



Residual alkali effect in LLZO-modified composite solid polymer electrolyte

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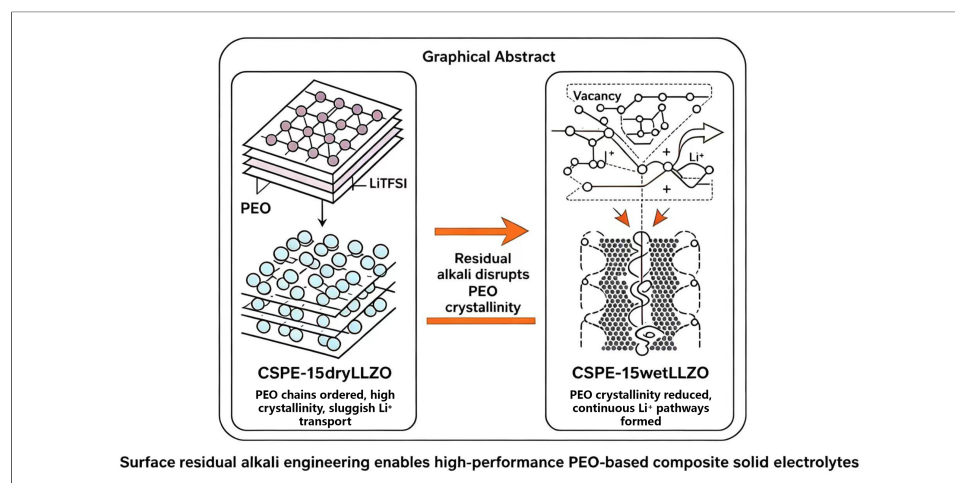
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Abstract

Solid polymer electrolytes (SPEs) are regarded as ideal solid electrolytes for next-generation lithium-ion batteries due to their high safety, but their low ionic conductivity limits practical applications. The incorporation of garnet-type Lithium Lanthanum Zirconium Oxide (LLZO)-based electrolytes with high Li^+ conductivity is an effective strategy to enhance the performance of polyethylene oxide (PEO)-based SPEs. In this study, highly Li^+ -conductive Ga-doped LLZO ($\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$) was prepared by wet and dry methods, Ga-doped ($\text{Ga} = 0.2$) LLZO is referred to as LLZO for brevity throughout this manuscript, yielding samples denoted as wet-LLZO and dry-LLZO, with abundant and minimal surface residual alkali, respectively. These LLZO nanoparticles with different residual alkali were incorporated as fillers in composite solid polymer electrolytes (CSPEs). Studies demonstrate that the residual alkali, such as Li_2CO_3 , on the LLZO surface effectively disrupts the ordered arrangement of PEO segments, significantly reducing their crystallinity and thus facilitating Li^+ transport. Based on this, CSPE with 15 wt% wet-LLZO achieves a high ionic conductivity of 0.80 mS cm^{-1} and a lithium-ion transference number of 0.36 at



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60 °C. The assembled Li/LiFePO₄ all-solid-state battery maintains a discharge specific capacity of 142.5 mAh g⁻¹ and a Coulombic efficiency exceeding 99% after 300 cycles at a 1.0 C rate. This work reveals the role of residual surface alkali in the LLZO composite solid electrolyte, providing novel insights for designing high-performance solid-state batteries through filler surface engineering.

INTRODUCTION

Solid-state lithium batteries (SSLBs) have become a key focus in next-generation energy storage technology development due to their inherent safety and high energy density. The performance of their core component - solid-state electrolytes (SSEs) - directly determines the overall battery performance^[1]. Among various solid-state electrolytes, polyethylene oxide (PEO)-based solid polymer electrolytes (SPEs) have been extensively studied for their excellent flexibility, good interfacial compatibility, and ease of processing^[4]. However, the high crystallinity of PEO results in low room-temperature ionic conductivity (typically 10⁻⁶-10⁻⁵ S cm⁻¹), which severely limits its practical applications at room temperature^[8]. To overcome this bottleneck, introducing inorganic fillers into the PEO matrix - has been proven to be one of the effective strategies^[11].

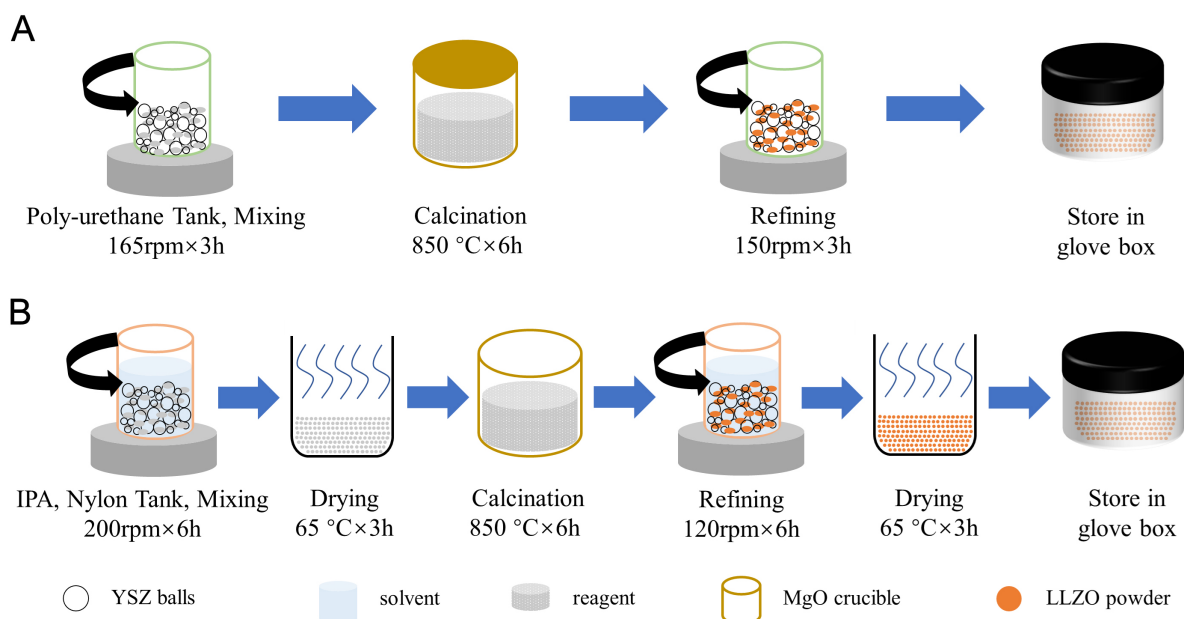
Among various inorganic fillers, garnet-type Lithium Lanthanum Zirconium Oxide (LLZO) has garnered significant attention due to its outstanding bulk lithium-ion conductivity and excellent electrochemical stability^[16]. There is much literature on the addition of LLZO nanoparticles and nanowires to polymer electrolytes to improve electrolyte performance^[22]. However, LLZO materials face a common practical challenge: their extreme sensitivity to moisture (H₂O) and carbon dioxide (CO₂) in the air, leading to frequent H⁺/Li⁺ exchange reactions on the surface, resulting in residual alkali layers such as LiOH and Li₂CO₃^[25,26]. Traditional research has typically regarded residual surface alkali as insulating impurity phases, believing they increase interfacial impedance and hinder ion transport^[27,28]. Consequently, extensive efforts have focused on removing residual alkali through post-processing techniques such as acid washing and heat treatment, aiming to achieve the filler's intrinsic high conductivity^[29,30].

