



Article Enhanced Electrochemical Performance of PEO-Based Composite Polymer Electrolyte with Single-Ion Conducting Polymer Grafted SiO₂ Nanoparticles

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Abstract: In order to enhance the electrochemical performance and mechanical properties of poly(ethylene oxide) (PEO)-based solid polymer electrolytes, composite solid electrolytes (CSE) composed of single-ion conducting polymer-modified SiO₂, PEO and lithium salt were prepared and used in lithium-ion batteries in this work. The pyridyl disulfide terminated polymer (py-ss-PLiSSPSI) is synthesized through RAFT polymerization, then grafted onto SiO₂ via thiol-disulfide exchange reaction between SiO₂-SH and py-ss-PLiSSPSI. The chemical structure, surface morphology and elemental distribution of the as-prepared polymer and the PLiSSPSI-*g*-SiO₂ nanoparticles have been investigated. Moreover, CSEs containing 2, 6, and 10 wt% PLiSSPSI-*g*-SiO₂ nanoparticles (PLi-*g*-SiCSEs) are fabricated and characterized. The compatibility of the PLiSSPSI-*g*-SiO₂ nanoparticles and the PEO can be effectively improved owing to the excellent dispersibility of the functionalized nanoparticles in the polymer matrix, which promotes the comprehensive performances of PLi-*g*-SiCSEs. The PLi-*g*-SiCSE-6 exhibits the highest ionic conductivity (0.22 mS·cm⁻¹) at 60 °C, a large t_{Li+} of 0.77, a wider electrochemical window of 5.6 V and a rather good lithium plating/stripping performance at 60 °C, as well as superior mechanical properties. Hence, the CSEs containing single-ion conducting polymer modified nanoparticles are promising candidates for all-solid-state lithium-ion batteries.

Keywords: composite solid electrolyte; single-ion conducting polymer grafting; SiO₂ modification; RAFT polymerization; all-solid-state battery

1. Introduction

Developing solid-state lithium-ion batteries with higher energy density and higher safety is one of the main research and development goals of next-generation batteries. Since Wright et al. [1] discovered that mixed polyethylene oxide (PEO) and alkali metal salts show ionic conductivity in 1973, solid polymer electrolytes (SPEs) have received extensive attention in lithium-ion batteries owing to their high flexibility, processability, shape versatility, and light weight [2]. Despite that various other polymers, such as poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN) and poly(vinylidene difluoride) (PVDF) are used as SPEs in lithium-ion batteries nowadays, PEO is still the focus of extensive research owing to its relatively low melting point (T_m), low glass transition temperature (T_g) [3,4], as well as its superior ability to dissolve large amounts of alkali metal salts [5]. However, linear PEO is typically in its semicrystalline state at room temperature, which may hamper the mobility of lithium ions [6]. To address this problem and to promote the



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). compatibility of nanoparticles and PEO, composite solid electrolytes (CSEs) are fabricated by introducing polymer functionalized nanoparticles into PEO [7–9], which can help to decrease the crystallinity of polymer chains and to increase the dispersion of nanoparticles in PEO, and consequently enhance the ionic conductivity as well as the mechanical strength of electrolytes.

Similar to commercial liquid electrolytes, most polymer electrolytes are double-ion conductors, and the lithium-ion transference number is low ($t_{Li+} < 0.5$). The anion as the main carrier can cause severe concentration polarization and can increase the internal resistance of the battery. This can result in voltage drop and severe side reactions, which would seriously affect the performance of solid-state batteries [10]. The polymer electrolyte obtained by chemically linking the anion to the polymer backbone or introducing anion acceptors to limit the movement of the anions is called a single-ion conducting solid polymer electrolyte (SIC-SPEs). The t_{Li+} of SIC-SPEs is usually close to 1, and SIC-SPEs can effectively suppress the concentration gradient of anions, reduce the internal impedance and increase the discharge voltage [11–13]. According to the model proposed by Chazalviel [14] electrolytes with t_{Li+} close to 1 can weaken the driving force for dendrites formation. Therefore, SIC-SPEs can avoid the disadvantages of traditional double-ion conductors, such as the formation of lithium dendrites and poor battery cycle performance, and are regarded as promising candidates for the electrolyte of all-solid-state batteries.

Strategies to combine the advantages of both functionalized nanoparticles and SIC polymers have been proposed. PEO-based CSE containing nanoparticles of SiO_2 and Al_2O_3 modified with lithium [(4-methylphenyl)sulfonyl][(trifluoromethyl) sulfonyl]amide or a mixture of this lithium salt with poly(ethylene glycol) strands exhibit a high ionic conductivity (0.19 mS·cm⁻¹ at 70 °C) and a high electrochemical stability (up to 5 V vs. Li⁺/Li) [15]. Solid electrolytes mixing lithium single-ion polymer (lithium (4-styrenesulfonyl) (trifluoromethanesulfonyl) imide (LiSTFSI)) grafted onto the surface of Ta-doped garnet Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (Li@LLZTO) nanoparticles with PEO show a high lithium ion conductivity (1.50 mS·cm⁻¹) at 60 °C, a wide electrochemical window (~5.3 V vs. Li⁺/Li) and a large t_{Li+} (0.77) [16]. Single-ion conducting polymeric nanoparticles (SIC-PNPs) are also used as functional fillers to promote the performances of PEO. SIC-PNPs prepared through emulsion polymerization of styrene and divinylbenzene with a precise size used in CSEs enable high ionic conductivities ranging from 0.2 to 1 mS·cm⁻¹, high $t_{I,i+}$ of 0.99, high electrochemical stabilities up to 5.5 V (vs. Li^+/Li), and stable storage moduli of >10 MPa at 25–90 °C [17]. Lithium sulfonamide surface-functionalized polymer nanoparticles prepared through a semibatch emulsion polymerization with the help of cross-linked poly(methyl methacrylate) deliver a significant stiffening effect on the PEO matrix (E' > 10 MPa at 80 °C) while the CSEs retain high ionic conductivity values ($\sigma = 0.66 \text{ mS} \cdot \text{cm}^{-1}$) [18].

