Experimental and theoretical study on enhanced electrochemistry of aluminum substitution LLZO garnet solid electrolytes

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Abstract
Although the wider electrochemical window, higher temperature stability, and better battery safety of Li$_7$La$_3$Zr$_2$O$_12$ (LLZO) electrolytes than organic liquid, organogels, and polyelectrolytes, the limited ionic conductivity still far away from the practical electrochemical applications. Herein, LLZO electrolytes were by solid phase method. In order to further improve its electrochemical performance, aluminum substitution was introduced to replace Li$^+$ sites and thus the highly conductive cubic phase was stabilized. The results show that with the increase of the substitution amount, the ion conductivity presents a trend of first increasing and then decreasing. It was found that 0.15Al-LLZO ceramics presented optimized ionic conductivity ($1.184 \times 10^{-4}$ S·cm$^{-1}$) and 92.5% of bulk density at 1150 °C for 21 h treatment. On the other hand, with the combination of molecular simulations, the relationship between the influence of aluminum substitution on the differential charge density of the garnet solid electrolyte and the electrochemical performance was investigated. It is believed that such an experimental-modeling combination will expand the fundamental understanding of elements variation/substitution effects on solid electrolytes, especially for lithium metal oxides.

Introduction

Compared with the state-of-the-art Li-ion batteries, solid-state batteries (SSBs) have been attracted wide attentions for next generation energy-storage devices due to the probability to realize higher energy density and superior safety performances [1]. In general, the main proposed benefit of solid-state batteries has been their increased safety [2], which mainly stems from the absence of flammable liquid electrolytes typically employed in Li-ion cells [3]. As a key component in SSBs, various types of solid-state electrolytes (SSEs) have been studied [4–7], including perovskite-type [8], sodium superionic conductor (NASICON)-type [9], lithium phosphorus oxynitride (LiPON) [10], sulfide-type [11], and garnet-type materials [12]. Among them, Li-containing garnet materials, particularly Li$_7$La$_3$Zr$_2$O$_12$ (LLZO) have been attracting considerable interest as potential solid-state electrolytes for Li ion batteries due to its excellent Li-ion conductivity at room temperature [13–16], and electrochemical stabilities [17] against Li metal. Moreover, it is also found that all-solid-state battery using LLZO as a promising solid electrolyte exhibited good thermal and chemical stability [18] against reactions with prospective electrode materials, environmental benignity [19], low cost (thus, it is easy to achieve kilogram-level or higher-scale production, which has a profound impact on practical applications) [20, 21], and ease of preparation and densification [22]. From the structural investigations, there are two polymorphs of LLZO have been reported—(i) a tetragonal (I41/acd, SG no. 142) low-temperature form [23] and (ii) a cubic (Ia3d, SG no. 230) polymorph that is thermodynamically stable above 400–625 K (The exact value depending on the sample impurity level) [24]. Interestingly, by substitution supervalent cations (i.e., Al$^{3+}$, Ga$^{3+}$ [13], Ta$^{5+}$ [26], Fe$^{3+}$ [27], Mg$^{2+}$ [28], Nb$^{5+}$ [5], Ba$^{2+}$ [29], Mo$^{6+}$ [30], etc), it enables the stabilization of the cubic...
form at room temperature, mainly because the position of Li ions in the cubic structure is partially occupied [31]. With abundant randomly distributed Li-ion vacancies, the migration of lithium ions becomes easier.

However, the challenge still remains: as the low ionic conductivity of garnet-type solid electrolytes is still no breakthrough, the commercial conversion of garnet-type solid electrolytes still remain an arduous task [32]. Aluminum (Al) substitution was the first to appear this substitution is caused by aluminum contamination using alumina crucibles for sintering and was the most common but effective since the substitution raw materials were cheap and easy to obtain [33]. Based on these abovementioned investigations [34], here we introduced the concept of reasonable design and modified it by elementary substitution to obtain a garnet-type solid electrolyte with high conductivity at room temperature. The substitution amount and corresponding ionic conductivity variation were systematically compared. It was found that when the substitution amount of Al element reaches 0.15, the obtained Al-LZLO with $1.184 \times 10^{-4}$ S cm$^{-1}$ of conductivity enabled to meet the performance requirements of assembled batteries. Taking advantage of Materials Studio CASTEP modules [35], we also calculated and discussed the relationship among the influence of aluminum substitution on the differential charge density maps of the garnet solid electrolyte and corresponding electrochemical performances. The dominated factor of enhanced electrochemical performance was partial replacement of Li-ion sites by Al ions.

