

Janus-particle-based composite solid electrolytes with a root-soil interlocking architecture

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Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94909055>

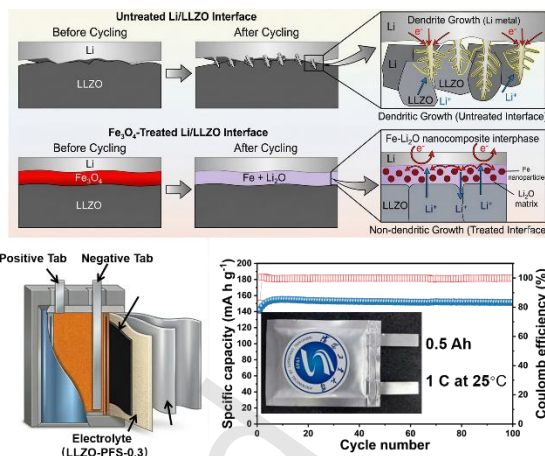
<https://www.sciopen.com/journal/1998-0124> on Jul. 23, 2026

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Interface Engineering for High-Performance Solid-State Lithium Batteries



This work proposes an interfacial engineering strategy based on $\text{Fe}_3\text{O}_4@\text{Si}/\text{PVDF}$ Janus particles to construct a “root-soil interlocking” structure. This architecture features dual asymmetric functionalities: the Fe_3O_4 side, rich in oxygen-containing groups, exhibits strong lithiophilicity, effectively adsorbing Li^+ and promoting uniform nucleation and deposition; the silane-coupler-modified Si/PVDF side establishes robust interfacial bonding with the LLZO surface and facilitates the self-assembly of a continuous three-dimensional ionic transport network.

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Received: 29 April 2026; **Revised:** 26 June 2026; **Accepted:** 23 July 2026

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Cite this article: *Nano Research*, 2026, 19, 94909055 <https://doi.org/10.26599/NR.2026.94909055>

Abstract

Garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) solid-state electrolytes are considered ideal candidates for solid-state Li metal batteries (SLMBs) due to their high ionic conductivity and excellent chemical stability toward Li metal. However, their practical application is hindered by high interfacial resistance, poor physical contact with Li metal, and the resultant inhomogeneous Li^+ flux, which collectively induce Li dendrite growth and premature battery failure. To address these challenges, this work proposes an interfacial engineering strategy based on $\text{Fe}_3\text{O}_4@\text{Si}/\text{PVDF}$ (PFS- x) Janus particles to construct a “root-soil interlocking” structure. This architecture features dual asymmetric functionalities: the Fe_3O_4 side, rich in oxygen-containing groups, exhibits strong lithiophilicity, effectively adsorbing Li^+ and promoting uniform nucleation and deposition; the silane-coupler-modified Si/PVDF side establishes robust interfacial bonding with the LLZO surface and facilitates the self-assembly of a continuous three-dimensional ionic transport network. Benefiting from this interlocking structure, the interfacial resistance is significantly reduced from $>1000 \text{ } \Omega \cdot \text{cm}^2$ to approximately $240 \text{ } \Omega \cdot \text{cm}^2$, accompanied by enhanced Li^+ transport kinetics with an activation energy lowered to 0.1806 eV. Consequently, symmetric Li cells achieve stable cycling for over 5000 h at a current density of 0.1 mA cm^{-2} . The prepared SLMBs deliver an initial discharge capacity of $165.4 \text{ mA h g}^{-1}$ at 0.5 C and retain $151.9 \text{ mA h g}^{-1}$ after 100 cycles with a coulombic efficiency exceeding 99%, whereas the unmodified system fails after approximately 30 cycles. Collectively, this study presents an effective interface optimization strategy using Janus composite materials, offering new insights for the development of high-performance all-solid-state Li metal batteries.

Keywords: garnet-type solid-state electrolytes, solid-state Li metal batteries, interfacial engineering, Janus composite particles, Li dendrite suppression

Introduction

Rechargeable batteries face significant challenges in meeting the ever-increasing demands associated with the transition from fossil fuels to renewable energy for a sustainable future [1-4]. Solid-state Li metal batteries (SLMBs) have garnered significant attention as next-generation energy storage systems due to their higher energy density and improved safety compared to conventional liquid electrolyte-based Li-ion batteries [5]. Among them, garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) stands out owing to its high ionic conductivity (10^{-4} - 10^{-3} S cm^{-1} at 25°C), wide electrochemical stability window, and excellent chemical compatibility with Li metal anodes [6,7]. However, the practical application of LLZO-based ASSLBs is severely limited by poor solid-solid interfacial contact between the rigid ceramic electrolyte and the Li metal anode. This issue leads to high interfacial resistance (typically exceeding $1000\ \Omega\cdot\text{cm}^2$), inhomogeneous Li^+ flux distribution, and subsequent Li dendrite growth, ultimately causing premature cell failure [8-10].

To address these interfacial challenges, various interface engineering strategies have been explored, including surface polishing, introduction of buffer layers (e.g., polymers, metal oxides, or hybrid interlayers), and three-dimensional (3D) electrode designs [11-13]. For instance, polymer interlayers such as PEO and PVDF can accommodate volume changes to some extent and improve physical contact. For example, Yang et al. [14] developed a polycarbonate buffer layer that accommodates volume changes and maintains interfacial contact, resulting in an interfacial resistance increase of only 20% after 150 cycles and stable cycling for over 360 h. However, their thermal stability and mechanical strength are often insufficient [15,16]. Inorganic buffer layers such as Al_2O_3 or Li_2O have also been explored to enhance lithiophilicity. Pakseresht et al. [17] fabricated an ultrathin Al_2O_3 coating via atomic layer deposition, achieving stable Li/LLZO cycling for over 1000 h at $0.5\ \text{mA cm}^{-2}$. This conformal coating improves interfacial contact and forms a lithiated Li-Al-O interphase that conducts Li^+ while blocking electrons, thereby stabilizing the interface and suppressing Li dendrite penetration. However, the rigid intrinsic of the interface may not fully eliminate interfacial stress concentration [18-20]. Recently, surface modification strategies using silane coupling agents or atomic layer deposition coatings have shown promise in improving wettability and reducing interfacial resistance [21-23]. Nevertheless, most existing approaches still focus on single-function interlayers, struggling to simultaneously meet multiple demands such as robust interfacial adhesion, uniform Li^+ flux regulation, and effective dendrite suppression. Therefore, there is an urgent need to develop a multifunctional, asymmetric interface design paradigm.

In this context, we propose a bioinspired “root-soil interlocking” interface engineering strategy based

on $\text{Fe}_3\text{O}_4@\text{Si}/\text{PVDF}$ Janus particles. The Fe_3O_4 side, rich in oxygen-containing groups, exhibits strong lithiophilicity, enabling Li^+ adsorption and promoting uniform nucleation. The silane coupling agent-modified Si/PVDF side ensures robust chemical bonding with the LLZO surface and facilitates the formation of a continuous 3D ionic transport network. At the macroscopic level, the self-assembled Janus particles form a 3D interlocking network that bridges the rigid ceramic electrolyte and the soft Li metal, achieving synergistic regulation of interfacial chemistry, mechanics, and ionic transport. Benefiting from this design, the symmetric Li/Li cells can achieve stable cycling for over 5000 h at a current density of 0.1 mA cm^{-2} . Solid-state $\text{LiFePO}_4\|\text{Li}$ cells deliver an initial discharge capacity of 165.4 mAh g^{-1} at 0.5 C , with a coulombic efficiency exceeding 99% after 100 cycles. Moreover, this strategy has also been validated in a pouch cell configuration. This work not only provides an effective solution to the Li -LLZO interfacial instability issue but also establishes a generalizable strategy for constructing stable solid-solid interfaces in high-performance solid-state batteries using asymmetric Janus materials.

2. Results and Discussion

2.1 Structural Characterization

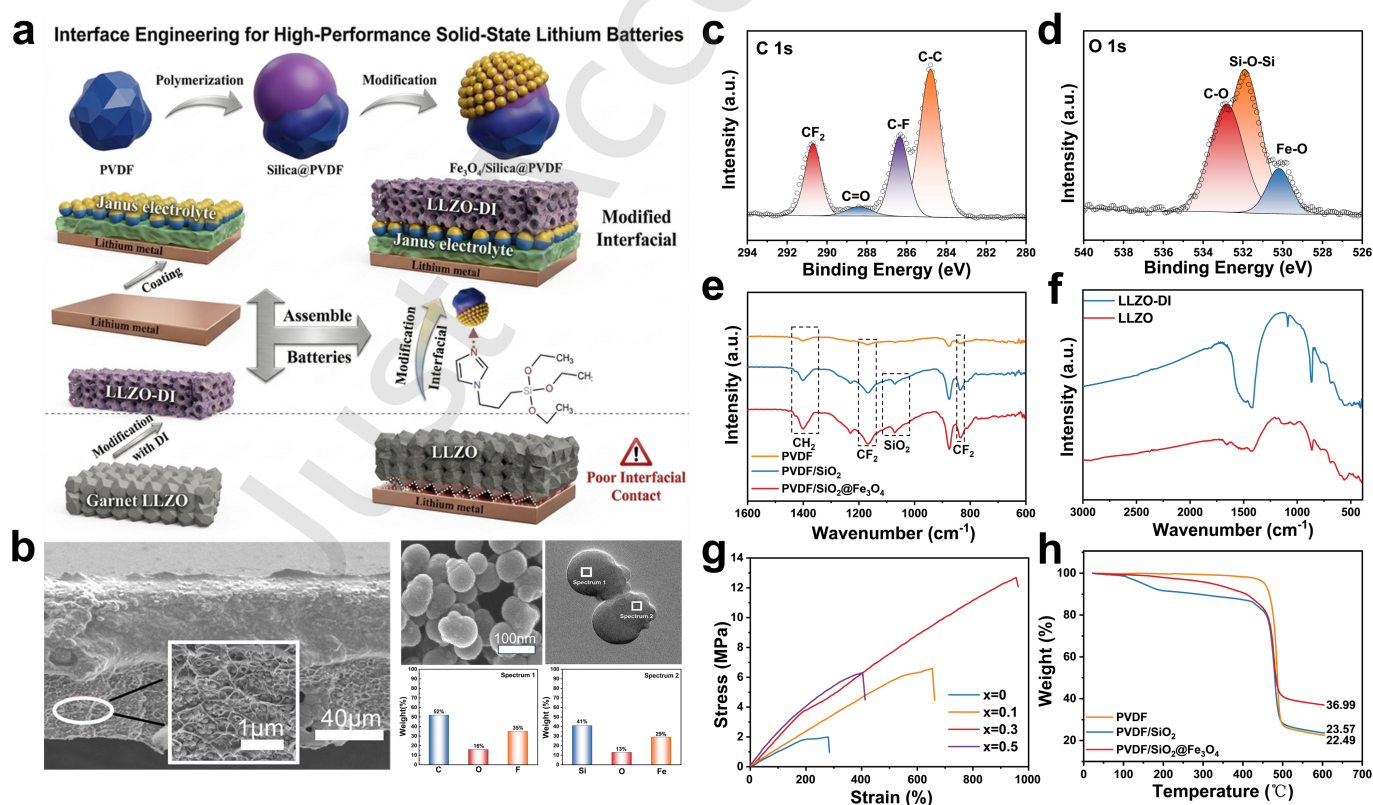


Fig. 1. (a) Schematic illustration of Janus particle fabrication via seed emulsion polymerization-induced phase separation and subsequent selective modification. (b) Interfacial bridging between the Janus organic-inorganic composite electrolyte and electrode surfaces. (c) SEM, TEM, and EDX characterization of PFS-0.3 Janus particles. (d-e) XPS spectra (C and O)

of PFS-x. (f) FTIR spectra of three Janus particles. (g) FTIR spectra of LLZO and LLZO-DI. (h) Tensile strength of membranes with different compositions at 80 °C. (i) Thermogravimetric analysis curves of three Janus particles.