In this study, a PEO-based composite solid electrolyte with PLiSSPSI-g-SiO₂ (poly (lithium (4-styrenesulfonyl)(phenylsulfonyl) imide)-grafted-SiO₂) nanoparticles (PLi-g-SiCSE) for solid-state lithium-ion battery was designed, with PEO as matrix and functionalized SiO₂ as filler, in which PLiSSPSI was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization, then simply grafted onto SiO₂ via thiol-disulfide exchange reaction. PEO/LiTFSI CSE was also prepared as the control. In terms of the single-ion conducting polymer layer on the surface of nanoparticle, the charge distribution on the surface of SiO₂ can be adjusted and the interfacial compatibility between SiO₂ and PEO can be also promoted, which results in the increased content of amorphous regions in polymer matrix. Hence, the PLi-g-SiCSE exhibits higher ionic conductivity, larger t_{Li+} , wider electrochemical stability window, and better cycling stability. This demonstrates that PLi-g-SiCSE has great potential for all-solid-state lithium batteries.

2. Materials and Methods

2.1. Materials

Sodium 4-vinylbenzenesulfonate (Macklin, \geq 98%), thionyl chloride (SOCl₂, Macklin, 99%), benzenesulfonamide (Macklin, 98%), triethylamine (Macklin, 99%), anhydrous LiOH

(Macklin, 98%), 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid (DTPA, Macklin, 98%), 2,2'-azobis(2-methylpropionitrile) (AIBN, Macklin, 98%), (3-mercaptopropyl)-trimethoxysilane (MPTMS, Macklin, 97%), 2,2'-dipyridyldisulfide (Macklin, 98%), methanol (Macklin, 99.5%), ethanol (Macklin, 99.5%), acetonitrile (Macklin, 99.5%), dimethyl formamide (DMF, Macklin, 99.5%), dichloromethane (DCM, Macklin, 99.5%), ethyl acetate (Macklin, 99.8%), hexane (Macklin, 99.8%), poly(ethylene oxide) (PEO, M_w = 600,000 g·mol⁻¹, Macklin), 4-dimethylaminopyridine (DMAP, Aladdin, 99%), 2-mercaptoethanol (Aladdin, 98%), N,N'-dicyclohexylcarbodiimide (DCC, Aladdin, 99%), NH₄OH solution (Aladdin), glacial acetic acid (Aladdin, 99.7%), anhydrous MgSO₄ (Aladdin, AR), NaHCO₃ (Aladdin, AR), hydrochloric acid (Aladdin, AR), bis(trifluoromethane)sulfonimide lithium (LiTFSI, Aldrich, 99.95%), ultrapure water was prepared using ultra-pure water equipment (Beijing Cheng Ruiyuan Technology Co., Ltd., Beijing, China).

2.2. Preparation of Single-Ion Conducting Polymer through RAFT Polymerization

2.2.1. Synthesis of Lithium (4-styrenesulfonyl)(phenylsulfonyl) imide (LiSSPSI) Monomer [19] A solution of thionyl chloride (SOCl₂, 208.20 g, 1.75 mmol) in anhydrous dimethyl formamide (DMF, 85 mL) was stirred in a double-neck flask immersed in an ice bath for 30 min. Sodium 4-vinylbenzenesulfonate (51.55 g, 0.25 mol) was progressively added into the solution during 30 min and the mixture was stirred for 2 h at 0 °C, then for 12 h at room temperature. After pouring the mixture into ice water (200 mL) to remove the unreacted SOCl₂, dichloromethane (DCM, 150 mL) was then added and the product was extracted in the organic phase after treating with ice water (3×100 mL). The organic phase was dried over anhydrous MgSO₄, then concentrated with a rotary evaporator after filtration to yield a yellow bright liquid 4-styrenesulfonyl chloride, which was stored in dry acetonitrile under an argon gas atmosphere at 0 °C.

Benzenesulfonamide (28.22 g, 0.18 mol), 4-dimethylaminopyridine (5.0 g, 0.04 mol) and triethylamine (27.25 g, 0.27 mol) were dissolved in dry acetonitrile (200 mL) under an argon gas atmosphere and stirred at 0 °C for 30 min. Then, the solution of 4-styrenesulfonyl chloride in dried acetonitrile was added slowly into the mixture via syringe for 20 min. Afterwards, the mixture was kept at 0 °C for 1 h, then stirred for 24 h at room temperature. After removing the solvent with a rotary evaporator, the resulting brown viscous liquid was dissolved in DCM. The solution was then washed with 0.5 M aqueous solution of NaHCO₃ and 1.0 M hydrochloric acid for three times. The acid monomer was obtained after removing DCM, then neutralized with LiOH to produce LiSSPSI monomer.

¹H NMR (400 MHz, D₂O): δ = 7.47 (Ph, 5H), 7.34-7.22 (Ph', 5H), 6.70 (CH₂=CH, 1H), 5.84 (CHH=CH, 1H), and 5.36 (CHH=CH, 1H).

