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Constructing Enhanced Composite Solid-State Electrolytes with Sb/Nb Co-Doped LLZO and PVDF-HFP

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Abstract: Composite solid-state electrolytes are viewed as promising materials for solid-state lithium-ion batteries due to their combined advantages of inorganic solid-state electrolytes and solid-state polymer electrolytes. In this study, the solid electrolytes $\text{Li}_{6.7-x}\text{La}_3\text{Zr}_{1.7-x}\text{Sb}_{0.3}\text{Nb}_x\text{O}_{12}$ (LLZSNO) with Sb and Nb co-doping were prepared by a high-temperature solid-phase method. Results indicate that Sb/Nb co-doping causes lattice deformation in LLZO and increases the lithium vacancy concentration and conductivity of LLZO. Then, with the co-doped LLZSNO as an inorganic filler, a composite solid electrolyte of polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) was prepared with a casting method. The obtained composite solid electrolyte exhibits a high ionic conductivity of 1.76×10^{-4} S/cm at room temperature, a wide electrochemical stable window of 5.2 V, and a lithium-ion transfer number of 0.32. The $\text{Li}|\text{LiFePO}_4$ coin battery with the composite solid electrolyte shows a high specific capacity of 161.2 mAh/g and a Coulombic efficiency close to 100% at 1 C. In addition, the symmetrical lithium battery $\text{Li}|\text{Li}$ with the composite electrolyte could cycle stably for about 1500 h without failure at room temperature.

Keywords: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$; co-doping; composite solid-state electrolyte; ionic conductivity



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1. Introduction

Since lithium-ion batteries (LIBs) were successfully commercialized by Sony in 1991 for the first time, they have been widely used in cell phones, notebook computers, and portable electronic products due to their high energy density, high voltage, low self-discharge, and long cycle life [1–3]. Today, the application field of LIBs has also expanded from small digital electronic devices to electric vehicles (EVs), energy storage power plants, and large-scale scenarios [4]. However, the current commercial lithium batteries use organic material as the electrolyte, which not only requires high environmental standards for the production and packing processes but also poses risks of potential safety hazards such as liquid leakage, fire, and explosions [5,6]. As a good substitute for organic electrolytes, solid electrolytes have received much attention because they may solve safety issues and enhance the energy density of lithium-ion batteries.

Solid-state electrolytes (SSEs) were usually divided into solid polymer electrolytes (SPEs), inorganic solid-state electrolytes (ISEs), and composite solid electrolytes (CSEs) [7,8]. ISEs include oxides [9,10], sulfides [11,12], nitrides [13], and hydrides [14]. Oxide electrolytes show good commercial value because of their high ionic conductivity, wide electrochemical window, high strength, and good thermal stability [15,16]. Among them, the common oxide solid electrolytes are lithium superionic conductors (LISICON), sodium superionic conductors (NASICON), perovskite $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO), and garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) [17]. Specifically, since garnet-type LLZO was first reported by Murugan in 2007 [18], it has been widely noticed and studied because of its potential advantages in energy density, thermal stability, and safety performance. However, for LLZO, there are two crystal phases present at room temperature: the tetragonal phase and the cubic

phase. Although the tetragonal phase is more stable, its ionic conductivity is two orders of magnitude lower than that of the cubic phase. LLZO also has some shortcomings that need to be improved [19], such as cubic phase LLZO with high ionic conductivity requiring a high sintering temperature; it was unstable at room temperature and easy to decompose or convert into tetragonal-phase LLZO with low ionic conductivity during the cooling process. From the reported results, it was observed that doping is an effective strategy for LLZO to overcome this challenge [20–22].

Additionally, the application of inorganic ceramic electrolytes (ICEs) still faces some challenges, such as poor contact with the electrode and high interfacial impedance. In contrast, SPEs have better interfacial contact properties and a simpler preparation process than ICEs [23] but lower conductivity and bad thermal stability. The composite solid-state electrolytes (CSEs), composed of polymers and ceramics, not only combine the advantages of inorganic and polymer solid electrolytes but also overcome their disadvantages and have become research hotspots. Adding inorganic fillers to the polymer matrix may improve the ionic conductivity of the CSEs [24]. Fan et al. [25] reported that composite electrolytes might achieve enhanced ionic conductivity and stability, resulting from the inorganic component and synergistic interactions between the polymer and inorganic phase. Since the amorphous phase in a polymer is more favorable for ion transport, combining inorganic fillers with the polymer electrolytes is an effective way to decrease glass transition temperature and suppress the crystallization of polymers. Wu et al. [26] found that polymer electrolytes with dissolved Li–salts interact with the ceramic fillers through surface interactions, which increase the amorphous phase zone, facilitate Li^+ migration, and decrease the activation energy for Li^+ transport. And, the stronger the binding between TFSI $^-$ and inorganic filler surface, the weaker its binding with Li^+ will be. The introduction of fillers minimizes the binding between Li^+ and TFSI $^-$, thereby maximizing the Li^+ migration number and Li^+ conductivity of the electrolyte.

Except for the doping of one single element increasing the ionic conductivity of LLZO to varying degrees, several studies have shown that co-doping is more helpful and synergistic in enhancing the performance of LLZO [27]. Liang et al. [28] found the structure of $\text{Li}_{6.7}\text{La}_3\text{Zr}_{1.7}\text{Sb}_{0.3}\text{O}_{12}$ to be stable and more favorable for improving ionic migration, and some studies have shown that Nb can form the garnet structure for co-doping with other elements [29,30]. Based on this consideration, the isovalent dopant Nb_2O_5 was chosen to further enhance the ion conductivity of LLZSO. Herein, cubic-phase LLZO co-doped with Sb and Nb was synthesized using a solid-phase sintering method; based on previous research, the content of Sb was fixed at 0.3 mol invariable, and the effects of the niobium dopant concentration on the relative density, ionic conductivity, and composite performance were investigated. Subsequently, composite solid electrolytes, with the co-doped garnet powder as a filler mix in the polymer matrix, were prepared using a solution casting method, and the batteries with the composite solid electrolytes were assembled for electrochemical performance and safety analysis. The prepared CSEs show high ionic conductivity at room temperature, wide electrochemical windows, good interface stability with lithium anode, and good safety.

