present study lays the groundwork for future research into halide-based ASSLMBS toward high energy density and excellent safety.

RESULTS
Ammonium-assisted wet-chemistry synthesis of solid-state halide electrolytes
We first tried to synthesize Li₃YCl₆ via a wet-chemistry approach with various solvents, such as ethanol, tetrahydrofuran, and acetonitrile, as these solvents can dissolve YCl₃ and LiCl. However, only impurities LiCl and yttrium oxychloride (YOCl) were observed by x-ray diffraction (XRD) patterns (fig. S1). Inspired by the traditional “ammonium halide routes” to produce highly pure MCl₃ in which NH₄Cl is used as the coordination reagent, we purposely added NH₄Cl into the solvents to coordinate with YCl₃ forming (NH₄)₃[YCl₆] intermediate (42, 43). During the following thermal decomposition process, LiCl reacts with (NH₄)₃[YCl₆] to produce Li₃YCl₆. Below is the proposed reaction route (42)

\[\text{MCl}_3 \cdot n\text{H}_2\text{O} + 3\text{NH}_4\text{Cl} \xrightarrow{\text{Heating}} \text{(NH}_4)_3\text{[MCl}_6] + 3\text{LiCl} \]  

\[ \text{(NH}_4)_3\text{[MCl}_6] \xrightarrow{\text{Heating}} \text{Li}_3\text{MCl}_6 + 3\text{NH}_3 + 3\text{HCl} \]

M³⁺ represents the trivalent Y³⁺, Sc³⁺, Er³⁺, etc. The solvent is deionized water, which is cheap, abundant, and environmentally friendly. The (NH₄)₃[YCl₆] intermediate was identified by XRD (fig. S2). The intermediate (NH₄)₃[YCl₆] LiCl composite can be completely decomposed at around 400°C, as analyzed by thermogravimetry analysis and differential scanning calorimetry (TGA-DSC) (Fig. 1A). The large endothermic peaks lower than 400°C are related to ammonium decomposition, while the small endothermic peaks above 400°C indicate the formation of the Li₃YCl₆ phase. On the basis of the TGA-DSC results, the complex chlorides were annealed at 350°, 400°, 450°, 500°, and 550°C for 5 hours under Ar atmosphere. As synthesized Li₃YCl₆ from different temperatures are named as Li₃YCl₆-350, Li₃YCl₆-450, Li₃YCl₆-500, and Li₃YCl₆-550, respectively. The XRD patterns of these Li₃YCl₆ samples are displayed in Fig. 1B. After heating at 350°C, the obtained powder contained a lot of LiCl precursor and barely any Li₃YCl₆, suggesting that 350°C was not enough to fully decompose the intermediate (NH₄)₃[YCl₆] or form Li₃YCl₆ phase. Heating above 400°C, both LiCl and Li₃YCl₆ were observed by XRD, suggesting that LiCl partially reacted with (NH₄)₃[YCl₆]. Further increasing the heating temperature to above 450°C, mainly XRD characteristics of Li₃YCl₆ were shown with the suppressed characteristic peak of LiCl at 34.55° (highlighted by a green bar). Heat treatment at higher temperatures can increase the crystallinity of Li₃YCl₆ and decrease the LiCl impurity, as suggested by the XRD results of Li₃YCl₆-500 and Li₃YCl₆-550. However, high-crystallinity may not be beneficial for its ionic conductivity, as suggested in previous studies (19). Figure 1C displays the slow-scanned XRD pattern and Rietveld refinement result of Li₃YCl₆-500. Li₃YCl₆ consists of a hexagonal close-packed anion arrangement with trigonal P-3m1 space group (ICSD no. 04-009-8882; all the cations are sited at the octahedral center. Table S1 shows the detailed structural information of the Rietveld refinement results, which are compared with the structure information of Li₃YCl₆ in the database. The XRD refinement result also showed that the content of LiCl impurity was about 4.3 weight % (wt %).

The particle size of the as-synthesized Li₃YCl₆-500 is around 400 nm, while the crystallite size is only 159.11 nm (Fig. 1D and fig. S3), which is significantly smaller than the micrometer size of Li₃YCl₆ synthesized by the mechanochemical method or comelting method (44). It is well known that the small size effect would induce localized microstrain in materials because of the localized disturbance in the lattice or defect formation. To understand the microstrain effect on the ionic conductivity of as-prepared halide electrolytes, we quantified the microstrain in small-size Li₃YCl₆ by the Williamson-Hall method. The microstrain in small Li₃YCl₆ was 0.118% (Fig. 1D). It was found that the bond lengths of Li—I—Cl, Li—I—Cl, and Li—I—Cl were elongated as compared in fig. S4, which is the result of the microstrain (ε) induced by the local structure change. It is anticipated that the elongated Li—I—Cl bonds accelerate Li-ion transport along the ab plane (Fig. 1D), thereby increasing the ionic conductivity (table S3).

