

Article

Comparative Study of Stability against Moisture for Solid Garnet Electrolytes with Different Dopants

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Abstract: The cubic garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (c-LLZO) is one of the most promising solid electrolytes due to its high ionic conductivity and large electrochemical window. However, the critical issue of Li_2CO_3 formation on the c-LLZO surface when exposed to air is problematic, which is detrimental to the ionic conductivity and storage. Herein, comparative studies were carried out on the air stability of Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (Al-LLZO), Al-Ta-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (Al-LLZTO), and Al-Nb-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (Al-LLZNO). It was found that Al-LLZTO and Al-LLZNO are less reactive with air than Al-LLZO. The morphology of Li_2CO_3 on Al-LLZTO micro-sized powders after air exposure was island-like with $\sim 1.5 \mu\text{m}$ in thickness. The interfacial resistance of Li/Al-LLZTO was also a factor of ~ 3 smaller than that of Li/Al-LLZO, leading to the improved cycle stability of Li/Al-LLZTO/Li symmetric cells. The first-principles calculations based on density functional theory (DFT) verified that the decomposition energy of Al-LLZTO was larger than that of Al-LLZO, inhibiting the reaction product of Li_2O and, thus, the next step product of Li_2CO_3 following the reactions of $\text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{LiOH}$ and $\text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3$.

Keywords: solid garnet electrolytes; air stability; Li_2CO_3 ; doped electrolytes



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1. Introduction

With the rapid development of electric vehicles, the requirements for energy density and safety of lithium-ion batteries (LIBs) have become critical [1–3]. Currently, commercial LIBs generally use flammable organic liquid electrolytes, which may cause accidents when the thermal runaway loses control [4–6]. Under this context, the replacement of liquid electrolytes with solid-state electrolytes (SSEs) is viewed as a powerful means of overcoming safety concerns [7,8]. Among various solid electrolytes, the cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has attracted extensive attention due to its relatively high ionic conductivity, wide electrochemical window, and good mechanical strength [9–12]. However, subsequent experimental and computational studies have demonstrated that LLZO tends to react with the humidity in air, resulting in the generation of surface Li_2CO_3 impurities, which leads to low ionic conductivity, crystal phase decomposition, poor electrochemical stability, poor contact with Li metal, and increased resistance of the garnet surface [13–15]. Previous reports indicated that Li^+/H^+ exchange occurred on the garnet surface when in contact with air [16,17]. The water first reacted with LLZO to form LiOH either as a surface layer or as a precipitate in solution when immersed in water [18]. The formed LiOH then subsequently

reacted with CO_2 in air to form surface Li_2CO_3 , the amount of which increased with exposure time, seriously deteriorating the ionic conductivity of garnet electrolytes [19]. Furthermore, other studies have also reported a single-step reaction pathway, where the garnet directly reacted with water and CO_2 to form Li_2CO_3 [20–22]. Various strategies have been developed to remove the Li_2CO_3 . For example, acid etching is proposed for its high efficiency in removing Li_2CO_3 from the LLZO surface, but the side reaction of Li^+/H^+ exchange is hard to avoid [23]. As the garnet electrolytes are used in solid-state batteries, such an inert carbonate contaminant induces a great increase in interfacial resistance at both cathode and anode sides, leading to performance decline and dendrite growth [24–28]. Therefore, the improvement of air stability for garnet electrolytes is important for electrolyte storage and battery performance [29].

Herein, we investigated the air stability of three different element-doped LLZO, i.e., Al-doped LLZO ($\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, Al-LLZO), Al-Ta-doped LLZO ($\text{Li}_{5.65}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$, Al-LLZTO), and Al-Nb-doped LLZO ($\text{Li}_{5.625}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.375}\text{Nb}_{0.625}\text{O}_{12}$, Al-LLZNO). The garnet surfaces were investigated after air exposure for 24 and 72 h. It was found that the growth rate of Li_2CO_3 on Al-LLZTO and Al-LLZNO was much slower than that on Al-LLZO. The theoretical study indicated that the decomposition product Li_2O could evolve into Li_2CO_3 when in contact with CO_2 and H_2O . As a result, the decomposition reactions for Al-LLZO, Al-LLZTO, and Al-LLZNO into product Li_2O were calculated through density functional theory (DFT) to account for the stability. It was demonstrated that Al-Ta- and Al-Nb-doped LLZOs showed a higher formation energy of Li_2O than Al-LLZOs, resulting in a slower Li_2CO_3 formation rate.

2. Materials and Methods

Cubic-phase $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Al-LLZO), $\text{Li}_{5.65}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (Al-LLZTO), and $\text{Li}_{5.625}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.375}\text{Nb}_{0.625}\text{O}_{12}$ (Al-LLZNO) ceramics were prepared via a conventional solid-state reaction in Al_2O_3 crucibles. The Al dopants were diffused from the crucibles during sinters. The stoichiometric LiOH , $\text{La}(\text{OH})_3$ (Alfa Aesar, 99.95%), ZrO_2 , Nb_2O_5 , and Ta_2O_5 (Aladdin Reagent, 99.99%) were uniformly mixed, and a 15 wt.% excess of LiOH was adopted to compensate for volatile Li components during synthesis. Then, the uniformly mixed powders were heated in air at 950°C for 12 h to ensure the formation of cubic-phase garnets. After that, the powders were pressed into pellets with a diameter of 12 mm at 100 MPa, and then sintered at 1140°C for 9 h in air. The Al-LLZO, Al-LLZTO, and Al-LLZNO pellets and the corresponding powders were exposed to air with a humidity of 70% and temperature of 25°C for 24 and 72 h for Li_2CO_3 analysis.