Fig. 1a schematically illustrates the fabrication route of PFS-x Janus particles. Specifically, 3-aminopropyltriethoxysilane (APTES)-modified SiO₂ nanoparticles were first incorporated into a PVDF matrix via a precipitation-induced coating process to form PVDF/SiO₂ Janus particles, followed by selective sulfonation to generate an asymmetric surface chemistry. Subsequently, Fe₃O₄ nanoparticles were in situ grown on the Si-rich side through a coprecipitation reaction, yielding PFS-x Janus particles with pronounced structural and compositional anisotropy. To enable robust interfacial coupling with the garnet-type electrolyte, N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (DI) silane coupling agents were employed as molecular bridges. The imidazole groups of DI can readily coordinate with coordinatively unsaturated Fe³⁺ species on the Fe₃O₄ surface, forming stable ionic coordination bonds and thereby facilitating the anchoring of Janus particles onto the LLZO surface. The interfacial modification process is schematically illustrated in **Fig. 1b**. Owing to the coordination interaction between LLZO-DI and the Janus particles, an intimate and chemically coupled LLZO/Janus/PVDF interface is established, which is favorable for the construction of fast Li⁺ conduction pathways across the interface.

The morphology and microstructure of the Janus particles were systematically characterized by SEM and TEM. As shown in **Fig. 1c**, the PFS-x Janus particles exhibit a distinct snowman-like morphology, consisting of two tightly connected domains with markedly different sizes and contrasts. This characteristic feature directly confirms the intrinsic asymmetry of the particles, rather than a homogeneous or conventional core-shell structure. TEM images further reveal a pronounced contrast difference between the upper and lower regions within individual particles, indicating substantial variations in composition and mass density. To clarify the spatial distribution of the constituent components, localized EDX analyses were performed. The upper region is dominated by C, F, and O signals, corresponding to the PVDF-rich polymer phase, whereas the lower region exhibits strong Fe, Si, and O signals, originating from the Fe₃O₄ and SiO₂ inorganic components.

X-ray photoelectron spectroscopy (XPS) was employed to elucidate the chemical states of individual elements and the interfacial interactions within the x-Fe₃O₄/SiO₂@PVDF composite. As shown in **Fig. S2g**, the Fe 2p spectrum displays characteristic Fe 2p_{3/2} and Fe 2p_{1/2} peaks at 710.8 and 724.5 eV with a satellite peak at 718.5 eV, and the Fe 2p_{3/2} deconvolution reveals Fe²⁺ (709.8 eV) and Fe³⁺ (711.2 eV) components with an area ratio of 0.5, consistent with the stoichiometry of Fe₃O₄ [24]. Interfacial chemical interactions

are further corroborated by the O 1s spectra (**Fig. 1e** and **Fig. S2d**). The emergence of a new component at 530.1 eV absent in the PVDF/SiO₂ sample is attributed to Fe-O bonding within the hybrid architecture. Meanwhile, the Si-O-Si peak shifts toward lower binding energy by approximately 0.3-0.5 eV, suggesting electron redistribution induced by interfacial chemical coupling, which facilitates robust interfacial adhesion and continuous ion-transport pathways across the Janus-modified polymer-ceramic interface. Consistently, the Si 2p_{3/2} peak also exhibits a negative shift from 103.7 eV to around 103.4 eV, accompanied by noticeable peak broadening (**Fig. S2c and f**). In contrast, the C 1s and F 1s spectra show that the characteristic CF₂ and C-F peaks of PVDF remain essentially unchanged in both binding energy and spectral shape, indicating that the polymer backbone is well preserved during the composite formation process (**Fig. 1d** and **Fig. S2b**). Moreover, no Fe-related signals are detected in the reference sample, excluding the possibility of extrinsic iron contamination. Collectively, these XPS results confirm the successful incorporation of Fe₃O₄ with a stable mixed-valence state and provide direct evidence for robust chemical bonding at the composite interface, which is crucial for the structural stability of the hybrid system.

Fig. S5 exhibits the tribological performance of the PFS-*x* Janus membranes. Among them, the one with *x* = 0.3 exhibits the lowest steady-state friction coefficient and the most uniform wear-depth evolution (~ 718.42 nm), without observable surface delamination or tearing (**Fig. S5f**), indicating a stable and wear-resistant friction process. This behavior can be attributed to the synergistic reinforcement between nanosized SiO₂ fillers and the PVDF matrix, which is highly consistent with the post-test surface SEM observations (**Fig. S4e-h**). FTIR spectroscopy further confirms the successful integration of the inorganic components and their influence on polymer structure (**Fig. 1f**). Typical PVDF absorption bands are observed in all samples, while the broad peak at 1100 cm⁻¹ verifies the incorporation of SiO₂. Notably, the β-phase characteristic peak of PVDF at 840 cm⁻¹ is significantly enhanced in the composite membrane, indicating that the Fe₃O₄@SiO₂ Janus particles effectively promote the α-to-β phase transition of PVDF [25,26]. This enhancement arises from the interfacial interaction between the particles and the polymer, which induces dipole orientation and conformational rearrangement of the C-F bonds, rather than disrupting the covalent structure. This is evidenced by the absence of CF-related bands or significant broadening of the original bands. Furthermore, a slight blue shift of the Fe-O related band (600 cm⁻¹) further suggests that the SiO₂ coating and polymer confinement effects induce interfacial electronic interactions.

Surface-modified LLZO exhibits a distinct absorption band at 1175 cm⁻¹, corresponding to the C=C skeletal vibration of imidazole groups, confirming the successful grafting of DI molecules and effective

organic functionalization of the LLZO surface (**Fig. 1g**). Mechanical properties of the composite electrolytes were evaluated by tensile testing (**Fig. 1h**). The $x = 0.3$ composite delivers the highest tensile strength (12.5 MPa), substantially outperforming other compositions. This enhancement is attributed to the asymmetric architecture of the Janus particles, in which the PVDF-rich side forms robust chain entanglements with the matrix, while the rigid Si/Fe₃O₄ side efficiently bears mechanical loads, enabling effective stress transfer across the composite. Thermal stability was further assessed by thermogravimetric analysis (**Fig 1i**). Pristine PVDF shows an onset decomposition temperature of 425°C with a residual mass of 22.49%. The introduction of SiO₂ increases the onset temperature to 440°C due to its barrier effect, while further incorporation of Fe₃O₄ raises it to 450 °C and significantly increases the residual mass to 36.99%, indicating enhanced char formation and reinforced thermal protection. These results demonstrate that the stepwise incorporation of SiO₂ and Fe₃O₄ synergistically improves the mechanical robustness, thermal stability, and structural integrity of the PVDF-based composite electrolyte.

2.2 Interfacial stability of Li||LLZO-PFS||Li symmetric cells

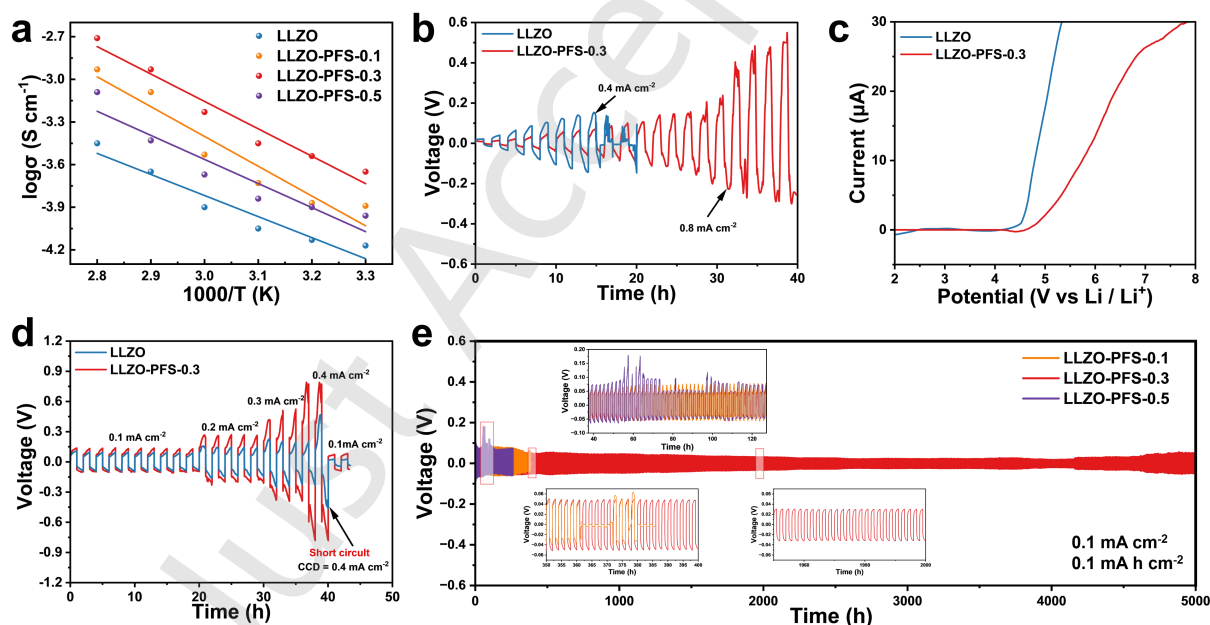


Fig. 2. (a) Arrhenius plots for LLZO and LLZO-PFS- x with different modified compositions. (b) Critical current density (CCD) profiles before and after modification. (c) LSV curves of LLZO and LLZO-PFS-0.3. (d) Rate performance under different current densities of LLZO and LLZO-PFS-0.3. (e) Cycling performance of Li|| LLZO-PFS- x ||Li symmetric cells with different modified compositions.

As shown in **Fig. S7a-d**, temperature-dependent impedance spectroscopy reveals that LLZO-PFS-0.3 exhibits the highest ionic conductivity at room temperature (25°C), approximately $1.2 \times 10^{-5} \text{ S cm}^{-1}$. Notably, in the LLZO-PFS- x system, the magnitude of variation in interfacial resistance with increasing temperature

is significantly reduced, indicating that the Janus interlayer effectively stabilizes the interface, facilitates Li^+ transport, and mitigates interfacial degradation. Arrhenius analysis (**Fig. 2a**) further shows that the LLZO-PFS-0.3 possesses the lowest activation energy ($E_a = 0.1806 \text{ eV}$), confirming that Janus modification can enhance interfacial lithiophilicity and accelerate Li^+ migration. The dendrite suppression capability of the composite electrolyte was systematically evaluated by critical current density (CCD) measurements using symmetrical Li cells (**Fig. 2b**). Under stepwise increasing current densities, the LLZO-PFS-0.3 exhibits significantly enhanced resistance against Li dendrite penetration, maintaining a stable deposition/stripping profile with minimal polarization at a current density of 0.8 mA cm^{-2} for over 30 h without any voltage mutation or short circuit. Rate performance tests further demonstrate stable and reversible Li deposition/stripping over a wide current density range from 0.1 to 0.8 mA cm^{-2} , with full recovery of interfacial stability upon returning to 0.1 mA cm^{-2} , highlighting excellent interfacial reversibility (**Fig. 2d**). In contrast, the pristine LLZO electrolyte suffers rapid short-circuiting at only 0.4 mA cm^{-2} . Especially, the $\text{Fe}_3\text{O}_4@\text{Si}/\text{PVDF}$ effectively improves the high-voltage stability of the solid electrolyte. As shown in **Fig. 2c**, the optimized LLZO-PFS-0.3 exhibits a high oxidation onset potential of 4.8 V , which is higher than the pristine LLZO of 4.5 V , indicating a widened electrochemical window. Especially, this wide electrochemical window confirms its compatibility with high-voltage cathode materials and underscores the effectiveness of the Janus interfacial design in simultaneously enhancing interfacial stability, ionic transport, and electrochemical robustness.