2. Materials and Methods

2.1. Preparation of LLZSNO

$\text{Li}_{6.7-x}\text{La}_3\text{Zr}_{1.7-x}\text{Sb}_{0.3}\text{Nb}_x\text{O}_{12}$ ($x = 0, 0.05, 0.10$, and 0.15 ; LLZSNO) was synthesized using a solid-state sintering method. In detail, Li_2CO_3 (99%, Damas-Beta, China), La_2O_3 (99.99%, MACKLIN), ZrO_2 (99%, Damas-Beta), Sb_2O_5 (99.99%, Damas-Beta), and Nb_2O_5 (99.99%, Damas-Beta) powders were accurately weighed according to their stoichiometric ratios (excessive 10 wt% Li_2CO_3 was used for the compensation of lithium losses during sintering). These raw materials were ball-milled at 300 rpm in an isopropanol solution for 6 h before being dried for 12 h at 80 °C. The mixtures were then put into a corundum crucible and sintered for 6 h at 950 °C to produce precursor powders. Then, the precursor powders were processed for 10 min in a mortar before being transferred to the corundum

crucible and sintered at 1150 °C for 6 h. The obtained garnet powder was ball-milled once again at 300 rpm for 6 h to get the final product.

2.2. Preparation of Composite Solid Electrolyte Membranes

The composite solid electrolyte was prepared through a solution casting process, as illustrated in Figure 1. Firstly, 1.8 g of PVDF-HFP (Kynar Flex 2801, France), 0.2 g of succinonitrile (SN, 99%, Damas-Beta), and 0.2 g of lithium bis(trifluoromethanesulphonyl)imide (LiTFSI, 99.95%, Sigma-Aldrich) were dissolved in 10 g of N,N-dimethylformamide (DMF, Damas-Beta), and 0.3 g of LLZSNO powder was then added to the solution. Then, the obtained homogenized slurry was scraped onto a clean glass plate. To ensure the sufficient volatilization of organic solvents, the CSEs were dried at 80 °C for 12 h. The prepared CSEs were named PVDF-HFP/LLZSNO (abbreviated as PL-x, where X is the content of Nb in LLZSNO). Moreover, polymer solid electrolyte membranes were prepared according to the same procedure for comparison. For the assembly of the coin cell, the electrolyte membranes were sliced into 20 µm thick wafers with 19 mm diameters, about 0.017 g.

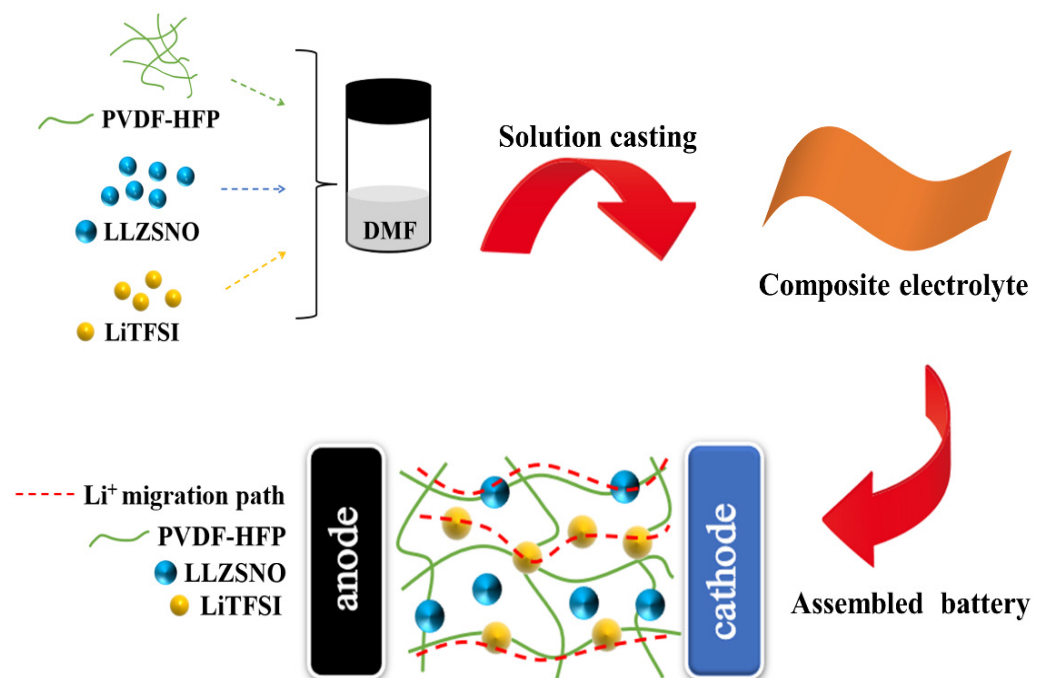


Figure 1. Preparation process of PVDF-HFP/LLZO composite solid electrolytes.

2.3. Battery Assembly

To evaluate the electrochemical performance of prepared composite solid electrolytes, Li/CSEs/LiFePO₄ coin batteries (CR2016) were assembled. The cathode active materials consist of LiFePO₄, carbon black, and PVDF in an 8:1:1 weight ratio. The active material load of the cathode (LiFePO₄) was around 1.2–1.5 mg/cm². Before the battery was packaged, a small amount of fluoroethylene carbonate (2 µL/cm²) was added between the cathode and the electrolyte to further improve the interface contact.

