Improvement of the Li-ion conductivity and air stability of the Ta-doped Li$_7$La$_3$Zr$_2$O$_{12}$ electrolyte via Ga co-doping and its application in Li–S batteries†

Kai Ma, a,b Bowen Chen, b Cheng-Xin Li, *a and Venkataraman Thangadurai b, *b

The garnet-type solid electrolyte Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) has emerged as a promising candidate for all-solid-state lithium-ion batteries (ASSLBs) due to its exceptional performance. However, it currently faces challenges related to low ionic conductivity and structural instability, which limit its widespread application. To obtain a garnet-type solid electrolyte with high ionic conductivity and stable structure, Ta and Ga co-doped Li$_{6.6-4x}$Ga$_x$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ (Ga–LLZT) was successfully synthesized using a solid-phase method. The influence of Ga-doping on crystal structure, morphology, relative density, ionic conductivity, and air stability was investigated. The results indicate that Ga-doping not only alters the Li occupancy distribution, enhancing ionic conductivity but also expedites the densification of the garnet electrolyte, reducing the required sintering temperature for densification. Specifically, Ga$_0.1$-LLZT sintered at 1050 °C for 6 h achieves a relative density of 95.3% and a total ionic conductivity of 8.09 × 10$^{-4}$ S cm$^{-1}$ at 25 °C. Remarkably, it exhibits excellent air stability, retaining 86% of the initial total ionic conductivity after 4 months of atmospheric exposure. Furthermore, the Li/Ga$_0.1$-LLZT/Li symmetric cell demonstrates excellent Li metal stability. The fabricated Li/Ga$_0.1$-LLZT/5–KB full cell maintains a discharge specific capacity of 392 mA h g$^{-1}$ after 600 cycles at 0.1C, confirming the potential of the Ga–LLZT electrolyte in ASSLBs.

1 Introduction

Lithium-ion batteries (LBs) play a pivotal role in modern society as essential energy storage devices, finding widespread applications in portable electronic devices and electric vehicles.1–3 Nevertheless, despite their high ionic conductivity, conventional liquid electrolytes are accompanied by a host of safety concerns, including easy leakage and pyrolysis problems.4,5 These safety concerns limit the reliability of batteries and entail certain environmental risks. Therefore, with the widespread application of lithium batteries in various fields, it is imperative to enhance the energy density of batteries and bolster their safety and reliability. All-solid-state lithium-ion batteries (ASSLBs), which employ solid electrolytes instead of traditional liquid electrolytes, have significantly elevated battery safety levels and are regarded as the next-generation energy storage solution with high energy density and better safety performance.6–8 Solid-state electrolytes play a pivotal role in ASSLBs, with high Li-ion conductivity and exceptional stability representing fundamental prerequisites for their utilization in ASSLBs.9–11

Among various types of solid-state electrolyte materials, the garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) is considered a promising solid-state electrolyte candidate due to its high ionic conductivity (∼10$^{-3}$ S cm$^{-1}$ at 25 °C), low electronic conductivity (∼10$^{-8}$ S cm$^{-1}$ at 25 °C), wide electrochemical stability window (>6 V vs. Li$^+/Li$) and excellent chemical stability towards Li metal.12–14 There are two crystalline phases of LLZO: tetragonal (space group $I4_1/acd$) and cubic (space group $Ia3d$). The tetragonal phase has high stability but low ionic conductivity (∼10$^{-8}$ S cm$^{-1}$ at 25 °C).15,16 In contrast, the cubic phase has two orders of magnitude higher ionic conductivity but is thermodynamically unstable at ambient temperature.17,18 Therefore, it is important to preferentially prepare cubic phase LLZO to obtain higher ionic conductivity.

To enhance the stability of the cubic phase LLZO, the substitution of elements with heterovalent cations has proven to be an effective approach.19–21 Substituting Zr$^{4+}$ with high-valent Ta$^{5+}$ not only stabilizes the cubic phase structure but also introduces more Li vacancies, making Ta-doped LLZO (LLZT) have high room temperature ionic conductivity, good

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*State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi’an Jiaotong University, Xi’an, Shaanxi, 710049, P. R. China. E-mail: lcs@mail.xjtu.edu.cn
aDepartment of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada. E-mail: vthangad@ucalgary.ca
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mechanical strength, and thermal stability.\textsuperscript{19,22} The single-crystal highest ionic conductivity of LLZT can reach $1.1 \times 10^{-3}$ S cm$^{-1}$ for the chemical formula $\text{Li}_{6.6-\text{x}}\text{La}_{3}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$.\textsuperscript{23} Typically, there are abundant low ionic conductivity grain boundaries in LLZO ceramics, leading to lower total ionic conductivity in polycrystalline garnet electrolyte samples. In addition, substituting Ga$^{3+}$ for Li$^{+}$ causes Li vacancies and disorder in the LLZO structure.\textsuperscript{24-26} It has been reported that Ga-doped LLZO can achieve the highest total Li-ion conductivity at room temperature, reaching $1.3 \times 10^{-3}$ S cm$^{-1}$.\textsuperscript{24,26,27} However, Ga-LLOZ is prone to abnormal grain growth (AGG) during high-temperature sintering, potentially leading to impurity phases and porous grain boundaries between grains.\textsuperscript{26,28} This not only reduces its mechanical strength but also increases the risk of Li dendrite penetration. Consequently, the fabrication of electrolytes that combine high ionic conductivity, high density, and the suppression of Li dendrite growth remains a substantial challenge.

Due to the differing preferred substitution sites for various dopant ions in LLZO, a multielement co-doping approach can effectively optimize both Li vacancy concentration and lattice dimensions, which can more effectively improve the stability and ionic conductivity of LLZO electrolytes.\textsuperscript{29-32} The microstructure of LLZO electrolytes plays a crucial role in determining air stability and the stability of Li plating and stripping.\textsuperscript{33,34} When the LLZO electrolyte comes into contact with CO$_2$ and H$_2$O in the air, it reacts to form Li$_2$CO$_3$, leading to a degradation in its performance.\textsuperscript{30,35,37} It has been demonstrated that the initial reaction usually occurs at grain boundaries. The growth of Li dendrite becomes a potential issue, particularly in the intergranular regions of polycrystalline LLZO, during battery cycling at high current densities.\textsuperscript{33} High fracture toughness is a key factor in inhibiting Li dendrite growth and is influenced by factors such as grain size, density, and grain boundary structure. The introduction of sintering aids can also help increase the density and improve the microstructure of LLZO, to enhance its air stability and suppress Li dendrite growth.\textsuperscript{31-34} Ga$_2$O$_3$ has been demonstrated as an optional sintering aid,\textsuperscript{42,45,46} as its introduction in LLST may contribute to increasing LLST's ionic conductivity and enhancing its air stability.