### Experimental section

**Preparation of Al-LZLO powders and ceramics**

Li$_{7-3x}$Al$_x$La$_3$Zr$_2$O$_{12}$ was prepared by the conventional high-temperature solid-state reaction procedures according to the following stoichiometric amounts: lithium carbonate (MACKLIN, >99.9%, dried at 200 °C, adding an excess of 10 wt% to compensate for lithium loss during annealing), La$_2$O$_3$ (MACKLIN, >99.99%; in Drying at 900 °C for 10 h), aluminum oxide (MACKLIN, >99.9%) and zirconium dioxide (MACKLIN, >99%). The lanthanum oxide is mixed with lithium carbonate and zirconium dioxide. The powder feedstock was thoroughly mixed in the solvent isopropanol(MACKLIN, AR, >99.5%) at a stoichiometric ratio by means of a planetary ball mill (48 h, 300 rpm). The obtained slurry was dried in a drying oven (120 °C, 6 h) to obtain a mixed powder, subsequently taken out the above powder and poured it into a crucible for sintering. After cooling, new mixed powders were obtained and underwent ball milling (15 h, 300 rpm), and the Al-modified LZLO solid electrolyte powders can be obtained by fully dried. 15 wt% binder PVA was added to Al-modified LZLO solid electrolyte powder, stir evenly and put it in a drying oven to dry (120 °C, 5 min). The aluminum-modified LZLO solid electrolyte powder was sieved and dried with a combined mesh. (40 mesh, 100 mesh), collect the powder (particle size between 40 mesh and 100 mesh), and use a mold with a diameter of 10 mm for tableting (tabletting conditions: 0.5 g/tablet, apply a vertical pressure of 28 MPa, and hold the pressure for 3 min); Appropriate heating stage and heat preservation sintering stage are set, and through final sintering, the crystal grains are fully grown and formed, and dense LZLO wafers are obtained. After the discs are pressed, they are stacked vertically into the crucible. Spread aluminum-modified LZLO solid electrolyte powder between the discs. Place the filled crucible in a muffle furnace and sinter it. The curve is divided into seven sections, including three sections of heating curve, three sections of heat preservation curve and one section of cooling curve, and the final sintering temperature is 1150 °C. The specific sintering curve is: from room temperature to 100 °C at 3 °C min$^{-1}$, holding for 2 h; from 100 °C to 450 °C at 3 °C min$^{-1}$, heat preservation for 2 h; then from 450 °C to 1150 °C at 1 °C min$^{-1}$, heat preservation for 21 h; then reduce from 1150 °C to 450 °C at 1.5 °C min$^{-1}$ and cool to room temperature naturally. The synthesized Li$_{7-3x}$Al$_x$La$_3$Zr$_2$O$_{12}$ powder and ceramics are recorded as Al $= 0.00 \sim 0.30$, indicating different Al substitution levels.

