Site-Occupation-Tuned Superionic LixScCl3+x Halide Solid Electrolytes for All-Solid-State Batteries

Jianwen Liang, Xiaona Li, Shuo Wang, Keegan R. Adair, Weihan Li, Yang Zhao, Changhong Wang, Yongfeng Hu, Li Zhang, Shangqian Zhao, Shigang Lu, Huan Huang, Ruying Li, Yifei Mo, and Xueliang Sun

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.0c00134 • Publication Date (Web): 26 Mar 2020

Downloaded from pubs.acs.org on March 26, 2020

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Site-Occupation-Tuned Superionic Li$_x$ScCl$_{3+x}$ Halide Solid Electrolytes for All-Solid-State Batteries

Jianwen Liang,1+ Xiaona Li,1+ Shuo Wang,2+ Keegan R. Adair,1 Weihan Li,1 Yang Zhao,1 Changhong Wang,1 Yongfeng Hu,3 Li Zhang,4 Shangqian Zhao,4 Shigang Lu,4 Huan Huang,5 Ruying Li,1 Yifei Mo,2,* and Xueliang Sun1,*

1Department of Mechanical and Materials Engineering, University of Western Ontario, 1151 Richmond St, London, Ontario, N6A 3K7, Canada.
2Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA
3Canadian Light Source, 44 Innovation Boulevard, Saskatoon, SK S7N 2V3, Canada.
4China Automotive Battery Research Institute Co. Ltd, 5th Floor, No. 43, Mining Building, North Sanhuan Middle Road, Beijing, China, 100088.
*Corresponding email: xsun9@uwo.ca, yfmo@umd.edu

Abstract

Enabling the high energy density of all-solid-state lithium batteries (ASSLBs) requires the development of highly Li$^+$-conductive solid-state electrolytes (SSEs) with good chemical and electrochemical stability. Recently, halide SSEs based on different material design principles have opened new opportunities for ASSLBs. Herein, we discovered a series of Li$_x$ScCl$_{3+x}$ SSEs ($x$=2.5, 3, 3.5, and 4) based on the cubic close-packed anion sublattice with room-temperature ionic conductivities up to $3 \times 10^{-3}$ S cm$^{-1}$. Owing to the low eutectic temperature between LiCl and ScCl$_3$, Li$_x$ScCl$_{3+x}$ SSEs can be synthesized by a simple co-melting strategy. Preferred orientation is observed
for all the samples. The influence of $x$ value in $\text{Li}_x\text{ScCl}_{3+x}$ on the structure and $\text{Li}^+$ diffusivity were systematically explored. With increasing $x$ value, higher $\text{Li}^+$, lower vacancy concentration, and less blocking effects from Sc ions are induced, enabling the ability to tune the $\text{Li}^+$ migration. The electrochemical performance shows that $\text{Li}_3\text{ScCl}_6$ possesses a wide electrochemical window of 0.9-4.3 V vs. $\text{Li}^+$/Li, stable electrochemical plating/stripping of Li for over 2500 hrs, as well as good compatibility with $\text{LiCoO}_2$. $\text{LiCoO}_2$/Li$_3$ScCl$_6$/In ASSLB exhibits a reversible capacity of 104.5 mAh g$^{-1}$ with good cycle life retention for 160 cycles. The observed changes in the ionic conductivity and tuning of the site occupations provide an additional approach towards the design of better SSEs.

**Keyword**: halide solid electrolyte, Li$_3$ScCl$_6$, co-melting, all-solid-state battery, ionic conductivity

**1. Introduction**

All-solid-state lithium batteries (ASSLBs) are more attractive compared to their conventional lithium-ion battery counterparts due to their improved safety, thermal stability, high energy density, and higher voltage compatibility. Thus, significant efforts have been made to develop suitable solid-state electrolytes (SSEs) for ASSLBs, such as oxides, polymers, borohydrides, and sulfides. Great research advancements have been made for the aforementioned electrolytes, especially improvements in ionic conductivity approaching $10^{-2}$ S cm$^{-1}$. Nonetheless, there are still many factors inhibiting their practical application in ASSLBs, such as the high-temperature sintering of oxides, narrow electrochemical windows of polymers and borohydrides, as well as air/moisture hypersensitivity and electrode instability of sulfides.

In addition to the above-mentioned SSEs, the recently emerged halide SSEs (such as Li$_3$YCl$_6$, Li$_3$YBr$_6$, and Li$_3$InCl$_6$) have proven promising. These SSEs exhibit high ionic conductivities around $10^{-3}$ S cm$^{-1}$ at room temperature (RT), good compatibility toward oxide cathodes, wide
electrochemical windows (for chloride-based electrolytes), and can be synthesized by liquid-phase methods\textsuperscript{14-15}. The good compatibility toward oxide cathodes and wide electrochemical windows are highly consistent with simulation results.\textsuperscript{16-17} For the case of fluorides, chlorides, and bromides, the oxidation limit electrochemical window can be as high as $\geq 6, 4, \text{ and } 3 \text{ V vs. Li}^+$/Li, respectively.\textsuperscript{18} Moreover, the good compatibility toward oxide cathodes should be a general characteristic intrinsic to most of the halide SSEs.\textsuperscript{16} Based on the tremendous success of recent halide SSEs, it is expected that research in the near future will further reveal the favorable attributes of halide-based systems for ASSLBs. Moreover, different from most of the reported highly conductive SSEs (sulfides, oxide, borohydrides and metal-organic framework, etc.) where Li$^+$ migration through the structural framework built of covalent bonds such as PS$_4$ tetrahedron, the structure of halide SSEs of Li-M-X (M is metal cation and X is halogen anion) are built by close anion stack based on ionic bonding. Originated from the essential chemical distinction between the covalent bond and ionic bond, the Li$^+$ migration through these frameworks will lead to the different phenomenon and diffusion mechanisms.