This study aims to further improve the ionic conductivity and stability of LLZO electrolytes by co-doping Ga (Gax-LLZT). The effects of varying Ga doping contents on the crystal structure, morphology, relative density, and ionic conductivity of Gax-LLZT were investigated. Additionally, we also paid attention to the air stability and Li metal stability of Gax-LLZT and explored its practical application potential by assembling Li-S batteries. In this study, we adopted a simple co-doping method to successfully stabilize the cubic phase structure, improve ionic conductivity, and enhance stability. This achievement presents novel strategies and possibilities for the commercialization and advancement of ASSLBs.

2 Experimental

2.1 Preparation of Gax-LLZT electrolytes

The Li$_{6.6-\text{x}}$Ga$_{\text{x}}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ (denoted as Gax-LLZT, where $x = 0.05, 0.1, 0.15, 0.2$) powders were synthesized via the solid-state reaction method as reported previously.\textsuperscript{47,48} Raw materials including LiNO$_3$ (99%, Alfa Aesar, 10 wt% excess), La$_2$O$_3$ (99.99%, Alfa Aesar, calcined at 900 °C for 12 h), Ga$_2$O$_3$ (99.999%, Alfa Aesar), ZrO$_2$ (99%, Aldrich) and Ta$_2$O$_5$ (99%, Alfa Aesar) were mixed with isopropanol in the zirconia ball-milling jars at 200 rpm for 6 h. After drying at 80 °C, the mixed powder was pre-sintered at 700 °C for 6 h in an alumina crucible. Subsequent ball-milling under the same conditions produced the precursor, which was then cold isostatically pressed into cylindrical pellets. Calcination at 900 °C for 6 h in an alumina crucible yielded Gax-LLZT powders. Additional ball-milling was conducted to refine particle size for subsequent characterization and pelletizing. For comparison, LLZT powder was prepared using the same synthesis procedure as described above.

The synthesized garnet powders were compacted through cold pressing at 250 MPa pressure, resulting in green pellets of 10 mm diameter and approximately 1 mm thickness. To achieve densification, these green pellets were stacked in alumina crucibles and sintered at 1050 °C or 1150 °C for 6 h with a heating rate of 5 °C min$^{-1}$. To counter lithium loss at high temperatures, the green pellets were surrounded by the parent powder. All pellet sintering processes were conducted in an ambient air atmosphere. The garnet pellets fabricated excluding the top and bottom portions were utilized for subsequent tests and transferred to an argon-filled glovebox to minimize atmospheric exposure and prevent deterioration. Both pellet sides were coated with gold paste, followed by a 1 hour, 700 °C heat treatment, establishing a gold electrode barrier for ensuing electrochemical testing.

2.2 Characterization of Gax-LLZT electrolytes

Powder X-ray diffraction (PXRD) analysis was carried out using a Bruker D8 powder X-ray diffractometer, operating at 40 kV and 40 mA with Cu-K$_\alpha$ radiation ($\lambda = 1.54$ Å). Data collection spanned 2θ from 10° to 80°, with 0.02° intervals. Rietveld refinement of XRD data was performed using the Fullprof software for phase analysis and crystal structure determination. Chemical composition analysis was performed by using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7800, USA). The density of the garnet pellets was determined using the Archimedes method with isopropanol as the immersion medium. Microscopic morphology and elemental distribution were examined by Field Emission Scanning Electron Microscopy (FE-SEM, MIRA3 LMH, TESCAN, Czech Republic) coupled with Energy Dispersive Spectroscopy (EDS). A scanning transmission electron microscope (STEM, Thermoscientific ThermoFisher Scientific, USA) equipped with a field emission gun and EDS detectors was used to investigate electrolyte composition. The Raman spectrum was recorded from 50 to 1200 cm$^{-1}$ using a Raman spectrometer (Renishaw inVia Qontor, UK) utilizing...
a 532 nm laser excitation source. Electrochemical impedance spectroscopy (EIS) was conducted via a Solartron SI 1260 impedance analyzer, measuring from 1 Hz to 1 MHz with a 10 mV AC amplitude. This analysis occurred across a temperature range of 25 °C to 125 °C. To evaluate extended air stability, pellets were air-exposed for 4 months, then heat-treated at 700 °C for 1 hour. Concurrently, EIS was employed to track changes in ionic conductivity. Within the glovebox, Li pieces were placed on pellets, heated to 230 °C on a hot stage, observing the interaction between garnet pellets with molten Li.

### 2.3 Fabrication and electrochemical performance tests of symmetric and full cells

In pursuit of exploring the potential application of Ga–LLZT electrolytes in Li–S batteries, a sulfur cathode was fabricated. A mixture of 80 wt% sulfur (S) and 20 wt% Ketjen black EC600JD (KB, Shenzhen Teensky Technology Co.) was heated at 155 °C in an Ar atmosphere for 15 h, forming S/KB composite powder. 80 wt% ground S/KB composite powder, 10 wt% carbon black (Super P Li), and 10 wt% poly(vinylidene fluoride) (PVDF) were dispersed in 1-methyl-2-pyrrolidone (NMP), and stirred for 4 h. The resulting slurry was cast onto aluminum foil, heated to 230 °C on a hot stage, observing the interaction between garnet pellets with molten Li.

Cyclic voltammetry (CV) was performed using a Solartron 1287 electrochemical interface in the −0.5 to 6 V potential range at 1 mV s⁻¹ scanning rate. A Swagelok-type cell configuration was employed, with gold serving as the working electrode and Li as the reference electrode. Critical current density (CCD) was tested using stepped current density. To address the issue of poor wettability of garnet pellets with molten Li and achieve low interfacial impedance, gold modification on the pellets’ surface was employed. Galvanostatic cycling tests of Li/Li symmetric cells were conducted at 0.1, 0.2, and 0.5 mA cm⁻² (30 min for plating/stripping, 100 cycles) to assess cycling performance. EIS was employed to monitor impedance changes of the symmetrical cells before and after cycling. The microstructural morphology of the Li/Ga-LLZT interface after cyclic testing was examined by SEM. A Li/Ga0.1-LLZT (1050 °C)−S–KB full cell was assembled with a Li metal anode and S–KB cathode (sulfur loading: 1.3 mg cm⁻²). To minimize interface resistance, 5 μl of liquid electrolyte [1 M LiTFSI solution in 1:1 volume ratio of 1,3-dioxolane (DOL) and dimethoxyethane (DME)] was added to the cathode. The charge/discharge performance of the Li–S full cell was measured within the 1.5–3.0 V voltage range at 0.1C rate. All electrochemical performance tests of cells were conducted at a room temperature of about 25 °C.

