Garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid-State Electrolyte: Environmental Corrosion, Countermeasures and Applications

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Abstract

Garnet-based $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), as a popular solid-state electrolyte, is easily corroded by wet air, leading to failure of mechanical strength, Li-ion conductivity, and wettability. In this work, corrosion behaviors of garnet electrolyte in the air (carbon dioxide, water vapor, $\text{CO}_2+\text{H}_2\text{O}$ mixed air, actual moist air) and solution (distilled water, NaCl solution, natural seawater) are investigated, and it is determined that the electrolyte has the worst corrosion resistance to water. Prohibition of direct contact between vapor/liquid water and garnet is the basic design standard. We report a straightforward physical deposition methodology to achieve the growth of a poly (vinylidene fluoride) (PVDF) nano-hydrophobic layer on garnet. Grain (R_g) and grain boundary (R_{gb}) resistances of the electrolyte with PVDF coating are increased by only 14% and 170% at room temperature for 50 hours during a relative humidity of 80%, respectively, which are significantly lower than 930% and 2240% of the unmodified sample. The modified electrolyte presents the original morphology even after being immersed in solution at 353 K for 15 days. Excellent chemical corrosion resistance makes as-prepared garnet have great potential applications in all-solid-state, air-based, and water-based batteries.

Keywords: Garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$; PVDF coating; Chemical corrosion; Grain resistance; Grain boundary resistance.

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1. Introduction

The safety of solid-state electrochemical devices is significantly better than conventional Li-ion batteries due to reduced risk of liquid electrolyte leakage/burning and electrode chemical/physical short circuits.^[1-8] The key scientific challenge for the development of solid-state devices is focused on solid-state electrolytes (SSEs), which require high Li-ion conductivity, good chemical/thermal stability, non-toxic, and a simple manufacturing process. Although a large number of SSE materials have been reported, the candidate materials are very limited for solid-state devices.^[9-12] Such as, $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP),^[13-15] $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS),^[16-18] and $\text{Li}_x\text{La}_{2/3-x}\text{TiO}_3$ (LLTO)^[19,20] have a high ionic conductivity (10^{-3} S cm^{-1}) but are not stable against Li metal. LiPON^[21-24] as a chemically stable material for Li exhibits a low ionic conductivity (10^{-6} S cm^{-1}). In comparison, garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)^[25-30] is the most-promising material

because of high ionic conductivity ($10^{-3} - 10^{-4}$ S cm^{-1}), superior chemical stability against Li metal and wide electrochemical window (up to 6 V).

One of the major challenges is the large interfacial resistance between the garnet LLZO solid-state electrolyte and metal Li electrode due to poor interfacial wetting. Large interfacial resistance is not inherent in the garnet material but originates from a small amount of Li_2CO_3 naturally formed on the surface of the garnet electrolyte in the air.^[31-33] Surface modification of the garnet electrolyte with anode materials, such as Al,^[34] Al_2O_3 ,^[35] ZnO,^[36] Ge,^[37] g- C_3N_4 ,^[38] is the mainstream method to improve interfacial wettability. It is based on the fact that the lithiation product can greatly enhance the binding force/energy with the metal Li electrode. Choosing Li alloy materials (such as Li-Mg,^[39] Li-graphite^[40-42]) to replace pure Li metal is another technical approach. Unfortunately, these modification methodologies cannot fundamentally inhibit the formation of Li_2CO_3 , which means that the garnet solid-state electrolyte has to be operated in a dry inert gas atmosphere. Cheng *et al.* showed that the large resistance at Li/LLZO interfaces was not inherent to the material but originates from a small amount of Li_2CO_3 that forms on LLZO surfaces because of exposure to ambient air.^[43] These reactions could be readily reversed by heating samples

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at 623 K under an inert atmosphere to recover LLZO surface chemistry and structure.^[44] In the large-grained LLZO sample, Al segregates at grain boundaries resulting in depletion from the bulk, while Al is retained in the grains of the small-grained sample. Small-grained samples formed less Li_2CO_3 on surfaces after both short and long-term ambient air exposures, compared to the large-grained sample.^[45] It is unfavorable for garnet SSE, whether in production, storage, transportation, or in broadening its applications.