The elemental composition was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) [30]. X-ray diffraction (XRD, Bruker D8 Advance) was used to detect the phase structures of samples with $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) with a 2θ range of $10\text{--}80^\circ$ and a step size of 0.02° . The cross-sectional morphology of the ceramic pellets was analyzed by a focused ion beam scanning electron microscope (FIB-SEM, Thermo Scientific, Scios2 DualBeam). The Scios 2 DualBeam microscope was equipped with an ion beam for sample cutting and an electron beam for morphology observation, allowing the direct observation of sample morphology after ion beam cutting. Raman spectroscopy (WITec Alpha 300) with an excitation source of 532 nm was used to collect spectra of samples with a $50\times$ objective lens. The Fourier-transform infrared (FTIR) spectra were recorded using a NETZSCH X70 FTIR spectrometer. Titration gas chromatography (TGC) [31,32] was carried out as follows: sample powders of 50 mg were weighed in an Ar-filled glovebox ($\text{H}_2\text{O} < 0.1 \text{ ppm}$, $\text{O}_2 < 0.1 \text{ ppm}$) and reacted in a closed sample container (42 mL) using an excess of dilute hydrochloric acid for 20 min, until no bubbles were observed in the bottle. CO_2 in the sample bottle was measured by gas chromatography (Shimadzu Nexis GC-2030) using He (99.9999%) as the carrier gas. A gastight syringe was used to transfer 50 μL of sample gas from the container into the gas chromatography (GC) system for every measurement. The content of Li_2CO_3 was determined by converting the corresponding CO_2 amount according to a pre-established standard calibration curve.

The electrochemical impedance spectra (EIS) of Li symmetric cells were recorded using a Princeton electrochemical workstation at a frequency range from 7 MHz to 0.1 Hz at 55 °C. The Li symmetric cells were cycled under a current density of 0.2 mA·cm^{−2} at 55 °C. Considering the stable contact between garnets and Li metals, polyoxyethylene (PEO)-based buffer layers were introduced at the Li/garnet interface. PEO, lithium (bis trifluoromethyl) sulfate (LiTFSI), and succinonitrile (SCN) with a mass ratio of 2:1:0.4 were added to anhydrous acetonitrile (ACN) solution (the mass ratio of ACN to total solution is 80%) and continuously stirred for 12 h. Then, 60 µL of PEO slurry was introduced into the garnet surface, followed by heat treatment at 80 °C for 30 min to evaporate the solvent in the slurry, and the Li foil was tightly pressed on the garnet with PEO electrolyte on the surface. An identical process was applied to both sides of the garnet electrolyte. Finally, the cells were sealed in a Swagelok-type cell mold in an Ar-filled glovebox. All electrochemical measurements were conducted at 55 °C.

First-principles calculations were performed using density functional theory (DFT), implemented in the PWmat package using a GPU [33,34]. For the treatment of the exchange–correlation potential, the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) functional [35] was adopted, and the NCPP-SG15-PBE pseudopotential [36,37] was used in the geometry optimization, with a force tolerance for the maximal residual force of 0.02 eV·Å^{−1} and an energy between two successive steps smaller than 2.7×10^{-6} eV as the convergence criteria. A plane wave basis set with a cutoff of 70 Ryd was used. The Brillouin zone was sampled using a $1 \times 1 \times 1$ Monkhorst–Pack *k*-point grid.

3. Results and Discussion

Figure 1 shows the XRD patterns of the Al-LLZO, Al-LLZTO, and Al-LLZNO with different hours of air exposure. Figure 1a shows that Li₂CO₃ appeared on Al-LLZO surfaces, the intensity of which increased with an increase in time of air exposure, due to the gradually increasing amount of Li₂CO₃ [38]. On the contrary, XRD patterns of the Al-LLZTO and Al-LLZNO showed a negligible intensity of Li₂CO₃ even after 72 h exposure (Figure 1b,c). The XRD results indicate that Al-LLZO surfaces had a larger amount of Li₂CO₃ than Al-LLZTO and Al-LLZNO surfaces.

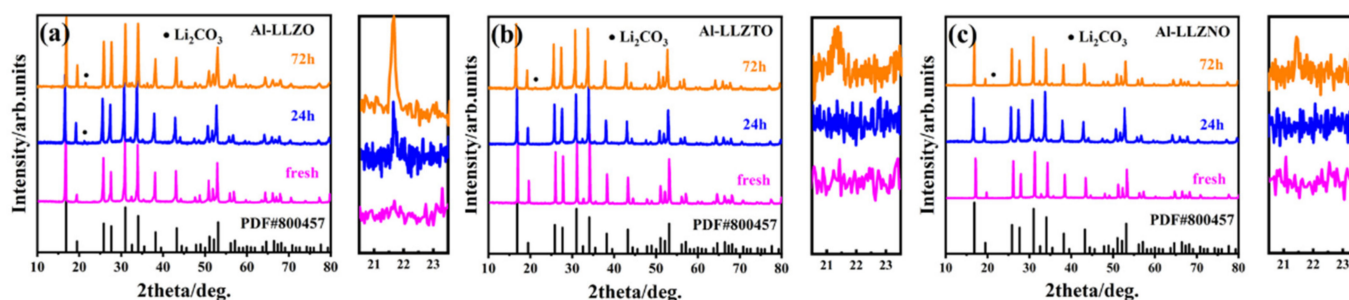


Figure 1. XRD patterns of (a) Al-LLZO, (b) Al-LLZTO, and (c) Al-LLZNO before and after 24 and 72 h of air exposure.