### 3 Results and discussion

#### 3.1 Structural analysis of Ga–LLZT powders

By the two-step ball-milling solid-state synthesis process depicted in Fig. 1, Ga–LLZT powders were successfully prepared. To validate their phase composition and crystal structure, PXRD analysis was performed. As shown in Fig. 2a, the PXRD pattern of the Ga–LLZT powders reveals an excellent match with the diffraction peaks of the standard cubic garnet phase (PDF#45-0109) without any impurity peaks. This observation suggests that, following the introduction of Ga, the garnets with dual substitutions of Ta⁵⁺ and Ga³⁺ still maintain a pure cubic structure. This indicates that Ga and Ta were successfully doped into the LLZO lattice to form a solid solution. Fig. 2b presents the crystal structure of Ga–LLZT. Ga³⁺ substitutes the Li⁺ at the interstitial tetrahedral 24d sites, and Ta⁵⁺ substitutes the Zr⁴⁺ at the octahedral 16a sites. Fig. 2c shows the morphological properties of the Ga0.1-LLZT particle and Fig. 2d–h are the corresponding elemental mappings. It is obvious that Ga, La, Zr, Ta, and O elements are evenly distributed, verifying the homogeneity of the microstructure. As shown in Table S1, the element content is consistent with the designed content, that is, the obtained garnet elemental composition complies with the designed chemical formula composition. It can be

![Fig. 1 Schematic illustration of the preparation procedure for garnet-based Li–S batteries.](Image)
concluded that Ga has been doped into the garnet during the powder synthesis process.

To gain a more profound understanding of the changes in the crystal structure of Ga\textsubscript{x}-LLZT, Rietveld refinement on these PXRD patterns was performed. The refinement results are shown in Fig. 3a–c, and the detailed crystal structure parameters are summarized in Table S2.† Error bars and refinement indices demonstrate the high reliability of the refined results. Notably, the doping of Ga did not alter the inherent cubic structure of LLZT (space group: \textit{Ia}3\textit{d}). The lattice constant, which was initially 12.9489 Å at \(x = 0\), experienced a slight reduction to 12.9464 Å at \(x = 0.2\) (Fig. 3f), attributable to the smaller ionic radius of Ga\textsuperscript{3+} (0.64 Å) compared to that of Li\textsuperscript{+} (0.76 Å). This result is consistent with the expectations of Vegard’s law.\textsuperscript{51}

The pentavalent Ta\textsuperscript{5+} substitution for tetravalent Zr\textsuperscript{4+} induces distortion in the ZrO\textsubscript{6} octahedra, stabilizing the cubic phase of LLZO while providing more Li vacancies.\textsuperscript{17,23} As depicted by the following equation, with the introduction of Ga, Ga\textsuperscript{3+} substitution occurs at Li sites, generating additional Li vacancies:

\[
\frac{1}{2}\text{Ga}_2\text{O}_3 + 3\text{Li}_{\text{Li}}^+ \rightarrow \text{Ga}_{\text{Li}}\text{Li}^+ + 3\text{Li}_0 + \frac{1}{2}\text{Ga}_2\text{O}_3
\]

Here, Li\textsubscript{Li} represents Li\textsuperscript{+} at the Li site, Ga\textsubscript{Li} represents Ga\textsuperscript{3+} at the Li site, and V\textsubscript{Li} represents Li vacancies. Ga\textsuperscript{3+} predominantly substitutes Li\textsuperscript{+} in the Li1(24d) positions, resulting in stronger Coulomb repulsion between Ga\textsuperscript{3+} and Li\textsuperscript{+}, which alters the Li site occupancy.\textsuperscript{24,26} As the Ga content increases, Li\textsuperscript{+} tends to occupy the Li1(96h) site. Li\textsuperscript{+} has a transport pathway of Li2(96h)–Li1(24d)–Li2(96h) in LLZO, and the migration of Li\textsuperscript{+} at Li2 sites requires jumping to the Li1 site pathway junction.\textsuperscript{41,47} Therefore, the Li site occupancy will affect the ionic conductivity.

3.2 Sintering of Ga\textsubscript{x}-LLZT electrolytes

The sintering behavior, densification process, and microstructural evolution of Ga\textsubscript{x}-LLZT ceramics were investigated using FE-SEM. Fig. 4 shows the cross-sectional morphology of the
Ga$_x$-LLZT ceramics sintered at 1050 °C and 1150 °C. To densify LLZT, a higher sintering temperature exceeding 1100 °C is often required.\textsuperscript{19,22,52} For LLZT, a sintering at 1050 °C for 6 h, although bonding between particles can be observed, a large number of pores still exist (Fig. 4a). The contact between particles is not sufficiently tight, resulting in a relative density of only 82.9%. When the sintering temperature was raised to 1150 °C, the LLZT ceramic exhibits a relatively dense microstructure (Fig. 4f), achieving a relative density of approximately 94%. The grain size is around 10 μm, and grain boundaries are visible. Nevertheless, due to incomplete intergranular shrinkage, some small pores are still observable at grain boundaries.

The addition of Ga, particularly for samples sintered at lower temperatures, significantly improves densification. At 1050 °C sintering, a minor Ga addition ($x = 0.05$) results in grain growth and a noticeable reduction in pores, with all particles interconnected, leading to a relative density of 92.1% (Fig. 4b). As Ga content increases, both the number and size of pores decrease, leading to increased densification (Fig. 4c–e). Notably, when $x \geq 0.1$, the relative density of the Ga$_x$-LLZT ceramic exceeds 95%. At this point, grains merge, and some grain boundaries disappear, facilitating Li-ion diffusion between grains, and effectively enhancing total Li-ion conductivity.\textsuperscript{23} Furthermore, the increased grain boundary strength shifts from the intergranular fracture mode to the transgranular fracture mode, reducing grain boundary resistance.\textsuperscript{19,21} Consequently, appropriate Ga doping is beneficial to the low-temperature densification of garnet ceramics. There are two possible reasons for this phenomenon. Firstly, Ga doping altered the Li vacancy concentration, affecting sintering kinetics, thus modifying the density and microstructure of the garnet ceramics. Secondly, the Ga dopant could form a LiGaO$_2$–Li$_2$GaO$_4$ binary system at relatively low sintering temperatures, enhancing the contacts between grains, eliminating grain boundaries, and reducing the number and size of pores, thereby promoting grain densification.\textsuperscript{34–36}

However, when sintered at 1150 °C, LLZT itself already possesses a considerably dense structure. With increasing Ga doping, grain-to-grain contact further improves, grains continue to grow, and densification increases. Especially when $x \geq 0.1$, the relative density of Ga$_x$-LLZT ceramic exceeds 96%, comparable to hot-pressed sintering of LLZT.\textsuperscript{52,57} However, the grain size already exceeds several hundred micrometers, and even the outlines of particles are observable in corresponding optical images (Fig. 4h–j). The presence of Ga results in the rapid mobility of grain boundaries at high temperatures, leading to abnormal grain growth.\textsuperscript{19–21,28} Large grains will compromise the mechanical strength of ceramics, which is detrimental to their application in ASSLBs.

