High Li ion conductivity in a garnet-type solid electrolyte via unusual site occupation of the doping Ca ions

Shufeng Song, Denis Sheptyakov, Alexander M. Korsunsky, Hai M. Duong, Li Lu

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ABSTRACT

The search for solid electrolytes with high stability and ionic conductivity is a long sought-after goal in the development of safe and high energy density Li-ion batteries. Garnet-type lithium conductors form a most promising family of materials due to their good chemical stability. However, the low conductivity at room temperature prevents wider application of these materials. It has long been recognized that alkaline earth metals are confined exclusively to dodecahedral 8-coordinated sites within the garnet framework. In contrast to this dominant viewpoint, we show that Ca2+ cations can occupy the octahedral 6-coordinated sites, leading to an enhanced room temperature conductivity of \(5.2 \times 10^{-4} \text{ S cm}^{-1}\) and reduced activation energy of 0.27 eV, together with a 0 to 9 V electrochemical stability window. This finding opens up a new opportunity for the design of ceramic electrolytes with higher conductivities, providing added impetus for further exploration of oxide electrolyte chemistry.

1. Introduction

Developing safe and high energy density lithium-ion batteries is a long sought-after goal for the scientific community [1]. However, use of lithium metal in contact with a polymer-based separator and liquid electrolytes gives rise to safety concerns because of the formation of lithium dendrite during cycling caused by uneven current distribution at the lithium-electrolyte interface. Lithium solid electrolytes are therefore being considered as a solution to mitigate the lithium dendrite problem since being reported by Weppner’s group [2]. The research results presented here reveal a route towards further conductivity enhancement by optimizing chemical substitutions and structural modifications. Alkaline earth ions (Ca2+, Mg2+, Sr2+, Ba2+) can be used to substitute La3+ in LiLa2M2O12 to increase the lithium concentration and ionic conductivity, and improved ionic conductivity of \(10^{-5} \text{ S cm}^{-1}\) at room temperature has been reported [3–8]. On the other hand, the larger size of dopant ions would cause lattice expansion, thus increasing the bottleneck size, and reducing the migration barrier and improving the conductivity. Accordingly, we screen the alkaline earth ions considering their much larger radii than Zr.

In 2007, Murugan et al. synthesized highly conductive cubic garnet-type Li7La3Zr2O12 (LLZO) by substitution of Zr for M in Li7La3M2O12 with ionic conductivity of \(2 \times 10^{-4} \text{ S cm}^{-1}\) [9]. The alkaline earth doping cations have been long thought to be confined exclusively to dodecahedral 8-coordinated sites (La sites) [3–12]. In this work, we report unusual Ca2+ occupancy at octahedral 6-coordinated sites. This is achieved through the controlled placement of Ca2+ ions into Zr4+ sites, which is achieved in two sequential steps. Firstly, a solid solution of CaO and ZrO2 is synthesized via mechano-chemical method. Subsequently an Al-containing garnet-type structure based on the prototype material LLZO is synthesized through solid-state reaction between lithium salt and the solid solution of CaO and ZrO2. The new chemical composition of Al-containing Li\(_7\)La\(_2\)Zr\(_{1.95}\)Ca\(_{0.05}\)O\(_{12}\) with garnet-type structure displays a room-temperature conductivity of \(5.2 \times 10^{-4} \text{ S cm}^{-1}\), which is twice higher than its prototype LLZO [9]. Furthermore, careful crystallographic analysis of X-ray and neutron diffraction data for the new material allows the detailed lattice structure to be reconstructed, and Li+ diffusion channels to be identified. This finding opens up a new opportunity for broadening the range of chemical substitutions, formulating new Li+ transport tunnels in garnet-type conductors, and provides impetus to look for further oxide systems with high conductivities.
2. Experimental