It is well known that the Li₂CO₃ formed on the garnet surface is generally not very thick, which leads to a weak peak intensity in XRD patterns. Due to the low thickness of surface Li₂CO₃ on the garnet matrix, the peak intensity of Li₂CO₃ is weak and unobvious to distinguish. The observable Li₂CO₃ peak for Al-LLZO implies that the Al-LLZO surfaces had a large amount of Li₂CO₃. No observable Li₂CO₃ peak for Al-LLZTO and Al-LLZNO does not indicate the absence of Li₂CO₃ on the surface. As revealed by focused ion beam scanning electron microscopy (FIB-SEM), shown in Figure 2a, the formed Li₂CO₃ is not continuous but island-like on the Al-LLZTO surface after 72 h of exposure, compared with the pristine SEM image of Al-LLZTO (inset of Figure 2a). The maximum island was approximately 1.5 µm in size. Furthermore, as can be seen in Figure 2b, titration gas

chromatography (TGC) analysis indicated that the growth of Li_2CO_3 on the Al-LLZTO surface occurred in two stages. Within the initial 24 h, the growth was fast with a rate of 0.053 mg/h. Then, the growth slowed down with a saturation tendency, the rate of which was approximately 0.007 mg/h. Initially, the pristine surface of garnet was fully exposed to the air, leading to a rapid reaction with $\text{H}_2\text{O}/\text{CO}_2$ in the air. Li_2CO_3 was quickly generated during this initial process, as indicated in Figure 2b. Afterward, the surface sites of garnet were gradually covered by Li_2CO_3 , leading to reduced contact area with air, thereby decreasing the generation rate of Li_2CO_3 . Thus, a decreased slope of Li_2CO_3 amount vs. time was detected during the middle process. Finally, when the garnet surface was fully covered by Li_2CO_3 , the growth of Li_2CO_3 reached a saturation state.

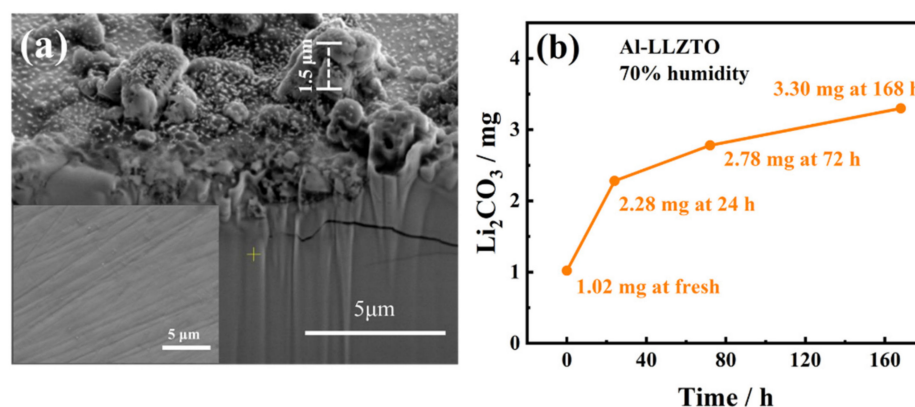


Figure 2. (a) The cross-sectional SEM image in combination with FIB for Al-LLZTO. The inset is the polished pristine SEM image of Al-LLZTO. (b) Quantitative analysis of Li_2CO_3 based on TGC technique for micro-sized Al-LLZTO.

Raman spectra were also used to identify Li_2CO_3 , as displayed in Figure 3. The peaks located at 243, 375, 645, and 728 cm^{-1} denote the characteristic peaks of the cubic garnet phase, which were present for all the three samples [14,39–41]. The broad Raman shift around 1100 cm^{-1} attributed to Li_2CO_3 was detected in Al-LLZO after 24 and 72 h of air exposure. However, no Li_2CO_3 could be found in Al-LLZTO and Al-LLZNO after 24 h of exposure. The Li_2CO_3 peaks were almost absent after 72 h of exposure for both Al-LLZTO and Al-LLZNO, as shown in Figure 3b,c.

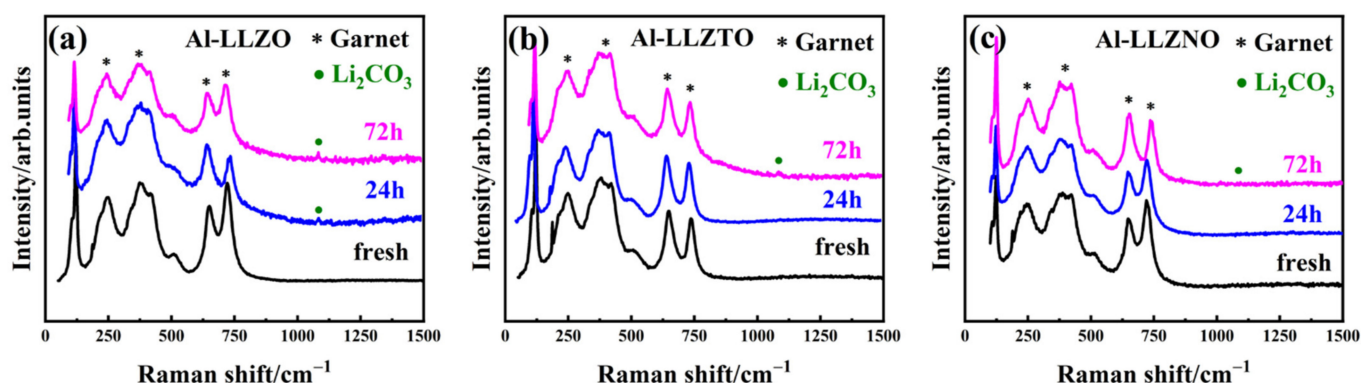


Figure 3. Raman spectra of as-prepared, 24 h air-exposed, and 72 h air-exposed (a) Al-LLZO, (b) Al-LLZTO, and (c) Al-LLZNO.