To date, there have only been a few successful examples of halide SSEs that possess high ionic conductivity. Therefore, it is essential to explore other potential halide SSEs to broaden the knowledge and their applications. One of the most critical factors for designing superionic halide SSEs is the structure, which is the dominant factor in determining the ionic conductivities. For example, the reported Li$_3$YBr$_6$, Li$_3$InCl$_6$, and high-temperature-phase Li$_3$InBr$_6$ SSEs with higher ionic conductivity of $1-2\times10^{-3}$ S cm$^{-1}$ possess cubic close-packed (ccp)-like anion arrangement with monoclinic structure (space group C2/m).\textsuperscript{12, 14, 19-20} Comparatively, the Li$_3$YCl$_6$ and Li$_3$ErCl$_6$ SSEs, which possesses hexagonal close-packed (hcp)-like anion arrangement with trigonal structure (space group P-3m1) displays relatively lower ionic conductivity of $10^{-5}$-$10^{-4}$ S cm$^{-1}$.\textsuperscript{12, 21-22} Experimentally, halide SSEs with ccp anion sublattices can display high ionic conductivities, though theoretical calculations predict that halide SSEs with hcp anion sublattices may supersede them.\textsuperscript{16}

When systemically exploring the developed halide materials, it is found that Li$_3$MX$_6$ (M = rare earth metal of La-Lu, Sc, Y; X = Cl, Br) materials with isomorph structures of Li$_3$InCl$_6$ and Li$_3$YBr$_6$
should be promising halide SSEs. Among the Li$_3$MX$_6$ materials, most of Li$_3$MBr$_6$ (M = Sm-Lu)$_{23}$ materials also possess ccp anion sublattices with monoclinic structure (space group C2/m), which is the same as Li$_3$YBr$_6$.\textsuperscript{12,23} Meanwhile, the ccp structure can only be formed for the chloride counterpart of Sc-based halide electrolyte-Li$_3$ScCl$_6$.\textsuperscript{24} In contrast, most of the other chlorides possess hcp anion sublattices with different space groups. For example, Li$_3$MCl$_6$ (M = Tb, Dy, Ho, and Er) possess a trigonal structure with a P-3m1 space group, and Li$_3$MCl$_6$ (M = Yb, Lu) possess an orthorhombic structure with a Pnma space group.\textsuperscript{24-26} Thus, when further taking into consideration the wide electrochemical window of chloride-based SSEs, Li$_3$ScCl$_6$ stands out from others due to the potential of simultaneously possessing high ionic conductivity and a wide electrochemical stability window.

Herein, inspired by the possibility of achieving fast Li$^+$ migration in ccp halide SSEs, we have obtained Li$_3$ScCl$_6$ as well as other Li$_x$ScCl$_{3+x}$ SSEs ($x$=2.5, 3.5, and 4) that also possess ccp anion sublattices based on a simple co-melting strategy from LiCl and ScCl$_3$. Using Rietveld refinement against X-ray diffraction data and Raman spectroscopy, the structural evolution in Li$_x$ScCl$_{3+x}$ was revealed. It was confirmed that Sc is indeed present in ScCl$_6^{3-}$ octahedral form with a Sc coordination number of six rather than 4 or 7 coordinated structures, thus only the site occupations within the Li$_x$ScCl$_{3+x}$ were changed. Impedance spectroscopy and first-principle calculations were performed to monitor the changing ionic transport and reveal the diffusion mechanisms. The Li$^+$ carrier concentration is found to increase with increasing $x$ value in Li$_x$ScCl$_{3+x}$, while the opposite trend is observed for the total vacancy concentration for hopping and Sc blocking effect within the structure. Thus, the best balance is achieved for Li$_3$ScCl$_6$ with appropriate Li$^+$ carrier concentration and vacancy concentration for Li$^+$ diffusion in the continuous ion diffusion channels. As a result, Li$_3$ScCl$_6$ possesses the highest RT ionic conductivity (3.02×10$^{-3}$ S cm$^{-1}$) and a wide electrochemical window of 0.9-4.3 V vs. Li$^+/Li$. Although Li$_3$ScCl$_6$ is not stable toward Li in the initial cycles of plating/stripping, a stabilized interface can be gradually formed, ensuring long cycling life over 2500 hrs for Li/Li$_3$ScCl$_6$/Li symmetric cells. Moreover, the remarkable reversibility of all-solid-state LiCoO$_2$/Li$_3$ScCl$_6$/In full cell over 160 cycles was demonstrated. This work reveals fast Li$^+$ conduction
within the Li$_x$ScCl$_{3+x}$ and demonstrates that the local structure, as well as the site occupations of metal/vacancies, affect Li$^+$ migration in the anion sublattice, which can open up a new route to explore and develop new superionic conductors.

2. Results and Discussion

![Gibbs triangle of the ternary Li-Sc-Cl composition diagram with formulae of known compounds.](image1)

![XRD patterns of Li$_x$ScCl$_{3+x}$ SSEs](image2)

The crystal chemistry of the ternary rare-earth halides with general composition A$_a$M$_b$X$_{a+3b}$, where A represents monovalent cations, M represents a rare-earth metal, and X represents a halide.
element, has been well developed. There are different types of $A_aM_bX_{a+3b}$ structures, mainly including
$AMX_4$, $A_2MX_5$, $A_3MX_6$, $A_4MX_7$, and $A_3R_2X_9$. Moreover, the composition of $A_aM_bX_{a+3b}$ in the
$AX/MX_3$ systems is highly dependent on the atomic radii of $A^+$, $M^{3+}$, and $X^-$. Among them, $A_3MX_6^{-}$
type is the most frequently obtained composition (such as $Li_3YCl_6/Li_3YBr_6$, $Li_3InCl_6$, and $Li_3ErCl_6$). In addition to the existing $Li_3ScCl_6$, we further investigated other possible
stoichiometric ratios of $LiCl$ and $ScCl_3$ within the Li-Sc-Cl Gibbs triangle (Figure 1a). The explored
nominal compositions of $Li_xScCl_{3+x}$ are based on the different molar ratios of $LiCl$ and $ScCl_3$, with $x$
values of $1, 1.5, 2, 2.5, 3, 3.5, and 4$, respectively.