**Characterizations**

Powder X-ray diffraction (XRD) (Seifert3000, CuK$_\alpha$) was used to monitor the phase formation, The crystal structure of Al-LZLO phase was characterized and confirmed by XRD in the range of 10°~80°. The Archimedes method was used to determine the density with alcohol as the liquid. Scanning electron microscope (SEM) was used to observe the cross section of LZLO solid electrolyte sheet after sintering. Before each impedance measurement, the sample was equilibrated at a constant temperature for 3~6 h. Electrochemical impedance spectroscopy (EIS) data were collected in the temperature range of 25 °C~85 °C, with Ag coating fabrication of blocking electrodes: sand the surface of the LZLO solid electrolyte sheet with 400-mesh, 800-mesh, 1200-mesh, and 1500-mesh sandpaper, and then apply silver paste (FERRO, 80%) on the surface of the LZLO sheet and place it in a muffle furnace to keep warm (850 °C, 0.5 h), the silver paste was shrunk and solidified, and it was completely bonded to the surface of the sheet), as the barrier electrode, and the heating/cooling rate was 20 °C~30 °C min$^{-1}$. The impedance value of the Garnet-type solid electrolyte Li$_{7-3x}$Al$_x$La$_3$Zr$_2$O$_{12}$ was calculated by Z-view fitting. The calculation is carried out using the material studio (MS) Refex module based on density functional theory (DFT) [36], and the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) is selected for the exchange correlation function [37]. The convergence criteria for structure and energy relaxation are set to 1.0 × 10$^{-5}$ eV and 0.01 eV Å$^{-1}$. 
Results and discussion

Synthesis and characterization of Al-modified LLZO solid electrolytes

The XRD patterns of Li$_{7-3x}$Al$_x$La$_3$Zr$_2$O$_{12}$ were shown in figure 1. Since the positions of the diffraction peaks in the XRD diffraction spectra for both Li$_7$La$_3$Zr$_2$O$_{12}$ and Li$_5$La$_3$Nb$_2$O$_{12}$ were roughly similar, Li$_5$La$_3$Nb$_2$O$_{12}$ here was selected as a standard specimen for comparison [38]. As shown in figure 2, there is not split diffraction peak near 31° in all samples, indicating that these Al-modified LLZO electrolyte are cubic phase. This may be attributed to the introduction of Al elements into LLZO, which stabilized the cubic phase of LLZO [18]. Furthermore, all diffraction peaks of Al-LLZO with varying Al substitution contents are shifted, indicating to Bragg’s equation ($2dsin\theta = n\lambda$), the displacement comes from the crystal phase lattice change [39]. On the other hand, when a Al ion successfully enters LLZO unit cell, three Li ions will be replaced according to the conservation of charge [40, 41], and the ionic radius of Al ions is larger than those of Li ions, which is the root cause of the increase in the lattice constant. It is worth mentioning that there are two additional peaks around 30.9° and 27.6° in the figure 2, and some broadening. By comparing the standard card [42], we can know that there are second phases La$_2$Zr$_2$O$_7$ in the powder. La$_2$Zr$_2$O$_7$ is an intermediate product that reacts with lithium oxide during the solid-state reaction to form Li$_7$La$_3$Zr$_2$O$_{12}$ [40, 43]. In high-Al-substituted LLZO, the lithium oxide is not sufficient to react with La$_2$Zr$_2$O$_7$, therefore, the La$_2$Zr$_2$O$_7$ impurity phase remains in the high-Al-substituted powder. However, due to the limited accuracy of XRD diffraction patterns for qualitative comparison analysis, low content of the impurity phase remains in the high-Al-substituted LLZO.
phase will result in weak diffraction peak intensity and reduce the credibility of the actual results. Next, Raman spectroscopy was performed to further clarify the results. Raman spectra to show the generation of impurity phases was judged by the vibration of non-polar molecular bonds at the wavenumber range of 100–1200 cm\(^{-1}\). The Raman spectra of Li\(_{7-3x}\)Al\(_x\)La\(_3\)Zr\(_2\)O\(_{12}\) were shown in figure 3. Tietz et al.\(^{[44]}\) reported the existence of LLZO through two typical peaks at 100 cm\(^{-1}\) and 350 cm\(^{-1}\) in the Raman spectrum. The peak near 650 cm\(^{-1}\) corresponds to the vibration of the Zr-O bond in the octahedral ZrO\(_8\)\(^{[44]}\), indicating that the environment of the skeleton element Zr in the LLZO unit cell conforms to the garnet-type structure where the octahedral skeleton elements are located. Compared with the detailed spectra of Al\(_{0.05}\)-LLZO, Al\(_{0.10}\)-LLZO, Al\(_{0.15}\)-LLZO, Al\(_{0.20}\)-LLZO, Al\(_{0.25}\)-LLZO, and Al\(_{0.30}\)-LLZO, the obvious Raman shift at around 1100 cm\(^{-1}\) presented the existence of impurity Li\(_2\)CO\(_3\). The impurity Li\(_2\)CO\(_3\) is mainly formed by the reaction among highly sensitive water molecules, carbon dioxide, and Li composites\(^{[7]}\). The liquid phase LiAlO\(_2\) produced at high temperature is obtained by the reaction of \(\gamma\)-Al\(_2\)O\(_3\) with Li composites\(^{[26]}\). On the other hand, higher Al substitution results in less Li composites in Li\(_{7-3x}\)Al\(_x\)La\(_3\)Zr\(_2\)O\(_{12}\). Li composites in Al = 0.00 and Al = 0.05 is supersaturated, so the Li\(_2\)CO\(_3\) impurity peaks of both are obvious. At the same time, the co-action of LiAlO\(_2\) and supersaturated Li composites leads to the generation of large-sized molten particles (figure 4). The content of Li\(_2\)O in Al = 0.15 is appropriate, resulting the Li\(_2\)CO\(_3\) impurity peak to be inconspicuous. With the further increase of \(\gamma\)-Al\(_2\)O\(_3\) to Al = 0.25, although there is enough LiAlO\(_2\), the Li composites content becomes significantly lower after the reaction, which eventually leads to abnormal grain growth (AGG) after sintering, resulting in a significantly increased number of isolated pores\(^{[45]}\). As the Al substitution amount increased, the Raman peak at 1100 cm\(^{-1}\) decreased, indicating that Al ions are beneficial to reduce the sensitivity of LLZO to carbon dioxide and water; while a large amount of substituted Al ions can block the absorption of carbon dioxide by LLZO to a certain extent, thereby greatly improving the stability of LLZO in the air\(^{[46]}\). However, the improvement of the electrochemical performance of Al-LLZO is limited due to the small number and intensity of secondary electrons collected in these regions. It is worth mentioning that, an additional peak can be clearly observed at 300 cm\(^{-1}\), and the corresponding substance is La\(_2\)Zr\(_2\)O\(_7\)\(^{[43]}\). This peak only appears in the experimental group with high aluminum substitution, which corroborates the experimental phenomenon in XRD.