To verify the security of the CSEs, the pouch battery with the LiFePO₄ cathode (length: 5 cm, width: 5 cm), the PL-0.05 CSE membrane (length: 7 cm, width: 7 cm), and a Li band (length: 5 cm, width: 5 cm) were assembled in an argon-filled glove box (O₂ < 0.01 ppm, H₂O < 0.01 ppm) and measured by the LAND-CT2001A system (China).

2.4. Characterization

LLZSNO powder crystalline phase was confirmed by a Bruker-D8 X-ray diffractometer (XRD, Germany). The testing was conducted using a Cu-K source with the following parameters: $\lambda = 0.15418$, a scanning range of $2\theta = 10\sim 80^\circ$, a scanning rate of $2^\circ/\text{min}$, a step

size of 0.02, a voltage of 40 KV, and a current of 50 mA. The theoretical densities of the ceramic samples were refined using the Rietveld method. The surface of the CSEs and the cross-section of garnet were observed with a scanning electron microscope (SEM, Japan), and energy dispersive X-ray spectroscopy (EDS, Japan) was then used to determine the elemental distribution on the surface of the samples. X-ray photoelectron spectroscopy (XPS, USA) was used to examine the valence state of Sb in LLZSNO. Then, the Sb/Nb co-doping effect was confirmed by Raman spectroscopy. The thermal properties of the PVDF-HFP and PVDF-HFP/LLZSNO solid electrolyte were investigated through TG-DSC (STA449C/3/G) at 10 °C min⁻¹ in an air atmosphere from room temperature to 600 °C.

2.5. Determination of the Relative Density of Ceramics

The actual density of ceramic electrolytes was measured using a hydrostatic weighing method. First, weigh the mass of the material in the air to m_1 , and then place the material in solution and test its mass in liquid to m_2 . The relative density of the material can be obtained through the Archimedes principle; here, ρ_R is the relative density of LLZO, ρ_L is the density of the ethanol, and ρ_T is the theoretical density of LLZO.

$$\rho_R = \frac{m_1}{(m_1 - m_2)} \rho_L / \rho_T \times 100\% \quad (1)$$

2.6. Electrochemical Measurement

The AC impedance method is usually used to test the ion conductivity of solid electrolytes. Before impedance testing, inorganic ceramic materials need to be coated with silver on both sides to form the blocking symmetrical electrode, while polymer and composite electrolytes are tested with stainless steel as the electrode. The impedance (R) of the solid electrolyte was measured through EIS, and its corresponding ionic conductivity also could be obtained by calculating Formula (2), where L is the thickness of the solid electrolyte and S is the area of the symmetrical electrode.

$$\sigma = \frac{L}{RS} \quad (2)$$

Based on the corresponding impedance of the electrolyte, the activation energy of the corresponding solid electrolytes could be calculated according to the following Formula (3), where σ , T, A, and K_B are the ionic conductivity, the absolute temperature, the finger-forward factor, and the Boltzmann constant, respectively.

$$\sigma T = A \exp(-E_a / K_B T) \quad (3)$$

The Li^+ transfer number could be obtained through the DC polarization method; in this study, the voltage was set to 10 mV, and the EIS test was performed before and after polarization. The Li-ion transfer number was calculated as follows in Formula (4), where the initial currents I_0 and stable currents I_{ss} were obtained from the DC polarization test. The interfacial impedance of the pre-test R_0 and post-test R_{ss} were obtained from AC impedance measurements with frequencies between 1 MHz and 10⁻¹ Hz.

$$t_{\text{Li}^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})} \quad (4)$$

3. Results and Discussion

The XRD patterns of LLZSNO with different contents of Nb are shown in Figure 2a. The diffraction peaks of the samples all match well with the cubic phase LLZO (PDF#80-0457) [31], indicating that LLZO with Sb/Nb co-doping was successfully synthesized. Interestingly, the diffraction peaks of the samples also show a tendency to shift toward higher angles. According to Bragg's law [32], this is related to the decrease in the interplanar distance. The variation of the lattice parameter after co-doping could be obtained through Rietveld

refinement, as shown in Figure 2b. It was found that the lattice parameter decreased with Sb/Nb co-doping; this is likely due to the crystal lattice deformation of garnet LLZO. There are three locations in the cubic LLZO that can accommodate Li: tetrahedral void 24 d, regular octahedral void 48 g, and partial octahedral void 96 h. Due to the mutual repulsion of Li^+ , it generally occupies void 96 h. Considering that the 96 h is very close and only half of it can be occupied by Li^+ , per formula unit $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ can provide a total of 9 Li^+ vacancies by the 24 d and 96 h. Li^+ in cubic LLZO is randomly disordered at 24 d and 96 h [33]. More significantly, due to the substitution of partial Zr^{4+} by high-valence Nb^{5+} and Sb^{5+} cations, Li^+ vacancies were generated, resulting in an increase in conductivity.