The $Li_xScCl_{3+x}$ SSEs were synthesized by a co-melting strategy from $LiCl$ and $ScCl_3$ with
different molar ratios. When $x=1, 1.5$ and $2$, though the main X-ray diffraction (XRD) patterns can be
indexed to the monoclinic phase, some other obvious peaks can still be observed (Figure S1-3).
Meanwhile, it was found that when $x$ $\geq$ $2.5$, all the XRD patterns (Figure 1b) can be indexed well with
$Li_3ScCl_6$ (C2/m, ICSD No. 04-009-8885, crystallographic data shown in Table S1), which is a
monoclinic structure based on a ccp anion arrangement. It should be noted that the XRD patterns of
these four samples show strong (001) and (200)/(-131) peaks, indicating a possible preferred
orientation. However, the intensity of the (003) peak (around 45.29°) does not show the same trend as
the (001) peak. In contrast, the (400)/(-262) peaks also exhibit much stronger intensity compared to
that found in the database, demonstrating the preferred orientation along (200)/(-131) of the
synthesized samples. As shown in Figure 1c, the peak intensity ratio of (200)/(-131) compared with
that of (131) of the $Li_xScCl_{3+x}$ samples range from 3.5716 to 9.6184, which is significantly higher than
that of 0.828 in the database. The ratio of the peak intensity of (200)/(-131) compared with that of
(131) gradually increased along with an increase of $x$, and reaches the maximum when $x=3.5$ followed
by a reduction when $x=4$. Correspondingly, the peak intensity ratio of (400)/(-262) compared to that
of (131) of $Li_xScCl_{3+x}$ samples exhibit the same trend as presented in Figure 1d. Another important
fact is that the presence of weak peaks is not observed for all the XRD patterns of $Li_xScCl_{3+x}$ ($x \geq 2.5$),
which might be caused by system extinction or higher symmetry properties of the as-prepared Li$_x$ScCl$_{3+x}$ samples compared to the monoclinic symmetry in the case of that found in the database.

![Figure 2](image_url)

**Figure 2.** (a) The XRD Rietveld refinement of Li$_3$ScCl$_6$ SSE (corresponding SEM image showed insert). (b) Typical crystal structure of Li$_3$ScCl$_6$ SSE based on the XRD Rietveld refinement result. (c) Obtained Raman spectra of Li$_x$ScCl$_{3+x}$ SSEs ($x$=2.5, 3, 3.5, and 4) showing the typical vibration of ScCl$_{6}^{3-}$ octahedra, (d) Normal modes of vibrations of ScCl$_{6}^{3-}$ octahedra.

Representative XRD Rietveld refinement of Li$_3$ScCl$_6$ SSE is shown in Figure 2a (detailed structural data are shown in Table S2,3). The typical structure of Li$_3$ScCl$_6$ based on the XRD Rietveld refinement result is shown in Figure 2b, which is quite different from that of the reported Li$_3$YBr$_6$ and Li$_3$InCl$_6$ that can be regarded as distorted LiCl structures.$^{12-13}$ The unit cell of Li$_3$ScCl$_6$ SSEs contains six crystallographic atom positions (Cl1, Li1, Li2, Li3, Sc1, Cl2). The structure is based on ccp of Cl
atoms in the $4i$ and $8j$ sites. Alternate octahedral voids formed by the stacking of Cl atoms are completed and ordered with occupation of Sc and Li atoms along the $c$ axis: one layer is fully occupied with Sc1 in $2a$ site and Li1 in $4g$ site with the ratio of 1:2 (denoted as Sc+Li layer); the other layer is statistically occupied with Li2 in $4h$ site and Li3 in $2d$ site as well as different amount of partial vacancy (denoted as vacancy+Li layer). Nevertheless, due to the low X-ray form factor for lithium, the detailed results of the lithium position and occupancy can not be obtained accurately. Rietveld refinement results and corresponding structures of other samples can be found in the supporting information (Figure S4-S6 and Table S4-6). It can be seen that similar to the Li$_3$ScCl$_6$, all the Li$_x$ScCl$_{3+x}$ SSEs ($x$=2.5, 3.5, and 4) also possess the same structure based on Li-Cl and Sc-Cl octahedral arrangements. The main difference is the occupations of the elements within the structure. For the Li$_{2.5}$ScCl$_{5.5}$ SSE with a higher content of Sc atoms compared with Li$_3$ScCl$_6$, besides the occupation in the pristine Sc+Li layer, partial Sc atoms will also occupy the $4h$ site in the vacancy+Li layer, indicating that Sc atoms occupy each layer of the structure along the $c$ axis. For Li$_{3.5}$ScCl$_{6.5}$ and Li$_4$ScCl$_7$ SSEs with lower content of Sc atoms compared with Li$_3$ScCl$_6$, Sc vacancies will be formed at the $2a$ site (Sc occupation of 0.98 for Li$_{3.5}$ScCl$_{6.5}$ and 0.83 for Li$_4$ScCl$_7$). The results indicate the high tolerance of the basic structure of typical Li$_3$ScCl$_6$, possessing tunable site occupations within the structure, which is a unique characteristic of halide SSEs and should influence the final ionic conductivity to some extent. The covalent Sc-Cl orbital mixing and high purity of the Li$_x$ScCl$_{3+x}$ SSEs samples without possible amorphous impurity phase were further confirmed by the Cl K-edge X-ray absorption near-edge structure (XANES) and the corresponding first derivatives shown in Figure R7. The preferred orientation of Li$_x$ScCl$_{3+x}$ SSEs indicated by XRD results was further reflected by the corresponding scanning electron microscopy (SEM) images (insert in Figure 2a and Figure S8-11), which showed obvious flakes like morphology.