In this work, we unveil the positive role of residual surface alkali in optimizing electrolyte interface transport. Through precise control of the synthesis pathway, we prepared two LLZO fillers with distinct surface chemical states. [Scheme 1A](#) demonstrates the dry-LLZO preparation using a solvent-free method (dry method)^[31], where ball milling and calcination were conducted under fully sealed, air-free conditions, yielding a clean surface with minimal residual alkali. As shown in [Scheme 1B](#), wet-LLZO was synthesized via solid-state synthesis and ground in isopropanol solvent and air (wet method)^[32], resulting in a surface rich in residual Li₂CO₃ alkali layer. Both fillers were incorporated into the PEO/LiTFSI system at equal proportions (15 wt%) to prepare the corresponding composite electrolytes CSPE-15 wet-LLZO and CSPE-15 dry-LLZO, enabling systematic investigation of the differential effects of surface residual alkali on electrolyte structure and performance. Comprehensive characterization reveals that residual alkali, such as Li₂CO₃ on the wet-LLZO surface, disrupts the regularity of PEO chain segments, thereby substantially decreasing their crystallinity. Benefiting from this, CSPE-15 wet-LLZO achieves a high ionic conductivity of 0.80 mS cm⁻¹ and a lithium-ion transference number of 0.36 at 60 °C. The assembled Li/LiFePO₄ all-solid-state battery maintains a discharge specific capacity of 142.5 mAh g⁻¹ and a coulombic efficiency exceeding 99% after 300 cycles at a 1.0 C rate. This study deepens the understanding of the surface characteristics of LLZO in SPEs and provides a novel, promising strategy for designing high-performance composite solid-state electrolytes.

EXPERIMENTAL

Materials

PEO (Aladdin, M_v = 600,000 g mol⁻¹) and LiTFSI (Aladdin, 99%) were dried under vacuum at 65 °C and 110 °C, respectively, for more than 24 h. After drying, the above materials were placed in a glove box filled with argon gas (less than 0.01 ppm H₂O and O₂).



Scheme 1. Schematic diagram of (A) dry-LLZO preparation via solvent-free method, (B) wet-LLZO preparation via solid-phase synthesis. LLZO: $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$, dry-LLZO: LLZO by a dry method; wet-LLZO: LLZO by a wet method; YSZ: yttria-stabilized zirconia

Preparation of Ga-LLZO particles

In this work, the LLZO particles were added into the SPEs. LLZO particles with a Ga = 0.2 doping level are confirmed as having the highest Li^+ conductivity, which is consistent with our previous work^[33].

Ga-doped (Ga = 0.2) LLZO was prepared via solid-state synthesis, with a stoichiometric ratio of lithium hydroxide monohydrate to lithium oxide. The starting materials - $\text{LiOH}\cdot\text{H}_2\text{O}$ (AR, 98%), La_2O_3 (99.99%, preheated at 900 °C for 12 h), ZrO_2 (AR, 3N), and Ga_2O_3 (AR, 99.99%) (total 0.2 mol, approximately 204.49 g) - were weighed to ensure no excess lithium source. Isopropanol (IPA, 300–350 g) was then used as the solvent, and yttria-stabilized zirconia (YSZ) beads (Φ 10 mm, 100 g; Φ 5 mm, 600 g) were employed as the grinding media. The mixture was ball-milled at 200 rpm for 6 h in a ball mill (MITR). After vacuum drying at 65 °C for 3 h, 80 g of the precursor powder was calcined for 6 h in an uncovered magnesium oxide crucible at 850 °C to obtain cubic-phase powder.

The powder was then subjected to wet ball milling at 120 rpm for 6 h. After drying, it was sieved through a 200-mesh sieve to obtain LLZO powder with particle sizes approaching the nanoscale. The powder was vacuum-dried at 65 °C for 3 h and stored in a glovebox for further use.

Dry-LLZO was prepared by a solvent-free method: 53.71 g of $\text{LiOH}\cdot\text{H}_2\text{O}$ (AR, 98%), 97.74 g of La_2O_3 (99.99%, preheated at 900 °C for 12 h), 49.29 g of ZrO_2 (AR, 3N), and 3.75 g of Ga_2O_3 (AR, 99.99%) (total 0.2 mol, ~204.49 g) were weighed in stoichiometric proportions, with the lithium source not exceeding the required amount. A polyurethane tank was used as the ball mill, and YSZ beads (Φ 10 mm, 100 g; Φ 5 mm, 600 g) were used as the grinding media. The mixture was ball-milled at 165 rpm for 3 h in a ball mill (MITR). The ball mill tank was sealed with high-temperature tape to prevent the entry of water vapor and carbon dioxide from the air. 80 g of the precursor powder was then calcined at 850 °C in a covered MgO crucible for 6 h to obtain cubic-phase LLZO powder. The powder was subsequently returned into the polyurethane tank and ball-milled at 150 rpm for 3 h, with the tank again sealed with high-temperature tape. The powder was filtered through a 200-mesh sieve in a glove box to obtain dry-LLZO powder with particle size approaching the nanoscale, which was then stored in the glove box.

Preparation of composite solid electrolytes

PEO and LiTFSI lithium salt were dissolved in anhydrous acetonitrile at a ratio of EO:Li⁺ = 18:1. Wet-LLZO or dry-LLZO fillers (15 wt%) were added to the mixture. The mixture was stirred at 60 °C for 12 h to form a homogeneous slurry, which was then cast into a film using solution casting. After initial drying at room temperature, the film was dried in a vacuum at 60 °C for 24 h, yielding composite electrolyte films with a thickness of approximately 80 μm (labeled as CSPE-15 wet-LLZO and CSPE-15 dry-LLZO).

Material characteristics

The LLZO fillers with varying surface residual alkali content were first prepared through solid-phase synthesis (wet method) and solvent-free synthesis (dry method). The wet synthesis method used isopropanol as the solvent, with the mixture calcined at 850 °C in an air environment for 6 h to form a rich LiOH/Li₂CO₃ residual alkali layer on the filler surface (denoted as wet-LLZO). The dry synthesis method involved solvent-free ball milling and calcination under strict sealed conditions to avoid air contact, yielding LLZO with minimal surface residual alkali (denoted as dry-LLZO). Subsequently, the composite electrolyte was prepared via solution casting: PEO and LiTFSI (EO:Li⁺ = 18:1) were dissolved in anhydrous acetonitrile, with 15 wt% wet-LLZO or dry-LLZO fillers added, respectively. The mixture was stirred at 60 °C for 12 h to form a homogeneous slurry, which was cast into a film and then vacuum-dried to obtain an electrolyte film with a thickness of approximately 80 μm (labeled as CSPE-15 wet-LLZO and CSPE-15 dry-LLZO, respectively). The physical properties were characterized by X-ray diffraction (XRD) to analyze the crystal structure of the filler and the crystallinity of PEO, Scanning Electron Microscopy - Energy Dispersive X-ray Spectrometry (SEM-EDS) to observe the morphology and dispersion of the filler, and X-ray photoelectron spectroscopy (XPS)/Fourier Transform Infrared Spectroscopy (FTIR)/Raman to characterize the surface chemistry (e.g., the lattice Li-O component of wet-LLZO exhibits a Li 1s binding energy of 54.2 eV, and the Li₂CO₃ peak position of C 1s is 289.85 eV). In [Supplementary Figure 1](#), Brunauer-Emmett-Teller (BET) was used to measure the specific surface area (wet-LLZO is 10.14 m² g⁻¹, higher than dry-LLZO's 2.45 m² g⁻¹). Differential scanning calorimetry (DSC)/Thermogravimetric Analysis (TGA) was employed to analyze the glass transition temperature and thermal stability.