Based on the relative density results of garnet ceramics obtained via the Archimedes method (Fig. 5) and observations from SEM images, it is evident that high-temperature conditions positively impact the densification of LLZT, and Ga doping also plays an important role in promoting the densification of LLZT, especially it is more significant at lower sintering temperatures. Under sintering at 1050 °C, Ga$_{0.1}$-LLZT achieves a relative density of 95.3%, whereas at 1150 °C, it reaches an even higher relative density of 96.4%. However, it is worth noting that with further increases in Ga doping, the relative density of Ga$_x$-LLZT slightly decreases. This is attributed to the higher Ga content, which makes it more prone to triggering abnormal grain growth and resulting in the formation of Ga-rich phases at grain boundaries, as well as the presence of micropores with sizes reaching up to 10 μm (as shown in Fig. 4j).
As depicted in Fig. 6, Ga-doped and undoped LLZT ceramics exhibit four main microstructures at different sintering temperatures: (1) at lower sintering temperatures (1050 °C), LLZT exhibits partial particle bonding with a significant number of pores and lower density; (2) raising the sintering temperature to 1150 °C leads to grain growth, a reduction in pores, and the formation of a relatively dense microstructure; (3) even at lower sintering temperatures (1050 °C), the introduction of Ga results in higher density, grain fusion, and partial disappearance of grain boundaries; (4) however, at 1150 °C, abnormal grain growth is observed, with some closed small pores within and between grains. In conclusion, the doping of Ga indeed contributes to enhancing the densification of LLZT ceramics and can lower their sintering temperature requirements. However, it is crucial to exercise special caution in controlling the amount of Ga doping and sintering temperature to prevent the occurrence of anomalous effects at grain boundaries, which could potentially have a detrimental impact on the performance of garnet ceramics.

To further clarify the elemental distribution within the grains, we selected the Ga0.1-LLZT sample for EDS analysis, which exhibited transgranular fracture morphology. Fig. S1† displays the EDS elemental mappings, confirming the uniform distribution of Ga, La, Zr, Ta, and O within the grains. This result substantiates the successful incorporation of Ga and Ta into the garnet-type LLZO lattice, consistent with the lattice constant variation shown in Fig. 3f.

### 3.3 Electrochemical performance of Ga₅(LLZT) electrolytes

EIS analysis of Ga₅(LLZT) pellets was conducted to evaluate their ionic conductivity. Fig. 7a and b show typical Nyquist impedance plots obtained at 25 °C for sintered pellets at 1050 °C and 1150 °C, respectively. The resistance of LLZO solid electrolytes primarily comprises two components: bulk resistance ($R_b$) and grain-boundary resistance ($R_{gb}$). However, our investigation reveals that the Nyquist plot of prepared pellets only includes an incomplete high-frequency semicircle originating from the grain boundary and a low-frequency tail stemming from electrode blocking. It’s noteworthy that, among all impedance spectra, no semicircle related to bulk resistance is observed. This can be attributed to the temperature effect that results in high dielectric constants and low ionic resistance at room temperature, resulting in the disappearance of the semicircle from the bulk resistance.32-58 The bulk resistance and grain-boundary resistance can be obtained using the equivalent circuit model of $R_b(R_{gb}CPE_{gb})CPE_{el}$. The effects of grains and grain boundaries on ionic conductivity can be well distinguished based on their

![Fig. 4 Cross-sectional SEM images of Ga₅(LLZT) electrolyte pellets sintered at (a–e) 1050 °C and (f–j) 1150 °C. The corresponding optical images are in the small image.](image-url)
typical capacitance values.\textsuperscript{24} The results for bulk and total ionic conductivity of the pellets are summarized in Table 1.

The dependence of bulk and total ionic conductivities on the Ga content are depicted in Fig. 7d. The LLZT pellet sintered at 1050 °C exhibits the lowest bulk ionic conductivity of 1.59 × 10\textsuperscript{−4} S cm\textsuperscript{−1} and the lowest total ionic conductivity of 4.20 × 10\textsuperscript{−5} S cm\textsuperscript{−1}. This is primarily due to the lower density resulting from the excessively low sintering temperature. With the introduction of Ga, both bulk and total ionic conductivities show an initial significant increase, followed by a slight

![Fig. 6 Idealized schematic diagram of Ga-doped LLZT morphology evolution.](image)

![Fig. 7 Nyquist plots of Ga\textsubscript{x}-LLZT electrolytes sintered at (a) 1050 °C and (b) 1150 °C. (c) Arrhenius plots of total ionic conductivities, (d) bulk and total ionic conductivity, and (e) activation energy of Ga\textsubscript{x}-LLZT electrolytes.](image)
decrease. When the doping content reaches $x = 0.1$, the body and total ionic conductivities peak at $8.81 \times 10^{-4}$ S cm$^{-1}$ and $8.09 \times 10^{-4}$ S cm$^{-1}$, respectively. This enhancement is attributed to the minor Ga doping, which elevates the relative density from 82.9% for LLZT to 95.3% for Ga0.1-LLZT. Ga sintering aids reduce the number of pores and grain boundaries, effectively reducing the resistance to Li-ion transport, favoring Li-ion diffusion between grains, and thus enhancing the total ionic conductivity.$^{26}$ Additionally, the partial substitution of Li$^+$ by Ga$^{3+}$ introduces additional Li vacancies, altering the Li-ion occupancy distribution through stronger coulombic repulsion, thus creating more pathways for Li-ion transport and enhancing Li-ion mobility.$^{26}$ However, as the Ga content continues to increase, despite the increase in Li vacancies, it leads to a decrease in Li-ion concentration, ultimately resulting in a reduction in ionic conductivity. It is evident from these findings that there exists an optimal range for both Li vacancy concentration and Li-ion concentration to achieve high Li-ion conductivity, consistent with previously reported results.$^{23,60,61}$