Raman spectroscopy was used to further elucidate the structure of Li$_x$ScCl$_{3+x}$ samples. Four typical Raman spectra of Li$_x$ScCl$_{3+x}$ SSEs ($x$=2.5, 3, 3.5, and 4) are shown in Figure 2c, presenting the
typical vibrational modes of the ScCl$_6^{3-}$ octahedra. Four bands at ~280, 206, 183, and 158 cm$^{-1}$ were observed for all the spectra, which can be assigned to the $\nu_1$, $\nu_2$, $\nu_4$, and $\nu_5$ vibrational modes (Figure 2d) of ScCl$_6^{3-}$ octahedra.$^{30-31}$ No other signals for possible ScCl$_4^-$ (310 cm$^{-1}$) and ScCl$_7^{4+}$ (260 cm$^{-1}$) species are found,$^{30-31}$ demonstrating that there’s no four-coordinated species (ScCl$_4^-$) nor seven-coordinated species (ScCl$_7^{4+}$) for all the Li$_x$ScCl$_{3+x}$ SSEs ($x=2.5, 3, 3.5, \text{ and } 4$), even for the stoichiometric Li$_4$ScCl$_7$ compound. The Raman results are in accordance with the XRD Rietveld refinement results shown in Figure 2a,b and Figure S4-6. Moreover, all the Li$_x$ScCl$_{3+x}$ SSEs ($x=2.5, 3, 3.5, \text{ and } 4$) possess the basic ScCl$_6^{3-}$ octahedral arrangement with Sc coordination number of six. The results are also consistent with the previous reports about A$_a$M$_b$X$_{a+3b}$ halide materials. The lack of ScCl$_7^{4+}$ is due to the small Sc$^{3+}$ radius of 74.5 pm compared to 181 pm for Cl$^-$, and until now the LiMCl$_4$-type compounds were only found for M=Sm-Gd.$^{27}$ The obtained Li$_x$ScCl$_{3+x}$ SSEs ($x=2.5, 3, 3.5, \text{ and } 4$) were found to have a similar ccp anion sublattice structure with the same basic ScCl$_6^{3-}$ octahedral arrangement (Sc coordination number of six), even in the case of the stoichiometric Li$_4$ScCl$_7$ compound. Thus, the highly tunable structure of halide SSEs is demonstrated.
Figure 3. (a) Nyquist plots of Li$_3$ScCl$_6$ at different temperatures ranging from -25 to 75 °C, (b) Impedance plots at 25 °C of the cold-pressed pellets of Li$_x$ScCl$_{3+x}$ SSEs ($x$=1, 1.5, 2, 2.5, 3, 3.5, and 4) and the impedance is normalized to the respective pellet thickness, (c) Arrhenius conductivity plots of Li$_x$ScCl$_{3+x}$ SSEs ($x$=1, 1.5, 2, 2.5, 3, 3.5, and 4), (d) Comparison of RT ionic conductivities and activation energies of Li$_x$ScCl$_{3+x}$ SSEs ($x$=1, 1.5, 2, 2.5, 3, 3.5, and 4).

The Li$^+$ conductivity of Li$_x$ScCl$_{3+x}$ was determined by impedance measurements at different temperatures in a blocking electrode configuration. Impedance spectra of typical Li$_3$ScCl$_6$ SSE at different temperatures are presented in Figure 3a, showing a semi-circle at high frequency and a tail at low frequency. The impedance spectra were fit with an equivalent circuit consisting of one parallel constant phase element (CPE)/resistor (R) in series with another CPE, where R includes both intragrain and grain boundary contributions within the SSE. The CPE/R exceeded the range of the impedance.
analyzer at a higher temperature (Figure 3a2), thus only the tail of the blocking electrodes was used during fitting. Impedance plots of all the Li$_x$ScCl$_{3+x}$ SSEs ($x$=1, 1.5, 2, 2.5, 3, 3.5, and 4) at 25 °C are shown in Figure 3b. Li$_3$ScCl$_6$ SSE exhibits the highest ionic conductivity of $3.02\times10^{-3}$ S cm$^{-1}$ based on the equation of $\sigma=d/RS$, where $d$ and $S$ is the thickness and the cross-sectional area of the pellets, respectively. Arrenhius conductivity plots of Li$_x$ScCl$_{3+x}$ SSEs based on the impedance spectra at different temperatures of all the samples were further compared in Figure 3c, and the resultant RT ionic conductivities and activation energies ($E_a$) of all the samples are summarized in Figure 3d and Table S7.

The relatively low ionic conductivity of LiScCl$_4$ and Li$_{1.5}$ScCl$_{4.5}$ SSEs ($1.23$-$2.42\times10^{-4}$ S cm$^{-1}$) also leads to relatively high $E_a$ values as presented in Figure 3d. However, all the other Li$_x$ScCl$_{3+x}$ SSEs ($x$=2.5, 3, 3.5, and 4) display faster Li$^+$ migration ranging from $1.98\times10^{-3}$ to $3.02\times10^{-3}$ S cm$^{-1}$, which are the best among the reported halide SSEs.$^{12-14,21-22}$ More importantly, the structure of the as-synthesized Li$_x$ScCl$_{3+x}$ SSEs (with high ionic conductivity over $10^{-3}$ S cm$^{-1}$) consists of a ccp anion sublattice, which is different from that of Li$_3$ScCl$_6$ with the hcp anion sublattice that has been previously reported based on theoretical results.$^{16}$ Indeed, as confirmed by the XRD Rietveld refinement and Raman results, all the Li$_x$ScCl$_{3+x}$ SSEs ($x$=2.5, 3, 3.5, and 4) possess a similar monoclinic structure (ccp sublattice) of Li$_3$ScCl$_6$ with configurational variability of Sc and Cl site occupations in the octahedral lattice. Correspondingly, the total vacancy content within the Li$_x$ScCl$_{3+x}$ SSEs is also adjusted by the $x$ value, with higher vacancy content achieved along with a decrease of $x$ (i. e., Li$^+$ concentration). As evidenced by the impedance test, Li$_3$ScCl$_6$ showed the highest RT ionic conductivity among Li$_x$ScCl$_{3+x}$ SSEs, though it only possesses Li vacancy within the structure. Thus, there should be a balance between Li$^+$ concentration and total vacancy content that dominates the final ionic conductivity. The typical electronic conductivity of Li$_3$ScCl$_6$ SSE determined by direct current (DC) polarization measurements in the range from 100 to 500 mV is about $2.92\times10^{-9}$ S cm$^{-1}$ (Figure S12), which can be regarded as almost insulating electron transport compared to the fast Li$^+$ migration.
Furthermore, the Li$_3$ScCl$_6$ SSE also exhibits good dry-air and temperature stability reflected by the thermogravimetric analysis (TGA) test (Figure S13).