Figure 4 shows the FTIR spectra of Al-LLZO, Al-LLZTO, and Al-LLZNO with different exposure time. The $\text{V}_{\text{as}}(\text{C}=\text{O})$ at 1438 and 863 cm^{-1} corresponds to the characteristic peaks of Li_2CO_3 [42–44]. The two peaks with large intensity for Al-LLZO confirmed the obvious Li_2CO_3 formation upon exposure to air for 24 h and 72 h. The peaks of Li_2CO_3 with weak

intensity shown in Figure 4b,c indicate that Al-LLZTO and Al-LLZNO contained a smaller amount of Li_2CO_3 after exposure to air compared to Al-LLZO.

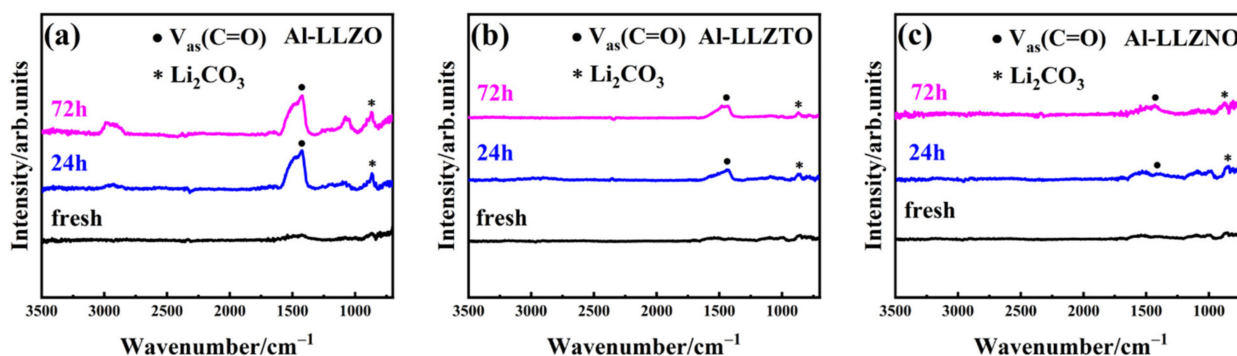


Figure 4. FTIR spectra of as-prepared, 24 h air-exposed, and 72 h air-exposed (a) Al-LLZO, (b) Al-LLZTO, and (c) Al-LLZNO.

To investigate the effect of Li_2CO_3 on interfacial resistance, Li symmetric cells with 24 h air-exposed pellets were assembled. The electrochemical impedance spectra (EIS) of Li symmetric cells are plotted in Figure 5. As can be seen in Figure 5a,b, all the fitted EIS lines consisted of two half-circles in the measuring ranges. The high-frequency half-circle corresponds to the resistance of bulk impedance, while the medium-frequency half-circle corresponds to the interfacial resistance. Considering the charge transfer across two Li/LLZO interfaces in each symmetric cell, the interfacial resistance determined by the half-circle should be divided by 2 to obtain the value for each Li/LLZO interface. The fitted results of interfacial resistance are listed in Figure 5c. After air exposure for 24 h, the interfacial area resistance of Li/Al-LLZO greatly increased from $160 \Omega \cdot \text{cm}^2$ to $836 \Omega \cdot \text{cm}^2$, which was attributed to the blocking effect of Li_2CO_3 coverage [45]. For Al-LLZTO and Al-LLZNO, the interfacial area resistance also increased after 24 h of air exposure. The specific values for the three samples are given in Figure 5c. The interfacial resistance for Al-LLZO increased by a factor of approximately 5 after 24 h exposure, while that for Al-LLZTO and Al-LLZNO increased by a factor of 2–3. The galvanostatic cycles of Li symmetric cells for the three types of samples are shown in Figure 5d–f. It can be seen that Al-LLZO after 24 h exposure showed a larger potential increase during cycles than Al-LLZTO and Al-LLZNO. This is consistent with the above conclusions drawn from XRD, Raman, and FTIR analyses, i.e., the amount of formed Li_2CO_3 for Al-LLZO was larger than that for Al-LLZTO and Al-LLZNO.

In order to deeply understand the mechanism of Li_2CO_3 formation, density functional theory (DFT) was further used to calculate the decomposition energy of Al-LLZO, Al-LLZTO, and Al-LLZNO, referring to the decomposition product of Li_2O [46]. Here, $\text{Li}_{5.625}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.375}\text{Ta}_{0.625}\text{O}_{12}$ was adopted instead of experimental $\text{Li}_{5.65}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ in consideration of the eight times supercell and the integer number of atoms. The decomposed Li_2O reacts with H_2O and CO_2 in air to form surface Li_2CO_3 . The energies of reactants and products are shown in Table 1, and the three decomposition reaction energies are presented in Table 2. Considering the partial substitution of Li^+ by introducing 0.25/f.u. (formula units) Al^{3+} in LLZO, the decomposition energy of $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ is -19.89 meV/atom , indicating the preferred decomposition trend and the intensive Li_2CO_3 formation [47]. The decomposition is significantly promoted in the existence of H_2O and CO_2 with the final formation of Li_2CO_3 . In comparison, when theoretically substituting 0.625/f.u. Ta^{5+} and Nb^{5+} in LLZO for Zr^{4+} , the cell parameters were close to the cubic phase, with the parameters shown in Table 3. In addition, an increment of 11.08 and 11.07 meV/atom were required for the decomposition reaction, indicating the better thermodynamic stability of Al-LLZTO and Al-LLZNO than Al-LLZO. In fact, the former samples were thermodynamically stable in the absence of CO_2 and H_2O . This is highly in agreement with the experimental results.