LLZT pellets sintered at 1150 °C already exhibit a relatively high relative density of 94% with the primary resistance contribution coming from the bulk resistance. Despite already possessing a high bulk ionic conductivity of $7.98 \times 10^{-4}$ S cm$^{-1}$ and total ionic conductivity of $7.68 \times 10^{-4}$ S cm$^{-1}$, the addition of a small amount of Ga can further enhance their bulk ionic conductivity. When $x = 0.05$, the bulk ionic conductivity reaches $9.52 \times 10^{-4}$ S cm$^{-1}$. While the total ionic conductivity also increases, it does not show as significant an improvement as the bulk ionic conductivity. As the Ga content continues to increase, similar to pellets sintered at 1050 °C, the bulk ionic conductivity of pellets sintered at 1150 °C decreases. However, it is noteworthy that, particularly when $x \geq 0.1$, the total ionic conductivity experiences a substantial reduction. As demonstrated in the results of microstructure analysis, Ga0.15-LLZT and Ga0.2-LLZT pellets sintered at 1150 °C exhibit a substantial growth of abnormal grains, with the presence of Ga oxide impurities at grain boundaries deteriorating their microstructure. It results in impedance spectra displaying larger incomplete semicircles (Fig. 7b), showing a lower total ionic conductivity. This issue is commonly observed in reported Ga-doped LLZO.$^{19,20}$

Furthermore, the total ionic conductivity of the pellets was measured in the temperature range of 25–120 °C, and the Arrhenius plots of total ionic conductivity for some samples are shown in Fig. 7c. Activation energies (E_a) were calculated using the Arrhenius equation and are listed in Table 1. Fig. 7e illustrates the variation of activation energy with increasing Ga doping content. For the pellets sintered at 1050 °C, their activation energy decreases with increasing Ga doping content. This can mainly be attributed to two factors. First, Ga doping contributes to the densification of the ceramics, improving grain contacts, and reducing the energy barriers for Li-ion transport.$^{62}$ Second, Ga$^{3+}$ substitution for Li$^+$ introduces more Li vacancies, altering the Li-ion site occupancy, and providing more Li-ion transport pathways. Multiple reports also have confirmed that Ga-doped LLZO often exhibits low activation energies.$^{24,55,61}$ In contrast, for the pellets sintered at 1150 °C, their activation energy initially decreases and then increases with increasing Ga doping content. The reason for the initial decrease in activation energy is similar to what was mentioned earlier. However, the subsequent increase is consistent with the significant decrease in ionic conductivity, which is attributed to the microstructural deterioration of Ga-containing garnet ceramics during high-temperature sintering. In summary, the introduction of Ga not only enhances the ionic conductivity of cubic LLZT but also lowers the required sintering temperature. Ga plays a crucial role in promoting the ionic conductivity of Ga-LLZT ceramics. Compared to previously published studies, the performance of Ga0.1-LLZT sintered at 1050 °C is notably outstanding, as shown in Table 2. Its room temperature ionic conductivity surpasses that of most garnet electrolytes sintered at higher temperatures and even exceeds the ionic conductivity of some highly dense garnets sintered via hot-pressing. This evidence indicates the high potential of this electrolyte in practical applications for ASSLBs.

### 3.4 Stability of the Ga-LLZT Electrolyte

The LLZO electrolyte has been proven to exhibit excellent chemical stability with metallic Li.$^{16,67}$ The use of high specific capacity Li anode can enhance the energy density of ASSLBs based on LLZO electrolytes. However, in this study, some GaLLZT pellets displayed instability when in contact with metallic Li. When the Ga0.1-LLZT pellet sintered at 1150 °C was in contact with molten Li, it can be observed that black streaks gradually appeared on the pellet, even throughout the entire pellet (Fig. S2a†). For the Ga0.2-LLZT pellet sintered at 1150 °C, the molten Li rapidly infiltrated the pellet and spread to the entire pellet, leading to pellet disintegration into particles several hundred micrometers in size (Fig. S2b†). The above

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<th>Table 1</th>
<th>Relative density, bulk ionic conductivity, total ionic conductivity, and activation energy of Ga_x-LLZT</th>
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<tr>
<td>Relative density (%)</td>
<td>$\sigma_{\text{bulk}}$ ($10^{-4}$ S cm$^{-1}$)</td>
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<tr>
<td>1050 °C</td>
<td>1150 °C</td>
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<tr>
<td>LLZT</td>
<td>82.9 ± 1.8$^a$</td>
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<tr>
<td>Ga0.05-LLZT</td>
<td>92.1 ± 1.2</td>
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<tr>
<td>Ga0.1-LLZT</td>
<td>95.3 ± 1.2</td>
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<tr>
<td>Ga0.15-LLZT</td>
<td>95.0 ± 1.6</td>
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<tr>
<td>Ga0.2-LLZT</td>
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$^a$ Standard deviation is obtained by measuring three samples.
phenomenon was not observed in the LLZT pellet and Ga0.05-LLZT pellet sintered at 1150 °C, and in all pellets sintered at 1050 °C. Hence, it can be inferred that at a certain content of Ga doping, there exists a mechanism that deteriorates the stability of a garnet towards metallic lithium after high-temperature sintering.

The XRD pattern of the Ga0.2-LLZT pellet sintered at 1150 °C closely matches its powder XRD pattern, and no presence of a second phase like LiGaO2 or other impurities is detected (Fig. S3†). As discussed in Section 3.3 regarding the microstructure of Ga-LLZT ceramics, it is evident that when the Ga content reaches a certain level (x ≥ 0.1), abnormal grain growth with larger intergranular gaps occurs under high-temperature (1150 °C) sintering conditions. The accumulation of Ga at the grain boundaries of Ga-LLZT ceramics sintered at 1150 °C can be observed (Fig. S4†), indicating the presence of Ga-enriched phases at the grain boundaries. Since LiGaO2 is regarded as the second phase in Ga-doped LLZO, the observed Ga-enriched phase might be LiGaO2.18,20,21,45,68 However, its content is too low and its characteristic peak cannot be detected by XRD. When the Ga-enriched phase at the grain boundaries comes into contact with molten Li, Ga leaches out from this phase and forms a Li–Ga alloy with Li. The formation of a small amount of Li–Ga alloy manifests as black streaks on the pellet’s surface. However, when a significant amount of Ga-enriched phase exists at the grain boundaries, the volume expansion associated with Li–Ga alloying leads to pellet disintegration along the grain boundaries.28 When Li–Ga alloying permeates the entire pellet, it results in a short circuit of the electrolyte, limiting its application in ASSLBs.

