High-Voltage Superionic Halide Solid Electrolytes for All-Solid-State Li-Ion Batteries

Kern-Ho Park, Kavish Kaup, Abdeljalil Assoud, Qiang Zhang, Xiaohan Wu, and Linda F. Nazar*

ABSTRACT: All-solid-state Li-ion batteries (ASSBs), considered to be potential next-generation energy storage devices, require solid electrolytes (SEs). Thiophosphate-based materials are popular, but these sulfides exhibit poor anodic stability and require specialty coatings on lithium metal oxide cathodes. Moreover, electrode designs aimed at high energy density are limited by their narrow electrochemical stability window. Here, we report new mixed-metal halide Li_{x−M_{1/3}}ZrCl_{6} (M = Y, Er) SEs with high ionic conductivity—up to 1.4 mS cm⁻¹ at 25 °C—that are stable to high voltage. Substitution of M (M = Y, Er) by Zr is accompanied by a trigonal-to-orthorhombic phase transition, and structure solution using combined neutron and single-crystal X-ray diffraction methods reveal a new framework. The employment of >4 V-class cathode materials without any protective coating is enabled by the high electrochemical oxidation stability of these halides. An ASSB showcasing their electrolyte properties exhibits very promising cycling stability up to 4.5 V at room temperature.

The provision of high energy density rechargeable Li-ion batteries has accelerated development of large-scale energy storage systems for electric vehicles and grid applications. The high energy density of current Li-ion batteries (LIBs) is achieved by increasing the cell voltage, which necessitates the use of organic liquid electrolytes and specialty additives. These can pose serious safety concerns. On the other hand, bulk-type all-solid-state Li-ion batteries (ASSBs) employing inorganic solid electrolytes (SEs) are considered promising candidates for large-scale energy storage devices, as they eliminate the liquid component and allow the possibility of implementing a lithium metal negative electrode to further increase energy density.

Oxide SEs were one of the first families that were widely explored. Perovskite-type Li_{1−x}La_{x}TiO_{3} (0 ≤ x ≤ 0.16), NASICON-type Li_{1/3}Al_{1/3}Ti_{1/3}(PO_{4})_{5/3}, and garnet-type Li_{1/2}La_{3/2}Zr_{2}O_{12} are the most notable oxide SEs and exhibit good ionic conductivity ranging between 10⁻⁴ and 10⁻³ S cm⁻¹. Nonetheless, their poor mechanical deformability makes effective contact with ceramic active materials very difficult, hindering ion transport at the interface. While favorable ionic contacts between oxide SE particles can be generated by high-temperature sintering, this cannot be used to improve the oxide SE/active material interface because of reactivity of the two components under these conditions. This problem is alleviated by the use of ductile sulfide SEs where intimate ionic contacts can be achieved by simple cold pressing. Superionic conductivities have been achieved for many sulfide SEs (e.g., Li_{10}GeP_{2}S_{12}, 1.2 × 10⁻² S cm⁻¹, Li_{3.33}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}, 2.5 × 10⁻² S cm⁻¹, argyrodites Li_{x}PS_{y}Cl_{z}, 0.5 × 10⁻² S cm⁻¹; and Li_{3.3}PS_{4.5}Cl_{1.5}, 0.94 × 10⁻² S cm⁻¹), and they have been proposed to be among the most plausible candidates for bulk ASSBs.

To utilize sulfide SEs in a 4 V-class cathode, a protective coating layer must be introduced on the surface of active materials because of the intrinsic instability of sulfide compounds at high potential. This originates from the oxidation of S²⁻ above 2.6 V. Intensive research has yielded numerous oxides to be potential coating materials, such as LiNbO₃, LiNb₀.₅Ta₀.₅O₃, Li₅Ti₃O₁₃, Li₅PO₄, Ta₂O₅, Al₂O₃, and Li₁₋ₓBₓC₂O₅. Nonetheless, solid electrolyte decomposition by reaction with other electronically active components such as the carbon additive or current collector is inevitable. It is also difficult to control the reproducibility and homogeneity of the coating process. While the poor electronic conductivity of the passivating coating layer (e.g., LiNbO₃: σ < 10⁻¹¹ S cm⁻¹) is necessary to reduce interfacial reaction, its typically low ionic conductivity (e.g., LiNbO₃: σ ≈ 10⁻⁷ S cm⁻¹) is not sufficient for efficient charge transport.
cm$^{-1}$) disrupts interparticle charge transport.$^{26,27}$ Overall, the quasi-stability of sulfide SEs limits the practical design of electrodes for ASSBs. Therefore, a search for new SEs with good electrochemical oxidative stability is critical for future improvement of ASSB performance.