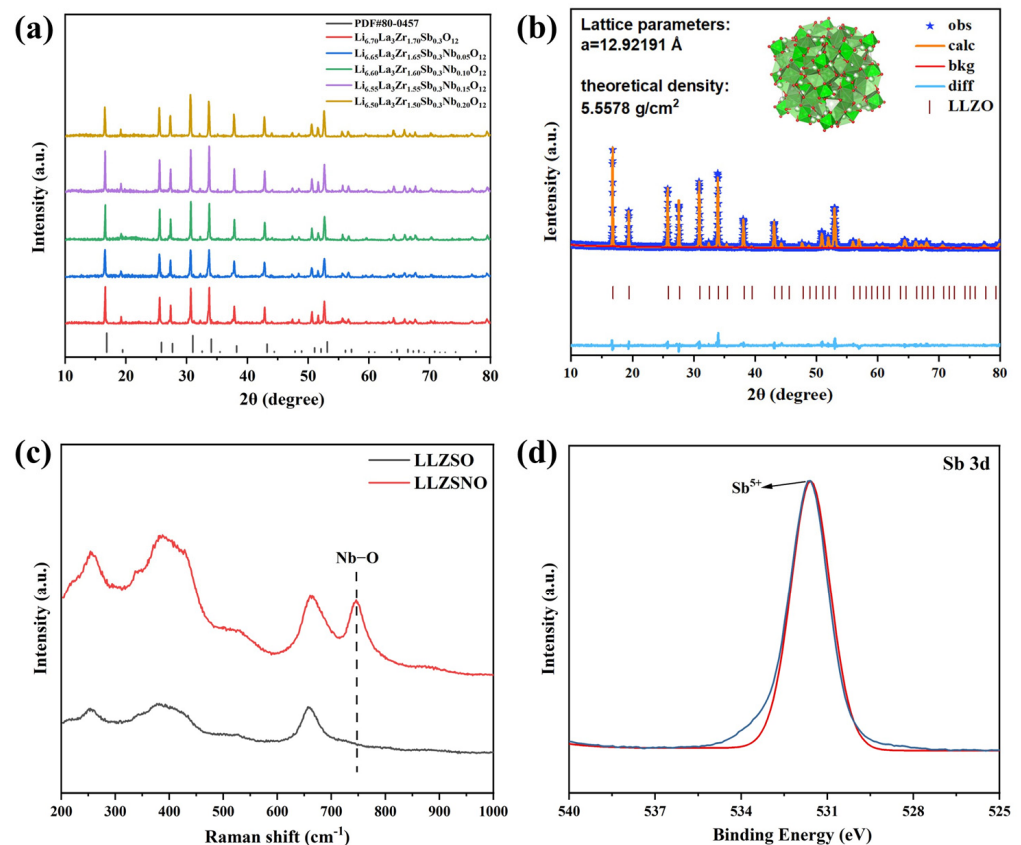


Figure 2. (a) XRD patterns of LLZSNO powder; (b) Rietveld Refined of XRD; (c) Raman of LLZSO and LLZSNO; and (d) XPS energy spectrum of LLZSNO in Sb 3d orbit.

As shown in Figure 2c, the Raman spectra of garnet further show the effect of co-doping on the LLZO. The peaks near 205, 240, 350, 393, 484, and 650 cm^{-1} are the characteristic peaks of cubic LLZO [34], which is consistent with the XRD results. This part of the characteristic peak shifts to the right as a whole, and the blue shift means an enhancement of the bonding energy in the region. The results show that LLZO with co-doping has a larger relative displacement than that with only Sb-doping, which indicates that the Nb substitution has a positive effect on the structure of LLZO. This is attributed to the partial structure change of LLZO, which leads to an increase in Li vacancy and more disorder characteristic of Li^+ in the lattice. The spectral bandwidth intensity increases at about 531 cm^{-1} after co-doping, indicating a higher degree of distortion of ZrO_6 [35]. Moreover, it can be observed that the peak of the Nb-O bond appears at 750 cm^{-1} after co-doping, while the intensity of the Zr-O bond decreases simultaneously, which suggests that the Nb occupies the Zr-site. The valence of Sb in the synthesized LLZSNO was determined by XPS, as shown in Figure 2d. The results show that, compared to the standard electron-binding energy, the peak of 531.1 eV proved that the valence state of the Sb in the LLZSNO should be Sb^{5+} , which achieves the expected goal of the experiment.

As displayed in Figure 3, all samples of $\text{Li}_{6.7-x}\text{La}_3\text{Zr}_{1.7-x}\text{Sb}_{0.3}\text{Nb}_x\text{O}_{12}$ ($x = 0.05, 0.10, 0.15$, and 0.20) show the Nyquist plots consisting of semicircular arcs and straight lines inclined at approximately 45° . The equivalent circuit consists of CPE1, CPE2, and R1, which represent grain-boundary capacitance, electrolyte resistance, and grain-boundary resistance, respectively [36]. It can be seen that the impedances of $\text{Li}_{6.7-x}\text{La}_3\text{Zr}_{1.7-x}\text{Sb}_{0.3}\text{Nb}_x\text{O}_{12}$ are about $1750\ \Omega$, $720\ \Omega$, $930\ \Omega$, and $1080\ \Omega$ (for $x = 0.05, 0.10, 0.15$, and 0.20), in which LLZSNO prepared when $x = 0.05$ has the smallest impedance. Chen [37] elucidated Li diffusion in LLZO using density-based trajectories calculated by molecular dynamics simulations. It is found that most Li jumps in cubic LLZO do not contribute to the diffusion rate because of the local reciprocating motion of its jump. Therefore, the low vacancy concentration is the main obstacle to Li^+ diffusion in LLZO. As observed in the experiment, it is an effective strategy to increase the vacancy concentration by substituting higher valence cations. The relative density and ion conductivity of LLZSNO are calculated using Formulas (1) and (2), as shown in Table 1. It was observed that the relative densities of the co-doped LLZSNO all increased compared with LLZO, and LLZSNO with $x = 0.05$ has the highest densities of 88.7%. $\text{Li}_{6.65}\text{La}_3\text{Zr}_{1.65}\text{Sb}_{0.3}\text{Nb}_{0.05}\text{O}_{12}$ also exhibits the highest ionic conductivity of $2.08 \times 10^{-4}\ \text{S/cm}$, which is a significant enhancement compared to LLZO and is related to its high densification. Moreover, with the increase in Nb content in co-doped garnets, the ionic conductivity of the studied garnets decreases as a result of the garnet lattice constant decreasing, which narrows the Li-ion transport paths.