The SEM fracture section micrographs were shown in figure 4. Specifically, the fracture mode of the grains can be observed on the fracture surface before and after substitution, which is a mixed fracture mode of intergranular fracture and transgranular fracture. Tetragonal Al = 0.00 ceramics contain polyhedral-like grains with loose grain boundaries, consistent with their lower relative density (figure 5). At the same time, the grain gaps are not uniform, and large-area grain pores appear in some areas. The grain size in Al = 0.05 sample became larger and uniform (figure 4). The grain size of Al = 0.15 is much smaller than that of Al = 0.05, Spherical isolated pores were detected on the surface of its grains (figure 4), with relatively uniform particle size, showing that the Al = 0.15 sample exhibited melting sintering behavior sample. The melting sintering behavior also exists in Al = 0.25, and the number of isolated pores in the grains increases significantly (figure 4). At the same time, it can be seen from figure 4 that the silver coating on the interface can well wrap the grains of the surface layer, so that the subsequent electrochemical tests can be carried out effectively. Compared with the counterweight in the

![Figure 3. Raman spectra of Al-LLZO solid electrolytes with the varied Al substitution contents from 0.05 to 0.30.](image-url)
sintering process, the sample has a compact structure, and there is no large gap between the grains. This is because during the sintering process, the sample acquires the pressure provided by the counterweight. As a result, the sample has a more compact structure, and the gap between the grains is effectively reduced.