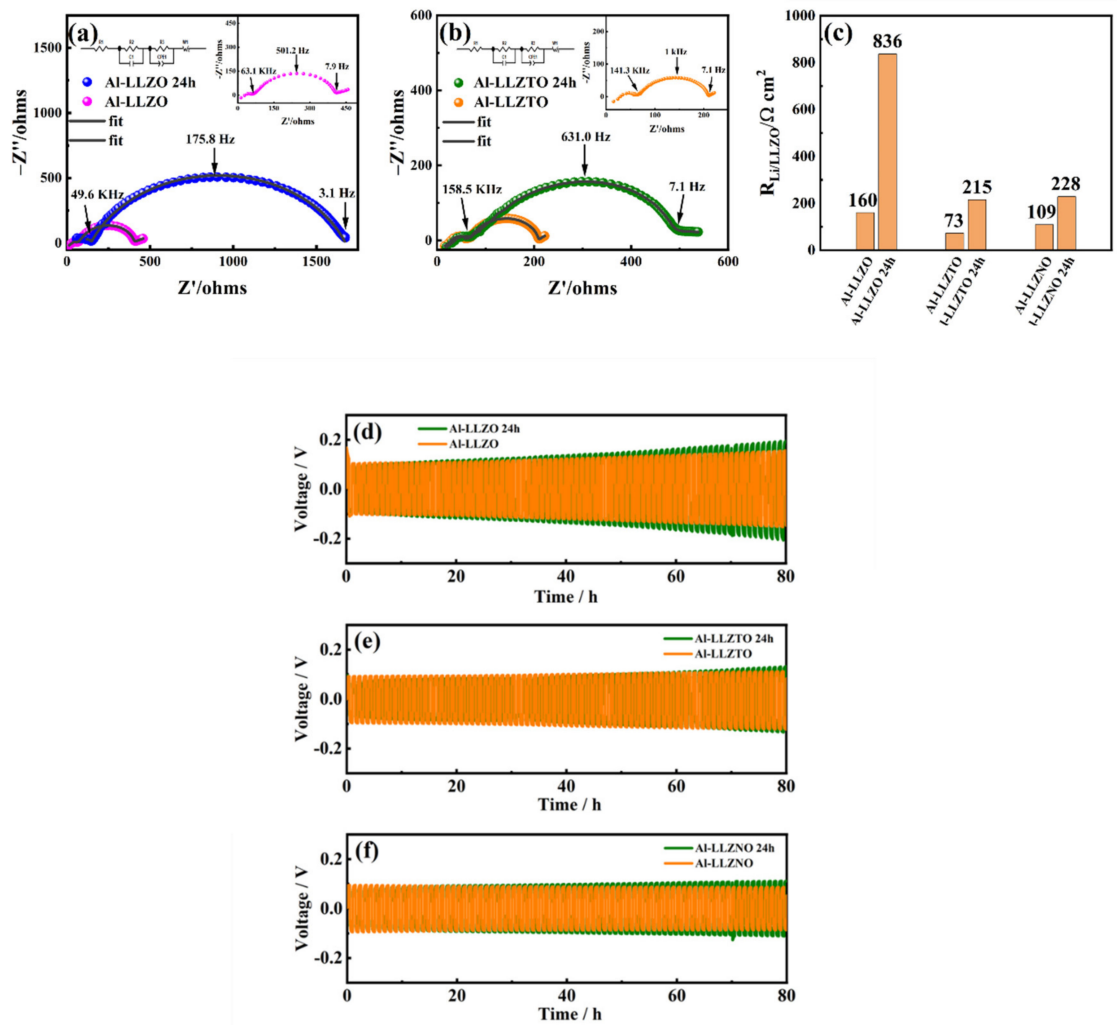


Figure 5. Comparison of EIS profiles of Li symmetric cells with (a) Al-LLZO and (b) Al-LLZTO at 55 °C. (c) The interfacial resistances of the Li/LLZO/Li symmetric cells with Al-LLZO, Al-LLZTO, and Al-LLZNO. The galvanostatic cycles of Li symmetric cells at a current density of $0.2 \text{ mA} \cdot \text{cm}^{-2}$ and a capacity of $0.1 \text{ mA} \cdot \text{h} \cdot \text{cm}^{-2}$ for as-prepared and 24 h air-exposed (d) Al-LLZO, (e) Al-LLZTO, and (f) Al-LLZNO.

Table 1. The energies of reactants and products.

Samples	Energy keV/f.u.
Li_2O	−0.825603
$\text{Li}_6\text{Zr}_2\text{O}_7$	−6.811825
La_2O_3	−3.053699
LiTaO_3	−3.101137
LiNbO_3	−3.057770
Al_2O_3	−5.079534
$\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$	−12.13005
$\text{Li}_{5.625}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.375}\text{Ta}_{0.625}\text{O}_{12}$	−12.19829
$\text{Li}_{5.625}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.375}\text{Nb}_{0.625}\text{O}_{12}$	−12.17118

Table 2. The simulated thermodynamic stability of Al-LLZO, Al-LLZTO, and Al-LLZNO.