Electrochemical testing

All coin cells were assembled in a glove box and stored in a constant temperature chamber awaiting testing. Electrochemical impedance spectroscopy (EIS) tests were performed using an Alternating Current (AC) impedance spectrometer (IVIUM nSTAT) with a frequency range of 0.1 HZ to 1 MHZ and a bias voltage of 10 mV. Coin cell cases of type CR2016 were used for assembly, and the electrolyte film (thickness ~80 μm) was sandwiched between two stainless steel plates (diameter = 16 mm) and tested at a temperature range of 30 °C to 80 °C. The AC impedance spectra (EIS) of the electrolyte films at different temperatures were obtained by this method to calculate the Li⁺ conductivity of the corresponding electrolytes [[Supplementary Figure 2](#)]. The calculation equation is as follows^[38]:

$$\sigma = \frac{L}{RS} \quad (1)$$

where σ is the Li⁺ conductivity, L is the thickness of the electrolyte membrane, R is the intrinsic impedance of the electrolyte (intercept of the Nyquist plot on the x-axis), and S is the effective area of the electrolyte.

Assembled with two lithium metal cells (diameter = 16 mm) as non-blocking electrodes using CR2032-type coin cell cases. The Li⁺ mobility of the electrolyte membrane was measured by the chrono-current method (potential applied to the cell was 10 mV) and AC impedance spectroscopy, calculated as follows^[21]:

$$t^+ = \frac{I_{SS} (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_{SS} R_{SS})} \quad (2)$$

where t^+ is the Li^+ transference number, I_0 and I_{ss} represent the initial and steady-state currents, respectively, ΔV denotes the external polarization voltage (10 mV), and R_0 and R_{ss} represent the electrolyte/Li interface resistance in the initial and steady states.

The electrochemical stability window was evaluated using linear sweep voltammetry (LSV) at a scan rate of 1 mV s^{-1} , within a voltage range of 0–6 V, and at a test temperature of 60°C . Critical current density (CCD) tests were conducted using Li/electrolyte/Li batteries, with current incrementally increased from 0.05 mA cm^{-2} in stepwise increments, each step lasting 1 h (0.5 h stripping + 0.5 h plating), until the battery short-circuited.

The full-cell performance evaluation utilized CR2032 battery casings to assemble Li/electrolyte/ LiFePO_4 batteries. The cathode active material loading was maintained at $1.5\text{--}4.0 \text{ mg cm}^{-2}$, with a voltage window set between 2.5 and 4.0 V. Using the Neware battery testing system, constant-current charge-discharge tests were conducted at rate ranges of 0.2–3.0 C ($1 \text{ C} = 170 \text{ mA g}^{-1}$), with test temperatures including 30 and 60°C . Cycle performance testing was performed at 0.2 C rate for 100 cycles, evaluating capacity retention and Coulombic efficiency. All battery assemblies were fabricated in an argon glove box ($\text{H}_2\text{O}/\text{O}_2 < 0.01 \text{ ppm}$) and pre-treated in a 60°C vacuum oven for 12 h prior to testing to ensure interface stability. The experimental chemicals and reagents, as well as the experimental instruments and equipment used, are listed in [Supplementary Tables 1](#) and [2](#), respectively.

RESULTS AND DISCUSSION

[Supplementary Figure 3](#) illustrates the preparation process of the PEO-based composite electrolytes containing LLZO fillers. The digital photographs in [Supplementary Figure 4](#) show the 18 mm-diameter SPE-blank, CSPE-15 dry-LLZO, and CSPE-15 wet-LLZO electrolyte membranes, confirming that flexible and self-standing films were successfully obtained. The morphologies of dry-LLZO and wet-LLZO were examined by SEM, as shown in [Figure 1A](#) and [1B](#). The particle-size distribution histograms inserted in these two figures were obtained from SEM image analysis. The average particle size of dry-LLZO is $0.908 \pm 0.346 \text{ }\mu\text{m}$, while that of wet-LLZO is $0.859 \pm 0.422 \text{ }\mu\text{m}$, indicating that both fillers are mainly distributed in the submicrometer range. Although the two samples show similar average particle sizes, wet-LLZO presents a slightly broader size distribution, which may be associated with partial aggregation during wet processing and subsequent drying. In terms of morphology, dry-LLZO exhibits a more distinct granular structure and a relatively dry surface, whereas wet-LLZO shows less pronounced granular features. This difference is likely related to IPA-assisted mixing and the formation of surface residual alkali during air exposure. EDS elemental mapping further confirms the successful preparation of both dry-LLZO and wet-LLZO. As shown in [Figure 1C–E](#), the electrolyte membrane of SPE-blank, CSPE-15 dry-LLZO, and CSPE-15 wet-LLZO exhibits a uniform thickness of approximately $80 \text{ }\mu\text{m}$. The cross-sections of SPE-blank and CSPE-15 wet-LLZO are relatively smooth and dense, whereas CSPE-15 dry-LLZO shows a considerably rougher cross-sectional morphology. This phenomenon can be ascribed to the inferior particle size uniformity of the dry-LLZO powder and its poor dispersibility in acetonitrile solvent without prior solvent infiltration.

The XRD patterns of dry-LLZO and wet-LLZO particles are shown in [Figure 2A](#). Both wet- and dry-LLZO particles exhibited cubic phases after calcination at 850°C for 6 h. Notably, the dry-LLZO displayed a broad full width at half maximum (FWHM) in its XRD pattern, accompanied by weak La_2O_3 impurity peaks (PDF#05-0602). This phenomenon is attributed to the high hardness of La_2O_3 , which led to incomplete pulverization and uneven mixing during the dry mixing process. However, trace amounts of La_2O_3 are not expected to significantly affect the final sintered powder^[39]. The FTIR spectrum of wet-LLZO [[Figure 2B](#)] exhibits distinct characteristic peaks assigned to $\text{LiOH}\cdot\text{H}_2\text{O}$ and Li_2CO_3 (labeled i–viii). The peaks