**Figure 4.** The diffusion mechanism of the Li$_x$ScCl$_{3+x}$ ($x=1, 1.8, 3,$ and $5$) SSEs based on AIMD simulations. (a, b) The Li$^+$ probability density marked by yellow isosurfaces from AIMD simulations. (c) The Li$^+$ migration pathways in ccp-anion stacking sublattice of Li$_3$ScCl$_6$ structure. (d-g) The Li$^+$ probability density marked by yellow isosurfaces of (d) Li$_5$ScCl$_8$ ($x=5$), (e) Li$_3$ScCl$_6$ ($x=3$), (f) Li$_{1.8}$ScCl$_{4.8}$ ($x=1.8$) and (g) LiScCl$_4$ ($x=1$) structures along $a$ axis. (h) The blocking effect of Sc due to the strong repulsion between Sc and Li. The green, purple, and blue ball represents the Cl, Sc, and blocked tetrahedral site for Li$^+$ migration, respectively. (i) Radial distribution function (rdf) of Sc-Li ions illustrating the blocking effect of Sc cation in the Li$_x$ScCl$_{3+x}$ ($x=1, 1.8, 3,$ and $5$) SSEs. (j) Arrhenius plot of Li$^+$ diffusivity in Li$_x$ScCl$_{3+x}$ ($x=1, 1.8, 3,$ and $5$) from AIMD simulations.
Moreover, first-principle calculations were performed to further reveal the diffusion mechanism in these new halide SSEs as a result of different configurations and site occupation of Sc and Li cations. All the calculations were carried out using the Vienna Ab initio Simulation Package (VASP)\(^{32}\) based on density functional theory (DFT). The projector augmented-wave\(^{33}\) (PAW) approach and Generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional\(^{34}\) were used for the energy calculations, structural optimization, and ab initio molecular dynamics (AIMD) simulations. The plane-wave energy cutoff and k-points density used in the calculations were consistent with those of Materials Project\(^{35}\). The detailed information about the calculation can be found in the supporting information. In all Li\(_x\)ScCl\(_{3+x}\) compounds with different occupations, stable Li and Sc positions are located at the octahedral sites of a Cl ccp-anion stacking sublattice. Based on the structures and site occupations from XRD refinement results, all symmetrically distinctive structures in a primitive cell were generated for the Li\(_x\)ScCl\(_{3+x}\) (x=1, 3) and 20 symmetrically distinctive structures were generated by minimizing the electrostatic energies from 1000 random configurations for the Li\(_x\)ScCl\(_{3+x}\) (x=1.8, 5) in a 2×1×2 supercell using the pymatgen package\(^{36}\) as in previous work\(^{37-38}\). Then, all these structures were structurally relaxed in the DFT calculations, and the structure with the lowest energy was identified as the ground state structure for other calculations. Table S8 and Figure S14 summarize all of these model structures and the related energies above the convex hull (ΔE\(_{\text{hull}}\)). Li\(_3\)ScCl\(_6\) possesses the lowest hull energy about 17 meV/atom, indicating good phase stability. We performed the AIMD simulations to investigate the Li\(^+\) diffusion in the Li\(_3\)ScCl\(_6\) structure. The Li\(^+\) probability density from AIMD simulation was marked as yellow iso-surfaces which illustrate the 3D Li\(^+\) diffusive channels (Figure 4a,b). As observed in AIMD simulations, the lithium-ion hops from one octahedral site to a neighboring octahedral site through a tetrahedral interstitial site (Oct-Tet-Oct, Figure 4c), forming a three-direction isotropic diffusion network (Figure 4b). For comparison, the Li\(^+\) migration pathways of other structural models based on x= 1, 1.8, and 5 exhibit notable differences in Li\(^+\) migration (Figure 4d-g). As mentioned above, there are two different positive ionic layers along the c axis, i.e. Sc+Li (2a and 4g sites) layer and vacancy+Li (4h and 2d sites) layer. When x is higher
than 3, the occupation of Sc1 in 2α decreases along with increased occupancy of Li in 4h and 2d sites, leading to an increased Li⁺ concentration but a decreased vacancies for lithium diffusion. The pathway of lithium ions in Li₅ScCl₈ (Figure 4d) is similar to Li₃ScCl₆ (Figure 4e). When x is lower than 3, more introduced Sc ions occupy the position of Li2 or Li3 sites in the vacancy+Li layer. Due to the repulsive coulombic interaction between Sc³⁺ and Li⁺, the tetrahedral interstitial sites adjacent to Sc³⁺ are blocked, which is shown as blue sites in Figure 4h. This blocking effect is further confirmed in the Li-Sc radial distribution function in AIMD simulations for all LiₓScCl₃+ₓ, as no peak exists at the tetrahedral site (i.e. blocking site) neighboring the Sc site at ~2.3 Å, which is consistent with the absence of Li⁺ probability around Sc³⁺ in Figure 4d-g and Figure S15-18. This explains the different Li⁺ migration pathways in Li₁.₈ScCl₄.₈ (Figure 4f) and LiScCl₄ (Figure 4g) compared with Li₃ScCl₆. Since partial Li⁺ migration pathways are blocked, the Li⁺ migration energy barrier may increase, which is consistent with the experimental results shown in Figure 3. Furthermore, the rate of effective ion hops from AIMD simulations were calculated (Figure S19), the effective rate of the ionic hopping for LiScCl₄ (x=1), Li₁.₈ScCl₄.₈ (x=1.8), Li₃ScCl₆ (x=3), and Li₅ScCl₈ (x=5) is 1.3, 1.1, 1.6, and 1.0 times per picosecond at 700 K, respectively. Li₃ScCl₆ also exhibits the highest rate of the ionic hopping. As a result, the Li₃ScCl₆ structure achieves the optimal vacancies concentration for Li⁺ conduction and continuous network of diffusion channels. The ionic conductivities and activation energies of the four structures based on AIMD simulation were compared in Figure 4j and Table S9. The ionic conductivity of LiScCl₄ (x=1), Li₁.₈ScCl₄.₈ (x=1.8), Li₃ScCl₆ (x=3), and Li₅ScCl₈ (x=5) at 300 K is 0.18, 0.44, 5.1 and 2.4 mS cm⁻¹, respectively, showing the same trend of experimental results (Figure 3 and Table S7). The Haven ratio for these compositions is close to 1 (Table S10), which suggests most of the ion hoppings are uncorrelated. The calculated $E_a$ of 0.25±0.04 eV for Li₃ScCl₆ is similar to that of Li₅ScCl₈ (0.26±0.07 eV), while the ionic conductivity of Li₅ScCl₈ is lower than that of Li₃ScCl₆. This is originated from the low rate of the ionic hopping in Li₅ScCl₈ due to the low concentration of vacancies in the structure. The calculated $E_a$ of LiScCl₄ (0.37±0.07 eV) and Li₁.₈ScCl₄.₈ (0.34±0.07 eV) is higher than that of Li₃ScCl₆, which is due to the blocking effect of extra Sc occupation in vacancy+Li layer.
Based on the variable site occupation configurations within Li$_x$ScCl$_{3+x}$ SSEs, it was proven that the Sc blocking effect, Li$^+$ carrier concentration, and vacancies concentration for hopping are the three key parameters to determine the Li$^+$ diffusion. The best balance can be obtained with appropriate vacancy concentration for Li$^+$ diffusion and continuous diffusive channels. The observed change of Li$^+$ diffusion mechanism in halide SSEs with site occupation tuning has not been observed from other highly conducting SSEs where Li$^+$ migration occurs through well-formed channels of the crystal structural frameworks. These findings indicate that the material design principles, especially regarding the local structure change and element/vacancy distribution in the structure, are critical in understanding and developing the halide SSEs.
Figure 5. Electrochemical performance of Li$_3$ScCl$_6$ SSE at 25 °C. (a) Thermodynamic equilibrium voltage profile and the phase equilibria for Li$_3$ScCl$_6$ based on first-principle calculations. (b) CV curves of all-solid-state Li/Li$_3$P$_3$S$_11$/Li$_3$ScCl$_6$/Li$_3$ScCl$_6$-C cell at 0.1 mV s$^{-1}$ (Li$_3$ScCl$_6$ and carbon mass ratio of 5:5). (c) Electrochemical performance of the symmetric all-solid-state Li/Li$_3$ScCl$_6$/Li cell at 0.1 mA cm$^{-2}$ (100 min per plating/stripping cycle). (d) Initial charge/discharge curves of all-solid-state LiCoO$_2$/Li$_3$ScCl$_6$/In cell at 0.13 mA cm$^{-2}$ at room temperature (corresponding dQ/dV curves shown insert). (e) Cycling stability and Coulombic Efficiency of all-solid-state LiCoO$_2$/Li$_3$ScCl$_6$/In cell at 0.13 mA cm$^{-2}$.
Besides the ionic conductivity, the thermodynamic intrinsic electrochemically stable window of Li$_3$ScCl$_6$ SSE was calculated by using the established scheme$^{40-42}$ based on the Materials Project$^{35}$ database. The equilibrium voltage profile and corresponding phase equilibria as a function of applied potential referenced to Li$^+/Li$ are shown in Figure 5a and Table S11. For Li$_3$ScCl$_6$ SSE, the electrochemical oxidation process originates from the Cl$^-$ anion chemistry with products such as ScCl$_3$ and Cl$_2$. On the other hand, the electrochemical reduction process is mainly caused by the Sc$^{3+}$ cation chemistry, resulting in LiCl and Sc-Cl compounds with different Sc/Cl ratios such as Sc$_5$Cl$_8$ and Sc$_7$Cl$_{10}$ followed by reduction to Sc metal. The Li$_3$ScCl$_6$ SSE shows a wide electrochemical window with an anodic limit of 4.26 V (vs. Li$^+/Li$) and cathodic limits of 0.91 V (vs. Li$^+/Li$). The thermodynamic window is significantly wider than many current SSEs, especially for the electrolytes with the ionic conductivity higher than 1 mS cm$^{-1}$ such as Li$_6$PS$_5$Cl (1.71-2.14)$^{40}$, LGPS (1.72-2.42 V)$^{43}$, Li$_{0.33}$La$_{0.56}$TiO$_3$ (1.75-3.71 V)$^{43}$, LISICON (1.44-3.39 V)$^{40}$, Li$_3$OCl (0-2.55 V)$^{44}$, Li$_3$YBr$_6$ (0.59-3.15),$^{16}$ and Li$_3$InCl$_6$ (2.38-4.3 V)$^{16}$.