The effect of Janus particle loading on interfacial stability was systematically investigated using $\text{Li}||\text{LLZO-PFS-x}||\text{Li}$ symmetric cells at a current density of 0.1 mA cm^{-2} . As shown in **Fig. 2e**, the cell with LLZO-PFS-0.1 exhibits relatively large polarization voltages with pronounced fluctuations during cycling, indicating that the insufficient concentration of Janus particles fails to provide enough interfacial “bridging” sites to construct a stable and continuous contact interface, resulting in high and unstable interfacial resistance. In contrast, the excessive loading of LLZO-PFS-0.3 leads to severe voltage fluctuations and premature short-circuiting after several hundred hours of cycling, which can be attributed to particle agglomeration-induced heterogeneity in local current density, thereby triggering Li dendrite nucleation and penetration through the electrolyte. Remarkably, the cells based on electrolyte with an intermediate Janus content of LLZO-PFS-0.3 demonstrate exceptional long-term cycling stability, maintaining low and highly stable overpotentials throughout more than 5000 h of continuous cycling without any signs of short circuiting. This result unambiguously identifies 0.3 wt.% as the optimal concentration for interfacial

performance optimization. At this loading level, Janus particles are uniformly dispersed and fully exert their bifunctional “interfacial bridge” role: the lithiophilic functional groups on one side stabilize the Li metal interface and homogenize Li^+ flux, while the polymeric chains on the opposite side integrate seamlessly with the electrolyte matrix, collectively suppressing interfacial instability and Li dendrite growth. For comparison, symmetric cells employing pristine LLZO electrolyte display large and unstable polarization voltages from the initial cycles and suffer rapid failure within a short time span, which originates from the intrinsic solid–solid contact issues and poor interfacial compatibility (**Fig. S8a**). In contrast, the Janus-modified LLZO electrolyte of LLZO-PFS-0.3 exhibits minimal polarization and highly stable voltage profiles throughout the entire testing period, confirming the effectiveness of interfacial regulation. Notably, even in the absence of a solid electrolyte, the Janus membrane enabled relatively stable Li plating/stripping for over 1000 h, demonstrating its intrinsic ionic transport capability and interfacial electrochemical activity (**Fig. S8b**). Nevertheless, its cycling stability remained inferior to that of the electrolyte-modified LLZO-Janus system, underscoring the critical role of the LLZO electrolyte in further reinforcing interfacial stability and accelerating ion-transport kinetics. In addition, SEM analysis after prolonged cycling reveals severe structural degradation in pristine LLZO, characterized by a loose and porous cross-section, grain boundary cracking, and extensive penetration of Li dendrites and “dead Li”, ultimately leading to short-circuit failure (**Fig. S6**). In contrast, the optimally modified LLZO electrolyte of LLZO-PFS-0.3 retains a dense and intact microstructure with tightly bonded grains and no observable dendrite penetration. This compact architecture acts as a rigid physical barrier that effectively blocks dendrite propagation along grain boundaries. EDS mapping further confirms a uniform elemental distribution, which contributes to homogenized ionic flux and local electric field distribution, thereby fundamentally suppressing Li dendrite nucleation and growth.

2.3 Interfacial Flux Regulation Mechanism Induced by Janus Particles and based on theoretical Calculation

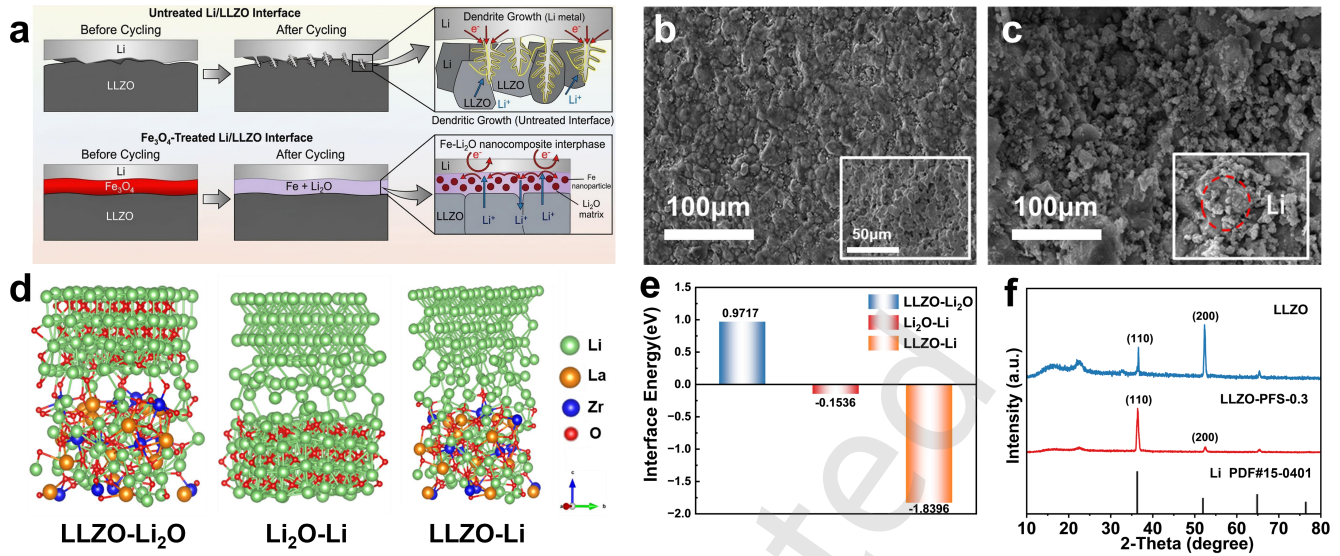


Fig. 3. (a) Janus Particles Schematic illustration of the interfacial regulation mechanism. (b, c) SEM comparison of LLZO electrolytes before and after Janus modification after repeated plating/stripping cycles. (d) First-principles calculations of interfacial energies for different contact configurations. (e) Bar chart summarizing the interfacial energies of various interfaces. (f) XRD patterns of Li metal anodes after cycling with unmodified and Janus-modified LLZO electrolytes.

The interfacial optimization mechanism enabled by the Janus-particle-modified electrolyte is schematically illustrated in **Fig. 3a**. For the pristine LLZO system, the rigidity of the LLZO electrolyte results in poor physical contact with the Li metal anode, giving rise to pronounced interfacial structural distortion, interfacial instability, and a high propensity for Li dendrite growth. Especially, the direct LLZO/Li contact is intrinsically unfavorable, as corroborated by first-principles calculations, which reveal a highly distorted interfacial configuration and a low interfacial energy (-1.8396 eV) for LLZO-Li. This indicates that the severe structural mismatch, weak interfacial compatibility, and a strong tendency toward parasitic interfacial reactions and non-uniform local electric field distribution (**Fig. S3d and e**) [27,28]. In contrast, introducing a Li₂O interlayer can significantly improve interfacial thermodynamic and structural stability. As shown in **Fig. 3d**, density functional theory (DFT) calculations show that the LLZO-Li₂O interface exhibits a markedly increased interfacial energy (0.9717 eV), reflecting enhanced interfacial bonding strength and improved structural coherence [29,30]. Atomic-scale analysis further indicates that Li₂O forms a continuous Li-O coordination network on the LLZO surface, which effectively alleviates lattice mismatch and mitigates interfacial stress concentration. Meanwhile, the Li₂O-Li interface maintains favorable compatibility, with a relatively low interfacial energy of -0.1536 eV, enabling a smooth and stable transition from the rigid

ceramic electrolyte to the soft metallic Li. These results collectively establish Li₂O as an energetically and structurally favorable buffer layer bridging LLZO and Li metal.

After Janus modification, the Fe₃O₄ component within the Janus particles undergoes an in situ interfacial reaction with Li metal (equation 1), generating a composite interphase composed of metallic Fe nanoparticles and Li₂O:



Consistent with the DFT predictions, the in situ formed Li₂O-rich interphase serves as a stable and compliant buffer layer. This hybrid interphase, characterized by its electronically insulating yet ionically conductive nature, establishes an intimate “soft contact” at the Li/LLZO interface. Consequently, the interfacial Li⁺ flux is effectively homogenized, local current density concentration is mitigated, and Li dendritic growth is significantly suppressed, leading to enhanced interfacial stability [31,32].

SEM observations provide direct experimental evidence for this interfacial regulation effect (**Fig. S3b-c**). After prolonged cycling, the surface of the Janus-modified LLZO electrolyte remains smooth and intact, with no other byproducts detected. In contrast, the surface of the pristine LLZO exhibits extensive pitting and highly uneven accumulation of byproducts. These results unequivocally demonstrate that the Janus-derived interlayer constructs a stable “root-soil interlocking” interfacial architecture, which effectively redistributes Li⁺ flux and eliminates localized current hotspots. In contrast, uncontrolled Li dendrite growth on unmodified LLZO originates from poor interfacial contact and surface defects, underscoring the critical role of Janus-enabled interfacial engineering in improving the cycling stability and safety of SLMBs. In addition, XRD reveals a pronounced crystallographic reorientation of the Li deposition based on LLZO-PFS-0.3. Notably, Li metal is a typical body-centered cubic (BCC) crystal, with the (110) crystal plane being its closest-packed plane and exhibiting the lowest migration energy barrier. Consequently, compared to other planes, Li atoms tend to form dense, planar deposition more readily on the (110) plane [33,34]. As shown in **Fig. 3f**, the pristine LLZO exhibits a dominant (200) crystal plane, indicating a primarily (200)-oriented deposition. In contrast, LLZO-PFS-0.3 undergoes a dramatic shift in crystal plane orientation. The (110) diffraction peak intensifies significantly, accompanied by a severe attenuation of the original (200) reflection. This unambiguously demonstrates a strong (110) preferred orientation of Li deposition. This profound crystallographic reconstruction of the interfacial regulation governed by the engineered Janus particles. By establishing an asymmetric physicochemical microenvironment at the interface, the Janus architecture effectively homogenizes local ion fluxes and reshapes the electric field

distribution, thereby fundamentally modulating the Li deposition kinetics. More importantly, this Janus-induced (110) preferred orientation serves to guide uniform Li^+ nucleation and planar growth, intrinsically enhancing interfacial stability and mitigating dendrite growth.