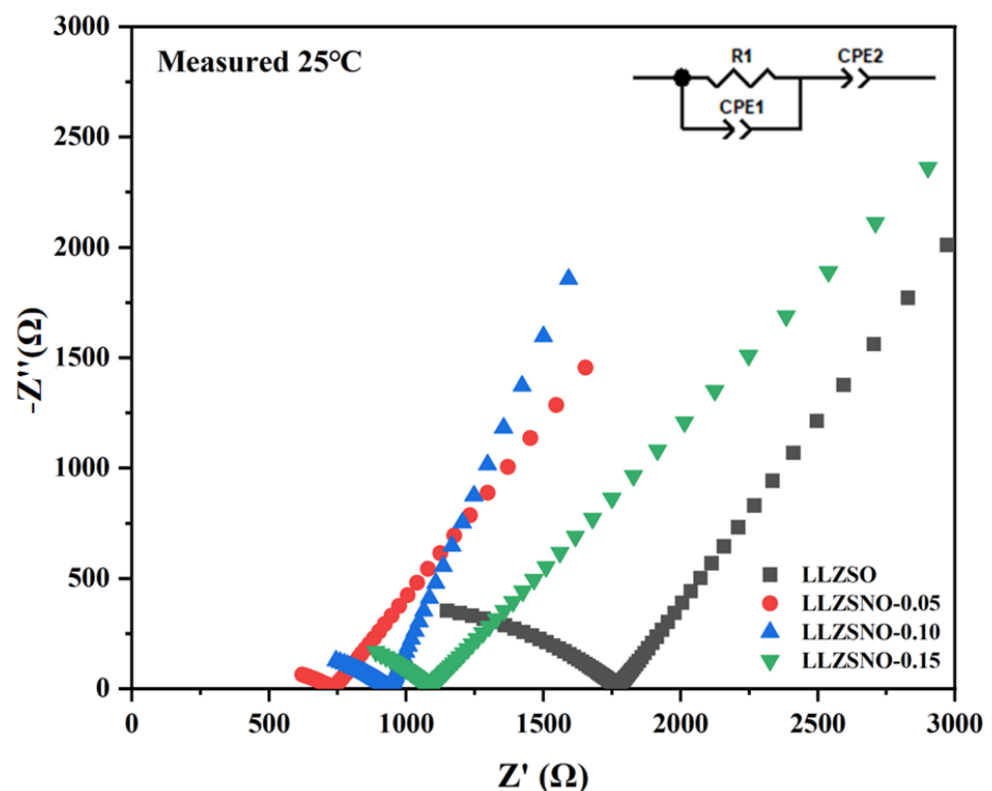


Figure 3. Nyquist plots of LLZO and LLZSNO at $25\ ^\circ\text{C}$.

The cross-sectional microstructure of $\text{Li}_{6.65}\text{La}_3\text{Zr}_{1.65}\text{Sb}_{0.3}\text{Nb}_{0.05}\text{O}_{12}$ ceramics is shown in Figure 4. Figure 4a shows the cross-section of the green pellet before sintering, where the ball-milled powder particles were uniformly pressed. The ceramic after sintering is observed overall at low magnification, as shown in Figure 4b; it can be seen that the ceramic is composed of large particles surrounded by some small particles. Figure 4c,d demonstrate that large particles with clear grain boundaries are observed at high magnification, and the filling of the voids between the large particles by small particles may increase the density of the ceramic. In addition, spherical pores can also be seen in the grain boundary, and these

voids are usually accompanied by a certain liquid-phase sintering process [38]. Figure 4e shows the elemental distribution of LLZSNO using EDS; the results indicate that in the prepared LLZSNO, the elements of La, Zr, O, Sb, and Nb all have a uniform distribution. The SEM image and EDS mapping of LLZSNO powder are shown in Figure S1. The particle morphology of LLZSNO powder after crushing in a high-speed ball mill, with a particle size of submicron, can be observed in the SEM images; the individual particles are very fine and present irregular polyhedrons, and some of the particles are clustered together.

Table 1. Impedance, Relative Density, and Ionic Conductivity of LLZSNO.

Nb Content	Impedance (Ω)	Relative Density (%)	Ionic Conductivity (S/cm)
0	1750	82.4	8.53×10^{-5}
0.05	720	88.7	2.08×10^{-4}
0.10	930	86.5	1.61×10^{-4}
0.15	1080	87.2	1.38×10^{-4}