2.1. Material synthesis

$Zr_{1.95}Ca_{0.05}O_{3.95}$ solid solution was prepared through mechanochemical reaction in a planetary high-energy ball-milling system (with stainless steel vessels and stainless steel balls with a diameter of 10 mm) for 2 h. To prevent excessive heating during milling, the mixture of $ZrO_2$ (Inframat Advanced Materials, 99.9%) and CaO ($CaCO_3$ decomposed at 950 °C for 5 h) was milled by alternately 30 min of milling followed by 30 min in standby. Then, Al-containing $Li_7La_3Zr_{1.95}Ca_{0.05}O_{12}$ was synthesized through solid-state reaction by mixing stoichiometric amounts of $Li_2CO_3$ (Sigma, 99%, with 10 wt.% excess to compensate for the loss of lithium during annealing), $La_2O_3$ (Sigma, 99.9%; dried at 900 °C for 12 h), and $Zr_{1.95}Ca_{0.05}O_{3.95}$, and ball-milling with zirconia balls for about 2 h in ethanol in air. Small amount of Al doping was the consequence of calcining the precursor at 900 °C and 1125 °C for 12 h in alumina crucibles, followed by repeated ball-milling for 2 h. The calcined powder was then cold pressed and sintered at 1230 °C for 16 h covered with the raw powders to avoid lithium loss.

2.2. Electrochemical characterization

Ionic conductivities of the conductors were measured using ionic blocking technique where the electrodes were made by sputtering gold on both faces of the pellets. Impedance spectroscopy measurements were performed using a Solartron 1260 + 1287 System, applying 10 mV in the frequency range of 1 MHz–10 Hz in the temperature range from 27 °C to 130 °C.

Cyclic voltammogram of the samples was measured using a linear sweep voltammetry run on $Pt|Li_{7.1}La_3Zr_{1.95}Ca_{0.05}O_{12}|Li$ cells in a voltage range from −0.5 V to 9 V vs. $Li^+/Li$ and with a 1 mV s$^{-1}$ scan rate.

2.3. Structure characterization

X-ray diffraction (Shimadzu XRD-6000 and 7000 Cu-K$\alpha$) was employed to detect the crystallographic structure of the samples in air. The microstructure was examined on polished surfaces of the sintered pellet using SEM (S-4300 Shimadzu). Fourier transform infrared spectroscopy (FTIR) was acquired in the range of 4000–350 cm$^{-1}$ with a SHIMADZU-8400 FTIR spectrometer.

$^6$Li and $^7$Li MAS NMR experiments were performed using a Bruker DRX400 wide bore solid state NMR spectrometer equipped with 4 mm CP/MAS BB probe. The spectra were recorded under single pulse experiment with magic angle spinning rate of 10 kHz, 1800 and 16 scans with relaxation delay at 2 s for $^6$Li and $^7$Li MAS NMR, respectively. The measurement of $^{27}$Al MAS NMR spectrum was carried out at 104.27 MHz using standard Bruker 4 mm MAS probe with sample spinning at 8 kHz. A recycle delay of 0.1 s was used and 4736 scans were accumulated.

Neutron powder diffraction data was collected on the HRPT high-resolution powder neutron diffractometer at SINQ spallation neutron source (Paul Scherrer Institut, PSI, Villigen, Switzerland) using thermal neutrons of wavelength $\lambda = 1.494 \AA$, and the high-intensity mode of the diffractometer [13]. A powder sample of $Li_7La_3Zr_{1.95}Ca_{0.05}O_{12}$ was enclosed into an 8-mm vanadium container, and the scattered neutrons were registered by a wide-angle position sensitive detector in the angular range from 5 to 165 deg. The refinement was performed using FullProf suite of programmes.

