

Strong Lewis Acid–Base and Weak Hydrogen Bond Synergistically Enhancing Ionic Conductivity of Poly(ethylene oxide)@SiO₂ Electrolytes for a High Rate Capability Li-Metal Battery

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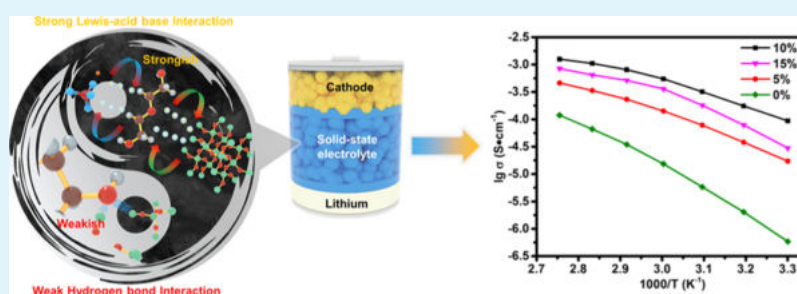
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ABSTRACT: Solid-state composite polymer electrolytes (CPEs) usually suffer from intrinsic low ionic conductivity and a solid–solid interface, badly inhibiting their widespread commercial application in all-solid-state Li-metal battery (ASSLMB) energy storage. Herein, a synergistic strategy using strong Lewis acid–base and weak hydrogen bonds was employed for self-assembly in situ construction of three-dimensional (3D) network-structured poly(ethylene oxide) (PEO) and SiO₂ CPEs (PEO@SiO₂). Ascribed to this synergistically rigid–flexible coupling dynamic strategy, a harmonious incorporation of monodispersed SiO₂ nanoparticles into PEO could remarkably reduce crystallinity of PEO, significantly enhancing the ionic conductivity ($\sim 1.1 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C) and dramatically facilitating solid electrolyte interface stabilization (electrochemical stability window > 4.8 V at 90 °C). Moreover, the PEO@SiO₂-based ASSLMs possess excellent rate capability over a wide temperature range ($\sim 105 \text{ mA h g}^{-1}$ under 2 C at 90 °C), high temperature cycling capacity (retaining 90 mA h g⁻¹ after 100 cycles at 90 °C), and high specific capacity (146 mA h g⁻¹ under 0.3 C at 90 °C). Unambiguously, these high ionic conductivity CPEs along with excellent flexibility and safety can be one of the most promising candidates for high-performance ASSLMs, evidently revealing that this synergistically rigid–flexible coupling dynamic strategy will open up a way to exploit the novel high ionic conductivity solid-state electrolytes.

KEYWORDS: all-solid-state Li-metal battery, ceramic-polymer composite electrolytes, in situ synthesis, ionic conductivity, rate capability

1. INTRODUCTION

Composite polymer electrolytes (CPEs) with greatly improved ionic conductivity and better mechanical properties compared to solid polymer electrolytes (SPEs) can potentially inhibit Li dendrite growth ascribed to their high mechanical strength.^{1–4} These unique CPEs will make it possible to fully exploit lithium-metal anodes (with an extremely high specific capacity of 3860 mA h g⁻¹ and the lowest electrochemical potential of –3.04 V vs the standard hydrogen electrode) for the state-of-the-art all-solid-state lithium-metal batteries (ASSLMs).^{5–7} Typically, poly(ethylene oxide) (PEO)-based CPEs have been extensively studied because of their high ionic conductivity, decent mechanism properties, simple large-scale fabrication, and low electrolyte–electrode interface resistance to date.^{8,9} Therefore, this kind of CPE-developed ASSLMB would be the most promising candidate for large-scale energy storage devices, such as electric vehicles, smart grids, and so forth.^{10–13}

For further enhancing ionic conductivity of PEO-based CPEs, some composite approaches such as adding plasticizers and forming the copolymer or cross-linking polymers had to slightly sacrifice mechanical strength and electrochemical stability of CPEs.^{14–16} In contrast, the appropriate addition of ceramic nanoscale fillers into the polymer skeleton can inhibit the recrystallization kinetics of the polymer chains for intensifying localized amorphization, ultimately increasing the ionic conductivity and electrochemical stability of the CPEs simultaneously.¹⁷ During this recrystallization process, the size and specific surface area of nanoparticles play crucial roles in

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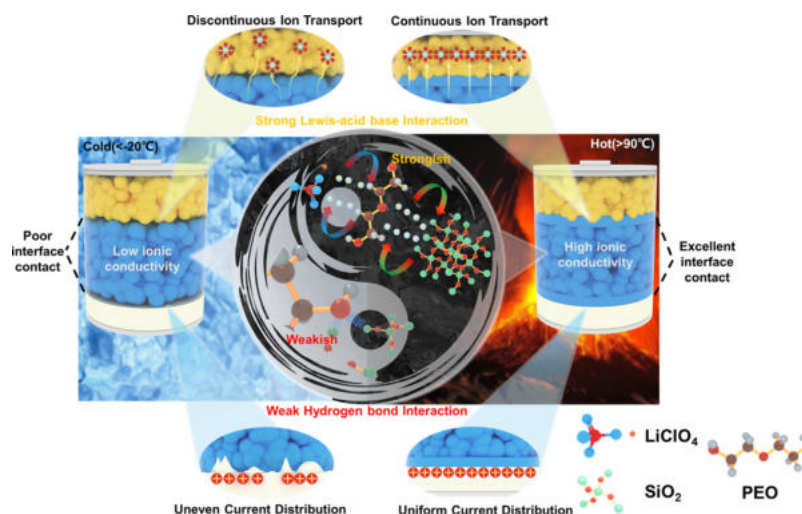