Considering the multiple requirements for SEs including high ionic conductivity, ductility, as well as oxidation stability, we believe that chloride compounds are among the most plausible candidates. While the ionic radius of the chloride ion ($r_{\text{Cl}^-} = 181$ pm) is almost equivalent to that of sulfide ($r_{\text{S}^{2-}} = 184$ pm), its lower charge means that it will bind more weakly with Li$^+$, which is beneficial for facile cation diffusion. A recent computational study on chloride compounds also predicts their robustness to electrochemical oxidation.$^{28}$ Moreover, even better deformability than sulfide compounds is expected for chloride compounds, according to Fajan’s rule that predicts greater covalency for chloride compounds.$^{29}$ The members of the Li$_3$MCl$_6$ family (M = Sc, In, Lu, Er, Y, Ho, etc.) are some of the most well-known materials that contain multiple Li$^+$ sites in their lattice. While trigonal Li$_3$YCl$_6$ was reported to be a rather poor ionic conductor ($\sim 10^{-7}$ S cm$^{-1}$ at 110°C),$^{30}$ a recent revision of this material reveals that it can exhibit moderate room-temperature ionic conductivity of $4 \times 10^{-3}$ S cm$^{-1}$ as a well-crystallized material and up to $5.1 \times 10^{-4}$ S cm$^{-1}$ in a poorly crystalline form.$^{31}$ Trigonal Li$_3$ErCl$_6$ also exhibits similar ionic conductivity (ball-milled, $3.3 \times 10^{-4}$ S cm$^{-1}$; subsequently annealed, $S \times 10^{-5}$ S cm$^{-1}$).$^{32}$ A high ionic conductivity of $1.49 \times 10^{-3}$ S cm$^{-1}$ was observed recently for Li$_3$InCl$_6$, a material that was earlier reported in 1992 but with much poorer ionic conductivity ($10^{-5}$ S cm$^{-1}$).$^{34}$

Herein, we report a class of chloride solid electrolytes, Li$_3$-$x$M$_1$-$x$Zr$_x$Cl$_6$ (M = Er, Y), with excellent room-temperature ionic conductivity up to 1.4 mS cm$^{-1}$ that is due to a unique new structure. The conductivity is one of the highest among the reported chloride compounds. Most importantly, the superior electrochemical oxidation stability of this class is directly demonstrated by enabling stable cycling of ASSBs using unprotected LiCoO$_2$ as the cathode material. This confirms a computational prediction.$^{28}$