2.4. Battery Performance

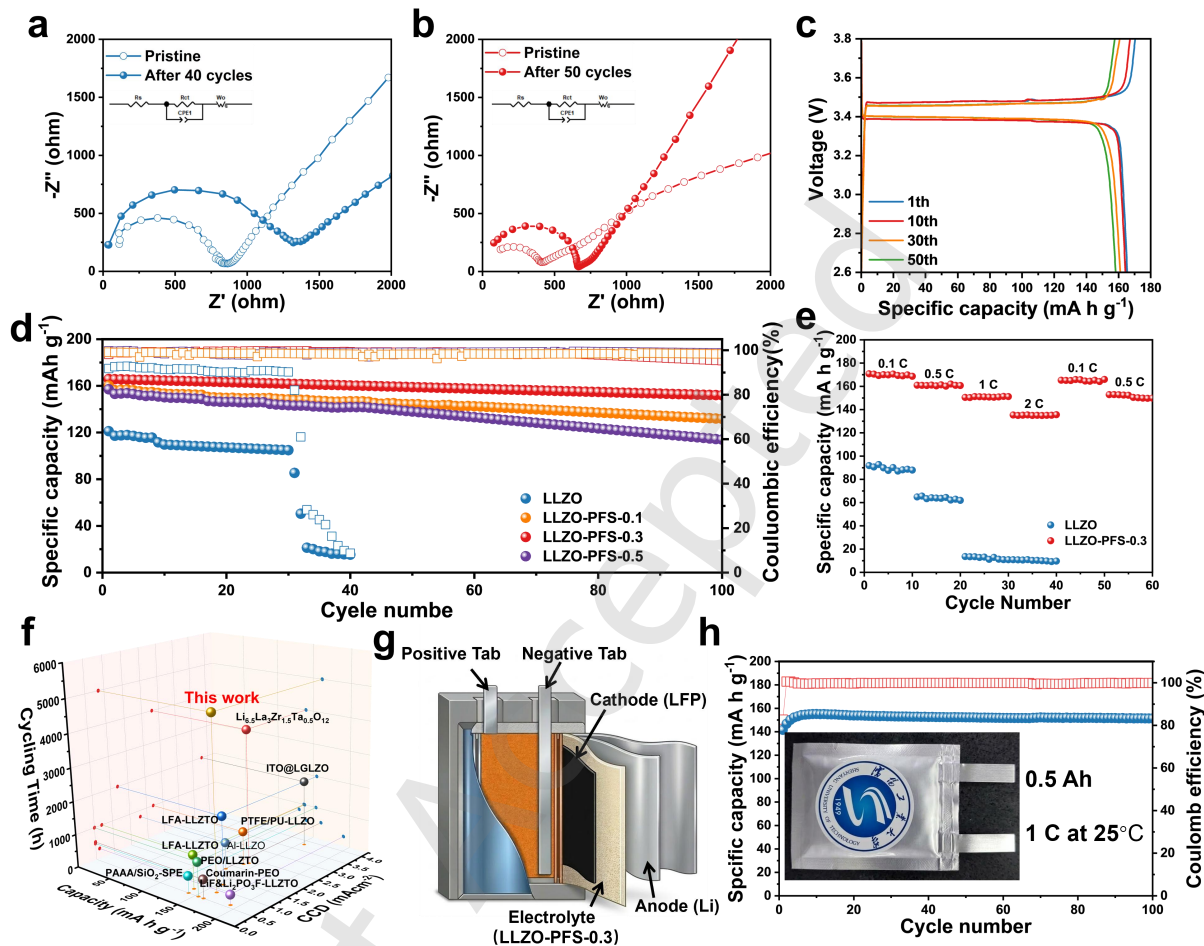


Fig. 4. (a, b) Electrochemical impedance spectra (EIS) of LLZO electrolytes before and after Janus modification following repeated charge–discharge cycling. (c) Charge–discharge profiles at 0.5 C of the cell with the $x = 0.3$ Janus-modified electrolyte. (d) Cycling curves at 0.5 C and corresponding Coulombic efficiency of cells with various Janus modified electrolytes. (e) Rate performance of cells with unmodified and Janus-modified LLZO electrolytes. (f) Performance comparison of recently reported LLZO modification strategies [22–29]. (g) Schematic illustration of the LLZO-based pouch cell configuration. (h) Discharge capacity and Coulombic efficiency of the pouch cell cycled at 1 C.

Electrochemical impedance spectroscopy (EIS) reveals distinct interfacial evolution behaviors between pristine and Janus-modified LLZO electrolytes. For the unmodified LLZO, the interfacial resistance rapidly increases from 712 Ω to 1320 Ω after only 50 cycles (**Fig. 4a**), indicating severe interfacial degradation and continuous parasitic reactions at the Li/LLZO interface. In contrast, LLZO-PFS-0.3 exhibits a substantially lower initial interfacial resistance (340 Ω) and maintains a much lower overall impedance even after

prolonged cycling. After 50 cycles, the resistance increases to 621 Ω (**Fig. 4b**), which remains less than half of that observed in the pristine system. Especially, the resistance evolution in the modified system is significantly more gradual, suggesting a suppressed interfacial degradation rate. Although interfacial evolution is not entirely eliminated, the Janus interlayer effectively stabilizes the Li/LLZO interface by reducing the initial interfacial barrier and mitigating its subsequent growth, thereby enabling a more durable and kinetically favorable interfacial environment. Consequently, the Li symmetric cell employing LLZO-PFS-0.3 delivers the favorable interfacial properties. As shown in **Fig. S9a**, the Nyquist plot exhibits a substantially smaller semicircle diameter than that of the control samples, corresponding to the lowest interfacial charge-transfer resistance. Especially, LLZO-PFS-0.3 maintains the smallest resistance growth after cycling, confirming the outstanding interfacial stability. This superior performance arises from an optimized Janus particle concentration, which provides sufficient active sites to construct a robust “root-soil interlocking” interfacial architecture while avoiding interfacial defects induced by excessive particle aggregation. Post-cycling EIS measurements of Li symmetric cells further corroborate that LLZO-PFS-0.3 exhibits the lowest interfacial resistance and the minimal resistance increase among all samples.

To evaluate the practical application performance, SLMBs were assembled using LLZO-PFS-0.3 as the electrolyte, Li metal as the anode, and LiFePO_4 as the cathode, forming $\text{LiFePO}_4\|\text{LLZO-PFS-0.3}\|\text{Li}$ cells. All electrochemical tests were conducted at room temperature (25°C). As shown in **Fig. 4c**, SLMBs with LLZO-PFS-0.3 exhibit a high initial discharge capacity of 165.4 mA h g⁻¹ at 0.5 C, and the highly overlapped discharge profiles from the 1st to the 50th cycles demonstrate excellent interfacial structural stability and electrochemical reversibility. The absence of additional voltage plateaus confirms the effective suppression of interfacial parasitic reactions, while the low overpotential indicates reduced kinetic barriers for Li⁺ stripping/plating and interfacial transport (**Fig. S9b**). These results demonstrate that Janus-enabled interfacial engineering simultaneously preserves high ionic conductivity and significantly enhances interfacial stability and cycling reversibility, thereby enabling the development of high-energy-density and long-lifespan solid-state Li metal batteries.

As shown in **Fig. 4d**, the galvanostatic cycling tests demonstrate that the modified LLZO-PFS-x electrolytes maintain discharge capacities of 131.7 mAh g⁻¹ (x = 0.1), 151.9 mAh g⁻¹ (x = 0.3), and 113.9 mAh g⁻¹ (x = 0.5) after 100 cycles, exhibiting relatively low capacity fading. In sharp contrast, the cell employing pristine LLZO suffers a rapid capacity decay due to short-circuit failure after 30 cycles and becomes completely inactive after 40 cycles. This premature failure is mainly attributed to the unstable

electrode-electrolyte interfaces in the pristine LLZO system, where poor interfacial compatibility leads to pronounced interfacial polarization and highly non-uniform Li^+ transport. The resulting localized current density amplification facilitates interfacial degradation and triggers internal short-circuit failure during prolonged cycling.

Rate performance was further evaluated for cells with LLZO and LLZO-PFS-0.3 (**Fig. 4e**). Notably, the cell with LLZO-PFS-0.3 exhibits superior rate capability and maintains high reversible capacity over a wide range of current densities. More importantly, the discharge capacity can be almost fully recovered when the current density is switched back to 0.1 C after high-rate cycling, demonstrating the robust interfacial stability and reversible Li^+ transport enabled by the Janus interlayer. In contrast, the pristine LLZO-based cell suffers from pronounced capacity decay at elevated current densities and exhibits limited capacity recovery upon rate reversal, reflecting aggravated interfacial polarization and irreversible interfacial degradation. Moreover, analysis of overpotential as a function of current density reveals that the LLZO-PFS-0.3 delivers the lowest polarization voltage across all tested current densities (**Fig. S9b**). This result reflects an optimal balance between interfacial structural stability and Li^+ transport kinetics, leading to minimized polarization and superior electrochemical performance. Especially, compared with other recent reports [22-29], the LLZO-PFS-0.3 exhibits a competitive advantage of electrochemical performance (**Fig. 4f**). Collectively, these results confirm that the LLZO-PFS-0.3 enables optimal interfacial ion-transport dynamics and significantly enhances the cycling stability and rate capability of SLMBs.

In addition, a pouch-type SLMB was successfully constructed using Janus-modified LLZO as the solid electrolyte. As illustrated in **Fig. 4g**, the pouch cell employs Li metal as the anode, LiFePO_4 as the cathode, and LLZO-PFS-0.3 serving as an integrated separator/electrolyte, encapsulated with an aluminum-plastic laminate. As shown in **Fig. 4h**, the $\text{Li}||\text{LLZO-PFS-0.3}||\text{LFP}$ pouch cell exhibits excellent cycling stability at 1C. An initial discharge capacity of 150 mAh g^{-1} is achieved and remains highly stable over 100 cycles with negligible capacity fading. Meanwhile, the coulombic efficiency is maintained at 99% throughout the entire cycling process, indicating highly reversible Li plating/stripping and effectively suppressed parasitic reactions. This excellent interfacial stability can be attributed to the in situ interfacial reaction of the Janus particles. Specifically, the Fe_3O_4 component within the Janus particles reacts with Li metal, generating a composite interphase composed of Li_2O and Fe nanoparticles. This interface precisely provides a flexible “soft contact”: Li_2O possesses a certain degree of plastic deformability, while the Fe nanoparticles buffer local stresses, and the synergistic effect enables the interface to maintain intimate contact even under

mechanical disturbance. In summary, these results demonstrate that even under a practical pouch cell configuration, the Janus-LLZO integrated separator/electrolyte achieves robust interfacial stability and efficient ion transport.

Conclusion

A Janus-particle-enabled interfacial engineering strategy is developed to address the intrinsic instability of the Li/LLZO solid–solid interface. By incorporating Janus particles, a biomimetic “root–soil interlocking” architecture is constructed, in which asymmetric functional domains synergistically regulate interfacial chemistry and ion transport. The lithiophilic Fe₃O₄ domain homogenizes Li⁺ flux and Li deposition, while the Si/PVDF domain ensures robust interfacial adhesion and mechanical compliance. As a result, the optimized LLZO electrolyte of LLZO-PFS-0.3 exhibits a significantly reduced interfacial resistance of 240 Ω·cm² and a low Li⁺ migration activation energy of 0.1806 eV. Benefiting from the stabilized interface, Li||LLZO-PFS-0.3||Li symmetric cells operate stably for over 5000 h at 0.1 mA cm⁻², demonstrating effective suppression of Li dendrite growth. When applied in solid-state LiFePO₄||LLZO-PFS-0.3||Li batteries, the Janus-modified LLZO electrolyte delivers an initial discharge capacity of 165.4 mA h g⁻¹ at 0.5 C and retains 151.9 mAh g⁻¹ after 100 cycles with coulombic efficiencies exceeding 99%, whereas the unmodified system fails rapidly. The feasibility of this strategy is further validated in a pouch-type solid-state cell with stable cycling performance. Mechanistically, the in situ formed Fe/Li₂O composite interphase provides an ionically conductive and electronically insulating buffer layer, mitigating local current concentration and interfacial degradation. Overall, this work demonstrates that exploiting the intrinsic anisotropy of Janus materials enables effective interfacial functional partitioning, offering a general strategy for constructing stable solid-solid interfaces in all-solid-state Li batteries.