Fig. 2A shows the corresponding Arrhenius plots of Li₃YCl₆ obtained from different temperatures. The activation energy (Ea) is calculated by the Arrhenius Eq. 1

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

where σ represents the ionic conductivity, σ₀ is a prefactor, T is the absolute temperature, and k_B is the Boltzmann constant. The RT ionic conductivities and corresponding activity energies of Li₃YCl₆ under various annealing temperatures are shown in Fig. 2B. The corresponding electrochemical impedance spectroscopy (EIS) profiles are shown in fig. S5.

The ionic conductivity of the Li₃YCl₆ increased with increasing annealing temperatures but decreases after 500°C. The highest RT ionic conductivity of 0.345 mS cm⁻¹ is obtained at 500°C, with the lowest activation energy of 0.39 eV (Fig. 2B). The Li₃YCl₆ showed a higher ionic conductivity and lower activation energy than that synthesized by the comelting method (0.058 mS cm⁻¹; fig. S6) (19). The enhancement in the ionic conductivity is attributed to local structure distortion caused by the localized microstrain. The Li⁺ transport...
Figure 1. Synthesis and structural analysis of wet-chemistry Li₃YCl₆. (A) TGA-DSC curves of (NH₄)₃[YCl₆]·3LiCl composite. (B) XRD patterns of Li₃YCl₆ annealed under different temperatures. (C) Rietveld refinement of slow-scanned Li₃YCl₆-500. (D) Williamson-Hall plot. FWHM, full width at half maximum. (E) Crystal structure of wet-chemistry Li₃YCl₆ obtained from XRD refinement. a.u., arbitrary units.

As the ammonium-assisted route is a universal approach in industry to produce various anhydrous MX₃ (M = Tb-Lu, Y, and Sc; X = Cl, Br, and I) (42-44), the ammonium-assisted wet-chemistry approach can probably be a universal approach to synthesizing various halide electrolytes with a small size. To prove the generality, Li₃ScCl₆, Li₃ErCl₆, and Li₃YBr₆ were further synthesized by the wet-chemistry approach. Figure 3A shows the XRD pattern of Li₃ScCl₆. Different from the structure of Li₃YCl₆, Li₃ScCl₆ belongs to a monoclinic structure (C2/m, ICSD no. 04-009-8885) consisting of a cubic close-packed anion arrangement (24). All the cations site in the octahedral sites (fig. S8). Figure 3B exhibits the Arrhenius plot of Li₃ScCl₆. Its RT ionic conductivity reached 1.25 mS cm⁻¹, and the corresponding activation
energy is 0.31 eV. The high ionic conductivity was also confirmed by the electron-blocking DC test (fig. S9), suggesting that the main charge carriers are lithium ions. The electronic conductivity of Li₃ScCl₆ is only 1.38 × 10⁻⁹ S cm⁻¹. The scanning electron microscopy (SEM) image in Fig. 3C displays that the size of Li₃ScCl₆ is 200 to 500 nm. In parallel, Fig. 3D shows the refinement results of Li₃ErCl₆ synthesized by the wet-chemistry method. It also shows 3.7% LiCl impurity based on XRD refinement results. The RT ionic conductivity of Li₃ErCl₆ is 0.407 mS cm⁻¹ with an activation energy of 0.47 eV, and the particle size is about 500 nm, as displayed in Fig. 3 (E and F). Not only the chloride-based halide electrolytes but also the bromide-based halide electrolytes can be synthesized. Figure S10A displays the refinement results of wet-chemistry Li₃YBr₆ with high purity, which have a high ionic conductivity of 1.08 mS cm⁻¹ and a low activation energy of 0.34 eV, and the particle size is about 500 nm, as displayed in Fig. 3 (E and F). Not only the chloride-based halide electrolytes but also the bromide-based halide electrolytes can be synthesized. The atomic occupancies of Li₃ScCl₆ in table S4 are kept unchanged for slow-scanned XRD refinement results (table S5). The Sc—Cl bonds are expanded as compared in table S6; thus, Li⁺ transport via [octa]-[tetra]-[octa] along the c axis is limited in comparison with the standard Li₃ScCl₆, which may be the underlying reason for the slightly lower ionic conductivity of Li₃ScCl₆ (Fig. 3B). The case of Li₃ErCl₆ is the same as the case of Li₃YCl₆, and the c axis is elongated, while the a axis and b axis are shrunk as compared in tables S7 and S8. The crystallite size of the Li₃ScCl₆ was determined to be 97.64 nm, and the microstrain is 0.166% (fig. S12), as calculated by the Williamson-Hall plot method. The microstrain in Li₃ErCl₆ was found to be 0.142%, and the crystallite size is 53.32 nm (fig. S12). In comparison, the wet-chemistry method may lead to microstrains that are several times...
larger than the solid-state reaction method. Overall, it is likely that the microstrain-induced local structural change is beneficial for Li-ion transport along the $ab$ plane in the halide electrolytes with a hexagonal closest packing anion framework (i.e., Li$_3$YCl$_6$ and Li$_3$ErCl$_6$), while the microstrain in halide electrolytes with a cubic closest packing sublattice (i.e., Li$_3$ScCl$_6$ and Li$_3$YBr$_6$) might not be favorable. These findings, while preliminary, suggest that understanding the role of localized microstrain in solid electrolytes is a bright direction to further boost their ionic conductivity.