2.2.2. Synthesis of 2-Methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid-2-(2-pyridyldithio) ethyl ester (Py-ss-DTPA) [20]

Initially, 2-(2-Pyridinyldithio)ethanol (PDE) was prepared as follows [21]. The 2,2'dipyridyldisulfide (9.90 g, 45.0 mmol) and glacial acetic acid (0.66 mL) were dissolved in methanol (90 mL) under N₂ atmosphere. Then, a solution of 2-mercaptoethanol (1.65 g, 22.1 mmol) in methanol (10 mL) was added dropwise into the mixture. The solution was stirred for 5 h at room temperature. A light-yellow oil was obtained after removing solvent with rotary evaporator and was purified by column chromatography on silica gel with a mixture of ethyl acetate: hexane (1:2/v:v).

To a solution containing 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid (DTPA, 0.9 g, 2.23 mmol), 2-(2-pyridinyldithio)ethanol (0.4 g, 2.14 mmol), 4-dimethylaminopyridine (26.1 mg, 0.214 mmol) and dry dichloromethane (20 mL), *N*,*N*'-dicyclohexylcarbodiimide (0.44 g, 2.14 mmol) were added dropwise, and the mixture was stirred overnight at room temperature. After filtration, the resulting product py-ss-DTPA was obtained, and further purified by column chromatography on silica gel with a mixture of ethyl acetate: hexane (1:8/*v:v*).

¹H NMR (400 MHz, CDCl₃): δ = 8.52 (Ph, 1H), 7.83-7.67 (Ph', 2H), 7.15 (Ph", 1H), 4.41 (CH₂-O, 2H), 3.32 (S=C-S-CH₂, 2H), 3.08 (S-S-CH₂, 2H), 1.73 (C-(CH₃)₂, (CH₂)₉-CH₂,8H), 1.30 (-(CH₂)₉-, 18H), 0.92 ((CH₂)₉-CH₃, 3H).

2.2.3. Synthesis of PLiSSPSI with Pyridyl Disulfide Terminal Group (py-ss-PLiSSPSI)

Pyridyl disulfide terminated PLiSSPSI was prepared through RAFT polymerization of LiSSPSI using Py-ss-DTPA as the chain transfer agent. A mixture of LiSSPSI (3.29 g, 10 mmol), AIBN (50 mg, 0.3 mmol) and Py-ss-DTPA (171 mg, 0.32 mmol) in DMF (7.8 g) was degassed via three freeze-pump-thaw cycles, backfilled with argon and placed in an oil bath at 70 °C. After 16 h, the reaction was stopped by cooling in liquid nitrogen. Conversion was determined by ¹H NMR in D₂O. The polymer was dried in vacuo. $(M_{n,theo} = 10,000 \text{ g} \cdot \text{mol}^{-1}, M_{n,SEC} = 10,100 \text{ g} \cdot \text{mol}^{-1}, D = 1.7).$

2.3. Preparation of PLiSSPSI Grafted SiO₂ Nanoparticles (PLiSSPSI-g-SiO₂)

2.3.1. Synthesis of Thiol-Functionalized Silica Particles (SiO₂-SH) [22,23]

MPTMS (5 mL) was dissolved in water (500 mL) with mechanical stirring, a certain amount of NH₄OH solution was added into the mixture to adjust pH to 11. After that, the mixture was stirred at room temperature for 24 h. The resulting microspheres were purified by repeated centrifugation and redispersion cycles, replacing supernatants with ethanol and H₂O, respectively. Finally, the SiO₂-SH microspheres were redispersed in water by repeated ultrasonication for a few hours.

2.3.2. Synthesis of PLiSSPSI-g-SiO₂ Nanoparticles

PLiSSPSI-*g*-SiO₂ nanoparticles were prepared by thiol-disulfide exchange reaction between thiols on SiO₂-SH and py-ss-PLiSSPSI. py-ss-PLiSSPSI (1.0 g) and SiO₂-SH (2.0 g) were dispersed in DMF (40 mL) under N₂ atmosphere. The exchange reaction was performed at 60 °C for 12 h after degassed by three freeze-pump-thaw cycles. The PLiSSPSI-*g*-SiO₂ nanoparticles were collected after centrifugation (10,000 rpm, 10 min), and washed with methanol. The PLiSSPSI-*g*-SiO₂ nanoparticles were redispersed in ethanol.

2.4. Preparation of PEO-Based Composite Solid Electrolyte with PLiSSPSI-g-SiO₂ Nanoparticles

A certain amount of PEO and LiTFSI ([EO]: $[Li^+] = 20$) were mixed for stirring with a mass ratio of 2, 6 and 10 wt% PLiSSPSI-*g*-SiO₂ nanoparticles (based on the mass of PEO), then the composite solid electrolytes were prepared by the solution casting method and dried in a vacuum oven at 60 °C for 48 h. After that, the films were pressed into a round piece with a diameter of 19 mm and stored in glove box. The corresponding composite solid electrolytes were denoted as PLi-*g*-SiCSE-x, where x represents the weight content of PLiSSPSI-*g*-SiO₂ nanoparticles.