Figure 1. Synergistic effect of strong Lewis acid–base interaction and relatively weak hydrogen bond interaction between the PEO matrix, SiO₂ nanoparticles, and Li salt along with the excellent solid–solid interface contact at high temperature resulting in fast ion transport and uniform current distribution, which is critical for the high rate capacity and favorable stability toward the lithium-metal anode.

overcoming the energy barrier of particle–particle junctions, which is essential for the ionic conductivity improvement of the CPEs.^{4,18} To further minimize the particle junctions and homogeneously disperse the nanofillers into polymer chains, the three-dimensional (3D) nanostructure networks based on the garnet-type fast lithium-ion conductor Li_{6.4}La₃Zr₂Al_{0.2}O₁₂ could effectively provide continuous Li⁺ transfer channels in PEO-based CPEs, presenting an improved ionic conductivity of 2.5×10^{-4} S cm⁻¹ at room temperature.¹⁹ However, Cui et al.⁸ integrated in situ-synthesized SiO₂ nanoparticles into the PEO–LiClO₄ CPE to significantly suppress the crystallization of the PEO matrix, achieving an ionic conductivity of 4.4×10^{-5} S cm⁻¹ at 30 °C. Despite the ionic conductivity of PEO-based CPEs being somewhat alleviated through the above-mentioned strategies, the synergistic rigid–flexible dynamics between polymer chains and nanoparticles in the 3D PEO-based CPEs have not been entirely optimized to fully extract their electrochemical performance.

Herein, we proposed a synergetic strategy using strong Lewis acid–base and weak hydrogen bonds (as shown in Figure 1) for self-assembly in situ construction of 3D network-structured PEO and SiO₂ CPEs (PEO@SiO₂) with different internal interface contacts between electrodes and electrolytes under different temperatures. The crystallinity of PEO was reduced remarkably because of this synergistically rigid–flexible coupling dynamic strategy, thus significantly enhancing the ionic conductivity ($\sim 1.1 \times 10^{-4}$ S cm⁻¹ at 30 °C) and dramatically facilitating solid electrolyte interface (SEI) stabilization (electrochemical stability window > 4.8 V at 90 °C). Hence, the PEO@SiO₂-based ASSLMBs possess excellent rate capability over a wide temperature range (~ 105 mA h g⁻¹ under 2 C at 90 °C), high temperature cycling capacity (retaining 90 mA h g⁻¹ after 100 cycles at 90 °C), and high specific capacity (147 mA h g⁻¹ @0.3 C at 90 °C). Evidently, this rigid–flexible coupling dynamic strategy will generate tremendous opportunities for achieving high-electrochemical performance CPEs and also promote the emerging state-of-the-art ASSLMBs.

2. EXPERIMENTAL SECTION

2.1. Materials. PEO (average $M_v = 600,000$, Sigma-Aldrich), lithium perchlorate (99%, Aladdin), and lithium iron phosphate (LiFePO₄, battery level) were vacuum-dried for 24 h before use. Tetraethyl orthosilicate (TEOS, AR), ammonium hydroxide (AR), *N*-methyl pyrrolidone (NMP, AR), and polyvinylidene fluoride (AR) were purchased from Kelong Chemical Reagents Company (Chengdu, China). Super P (C6S, Timical) and lithium foil (battery level) were directly used without further treatment.

2.2. Characterization. Fourier transform infrared (FT-IR) spectra were recorded with a Thermo Fisher company Nicolet iS10 infrared instrument, applying the reflection and transmission patterns. A transmission electron microscope (TEM, JEM-2100F) was utilized to characterize the morphology and distribution of materials. A JFOF JSM-7800F field-emission scanning electron microscope was used to obtain the microstructure and morphologies of SiO₂ nanoparticles and SPEs (sprayed with Au ~ 50 s). An energy-dispersive spectrometer of Oxford Instruments was used to detect the distribution of SiO₂ nanoparticles in the CPEs. To acquire the crystallinity variation of the SPE, X-ray diffraction (XRD) spectra were recorded on a Dutch PANalytical Panaco X'pert powder automated multifunctional X-ray diffractometer with Cu K α X-ray radiation. Differential scanning calorimetry (DSC) was performed using a Discovery 2500 fabricated by TA Instruments to acquire phase transition temperature. Solid-state nuclear magnetic resonance (SSNMR, Bruker ADVANCE III 400 MHz) was applied to characterize the hydrogen bond interaction between the PEO matrix and SiO₂ nanoparticles. All the measurements mentioned above were performed under the same conditions that included the same area and thickness of films at room temperature except for the high temperature XRD and DSC.