The aliovalent substitution of metal ions as a strategy to introduce vacancies in a mobile ion sublattice is an established approach to improve the ionic conductivity of inorganic materials.$^{3,13}$ In our case, the metal ion Zr$^{4+}$ ($r = 72$ pm) was selected as a substituent for either Er$^{3+}$ ($r = 89$ pm) or Y$^{3+}$ ($r = 90$ pm) because of its large ionic radius compared to other tetravalent metal ions. The Li$_3$-$x$M$_1$-$x$Zr$_x$Cl$_6$ (M = Er, Y) microcrystalline powders were prepared by a simple solid-state reaction at 450°C. Figure 1a shows the X-ray diffraction (XRD) patterns of Li$_3$-$x$Er$_1$-$x$Zr$_x$Cl$_6$ materials over the range of $x = 0$–0.6. The XRD pattern of Li$_3$ErCl$_6$ ($x = 0$) is in accord with its reported trigonal structure (space group: $P3\bar{m}1$).$^{30}$ The original framework which contains two octahedral Li sites is...
preserved up to $x = 0.1$ and is denoted as phase-I. When more Zr$^{4+}$ ions are introduced, a new XRD pattern is obtained at $x = 0.2$ that crystallizes in the $Pnma$ space group (phase-II) and is isostructural to Li$_3$LuCl$_6$.30 This structure is also adopted by Li$_3$YCl$_6$ at elevated temperatures.30 The average transition metal ion radius of Li$_{2.8}$Zr$_{0.2}$Er$_{0.8}$Cl$_6$ ($r = 85.6$ pm) is close to that of Lu$^{3+}$ ($r = 86.1$ pm), which is likely responsible for this behavior. As more Er$^{3+}$ is substituted by Zr$^{4+}$, following an excursion through a short two-phase region ($0.2 \leq x \leq 0.3$), another new solid-solution region (phase-III) is observed from $x = 0.367 - 0.6$, which exhibits a distinctly different and unique XRD pattern. Moreover, the same structural evolution is observed for Li$_{3-x}$Y$_x$Zr$_x$Cl$_6$ ($0 \leq x \leq 0.6$) (Figure 1b). Namely, at $x = 0$ and 0.1, the parent trigonal structure is maintained, whereas the Li$_3$LuCl$_6$-like structure (phase-II) is observed for Li$_{3-x}$Y$_x$Zr$_x$Cl$_6$ in the region $0.2 \leq x \leq 0.3$. At higher substitution levels ($0.367 \leq x \leq 0.600$), XRD patterns identical to those of phase-III in Li$_{3-x}$Er$_{1-x}$Zr$_x$Cl$_6$ are obtained (Figure S1). Thus, the average transition metal ion size is likely a key factor in determining the crystal structure of these materials.
The ionic conductivities at 25 °C and activation energies of Li$_{3-x}$Er$_x$Zr$_x$Cl$_6$ are shown in Figure 1c where the activation energies were determined according to the Arrhenius equation:

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

where $\sigma$ is the ionic conductivity, $T$ the temperature in K, $A_T$ the pre-exponential factor, $E_a$ the activation energy, and $k_B$ the Boltzmann constant. Typical Nyquist plots of a Ti|SE|Ti cell and Arrhenius plots are shown in Figure S2. The trends of ionic conductivities and activation energy parallel that of structural evolution upon Zr-substitution. Li$_3$ErCl$_6$ (x = 0) exhibits moderate ionic conductivity (8.7 × 10$^{-5}$ S cm$^{-1}$ at 25 °C). The conductivity increases to 3.6 × 10$^{-4}$ S cm$^{-1}$ for x = 0.1 where the original trigonal structure is preserved (phase-I) and increases further to 7.7 × 10$^{-3}$ S cm$^{-1}$ at x = 0.2 owing to the formation of phase-II. In the subsequent two-phase region (0.2 ≤ x ≤ 0.367) that encompasses phase-II and III, the ionic conductivity continues to increase as phase-III grows in relative fraction. The maximum ionic conductivity of 1.1 × 10$^{-3}$ S cm$^{-1}$ is obtained at x = 0.367 where pure phase-III is obtained. Particularly important is that the electronic conductivity of the material at x = 0.367 is very low, ~10$^{-10}$ S cm$^{-1}$, indicative of a pure single-ion conductor (Figure S3). Figure 1d shows the ionic conductivities of the Li$_{3-x}$Y$_x$Zr$_x$Cl$_6$ series. Similar to the Er compositions, the ionic conductivity increases as more Y$^{3+}$ ions are replaced by Zr$^{4+}$ ions. The maximum ionic conductivity (1.4 × 10$^{-3}$ S cm$^{-1}$ at 25 °C) is achieved for x = 0.5 (phase-III), which also exhibits the lowest activation energy (0.33 eV).