3. Results and discussion

3.1. Electrochemical properties

The room-temperature ionic conductivity was measured with ionic blocking Au electrodes for typical $Li_7La_3Zr_{1.95}Ca_{0.05}O_{12}$ sintering pellet (Fig. 1a). It shows a depressed semicircle and inclined capacitive tail. The appearance of the inclined tail at low frequencies in the case of ionic blocking electrodes is an indication that the material is ionically conducting inherently [14,15]. The EIS profiles show a partial semicircle at the frequency range of 1 MHz to 158 kHz, which is attributed to the grain boundary resistance. The intercept of the semicircle on the real axis at higher frequency range represents the grain resistance. An ($R_b$)($R_{gb}$CPE$_g$)($W_1$) equivalent circuit (see inset of Fig. 1a) was used to fit the EIS data, where $R_b$ represents the grain resistance, $R_{gb}$ represents the grain boundary resistance, CPE represents a constant phase element, and $W$ represents a Warburg element. The total resistance ($R_b + R_{gb}$) is determined from the fit. The total conductivity of the pellet (0.14 cm in thickness and 0.44 cm in diameter) measured at 27 °C is calculated to be $5.2 \times 10^{-4} - S cm^{-1}$. The activation energy, $E_a$, for transport, calculated from the Arrhenius plot (Fig. 1b), is a significant data for assessing ionic conductivity, because it represents the barrier height of ions transport. The activation energies for heating and cooling cycles were 0.27 eV and 0.271 eV, respectively. There is no obvious shift in the conductivities for heating and cooling cycles, which implies that the present material is thermally stable without any decomposition in the investigated temperature range between room temperature and 130 °C. The activation energy $E_a = 0.27$ eV for $Li_7La_3Zr_{1.95}Ca_{0.05}O_{12}$ is much lower than that of the parent LLZO (0.34 eV) [9]. Dense and white colour pellets are obtained after sintering at 1230 °C for 16 h. The microstructure of the present material is examined on polished surfaces using SEM (Fig. 1c, d). The grains are fairly equi-axed and uniform, with an average grain size of about 0.5 μm. Uniform grain size is helpful for lithium ion conduction. Although some micropores are found, it is known that advanced sintering technology like hot-pressing and spark plasma sintering can produce denser pellets and further improve the conductivity [16,17].

Besides the good conduction performance, a necessary demand for solid electrolytes is their electrochemical stability window. The potential was first swept from open voltage to −0.5 V (cathodic direction) and then from −0.5 V to 9 V (anodic direction) (Fig. 2). The cathodic current represents lithium deposition, and the anodic current represents lithium dissolution. No obvious current was observed except the ones due to the lithium deposition and dissolution, implying that this material has a wide electrochemical stability window up to 9 V, making it a solid electrolyte with one of the widest electrochemical stability ranges.

3.2. Compositional characterization

The molar ratio of the elements Li$:La^3+:Zr^4+:Ca^2+:Al^{3+}$ for Al-containing garnets is 6.4 (0.1): 3.0 (0.04): 2.08 (0.02): 0.05 (0.002): 0.26 (0.04) determined by ICP-OES (inductively coupled plasma optical emission spectroscopy). The solid samples are digested with HF, and clear digestes are obtained for analysis. Comparing with the designed composition of $Li_7La_3Zr_{1.95}Ca_{0.05}O_{12}$, this material shows an Al content of −0.26 mol per mol garnet formula unit. The Al content is comparable to that of reports by Geiger et al. (0.23 mol) [18], Buschmann et al. (0.28 mol) [19], and Sakamoto et al. (0.24 mol) [20]. Al is likely to affect the structure and properties in ways: (1) occupying lattice sites in substitution for Li, and stabilizing the cubic garnet structure, and/or (2) serving a sintering aid to improve the density [20]. The mechanism of Al in the stabilization of the cubic garnet phase is not yet well-understood. $^{27}$Al MAS NMR was performed to examine the Al role in the present work. Two signals −60 ppm and −75 ppm can be identified (Fig. 3). These two signals are also reported by other groups, and are assigned to tetrahedral sites [21,22]. Besides the two signals, the third signal at 233 ppm for transport, calculated data for assessing
ball-milling. The real Li content is ~6.4 mol per mol garnet formula unit, which is lower than the designed Li content of 7.1 mol per mol formula unit. The Li volatilization and Al diffusion from alumina crucibles during preparation would result in the “depleted” garnet noted as Li$_{7.1}$La$_3$Zr$_{1.95}$Ca$_{0.05}$O$_{12}$. 