2.3. Synthesis of All-Solid-State Li-Metal Batteries. **2.3.1. Synthesis of SPE Membranes.** For in situ synthesis of SiO₂ nanoparticles and assembling SiO₂ into the SPE, 1.5 g of PEO was dispersed in 50 mL of deionized (DI) water homogeneously. The pH of the solution was changed to approximately 11 and NH₃·H₂O was used to facilitate the hydrolysis reaction. Typically, 0.34 g (5%), 0.68 g (10%), and 1.02 g (15%) of TEOS were added into the solution dropwise as the SiO₂ nanoparticle precursor. The obtained heterogeneous system was stirred intensely at 500 rpm and 60 °C for 24 h in a water bath. After the hydrolysis reaction was complete, 0.45 g of LiClO₄ was added into the solution to maintain the EO/Li = 8:1. The solvent was partially evaporated to obtain appropriate viscosity. Through solution casting on the PTFE pattern, SPE membranes with an average thickness of 150 μ m were prepared. They were then moved into an argon-filled

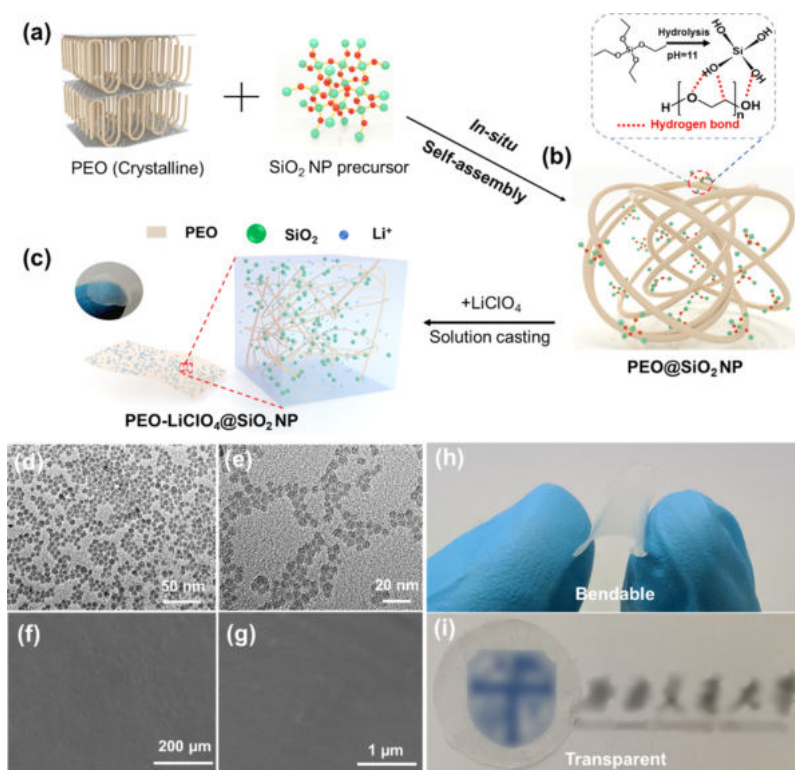


Figure 2. Synthetic routes and morphology of the PEO–LiClO₄@SiO₂ CPEs. (a) Crystalline PEO and SiO₂ nanoparticle precursor (TEOS). (b) SiO₂ nanoparticles self-assemble into PEO amorphous chains through a hydrogen bond. The inset shows the in situ hydrolysis reaction of TEOS. (c) PEO-based CPE membranes obtained by solution casting. (d,e) TEM images of in situ SiO₂ nanoparticles with a size of ~10 nm. (f,g) Surface SEM images of in situ CPEs membranes. (h,i) CPE films show desirable transparency and shape conformity properties.

glovebox (O₂ and H₂O < 0.1 ppm) and preserved for another 24 h to completely eliminate the solvent prior to the test and assembly of the batteries.

2.3.2. Synthesis of LiFePO₄ Electrodes. For preparing LiFePO₄ (LFP) electrodes, in a typical procedure, dehydrated LFP, Super P, and polyvinylidene fluoride solution (4 wt %) at a weight ratio of 85:10:5 were mixed with a moderate amount of *N*-methyl pyrrolidone under ball-mill stirring at 400 rpm for 2 h. Moreover, the electrodes were made by doctor blading on aluminum foil. The as-obtained electrodes were dried in a vacuum oven at 120 °C for 24 h and moved into the glovebox. The areal loading of the LFP electrode is approximate 7 mg cm⁻².

2.4. Electrochemical Measurements. The ionic conductivities of the CPEs were measured on an electrochemical workstation (CHI660E, Shanghai, China), through electrochemical impedance spectroscopy (EIS) with the symmetric SS/CPE/SS cell. The ac amplitude was 5 mV, the frequency ranged from 10⁶ to 1 Hz, and the temperature was controlled using an environmental chamber (T-HWS-150H, Dongguan, China) between ambient temperature and 90 °C. Moreover, the ionic conductivity can be acquired by the following equation

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

where L is the thickness of the CPE, R is the interfacial impedance between the CPE and block electrode, and S is the contact area of the SS and CPE.

The electrochemical stability window of the CPEs was measured through linear sweep voltammetry (LSV) with the Li/CPE/SS cell at a scan rate of 10 mV s⁻¹ from 0 to 6 V (Li⁺/Li). Cyclic voltammetry (CV) was used to test the compatibility of the CPEs and the electrode with the Li/CPE/LFP cell with different scanning rates in the voltage range of 2.5–4.3 V.