CRedit authorship contribution statement

Tiantian Yang and **Shuai Guo**: Conceptualization, Investigation, Writing-original draft. **Haixiong Huang**: Investigation. **Linxiang Wang**: Validation. **Ming Gao**: Data curation. **Jiangtao Fan** and **Fuxin Liang**: Visualization, Project administration, Writing-review & editing.

Declaration of Competing Interest

The authors declare no competing financial interest.

Acknowledgments

The work was supported by the National Key Research and Development Program of China (No.

References

- [1] X. Yang, H. Zhang, Q. Liu, G. Jiang, The Li-ion battery industry and its challenges, *Nature Reviews Chemistry* 9 (2025) 497-498. <https://doi.org/10.1038/s41570-025-00742-2>.
- [2] Y. Chen, Z. Shadike, Shatter existing lifetime limit of Li-ion battery, *Joule* 9 (2025) 101920. <https://doi.org/https://doi.org/10.1016/j.joule.2025.101920>.
- [3] S. Guo, Y. Chen, L. Tong, Y. Cao, H. Jiao, Z. long, X. Qiu, Biomass hard carbon of high initial coulombic efficiency for sodium-ion batteries: Preparation and application, *Electrochimica Acta* 410 (2022) 140017. <https://doi.org/https://doi.org/10.1016/j.electacta.2022.140017>.
- [4] S. Guo, L. Shi, X. Gao, B. Ren, Y. Yang, M. Gao, X. Guo, L. He, J. Ban, F. Liu, G. Cao, S.R.P. Silva, J. Hu, Molecular design and structural hybridization of hydrogel electrolytes toward high-performance Zn-based energy storage devices under extreme conditions, *Progress in Materials Science* 160 (2026) 101675. <https://doi.org/https://doi.org/10.1016/j.pmatsci.2026.101675>.
- [5] Y. Tian, G. Zeng, A. Rutt, T. Shi, H. Kim, J. Wang, J. Koettgen, Y. Sun, B. Ouyang, T. Chen, Z. Lun, Z. Rong, K. Persson, G. Ceder, Promises and Challenges of Next-Generation “Beyond Li-ion” Batteries for Electric Vehicles and Grid Decarbonization, *Chemical Reviews* 121 (2021) 1623-1669. <https://doi.org/10.1021/acs.chemrev.0c00767>.
- [6] Y. Zhu, J.G. Connell, S. Tepavcevic, P. Zapol, R. Garcia-Mendez, N.J. Taylor, J. Sakamoto, B.J. Ingram, L.A. Curtiss, J.W. Freeland, D.D. Fong, N.M. Markovic, Dopant-Dependent Stability of Garnet Solid Electrolyte Interfaces with Li Metal, *Advanced Energy Materials* 9 (2019) 1803440. <https://doi.org/https://doi.org/10.1002/aenm.201803440>.
- [7] T. Krauskopf, R. Dippel, H. Hartmann, K. Peppler, B. Mogwitz, F.H. Richter, W.G. Zeier, J. Janek, Li-Metal Growth Kinetics on LLZO Garnet-Type Solid Electrolytes, *Joule* 3 (2019) 2030-2049. <https://doi.org/https://doi.org/10.1016/j.joule.2019.06.013>.
- [8] J.G. Connell, T. Fuchs, H. Hartmann, T. Krauskopf, Y. Zhu, J. Sann, R. Garcia-Mendez, J. Sakamoto, S. Tepavcevic, J. Janek, Kinetic versus Thermodynamic Stability of LLZO in Contact with Li Metal, *Chemistry of Materials* 32 (2020) 10207-10215. <https://doi.org/10.1021/acs.chemmater.0c03869>.
- [9] W. Lu, T. Wang, M. Xue, C. Zhang, Improved Li_{6.5}La₃Zr_{1.5}Nb_{0.5}O₁₂ electrolyte and effects of atmosphere exposure on conductivities, *Journal of Power Sources* 497 (2021) 229845. <https://doi.org/https://doi.org/10.1016/j.jpowsour.2021.229845>.
- [10] B. Huang, B. Xu, J. Zhang, Z. Li, Z. Huang, Y. Li, C.-A. Wang, Li-ion conductivity and stability of hot-pressed LiTa₂PO₈ solid electrolyte for all-solid-state batteries, *Journal of Materials Science* 56 (2021) 2425-2434. <https://doi.org/10.1007/s10853-020-05324-9>.
- [11] R. Chen, A.M. Nolan, J. Lu, J. Wang, X. Yu, Y. Mo, L. Chen, X. Huang, H. Li, The Thermal Stability of Li Solid Electrolytes with Metallic Li, *Joule* 4 (2020) 812-821. <https://doi.org/https://doi.org/10.1016/j.joule.2020.03.012>.
- [12] A.C. Moy, A. Manjón-Sanz, T.C. Caracciolo, M.V. Lobanov, G.M. Veith, J. Sakamoto, Effects of Al concentration on the structure and conductivity of Li lanthanum zirconium oxide, *Journal of Materials Chemistry A* 12 (2024) 28193-28210. <https://doi.org/10.1039/D4TA04862H>.
- [13] G. Zhong, J. Ma, T. Jia, K. Cai, S. Huang, X. Ren, R. Yin, K. Yu, Y. He, L. Qiu, W. Ding, X. Yu, F. Kang, Y. Cao, Triazine crosslinked polyionic liquid: An electrolyte-stable, lithiophilic and electrostatic shielding layer for uniform Li plating/stripping, *Nano Energy* 103 (2022) 107828. <https://doi.org/https://doi.org/10.1016/j.nanoen.2022.107828>.
- [14] H. Yang, Y. Zhang, M.J. Tennenbaum, Z. Althouse, Y. Ma, Y. He, Y. Wu, T.-H. Wu, A. Mathur, P. Chen,

- Y. Huang, A. Fernandez-Nieves, P.A. Kohl, N. Liu, Polypropylene Carbonate-Based Adaptive Buffer Layer for Stable Interfaces of Solid Polymer Li Metal Batteries, *ACS Applied Materials & Interfaces* 11 (2019) 27906-27912. <https://doi.org/10.1021/acsami.9b08285>.
- [15] Z. Xie, Z. Wu, X. An, X. Yue, P. Xiaokaiti, A. Yoshida, A. Abudula, G. Guan, A sandwich-type composite polymer electrolyte for all-solid-state Li metal batteries with high areal capacity and cycling stability, *Journal of Membrane Science* 596 (2020) 117739. <https://doi.org/10.1016/j.memsci.2019.117739>.
- [16] H. Jiang, J. Liu, B. Tang, Z. Yang, X. Liang, X. Yu, Y. Gao, J. Wei, Z. Zhou, Regulation Mechanism on A Bilayer Li₂O-Rich Interface between Li Metal and Garnet-Type Solid Electrolytes, *Advanced Functional Materials* 34 (2024) 2306399. <https://doi.org/10.1002/adfm.202306399>.
- [17] S. Pakseresht, V. Miikkulainen, F.A. Obrezkov, A.W.M. Al-Ogaili, J. Lahtinen, T. Kallio, Atomic layer deposition for protecting Li metal anodes to high-voltage battery applications, *Journal of Power Sources* 653 (2025) 237731. <https://doi.org/10.1016/j.jpowsour.2025.237731>.
- [18] Y. Hui, Y. Wu, W. Sun, X. Sun, G. Huang, Z. Na, Nanosecond Pulsed Laser-Assisted Deposition to Construct a 3D Quasi-Gradient Lithiophilic Skeleton for Stable Li Metal Anodes, *Advanced Functional Materials* 33 (2023) 2303319. <https://doi.org/10.1002/adfm.202303319>.
- [19] X. Sun, M. Jing, H. Dong, W. Xie, F. Luo, CuO-ZnO submicroflakes with nanolayered Al₂O₃ coatings as high performance anode materials in Li-ion batteries, *Journal of Alloys and Compounds* 953 (2023) 170137. <https://doi.org/10.1016/j.jallcom.2023.170137>.
- [20] Z. Pan, S. Cao, X. Lu, G. Zhang, Q. Shen, C. Mao, X. Dai, F. Chen, Ammonium fluoride induced barrier-free and oxygen vacancy enhanced LLZO powder for fast interfacial Li-ion transport in composite solid electrolytes, *Journal of Materials Chemistry A* 11 (2023) 20676-20685. <https://doi.org/10.1039/D3TA03195K>.
- [21] A. Gruendl, S. Weinmann, J. Goehmann, J. Landau, M. Lechner, L. Mueller, K.J. Kim, J.L.M. Rupp, M.F. Zaeh, Process strategies for the laser-based surface treatment of garnet-type ceramics used in solid-state batteries, *Optics & Laser Technology* 189 (2025) 113118. <https://doi.org/10.1016/j.optlastec.2025.113118>.
- [22] V. Thangadurai, S. Narayanan, D. Pinzaru, Garnet-type solid-state fast Li ion conductors for Li batteries: critical review, *Chemical Society Reviews* 43 (2014) 4714-4727. <https://doi.org/10.1039/C4CS00020J>.
- [23] J. Li, L. Su, L. Qiu, J. Zheng, Z. Lin, S. Bai, Highly integrated silk fibroin/nanohydroxyapatite hybrid composites via interface engineering for enhancing bone regeneration, *Chemical Engineering Journal* 521 (2025) 166676. <https://doi.org/10.1016/j.cej.2025.166676>.
- [24] L. Xiang, D. Jiang, Y. Gao, C. Zhang, X. Ren, L. Zhu, S. Gao, X. Zhan, Self-Formed Fluorinated Interphase with Fe Valence Gradient for Dendrite-Free Solid-State Sodium-Metal Batteries, *Advanced Functional Materials* 34 (2024) 2301670. <https://doi.org/10.1002/adfm.202301670>.
- [25] A. Morali, A. Mandal, M. Skorobogatiy, S. Bodkhe, Unleashing the piezoelectric potential of PVDF: a study on phase transformation from gamma (γ) to beta (β) phase through thermal contact poling, *RSC Advances* 13 (2023) 31234-31242. <https://doi.org/10.1039/D3RA05068H>.
- [26] K. Liu, Y. Ma, M. Cui, Q. Yu, M. Yuan, L. Tang, Hydrogen bonding and ion-dipole synergistic interactions enhance the $\alpha \rightarrow \gamma'$ phase transformation in PVDF/PMMA blend films, *Polymer* 350 (2026) 129783. <https://doi.org/10.1016/j.polymer.2026.129783>.
- [27] D. Avadanii, S. Ganschow, M. Stypa, S. Müller, S. Lang, D. Kramer, C. Kirchlechner, R. Mönig, Disconnected Li Metal Damages Solid-State Electrolytes, *ACS Energy Letters* 10 (2025) 2061-2067. <https://doi.org/10.1021/acsenenergylett.5c00101>.
- [28] V. Raj, N.P.B. Aetukuri, J. Nanda, Solid state Li metal batteries – Issues and challenges at the Li-solid

electrolyte interface, *Current Opinion in Solid State and Materials Science* 26 (2022) 100999.