2.5. Characterization

The ¹H NMR spectra were recorded on a nuclear magnetic resonance spectrometer (NMR, AMX-400, Bruker, Karlsruhe, Germany) with CDCl₃ or D₂O as the solvent. The molecular weight was measured by size exclusion chromatography (SEC, 1260 Infinity II, Agilent, Santa Clara, CA, USA) with the PS standard for calibration and THF as the eluent. Fourier-transform infrared spectroscopy was recorded on a spectrophotometer (FT-IR, INVENIO, Bruker, Germany) in a range of 4000–400 cm⁻¹ employing KBr pellets. UV-Vis analyses were performed on a Shimadzu UV-2600 spectrometer (UV-Vis, Shimadzu, Kyoto, Japan) using quartz cuvettes with 10 mm path length. The surface elemental and surface functional groups of SiO₂-SH and PLiSSPSI-*g*-SiO₂ were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS SUPRA, Shimadzu, Japan). DLS was conducted on a Zetasizer Nano ZS90 (Malvern Instruments, Ltd., Malvern, UK) at a scattering angle of 90° (25 °C), SiO₂-SH and PLiSSPSI-*g*-SiO₂ were dispersed in ethanol under ultrasonication at 25 °C before measurement. The surface nanostructures of SiO₂-SH and PLiSSPSI-*g*-SiO₂ were recorded on a FEI Verios 460 SEM (FEI, Hillsboro, OR, USA) at an operating voltage of

2.0 kV. Elemental mapping was further performed using an analytical TEM instrument (FEI Tecnai G2 F20, FEI, USA) equipped with an energy-dispersive spectroscopy (EDS) system. The crystallization of PLi-*g*-SiCSE-x were analyzed by X-ray diffraction (XRD, D/max 2200PC, Tokyo, Japan) equipped with CuK α radiation, the angle of 2 θ ranged from 10° to 80°, and the scan rate was 5° min⁻¹. Glass transition temperature (T_g) of Pli-*g*-SiCSE-x was recorded by differential scanning calorimetry (DSC, DSC7020, HITACHI, Japan) at a heating rate of 10 °C min⁻¹ under nitrogen. The mechanical properties of Pli-*g*-SiCSE-x were studied by the stress-strain test using Hengyi HY-0580 universal testing machine with a 500 N loading cell at the tensile rate of 30 mm min⁻¹.

SS | Pli-g-SiCSE-x | SS symmetric cells (SS = stainless steel) were assembled for ionic conductivity measurement. The ionic conductivities of Pli-g-SiCSE-x were measured by electrochemical impedance spectroscopy (EIS) by using electrochemical working station (PARSTAT 3000A DX, PAR, USA) with the frequency range from 1 MHz to 0.1 Hz and temperature between 25 and 80 $^{\circ}$ C. The ionic conductivity was calculated as follows:

$$\sigma = \frac{L}{R \cdot S} \tag{1}$$

in which σ is the ionic conductivity, R is the bulk resistance, L is the thickness of the Pli-*g*-SiCSE-x, and S is the contact area of SS electrode and Pli-*g*-SiCSE-x.

Li | Pli-g-SiCSE-x | Li symmetric cell was used to determine t_{Li+} of the Pli-g-SiCSE-x membrane based on EIS with a frequency range from 1 MHz to 0.1 Hz and with the alternating voltage amplitude of 10 mV at 60 °C. The t_{Li}^+ was measured as Equation (2):

$$t_{Li^{+}} = \frac{I_{S}(\Delta V - I_{0}R_{0})}{I_{0}(\Delta V - I_{S}R_{S})}$$
(2)

where ΔV , I_S, and I₀ are the polarization potential, steady-state current, and initial-state current, respectively. R_S and R₀ represent the steady-state resistance and initial-state resistance.

The electrochemical stability of PLi-*g*-SiCSE-x was evaluated by linear sweep voltammetry (LSV) using a SS | PLi-*g*-SiCSE-x | Li cell with a scan rate of 0.1 mV s⁻¹ from 0 to 6 V (vs. Li/Li⁺) at room temperature.

The charge/discharge performance of LFP | PLi-g-SiCSE-x | Li batteries (LFP = LiFePO₄) was carried out on a battery testing system (LANHE CT 2001 A) with a voltage range from 2.5 to 4.0 V (1 C = 170 mA g⁻¹) at 60 °C. All batteries were assembled in an Ar-filled glove box with oxygen and H₂O content less than 0.1 ppm.

3. Results and Discussion

3.1. Preparation of PLiSSPSI-g-SiO₂ Nanoparticles

Lithium (4-styrenesulfonyl)(phenylsulfonyl) imide (LiSSPSI) as single-ion monomer used in this work was prepared according to the previous report [19], and the ¹H NMR spectrum and peak assignments of LiSSPSI are presented in Figure S1. RAFT agent, 2methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid-2-(2-pyridyldithio) ethyl ester (py-ss-DTPA), was synthesized via an esterification reaction between 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid (DTPA) and 2-(2-pyridinyldithio)ethanol (PDE) [20], and the ¹H NMR spectra and peak assignments of DTPA, PDE and pyss-DTPA are shown in Figures S2–S4, respectively. Py-ss-PLiSSPSI was synthesized through RAFT polymerization using py-ss-DTPA as RAFT agent and 2,2'-azobis(2-methylpropionitrile) (AIBN) as initiator (Scheme 1). The ¹H NMR spectrum and peak assignments of py-ss-PLiSSPSI are shown in Figure S5. Based on the ¹H NMR results, the average number of repeating units is calculated, and size exclusion chromatography (SEC) curves and the molecular weight dispersity of the polymer are shown in Figure S6.



Scheme 1. Synthesis of py-ss-PLiSSPSI and PLiSSPSI-g-SiO₂.

Thiol-functionalized silica particles (SiO₂-SH) were prepared following the previous work [23], and py-ss-PLiSSPSI brushes on silica particles (PLiSSPSI-g-SiO₂) were prepared after thiol-disulfide exchange reaction between SiO₂-SH and py-ss-PLiSSPSI (Scheme 1). Pyridine-2-thione yielded in the exchange reaction has a characteristic absorption at 375 nm in DMF in UV-vis spectra (Figure 1a). Based on a standard curve (Figure 1b), the amount of pyridine-2-thione is obtained and the grafting density of py-ss-PLiSSPSI on silica particles is calculated to be 0.67 mg·g⁻¹ [20].