Samples	Decomposition Equations	Δ Energy meV/atom
$\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$	$1/8\text{Li}_2\text{O} + \text{Li}_6\text{Zr}_2\text{O}_7 + 3/2\text{La}_2\text{O}_3 + 1/8\text{Al}_2\text{O}_3$	−19.89
$\text{Li}_{5.625}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.375}\text{Ta}_{0.625}\text{O}_{12}$	$7/16\text{Li}_2\text{O} + 11/16\text{Li}_6\text{Zr}_2\text{O}_7 + 5/8\text{LiTaO}_3 + 3/2\text{La}_2\text{O}_3 + 1/8\text{Al}_2\text{O}_3$	+11.08
$\text{Li}_{5.625}\text{Al}_{0.25}\text{La}_3\text{Zr}_{1.375}\text{Nb}_{0.625}\text{O}_{12}$	$7/16\text{Li}_2\text{O} + 11/16\text{Li}_6\text{Zr}_2\text{O}_7 + 5/8\text{LiNbO}_3 + 3/2\text{La}_2\text{O}_3 + 1/8\text{Al}_2\text{O}_3$	+11.07

Table 3. Lattice parameters for calculated crystals and XRD refinement.

Samples	Calculated Lattice Parameter						Refinement Lattice Parameter	
	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	a = b = c (Å)	$\alpha = \beta = \gamma$ (°)
Al-LLZO	12.9441	12.9707	13.0724	89.9	90.1	89.9	12.9387	90
Al-LLZTO	13.0032	12.9055	12.9431	90.0	90.0	89.9	12.9243	90
Al-LLZNO	13.0167	12.9176	12.9291	90.1	90.1	89.9	12.9288	90

4. Conclusions

Differently doped garnets Al-LLZO, Al-LLZTO, and Al-LLZNO were prepared to investigate their air stabilities. The results demonstrated that there was less Li_2CO_3 on the surface of Al-LLZTO and Al-LLZNO than on Al-LLZO after air exposure. Titration gas chromatography (TGC) analysis showed that the growth of Li_2CO_3 on the Al-LLZTO surface occurred in two stages: a fast growth stage and a slow growth stage with a tendency to saturation. FIB-SEM indicated Li_2CO_3 grew in an island-like manner on the garnet surfaces. In theory, the decomposition energies of Al-, Ta-, and Nb-doped LLZOs were calculated, with the product of Li_2O as the cause of Li_2CO_3 formation. The negative decomposition energy of Al-LLZO indicated that it is unstable and tends to decompose compared with the positive decomposition energy of Al-LLZTO and Al-LLZNO. Therefore, the development of such doped electrolytes is one step closer to the practical application of lithium metal batteries and offers prospects and directions for solid-state batteries.

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References

1. Fu, K.; Gong, Y.; Dai, J.; Gong, A.; Han, X.; Yao, Y.; Wang, C.; Wang, Y.; Chen, Y.; Yan, C.; et al. Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries. *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 7094–7099. [\[CrossRef\]](#)
2. Goodenough, J.B.; Park, K.-S. The Li-Ion Rechargeable Battery: A Perspective. *J. Am. Chem. Soc.* **2013**, *135*, 1167–1176. [\[CrossRef\]](#)
3. Zheng, F.; Kotobuki, M.; Song, S.; Lai, M.O.; Lu, L. Review on solid electrolytes for all-solid-state lithium-ion batteries. *J. Power Sources* **2018**, *389*, 198–213. [\[CrossRef\]](#)
4. Han, F.; Westover, A.S.; Yue, J.; Fan, X.; Wang, F.; Chi, M.; Leonard, D.N.; Dudney, N.; Wang, H.; Wang, C. High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes. *Nat. Energy* **2019**, *4*, 187–196. [\[CrossRef\]](#)
5. Bi, Z.; Zhao, N.; Ma, L.; Fu, Z.; Xu, F.; Wang, C.; Guo, X. Interface engineering on cathode side for solid garnet batteries. *Chem. Eng. J.* **2020**, *387*, 124089. [\[CrossRef\]](#)
6. Bi, Z.; Zhao, N.; Ma, L.; Shi, C.; Fu, Z.; Xu, F.; Guo, X. Surface coating of LiMn_2O_4 cathodes with garnet electrolytes for improving cycling stability of solid lithium batteries. *J. Mater. Chem. A* **2020**, *8*, 4252–4256. [\[CrossRef\]](#)
7. Bi, Z.; Huang, W.; Mu, S.; Sun, W.; Zhao, N.; Guo, X. Dual-interface reinforced flexible solid garnet batteries enabled by in-situ solidified gel polymer electrolytes. *Nano Energy* **2021**, *90*, 106498. [\[CrossRef\]](#)
8. Bi, Z.; Mu, S.; Zhao, N.; Sun, W.; Huang, W.; Guo, X. Cathode supported solid lithium batteries enabling high energy density and stable cyclability. *Energy Storage Mater.* **2021**, *35*, 512–519. [\[CrossRef\]](#)
9. Liu, Q.; Geng, Z.; Han, C.; Fu, Y.; Li, S.; He, Y.-B.; Kang, F.; Li, B. Challenges and perspectives of garnet solid electrolytes for all solid-state lithium batteries. *J. Power Sources* **2018**, *389*, 120–134. [\[CrossRef\]](#)
10. Zhao, N.; Khokhar, W.; Bi, Z.; Shi, C.; Guo, X.; Fan, L.-Z.; Nan, C.-W. Solid Garnet Batteries. *Joule* **2019**, *3*, 1190–1199. [\[CrossRef\]](#)
11. Jia, M.; Bi, Z.; Shi, C.; Zhao, N.; Guo, X. Air-stable dopamine-treated garnet ceramic particles for high-performance composite electrolytes. *J. Power Sources* **2021**, *486*, 229363. [\[CrossRef\]](#)