Cyclic voltammetry (CV) testing of all-solid-state Li/Li$_3$ScCl$_6$/Li$_3$ScCl$_6$+C and Li/Li$_7$P$_3$S$_{11}$/Li$_3$ScCl$_6$/Li$_3$ScCl$_6$-C cells at 0.1 mV s$^{-1}$, in which Li$_3$ScCl$_6$ is mixed with 50wt% carbon to improve the electron conduction were further performed to evaluate its actual electrochemical stability window.$^{45-47}$ As presented in Figure S20, two obvious reduction peaks at 0.53 V and 0.15 V, as well as one oxidation peak at 4.08 V (with oxidation onset of 3.72 V), are identified in the cell configuration of Li/Li$_3$ScCl$_6$/Li$_3$ScCl$_6$+C. However, it should be noted that the oxidation voltage reflected here is not fixed at Li$^+/Li$ redox potential since the reference electrode potential was changed due to the reaction between Li$_3$ScCl$_6$ SSE and Li metal. Thus, a layer of commercial Li$_7$P$_3$S$_{11}$ was inserted between Li$_3$ScCl$_6$ SSE and bare Li metal to fix the reference electrode potential. The CV curve of Li/Li$_7$P$_3$S$_{11}$/Li$_3$ScCl$_6$/Li$_3$ScCl$_6$-C cell in Figure 5b shows slightly different reduction/oxidation behavior compared to the cell without Li$_7$P$_3$S$_{11}$ protection layer, in which there are two reduction peaks at 0.75 V and 0.5 V and no obvious oxidation peak up to 5.0 V. The experimentally measured
The electrochemical stability window of Li$_3$ScCl$_6$ SSE is diverged from that of 0.91-4.26 vs. Li$^+$/Li as theoretically calculated, which can be attributed to the polarization as well as the interface formation during CV testing. To evaluate the anodic stability, symmetric all-solid-state Li cells using Li$_3$ScCl$_6$ as the electrolyte were further constructed. The charge/discharge profiles of Li/Li$_3$ScCl$_6$/Li at 0.1 mA cm$^{-2}$ with 100 min per cycle are shown in Figure 5c. Initially, Li plating/stripping occurred at around ± 400 mV, then gradually increased to ± 1500 mV (~ 400 hrs) and finally decreased to ± 510 mV over 2500 hrs. The initial increase of plating/stripping potentials should be caused by the severe interfacial reaction between Li and Li$_3$ScCl$_6$ SSE, and the decrease of the plating/stripping voltage in subsequent cycles might be due to the gradual formation of a stable interface as well as a higher area contact between active Li and SSE. The electrochemical impedance spectra (EIS) evolution of the Li/Li$_3$ScCl$_6$/Li cell recorded at different aging times and cycle numbers presented in Figure S21,22 also showed the formation of a gradually stabilized interface, as reflected by the almost unchanged interfacial resistance after a certain period of time during the plating/stripping process. The same trend was also observed for the Li/Li$_3$ScCl$_6$/Li cell at a higher capacity of 0.5 mAh cm$^{-2}$ as presented in Figure S23, with a steady overpotential of ± 620 mV over 2800 hrs. To the best of our knowledge, this is the first time to report a Li-M-Cl (M is a metal element) halide SSE that can be cycled directly against bare Li metal although it still reveals a high polarization voltage. Based on this, suitable Li protection strategies might be able to reduce this high polarization voltage and provide improved Li symmetric cell performances.