Lowering the sintering temperature to 1050 °C can prevent abnormal grain growth and the formation of Ga-enriched phases. Even after 30 minutes of contact with molten Li, the Ga0.1-LLZT pellet sintered at 1050 °C remained stable and did not experience disintegration or short-circuiting (Fig. S2c†). This indicates its excellent chemical stability with metallic Li. Considering both the electrochemical performance and sintering cost of Ga-LLZT ceramics, Ga0.1-LLZT pellets sintered at 1050 °C were used in subsequent tests to assess the possibility of their application in ASSLBs.

Table 2  A summary of some LLZO electrolytes. RT: room temperature

<table>
<thead>
<tr>
<th>Sintering conditions</th>
<th>a = b = c (Å)</th>
<th>Relative density (%)</th>
<th>d_{total} (10^{-4} S cm^{-1})</th>
<th>E_a</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_4$La$_3$ZrNb$_0.5$Y$<em>0.5$O$</em>{12}$ 1230 °C, 15 h</td>
<td>—</td>
<td>90.7</td>
<td>8.29 (30 °C)</td>
<td>0.307 (21–110 °C)</td>
<td>Gai et al. 64</td>
</tr>
<tr>
<td>Li$_6$Ga$_0.1$La$<em>3$Zr$</em>{1.8}$Nb$<em>0.2$O$</em>{12}$</td>
<td>1150 °C, 6 h</td>
<td>—</td>
<td>94.46</td>
<td>7.39 (30 °C)</td>
<td>0.342 (−20–50 °C)</td>
</tr>
<tr>
<td>Li$_6$.Ga$<em>0.2$.La$<em>3$.Zr$</em>{1.5}$.O$</em>{12}$</td>
<td>1100 °C, 12 h</td>
<td>12.979</td>
<td>93.1</td>
<td>4.244 (RT)</td>
<td>0.257 (20–86 °C)</td>
</tr>
<tr>
<td>Li$<em>6$.Ga$<em>0.2$.La$<em>3$.Yb$</em>{0.05}$.Zr$</em>{2}$.O$</em>{12}$</td>
<td>1160 °C, 6 h</td>
<td>12.9540</td>
<td>94.8</td>
<td>8.96 (30 °C)</td>
<td>0.28 (−60–150 °C)</td>
</tr>
<tr>
<td>Li$_6$.La$<em>2$.Mg$</em>{0.2}$.Zr$_1$.Nb$<em>0.5$O$</em>{12}$</td>
<td>1150 °C, 6 h</td>
<td>12.9313</td>
<td>92</td>
<td>5.28 (25 °C)</td>
<td>0.38 (−15–210 °C)</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{1.5}$.Zr$<em>{1.5}$.Ta$</em>{0.5}$O$_{12}$ + 2 wt% Li$_3$WO$_4$</td>
<td>1230 °C, 30 min</td>
<td>12.927</td>
<td>98.25</td>
<td>6.25 (25 °C)</td>
<td>—</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{2.5}$.Ta$<em>{0.5}$.Zr$</em>{1.5}$O$_{12}$</td>
<td>1225 °C, 40 min, 47 MPa (hot-pressed)</td>
<td>12.929</td>
<td>97.12</td>
<td>7.5 (25 °C)</td>
<td>—</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{1.5}$.Al$<em>{0.5}$.Zr$</em>{2}$.O$_{12}$</td>
<td>1225 °C, 40 min, 47 MPa (hot-pressed)</td>
<td>12.985</td>
<td>98.16</td>
<td>6.8 (25 °C)</td>
<td>—</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{2.5}$.Ga$<em>{0.2}$.Zr$</em>{2}$.O$_{12}$</td>
<td>1100 °C, 40 min, 47 MPa (hot-pressed)</td>
<td>12.967</td>
<td>99.23</td>
<td>10.4 (25 °C)</td>
<td>—</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{1.5}$.Zr$<em>{1.75}$.Ta$</em>{0.25}$O$_{12}$</td>
<td>1050 °C, 4 h, 40 MPa (hot-pressed)</td>
<td>12.96</td>
<td>96</td>
<td>8.7 (25 °C)</td>
<td>0.22 (−20–80 °C)</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{1.5}$.Zr$<em>{1.75}$.Ta$</em>{0.25}$Al$<em>{0.2}$.O$</em>{12}$</td>
<td>1050 °C, 4 h 40 MPa (hot-pressed)</td>
<td>12.95</td>
<td>98</td>
<td>3.7 (25 °C)</td>
<td>0.30 (−20–80 °C)</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{1.5}$.Zr$<em>{1.75}$.Ta$</em>{0.25}$Ga$<em>{0.2}$.O$</em>{12}$</td>
<td>1050 °C, 4 h, 40 MPa (hot-pressed)</td>
<td>12.95</td>
<td>98</td>
<td>4.1 (25 °C)</td>
<td>0.27 (−20–80 °C)</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{1.5}$.Zr$<em>{1.75}$.Ta$</em>{0.25}$O$_{12}$</td>
<td>1050 °C, 4 h, 40 MPa (hot-pressed)</td>
<td>12.9629</td>
<td>99.6</td>
<td>4.3 (RT)</td>
<td>0.32 (20–120 °C)</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{2.0}$.Ba$<em>{0.0}$.Zr$</em>{1.75}$.Ta$<em>{0.25}$O$</em>{12}$</td>
<td>1000 °C, 4 h, 40 MPa (hot-pressed)</td>
<td>13.0186</td>
<td>99.7</td>
<td>6.5 (RT)</td>
<td>0.29 (20–120 °C)</td>
</tr>
<tr>
<td>Li$<em>6$.Ga$</em>{0.05}$.La$<em>{2.0}$.Ba$</em>{0.0}$.Zr$<em>{1.75}$.Ta$</em>{0.25}$O$_{12}$</td>
<td>1000 °C, 4 h, 40 MPa (hot-pressed)</td>
<td>13.0386</td>
<td>99.9</td>
<td>7.2 (RT)</td>
<td>0.28 (20–120 °C)</td>
</tr>
<tr>
<td>Li$<em>6$.La$</em>{1.6}$.Zr$<em>{1.0}$.Ta$</em>{0.4}$.O$_{12}$</td>
<td>1150 °C, 6 h</td>
<td>12.9489</td>
<td>94.0</td>
<td>7.68 (25 °C)</td>
<td>0.368 (25–125 °C)</td>
</tr>
<tr>
<td>Li$<em>6$.Ga$</em>{0.1}$.La$<em>{1.6}$.Zr$</em>{1.0}$.Ta$<em>{0.4}$.O$</em>{12}$</td>
<td>1050 °C, 6 h</td>
<td>12.9471</td>
<td>95.3</td>
<td>8.09 (25 °C)</td>
<td>0.350 (25–125 °C)</td>
</tr>
</tbody>
</table>