12. Gai, J.; Zhao, E.; Ma, F.; Sun, D.; Ma, X.; Jin, Y.; Wu, Q.; Cui, Y. Improving the Li-ion conductivity and air stability of cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ by the co-doping of Nb, Y on the Zr site. *J. Eur. Ceram. Soc.* **2018**, *38*, 1673–1678. [\[CrossRef\]](#)
13. Huo, H.; Luo, J.; Thangadurai, V.; Guo, X.; Nan, C.-W.; Sun, X. Li_2CO_3 : A Critical Issue for Developing Solid Garnet Batteries. *ACS Energy Lett.* **2020**, *5*, 252–262. [\[CrossRef\]](#)
14. Wu, J.F.; Pu, B.W.; Wang, D.; Shi, S.Q.; Zhao, N.; Guo, X.; Guo, X. In Situ Formed Shields Enabling Li_2CO_3 -Free Solid Electrolytes: A New Route to Uncover the Intrinsic Lithiophilicity of Garnet Electrolytes for Dendrite-Free Li-Metal Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 898–905. [\[CrossRef\]](#)
15. Duan, H.; Zheng, H.; Zhou, Y.; Xu, B.; Liu, H. Stability of garnet-type Li ion conductors: An overview. *Solid State Ion.* **2018**, *318*, 45–53. [\[CrossRef\]](#)
16. Galven, C.; Fourquet, J.-L.; Crosnier-Lopez, M.-P.; Le Berre, F. Instability of the Lithium Garnet $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$: Li_+/H_+ Exchange and Structural Study. *Chem. Mater.* **2011**, *23*, 1892–1900. [\[CrossRef\]](#)
17. Larraz, G.; Orera, A.; Sanjuán, M.L. Cubic phases of garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$: The role of hydration. *J. Mater. Chem. A* **2013**, *1*, 11419–11428. [\[CrossRef\]](#)
18. Jia, M.; Zhao, N.; Huo, H.; Guo, X. Comprehensive Investigation into Garnet Electrolytes Toward Application-Oriented Solid Lithium Batteries. *Electrochem. Energy Rev.* **2020**, *3*, 656–689. [\[CrossRef\]](#)
19. Wang, C.; Fu, K.; Kammampata, S.P.; McOwen, D.W.; Samson, A.J.; Zhang, L.; Hitz, G.T.; Nolan, A.M.; Wachsman, E.D.; Mo, Y.; et al. Garnet-Type Solid-State Electrolytes: Materials, Interfaces, and Batteries. *Chem. Rev.* **2020**, *120*, 4257–4300. [\[CrossRef\]](#)
20. Cheng, L.; Crumlin, E.J.; Chen, W.; Qiao, R.; Hou, H.; Lux, S.F.; Zorba, V.; Russo, R.; Kostecki, R.; Liu, Z.; et al. The origin of high electrolyte-electrode interfacial resistances in lithium cells containing garnet type solid electrolytes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 18294–18300. [\[CrossRef\]](#)
21. Cheng, L.; Wu, C.H.; Jarry, A.; Chen, W.; Ye, Y.F.; Zhu, J.F.; Kostecki, R.; Persson, K.; Guo, J.H.; Salmeron, M.; et al. Interrelationships among Grain Size, Surface Composition, Air Stability, and Interfacial Resistance of Al-Substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolytes. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17649–17655. [\[CrossRef\]](#)
22. Ishiguro, K.; Nemori, H.; Sunahiro, S.; Nakata, Y.; Sudo, R.; Matsui, M.; Takeda, Y.; Yamamoto, O.; Imanishi, N. Ta-Doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ for Water-Stable Lithium Electrode of Lithium-Air Batteries. *J. Electrochem. Soc.* **2014**, *161*, A668–A674. [\[CrossRef\]](#)
23. Huo, H.; Chen, Y.; Zhao, N.; Lin, X.; Luo, J.; Yang, X.; Liu, Y.; Guo, X.; Sun, X. In-situ formed Li_2CO_3 -free garnet/Li interface by rapid acid treatment for dendrite-free solid-state batteries. *Nano Energy* **2019**, *61*, 119–125. [\[CrossRef\]](#)
24. Fu, K.; Gong, Y.; Liu, B.; Zhu, Y.; Xu, S.; Yao, Y.; Luo, W.; Wang, C.; Lacey, S.D.; Dai, J.; et al. Toward garnet electrolyte-based Li metal batteries: An ultrathin, highly effective, artificial solid-state electrolyte/metallic Li interface. *Sci. Adv.* **2017**, *3*, e1601659. [\[CrossRef\]](#)
25. Murugan, R.; Thangadurai, V.; Weppner, W. Fast lithium ion conduction in garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Angew. Chem. Int. Ed.* **2007**, *46*, 7778–7781. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Yu, S.; Schmidt, R.D.; Garcia-Mendez, R.; Herbert, E.; Dudney, N.J.; Wolfenstine, J.B.; Sakamoto, J.; Siegel, D.J. Elastic Properties of the Solid Electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO). *Chem. Mater.* **2016**, *28*, 197–206. [\[CrossRef\]](#)
27. Zhao, N.; Fang, R.; He, M.-H.; Chen, C.; Li, Y.-Q.; Bi, Z.-J.; Guo, X.-X. Cycle stability of lithium/garnet/lithium cells with different intermediate layers. *Rare Met.* **2018**, *37*, 473–479. [\[CrossRef\]](#)
28. Gao, J.; Zhu, J.; Li, X.; Li, J.; Guo, X.; Li, H.; Zhou, W. Rational Design of Mixed Electronic-Ionic Conducting Ti-Doping $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ for Lithium Dendrites Suppression. *Adv. Funct. Mater.* **2020**, *31*, 2001918. [\[CrossRef\]](#)
29. Samson, A.J.; Hofstetter, K.; Bag, S.; Thangadurai, V. A bird's-eye view of Li-stuffed garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ceramic electrolytes for advanced all-solid-state Li batteries. *Energy Environ. Sci.* **2019**, *12*, 2957–2975. [\[CrossRef\]](#)
30. Li, Y.; Wang, Z.; Li, C.; Cao, Y.; Guo, X. Densification and ionic-conduction improvement of lithium garnet solid electrolytes by flowing oxygen sintering. *J. Power Sources* **2014**, *248*, 642–646. [\[CrossRef\]](#)
31. Zhang, X.; Weng, S.; Yang, G.; Li, Y.; Li, H.; Su, D.; Gu, L.; Wang, Z.; Wang, X.; Chen, L. Interplay between solid-electrolyte interphase and (in)active Li_xSi in silicon anode. *Cell Rep. Phys. Sci.* **2021**, *2*, 100668. [\[CrossRef\]](#)
32. Fang, C.; Li, J.; Zhang, M.; Zhang, Y.; Yang, F.; Lee, J.Z.; Lee, M.H.; Alvarado, J.; Schroeder, M.A.; Yang, Y.; et al. Quantifying inactive lithium in lithium metal batteries. *Nature* **2019**, *572*, 511–515. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Jia, W.; Cao, Z.; Wang, L.; Fu, J.; Chi, X.; Gao, W.; Wang, L.-W. The analysis of a plane wave pseudopotential density functional theory code on a GPU machine. *Comput. Phys. Commun.* **2013**, *184*, 9–18. [\[CrossRef\]](#)
34. Jia, W.; Fu, J.; Cao, Z.; Wang, L.; Chi, X.; Gao, W.; Wang, L.-W. Fast plane wave density functional theory molecular dynamics calculations on multi-GPU machines. *J. Comput. Phys.* **2013**, *251*, 102–115. [\[CrossRef\]](#)
35. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Schlupf, M.; Gygi, F. Optimization algorithm for the generation of ONCV pseudopotentials. *Comput. Phys. Commun.* **2015**, *196*, 36–44. [\[CrossRef\]](#)
37. Hamann, D.R. Erratum: Optimized norm-conserving Vanderbilt pseudopotentials. *Phys. Rev. B Condens. Matter Mater. Phys.* **2013**, *88*, 085117. [\[CrossRef\]](#)
38. Sharafi, A.; Yu, S.; Naguib, M.; Lee, M.; Ma, C.; Meyer, H.M.; Nanda, J.; Chi, M.; Siegel, D.J.; Sakamoto, J. Impact of air exposure and surface chemistry on $\text{Li-Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ interfacial resistance. *J. Mater. Chem. A* **2017**, *5*, 13475–13487. [\[CrossRef\]](#)