Figure 1. (a) Absorptions of pyridine-2-thione yielded in the thiol-disulfide exchange reaction between SiO₂-SH and py-ss-PLiSSPSI in DMF and (b) standard curve of pyridine-2-thione in DMF.

FT-IR spectra of SiO₂-SH, py-ss-PLiSSPSI and PLiSSPSI-*g*-SiO₂ are presented in Figure 2, and the characteristic peak of -SH in SiO₂-SH measured by Raman spectroscopy is shown in Figure S7. As observed in FT-IR spectra, the peak at 3061 cm⁻¹ belongs to the stretching vibration of aromatic heterocycle of py-ss-PLiSSPSI. The peaks at 2930 and 746 cm⁻¹ can be assigned to the saturated C-H bonds and S-N bonds of PLiSSPSI segments, respectively. Peaks at 1667, 1443 and 1407 cm⁻¹ are originated from the vibration of benzene rings of PLiSSPSI. The strong absorption peak appears at 470 cm⁻¹ corresponds to the stretching vibration of -Si-O-Si- of SiO₂. Compared to pristine SiO₂-SH, PLiSSPSI-*g*-SiO₂ owns the characteristic absorption peaks of py-ss-PLiSSPSI, which indicates that the pyridyl disulfide functionalized polymer py-ss-PLiSSPSI was grafted onto SiO₂ successfully.



Figure 2. FTIR spectra of SiO₂-SH, py-ss-PLiSSPSI and PLiSSPSI-g-SiO₂.

The surface structures of SiO₂-SH and PLiSSPSI-g-SiO₂ are further investigated by XPS (Figure 3). Figure 3a shows the XPS deconvoluted C 1s peaks. For the SiO₂-SH, the peak at 284.80 eV is originated from the C-C bonds. The deconvoluted peaks at 284.80, 286.12 and 288.82 eV exist in the PLiSSPSI-g-SiO₂ correspond to the C-C, C-S and -O-C=O bonds, respectively [24]. The deconvoluted O 1s spectra are shown in Figure 3b. For the SiO₂-SH, one peak presents at 530.60 eV, which matches the Si-O bonds [25]. In comparison, the PLiSSPSI-g-SiO₂ shows two deconvoluted peaks at 530.60 and 531.70 eV, which can be assigned to the Si-O bonds and the SO₂-N bonds, respectively [25,26]. In Figure 3c, the S 2p peaks can be fitted into two spin orbit doublets with a splitting of 1.18 eV and a 2:1 area ratio. The S 2p spectra of the SiO₂-SH and PLiSSPSI-g-SiO₂ both show deconvoluted peaks at 163.50 $(2p_{3/2})$ and 164.48 eV $(2p_{1/2})$, which are originated from the S-H or S-C bonds. For the PLiSSPSI-g-SiO₂, and a small peak at around 167.33 eV corresponds to the structure of -SO₂-C- [26]. Figure 3d shows the deconvoluted spectra of the Si 2p region. Both SiO₂-SH and PLiSSPSI-g-SiO₂ show only one peak at 100.80 eV originated from the Si-O bonds [25]. The existence of C-C, C-S, -O-C=O and -SO₂-C- bonds demonstrates the py-ss-PLiSSPSI are successfully grafted onto the surface of SiO₂ nanoparticles.

Figure 4a shows the SEM of SiO₂-SH and PLiSSPSI-*g*-SiO₂. The diameters of SiO₂-SH and PLiSSPSI-*g*-SiO₂ are around 600 nm and 700 nm, respectively, consistent with the DLS results in methanol (Figure S8). The surface for the SiO₂-SH appears smooth, but the surface of PLiSSPSI-*g*-SiO₂ particles is rougher. This indicates that the py-ss-PLiSSPSI is successfully grafted onto the SiO₂ surface. The chemical compositions and element distributions of SiO₂-SH and PLiSSPSI-*g*-SiO₂ particles are characterized by scanning transmission electron microscopy (STEM). The results demonstrate that both Si and O are homogeneously distributed (Figure 4b). The EDS analysis indicates that the content of the S is less in SiO₂-SH particles than that of PLiSSPSI-*g*-SiO₂ (Figure 4c). The N (1%) is observed in PLiSSPSI-*g*-SiO₂ particles. Therefore, XPS, SEM and EDS results indicate that PLiSSPSI are successfully grafted onto SiO₂.



Figure 3. High-resolution XPS spectra of (**a**) C 1s, (**b**) O 1s, (**c**) S 2p and (**d**) Si 2p for SiO₂-SH and PLiSSPSI-*g*-SiO₂.



Figure 4. (a) SEM images, (b) elemental mapping and (c) EDS analysis of SiO₂-SH and PLiSSPSI-g-SiO₂.

3.2. Composite Solid Polymer Electrolytes Based on Poly(ethylene oxide) and PLiSSPSI-g-SiO₂ Nanoparticles

Nowadays, the application of PEO solid electrolytes is still limited by their poor mechanical properties and low ionic conductivity at room temperature [8]. Efforts have been made to decrease the crystallinity of PEO in order to improve the ionic conductivity of PEO-based solid electrolytes, such as fabricating PEO with cross-linking structure [27], blending PEO with other polymers [28] and forming PEO-based block copolymers [29,30]. Inorganic nanoparticles, e.g., SiO₂ and TiO₂ have been introduced into PEO-based composite solid electrolytes (CSE) to enhance their mechanic properties [31,32]. In this work, a kind of single-ion conduction polymer modified SiO₂ (PLiSSPSI-g-SiO₂) is utilized as the functional filler to prepare composite solid electrolytes PLi-g-SiCSE-x, where x represents the weight content of PLiSSPSI-g-SiO₂ nanoparticles. The concentration of PLiSSPSI-g-SiO₂ nanoparticles in the composites is varied between 2 and 10 wt% with respect to the total weight.