**Interfacial stability toward lithium metal anodes**

So far, ASSLMBs based on halide electrolytes have seldom been demonstrated because of the incompatibility between lithium metal and halide electrolytes (36, 37, 41). To address this dilemma, we adopted the most common strategy, interface modification. On the basis of our previous studies, sulfide electrolytes demonstrated excellent stability against lithium metal (49). Sulfide electrolytes are not thermodynamically stable against lithium metal; however, the self-limited reactions between lithium metal and Li$_6$PS$_5$Cl can generate a stable interface consisting of Li$_2$S, Li$_3$P, and LiCl, constructing a Li$^+$-conductive interface (fig. S13) (50). In addition, it was recently found that the interface resistance between sulfide electrolytes and lithium metal is almost negligible (41). Therefore, it is reasonable to construct a stable Li$^+$-conductive interface between halide electrolytes and lithium metal by inserting a thin layer of Li$_6$PS$_5$Cl. Figure 4A shows the EIS of Li/Li$_3$YCl$_6$/Li symmetrical cells in a function of time. The semicircle at the high frequency corresponds to the Li$_3$YCl$_6$ bulk resistance. With the increase in time, another semicircle at the middle frequency appeared and enlarged, suggesting that a new interface was growing at the Li/Li$_3$YCl$_6$ interface (41). This phenomenon is reasonable because Li$_3$YCl$_6$ is easily reduced by lithium metal (37), forming Li$_3$Y alloys with high electronic conductivity (Fig. 4D). Therefore, Li$_3$YCl$_6$/Li interface is a mixed Li$^+$/e$^-$-conductive interface, leading to a continuous reduction of Li$_3$YCl$_6$ during the Li$^+$ plating/stripping process. To prevent the formation of the unfavorable mixed Li$^+$/e$^-$-conductive interface, a thin layer of highly Li$^+$-conductive Li$_6$PS$_5$Cl was inserted at the Li$_3$YCl$_6$/Li interface. Figure 4B shows the EIS profile of Li/Li$_6$PS$_5$Cl/Li$_3$YCl$_6$/Li$_6$PS$_5$Cl/Li symmetric cells. Comparatively, the semicircle at the middle frequency was absent, suggesting that the interfacial reactions between halide electrolytes and lithium metal were successfully suppressed. However, the overall impedance still increased with time, suggesting that interfacial reactions between Li$_6$PS$_5$Cl and lithium metal occurred. Considering the narrow electrochemical windows of Li$_6$PS$_5$Cl, Li$_6$PS$_5$Cl reacts with lithium metal spontaneously even without electrochemical process, generating Li$_3$S, Li$_3$P, and LiCl. Li$_3$P is highly Li$^+$ conductive, while Li$_3$S and LiCl are electronically insulative (Fig. 4E). Therefore, the formed interface between Li$_6$PS$_5$Cl and lithium metal is an excellent Li$^+$-conductive interface that is highly preferable in ASSLMBs. Figure 4C shows the Li$^+$ plating/stripping behaviors of Li/Li$_3$YCl$_6$/Li and Li/Li$_6$PS$_5$Cl/Li$_3$YCl$_6$/Li$_6$PS$_5$Cl/Li symmetrical cells over 500 hours. The overpotential of Li/Li$_3$YCl$_6$/Li gradually increased to about 600 mV. As a sharp contrast, the Li/Li$_6$PS$_5$Cl/Li$_3$YCl$_6$/Li$_6$PS$_5$Cl/Li can be stably cycled for up to 500 hours with a small overpotential of less than 100 mV.
Furthermore, x-ray photoelectron spectroscopy (XPS) was performed to analyze the Li$_3$YCl$_6$/Li interface and Li$_3$YCl$_6$/Li$_6$PS$_5$Cl/Li interface after cycling (fig. S14). As confirmed by XPS analysis, Li$_3$YCl$_6$ was reduced or decomposed by lithium metal after 100 hours of cycling, which is the reason for the increasing overpotential observed during the plating/stripping process. As a sharp comparison, the interface is changed into a solely ionic conductive interface consisting of Li$_2$S, LiCl, and Li$_3$P, which effectively blocks electrons across the interface, thus well stabilizing the anode interface for ASSLMBs.