**Electrochemical performances for Al-modified LLZO solid electrolytes**

For electrochemical performance characterizations, the silver coating was used as the barrier electrodes and electrochemical impedance spectroscopy (EIS, Solartron 1260A) was used to determine the ionic conductivity of the ceramic at the amplitude of 20 mV and the frequency of 5 M ～ 10 Hz. By selecting four temperature points of 25 °C, 45 °C, 65 °C, and 85 °C for testing, and model the equivalent circuit of the data. By calculating the conductivity of Al-LLZO at different temperatures, the relationship between conductivity and temperature was obtained by the Arrhenius equation fitting. Here, we applied Z’ value as the inflection point and the blocking electrode of Al = 0.05 ～ 0.15 ceramic is determined as the total impedance contributed by the ceramic microspheres to calculate the ion conductivity [47]. As shown in figure 6, the low density of Al = 0.00 ceramics

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**Figure 4.** SEM images of Al-LLZO solid electrolytes with the varied Al substitution contents from 0 to 0.25.

**Figure 5.** Conductivities at 25°C and Elative densities (Al = 0.00 ～ 0.15, ρtheoretical = 5.061 g cm⁻³; Al = 0.20 ～ 0.30, ρtheoretical = 5.003 g cm⁻³), and part appearances.
provides considerable impedance and low conductivity of $2.5 \times 10^{-7}$ S cm$^{-1}$, while the density of Al = 0.05 ~ 0.30 ceramics is relatively higher than 90%. Detailed electrical conductivity value of LLZO ceramics with a specific composition increases with the increase of the relative density before 92%, and then remains unchanged with the further increase of the relative density. The highest conductivity can be achieved at $1.184 \times 10^{-4}$ S cm$^{-1}$ when the Al substitution concentration is 0.15. More interestingly, the semicircle with Al = 0.15 ~ 0.30 is not obvious enough, while the semicircle with Al = 0.20 ~ 0.30 is flat.

Figure 6. Impedance diagrams of Al-LLZO solid electrolytes at different temperatures from 0 to 0.30, Arrhenius curves and equivalent circuit diagrams of GaAl-LLZO at different Al substitution levels.
The experimental difference was represented by M, the formula of M can be obtained below [48]:

$$M = \sum W_i(Y_{oi} - Y_{ci})$$

Where $W_i$ and $Y_{oi} - Y_{ci}$ represented as the weighting factor and the difference between the experimental value and the fitted value in this equation, respectively [49]. When the difference between the experimental value and the fitted value is small, the fitted crystal structure information can be in line with the actual experimental value. To analyze the atomic vibration better quantitatively in the unit cell, thermogravimetric factor or temperature factor was used to describe the degree of atomic thermal vibration. The area over 80° in XRD patterns is a high diffraction angle area, and there are still a small number of diffraction peaks [50], which are very sensitive to the thermal vibration of the atoms in the unit cell (figure 7). Therefore, the range of XRD refinement is 10°–120°.

The results of XRD refinement used the confidence factors $R_p$ and $wR_p$ to evaluate the degree of fit: the smaller the confidence factors $R_p$ and $wR_p$, the higher the fit degree. In summary, when $wR_p$ was less than 0.15 and $R_p$ was less than 0.10, it can indicate that a good fitting degree can be achieved to quantitatively characterize the practical materials. The Reflex module from Materials Studio can further refine the obtained XRD pattern of Al0.15-LLZO electrolytes. From the results, the refinement ($wR_p = 0.1235/0.15$, $R_p = 0.0871/0.10$) make it possible to match the construction model crystal structure, lattice constant and actual structure of the model. Therefore, the interpretation of the corresponding structure through this model has a high degree of credibility. The comparison between XRD and refinement (figure 7) supports the presence of LiAlO$_2$. LiAlO$_2$ is soluble in acidic hot water [51]. Meanwhile, the sintered LLZO solid electrolyte pellets as the host are highly sensitive to water molecules and CO$_2$, and can only be stored in a vacuum oven with a relative humidity of less than 5% [52]. Therefore, the LiAlO$_2$ in the sintered LLZO solid electrolyte pellets cannot be removed by acidic heat.