Figure 5 showed the XRD patterns and DSC curves of PEO-based CSE with various concentrations of PLiSSPSI-g-SiO₂ nanoparticles, as well as the PEO/LiTFSI ([EO]: $[Li^+] = 20$) for comparison. In Figure 5a, for the PEO/LiTFSI, two sharp diffraction peaks appear at $2\theta = 19$ and 23° , respectively, indicative of the presence of highly crystalline phase in PEO [33]. Upon addition of the PLiSSPSI-g-SiO₂ nanoparticles into PEO/LiTFSI, the intensities of these two XRD peaks decrease, and the peaks become broad compared to PEO/LiTFSI. This can be attributed to the random distribution of PLiSSPSI-g-SiO₂ nanoparticles into PEO interrupts the ordered arrangement of PEO polymer chains, and consequently increases the content of amorphous phase of CSE. In Figure 5b, for PEO/LiTFSI electrolyte, the T_g was -49.3 °C and the T_m is 27.9 °C. With the rise in the content of PLiSSPSI-g-SiO₂ nanoparticles, the T_g of PLi-g-SiCSE drops from -50.8 °C (2 wt%) to -54.3 °C (6 wt%), then increases to -50.0 °C (10 wt%). Meanwhile, the T_m of PLi-g-SiCSE decreases from 25.6 °C (2 wt%) to 22.8 °C (6 wt%), then increases to 23.6 °C (10 wt%). Both T_g and T_m of PLi-g-SiCSEs are lower than those of PEO/LiTFSI electrolyte, which indicates that the introduction of PLiSSPSI-g-SiO₂ nanoparticles can increase the content of amorphous phase of PLi-g-SiCSEs, consist with the XRD results. The PLi-g-SiCSE-6 exhibits the lowest T_g and T_m , which suggests that its content of the amorphous phase is the highest. The high content of amorphous phase is beneficial to promoting the movement of EO segment and to enhancing the ionic conductivity of the CSE.



Figure 5. (a) XRD patterns and (b) DSC of the prepared CSEs containing PEO/LiTFSI and different amounts of PLiSSPSI-*g*-SiO₂ nanoparticles.

Figure 6 shows the SEM images of the surface and cross-section morphologies of the prepared CSEs containing PEO/LiTFSI and different amounts of PLiSSPSI-*g*-SiO₂ nanoparticles. The surface of all CSEs is smooth, while the cross-section of the CSEs containing PLiSSPSI-*g*-SiO₂ nanoparticles is smoother than that of PEO/LiTFSI CSE. In addition, PLi-*g*-SiCSEs-10 exhibits nanoparticle aggregations in film as shown in Figure 6(d3) compared to PLi-*g*-SiCSEs-2 (Figure 6(b3)) and PLi-*g*-SiCSEs-6 (Figure 6(c3)).



Figure 6. Surface and cross-section SEM images of the prepared CSEs containing (**a1–a3**) PEO/LiTFSI, (**b1–b3**) 2 wt% PLiSSPSI-g-SiO₂, (**c1–c3**) 6 wt% PLiSSPSI-g-SiO₂, and (**d1–d3**) 10 wt% PLiSSPSI-g-SiO₂ nanoparticles.

The mechanical properties of PLi-*g*-SiCSEs were also investigated. The stress-strain behavior of PLi-*g*-SiCSEs was studied (Figure 7), and the tensile strength and elongation of the PLi-*g*-SiCSEs was characterized. The results are summarized in Table 1.





Figure 7. (a) Stress-strain measurement of PLi-*g*-SiCSEs, (b) Stress-strain curves of the prepared CSEs membranes containing PEO/LiTFSI and different amounts of PLiSSPSI-*g*-SiO₂ nanoparticles.

Table 1.	Mechanical properties of the prepared CSEs membranes cor	ntaining PEO/LiTFSI and
different	amounts of PLiSSPSI-g-SiO ₂ nanoparticles.	

	PEO/LiTFSI	PLi-g-SiCSE-2	PLi-g-SiCSE-6	PLi-g-SiCSE-10
Stress (MPa)	0.97	2.22	3.63	3.37
Strain (%)	830	657	911	1147

The PEO/LiTFSI electrolyte shows a tensile strength of 0.97 MPa and maximum elongation of 830%. In the presence of PLiSSPSI-*g*-SiO₂ nanoparticles, the tensile strength of membranes increases to 3.63 MPa (6 wt%), then decreases to 3.37 MPa (10 wt%). With the increased content of the PLiSSPSI-*g*-SiO₂ nanoparticles, the breaking elongation decreases to 657% (2 wt%), then increased to 1147% (10 wt%). This phenomenon is due to the plasticized effect and conforms to the stress and strain law of solid membrane. Especially, the PLi-*g*-SiCSEs-6 membrane shows the most favorable mechanical properties, with a tensile strength of 3.63 MPa and a breaking elongation of 911%.