ASSLMBs based on bilayer solid electrolytes

As a stable interface between halide electrolytes and lithium metal was successfully constructed, an ASSLMB based on halide electrolyte can be fabricated. Figure 5A illustrates the configuration of ASSLMBs based on Li$_3$YCl$_6$, in which a thin layer of Li$_6$PS$_5$Cl is inserted between Li$_3$YCl$_6$ and lithium metal anode to form a stable anode interface. It should be mentioned that LiCoO$_2$ (LCO) is used without any interfacial coating because of the high oxidative stability of Li$_3$YCl$_6$ (>4.25 V versus Li$^+$/Li). Figure 5B shows the initial charge/discharge curves of the ASSLMBs at 0.1 C. The discharge capacity was 139.1 mA·hour g$^{-1}$, and the initial coulombic efficiency (CE) was as high as 98.1%. The high discharge capacity is due to the intimate solid-solid contact between Li$_3$YCl$_6$ and LCO (figs. S15 to S17). The high CE is ascribed to the use of lithium metal as the anode, which could supply any deficient Li ions unlike pure indium (In) foil or Li-In alloys. Figure 5C shows the cycling stability of ASSLMBs. It maintained a capacity of 118.5 mA·hour g$^{-1}$ with a high CE of ~99.3% on average over 50 cycles. Figure 5D exhibits the rate performance of ASSLMBs. Because of the limited ionic conductivity of Li$_3$YCl$_6$, the RT rate performance was limited, but much better rate performance can be demonstrated at an elevated testing temperature of 60°C. A discharge capacity of 58.6 mA·hour g$^{-1}$ was delivered at a current rate of 1 C, indicating that not only the solid-solid contact but also the high ionic conductivity of solid electrolytes is crucial for the rate performance of ASSLMBs. To verify this assumption, we further tested the rate performance of Li$_3$ScCl$_6$-based ASSLMBs (Fig. 5E), in which single-crystal LiNi$_0.6$Mn$_{0.2}$Co$_{0.2}$O$_2$ (SC-NMC622) was chosen as the active material because of its advantages in mechanical integrity and ion dynamics (51). Because of the high ionic conductivity of Li$_3$ScCl$_6$ (1.25 mS cm$^{-1}$), ASSLMBs with a configuration of SC-NMC622|Li$_3$ScCl$_6$|Li$_6$PS$_5$Cl|Li showed a high initial capacity of 166.9 mA·hour g$^{-1}$ with a CE of 85.6%. The ASSLMB retained a capacity of 81.1 mA·hour g$^{-1}$ at 1 C and 38.6 mA·hour g$^{-1}$ at 2 C at RT. The capacity remained at 85.9 mA·hour g$^{-1}$ at 0.2 C after 100 cycles. The energy density of ASSLMBs demonstrated in this work outperforms previous results, as compared in table S9.

DISCUSSION

In summary, ammonium-assisted wet chemistry is reported to be a universal strategy to synthesize various solid-state halide electrolytes with a submicrometer size. The obtained halide electrolytes can exhibit decent RT ionic conductivity (up to 1.25 mS cm$^{-1}$). Moreover, a thin layer of sulfide electrolyte was proven to be effective in preventing anode interfacial reactions between halide electrolytes and lithium metal. As a result, halide-based ASSLMBs with excellent electrochemical performance have been successfully demonstrated. This work provides an exemplary platform for developing halide-based ASSLMBs with high energy density. We believe that this universal ammonium-assisted wet chemistry can be further explored to synthesize other
solid-state electrolytes with a general formula of A<sub>3</sub>MX<sub>6</sub> (A = Li and Na; M = trivalent metals; X = Cl, Br, and I).