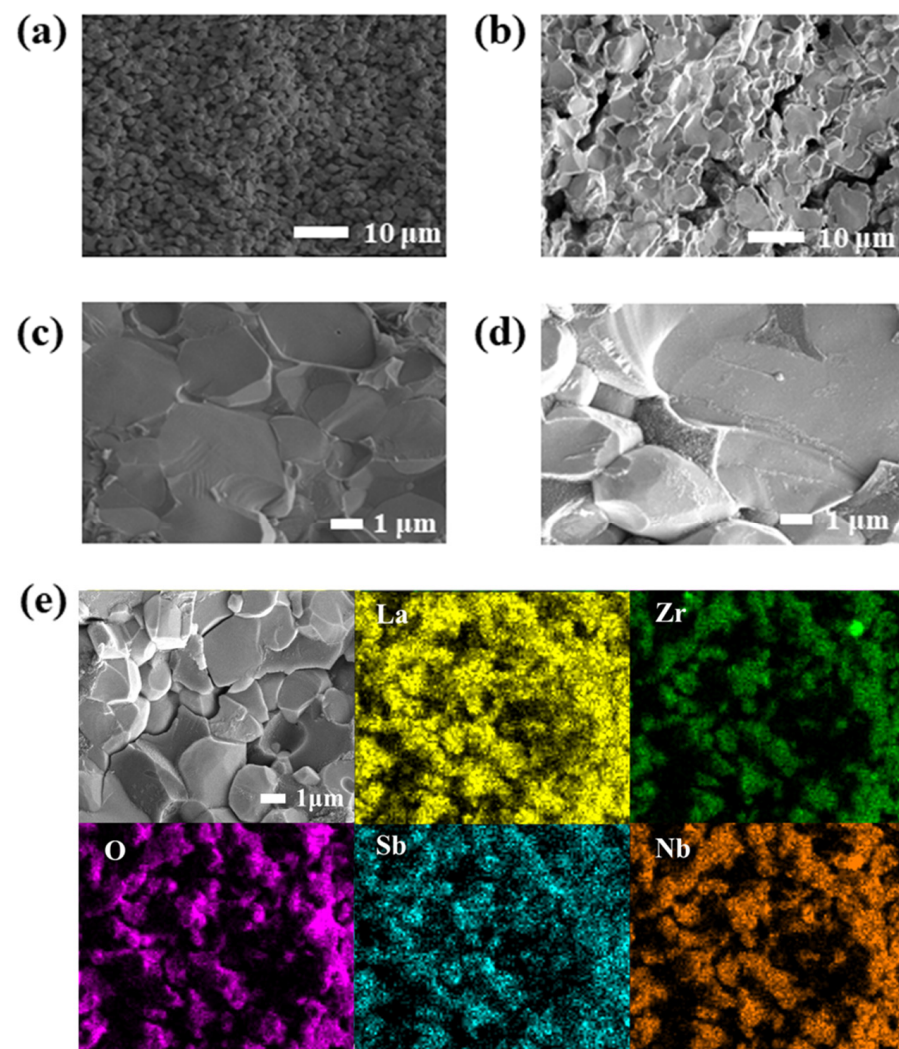


Figure 4. (a–d) SEM image of LLZSNO, and (e) EDS mapping of La, Zr, O, Sb, and Nb in LLZSNO.

Since the interface problem is still a big obstacle for the application of ceramic electrolytes [39], $\text{Li}_{6.65}\text{La}_3\text{Zr}_{1.65}\text{Sb}_{0.3}\text{Nb}_{0.05}\text{O}_{12}$ was used as the inorganic filler to prepare CSE membranes for displaying their electrochemical performance. The thermal stability

of the solid polymer electrolyte PVDF-HFP and the composite solid electrolyte PVDF-HFP/LLZSNO (PL-x) was conducted by TG-DSC; the results are shown in Figure S2. It can be seen that the thermal stability of the CSE membrane has not been lost compared to the PVDF-HFP membrane. In a way, the CSE membrane's thermodynamic property might be able to satisfy the application requirements of most LIBs. Figure S3 shows the microscopic morphology of the PVDF-HFP/LLZSNO. From the overall view, it could be observed that LLZSNO particles distribute uniformly on the surface of CSE, and the film is smooth and dense. Moreover, the concrete image in Figure S4 shows that the SSEs have good flexibility, recoverability, and film-forming properties.

Li | PVDF-HFP | LiFePO₄ and Li | PVDF-HFP/LLZSNO | LiFePO₄ batteries were assembled to study the electrochemical performance of SSEs. Figure 5a,b display the charging and discharging capacity of coin batteries at room temperature. The results show that the two batteries can cycle for more than 100 cycles at a rate of 1 C. The initial discharge-specific capacity of the pure polymer electrolyte is about 138.6 mAh/g, and the CSE PL-0.05 shows a higher initial specific capacity of 161.2 mAh/g with a specific capacity retention of 92.7% after 100 cycles, and during the 100 cycles, the CSE battery keeps a high Coulombic efficiency of 99.5~100%. Figure 5c,d exhibit that the voltage change of SSEs is small, which indicates that the solid-state lithium batteries have perfect cycling stability.