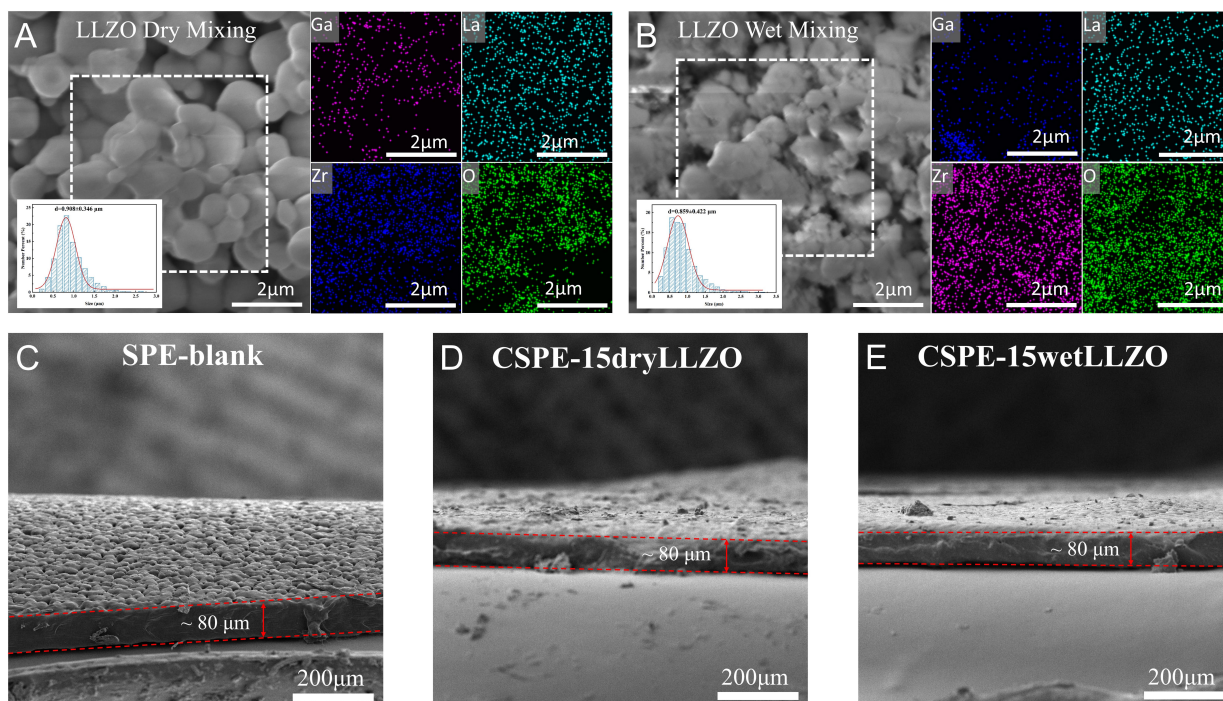


Figure 1. (A) Surface SEM image of LLZO prepared by the solvent-free method, (B) Surface SEM image of LLZO prepared by the solid-state synthesis method, and the insets in Figure 1A and B show the corresponding particle-size distribution histograms obtained from SEM image analysis. Cross-sectional SEM images of (C) SPE-blank, (D) CSPE-15 dry-LLZO, and (E) CSPE-15 wet-LLZO. SEM: Scanning electron microscopy; LLZO: $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_{12}\text{O}_{12}$.

corresponding to $\text{LiOH}\cdot\text{H}_2\text{O}$ are identified as follows: the O-H stretching vibration at $3,566\text{ cm}^{-1}$ (i), the H-O-H bending vibrations at $1,579\text{ cm}^{-1}$ (ii) and 999 cm^{-1} (iii), and the O-H-related vibrational modes at 678 cm^{-1} and 632 cm^{-1} (iv and v). Meanwhile, the characteristic peaks of Li_2CO_3 are observed at $1,504\text{ cm}^{-1}$ and $1,438\text{ cm}^{-1}$ (vi and vii, assigned to the C=O stretching of CO_3^{2-}) and at 863 cm^{-1} (viii, assigned to the C=O bending of CO_3^{2-}). These results confirm the presence of substantial $\text{LiOH}\cdot\text{H}_2\text{O}$ and Li_2CO_3 on the surface of wet-LLZO particles. This surface residual alkali can be rationalized by the following mechanism: during ball milling, H^+ ions derived from IPA and adsorbed moisture undergo ion exchange with Li^+ ions in the LLZO lattice, generating $\text{CH}_3\text{CH}(\text{OLi})\text{CH}_3$ and $\text{LiOH}/\text{LiOH}\cdot\text{H}_2\text{O}$. During the subsequent drying process, these reaction products further react with atmospheric H_2O (ambient concentration: $10\sim 16\text{ g m}^{-3}$) and CO_2 (atmospheric concentration: $\sim 0.8\text{ g m}^{-3}$), ultimately leading to the formation of Li_2CO_3 on the surface of wet-LLZO^[40]. In contrast, the FTIR spectrum of dry-LLZO exhibits almost no characteristic peaks assignable to $\text{LiOH}\cdot\text{H}_2\text{O}$ (i-v), with only extremely weak residual signals corresponding to Li_2CO_3 (vi-viii), confirming the presence of only a negligible amount of surface residual alkali (LiOH and Li_2CO_3). Raman spectroscopy [Figure 2C] reveals that the characteristic peaks of both dry-LLZO and wet-LLZO are derived from the same LLZO matrix. Specifically, the Raman spectrum of wet-LLZO exhibited a distinct characteristic peak of Li_2CO_3 , while dry-LLZO showed only a weak Li_2CO_3 peak. This result further confirms that the surface of dry-LLZO contains negligible residual alkali.

To further elucidate differences between LLZO particles synthesized by wet and dry methods, XPS was performed on both wet-LLZO and dry-LLZO samples. In the Li 1s spectrum [Figure 2D], Li_2CO_3 exhibits characteristic Li-O peaks at 54.83 eV (dry-LLZO) and 55.18 eV (wet-LLZO), while the peaks centered near 54.2 eV correspond to the Li-O bond within the LLZO lattice. Comparison of the two samples reveals a significantly stronger Li_2CO_3 peak for wet-LLZO relative to dry-LLZO. Analysis of the C 1s spectrum [Figure 2E] shows a peak at 289.85 eV , which, according to literature assignments, is associated with the C-O bond