Herein, we have characterized the corrosion behavior of the garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid-state electrolyte in an air atmosphere (carbon dioxide, water vapor, $\text{CO}_2+\text{H}_2\text{O}$ mixed air, real humid air) and aqueous solution (distilled water, 3.5wt% NaCl, natural seawater), and determine that garnet has the weakest chemical resistance to water. Therefore, we have designed a simple modification technique, which is to coat the surface of garnet with hydrophobic PVDF. Even if the as-prepared PVDF-SSE sample is placed at 298 K for 50 hours during the relative humidity of 80%, its R_g and R_{gb} resistances are increased by only 0.14 and 1.7 times, respectively. A simple coping strategy can greatly improve the corrosion resistance of garnet electrolytes and basically solve the obstacles in production, transportation, and application.

2. Experimental section

2.1 Material preparation

All the experimental chemicals, supplied by the Aladdin Company, were of analytical grade and used without further purification. The $\text{Li}_{6.75}\text{La}_3\text{Al}_{0.25}\text{Zr}_2\text{O}_{12}$ (LLAZO) powder was synthesized via the solid phase sintering technique. The starting materials were LiOH (99%, Aladdin), $\text{La}(\text{NO}_3)_3$ (99.9%, Aladdin), $\text{Zr}(\text{NO}_3)_4$ (99.9%, Aladdin), and Al_2O_3 (99.99%, Aladdin). Stoichiometric amounts of these chemicals were dispersed in deionized water and a 10% excess of LiOH was added to compensate for Li volatilization during the high-temperature pellet preparation. The ball-milled mixture was evaporated at 393 K for 12 hours and then calcined to 1173 K for 12 hours to synthesize the precursor powder. The powders were then pressed into pellets, which were sintered at 1423 – 1523 K for 24 hours. The sintered LLAZO pellets were polished to ~1 mm thickness with a smooth surface.

The self-made solid-state electrolytes were soaked in PVDF transparent liquid (N-methyl pyrrolidone, NMP, as a solvent) at 298 K for 24 hours, and the dried samples were recorded as PVDF $_x$ -SSE-yd. x represents the concentration of PVDF, mg ml^{-1} ; y represents the time left in the air.

2.2 Material characterization

Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 analytical scanning electron microscope. The crystal phase analysis was performed by powder X-ray diffraction with a D8 ADVANCE with LynxEye and SolX (Bruker AXS) using a Cu $K\alpha$ radiation source operated at 40 kV and 40 mA. The contact angle between seawater and the

garnet LLAZO solid-state electrolyte was determined using a contact angle meter.

The garnet LLAZO pellet was wet-polished using sandpaper and rinsed with ethanol several times. The thickness (~1 mm) of the garnet ceramic was controlled. To measure the ionic conductivity of the garnet SSE, both sides of the ceramic pellet were coated with an Au layer, which served as a blocking electrode. Electrochemical impedance spectroscopy (EIS) was performed across a frequency range of 1 MHz to 0.01 Hz with a 50 mV perturbation amplitude. Conductivities were calculated using $\sigma = h/(Z \times A)$, where Z is the impedance for the real axis in the Nyquist plot, h is the garnet ceramic disc length, and A is the surface area. Electrochemical performances, such as constant current charge/discharge curves, cyclic voltammogram, linear sweep voltammetry, and AC electrochemical impedance spectroscopy, were carried out using an electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., CHI660e).