### 3.3. Crystal chemistry and structure

XRD patterns (Fig. 4a) show that the diffraction peak of Zr$_{1.95}$Ca$_{0.05}$O$_{3.95}$ is consistent with ZrO$_2$ rather than CaO. It is a clear piece of evidence that CaO in ZrO$_2$ forms solid solution by high energy...
ball milling 2 h. The XRD pattern (Fig. 4a) of sintered Al-containing Li$_{7.1}$La$_2$Zr$_{1.95}$Ca$_{0.05}$O$_{12}$, shows no impurity peaks of calcium oxide, and matches well with the prototype LLZO (Powder Diffraction Files 45–0109, Space group Ia–3d). Direct determination of Ca$^{2+}$ coordination environment can be achieved by Fourier transform infrared spectroscopy (FTIR) (Fig. 4b). At lower frequency the complex exhibits a band at about 418 cm$^{-1}$ which may be assigned to CaO$_6$ octahedron vibration [25,26], indicating that Ca$^{2+}$ probably enters the lattice and locates at the octahedral 16a sites. Ceder et al. [27] indicated that some subvalent dopants (site) like Sc$^{3+}$ (Zr), Ca$^{2+}$ (Zr), Bi$^{3+}$ (Zr), Mg$^{2+}$ (Zr) that do not appear to have been tried before are proved to have relative low defect energies through first-principles calculation and are predicted to be stable. The bands at 630 cm$^{-1}$ and 841 cm$^{-1}$ are related to the characteristic Zr–O vibration [28–30]. The band at 482 cm$^{-1}$ may be attributed to the La–O vibration [31]. The bands viewed in the region of 1000–1650 cm$^{-1}$ are assigned to the absorbed carbonate species from the atmosphere [32]. Broad band at 3301 cm$^{-1}$ is assigned to the OH group and arises to some moisture absorption by the sample [33].

$^6$Li solid-state MAS NMR is used to examine the local lithium distribution. A single manifold of narrow spinning sidebands is observed from $^6$Li MAS NMR spectrum of Al-containing Li$_{7.1}$La$_2$Zr$_{1.95}$Ca$_{0.05}$O$_{12}$, which is centred at +5 ppm (Fig. 5a), and similar data is reported for several garnet-type structures in the literature [34–36]. Li$^+$ ions that differ in terms of their crystallographic coordination cannot be distinguished from the $^6$Li MAS NMR data. The $^6$Li MAS NMR line shows very narrow resonance at room temperature, which reflects fast ion-diffusion in this material at room temperature. This is in agreement with the high room-temperature diffusion coefficient ($\sim 10^{-11}$ cm$^2$ s$^{-1}$), obtained from the linear sweep voltammetry and high room-temperature conductivity ($\sim 10^{-3}$ S cm$^{-1}$) of this material. For $^6$Li MAS NMR, the low magnetogeric ratio and quadrupole moments result in better resolution of different local Li environments. Unfortunately, the Li sites cannot be well-resolved by the $^6$Li MAS NMR. A single peak at a chemical shift of around +31 ppm (Fig. 5b) seems to be attributed to the distribution of Li$^+$ at the octahedral coordination according to Cussen [37].

In order to determine lithium distribution and to clarify how Li–Li interactions affect the conductivity, neutron diffraction was used, since it is characterized by better balance between the scattering lengths of constitutive elements, including Li. Even though lithium remains the weakest scatterer among the other elements in the compound, the scattering strength difference is no longer as dramatic as for the X-ray case. Furthermore, lithium scattering length is actually negative, which makes its identification and quantitative refinement far more reliable. The refinement of the data collected on HRPT instrument at PSI (Paul Scherrer Institut, Villigen, Switzerland) is performed using FullProf suite of programmes [38]. Our analysis shows that the La (24c) and O (96h) sites are 100%-occupied by lanthanum and oxygen, correspondingly. Assigning the octahedral void (16a site) to be filled with Zr provides a very weak refined underoccuption (fractional occupancy -98%). Assuming instead that Ca (a weaker neutron scatterer than Zr) to be doping on this site allows excellent match to the ideal design composition assumed in the synthesis. The scatterers in the tetrahedral voids (24d sites) and in the clearly detectable in the difference Fourier maps 96h interstitial sites definitely have negative scattering lengths on average, and for that reason are (predominantly) Li atoms. Based on the $^{27}$Al MAS NMR data (Fig. 3) we assume -0.23 Al to be also located in the 24d sites, and the 96h interstitials to be occupied exclusively by lithium. This leads us to the final refinement illustrated in Fig. 6 with the following agreement factors: $R_p = 3.36$, $R_{exp} = 4.28$, $\chi^2 = 1.48$. The refined structure parameters are presented in Table 1.