To further analyze the structure, the respective differential charge density maps of constructed Al0-LLZO, Al0.05-LLZO, Al0.10-LLZO, Al0.15-LLZO, Al0.20-LLZO, Al0.25-LLZO, and Al0.30-LLZO were established (figure 8). The blue area indicates a higher electron density derived from the dense electron cloud in this area, while a lower electron density (thin electron cloud) can be observed in gray area. In addition, each O ion or/ and Li ion was surrounded by gray area (inner layer) and blue area (outer layer). This shows that there is a deficit in the migration rate of electrons near O ions and Li ions therefore, the direction of the formed Li-O bond can be judged, and the O ions are used as nodes and connected in sequence according to the regional distribution. We can also know that Li–O bond can build a Li ion transmission path, as evidenced by the generation of two types of Li-ion transmission paths: (i) one is from the octahedral gap to the tetrahedral gap (48g/96h–24d) [53]; (ii) Another one is from the octahedral gap to the octahedral gap, (48g/96h–48g/96h) [54]. Further observations indicated that there were six larger gray areas in the figure—two of which are distributed on the central hexatomic ring, while the other four are distributed near the end of long Li chains. According to the ion movement trajectory, when the four Li ions (from long Li chain) are removed to form vacancies, the nearby free Li ions will move closer to the central hexatomic ring due to the minimum energy principle. Specifically, this is because after removing Li ions, the nearby free Li ions are subjected to uneven Coulombic forces, and the direction of the

![Figure 7. Comparison of simulated XRD and refined XRD patterns.](image)
resulting force points to the hexatomic ring. By adjusting the position of the Li ions, the force exerted by Li ions can be balanced, thereby reducing the internal potential energy of the entire cubic LLZO unit cell.

In the cubic LLZO unit cell, four Li ions are removed from the entire central hexatomic ring, two Li ions in the tetrahedral gap and the other two in the octahedral gap. It can be found that the local area of the octahedral gap vacancy in the hexatomic ring has no change in electron density. The electron density of the local area for tetrahedral gap vacancies is reduced, indicating that this area is easier to attract Li ions to migrate to nearby bonds, that is, Li ions are more easily transported through the tetrahedral gap vacancies rather than through the octahedral gap vacancies [55]. Therefore, reducing the Li site occupancy rate in cubic LLZO and increasing the number of tetrahedral gap vacancies are beneficial to increase the transmission of Li ions, thereby enhancing the ionic conductivity of cubic LLZO [56]. Compared with the differential charge density map of Al0.05-LLZO and Al0.10 -LLZO, Al0.15-LLZO, Al0.20-LLZO, Al0.25-LLZO, and Al0.30-LLZO specimens, it can be found that Li sites occupy in cubic phase LLZO in Al0.15-LLZO with the lowest value of bit rate. Simultaneously, the effect of enhancing the ionic conductivity of cubic LLZO for Al0.15-LLZO is also the most significant, corroborating the experiment from the side.

Conclusions

In summary, we rationally designed the Garnet-type solid electrolyte Al-LLZO by using a heteroatomic substitution strategy. We systematically explored preparation method and the sintering process for LLZO powders. The resultant Al-LLZO with well-designed crystal structures possessed a higher density as partial replacement of Li ions by Al ions. At the meantime, the Li-ion positions in the structure are partially occupied and there are abundant randomly distributed Li-ion vacancies in the crystal, and the migration of lithium ions becomes easy, thereby increasing the ion conductivity. But virtue of relevant characterizations, the influence of Al element substitution on the electrochemical performance of LLZO, combined with the phase analysis of Al-LLZO with different Al substitution amounts, electrochemical performance analysis was fully analyzed. Furthermore, we use modeling (Materials Studio) to verify the possibility of performances enhancement of Al-LLZO solid electrolytes. The results showed that the unequal substitution will induce the lattice structure changed from tetragonal phase to cubic phase, while the unit cell Distortion and abundant vacancy defects promoted the movement of Li ions. With the increase of Al ion substitution, a lattice structure dominated by Al ions was gradually formed, so that the structure was reordered and thus limited the transport efficiency of Li ions. Such a combination also explains the trend of ion conductivity (first increases and then decreases) as the increase of the substitution amount.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

There are no conflicts to declare.

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