The crystal structure of phase-III was solved by single-crystal X-ray diffraction for Li$_2.5$Er$_0.5$Zr$_0.5$Cl$_6$ at 280 and 200 K (see Tables S1–S6 for details). The structure of Li$_2.5$Y$_0.5$Zr$_0.5$Cl$_6$ is assumed to be isomorphous, given its identical XRD pattern (Figures 1 and S1). While three Li sites were easily refi nable from single-crystal analysis despite the dominant heavy atoms, time-of-flight powder neutron diffraction (PND) was performed on polycrystalline Li$_2.5$Er$_0.5$Zr$_0.5$Cl$_6$ to more accurately locate the three Li sites and refi ne their occupancies. Lithium's negative neutron scattering length allows it to be easily distinguished (Er, 7.8; Zr, 7.2; Cl, 9.6; Li, −1.9 fm). The PND

### Table 1. Atomic Parameters of Li$_{2.5}$Er$_{0.5}$Zr$_{0.5}$Cl$_6$ Obtained from Refinement of Powder Neutron Diffraction at 280 K in Pnma (no. 62)$^a$

<table>
<thead>
<tr>
<th>atom</th>
<th>site</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>occ.</th>
<th>$U_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er1</td>
<td>4c</td>
<td>0.3677(3)</td>
<td>=1/4</td>
<td>0.5952(10)</td>
<td>0.533</td>
<td>0.0178(5)</td>
</tr>
<tr>
<td>Zr1</td>
<td>4c</td>
<td>=Er1 =Er1 =Er1</td>
<td>=Er1</td>
<td>=Er1 =Er1 =Er1</td>
<td>=Er1</td>
<td>=Er1</td>
</tr>
<tr>
<td>Cl1</td>
<td>8d</td>
<td>0.0096(2)</td>
<td>0.5852(4)</td>
<td>0.2450(5)</td>
<td>1</td>
<td>0.0264(3)</td>
</tr>
<tr>
<td>Cl2</td>
<td>8d</td>
<td>0.2541(2)</td>
<td>0.0856(4)</td>
<td>0.4212(4)</td>
<td>1</td>
<td>0.0265(3)</td>
</tr>
<tr>
<td>Cl3</td>
<td>4c</td>
<td>0.0023(4)</td>
<td>=1/4</td>
<td>0.2244(6)</td>
<td>1</td>
<td>0.0267(6)</td>
</tr>
<tr>
<td>Cl4</td>
<td>4c</td>
<td>0.7515(4)</td>
<td>=1/4</td>
<td>0.5835(8)</td>
<td>1</td>
<td>0.0286(6)</td>
</tr>
<tr>
<td>Li1</td>
<td>8d</td>
<td>0.1366(11)</td>
<td>0.076(2)</td>
<td>0.089(4)</td>
<td>0.77(2)</td>
<td>0.049(3)</td>
</tr>
<tr>
<td>Li2</td>
<td>8d</td>
<td>0.376(3)</td>
<td>0.070(4)</td>
<td>1.03(9)</td>
<td>0.30(2)</td>
<td>0.038(7)</td>
</tr>
<tr>
<td>Li3</td>
<td>8d</td>
<td>0.561(5)</td>
<td>0.085(7)</td>
<td>1.01(19)</td>
<td>0.193(13)</td>
<td>0.016(7)</td>
</tr>
</tbody>
</table>

$^a$Refined lattice parameters: a = 12.0389(2) Å, b = 11.1664(2) Å, and c = 6.4069(1) Å. Refined composition: Li$_{2.5}$Er$_{0.5}$Zr$_{0.5}$Cl$_6$. 

Figure 3. Phase evolution of Li$_3$M$_{1-x}$Zr$_x$Cl$_6$ (M = Er, Y) upon Zr substitution.
pattern and corresponding Rietveld fit are shown in Figure 2a. The data was initially fit using the single-crystal model (fixing the framework ions; Er, Zr, and Cl) and refining the positions of the lithium sites. Finally, because of the large neutron absorption cross section of Er, the Er/Zr ratio was fixed to the single-crystal value, and the other parameters were freely refined except for a constraint on total Li occupancy for charge balance (see Experimental Methods in the Supporting Information for details). The result (Table 1) is almost identical to the single-crystal solution (Table S1).