<https://doi.org/https://doi.org/10.1016/j.cossms.2022.100999>.

[29] H. Hao, Y. Liu, S.M. Greene, G. Yang, K.G. Naik, B.S. Vishnugopi, Y. Wang, H. Celio, A. Dolocan, W.-Y. Tsai, R. Fang, J. Watt, P.P. Mukherjee, D.J. Siegel, D. Mitlin, Tuned Reactivity at the Li Metal–Argyrodite Solid State Electrolyte Interphase, *Advanced Energy Materials* 13 (2023) 2301338.

<https://doi.org/https://doi.org/10.1002/aenm.202301338>.

[30] Q. Zhou, Z. Huang, T. Yang, H. Zhang, X. Yao, W. Zhang, H. Huang, Y. Xia, X. Tao, J. Zhang, Sulfone electrolyte based quasi-solid-state high-voltage Li metal batteries enabled by component design and interfacial engineering, *Chemical Engineering Journal* 504 (2025) 158719.

<https://doi.org/https://doi.org/10.1016/j.cej.2024.158719>.

[31] Z. Zhang, J. Zhao, J. Zhou, Y. Zhao, X. Tang, S. Zhuo, Interfacial engineering of metal oxide/graphene nanoscrolls with remarkable performance for Li ion batteries, *Energy Storage Materials* 8 (2017) 35-41.

<https://doi.org/https://doi.org/10.1016/j.ensm.2017.03.003>.

[32] X. Wu, Z. Liu, K. He, J. Feng, P. Hu, F. Zhang, C. Shang, Li surface engineering with in-situ generated Fe/Li₂O/LiCl mixed electron/ion conductive layer for stable Li metal batteries, *Chemical Engineering Journal* 496 (2024) 153842. <https://doi.org/https://doi.org/10.1016/j.cej.2024.153842>.

[33] Q. Zhao, Y. Deng, N.W. Utomo, J. Zheng, P. Biswal, J. Yin, L.A. Archer, On the crystallography and reversibility of Li electrodeposits at ultrahigh capacity, *Nature Communications* 12 (2021) 6034.

<https://doi.org/10.1038/s41467-021-26143-9>.

[34] J. Tan, L. Ma, P. Yi, Y. Wang, Z. Li, Z. Fang, X. Li, S. He, X. Wang, M. Ye, J. Shen, Scalable Customization of Crystallographic Plane Controllable Li Metal Anodes for Ultralong-Lasting Li Metal Batteries, *Advanced Materials* 36 (2024) 2403570. <https://doi.org/https://doi.org/10.1002/adma.202403570>.

Electronic Supplementary Material

Janus-particle-based composite solid electrolytes with a root-soil interlocking architecture

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Supporting information to <https://doi.org/10.26599/NR.2026.94909055>

1. Experimental Procedures

Material Synthesis

SiO₂ nanoparticles were dispersed in deionized water and subjected to ultrasonic treatment for a fixed duration to obtain a homogeneous suspension. Surface modification of SiO₂ was carried out using 3-aminopropyltriethoxysilane (APTES) as the silane coupling agent. Specifically, the predetermined number of APTES was added to the SiO₂ dispersion under continuous stirring, and the reaction was allowed to proceed under controlled conditions. After completion, the modified SiO₂ nanoparticles were collected by centrifugation, followed by repeated washing to remove excess and physically adsorbed coupling agents.

Poly(vinylidene fluoride) (PVDF) was dissolved in N-methyl-2-pyrrolidone (NMP) to obtain a homogeneous polymer solution. Separately, sodium dodecyl sulfate (SDS) was dissolved in deionized water as a surfactant, and potassium persulfate (KPS) was introduced as a radical initiator. The mixture was magnetically stirred at room temperature to form a stable seed emulsion. Reaction parameters, including temperature and stirring rate, were carefully controlled to promote the formation of polymer seed particles with a narrow size distribution.

Vinylidene fluoride monomer was subsequently introduced into the seed emulsion at a controlled rate to maintain emulsion stability. Polymerization was initiated by the addition of KPS at a designated reaction temperature. During polymerization, monomer molecules preferentially polymerized on the surface of the seed particles, gradually forming PVDF shells on the SiO₂ cores, resulting in PVDF@SiO₂ composite particles. Upon completion of polymerization, carbon disulfide was added as a terminating agent to quench the radical reaction. The obtained composite particles were separated by centrifugation to remove unreacted monomers, solvents, and residual initiators, followed by repeated washing with deionized water and ethanol. The purified Si@PVDF composite particles were dried under vacuum to constant weight.

For the fabrication of Fe₃O₄/Si@PVDF Janus particles, the as-prepared Si@PVDF Janus particles were ultrasonically dispersed in distilled water in a three-neck flask and mechanically stirred under an argon atmosphere to prevent oxidation. Anhydrous ferric chloride and ferrous sulfate heptahydrate were then added sequentially according to a fixed molar ratio. Aqueous ammonia was introduced dropwise to adjust the pH to alkaline conditions, inducing the in situ co-precipitation

of Fe₃O₄ nanoparticles on the composite particle surface. The reaction mixture was maintained under stirring for 2 h to ensure sufficient growth and anchoring of Fe₃O₄. The resulting products were collected by centrifugation, washed multiple times with ethanol and deionized water, and finally freeze-dried under vacuum for approximately 24 h to obtain the final Fe₃O₄/Si@PVDF Janus particles.

Garnet-type Li₇La₃Zr₂O₁₂ (LLZO) solid electrolyte was synthesized via a conventional solid-state reaction route. The precursor powders were thoroughly mixed and subjected to a pre-calcination and binder burnout process, followed by final sintering in a muffle furnace. Dense LLZO ceramic pellets with a diameter of 12 mm and a thickness of approximately 1 mm were obtained after sintering.

To activate the surface of the LLZO pellets, a 20 wt% NaOH aqueous solution was prepared, and the LLZO ceramics were immersed for a predetermined duration. After treatment, the pellets were thoroughly rinsed with ethanol to remove residual NaOH. Subsequently, a mixed solution consisting of ethanol, water, and a DI-type silane coupling agent was prepared with a volume ratio of V_{Ethanol}: V_{Water}: V_{DI} = 9: 2.5: 1 and transferred into a two-neck flask. The treated LLZO ceramic electrolyte was added and ultrasonically dispersed to ensure sufficient surface exposure. The suspension was then heated to 75 °C in an oil bath and maintained under reflux using a spherical condenser with continuous mechanical stirring. The reaction was allowed to proceed for 24 h under controlled conditions to facilitate effective surface functionalization.

For the preparation of the Janus-modified coating layer, N, N-dimethylformamide (DMF), poly(vinylidene fluoride) (PVDF), and Fe₃O₄/Si@PVDF Janus particles were added into a glass vial at predefined mass ratios. The mixture was magnetically stirred for 24 h to obtain a homogeneous slurry. The resulting suspension was uniformly cast onto the surface of the LLZO ceramic electrolyte. The coated LLZO pellets were subsequently dried in a vacuum oven at 80 °C for 24 h to remove residual solvent and to form a dense and uniform composite modification layer.

Characterization methods

The phase structure of the samples was analyzed by X-ray diffraction (XRD, Bruker D8 Advance) using Cu K α radiation (λ = 0.15406 nm), operated at 40 kV and 40 mA. The diffraction patterns were collected over a 2 θ range of 10–80° with a scanning rate of 8° min⁻¹.

The surface and cross-sectional morphologies of the sintered pellets were examined by scanning electron microscopy (SEM, SU8010, Hitachi, Japan). A field-emission scanning electron microscope equipped with an energy-dispersive X-ray spectroscopy (FESEM-EDS, Quanta FEG, USA) was employed to further investigate the microstructure and elemental composition of the samples.

Fourier-transform infrared (FTIR) spectroscopy was performed using a Nicolet iS50 spectrometer (Thermo Fisher Scientific, USA) to analyze the molecular structure and chemical bonding characteristics based on infrared absorption behavior. The mechanical properties of the membranes were evaluated by tensile tests using a universal testing machine (Instron 5982, USA).

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI 5600 VersaProbe II system (PHI, Chanhassen, USA) to analyze the surface chemical composition and elemental valence states. Simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC-TGA, PerkinElmer Diamond DSC, USA) was conducted to obtain thermal transitions and mass variation information of the Janus materials, providing comprehensive insight into their thermal stability. Specifically, the TGA tests were performed at a heating rate of 10°C min⁻¹ from room temperature to 700°C under a continuous N₂ atmosphere.

The microstructure and composition of the Janus materials were further observed by transmission electron microscopy (TEM, FEI Tecnai F20, USA). The tensile stress of the Janus membranes was also measured using an Instron universal testing machine. Electrochemical performance was evaluated using an electrochemical workstation (Metrohm Autolab PGSTAT302N, Switzerland).

The frictional behavior of membranes with different compositions was evaluated using a friction coefficient tester (UMT-3). The friction-induced scratch morphology and the average friction coefficient (SA) were measured under 2000-grit sandpaper conditions. During the tests, the composite membrane was placed in contact with 2000-grit sandpaper, and a standard weight of 100 g was applied on top of the membrane to provide a constant normal load. A thin string was attached to the weight, and the membrane was pulled by the string in a direction perpendicular to the loading direction (90°). A reciprocating sliding distance of 10 cm was defined as one cycle, and the friction test was conducted continuously for 3 min under controlled conditions. The friction traces and corresponding average friction coefficients were recorded for analysis.

The electrochemical performance was evaluated by assembling CR2032-type coin cells. Cathode was prepared by mixing 95 wt% of LiFePO₄, 3 wt% acetylene black, and 2 wt% polyvinylidene fluoride (PVDF) in NMP. The slurry was coated on Al foil using a doctor blade and dried in a vacuum at 120 °C for 12 h. The mass loading of the active material is about 20 mg cm⁻². The thickness of the Li foil is 50 μm, and the thickness of the solid electrolyte is 0.5 mm. The parameters of the Li metal pouch cell are the same as those mentioned above.

Calculation section

In this study, density functional theory (DFT) calculations were performed using the Vienna *ab initio* Simulation Package (VASP) [1]. The exchange–correlation interactions were described within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional [2]. The projector augmented-wave (PAW) method was employed to accurately describe the interaction between ion cores and valence electrons [3]. A plane-wave kinetic energy cutoff of 400 eV was applied in all calculations. To eliminate spurious interactions between periodically repeated slabs, a vacuum layer of approximately 30 Å was introduced along the *z* direction. Brillouin zone sampling was carried out using a 3 × 3 × 1 Monkhorst–Pack *k*-point mesh. Structural optimizations were performed until the total energy and atomic forces converged to 10⁻⁵ eV and 0.02 eV Å⁻¹, respectively. To evaluate the interfacial stability between the garnet-type LLZO solid electrolyte and metallic Li, three representative interface models were constructed, including the direct LLZO/Li interface, the LLZO/Li₂O interface, and the Li₂O/Li interface. All interface structures were fully relaxed to obtain optimized atomic configurations. The interfacial energies were calculated to quantitatively assess the thermodynamic stability of different interfaces and to clarify the role of the Li₂O interlayer in regulating interfacial compatibility between LLZO and Li metal.