The lithium-ion migration number (t_{Li^+}) of the CPEs was obtained by the lithium/CPE/SS cell via EIS and dc polarization, and t_{Li^+} was obtained using the following equation

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

where ΔV is the self-defined voltage (10 mV), R_0 and R_{SS} represent the interfacial impedance before and after the dc polarization, respectively, and I_0 and I_{SS} are the initial current before the dc polarization and the stable current after the dc polarization, respectively.

Galvanostatic cycling of the Li/Li symmetric cell using PEO–LiClO₄@SiO₂ was conducted at a current density of 0.1 mA cm⁻² (cycled at 90 °C). Both the charge and discharge times were 0.5 h.

The rate capacity and cycling performance of the CPE were evaluated using all-solid-state batteries of LFP/CPE/Li. A Neware battery testing system was used for testing the cells at the 60 and 90 °C with the voltage ranging from 2.5 to 4.3 V.

3. RESULTS AND DISCUSSION

3.1. In Situ Synthesis and Morphology of PEO Composite (PEO@SiO₂ NP) Electrolytes. Figure 2 shows the integrated synthetic routes and morphology of the in situ SiO₂ nanoparticle-doped PEO-based CPE membranes. The crystalline PEO polymer chains and SiO₂ nanoparticle precursor (Figure 2a) were self-assembled into the homogeneous phase by in situ hydrolysis reaction. The LiClO₄ salt was added to the mixed solution to provide Li⁺ for CPEs via the dissociation process. It can be seen from Figure 2b that the SiO₂ nanoparticles dramatically stimulate the movement of PEO polymer chains via the synergistic effect of strong Lewis acid and hydrogen bond interactions. It was proved that the

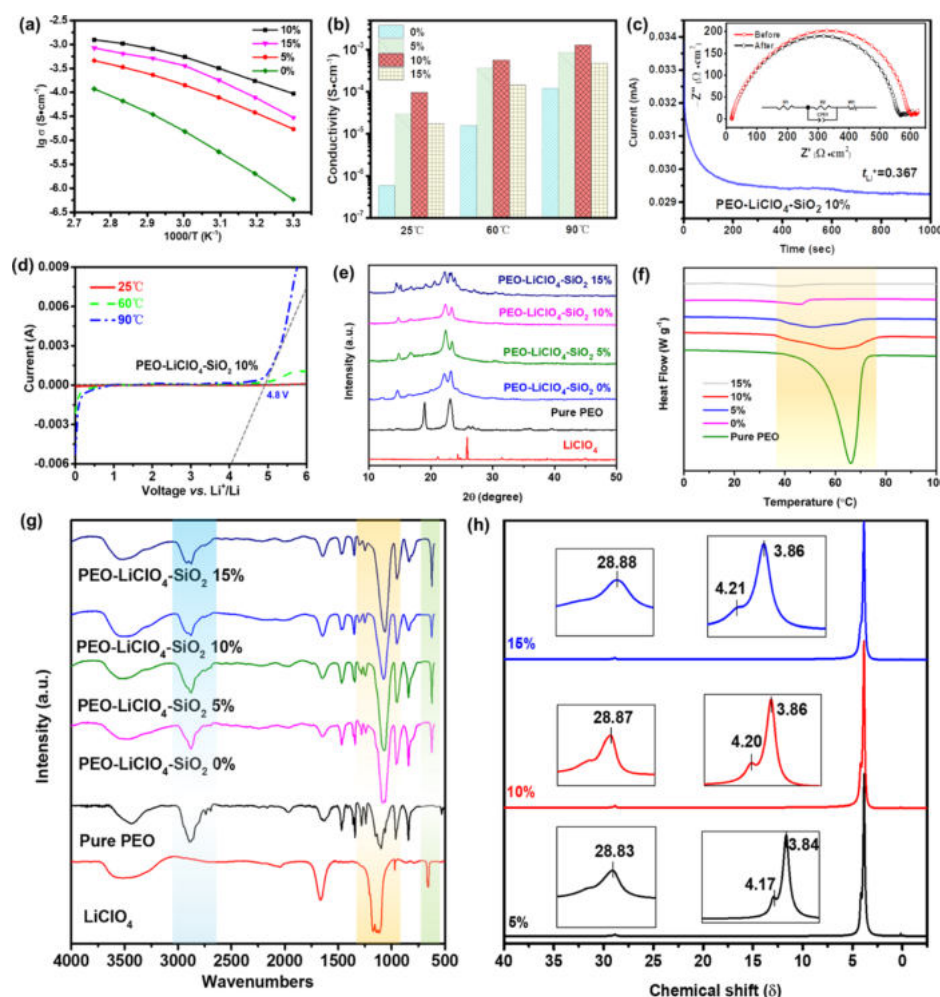


Figure 3. Characterizations of strong Lewis acid–base and weak hydrogen bond interactions toward the electrochemical performance of in situ CPEs. (a) Arrhenius plots and (b) histogram of ionic conductivity of different in situ SiO_2 -doped CPEs. (c) Lithium-ion migration number of 10% doped CPEs. (d) Electrochemical stability windows of 10% doped CPEs at room temperature, 60, and 90 °C. (e) Comparison of XRD spectra of pure PEO, pure LiClO_4 , and different doping ratio CPEs. (f) DSC curves of the different doped ratio CPEs. (g) FT-IR absorbance spectra of pure PEO, pure LiClO_4 , and different doped ratio CPEs. (h) SSMNR spectra of different doped ratio CPEs.