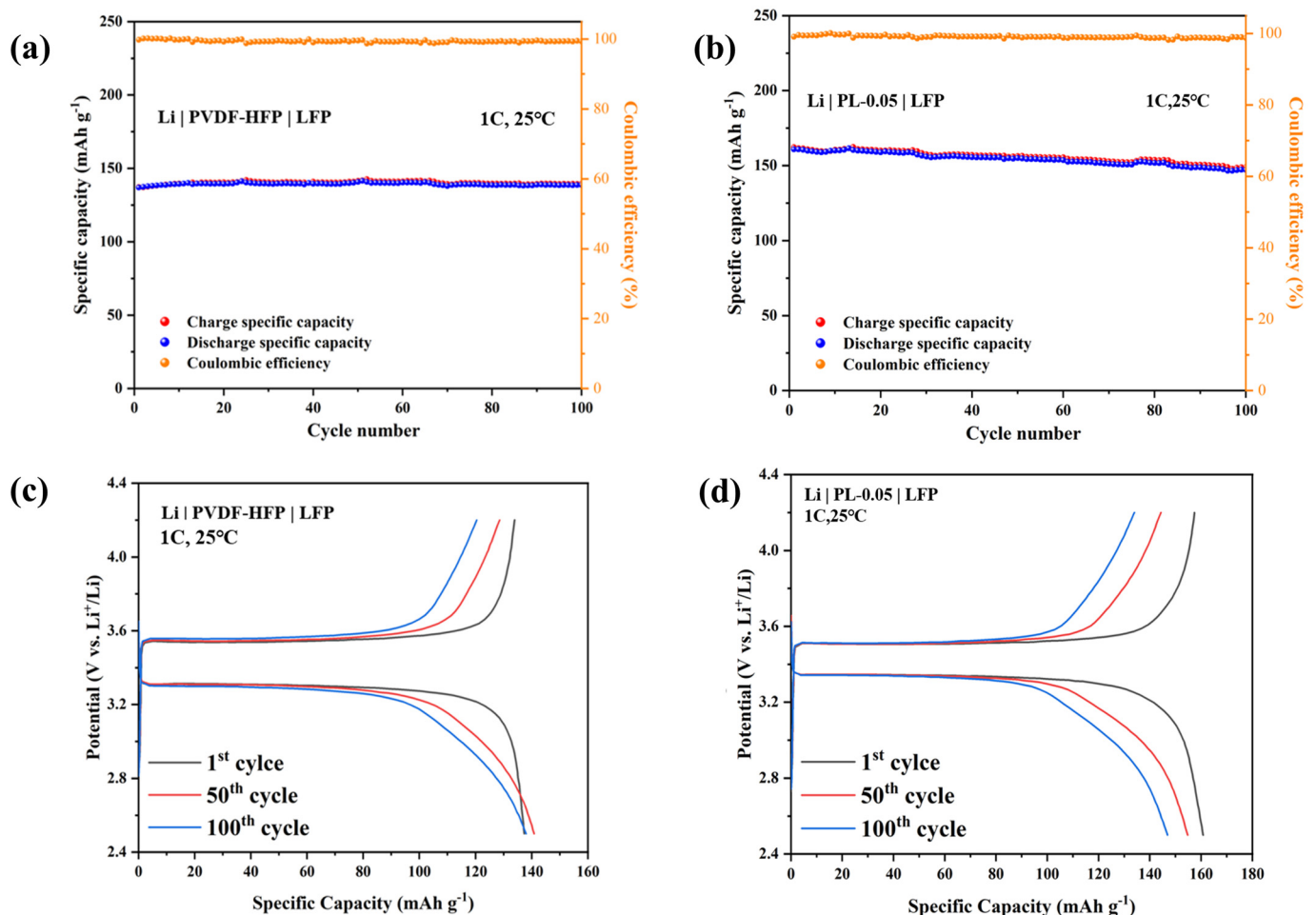


Figure 5. (a,b) Cycle performance comparison graphs, and (c,d) charge and discharge voltage platform of PVDF-HFP and PL-0.05 at room temperature and 1 C.

Figure S5 shows the Arrhenius plots of the SSEs at different temperatures (25~80 °C). The results indicate that the impedance of the samples decreases along with the temperature increase throughout the reheating process, and their ionic conductivities are all

improved along with the temperature. As shown in Table S1, the composite solid electrolyte PL-0.05 has the highest ionic conductivity of 1.76×10^{-4} S/cm at room temperature and the lowest activation energy of 0.76 eV. Composite solid electrolytes have higher ionic conductivity than polymer solid electrolytes, which is a contribution made by inorganic ceramic fillers. Because the LLZO is a fast ionic conductor, it greatly improves the ionic conductivity of the CSE, and the garnet also reduces the crystallinity of the polymer, thus increasing the mobility of the polymer chains and improving the lithium-ion transport efficiency inside the composite solid electrolyte.

As shown in Figure 6a, the important role of inorganic fillers is also emphasized by the results that the electrochemical window of pure polymer electrolytes is only 4.5 V, while the best-performing PL-0.05 composite solid-state electrolyte can reach 5.2 V. The improvement of the electrochemical window of the CSEs containing inorganic ceramic filler is attributed to the fact that LLZO possesses a high electrochemical window of more than 6 V. In addition, Lewis acid-base interactions on the surface of the LLZSNO stabilize the TFSI[−] and inhibit their migration, which also contributes to the oxidative stability of the CSEs. The solid electrolyte with a higher electrochemical window could be more adaptable to match the high-voltage cathode, laying the foundation for improving the overall energy density of the battery. Figure S6 shows the AC impedance and DC polarization test results of the SSEs at 25 °C. The Li⁺ transfer number of the PVDF-HFP solid electrolyte is about 0.24, while that of the PL-0.05 CSE is increased to 0.32. This enhancement could be explained by the following mechanism: the LLZO ceramic is an active conductor with a Li-ion transfer number near 1. The addition of LLZO ceramic filler can effectively enhance the Li transfer number of the polymer.

Figure 6b shows the rate performance of PVDF-HFP and PL-x. The results exhibit that when the rate was gradually increased, the PVDF-HFP electrolyte did not perform as well as the composite electrolyte, and its specific capacity decreased very quickly, to only 96 mAh/g at a rate of 5 C. When the rate was returned to 2 C, the overall specific capacity recovered. These test results indicate that the solid-state batteries equipped with PVDF-HFP/LLZSNO have a better rate performance and can adapt to more scenarios. Li | PL-0.05 | Li symmetric batteries were assembled for constant-current charge/discharge tests.

As shown in Figure 6c, the symmetric battery with a PL-0.05 composite solid electrolyte was able to cycle stably at room temperature and a current density of 0.1 mA/cm² for more than 1500 h without short-circuiting, and the polarization voltage did not increase and remained around 0.02 V when comparing the data of the first and last 5 turns. In the cycling stage of a symmetrical battery, if there is a sudden drop in voltage during the cycling process, it indicates that there is a short circuit caused by lithium dendrite piercing inside the battery, causing direct contact between the positive and negative electrodes, thus reducing the potential difference. This test result indicates that the PVDF-HFP/LLZSNO solid electrolytes have good interfacial stability and can be well contacted with lithium metal, with no lithium penetration.

In order to demonstrate the safety performance of the prepared composite solid-state electrolyte, the Li | PL-0.05 | LiFePO₄ pouch battery was assembled and tested for stability. As shown in Figure 6d, the pouch battery is able to work well in its initial state (the small bulb emits a red light). Subsequently, the battery was bent at 90° and 180° and still succeeded in lighting up the bulb under the bent condition. Next was impaling: when the battery was pierced by a nail, it worked as usual. Then, the battery was cut partially and it was found that the battery could continue to work without burning. The above experiments show that the PVDF-HFP/LLZSNO solid electrolyte has a high safety and reliability performance.