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J. Mater. Chem. A
To assess the air stability of Ga0.1-LLZT, it was exposed to the atmosphere, and changes in its total ionic conductivity were monitored. Meanwhile, LLZT pellets sintered at 1150 °C were used as a control. The ambient humidity range is 30–50%, and the temperature range is 24–27 °C. Fig. S5† shows the Nyquist plots of the pellets over atmospheric exposure time. With increasing atmospheric exposure time, the impedance plots of the LLZT pellet exhibit a significant rightward shift, and the size of the incomplete semicircle gradually increases. However, the impedance plots of Ga0.1-LLZT do not change significantly. As shown in Fig. 8a, the total ionic conductivity of Ga0.1-LLZT gradually decreases with increasing atmospheric exposure time. After 4 months of atmospheric exposure, its total ionic conductivity reduces to 86% of the initial value (Table S3†), with an average monthly aging rate of only 3.5%. This rate is significantly lower than LLZT’s average monthly aging rate of 9.8% and even lower than the reported Al-LLZT manufactured in a platinum crucible (6.5% per month).30 It’s worth noting that LLZT exhibited rapid decay in total ionic conductivity during the first 20 days of exposure to the atmosphere, followed by a slower decline.

In the Raman spectrum depicted in Fig. 8b, it is evident that after 120 days of atmospheric exposure, both LLZT and Ga0.1-LLZT exhibit a response peak at 1090 cm\(^{-1}\), attributable to CO\(_2\). Notably, this peak is more pronounced in LLZT. Some reports suggest that LLZO with small grains and a large number of grain boundaries is more stable in air.34,36 However, multiple studies have shown that the reaction between atmospheric CO\(_2\)/H\(_2\)O and LLZO, leading to the formation of Li\(_2\)CO\(_3\), is the primary cause of the decline in ionic conductivity.35,37 This reaction initially occurs at grain boundaries, so low grain boundary content and high density can effectively improve air stability and mitigate the degradation of ionic conductivity. The small amount of Ga doping in Ga0.1-LLZT reduces grain boundaries and results in high relative density (95.3%), effectively preventing the penetration of CO\(_2\)/H\(_2\)O along grain boundaries, and leading to excellent air stability. At the same time, Ga doping leads to lithium loss, which helps inhibit Li/H exchange and enhance air stability. In LLZT pellets, there are numerous grain boundaries, and exposure to air involves more grain boundaries in the reaction. Therefore, it exhibits rapid degradation in ionic conductivity. As the reaction progresses, Li\(_2\)CO\(_3\) hinders further penetration of CO\(_2\)/H\(_2\)O, and with Li consumption, it also slows down the rate of Li\(_2\)CO\(_3\) formation.

After annealing the exposed pellets at 700 °C, the ionic conductivity partially recovered in both Ga0.1-LLZT and LLZT pellets (Fig. 8c). The total ionic conductivity of the Ga0.1-LLZT pellet recovered from 86% to 94% of the initial value, while the total ionic conductivity of LLZT recovered from 61% to 78% of the initial value. This is because the heat treatment can decompose the poorly conducting Li\(_2\)CO\(_3\), reduce obstacles to Li-ion transport, and replenish the lost Li.69–71 In summary, a small amount of Ga doping in LLZT can effectively enhance its air stability, promoting its potential application in ASSLBs.

3.5 Electrochemical evaluation of the symmetric cell

The Li stability of the prepared Ga0.1-LLZT electrolyte was further evaluated through cyclic voltammogram tests and galvanostatic cycling tests to determine its suitability for ASSLBs with Li metal anodes. As shown in Fig. 8d, the CV curve of the Li/Ga0.1-LLZT/Au cell exhibits a pair of oxidation–reduction peaks attributed to Li plating/stripping within the range of −0.5 V to 0.5 V, with no other peaks observed. This suggests that Ga0.1-LLZT is relatively stable concerning Li metal. In the CCD test, a current density gradient was applied to symmetric cells, with an increase of 0.1 mA cm\(^{-2}\) every five cycles. As shown in Fig. 9a, the Li/LLZT/Li symmetric cell exhibits stable cycling at the current density below 0.5 mA cm\(^{-2}\). When the current density increases to 0.5 mA cm\(^{-2}\), the voltage fluctuates after three cycles and experiences a sharp decline in the fifth cycle, indicating the occurrence of a soft short circuit. In contrast, as shown in Fig. 9b, the Li/Ga0.1-LLZT/Li symmetric cell cycles stably at current densities below 0.7 mA cm\(^{-2}\). A short circuit occurs after running four cycles when the current density is increased to 0.7 mA cm\(^{-2}\).

Li plating/stripping cycling tests were conducted continuously at current densities of 0.1, 0.2, and 0.5 mA cm\(^{-2}\) for 100 cycles. Fig. 9c and d show the voltage–time plots of the two symmetric cells during Li plating/stripping. The Li/LLZT/Li symmetric cell exhibits stable cycling at a current density of 0.1 mA cm\(^{-2}\). However, when the current density increases to 0.2 mA cm\(^{-2}\), there is a rise in voltage during each cycle, although

![Fig. 8](https://example.com/fig8.jpg)

**Fig. 8**  (a) Variation of the total ionic conductivity of LLZT and Ga0.1-LLZT along atmospheric exposure time. (b) Total ionic conductivity and (c) Raman spectrum of LLZT and Ga0.1-LLZT before and after atmospheric exposure. All the tests were performed at room temperature.
no short circuit occurs. Notably, at a current density of 0.5 mA cm\(^{-2}\), the voltage drops sharply after the first cycle, indicating that potential Li dendrite grows and diffuses into the solid electrolyte, leading to a short circuit in the cell. In contrast, the symmetric cell using Ga0.1-LLZT, as depicted in Fig. 9d, remains stable even at a current density of 0.5 mA cm\(^{-2}\). Thanks to the high ionic conductivity and high density of the Ga0.1-LLZT electrolyte, there is no significant change in cell voltage during cycling at the same current density, and no short-circuit occurs. Li metal is uniformly plated/stripped during cycling. Fig. S7† shows no significant change in the electrochemical impedance plots of the Li|Ga0.1-LLZT|Li symmetric cell before and after the Li plating/stripping cycles, demonstrating the exceptional stability of the Ga0.1-LLZT electrolyte in Li plating/stripping cycle test.