siloxane polar group could efficiently promote PEO polymer chains to cross-link into the infinity 3D network.^{20,21} Therefore, we take advantage of this synergistic effect to in situ grow SiO_2 nanoparticles instead of just cross-linking the PEO network. Solution casting was adopted to prepare the PEO-based CPE membranes (Figure 2c) (a more detailed process is shown in Figure S1). During the in situ hydrolysis reaction, the hydroxyl groups at the end of PEO chains will chemically interact with high specific surface area SiO_2 nanoparticles and LiClO_4 according to Lewis acid–base theory,²² resulting in a remarkable decrease of the PEO crystallinity (a brief mechanism is illustrated in Figure S2). The SiO_2 nanoparticles invade into PEO between the molecular chains, and the intermolecular interaction impaired because of the increase of the molecular internal rotation resistance.²³ Also, the existence of the hydrogen bond between SiO_2 and PEO can physically increase the friction of PEO molecular chains, and the cross-linked 3D network structure can further inhibit the wriggle of segments.^{24,25} These synergistically rigid–flexible coupling dynamics can locally restrain the movement of polymer chains and eventually prevent their recrystallization.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were employed to characterize the morphology and distribution of the acquired in situ SiO_2 nanoparticles and composite SPE films. Figure 2d,e indicates that the in situ synthesis is feasible and the SiO_2 nanoparticles are dispersed homogeneously regardless of in PEO matrix or not (more SEM figures are shown in Figures S3 and S4). This result can also be confirmed by energy-dispersive spectrometry (EDS) elemental analysis (Figure S5). The surface of the CPE films is smooth and clear (Figure 2f,g). They can be bent freely without breaking, revealing superior flexibility (as shown in Figure 2h) which is critical in wearable electronics and wireless monitoring systems.^{26,27} These membranes also show a favorable transparent pattern, as indicated in Figure 2i.

3.2. Synergistic Effect of Lewis Acid–Base and Hydrogen Bond Interaction toward Enhanced Electrochemical Performance of in Situ CPEs. Ionic conductivity is a critical parameter for a solid-state electrolyte to be applied in ASSLMs. Figure 3a,b show the Arrhenius plots of ionic conductivity for different doped PEO-based CPE membranes at the temperature ranging from 25 to 90 °C. It can be clearly seen that the adulteration of SiO_2 nanoparticles through the in situ method significantly increases the ionic conductivity over

an order compared to the pure PEO–LiClO₄ SPE at the same temperature. Notably, 10% doped in situ SiO₂ exhibits the highest ionic conductivity ($\sim 1.1 \times 10^{-4}$ S cm⁻¹ at 30 °C) among all the SiO₂ nanoparticle-doped CPEs (more Nyquist plots at different temperatures can be seen in Figure S6). Generally, the ionic conductivity of the CPE may exhibit a “threshold effect”, which means that only suitable contents of SiO₂ nanoparticles are available to promote the movement of PEO molecular chains for the fast lithium ion transport.²⁶ The 5% concentration shows a relatively lower ionic conductivity because of the higher crystallinity of the PEO matrix, while that with the 15% concentration is because of the relatively weak synergetic interaction and less ratio of free ClO₄⁻ and bonded ClO₄⁻. Moreover, the mechanical property of 20% doped CPEs includes high hardness but also high fragility, which is unsuitable for practical application.

In order to achieve high rate performance of ASSLMBs, the lithium ion migration number of the CPEs needs to be high enough to achieve rapid movement of Li⁺. EIS and dc polarization were carried out to calculate the lithium-ion migration number of different SiO₂ nanoparticle doping ratios of CPEs at ambient temperature. dc polarization, EIS curves, and their equivalent circuits are shown in Figures 3c and S7. The 10% doped CPE exhibits the most potent ability of lithium ion migration, whose calculated number is 0.367. The electrochemical stability window of a solid electrolyte is another essential factor for its application in ASSLMBs. The electrolyte which is stable enough to inhibit the decomposition reaction itself at high potential versus Li/Li⁺ can coordinate with high potential cathode materials to increase the energy and power density.^{28,29} Here, LSV curves of 10% SiO₂ nanoparticle-doped CPEs at three typical temperatures are shown in Figure 3d. In contrast, 0% doped was also tested, as shown in Figure S8. For the 0% doped PEO electrolyte, the decomposition reaction occurs at ~ 4.5 V versus Li/Li⁺ at 60 °C, where the current flow increases significantly. However, the higher electrochemical stability window (>5 V at 60 °C) can be observed in 10% SiO₂ nanoparticle-doped CPEs. We attribute this result to the unique 3D network structure between the PEO segment and in situ SiO₂ nanoparticles and the excellent electrode–electrolyte interface contact at high temperature. Moreover, the high specific surface of SiO₂ nanoparticles and strong interaction between the polar group on PEO molecular chains play critical roles in absorbing H₂O and other impurities in the PEO matrix. The expansion of the electrochemical stability window verifies that the in situ SiO₂ nanoparticle can promote not only the ion migration but also the stability of the PEO matrix even at relatively high temperature.