The refined crystal structure is composed of LaO$_6$ dodecahedra and Zr/CaO$_6$ octahedra in which Li atoms occupy two crystallographic sites, namely, the tetrahedral 24d sites and interstitial 96h sites. Li diffusion pathway is constructed by interlocking Li(24d)–Li(96h)–Li(96h)–Li(24d) chain segments which form a 3D-loop structure. The extra Li atoms located at the interstitial 96h sites are actually located in such a way that their positions are likely to contribute to the migration paths for the Li atoms via tetrahedral 24d sites: the distances in the Li(24d)–Li(96h)–Li(96h)–Li(24d) are 1.62(2)–1.77(x) Å only. It should be noted that the very short and unphysical distance of -0.77 Å between the two 96h “twin sites”, together with the incomplete – on the order of 40% – occupation thereof actually indicates that these sites are probably not stationary, but are most probably intermediate Li sites in between the two adjacent tetrahedra [6]. Not more than one of these sites is expected to be occupied at any moment, thus leading to the typical Li-Li distance pattern of 1.62(2)–2.36(4) Å. Also noteworthy is the systematic underoccupation of both Li sites involved in this likely ions migration paths: both the 24d tetrahedral and the 96h interstitial sites are filled to the order of 40–50%, thus indicating that the whole ensemble of lithium atoms is randomly uniformly distributed across these sites forming a continuous migration path.

3.4. Enhanced high ionic conductivity

We have successfully developed a new garnet-type material with the designated composition Li$_{7.1}$La$_2$Zr$_{1.95}$Ca$_{0.05}$O$_{12}$ that possesses high room temperature ionic conductivity of $5.2 \times 10^{-4}$ S cm$^{-1}$. The high measured conductivity is ascribed to the following effects: (1) alkaline

![Fig. 4. XRD patterns of CaO, ZrO$_2$, Zr$_{1.95}$Ca$_{0.05}$O$_{12}$, Al-containing Li$_{7.1}$La$_2$Zr$_{1.95}$Ca$_{0.05}$O$_{12}$ (a); FTIR spectrum of Al-containing Li$_{7.1}$La$_2$Zr$_{1.95}$Ca$_{0.05}$O$_{12}$ (b).]}
earth cations location, (2) Al diffusion and incorporation into the lattice, and (3) Li\(^+\) ions occupancy and concentration.

Ca\(^{2+}\) cations are located at octahedral 6-coordination sites (Zr\(^{4+}\) sites) in the present family of materials. The larger ionic radius of Ca\(^{2+}\) (1.0 Å) than Zr\(^{4+}\) (0.72 Å) causes lattice expansion, thus increasing the bottleneck size, and reducing the migration barrier and improving the conductivity. The lattice constant of Al-containing Li\(_{7.1}\)La\(_{3}\)Zr\(_{1.95}\)Ca\(_{0.05}\)O\(_{12}\) is 12.96669 (14) Å, which is somewhat larger than that of the parent LLZO (12.94927(17) Å)\([39]\). The mobility of the ions mainly depends on the activation energy for ion conduction, whereas the bottleneck size is the predominant factor of the activation energy. The activation energy of the present material is 0.27 eV which is much smaller than that of the parent LLZO (0.34 eV)\([9]\). Moreover, the Ca doping improves the sinterability of present material, because of much lower melting point of CaCO\(_3\) than that of ZrO\(_2\). The dense microstructure with uniform grains is helpful for lithium ion conduction.