3. Results and discussion

3.1 Characterization of physical properties of garnet LLZO SSE

Al-doped LLAZO has been synthesized by a conventional solid phase sintering since trivalent Al enhances the concentration of Li-ion holes. Fig. S1 shows the SEM image of the cross-sectional morphology of the as-sintered garnet. Primary grain exhibits a uniform morphology with a size of 0.5 – 10 μm . The dense nature of the solid-state electrolyte is confirmed by the results of density measurements (carried out in ethanol by the Archimedes method), which affords a value $10 \pm 5\%$ less than that theoretically calculated for non-porous LLAZO. As shown in Fig. S2, X-ray diffraction (XRD) is used to analyze the crystal phase of the LLAZO SSE. The pattern of the as-prepared LLAZO matches that of cubic-garnet-phase $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (PDF #80-0457), which has higher Li-ion conductivity than the tetragonal garnet phase. The Li-ion conductivity of the garnet LLAZO at 298 – 328 K is evaluated by electrochemical impedance spectroscopy (EIS) with Au electrodes, and the corresponding Nyquist diagrams include two semicircles at high/medium frequencies and a nearly vertical low-frequency tail (Fig. S3). The contributions of bulk and grain boundary resistances are calculated using the low-frequency intercept. The resistance of LLAZO decreases with increasing temperature, with the Arrhenius behavior of total Li-ion conductivity, plotted in Fig. S3. The activation energy and Li-ion conductivity of the pure LLAZO SSE are 0.44 eV and $1.6 \times 10^{-4} \text{ S cm}^{-1}$ at 298 K, respectively, consistent with the literature values for garnet electrolytes.^[25-30]

3.2 Characterization of environmental corrosion of garnet LLZO SSE

3.2.1 Garnet-humid air

To evaluate the influence of humid air on the interfacial resistance, the polished SSE pellets were located at 298 K under a relative humidity of 80%. All EIS spectra are

composed of two semicircles and an inclined straight line in Fig. 1a. The intersection of the first semicircle and the x -axis corresponds to the grain resistance, while the second semicircle reflects the information of the grain boundary.^[33-35] The R_g and R_{gb} are equal to 340 and 480 $\Omega \text{ cm}^2$ for the fresh LLAZO SSE in Table 1, respectively, and the corresponding values are increased to 1,400 and 2,600 $\Omega \text{ cm}^2$ after 5 hours. By extending the storage time to 50 hours, the resistance values of the garnet are increased to 10.3 and 23.4 times, respectively. Fig. 1b is the XRD pattern of the garnet SSE eroded by humid air at room temperature for 7 days. Diffraction peaks of various impurities, such as Li_2CO_3 (PDF #22-1141), La_2O_3 (PDF #40-1281, #40-1284), ZrO_2 (PDF #37-1484), were found within $20 - 60^\circ$ diffraction angle. Li_2CO_3 is the most important impurity phase. According to the FE-SEM images in Figs. 1c and d, the impurity phase with an average size of about 1 μm is observed on the surface of the garnet SSE.

3.2.2 Garnet-simulated air

Using carbon dioxide, water vapor, and $\text{CO}_2+\text{H}_2\text{O}$ mixed gas to chemically corrode the fresh solid-state electrolyte ceramic sheets for 15 days, the schematic diagram and corresponding test results are shown in Fig. 2. In pure carbon dioxide atmosphere, the microscopic morphology of the corroded garnet is shown in Figs. 2a and d. The newly formed lithium

carbonate coating prevents the garnet electrolyte from being deeply corroded by carbon dioxide, so the corroded sample still retains the characteristic morphology of the garnet in the area of $250 \times 150 \mu\text{m}^2$. Inert N_2 is passed into liquid water to obtain high-humidity air. After 15 days of corrosion in water vapor, a large number of micro-scale protrusions grow on the electrolyte surface. It cannot be ignored that the primary particle size of the corroded electrolyte is significantly reduced, indicating that water vapor has caused grain boundary corrosion. Using $\text{CO}_2+\text{H}_2\text{O}$ mixed gas as the corrosive medium, the garnet solid-state electrolyte is subject to very severe grain boundary corrosion in Figs. 2c and f. The corrosion products are filled in the pores of the garnet in situ, and the corrosion depth exceeds 500 microns. In general, the corrosion chemical reaction of garnet in the air mainly occurs on the surface and grain boundaries, and the law of corrosion rate (v) is: $v(\text{CO}_2+\text{H}_2\text{O}) > v(\text{H}_2\text{O}) \gg v(\text{CO}_2)$.