In order to discuss the mechanism of improved electrochemical performance of CPEs, XRD spectra are shown to verify the influence of different doped SiO₂ precursors on the crystallinity of PEO (Figure 3e). The spectrum of pure PEO shows two sharp peaks at around 19.0 and 23.0°, which are identified with the JCPDS card #52-2279 (18.9 and 22.9°). These two strong peaks are a consequence of highly crystallized PEO at room temperature. After incorporating into LiClO₄ salts, the intensity of the PEO characteristic peak greatly reduced, evidently proving that Li salts as a plasticizer can effectively tailor the crystallinity of PEO via strong Lewis acid–base interaction.⁸ However, with increasing doped proportion of SiO₂, the crystalline peak intensity further decreases because of the accompanying weak hydrogen bond

interaction. Typically, the PEO–LiClO₄@SiO₂ with the optimal 10% incorporation of SiO₂ exhibits an almost indistinguishable and dispersed PEO characteristic peak, indicating the high amorphous proportion in the PEO matrix.

For further understanding toward the interaction between the PEO matrix, SiO₂ nanoparticles, and Li salt, we characterized the endothermic peak of DSC (Figure 3f), the absorbance intensity of FT-IR (Figure 3g), and the chemical shift of solid-state NMR (Figure 3h) in detail. From Table S1 and Figure S9, the pure PEO presents the highest $X_c \approx 87.85\%$, which is well consistent with the XRD results. When LiClO₄ was added into the PEO matrix, the crystallinity dramatically decreased to 15.46%, mainly scribing to the stronger Lewis acid–base interaction between PEO and LiClO₄. Such remarkably declined crystallinity will greatly promote rapid ion transport in the amorphous electrolyte phase, resulting in 2 or 3 orders of magnitude for ionic conductivity compared to that in the crystalline regions. With the further addition of the SiO₂ nanoparticle into the abovementioned CPE, the further increase of T_g and decrease of T_m evidently authenticate a synergetic interaction between PEO/LiClO₄ and PEO/SiO₂. This synergetic interaction will also influence the dynamics of the PEO chain, that is, once the single Li⁺ ion with multiple coordination sites interacts with ether oxygen atoms on PEO chains, it serves as cross-linking agents for the copolymer.³⁰ Its crystallinity is suppressed by the coordinating and cross-linking effect of Li⁺, which can effectively hinder the chain movement as well. The extent of this cross-linking is enhanced by further adopting SiO₂ nanoparticles and the ion migration.^{30,31} In order to deeply explore the interaction among the groups and properties of CPEs, in situ XRD is conducted from 30 to 90 °C (as shown in Figure S10). The characteristic peak density of PEO ($\sim 23.0^\circ$) significantly decreases with the increase of temperature, which is consistent with the results of DSC. When the temperature approaches T_m , the chain segment motion of PEO increases, resulting in lower crystallinity and higher ion migration rate.

In a word, this synergetic interaction could be attributed to the synergetic effects of strong Lewis acid–base interaction and weak hydrogen bonds. In the case of the PEO–LiClO₄ system, complex cross-links are formed between oxygen atoms, leading to the shift of FT-IR peaks³² (Table S2). As shown in Figure S11, with the addition of LiClO₄, the peaks of C–O–C stretching, CH₂ twisting, CH₃ symmetric deformation, and symmetric C–H stretching of CH₂ become weak and broad. When SiO₂ nanoparticles are added, two types of Lewis base centers (O atoms on the SiO₂ surface and ether oxygen on PEO chains) can synergistically form complexes with Lewis acid alkali metal cations. With the doping ratio increased, the peak continuously shifts toward high wavenumbers, indicating the solvation of cations in PEO@SiO₂ because of the synergistic interaction. Typically, FT-IR spectra within the range of 600–650 cm⁻¹ could directly verify the solvation of LiClO₄. In the PEO@SiO₂–LiClO₄ systems, ClO₄⁻ would either dissociate from LiClO₄ (free ClO₄⁻ ~ 620 cm⁻¹) or incorporate into the bonded ion pair (bonded ClO₄⁻ ~ 635 cm⁻¹).³³ Figure S12 and Table S3 exhibited the Gaussian fitting results of two types of ClO₄⁻ in different CPEs. The 10% doped CPE exhibited the highest percentage of free ClO₄⁻ (95.28%) with the highest interaction among PEO, SiO₂, and LiClO₄. This result is also consistent with its highest ionic conductivity. However, a relatively weak hydrogen bond