The high oxidation stability of Li$_3$ScCl$_6$ at >4.2 V supports the use of current commercial 4 V-class cathode materials such as LiCoO$_2$ in ASSLBs. Thus, the as-synthesized Li$_3$ScCl$_6$ is further evaluated in ASSLBs using indium (In) as the anode and LiCoO$_2$ as the cathode at 25 °C. Similar to other halide SSEs, Li$_3$ScCl$_6$ was directly hand-milled with bare LiCoO$_2$ to fabricate cathode composites (mass ratio of Li$_3$ScCl$_6$/LiCoO$_2$ of 3:7) without any protective coating layers for LiCoO$_2$. The EIS evolution at steady state over 24 h is presented in Figure S24 and indicates the stability of the
electrolyte/electrode interfaces in the LiCoO$_2$/Li$_3$ScCl$_6$/In full cell. Figure 5d shows the initial charge/discharge voltage profiles of the LiCoO$_2$/Li$_3$ScCl$_6$/In cell at 0.13 mA cm$^{-2}$ (LiCoO$_2$ loading of 8.92 mg cm$^{-2}$). The LiCoO$_2$/Li$_3$ScCl$_6$/In cell shows an initial charge capacity of 139.7 mAh g$^{-1}$ and a discharge capacity of 126.2 mAh g$^{-1}$, corresponding to an initial Coulombic efficiency of 90.3%.

Typical redox reaction peak associated with cobalt can be clearly observed in the dQ/dV curves (insert in Figure 5d). Figure 5e displays the cycling performance of the LiCoO$_2$/Li$_3$ScCl$_6$/In full cell at 0.13 mA cm$^{-2}$. After the slight decrease in the initial several cycles, the LiCoO$_2$/Li$_3$ScCl$_6$/In full cell displays stable cycling with a capacity of 104.5 mAh g$^{-1}$ maintained as well as a high Coulombic efficiency of 99.2% after 160 cycles.

**Figure 6.** Compatibility between Li$_3$ScCl$_6$ SSE and LiCoO$_2$. (a) Calculated Mutual reaction enthalpy between SSE and LiCoO$_2$ as a function of mixing ratio and the corresponding phase equilibria (in box) at the lowest point along the energy convex hull. *Ex-situ* (b) Sc K-edge and (c) Cl K-edge XANES spectra of Li$_3$ScCl$_6$-LiCoO$_2$ (Li$_3$ScCl$_6$-LCO) cathode composites at different charge-discharge states, i.e., (b1, c1) pristine Li$_3$ScCl$_6$-LCO, (b2, c2) charged to 3.35 V, (b3, c3) charged to 3.45 V, (b4, c4) fully charged to 3.60 V, (b5, c5) discharged.
to 3.35 V, (b6, c6) fully discharged to 1.90 V, and (b7, c7) fully discharged to 1.90 V after 50 cycles. *Ex-situ* (d) Sc 2p and (e) Cl 2p XPS spectra of Li$_3$ScCl$_6$-LCO cathode composites at different charge-discharge states, i.e., pristine Li$_3$ScCl$_6$-LCO, charged to 3.45 V, fully charged to 3.60 V, discharged to 3.25 V, fully discharged to 1.90 V. All the charge/discharge voltages versus Li$^+$/LiIn here.