Figure 2g exhibits the XRD patterns of the garnet LLAZO SSEs eroded by CO_2 , H_2O , and $\text{CO}_2+\text{H}_2\text{O}$ at 298 K for 15 days. The pattern of all the LLAZO matches that of cubic-garnet-phase $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (PDF #80-0457), but the eroded samples contain the diffraction peaks of the impurity phase. It is easy to know that mixed gas has the strongest corrosive ability, and pure carbon dioxide is the weakest. The chemical corrosion reactions involved in the garnet solid-state electrolyte are shown below:

Fig. 1 Stability test of the garnet $\text{Li}_{6.75}\text{La}_3\text{Al}_{0.25}\text{Zr}_2\text{O}_{12}$ solid-state electrolyte in the humid air. (a) Impedance plot (0.01 – 1 MHz) of the LLAZO SSEs measured in air at 298 K for 0 – 50 hours; (b) XRD pattern of the garnet placed by humid air at room temperature for 7 days; (c, d) FE-SEM images of the SSE-7d sample.

Fig. 2 Characterization of the stability of garnet LLAZO solid-state electrolyte. (a, d) SEM images of the garnet SSE placed by pure CO₂ gas at 298 K for 15 days; (b, e) in the N₂-H₂O mixed gas for 15 days; (c, f) in the CO₂-H₂O mixed gas for 15 days; (g) XRD patterns of the LLAZO pellets. Note (1) Pristine LLAZO pellet; (2) in pure CO₂ gas for 15 days; (3) in the CO₂-H₂O mixed gas for 5 days; and (4) in the CO₂-H₂O mixed gas for 15 days.

Table 1. Corrosion resistance-time values of the garnet with/without PVDF coating

	Corrosion resistance (Ω)											
	0 h		2 h		5 h		20 h		30 h		50 h	
	R_g	R_{gb}	R_g	R_{gb}	R_g	R_{gb}	R_g	R_{gb}	R_g	R_{gb}	R_g	R_{gb}
SSE	340	480	950	1,650	1,400	2,600	1,950	7,000	2,200	7,400	3,500	11,250
PVDF5-SSE	700	340	710	400	760	490	770	670	800	920	800	920
PVDF10-SSE	700	300	800	380	800	400	880	530	880	630	880	690
PVDF20-SSE	720	260	840	310	850	330	880	500	890	550	890	680

3.2.3 Garnet-aqueous solution

We further tested the corrosion experiments of the garnet SSE in an aqueous solution. The fresh garnet solid-state electrolyte was sealed in distilled water at room temperature to eliminate the interference of CO₂ in the experiment. After the garnet was soaked for 5 days, impurity particles with the size of a few microns precipitated at the grain boundary and surface in Fig. 3a. As the corrosion time increases, the primary particle size of the garnet electrolyte (Figs. 3b and c) decreases sharply from 10 μm to 2 μm, indicating that the chemical corrosion reaction mainly occurs at the grain boundary.