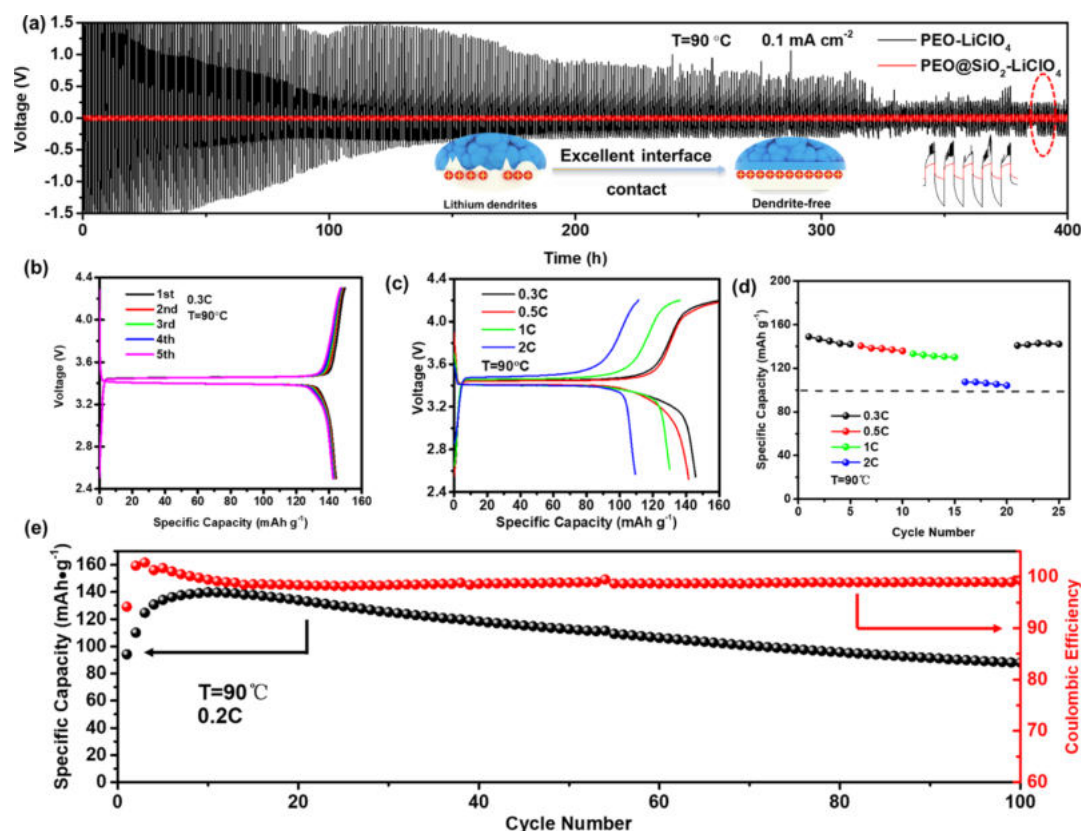


Figure 4. Electrochemical performance of Li/Li symmetric cells and LFP/CPEs/Li ASSLMBs at high temperature. (a) Voltage profiles for the lithium plating/stripping experiment with a symmetric Li/in situ CPEs/Li cell as a function of time cycled at a current density of 0.1 mA cm^{-2} at 90°C . (b) Charge/discharge profiles of a Li/in situ CPEs/LFP cell at 90°C under 0.3 C . (c,d) C-rate performance of ASSLMBs at 90°C under $0.3\text{--}2 \text{ C}$. (e) Cycling performance of ASSLMBs at 90°C under 0.2 C .

interaction also exists between the SiO_2 nanosphere and PEO (as shown in Figure S13).

Furthermore, the coordination and solvation of particles can be uncovered by NMR relaxation rates for further insight into the short-range dynamics of the $\text{PEO@SiO}_2\text{--LiClO}_4$ system. The solid-state NMR spectra of different doped CPEs are shown in Figure 3h, and these simulated multiple peak results are summarized in Table S4. As the doping ratio increases, the PEO segments become trapped partially, allowing great prevention from recrystallization, whose molecular tumbling enhances the local hydrogen bond interactions and results in a much-narrowed NMR peak.³⁴ This slight chemical shift result apparently confirms that the SiO_2 nanosphere should assist in the breakdown of PEO for lower crystallinity. The information of the measured nuclei and the assignment of the peak are shown in Table S5. According to Table S5, the peaks at around 3.8 and 28.8 of the 10% doped CPE exhibit the narrowest peak width. These narrowest peaks indicate the higher ionic conductivity of 10% doped CPEs. Moreover, the electrochemical performance of CPEs synergistically enhanced with strong Lewis acid–base and weak hydrogen bond interaction.³⁵ In general, this work demonstrates a novel rigid–flexible coupling dynamic strategy in enhancing ionic conductivity and experimentally understands this strategy, which is of great importance for further explicating and utilizing the CPE.

All this evidence mentioned above unambiguously proves that 10% doped in situ SiO_2 nanoparticles are the most efficient ratios toward decreasing the crystallinity of PEO and

solvation toward LiClO_4 . On the one hand, the Lewis acid and hydrogen bond interaction creates a synergistic effect to restrict the PEO molecular chain movement and subsequent recrystallization partially.^{24,25} On the other hand, 10% doped membranes exhibit an ideal balance between the crystallinity decline level to acquire high ionic conductivity and mechanical strength (Figure S14) to suppress lithium dendrite in ASSLMBs.