The ionic conductivity of PLi-g-SiCSEs at different temperature is calculated based on the intercept of the high-frequency region measuring by electrochemical impedance spectroscopy (EIS) (Figure S9 and Table S1), and the conductivity of CSEs at 60 °C is summarized in Table S2. Figure 8 compares the conductivities as a function of temperature for the CSEs with various contents of PLiSSPSI-g-SiO₂ nanoparticles, as well as the PEO/LiTFSI CPE. All the PLi-g-SiCSEs exhibit higher ionic conductivity than that of PEO/LiTFSI CPE in all temperature. This might be caused by the chain entanglement between LiSTFSI on PLiSSPSI-g-SiO₂ and PEO that reduces the crystallinity of PEO, and improves the compatibility of heterogeneous interface. A lower T_g is favorable to increase the amorphous phase and thus enhance the ionic conductivity of the CSE due to the relaxation of polymer chains. Hence, based on the T_g values shown in Figure 5b, the higher ionic conductivity is obtained in PLi-g-SiCSE-6. At 60 °C, with the increase of the content of PLiSSPSI-g-SiO₂ nanoparticles, the ionic conductivity increased from 0.17 mS cm⁻¹ of PLi-g-SiCSE-2 to 0.22 mS cm⁻¹ of PLi-g-SiCSE-6, then decreased to 0.13 mS cm⁻¹ of PLi-g-SiCSE-10. With low amounts of PLiSSPSI-g-SiO₂ nanoparticles, the single-ion conducting polymer-modified SiO₂ can disperse well in PEO/LiTFSI CSE, which can create more amorphous regions in CSEs, therefore the ionic conductivity is increased. However, higher amounts of PLiSSPSI-g-SiO₂

nanoparticles are inclined to agglomerate within the PEO, which could cause the obstruction of ion transport. The ionic conductivity of PLi-*g*-SiCSE-6 reaches 0.22 mS cm⁻¹ at 60 °C (Table S1), higher than those reported CSEs containing PEGMA-modified SiO₂ [34] and PEGMA/single-ion monomer-modified SiO₂ and Al₂O₃ [15] owing to the better dispersion caused by PLiSSPSI, while lower than the CSEs containing polymer-grafted SiO₂ [35,36] and neat polymeric nanoparticles[17,18] which can be attributed to the much larger particle size (around 700 nm as shown in Figure 4 and Figure S8).



Figure 8. Ionic conductivity plots of the prepared CSEs membranes containing PEO/LiTFSI and different amounts of PLiSSPSI-*g*-SiO₂ nanoparticles.

The lithium-ion transference number (t_{Li+}) is also a key parameter of SPE. The t_{Li+} for the PLi-*g*-SiCSEs and the classic PEO/LiTFSI ([EO]: [Li⁺] = 20) CSE at 60 °C are measured by a combination of impedance and potentiostatic polarization method. The impedance spectra and the *I*-*t* curve of PLi-*g*-SiCSE-6 are measured using the Li/PLi-*g*-SiCSE-x/Li symmetric cell at 60 °C (Figure 9a). The results of t_{Li+} for CSEs are calculated by Equation (2) and are presented in Figure 9b. The t_{Li+} of PEO/LiTFSI, PLi-*g*-SiCSE-2, PLi-*g*-SiCSE-6, and PLi-*g*-SiCSE-10 are 0.32, 0.48, 0.77 and 0.51, respectively. Obviously, all the t_{Li+} of PLi-*g*-SiCSEs are higher than that of PEO/LiTFSI CSE, which is caused by the grafting of PLiSSPSI on the surface of SiO₂ that can not only inhibit the movement of anions in CSE, but also promote the dissociation of lithium salt and increase the mobility of Li⁺. The t_{Li+} of PLi-*g*-SiCSE varies with the content of PLiSSPSI-*g*-SiO₂ nanoparticles, which indicates that well-dispersed PLiSSPSI-*g*-SiO₂ nanoparticles can improve the t_{Li+} effectively, and that the agglomeration resulted by high concentration of nanoparticles would reduce the t_{Li+} .

Furthermore, the electrochemical window is crucial for developing high voltage and high-power lithium batteries. Traditional PEO/LiTFSI CSE is usually oxidized at a relatively low voltage, which limits the energy density [37]. The electrochemical window is measured by linear sweep voltammetry using SS | PLi-g-SiCSE-x | Li cell at 0.1 mV s⁻¹ and the results are shown in Figure 10. All the PLi-g-SiCSEs are stable up to 4.2 V vs. Li/Li⁺. The electrochemical window for PLi-g-SiCSE-6 even reaches 5.6 V, indicating that it possesses good electrochemical stability and feasibility in high-voltage lithium batteries.



Figure 9. (a) The chronoamperometry profiles and AC impedance spectra before and after polarization for the Li | PLi-g-SiCSE-6 | Li symmetric cell with PLi-g-SiCSE-6, (b) t_{Li+} of the prepared CSEs membranes containing PEO/LiTFSI and different amounts of PLiSSPSI-g-SiO₂.



Figure 10. LSV curves of the SS | PLi-g-SiCSE-x | Li cell at 0.1 mV s^{-1} .

The PLi-*g*-SiCSEs are sandwiched between two lithium metal electrodes to assemble all-solid-state Li/Li symmetrical batteries. Figure 11a shows the time-dependent plating/stripping profile of the cell with PLi-*g*-SiCSE-6 as electrolyte over 480 h at a constant current density of 0.2 mA·cm⁻² and at 60 °C. A stable overpotential of 27 mV demonstrate that reversible lithium plating/stripping performance can be achieved in Li | PLi-*g*-SiCSE-6 | Li cell, and no short circuit is observed. Figure 11b exhibits an enlarged plot of the lithium plating/peeling cycling curves of Li | PLi-*g*-SiCSE-6 | Li symmetric cell at 70–80 h. The overpotential voltage is around 27 mV, indicating its superior interfacial stability with the lithium electrodes.



Figure 11. (a) Voltage-time curves of Li | PLi-*g*-SiCSE-6 | Li symmetric cell at a constant current density of 0.2 mA·cm⁻² at 60 °C, (b) enlarged voltage-time profiles at 70–80 h.