The corrosion behavior of the garnet solid-state electrolyte in 3.5 wt% NaCl solution (simulated seawater) was carried

out, and the relevant test results were shown in Figs. 3d-f. The LLAZO SSE with a thickness of 1 mm completely converts from a dense into a loose porous structure at 298 K for 5 days, showing that Na-ions can significantly enhance the grain boundary corrosion of garnet. More impurities appear as the corrosion time increases, but the grain size of the garnet does not change significantly. The filtered natural seawater was selected as the corrosive medium in order to further analyze the influence of salt solution on garnet in Figs. 3g-i. After being soaked for 5 days, the surface of the garnet is covered with nano-scale impurity particles, and the primary particles of the solid-state electrolyte are changed from angular polyhedrons to spheroids. Extending the immersion time, the

Fig. 3 SEM images of the garnet SSE soaked by distilled water (a-c), 3.5 wt% NaCl (d-f), and natural seawater (g-i) at 298 K for 5 (a, d, g), 10 (b, e, h) and 15 (c, f, i) days.

the apparent density of the solid-state electrolyte further reduces. In general, the law of corrosion rate (v) is $v(\text{seawater}) > v(\text{NaCl}) > v(\text{water})$. **Fig. 4** exhibits the XRD patterns of the garnet LLAZO SSEs soaked by distilled water, 3.5 wt% NaCl solution, and natural seawater at 298 K, and supports the corresponding micro-topography photo results. The chemical corrosion reactions involved in the garnet solid-state electrolyte are shown below:

Fig. 4 XRD patterns of the garnet LLAZO solid-state electrolyte-soaked aqueous solution. (1) Fresh garnet; (2) in distilled water for 5 days; (3) in distilled water for 10 days; (4) in distilled water for 15 days; (5) in 3.5% NaCl solution for 5 days; (6) in 3.5% NaCl solution for 10 days; (7) in 3.5% NaCl solution for 15 days; (8) in natural seawater for 5 days; (9) in natural seawater for 10 days and (10) in natural seawater for 15 days.

In short, the garnet solid-state electrolyte cannot withstand the chemical corrosion of water, while the corrosion of the electrolyte by carbon dioxide is negligible. Avoiding direct contact between garnet and water is the basic design criterion to improve chemical resistance.

3.3 Surface modification of the garnet LLZO SSE

To ensure the formation of a dense PVDF coating on the uneven surface, physical liquid deposition is applied to improve the hydrophobicity of the garnet SSE. PVDF x -SSE ($x = 5, 10$, and 20 mg ml^{-1}) was characterized by EIS, XRD, and SEM, and test results are shown in Fig. 5. The activation energy and Li-ion conductivity of the PVDF x -SSE is about 0.34 eV and $1.3 \times 10^{-4} \text{ S cm}^{-1}$, respectively, which are close to

the values of the uncoated sample. Thus, the negative influence of the PVDF coating on the Li-ion conductivity of the garnet SSE can be ignored.

The XRD peaks of the garnet SSE with PVDF coating match well with those of the cubic garnet-phase $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (PDF 80-0457) in Fig. 5e, but the diffraction peak corresponding to PVDF is not detected. As shown in Fig. 5f, a dense PVDF coating is found on the surface of the garnet SSE. The initial infiltration angle of the unmodified SSE pellet was about 39° in Fig. S4, which was reduced to 22° during 20 seconds. The PVDF5-SSE sample exhibited a strong hydrophobic character because the angle changes from 70° to 40° at the same time.

Fig. 5 Chemical resistance of the PVDF-SSE materials to humid air. (a-c) EIS profiles of the garnets with a PVDF coating at the temperature of 298 – 328 K; (d) Arrhenius plot of the SSE ionic conductivity; (e) XRD patterns of the fresh LLZO, PVDF, and PVDF20-SSE samples; (f) FE-SEM image of the solid-state electrolyte with a PVDF coating.

Fig. 6 Stability test of the garnet $\text{Li}_{6.75}\text{La}_3\text{Al}_{0.25}\text{Zr}_2\text{O}_{12}$ solid-state electrolyte in the humid air. (a) Impedance plot (0.01 – 1 MHz) of the LLZO SSEs measured in air at 298 K for 0 – 50 hours; (b) FE-SEM images of the PVDF5-SSE-7d sample; (c) XRD pattern of the garnet coated PVDF; (d, g) corrosion images (d, surface; g, cross-section) of the fresh garnet soaked by distilled water at 298 K for 90 days; (e, h) corrosion images (e, surface; h, cross-section) of the fresh garnet soaked by distilled water at 353 K for 15 days; and (f, i) corrosion images (f, surface; h, cross-section) of the PVDF5-SSE sample soaked by distilled water at 353 K for 15 days.