Besides, in the present material, Al probably enters the lattice and is located at tetrahedral sites to stabilize the cubic phase, as evidenced by the \(^{27}\)Al MAS NMR spectrum. A heterovalent substitution of Al\(^{3+}\) → 3Li\(^+\) leads to a reduction in the Li content and an increased Li vacancy concentration, both potentially improving phase stability and conductivity. Another factor is the Li\(^+\) ions occupancy and concentration. The refinement of crystal structure shows that the interstitial 96h sites are not stationary, and can lead to the typical Li–Li distance pattern of 1.62(2)–2.36(4) Å between tetrahedral 24d and interstitial 96h sites that are 40–50% occupied, thus indicating that the whole ensemble of lithium atoms is actually randomly distributed over these sites forming continuous migration paths consisting of interlocking Li(24d)–Li(96h)–Li(96h)–Li(24d) chain segments. This significant feature of Li distribution contributes to the superior Li-ion-conduction.

The finding that the present material with the real Li content of 6.4 per mol formula unit displays high ionic conductivity is in good agreement with Xie, and Li generic strategy is identified for doping garnet structure with rare earth oxides to improve electrochemical properties predictions that the highest ionic conductivity will be found where the Li content at 6.4 ± 0.1, based on the Li variation at 24d sites and 96h sites from neutron diffraction\([40,41]\).

4. Conclusion

In summary, we have successfully developed new Al-containing garnet-type material with the designed compositions of Li\(_{7.1}\)La\(_{3}\)Zr\(_{1.95}\)Ca\(_{0.05}\)O\(_{12}\). Different from other reports, we show that the alkaline earth cations can locate at octahedral 6-coordinated sites in the garnet-related materials. High room-temperature ionic conductivity of 5.2 × 10\(^{-4}\) S cm\(^{-1}\) is achieved by the unusual alkaline earth cations site occupancy. It is worth noting that ZrO\(_2\) can form solid solutions with a series of alkaline earth and rare earth oxides, combined with the ability of the garnet structure to accommodate cations of

Table 1

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Occupation</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Biso (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/Al</td>
<td>24d</td>
<td>0.468/0.077(^a)</td>
<td>3/8</td>
<td>0</td>
<td>1/4</td>
<td>2.7818(^b)</td>
</tr>
<tr>
<td>Li</td>
<td>96h</td>
<td>0.418</td>
<td>0.67156</td>
<td>0.56307</td>
<td>0.15247</td>
<td>2.78 18(^b)</td>
</tr>
<tr>
<td>La</td>
<td>24c</td>
<td>1</td>
<td>1/8</td>
<td>0</td>
<td>1/4</td>
<td>0.885 16</td>
</tr>
<tr>
<td>Zr/Ca</td>
<td>16a</td>
<td>0.975/0.025(^c)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.702</td>
</tr>
<tr>
<td>O</td>
<td>96h</td>
<td>1</td>
<td>0.96804</td>
<td>0.05419</td>
<td>0.15007</td>
<td>1.1504</td>
</tr>
</tbody>
</table>

Agreement factors: R\(_p\) = 3.36%, R\(_wp\) = 4.28%, \(\chi^2\) = 1.48
\(a = 12.96669(14)\) Å, V = 2180.15(4) Å\(^3\)
Refined Li composition: 6.42(1)

\(^a\) Value fixed based on ICP-OES.
\(^b\) The numbers for the Biso for both Li atoms were refined with constraint to equality.
\(^c\) Occupation ratio for Zr:Ca in this site has been fixed to 1.95:0.05. If refined, it converges to a very close value.
different valence states and different sizes, our results thus broaden the chemical substitutions and define a different direction to stabilize the garnet structure and enhance the ionic conductivity, and challenge us to seek new oxide electrolytes to substitute liquid electrolytes.

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