Fig. 10a and b display the cross-sectional SEM images of post-cycling LLZT electrolytes. There is good contact between Li metal and LLZT electrolyte, however, Li dendrites can be observed at the grain boundaries inside the electrolyte. As illustrated in Fig. 10c, due to the abundance of grain boundaries in the LLZT electrolyte, Li dendrites grew along these boundaries during cycling in the symmetric cell, eventually penetrating the entire electrolyte and causing a short circuit. In contrast, the cross-sectional SEM images of the post-cycling Ga0.1-LLZT electrolyte, as shown in Fig. 10d and e, indicate good contact between Li metal and the Ga0.1-LLZT electrolyte without any visible lithium dendrites. As depicted in Fig. 10f, the excellent cycling performance of Ga0.1-LLZT can be primarily attributed to its dense microstructure and low grain boundary content, providing structural rigidity and inhibiting the formation of Li dendrites during cell charging and discharging. Overall, this straightforward co-doping strategy effectively enhances the stability of the LLZO electrolyte with Li, holding significant importance for the commercialization of ASSLBs.

3.6 Performance of the Li–S battery based Ga0.1-LLZT electrolyte

To evaluate the commercial potential of the Ga\(_x\)-LLZT electrolytes in ASSLBs, we assembled a Li|Ga0.1-LLZT|S–KB full cell, as depicted in Fig. 11a, and conducted charge–discharge tests at 25 °C. Fig. 11b and c illustrate the charge–discharge curves and cycling performance of the S–KB cathode, operating at a current density of 0.22 mA cm\(^{-2}\) (0.1C) within a voltage range of 1.5 to 3.0 V. The charge–discharge curves exhibit two smooth voltage plateaus during both charging and discharging, characteristic of typical Li–S battery charge–discharge behavior.\(^{22,70}\) The first discharge specific capacity of the S–KB cathode in the
assembled Li–S cell is 1120 mA h g$^{-1}$, which is lower than the theoretical discharge capacity of 1673 mA h g$^{-1}$. This discrepancy can be attributed to the limited utilization of sulfur due to the presence of isolated sulfur particles. During the first 25 cycles, there is a substantial drop in the charge and discharge specific capacity, accompanied by a continuous increase in

![Fig. 10](image-url)  
(a) SE SEM images, (b) BSE SEM images, and (c) schematic diagram of the Li/LLZT interface after galvanostatic cycling. (d) SE SEM images, (e) BSE SEM images, and (f) idealized schematic diagram of the Li/Ga0.1-LLZT interface after galvanostatic cycling.

![Fig. 11](image-url)  
Electrochemical performance of the Li|$\text{Ga0.1-LLZT}$|$\text{S–KB}$ full cell. (a) Schematic diagram of the Li|$\text{Ga0.1-LLZT}$|$\text{S–KB}$ full cell. (b) Charge and discharge voltage profiles and (c) cycling performance of the Li–S full cell.
overpotential. Such irreversible capacity loss is likely attributed to the structural rearrangement of the S–KB cathode. The first charge–discharge coulombic efficiency is only 90%, but as the cathode restructuring process completes, the coulombic efficiency gradually rises. After 25 charge–discharge cycles, the full cell stabilizes, with a cathode discharge specific capacity of 628 mAh g$^{-1}$ and an areal capacity of 0.816 mA h cm$^{-2}$. In contrast to the initial 25 cycles, subsequent tests reveal good reversibility in the charge–discharge curves, with a slow decline in specific capacity. Even after 600 cycles, a discharge specific capacity of 392 mA h g$^{-1}$ is retained (areal capacity of 0.509 mA h cm$^{-2}$), with an average coulombic efficiency exceeding 99.9% during this period. The Li–S batteries with the Ga0.1-LLZT electrolyte did not suffer from battery short circuits or failure during long-term operation. In summary, the above research results underscore the stability of Ga0.1-LLZT within Li–S batteries, indicating the significant commercial potential for Ga$_x$-LLZT in ASSLB applications.

4 Conclusions

In this study, a multi-step ball-milling solid-state reaction method was successfully employed to prepare Ga and Ta co-doped LLZO electrolytes. The co-doping of Ga in LLZT proves to be effective in enhancing the sinterability of the LLZT electrolyte, leading to high ionic conductivity and superior chemical stability. At a sintering temperature of 1050 °C, Ga doping significantly increases the relative density and ionic conductivity of LLZT. The relative density improves from approximately 83% for LLZT to 95.3% for Ga0.1-LLZT. The total ionic conductivity increases from $0.42 \times 10^{-4}$ S cm$^{-1}$ for LLZT to $8.81 \times 10^{-4}$ S cm$^{-1}$ for Ga0.1-LLZT. However, when Ga$_x$-LLZT was sintered at 1150 °C, Ga tended to accumulate at grain boundaries, resulting in abnormal grain growth and the formation of weak grain boundaries, which deteriorated the microstructure of the LLZO electrolyte. This degradation became more severe with higher Ga content. The presence of abnormally grown grains and Ga-enriched phases at grain boundaries leads to poor stability of Ga$_x$-LLZT concerning Li metal. Ga0.1-LLZT sintered at 1050 °C exhibits good Li metal stability and excellent air stability. Its densified microstructure not only hinders the decay of ionic conductivity after exposure to the atmosphere but also suppresses the formation of Li dendrites during Li plating/stripping. After exposure to the atmosphere for 4 months, the total ionic conductivity at 25 °C remained at $6.94 \times 10^{-4}$ S cm$^{-1}$. The assembled Li–S full cell also confirms its promising prospects in ASSLBs. Overall, doping Ga in LLZT provides three key advantages: (1) Ta$^{5+}$ replacing Zr$^{4+}$ stabilizes the cubic structure and introduces Li vacancies, and a small amount of Ga$^{3+}$ replacing Li$^+$ further provides Li vacancies, facilitating Li-ion transport and enhancing ionic conductivity. (2) It promotes good grain connectivity by reducing grain boundaries, forming a rapid Li-ion transport pathway, enhancing Li-ion conductivity, and inhibiting Li dendrite formation. (3) Lowering the sintering temperature required for LLZT densification not only prevents undesirable Li losses from prolonged high-temperature sintering but also reduces production costs. This study provides valuable insights for optimizing LLZO electrolytes and establishes a solid foundation for their application in ASSLBs. In future research, further exploration of the optimal combination of doping concentrations and sintering conditions can enhance the performance of LLZO ceramics.

Author contributions

Kai Ma: conceptualization, methodology, validation, investigation, formal analysis, writing – original draft, writing – review & editing. Bowen Chen: validation, investigation, formal analysis, writing – review & editing. Cheng-Xin Li: conceptualization, supervision, writing – review & editing. Venkataraman Thangadurai: conceptualization, methodology, supervision, reviewing, editing, project administration.

Conflicts of interest

There are no conflicts to declare.

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