Figure 6a is the EIS curves of the $\text{PVDF}_x\text{-SSE}$ samples at 298 K under the relative humidity of 80%. R_g and R_{gb} of the PVDF5-SSE pellet are increased from 700 and 340 $\Omega \text{ cm}^2$ to 800 and 920 $\Omega \text{ cm}^2$ after 50 hours, respectively, with growth rates of 14% and 170%. R_g and R_{gb} in the PVDF10-SSE sample are increased to 880 and 690 $\Omega \text{ cm}^2$ after 50 hours; these of the PVDF20-SSE sample is enhanced to 890 and 680 $\Omega \text{ cm}^2$. In comparison, the resistance value of the garnet without PVDF coating is increased from 340 and 480 $\Omega \text{ cm}^2$ to 3,500 and 11,250 $\Omega \text{ cm}^2$, respectively.

XRD and SEM images were tested for the LLZO SSE with a PVDF coating after 7 days of exposure to wet air. A uniform thickness of PVDF nano-coating is grown on the surface of the solid-state electrolyte in Fig. 6b, which is different from the

microscopic morphology of impurities (Fig. 1c). Although the garnet SSE coated with PVDF has been eroded by humid air for 7 days, almost no impurities are visible in Fig. 6c. In comparison, diffraction peaks of the impurities are found for the unmodified garnet SSE, such as Li_2CO_3 , La_2O_3 , and ZrO_2 (Fig. 1b). Even after the modified SSE is immersed in distilled water at 353 K for 15 days, it still shows the original shape of garnet grains on the surface and cross-section (Figs. 6f and i). However, loose nanochips are observed in Figs. 6e and h for the uncoated sample at 353 K. These results show that hydrophobic PVDF can greatly enhance the chemical resistance of garnet to water or humid air.

To characterize the electrochemical performance of SSE, all-solid-state Li/SSE/Li symmetric batteries were assembled

under an argon atmosphere according to the schematic Fig. 7a. The Li/SSE/Li cell without PVDF coating involves a total resistance of 9.5 k Ω in Fig. 7b; however, the Li/PVDF5-SSE/Li cell exhibits a lower resistance of 3.8 k Ω . This is attributed to PVDF, as a good conductor of Li-ions, which enhances the wettability between metallic Li and the garnet electrolyte.^[46,47] The garnet solid-state electrolytes are exposed at 298 K during the relative humidity of 80% for 7 days. The total resistance amounts to 300 k Ω for Li/SSE-7d/Li cell, which is about 30 times higher than that of the corresponding fresh LLAZO cell. In comparison, the resistance value of the Li/PVDF5-SSE-7d/Li cell is only raised by 6.2 k Ω , accounting for only 2.1% of the growth of the unmodified symmetric cell. We further carry out d.c. Li plating and stripping experiments

to evaluate the Li-ion transport capability across the garnet SSE (Figs. 7c-e). Both Li/SSE-0d/Li and Li/PVDF5-SSE-0d/Li cells show perfect cycle performances within 1200 min, with corresponding resistances of about 8.8 and 4.4 k Ω , respectively. The results are consistent well with the EIS spectrum in Fig. 7b. Even at a current of 10 $\mu\text{A cm}^{-2}$, the control Li/SSE-7d/Li cell without PVDF coating displays a noisy potential with the max voltage polarization of 3 V. On the other hand, the Li/PVDF5-SSE-7d/Li cell stabilizes at 10 mV for 250 cycles. Therefore, the PVDF amorphous coating essentially negates the primary challenge of rapid deep corrosion in wet air for the practical application of garnet electrolyte.