The interfacial energy (γ) of the constructed interface models was calculated according to the following equation:

$$\gamma = \frac{E_{interface} - E_{slab1} - E_{slab2}}{A} \quad \#(1)$$

where $E_{interface}$ is the total energy of the relaxed interface supercell, E_{slab1} and E_{slab2} are the total energies of the two isolated slabs (LLZO, Li₂O, or Li) with identical atomic configurations and cell dimensions as those in the interface model, and A denotes the interfacial contact area.

For asymmetric interface models, the calculated interfacial energy represents the average value over the interface region. All energies were obtained from fully relaxed structures using the same computational parameters to ensure consistency and comparability among different interface systems.

Just Accepted

Supplementary data

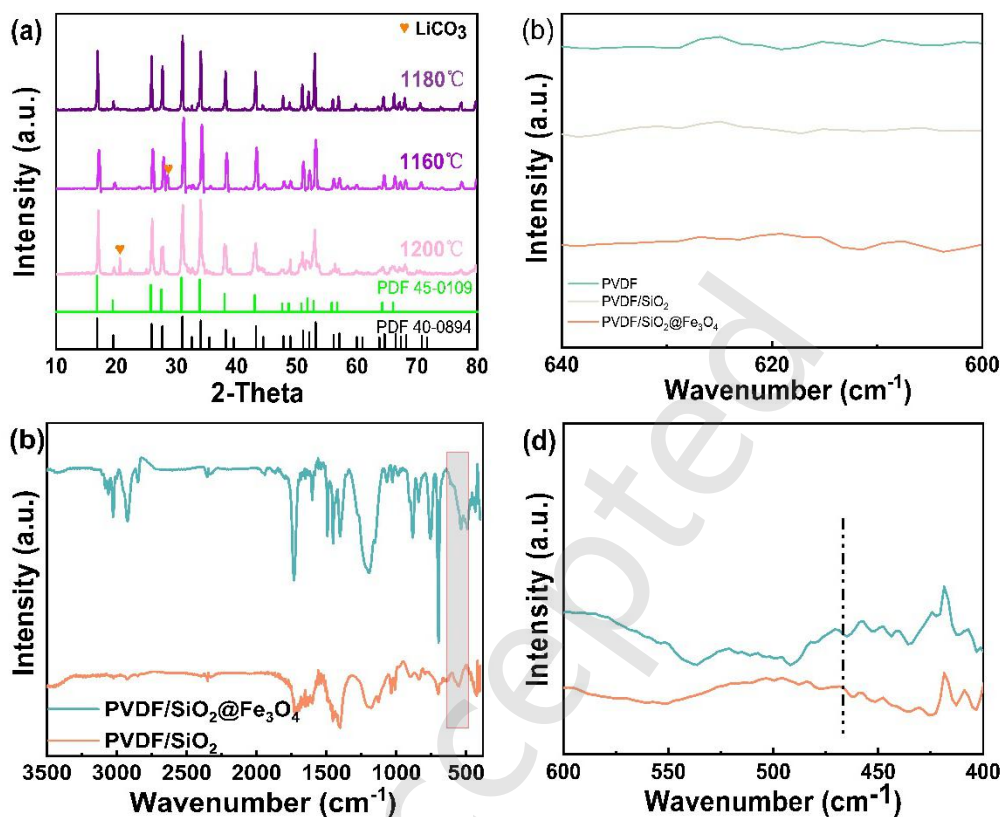


Figure S1. (a) XRD patterns of LLZO sintered at different temperatures. (b) Enlarged FTIR spectra of the composite membrane. (c) FTIR spectrum of Janus particles and (d) the corresponding enlarged view.

Firstly, the optimal sintering temperature of LLZO was determined by XRD (**Fig. S1a**) and cross-sectional SEM observations (**Fig. S4a-d**). LLZO sintered at lower temperatures exhibits pronounced porosity, insufficient grain growth, and poorly defined grain boundaries. Upon increasing the sintering temperature to 1180 °C, strong intergranular bonding is achieved, leading to a highly dense microstructure with significantly reduced porosity. Further temperature elevation induces abnormal grain growth accompanied by increased porosity, which is attributed to aggravated Li volatilization. EDS mapping confirms a homogeneous elemental distribution without detectable segregation.

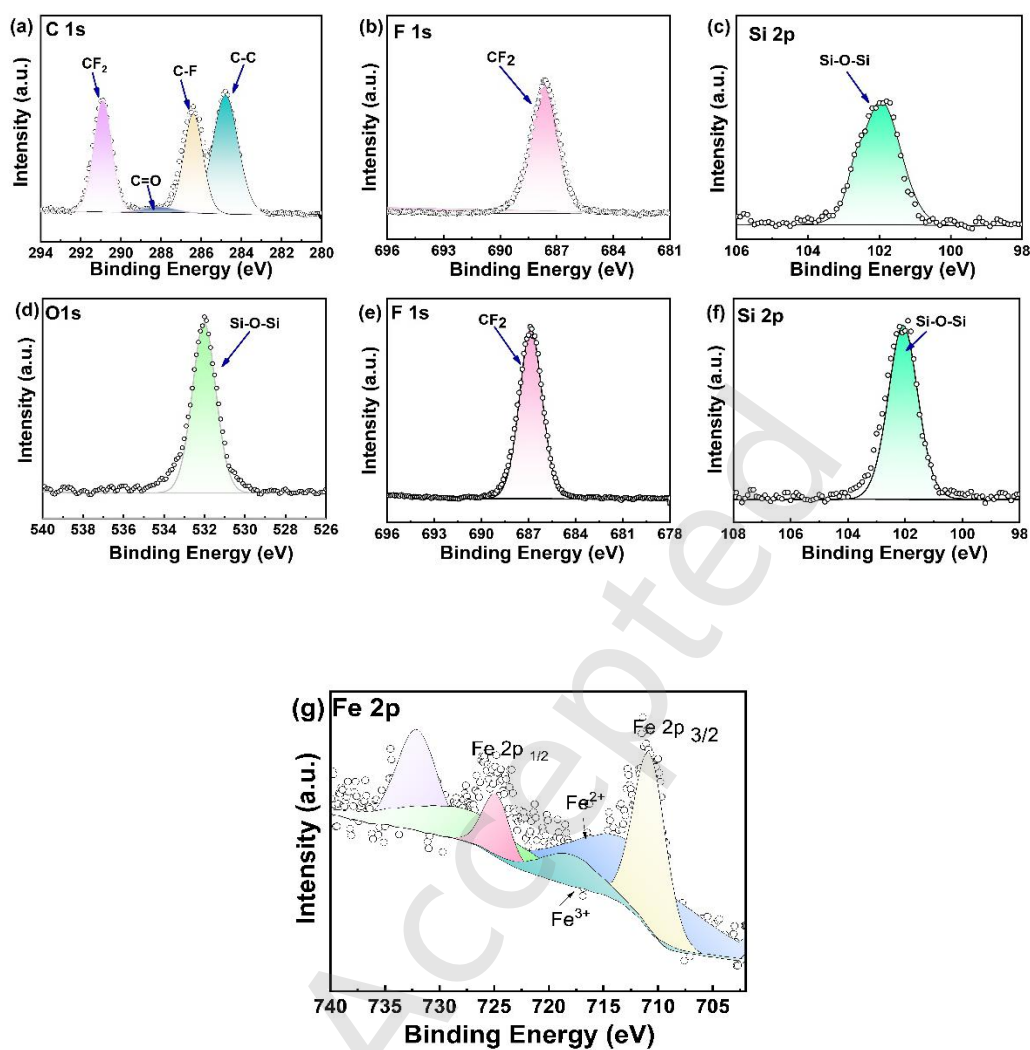


Figure S2. High-resolution XPS spectra of PVDF@SiO₂ (a–d) and Fe₃O₄/SiO₂@PVDF (e–g).

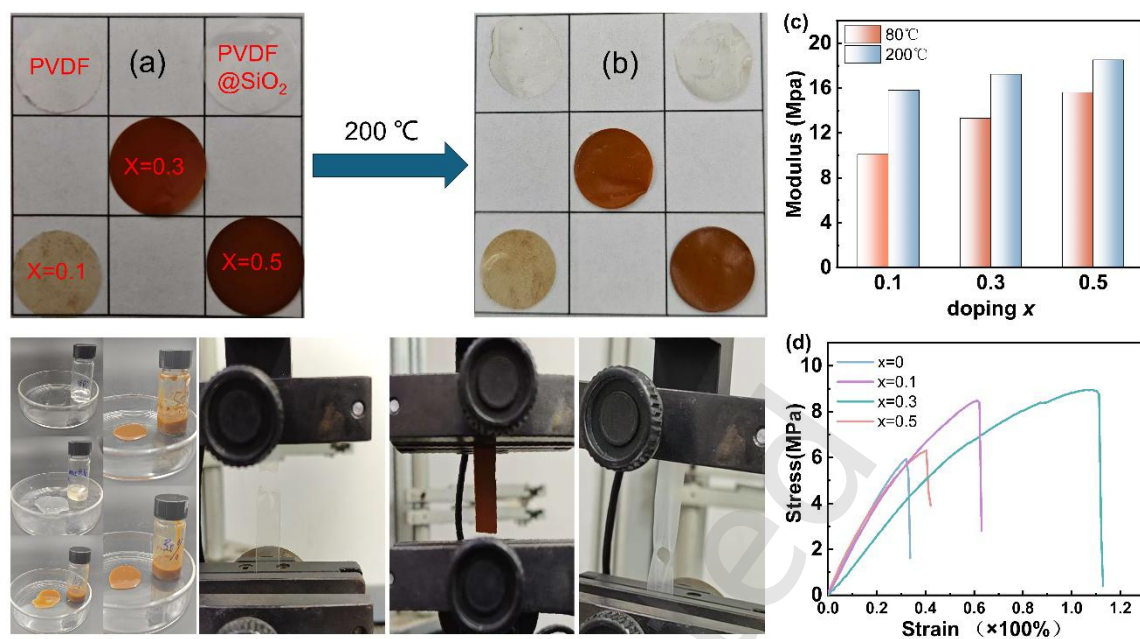


Figure S3. Morphology of the composite membranes at different temperatures: (a) 80 °C and (b) 200 °C. Tensile properties of membranes with different compositions measured at elevated temperatures: (c) tensile stress–strain curves at 200 °C and (d) Young’s modulus of membranes at different temperatures.