Compared to sulfide and oxide SSEs, on the cathode side, Li$_3$ScCl$_6$ SSE reveals a significant advantage in compatibility toward oxide cathodes without any interfacial modification. Typically, the side reactions and interface formation between the SSE and cathode material are critical factors affecting the performance of ASSLBs. The possible interfacial component between Li$_3$ScCl$_6$ and LiCoO$_2$ using the pseudo-binary model was calculated and shown in Figure 6a and Table S12, the calculation of some other common SSEs was also presented as a comparison. The reaction energy of Li$_3$ScCl$_6$ with LiCoO$_2$ cathode is around 60 meV/atom, which is one order of magnitude less than sulfide SSEs and half of LiPON SSEs, suggesting good interfacial stability between LiCoO$_2$ and Li$_3$ScCl$_6$ SSEs (Table S12). Moreover, the Li$_3$ScCl$_6$ electrolyte remains compatible with delithiated Li$_{0.5}$CoO$_2$, with an even smaller reaction energy of 35 meV/atom. Thus, the good interfacial stability between Li$_3$ScCl$_6$ and LiCoO$_2$ cathode during electrochemical cycling is revealed, which is consistent with the high Coulombic Efficiency (90.3%) as well as the stable cycling of LiCoO$_2$/Li$_3$ScCl$_6$/In cell.

The compatibility of the Li$_3$ScCl$_6$ toward LiCoO$_2$ cathode was further proved through use of XANES and X-ray photoelectron spectroscopy (XPS) analysis (Figure 6b-e). The collected Sc and Cl K-edge XANES spectra of Li$_3$ScCl$_6$-LiCoO$_2$ cathode composite and those at different charge/discharge states are presented in Figure 6b,c. For the Sc K-edge spectra, all samples display a split pre-edge feature (peak splitting about 1.5 eV, insert in Figure 6b) due to the 1s→3d ($t_{2g}$ and $e_g$) transition, demonstrating the octahedral environment of Sc atoms. The other pronounced feature of >4503 eV corresponds to the main edge resonance of $E_1$ transitions towards the empty 4p state of the Sc atoms (1s→4p). For the Cl K-edge spectra, two well-resolved pre-edge features at 2823.4 eV (1s→$t_{2g}$) and 2824.7 eV (1s→$e_g$) that indicative of covalent Sc-Cl orbital mixing were observed.
Overall, the Sc and Cl K-edge XANES spectra of all the samples are quite similar without obvious change, demonstrating the good compatibility between Li$_3$ScCl$_6$ and LiCoO$_2$ cathode during cycling. Most obviously, the quite same first derivatives of the Sc and Cl K-edge XANES spectra (Figure S25,26) further support this conclusion. Furthermore, the Sc 2p and Cl 2p XPS spectra of Li$_3$ScCl$_6$-LiCoO$_2$ cathode composites at different charge/discharge states (Figure 6d,e) also showed no obvious change of peak shift. Combined with the theoretical calculations, ex-situ XANES, and ex-situ XPS, the good stability of Li$_3$ScCl$_6$ SSE toward LiCoO$_2$ (as well as Li$_{0.5}$CoO$_2$ in a delithiated state) and the stability of Li$_3$ScCl$_6$ SSE itself within the applied voltage range can be concluded.

3. Conclusions

In summary, tuning of the local structure, as well as the site-occupation of Sc/vacancies in Li$_x$ScCl$_{3+x}$ SSEs ($x$=2.5, 3, 3.5, and 4) was successfully demonstrated by a simple co-melting synthesis strategy. XRD and SEM results indicate the Li$_x$ScCl$_{3+x}$ SSEs have a highly preferred structural orientation. Complementary analysis by XRD Rietveld refinement and Raman measurements reveal the same basic ScCl$_6^{3-}$ octahedral arrangement with Sc coordination number of six for Li$_x$ScCl$_{3+x}$, even for the firstly reported stoichiometric Li$_4$ScCl$_7$ compound. The variability of site occupation configurations, vacancy content in the octahedral lattice, and Li$^+$ diffusion mechanism upon changing the Li concentration in Li$_x$ScCl$_{3+x}$ SSEs is also illuminated. The Li$_x$ScCl$_{3+x}$ SSEs showed high RT ionic conductivity over $10^{-3}$ S cm$^{-1}$, with the highest value of $3.02 \times 10^{-3}$ S cm$^{-1}$ achieved for Li$_3$ScCl$_6$ through balancing of the Li$^+$ carrier and vacancy for hopping concentrations getting rid of Sc blocking effect. Our study further highlights the good electrochemical stability of these SSEs. Typical Li$_3$ScCl$_6$ showed a significantly wide electrochemical window, good compatibility with bare LiCoO$_2$, and gradually increased stability toward Li during the plating/stripping process. Our findings demonstrate that Li$_x$ScCl$_{3+x}$ are promising SSEs for ASSLBs, the structure of halide SSEs are highly tunable, and the Li$^+$ diffusivity of halide SSEs can be adjusted by tuning the site occupations within the structure.
**Supporting Information**

Complete experimental details, electrochemical/interface stability calculation, ab initio molecular dynamics simulations, supplementary figures and tables.

**Author Contributions**

‘J.L., X.L., and S.W. contributed equally to this work.

**Acknowledgments**

This research was supported by Natural Sciences and Engineering Research Council of Canada (NSERC), GLABAT Solid-State Battery Inc., China Automotive Battery Research Institute Co. Ltd, Canada Research Chair Program (CRC), Canada Foundation for Innovation (CFI), Ontario Research Fund, the Canada Light Source at University of Saskatchewan (CLS), Canada MITACS fellowships, and University of Western Ontario. Y.M. acknowledges the support from National Science Foundation under award No. 1550423. This research used computational facilities from the University of Maryland supercomputing resources and the Maryland Advanced Research Computing Center (MARCC).

**Declaration of interests**

The authors declare no competing interests.

**References**


10. Ohta, S.; Kobayashi, T.; Asaoka, T., High lithium ionic conductivity in the garnet-type oxide Li$_{2-x}$La$_2$(Zr$_{2-x}$Nb$_x$)O$_{12}$ (X= 0–2). *J. Power Sources* **2011**, *196*(6), 3342-3345.


20. Yamada, K.; Kumano, K.; Okuda, T., Lithium superionic conductors Li$_3$InBr$_6$ and LiInBr$_4$ studied by $^7$Li, $^{115}$In NMR. *Solid State Ionics* 2006, 177 (19-25), 1691-1695.


37. He, X.; Mo, Y., Accelerated materials design of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ oxygen ionic conductors based on first principles calculations. Phys. Chem. Chem. Phys. 2015, 17 (27), 18035-18044.