Figure 2b shows the [010] view of the phase-III Li2.5Er0.5Zr0.5Cl6 lattice, illustrating the arrangement of the (Er/Zr)Cl6 octahedra and the Li ions populating the b-axis channel. A comparison of the frameworks of phase-I (Li3ErCl6), phase-II (akin to Li3LuCl6), and phase-III is shown in Figure 3, illustrating the differences between them. While the phase transformation from phase I to II involves rearrangement of the metal ions, the transition of phase-II to phase-III includes tilting the (Er/Zr)Cl6 octahedra. The molar volumes of Li3-xEr1-xZrCl6 and the lattice parameters of phase-III obtained from a full pattern (Le Bail) fit are shown in Figure S5. The linear relationship with variation in x confirms the existence of a solid solution in phase III, as expected. The very significant difference between the phase-I, II, and III frameworks is that whereas phase-I and phase-II contain two octahedral Li sites, an additional tetrahedral Li site is created in phase-III (Table 1 and Figure S4) that is about 20% occupied. In this structure, the Li1 and Li2 octahedra share a face, and the additional Li3 tetrahedra connect the Li1/Li2 pairs via trigonal face sharing to form Li+-ion chains along the a axis (Figure 2c). The lithium is distributed over all three sites, with significant vacancy population in each, between 25% and 80% (Table 1).

Migration pathways for Li+ ions were analyzed by the bond valence site energy (BVSE) method developed by Adams et al.35,36 The calculated energy landscape of the lowest activation-energy Li-ion pathway is shown in Figure 2d (note that owing to the accuracy of softBV, the overall activation energy is higher than the experimental value, but it still provides an approximate assessment of the relative height of the barriers35). The BVSE study suggests one metastable site for Li+ ions, namely, an octahedral interstitial site (“Oct”, 8d, at (0.104, 0.250, 0.569)) that shares a trigonal face with (Er1/Zr1) octahedra (Figure S3). The [Li3−Oct−Li3−Li2] zigzag chain running along the [010] direction is predicted to be the most favorable 1D ion transport pathway, shown as the portion of the landscape in red. This pathway along the b-axis in the ab plane intersects with other chains of [Li2−Li3−Li1] running in the ac plane (Figure S6) to form a 3D transport network (overall pathways highlighted in green and blue). The 1D migration pathway is explicitly shown in the bond valence energy map (Figure 2e) viewed as the yellow isosurface of constant E_{BVSE} for lithium in the model, superimposed on the crystal structure. In comparison, the BVSE map for the x = 0 composition (trigonal Li3ErCl6, space group, P3m1, exhibits energy barriers for Li-ion migration that are about 1.5-fold higher (Figure S7). This analysis highlights the vital role that the new Li3 site induced by Zr substitution plays in changing the overall energy landscape. It explains the observed high ionic conductivity, which is also facilitated by the relatively weak interaction of Li+ with the monovalent Cl− anion. The vacancies introduced in the Li sites are undoubtedly also a key factor for the enhanced ionic conductivity.
dynamics studies are underway to further confirm these findings but are beyond the scope of this work.

These fast-ion conducting lithium metal (Zr, Er, Y) halides show high promise as solid electrolytes that obviate the need for cathode coating layers. To demonstrate this, we compared the electrochemical performance of bare LiCoO₂ with either Li₃PS₄ glass or Li₁₋ₓMₓZrxCl₆ (M = Y, Er) as the SSE within the cathode composite and using Li₃PS₄ glass as the “separator” in the cell in both cases. The first and second charge–discharge profiles of LiCoO₂/SELi₁₋ₓPSₓJLi₁₁Snₓ cells with a current density of 0.11 mA cm⁻² are shown in Figure 4a. The composite electrode was prepared by mixing LiCoO₂ and chloride solid electrolyte at a weight ratio of 70:30. For the counter electrode, Li₁₋ₓMₓZrxCl₆ powder (20 wt %) was added to Li₁₁Snₓ (80 wt %) to enhance Li⁺ diffusion. When Li₃PS₄ is employed as an electrolyte in the working electrode, the charge capacity was only 93 mA h g⁻¹, and poor initial Coulombic efficiency of 62.7% is obtained. A plateau that is attributed to sulfide oxidation was observed at the early stage of charging (Figure 4a, inset), which was also observed in a previous study. In contrast, Figure 4a reveals that no oxidative side reaction occurs prior to Li⁺ deintercalation from LiCoO₂ when Li₁₋ₓMₓZrxCl₆ (Figure 4a, inset) was also observed in a previous study. In contrast, Figure 4a reveals that no oxidative side reaction occurs prior to Li⁺ deintercalation from LiCoO₂ when Li₁₋ₓMₓZrxCl₆ (Figure 4a, inset) was used as the cathode electrolyte. This cell exhibits a discharge capacity of more than 110 mA h g⁻¹ with a high initial Coulombic efficiency of 96.4%. Figure 4b shows the charge–discharge curves of the electrodes employing Li₃ₓY₀.₅Zr₀.₅Cl₆, which exhibit similar characteristics. In fact, the electrode containing 15 wt % solid electrolyte exhibits higher capacity than the cathode with 30 wt % solid electrolyte. This can be explained by the fact that some LiCoO₂ may be electronically isolated by the solid electrolyte at the higher electrolyte content. There is no sulfide SE oxidation plateau although Li₃PS₄ was used as the solid electrolyte separator. This means any interfacial side reactions between the electrode and the solid electrolyte separator are almost negligible. Thus, such a cell could employ any type of solid electrolyte, which is important for cell design flexibility. The absence of undesirable SE decomposition remarkably improves the cell performance.