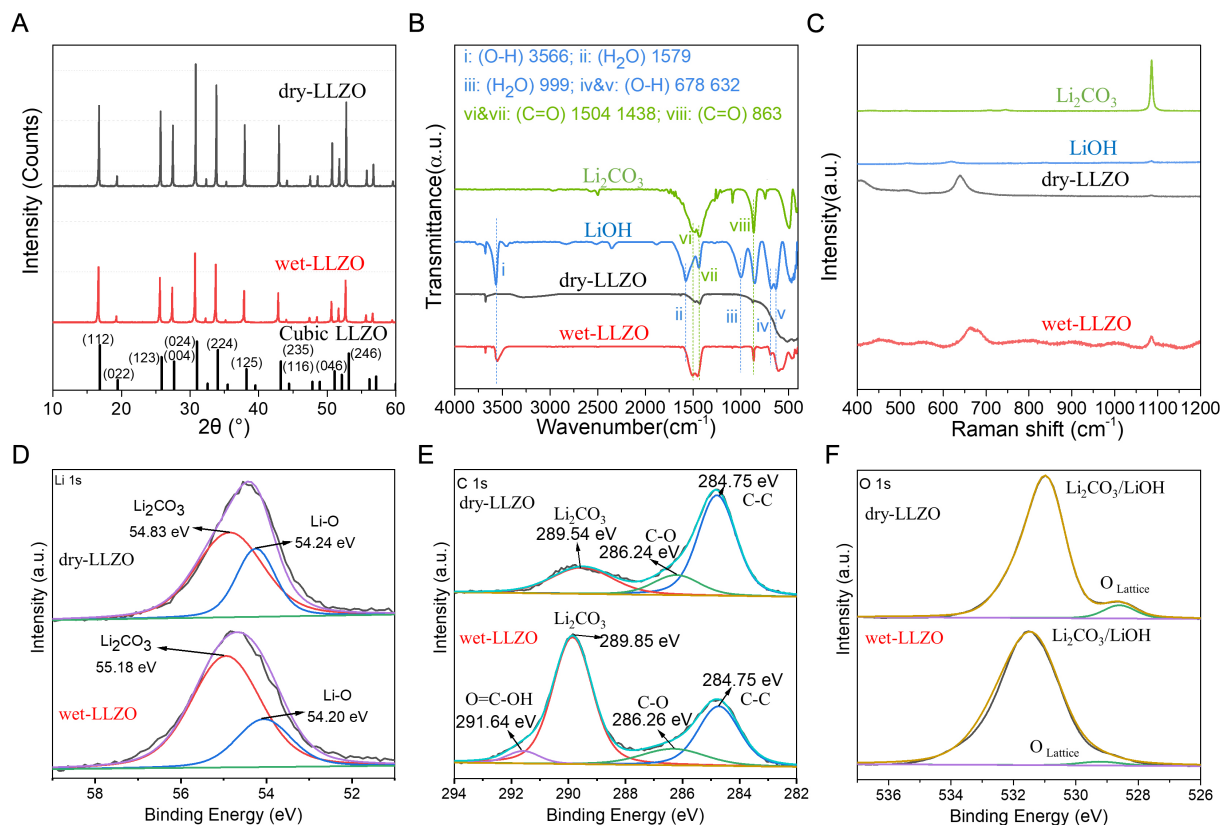


Figure 2. (A) XRD patterns of wet-LLZO and dry-LLZO, (B and C) FTIR and Raman spectra of wet-LLZO, dry-LLZO, LiOH, and Li₂CO₃, (D–F) high-resolution spectra of Li 1s, C 1s, and O 1s for dry-LLZO and wet-LLZO. XRD: X-ray diffraction; dry-LLZO: LLZO by a dry method; wet-LLZO: LLZO by a wet method; FTIR: fourier transform infrared spectroscopy; LLZO: Li_{6.4}Ga_{0.2}La₃Zr₂O₁₂.

in Li₂CO₃ [41,42]. This carbonate-related peak is markedly more intense in wet-LLZO than in dry-LLZO, consistent with the observations in the Li 1s spectrum. In the O 1s spectrum [Figure 2F], peaks centered near 531.0 eV are attributed to Li₂CO₃ and LiOH species, while the peak at approximately 529 eV arises from lattice oxygen within LLZO. Wet-LLZO exhibits a significantly higher peak intensity ratio of residual alkali (Li₂CO₃/LiOH) to lattice oxygen than dry-LLZO, indicating more abundant surface alkali residues in the wet-synthesized material [43]. Taken together, these XPS results demonstrate that wet- and dry-processed LLZO powders possess distinctly different surface alkali characteristics: wet-LLZO exhibits substantial residual Li₂CO₃ and LiOH, whereas dry-LLZO shows minimal surface alkali.

XRD was employed to evaluate the crystallinity of CSPE-15 wet-LLZO, CSPE-15 dry-LLZO, and SPE-blank [Figure 3A]. The SPE-blank sample displayed well-defined PEO crystalline peaks at the 2θ positions of 19° and 23°, corresponding to the (120) and (112) planes, respectively, as indexed in the PEO reference pattern (PDF card 45-0109). Incorporation of either wet-LLZO or dry-LLZO particles decreased the intensities of these PEO crystalline peaks, reflecting reduced polymer crystallinity. Notably, CSPE-15 wet-LLZO exhibited a more pronounced attenuation of PEO diffraction intensity compared to CSPE-15 dry-LLZO. DSC measurements [Figure 3B] further corroborated these findings. The glass transition temperature (T_g) of CSPE-15 wet-LLZO was -44.51 °C, lower than that of CSPE-15 dry-LLZO (-42.86 °C) and substantially lower than that of SPE-blank (-41.96 °C). This progressive decrease in T_g indicates enhanced disruption of PEO chain packing and reduced crystallinity upon LLZO incorporation, with wet-LLZO exerting a stronger effect than dry-LLZO. Collectively, XRD and DSC analyses consistently demonstrate that wet-LLZO incorporation is more effective than dry-LLZO in suppressing PEO crystallinity, which may be attributed to differences in particle-polymer interfacial interactions and dispersion behavior.