Figure 12 shows the rate capability and initial charge-discharge curves of LFP | PLig-SiCSE-6 | Li at 60 °C. The reversible discharge specific capacities are 140, 139, 132 and 121 mAh·g⁻¹ at current densities of 0.1, 0.2, 0.5 and 1 C, respectively (Figure 12a). After five cycles, the specific capacity at 0.1 C recovered to 140 mAh·g⁻¹, which indicates good rate performance of the PLi-g-SiCSE-6 in lithium batteries. Typical charge-discharge potential curves at different rates show that the voltage gaps between the charge and discharge plateaus are 0.09 V, 0.15 V, 0.30 V, and 0.53 V at 0.1 C, 0.2 C, 0.5 C, and 1 C, respectively (Figure 12b) [38]. The approximate linear variation of the voltage gap with current density further illustrates the selective Li⁺ conductivity of PLi-g-SiCSE-6, which improves the rate capability of the assembled cell. This phenomenon is attributed to the presence of organic-inorganic hybrid nanoparticles that enhance the interfacial compatibility between the membrane and the electrode, thereby reducing polarization [36].



Figure 12. (a) Rate capability and (b) initial charge-discharge curves of LFP | PLi-*g*-SiCSE-6 | Li batterie with various C rates.

Meanwhile, the high-rate cycling performance of the LFP | PLi-g-SiCSE-6 | Li battery was investigated (Figure 13a). The results show that the battery exhibits a specific capacity

of 124 mAh·g⁻¹ at 1 C (60 °C) and with a coulombic efficiency of 100%. After 130 cycles, the specific capacity decayed to 80%, while the coulombic efficiency remains 100%. As shown in Figure 13b, the polarization potential is within 0.4 V after 20 cycles. After 130 cycles, the polarization potential increases to 0.5 V which is possibly caused by the exfoliation of the cathode active material and the loss of the interfacial contact after long cycles at high current densities [16].



Figure 13. (a) Long-term cyclic performance and (b) charge and discharge profiles of LFP | PLi-*g*-SiCSE-6 | Li batterie at 1 C (60 °C).

4. Conclusions

In this work, a single-ion conducting polymer modified SiO₂ (PLiSSPSI-g-SiO₂) was served as a functional filler in PEO SPE. The SiO₂-SH nanoparticles were prepared via solgel process, then PLiSSPSI-g-SiO2 nanoparticles were synthesized through thiol-disulfide exchange reaction of the SiO₂-SH and py-ss-PLiSSPSI. The uniform distribution of singleion conducting polymer layer on the surface of SiO_2 reduces the crystallinity of the PEO effectively which can promote the transference of Li⁺. The composite solid electrolyte with 6 wt% of PLiSSPSI-g-SiO₂ nanoparticle exhibits a relatively high ionic conductivity $(0.22 \text{ mS} \cdot \text{cm}^{-1})$ at 60 °C, a wide electrochemical window (5.6 V vs. Li/Li⁺) and a large t_{Li+} (0.77). PLi-g-SiCSE-6 also shows superior mechanical properties with the tensile strength of 3.63 MPa and breaking elongation of 911%. Meanwhile, when charged and discharged at 0.2 mA·cm⁻² current densities, the Li|PLi-g-SiCSE-6|Li cell could cycle for more than 480 h without short circuit. The improved properties of the PLi-g-SiCSE-6 endow the LFP | PLi-g-SiCSE-6 | Li battery with good cycling performance (the specific discharge capacity reaches 140 mAh \cdot g⁻¹ at 0.1 C) and rate capability (average specific discharge capacities of 140, 139, 132 and 121 mAh \cdot g⁻¹ at the C-rates of 0.1, 0.2, 0.5 and 1 C, respectively). Furthermore, the all-solid-state LFP | PLi-g-SiCSE-6 | Li battery demonstrates stable cycling performance for 120 cycles at 1 C and 60 °C. Hence, the single-ion conducting polymer functionalized nanoparticles possess great potential as novel fillers to promote the utilization of corresponding CSEs used in the next generation of all solid-state high-voltage lithium-ion batteries. Moreover, the size effect of single-ion conducting polymer modified nanoparticles on the performances of CSEs is expected to be further investigated.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/polym15020394/s1, Figure S1: ¹H NMR spectrum of LiSSPSI in D₂O; Figure S2: ¹H NMR spectrum of DTPA in CDCl₃; Figure S3: ¹H NMR spectrum of PDE in CDCl₃; Figure S4: ¹H NMR spectrum of py-ss-DTPA in CDCl₃; Figure S5: ¹H NMR spectrum of py-ss-PLiSSPSI in D₂O; Figure S6: overlays of SEC chromatograms (RI detection, in THF) for py-ss-PLiSSPSI; Figure S7. Raman spectrum of SiO₂-SH; Figure S8: particles size statistics of SiO₂-SH and PLiSSPSI-*g*-SiO₂; Figure S9: the impedance plots of SS | PLi-*g*-SiCSE-x | SS symmetric cells: (a) PEO/LiTFSI, (b) PLi-*g*-SiCSE-2, (c) PLi-*g*-SiCSE-6, (d) PLi-*g*-SiCSE-10; Table S1. EIS fitting results of SS | PLi-*g*-SiCSE-6 | SS; Table S2: The ionic conductivity (60 °C) of the prepared CSEs membranes containing PEO/LiTFSI and different amounts of PLiSSPSI-*g*-SiO₂ nanoparticle.

Author Contributions: X.L. supervised the experiments. X.L. and C.W. designed the experiments, W.M., J.G., H.L., Y.S. and L.S. carried out the laboratory experiments, analyzed the data, interpreted the results, and prepared the figures. X.L. and C.W. did formal analysis. X.L., W.M., H.W. and C.W. wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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