39. Zhang, Z.; Zhang, L.; Yu, C.; Yan, X.; Xu, B.; Wang, L.-m. Lithium halide coating as an effective intergrain engineering for garnet-type solid electrolytes avoiding high temperature sintering. *Electrochim. Acta* **2018**, *289*, 254–263. [[CrossRef](#)]
40. Shalev, T.; Gopin, A.; Bauer, M.; Stark, R.W.; Rahimipour, S. Non-leaching antimicrobial surfaces through polydopamine bio-inspired coating of quaternary ammonium salts or an ultrashort antimicrobial lipopeptide. *J. Mater. Chem.* **2012**, *22*, 2026–2032. [[CrossRef](#)]
41. Li, C.; Zhang, Z.; Sui, J.; Jiang, X.; Waterhouse, G.I.N.; Zhang, Z.; Yu, L. Microwave-based synthesis of (NiCo)_x/(MnO)_y/C composites and their tunable wave absorption properties in the K band. *Ceram. Int.* **2020**, *46*, 9353–9362. [[CrossRef](#)]
42. Nam, C.; Zimudzi, T.J.; Geise, G.M.; Hickner, M.A. Increased Hydrogel Swelling Induced by Absorption of Small Molecules. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14263–14270. [[CrossRef](#)] [[PubMed](#)]
43. De Geyter, N.; Morent, R.; Leys, C. Surface characterization of plasma-modified polyethylene by contact angle experiments and ATR-FTIR spectroscopy. *Surf. Interface Anal.* **2008**, *40*, 608–611. [[CrossRef](#)]
44. Yow, Z.F.; Oh, Y.L.; Gu, W.; Rao, R.P.; Adams, S. Effect of Li⁺/H⁺ exchange in water treated Ta-doped Li₇La₃Zr₂O₁₂. *Solid State Ion.* **2016**, *292*, 122–129. [[CrossRef](#)]
45. Qiao, Y.; Yi, J.; Wu, S.; Liu, Y.; Yang, S.; He, P.; Zhou, H. Li-CO₂ Electrochemistry: A New Strategy for CO₂ Fixation and Energy Storage. *Joule* **2017**, *1*, 359–370. [[CrossRef](#)]
46. Gao, J.; Guo, X.; Li, Y.; Ma, Z.; Guo, X.; Li, H.; Zhu, Y.; Zhou, W. The Ab Initio Calculations on the Areal Specific Resistance of Li-Metal/Li₇La₃Zr₂O₁₂ Interphase. *Adv. Theory Simul.* **2019**, *2*, 1900028. [[CrossRef](#)]
47. Zhu, J.; Li, X.; Wu, C.; Gao, J.; Xu, H.; Li, Y.; Guo, X.; Li, H.; Zhou, W. A Multilayer Ceramic Electrolyte for All-Solid-State Li Batteries. *Angew. Chem. Int. Ed. Engl* **2021**, *60*, 3781–3790. [[CrossRef](#)]