3.3. Cell Performance of Li/Li Symmetric Cells and LFP/CPEs/Li ASSLMBs. Galvanostatic cycling of the Li/Li symmetric cell using the 10% doped CPE and SPE was conducted at a current density of 0.1 mA cm^{-2} (cycled at 90°C) for identifying the interface compatibility and lithium dendrite stability, and the result is shown in Figure 4a (as a reference, the results tested at 30°C are shown in Figure S15). The positive and negative voltages, respectively, represent Li stripping and Li plating processes.^{18,19} After long cycling (400 h), approximately 0.02 V increase of voltage occurs compared to the initial cycle in the CPE, while the SPE exhibited a lot of noise. Moreover, even in the higher current density, the curves are still smooth, which demonstrates the excellent interface stability of the in situ SiO_2 -doped CPE (Figure S16). The surface SEM images of Li foil are exhibited in Figure S17. The barely visible dead lithium and smooth voltage curves after cycling indicate that the SiO_2 nanoparticle-doped CPE has the favorable ability to realize a dendrite-free interface at high temperature for a long time, which is beneficial for ASSLMB lifespan.

In consideration of the high ionic conductivity, broad electrochemical stability window, and good interface compatibility of the 10% doped CPEs, we are able to assemble PEO–LiClO₄@SiO₂-based ASSLMs to demonstrate their potential application. A cell of LFP/PEO–LiClO₄@SiO₂/Li was employed to study the rate capacity and cycling performance. The galvanostatic charge/discharge curves of the cell at 0.3 C at 60 and 90 °C are shown in Figure S18a,b, respectively. A small polarization voltage during cycling can be observed in both 60 °C (0.07 V) and 90 °C (0.04 V), indicating excellent interface stability, fast kinetics of Li⁺ diffusion, and low internal resistance (Figure S19) in the SiO₂-doped composite electrolyte. In addition, the cycling voltammetry curves of this ASSLM can be seen in Figure S20. Figures 4c,d and S15b,c present the rate performance of the cell at C-rates of 0.3, 0.5, 1, and 2 C (cycled at 60 and 90 °C), respectively. This cell exhibits excellent rate capacities and a capacity retention of 146 mA h g^{−1} at 0.3 C and 90 °C, which is the approach to the theoretically capacity of LFP (170 mA h g^{−1}). Moreover, even at a relatively low temperature (60 °C), an excellent specific discharge capacity can still be observed over 100 mA h g^{−1} under 2 C, which shows a superior performance compared to most of the previously reported PEO-based systems (Table S6). These results prove that the interfaces between the electrolyte and electrodes are chemically stable at both high rate and high temperature. As illustrated in Figure S21, when the temperature is relatively low, the poor electrode–electrolyte interface contact results in high resistance and lithium dendrites.^{36,37} As the temperature elevates, the formation of excellent interface contacts via PEO matrix melting and infiltration provides the fast Li⁺ transfer channel.³⁸ In this circumstance, the ASSLMs employing these PEO@SiO₂ CPEs possess the advantages of high operation temperature and excellent safety compared with conventional LIBs using the liquid organic electrolyte.

The cycling performance of the cells at 0.2 C at 90 °C is illustrated in Figure 4e (as a reference, the results tested at 30 °C are shown in Figure S22). In the first few cycles, the specific capacity and the coulombic efficiency are limited and disordered because of the instability of the SEI layer.^{39–41} With the evolution of the reaction, a thermodynamically unstable but kinetically stable interface can be obtained so that the specific capacity and Coulombic efficiency come back to normal.⁴² The voltage profile of ASSLMs with in situ CPEs at different numbers of cycles can be seen in Figure S23. After 100 cycles, over 70% of specific capacity retention can be observed, which is reliable at such a high temperature. The Nyquist plots of ASSLMs before and after cycling are shown in Figure S24. The excellent performance of the LFP/SiO₂ nanoparticle CPE/Li cell can be attributed to the high ionic conductivity, broad electrochemical stability window, and favorable interfacial compatibility with both electrodes.

4. CONCLUSIONS

In summary, we designed a synergetic strategy using strong Lewis acid–base and weak hydrogen bonds for in situ self-assembly construction of 3D network-structured PEO@SiO₂ CPE. This rigid–flexible coupling dynamic strategy significantly reduced the crystallinity of PEO, resulting in a high ionic conductivity of $\sim 1.1 \times 10^{-4}$ S cm^{−1} at 30 °C. Also, the dramatically improved solid–solid interface stabilization facilitated the electrochemical stability window of up to 4.8 V at 90 °C. Based on the PEO@SiO₂ CPE, the developed

ASSLMs exhibited an excellent high-temperature rate capability of ~ 105 mA h g^{−1} under 2 C at 90 °C, high cycling capacity of retaining 90 mA h g^{−1} after 100 cycles at 90 °C, and high specific capacity of 147 mA h g^{−1} under 0.3 C at 90 °C. Evidently, this advanced synergetic strategy may provide a new platform for the expanded exploitation of high performance CPEs and the state-of-the-art ASSLMs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.9b20128>.

Detailed synthetic process of CPEs; brief mechanism of strong Lewis acid–base interaction; SEM images of SiO₂ nanoparticles and CPEs; EDS results of CPEs; electrochemical performance of CPEs; in situ XRD spectra of CPEs; FT-IR spectra and fitting results of CPEs; brief mechanism of hydrogen bonds; stress–strain curves of CPEs; electrochemical performance of batteries; SEM images of electrodes before and after cycling; thermal properties of CPEs; FT-IR peak assignment and fitting results of CPEs; solid-state NMR peak assignment and multiple peak analysis of CPEs; and electrochemical performance comparison of different CPEs (PDF)

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