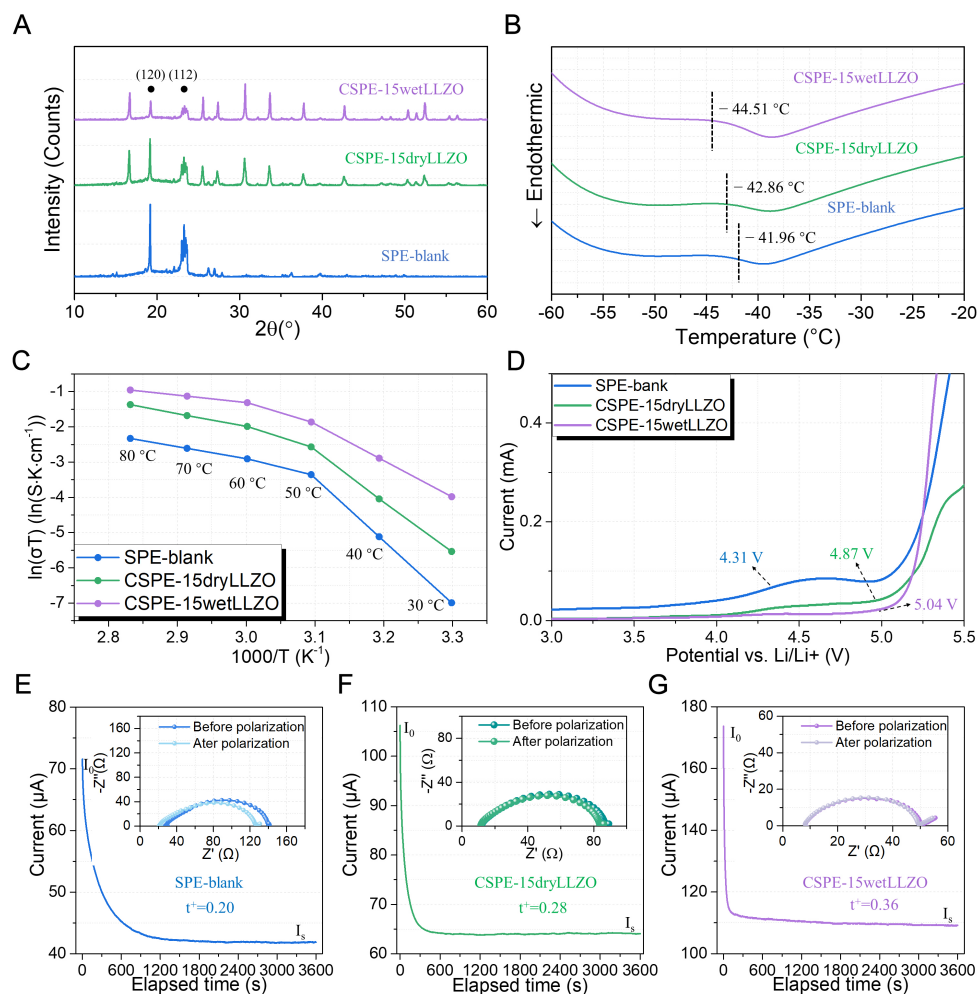


Figure 3. (A) XRD patterns of CSPE-15 wet-LLZO, CSPE-15 dry-LLZO, and SPE-blank, (B) DSC curves of CSPE-15 wet-LLZO, CSPE-15 dry-LLZO, and SPE-blank, (C) Lithium-ion conductivity curves at 30–80 °C; (D) LSV curves at 60 °C for SPE-blank, CSPE-15 dry-LLZO, and CSPE-15 wet-LLZO, (E–G) Chronoamperometry (CA) curves and EIS spectra before and after polarization at 60 °C and a potential of 0.01 V for the same materials. XRD: X-ray diffraction; DSC: differential scanning calorimetry; SPE: solid polymer electrolyte; LSV: linear sweep voltammetry; EIS: electrochemical impedance spectroscopy; LLZO: $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$.

The thermal stability of SPE-blank, CSPE-15 wet-LLZO, and CSPE-15 dry-LLZO was evaluated and analyzed using TGA curves [Supplementary Figure 5]. Before 200 °C, all three samples exhibited approximately 2% to 3% weight loss due to water vapor evaporation. Between 240 and 700 °C, significant weight loss was observed, caused by the decomposition of PEO and LiTFSI. Further TGA analysis using Derivative Thermogravimetry (DTG) revealed that the thermal decomposition temperature of the SPE-blank electrolyte was 402 °C. After adding the fillers, the decomposition temperatures of CSPE-15 dry-LLZO and CSPE-15 wet-LLZO increased to 417 and 414 °C, respectively. Therefore, the addition of wet-LLZO and dry-LLZO fillers can enhance the thermal stability of CSPEs.

To investigate the electrochemical effects of residual alkali on the surface of LLZO on composite electrolytes, fundamental electrochemical performance tests were conducted on SPE-blank, CSPE-15 dry-LLZO, and CSPE-15 wet-LLZO. The Li^+ conductivity curves with temperature variation are shown in Figure 3C. At 60 °C, the Li^+ conductivity of CSPE-15 wet-LLZO was 0.8 mS cm^{-1} , while that of CSPE-15 dry-LLZO and SPE-blank were only 0.41 mS cm^{-1} and 0.16 mS cm^{-1} , respectively. This is mainly attributed to the abundant residual alkali of Li_2CO_3 on the wet-LLZO surface, which further reduces the crystallinity of PEO on the basis

of LLZO. As the PEO segment moves, the ionic conductivity is enhanced. The non-uniform particle size of dry-LLZO results in poor dispersion within acetonitrile, leading to suboptimal interfacial contact between the composite electrolyte film and the electrode. Furthermore, the presence of large particles impedes Li^+ migration by obstructing efficient transport pathways. Consequently, the ionic conductivity of CSPE-15 dry-LLZO is lower than that of CSPE-15 wet-LLZO.

The electrochemical stability of the PEO-based solid electrolytes was evaluated using LSV, as shown in Figure 3D. CSPE-15 wet-LLZO maintained a stable voltage plateau up to approximately 5.04 V, indicating superior oxidative stability. In contrast, CSPE-15 dry-LLZO and SPE-blank reached instability at lower potentials of about 4.87 and 4.31 V, respectively, highlighting their limited voltage tolerance. Figure 3E-G present the Li^+ transference number (t_{Li^+}) for the three samples: CSPE-15 wet-LLZO exhibited a t_{Li^+} of 0.36, significantly higher than that of CSPE-15 dry-LLZO (0.28) and SPE-blank (0.20). This trend suggests that the incorporation of wet-LLZO not only enhances ionic conductivity but also improves the selective transport of Li^+ ions, which is critical for the performance of solid-state battery systems.

The critical current density (CCD) is a key parameter for assessing a polymer electrolyte's ability to suppress lithium dendrite penetration under high current conditions. Symmetric Li/SPEs/Li cells were assembled to determine CCD, with results illustrated in Figure 4A-C. The current density was increased stepwise at a rate of 0.05 mA cm^{-2} per hour (0.5 h stripping followed by 0.5 h plating), and the corresponding cell voltage was monitored continuously. Lithium symmetric cells incorporating CSPE-15 dry-LLZO and SPE-blank exhibited pronounced polarization at current densities of 0.4 mA cm^{-2} and 0.1 mA cm^{-2} , respectively, indicative of internal short circuits that precluded sustained cycling. In contrast, the cell employing CSPE-15 wet-LLZO maintained stable operation until reaching a short-circuit event at 0.65 mA cm^{-2} . This demonstrates that CSPE-15 wet-LLZO possesses markedly superior lithium dendrite suppression capability, enabling stable lithium stripping/plating at higher current densities compared with both dry-LLZO and blank polymer electrolyte systems.

EIS of the three lithium symmetric cells are shown in Figure 4D. The semicircular feature in the high- to mid-frequency range corresponds to the charge transfer resistance (R_{ct})^[44]. Among the samples, the Li/CSPE-15 wet-LLZO/Li cell exhibited the lowest R_{ct} value, indicating that the presence of wet-LLZO effectively buffers interfacial potential fluctuations and thereby promotes interfacial stability during cycling. The long-term galvanostatic cycling performance of the lithium symmetric cells was evaluated at 60°C under a current density of 0.1 mA cm^{-2} with a fixed capacity cutoff of 0.1 mAh cm^{-2} , as shown in Figure 4E. The Li/CSPE-15 wet-LLZO/Li cell demonstrated exceptional electrochemical durability, sustaining stable cycling for over 1,000 h with a steady polarization voltage stabilized at approximately 30 mV. In contrast, the Li/SPE-blank/Li and Li/CSPE-15 dry-LLZO/Li cells maintained relatively high initial polarization voltages and experienced a rapid decline in polarization voltage to 0 V after 248 and 381 h, respectively. This abrupt voltage drop is attributed to irreversible degradation of the electrolyte-electrode interfacial layer induced by repeated lithium deposition and stripping. Consequently, these results underscore that the CSPE-15 wet-LLZO composite effectively preserves the structural and electrochemical integrity of the electrolyte/lithium metal interface. This interfacial robustness is pivotal to the superior long-term stability observed in the wet-LLZO-based system.