Fig. 7 Electrochemical stability of the Li/SSE/Li cell. (a) Schematic of the symmetric cell preparation; (b) comparison of Nyquist plots of Li/SSE/Li, Li/SSE-7d/Li, Li/PVDF-SSE/Li, and Li/PVDF-SSE-7d/Li in the frequency of 1 MHz to 0.01 Hz at room temperature; (c) voltage profile depicting the Li plating/stripping behavior for the Li/SSE/Li and Li/PVDF-SSE/Li cells at a current density of $10 \mu\text{A cm}^{-2}$ for 1200 min; (d) voltage-time curve of the Li/SSE-7d/Li; (e) voltage curve of the Li/PVDF-SSE-7d/Li.

Fig. 8 Anti-corrosion mechanism (a, b) and related applications (c-e) of the garnet solid-state electrolyte with a PVDF coating.

3.4 Potential applications of modified electrolyte

Figure 8 describes the corrosion mechanism and potential applications of garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid-state electrolyte coated with PVDF. Garnet has poor chemical stability to H_2O and CO_2 , which leads to a significant decrease in mechanical strength and ionic conductivity. Improving the corrosion resistance of garnet SSE should no longer be ignored. In a humid air environment, the irreversible corrosion chemical reaction mainly occurs on the surface of the LLZO SSE and generates impurity oxides such as lithium carbonate. Li_2CO_3 is unlikely to conduct Li-ions, causing the interface resistance of the solid-state electrolyte to increase by several orders of magnitude. Li_2CO_3 has poor wettability to metallic lithium, which inevitably increases the interface resistance between the Li metal electrode and garnet SSE. Obvious grain boundary corrosion can be observed when garnet LLZO is soaked in distilled water. The loose corrosion products help liquid water migrate into the garnet SSE, resulting in a gradual acceleration of the chemical corrosion rate. Sodium chloride further increases the corrosion rate of the garnet electrolyte, eventually forming a three-dimensional porous microscopic morphology.

We have succeeded in developing a straightforward physical deposition methodology to modify the surface of the LLZO SSE with a dense PVDF amorphous layer for advanced chemical resistance. The garnet with hydrophobic PVDF coating maintains the original microscopic morphology and composition whether in moist air or liquid. The easy-to-industrial modification method not only improves the safety of the garnet LLZO SSE in storage, transportation, and use but also expands the application field from a single all-solid-state Li-ion battery to air-based,^[42,48-50] water-based^[51-53] chemical batteries and electrolytic cells.^[54-58]

4. Conclusions

Although the garnet solid-state electrolyte has a large Li-ion conductivity of $10^{-4} \text{ S cm}^{-1}$, it is susceptible to corrosion. After the SSE ceramic pellet is exposed to the wet air for 50 hours,

its total resistance increases from $820 \Omega \text{ cm}^2$ to $14,750 \Omega \text{ cm}^2$. The 17-fold increase reveals the fact that the intrinsic Li-ion conductivity of the garnet SSE is severely attenuated. It can be known from the corrosion experiments that garnet is easily corroded by water vapor/solution, but the corrosiveness of pure carbon dioxide can be ignored. Cutting off the path of water diffusion to garnet is the basic criterion of the anti-corrosion strategy.

For the first time, the hydrophobic PVDF polymer is applied to modify the surface of the LLZO SSE. The nano-scale film blocks the LLZO pellet from contact with moist air, which significantly improves the chemical stability of the as-prepared SSE. The total resistance ($R_b + R_{gb}$) of the PVDF-SSE-50h sample has increased only by 65%, obviously lower than the 17-fold value of the uncoated SSE. All the microscopic morphology, crystal structure, and electrochemical performance results exhibit the benefits of the PVDF coating. This extremely simple modification method provides potential feasibility for the large-scale industrialization of garnet solid-state electrolytes.

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Supporting information

Applicable.

Conflict of interest

There are no conflicts to declare.

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