A diagnostic electrochemical analysis was conducted by using electrochemical impedance spectroscopy. The Nyquist plots measured after the end of the sixth charging process are shown in Figure 4c. A typical Nyquist plot is exhibited for the LiCoO₂/chloride-SELi₁₋ₓPSₓJLi₁₁Snₓ cell, which consists of two semicircles followed by a low-frequency Warburg tail. The semicircle in the high-frequency region is attributed to the resistance of the Li₃PS₄ SE layer, and the other in the low-frequency region originates from the interfacial charge transport phenomena at the LiCoO₂/SE interface. The charge-transfer resistance for the electrode employing Li₃PS₄ (∼950 Ω) is almost 25-fold higher than that using the chloride SE (∼40 Ω), accounting for the sub-par performance of the electrode containing only Li₃PS₄ as the SE. Figure 4d displays the room-temperature cycling performance of the LiCoO₂ 2 cell using Li₁₋ₓMₓZrₓCl₆. The galvanostatic cycling test was conducted with a current density of 0.55 mA cm⁻² (~0.5 C) in a voltage range of 3.0–4.3 V (vs Li/Li⁺), showing very good capacity retention with high Coulombic efficiency over 200 cycles. The cell also exhibits good cycling performance with a cutoff voltage up to 4.5 V (vs Li/Li⁺) in spite of a small oxidation current in that voltage range (Figure S8a); typical voltage profiles are shown in Figure S8b.

In summary, we report a new class of mixed-metal chloride solid-state electrolytes, Li₃₋ₓM₁₋ₓZrxCl₆ (M = Er, Y), that exhibits high ionic conductivity of up to 1.4 mS cm⁻¹ at 25 °C, as a result of the evolution of a new ionically conductive phase upon Zr-substitution. Most importantly, the excellent electrochemical oxidation stabilities of those chloride SEs are directly demonstrated in full cells, which enable the use of noncoated 4 V-class cathode material without any noticeable oxidative interfacial decomposition. We believe these developments provide an important breakthrough for practical design of ASSBs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.9b02599.

Experimental methods, crystallographic details, Nyquist plots, additional electrochemical data, and Li migration pathways calculated by BVSE methods (PDF)

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REFERENCES

(4) Zhang, Z.; Shao, Y.; Lotts, B.; Hu, Y.-S.; Li, H.; Janek, J.; Nazar, L. F.; Nan, C.-W.; Maier, J.; Armand, M.; Chen, L. New horizons for

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REFERENCES

(4) Zhang, Z.; Shao, Y.; Lotts, B.; Hu, Y.-S.; Li, H.; Janek, J.; Nazar, L. F.; Nan, C.-W.; Maier, J.; Armand, M.; Chen, L. New horizons for...
(9) Murugan, R.; Thangadurai, V.; Weppner, W. Fast Lithium Ion Conduction in Garnet-Type \([\text{Li}_x\text{La}_2\text{Zr}_2\text{O}_{12}]^{2+}\). Angew. Chem. Int. Ed. 2007, 46, 7778–7781.