The EIS measurement of $\text{Li}|\text{LiFePO}_4$ full cells with different SPEs was tested at 60°C [Figure 5A]. The obtained EIS spectra consist of ohmic impedance (first semicircle), charge transfer impedance (middle semicircle), and diffusion resistance (linear portion)^[45]. Compared to the SPE-blank control, the full cell incorporating CSPE-15 wet-LLZO exhibited a significant reduction in ohmic impedance from 21.4Ω to 18.2Ω and charge transfer impedance from 101.0Ω to 28.5Ω . These findings indicate that the addition of

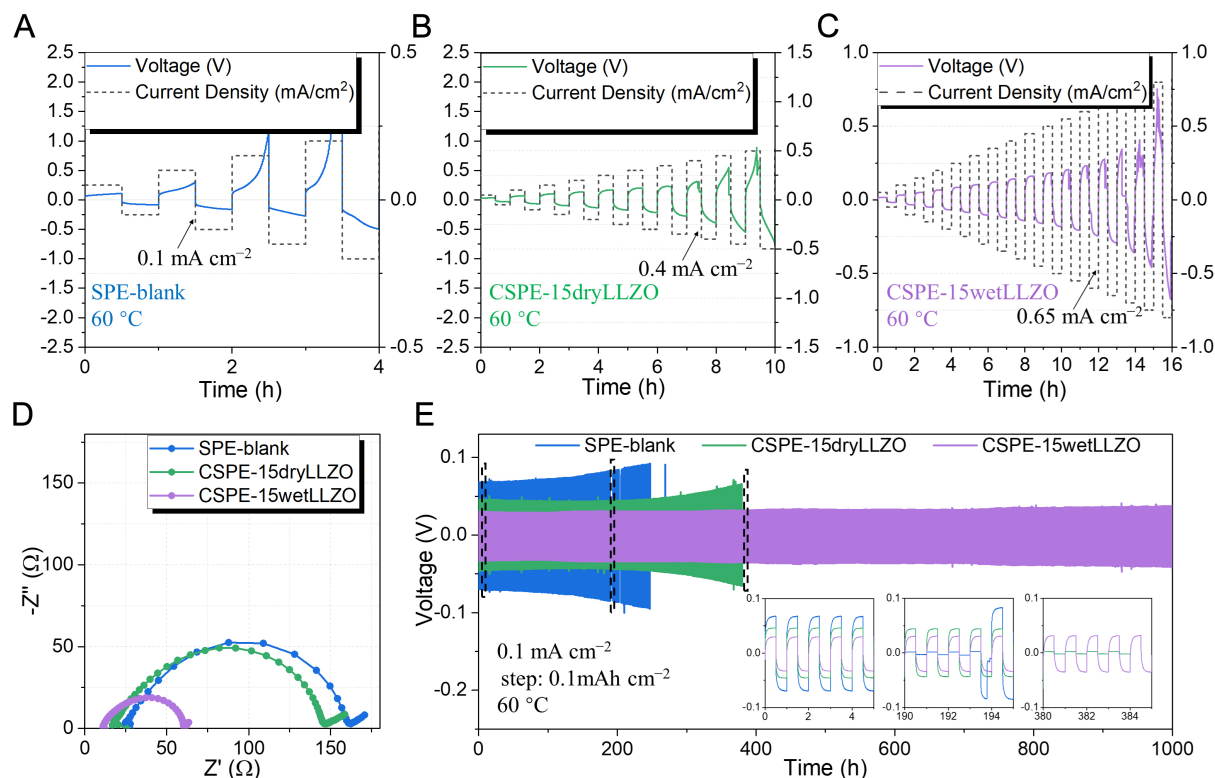


Figure 4. (A–C) CCD curves of Li/SPE-blank/Li, Li/CSPE-15 dry-LLZO/Li, and Li/CSPE-15 wet-LLZO/Li batteries at 60 °C, (D and E) EIS spectra and voltage-time curves at 0.1 mA cm⁻² before long cycling for the same batteries; and (insert) magnified view of local voltage distribution. CCD: Critical current density; EIS: electrochemical impedance spectroscopy; SPE: solid polymer electrolyte; LLZO: Li_{6.4}Ga_{0.2}La₃Zr₂O₁₂.

wet-LLZO effectively facilitates Li⁺ migration and lowers the overall impedance within the SPEs. **Figure 5B** presents the rate performance of Li/SPEs/LiFePO₄ full cells. At current rates of 0.2, 0.5, 1.0, and 3.0 C, the Li/CSPE-15 wet-LLZO/LiFePO₄ cell delivered discharge-specific capacities of 167.7, 166.8, 159.9, and 105.3 mAh g⁻¹, respectively. In comparison, the Li/CSPE-15 dry-LLZO/LiFePO₄ and Li/SPE-blank/LiFePO₄ cells exhibited notably lower capacities at the corresponding rates: 150.6, 147.3, 138.4, and 70.4 mAh g⁻¹ for the dry-LLZO composite, and 120.7, 115.8, 105.6, and 64.5 mAh g⁻¹ for the blank electrolyte. These results clearly indicate that the wet-LLZO-containing cell outperforms the other two electrolytes over all applied current rates. Moreover, when the current rate was returned from 3.0 C to 0.5 C, the specific capacity of the Li/CSPE-15 wet-LLZO/LiFePO₄ full cell fully recovered to its initial value, demonstrating excellent rate capability and electrochemical reversibility. This recovery underscores the excellent structural and interfacial stability imparted by the CSPE-15 wet-LLZO composite electrolyte during dynamic cycling under varied current loads.

The long-term cycling stability of solid-state lithium metal batteries was systematically investigated at 60 °C and 30 °C. The Li|LiFePO₄ battery using CSPE-15 wet-LLZO maintained a specific capacity of 156.8 mAh g⁻¹ and a capacity retention rate of 99.7% after 100 cycles at 0.2 C and 60 °C [**Figure 5C**]. By contrast, under identical test conditions, the discharge specific capacities of the cells based on CSPE-15 dry-LLZO and SPE-blank decreased to 128.3 mAh g⁻¹ and 116.8 mAh g⁻¹, respectively, after 100 cycles. Furthermore, the Li/CSPE-15 wet-LLZO/LiFePO₄ cell exhibited a more stable voltage plateau and lower polarization [**Figure 5D**]. **Supplementary Figure 6** further compares the cycling performance of the three solid-state Li|LiFePO₄ cells at 0.5 C and 1.0 C under 60 °C with a LiFePO₄ loading of 1.5 mg cm⁻². The long-cycle results over 100 cycles at 0.5 C [**Supplementary Figure 6A**] demonstrate that the CSPE-15 wet-LLZO battery delivers the