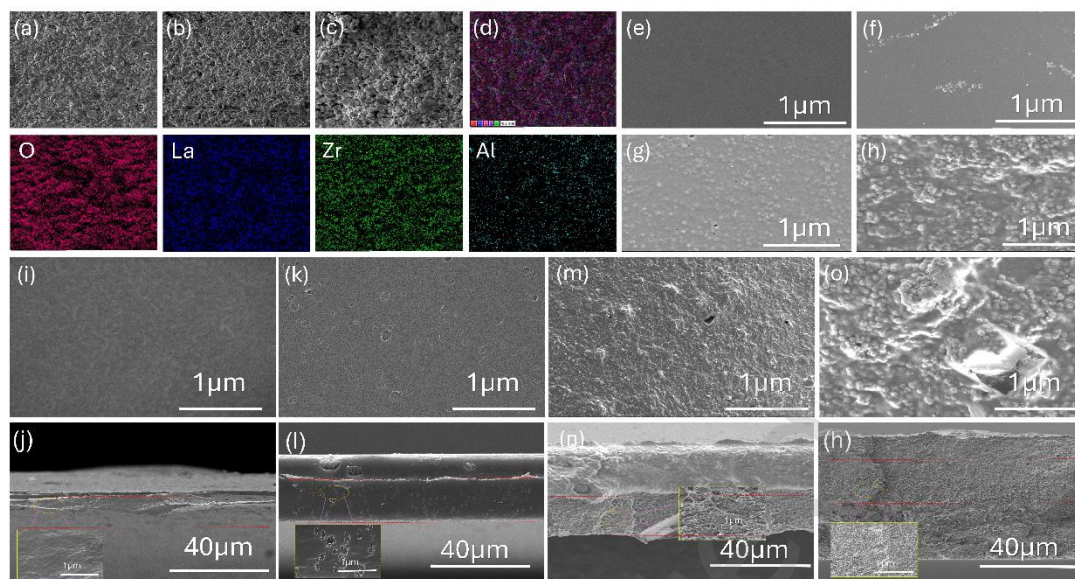


Figure S4. Cross-sectional SEM images of LLZO ceramics sintered at different temperatures: (a) 1160 °C, (b) 1180 °C, and (c) 1200 °C. (d) EDS elemental mapping of LLZO sintered at 1180 °C. Surface roughness of membranes with different compositions: (e) $x = 0$, (f) $x = 0.1$, (g) $x = 0.3$, and (h) $x = 0.5$. Plan-view and cross-sectional morphologies of $\text{Fe}_3\text{O}_4 @\text{Si}/\text{PVDF}$ Janus composite membranes with different contents ($x = 0, 0.1, 0.3$, and 0.5): (i, k, m, o) top-view images and (j, l, n, p) corresponding cross-sectional images with magnified views.

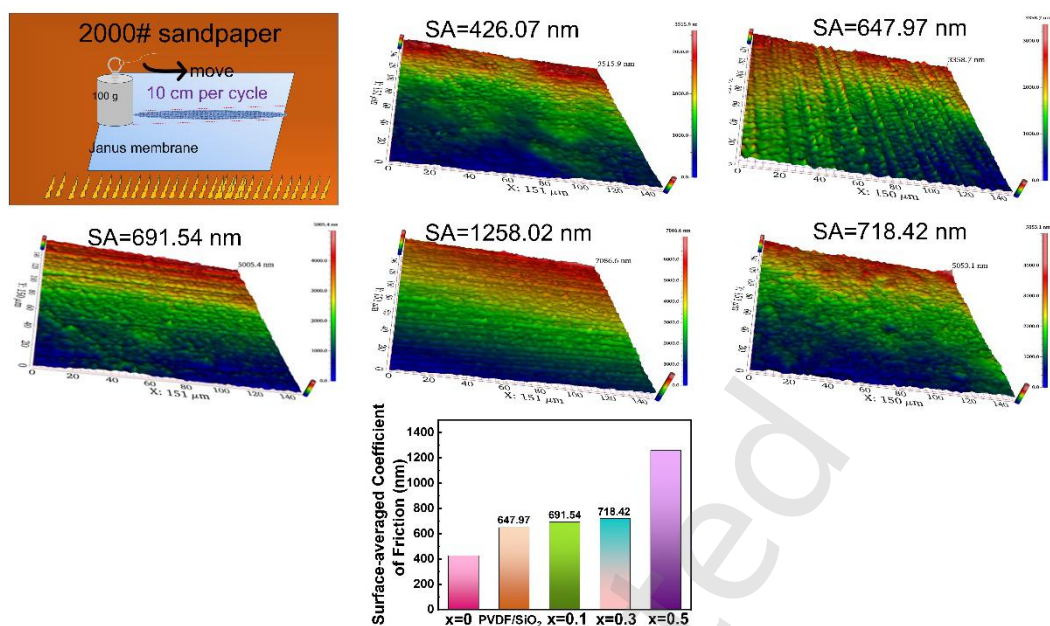


Figure S5. Friction properties of membranes with different compositions: (a) schematic illustration of friction-induced crack formation, (b) PVDF, (c) PVDF/SiO₂, and (d, e, f) Fe₃O₄@Si/PVDF Janus composite membranes with different contents ($x = 0.1, 0.5$, and 0.3). (g) surface-averaged coefficient of friction histogram

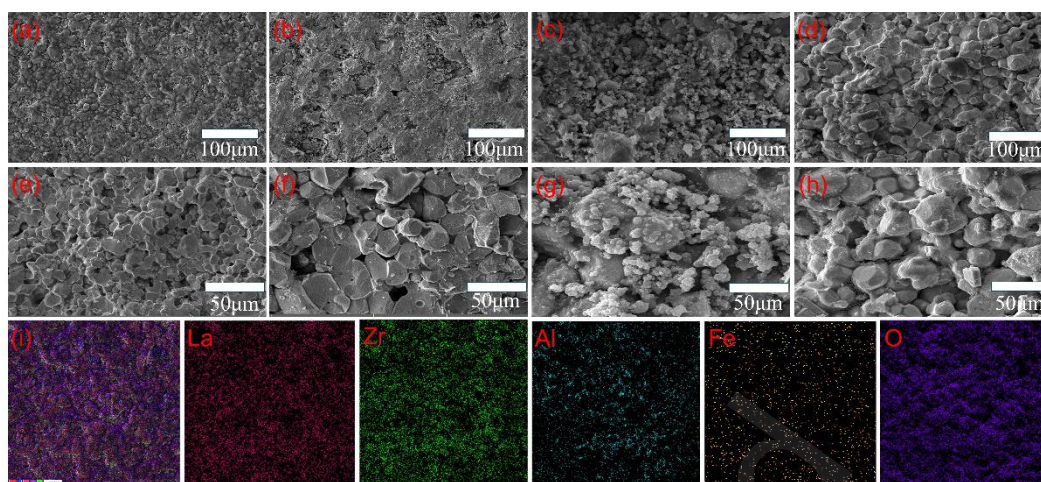


Figure S6. SEM images of LLZO before and after interfacial treatment and electrochemical reaction: (a, e) surface and cross-sectional morphologies of pristine LLZO, (b, f) cross-sectional morphology of LLZO after cycling, (c, g) cross-sectional SEM images and corresponding magnified views of LLZO after reaction with the composite electrolyte without DI silane modification, (d, h) cross-sectional SEM images and corresponding magnified views of LLZO after reaction with the fully DI-silane-modified composite electrolyte. (i) EDS elemental mapping corresponding to panel (d).

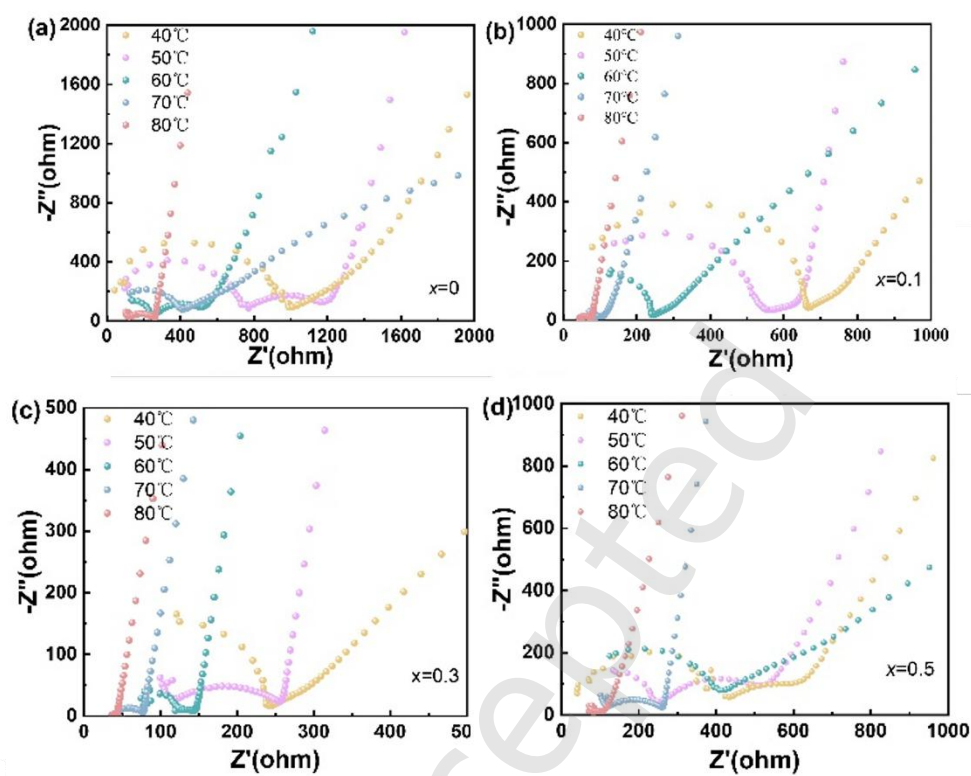


Figure S7. (a–d) Temperature-dependent electrochemical impedance spectra (EIS) of LLZO with different doping contents.

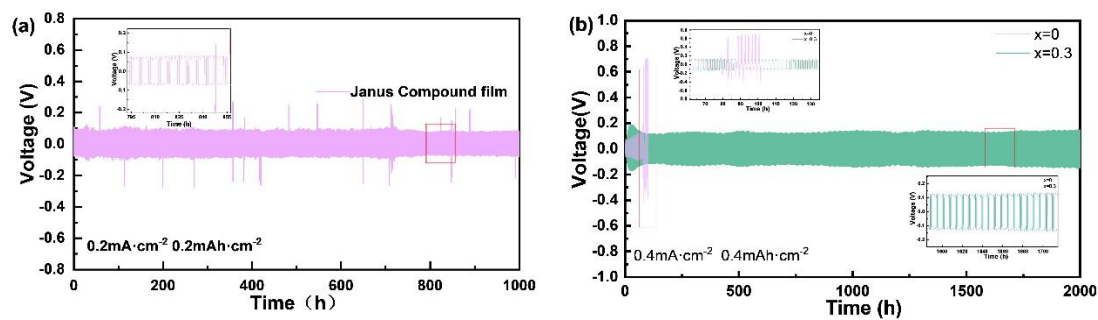


Figure S8. (a) Cycling performance of Li||Li symmetric cells before and after modification. (b) Cycling performance of Li||Li symmetric cells using the $\text{Fe}_3\text{O}_4@\text{Si}/\text{PVDF}$ Janus membrane as a separator without a solid electrolyte.

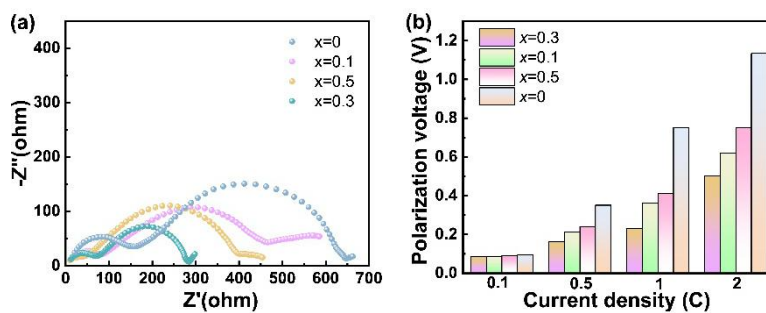


Figure S9. (a) Nyquist plots of Li||Li symmetric cells employing LLZO electrolytes with different Janus particle contents. (b) Overpotentials of cells with different Janus particle contents measured at various current densities.

Supporting references

- [1] G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758; b) G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169.
- [2] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
- [3] P. E. Blöchl, Phys. Rev. B 1994, 50, 17953.

Just Accepted