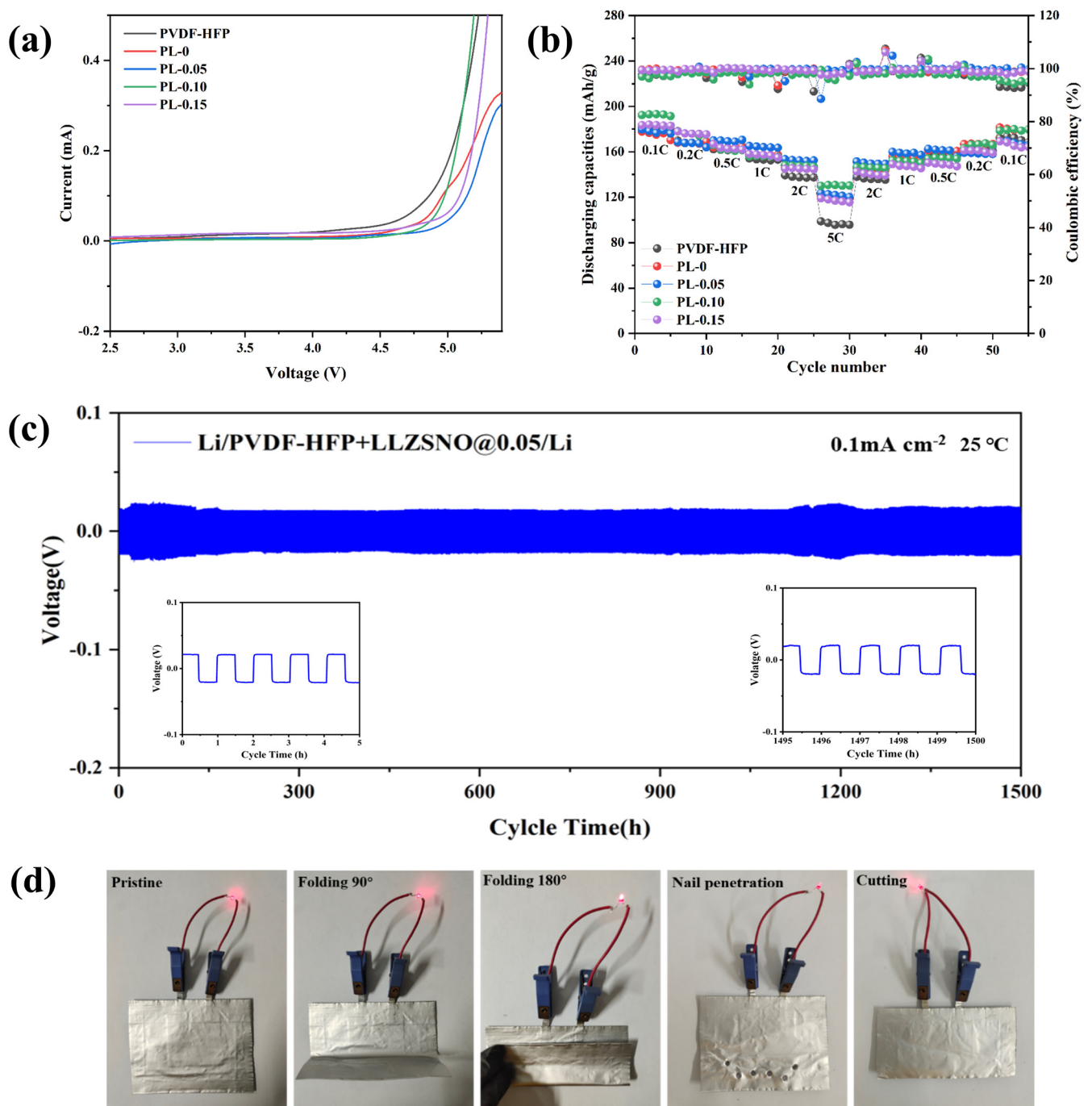


Figure 6. (a) LSV curve of PL-x electrolyte; (b) rate performance of PVDF-HFP and CSE; (c) constant current cycle test of lithium symmetric battery with PL-0.05; and (d) different states of pouch batteries light up small bulbs.

4. Conclusions

In this study, co-doped garnet-type LLZSNO solid electrolytes were successfully prepared by the high-temperature solid-phase method. The effects of different Nb contents on the structural properties and electrochemical performance and the performance of the composite solid electrolytes PVDF-HFP/LLZSNO were investigated. The co-doped LLZSNO shows the maximum ionic conductivities of 2.08×10^{-4} S/cm at room temperature and high relative densities of 88.7%. The results suggest that Sb/Nb dual substitution increases the Li vacancy concentration and transport channel. Due to the addition of LLZSNO

increasing the disorder of the polymer chain segments, the ionic conductivity, and thermal stability of CSEs, the prepared composite solid-state electrolyte PL-0.05 shows an ionic conductivity of 1.76×10^{-4} S/cm, an electrochemical stability window of 5.2 V, and a lithium-ion transfer number of 0.32. The Li/PL-0.05/Li symmetric battery could cycle for more than 1500 h at a current density of 0.10 mA/cm², and the Li/PL-0.05/LiFePO₄ battery exhibits excellent cycle and rate performance. The results show that the co-doped LLZSNO solid electrolyte has a potential application in composite solid electrolytes for higher energy density Li-ion batteries.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/app14073115/s1>: Figure S1: SEM and EDS mapping of LLZSNO powders; Figure S2: TG-DSC synchronous thermal analysis of solid electrolyte (a) PVDF-HFP, (b) PVDF-HFP/LLZSNO; Figure S3: SEM images comparison of surface morphology between (a) PVDF-HFP, and (b) PVDF-HFP/LLZSNO; Figure S4: Flexibility of (a) Polymer SSE membrane, and (b) CSE membrane; Figure S5: (a–e) EIS, and (f) Arrhenius plot of PVDF-HFP and PL-x solid electrolytes; Figure S6: EIS and DC polarization curves of (a) PVDF-HFP, and (b) PL-0.05; Table S1: Ionic Conductivity and Activation Energy of SSEs at Room Temperature.

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