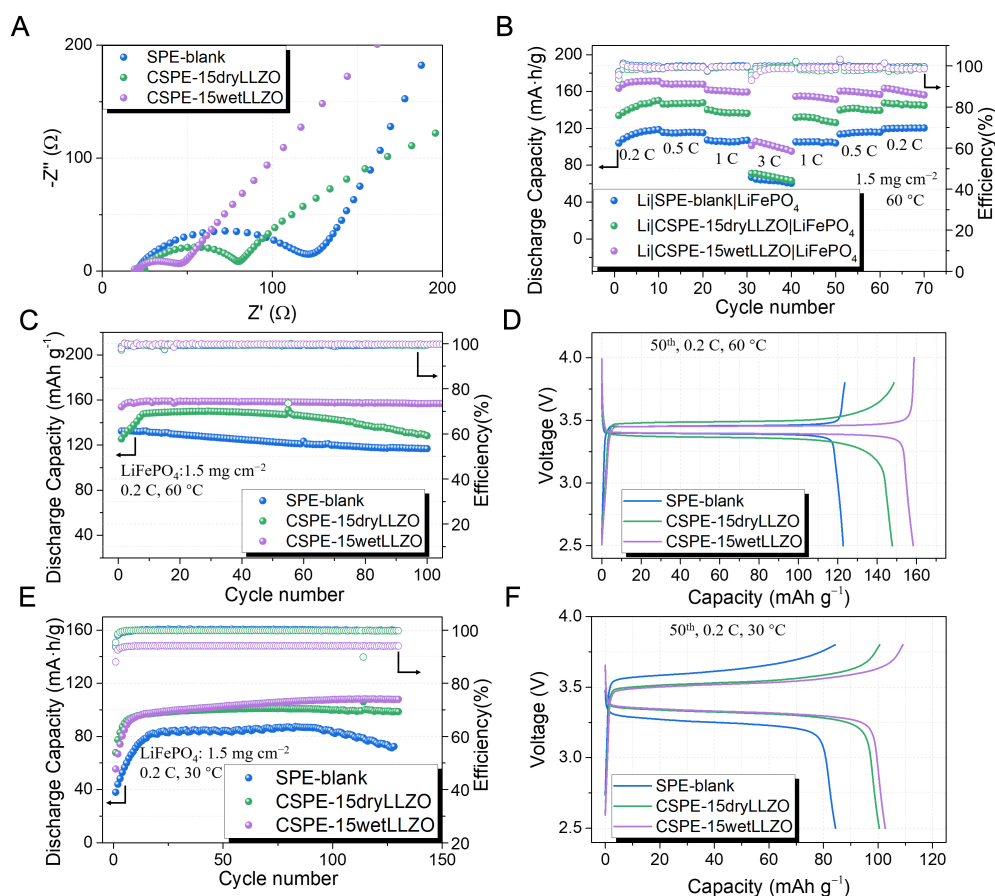


Figure 5. (A and B) EIS spectra before cycling and rate performance of Li/SPE-blank/LiFePO₄, Li/CSPE-15 dry-LLZO/LiFePO₄, and Li/CSPE-15 wet-LLZO/LiFePO₄ batteries, (C and D) Long-cycle performance and charge-discharge curves of Li/SPEs/LiFePO₄ batteries at 0.2 C at 60 °C, with the 50th cycle included, (E and F) Long-term cycling performance of Li/SPEs/LiFePO₄ batteries at 30 °C and 0.2 C, and the charge-discharge curves of the 50th cycle. EIS: Electrochemical impedance spectroscopy; SPE: solid polymer electrolytes; LLZO: Li_{6.4}Ga_{0.2}La₃Zr₂O₁₂.

highest discharge-specific capacity among all samples within these 100 cycles. Its charge-discharge profiles recorded up to 150 cycles [Supplementary Figure 6B] further reveal a stable voltage plateau from the 10th to 150th cycle. At 1.0 C, the long-cycle performance after 300 cycles [Supplementary Figure 6C] indicates that CSPE-15 wet-LLZO maintains a discharge specific capacity of 142.5 mAh g⁻¹, with its coulombic efficiency exceeding 99%. In contrast, CSPE-15 dry-LLZO shows significant capacity degradation after only 200 cycles, while SPE-blank exhibits substantial capacity loss after merely 133 cycles, as evidenced by its charge-discharge curves [Supplementary Figure 6D], which confirm minimal polarization deterioration over 50–200 cycles. Collectively, the results from these subfigures demonstrate that the CSPE-15 wet-LLZO composite electrolyte achieves both high reversible capacity and excellent long-cycle stability. The long-term cycling stability of Li/SPEs/LiFePO₄ full cells was also evaluated at 30 °C via galvanostatic charge-discharge at 0.2 C. As shown in Figure 5E, the Li/CSPE-15 wet-LLZO/LiFePO₄ cell retains 107.9 mAh g⁻¹ after 130 cycles, while the Li/CSPE-15 dry-LLZO/LiFePO₄ and Li/SPE-blank/LiFePO₄ cells only deliver 98.6 mAh g⁻¹ and 72.4 mAh g⁻¹, respectively, under the same conditions. Notably, the wet-LLZO cell exhibits a flatter voltage profile with minimal polarization throughout cycling [Figure 5F], confirming superior interfacial stability and efficient charge transport. These results verify that the wet-LLZO composite electrolyte enables high-capacity, long-life operation of LiFePO₄ full cells even at 30 °C.

CONCLUSION

This study investigates the positive effect of residual alkali on the surface of LLZO on CSPEs. Combined with characterization results from DSC and XRD, it was found that residual alkali on the LLZO surface can reduce the crystallinity of PEO, thereby enhancing the lithium-ion conductivity of CSPEs. Consequently, CSPE with 15 wt% wet-LLZO exhibits favorable Li^+ conductivity (0.80 mS cm^{-1}) and Li^+ transference number (0.36) at 60°C . The Li/CSPE-15 wet-LLZO/Li battery can achieve stable cycling for 1,000 h at 60°C and 0.1 mA cm^{-2} current density, with a critical current density of up to 0.65 mA cm^{-2} . Additionally, the Li|LiFePO₄ battery using CSPE-15 wet-LLZO demonstrates excellent rate performance (cycling specific capacity of 105.3 mAh g^{-1} at 60°C and 3.0 C) and good long-cycle performance (discharge specific capacity maintained at 156.8 mAh g^{-1} after 100 cycles at 60°C and 0.2 C). This study enhances the understanding of LLZO surface characteristics in solid polymer electrolytes and offers a new, effective approach for developing high-performance composite solid-state electrolytes.

DECLARATIONS

Authors' contributions

Study design, experimental validation, data curation and analysis, figure preparation: He, Y.
Experimental design, experimental validation, data analysis, writing of the original draft: Liu, G.
Research supervision, resource coordination, project administration, manuscript revision: Ao, X.
Research supervision, resource support, project management, manuscript review and revision: Tian, B.
All authors discussed the results and commented on the manuscript, and all authors have read and approved the final submitted version.

Availability of data and materials

The data supporting our findings can be found in the [Supplementary Materials](#).

AI-assisted tools statement

During the preparation of this manuscript, the AI tool ChatGPT (version 1.0, released 2026-07-22) was used solely to generate part of the particle elements in the Graphical Abstract. The tool did not influence the study design, data collection, analysis, interpretation, or the scientific content of the work. All authors take full responsibility for the accuracy, integrity, and final content of the manuscript.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Supplementary Materials

[Supplementary Materials](#)

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