**MATERIALS AND METHODS**

**Ammonium-assisted synthesis of Li<sub>3</sub>MX<sub>6</sub> (M = Y, Sc, and Er; X = Cl and Br)**

First, stoichiometric mixtures of LiCl (99.9%; Sigma-Aldrich), NH<sub>4</sub>Cl (>99.5%; Sigma-Aldrich), and YCl<sub>3</sub>·6H<sub>2</sub>O (99.99%; Sigma-Aldrich) were weighed and dissolved into water. After complete dissolution, the mixture solution was transferred to a glass oven (Buchi glass oven, B-585) for drying at 80°C under vacuum. After drying, the white powder was transferred to a glove box and pressed into pellets for annealing at various temperatures (350° to 550°C) for 5 hours, respectively. The heating rate was 2°C min<sup>−1</sup>. Similar procedures were followed to synthesize Li<sub>3</sub>YBr<sub>6</sub>, Li<sub>3</sub>ScCl<sub>6</sub>, and Li<sub>3</sub>ErCl<sub>6</sub>, but changing the YCl<sub>3</sub>·6H<sub>2</sub>O to YBr<sub>3</sub> (99.9%; Sigma-Aldrich), ScCl<sub>3</sub> (99.99%; Sigma-Aldrich), and ErCl<sub>3</sub> (99.99%; Sigma-Aldrich), respectively.

**Characterizations**

The XRD patterns were obtained over the range of 10° to 120° using Cu Kα x-ray radiation with λ = 1.54178 Å (Bruker AXS D8 Advance). As-prepared halide electrolytes were sealed in an air-tight holder to avoid air exposure to protect them from ambient air. The
data for the XRD Rietveld refinement were collected by scanning 5 s per step with one step of 0.02°. Neutron diffraction data were collected at the NOMAD (Nanoscale-Ordered Materials Diffractometer) beamline at the Spallation Neutron Source, Oak Ridge National Laboratory. The Rietveld refinement was performed using GSAS-II (52). The crystal structure was visualized using VESTA (53). SEM images were recorded using a Hitachi S-4800 field emission SEM equipped with energy-dispersive spectroscopy. The XPS data were collected with a monochromatic Al Kα source (1486.6 eV) using the Thermo Scientific K-Alpha Spectrometer at the University of Toronto.

Electrochemical characterizations

Ionic conductivities of as-prepared halide electrolytes Li3MCl6 (M = Er, Y, and Sc) with a configuration of carbon|Li3MCl6|carbon were measured by the AC impedance technique on a VMP3 potentiostat/galvanostat (BioLogic). The halide electrolyte pellet was isostatically pressed under 500 MPa. Impedance was measured at a frequency range of 7 MHz to 0.1 Hz using an SP-300 impedance analyzer (BioLogic). The electrochemical stability was evaluated by cyclic voltammetry measurements using versatile multichannel potentiostat 3/Z (VMP3) with a Li|Li3YCl6|Li3YCl6—AB cell in a scan range of 0 to 5 V (versus Li’/Li) at 0.1 mV s⁻¹. To evaluate cycling performance, ASSLMs with a configuration of cathode|halide electrolyte|Li6PS5Cl|Li metal are fabricated. First, 70-mg halide electrolytes (Li3YCl6 or Li3ScCl6) and 30-mg Li6PS5Cl were pressed at 100 MPa. Second, 12-mg cathode composites (active materials|halide electrolyte = 85%:15%) were spread on one side of halide electrolyte pellets and pressed at 500 MPa. Third, a Li foil was attached to another side of halide electrolyte pellets and pressed at 50 MPa. Last, the mold cells were added with some pressure by a torque wrench (60 N·m). The LCO|Li3YCl6|Li6PS5Cl|Li battery was charged to 4.4 V at 0.1 C and then discharged to 2.8 V (versus Li’/Li). The SC-NMC622|Li3ScCl6—Li6PS5Cl|Li battery was charged to 4.4 V at 0.1 C and then discharged to 2.8 V (versus Li’/Li). The cathode composite mass is 12 mg. The electrochemical performance was evaluated using the Neware system.

SUPPLEMENTARY MATERIALS

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