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Novel PEO-based solid composite polymer electrolytes with inorganic–organic hybrid polyphosphazene microspheres as fillers

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Abstract Novel solid-state composite polymer electrolytes based on poly (ethylene oxide) (PEO) by using $LiClO_4$ as doping salts and inorganic–organic hybrid poly (cyclotriphosphazene-*co*-4,4′-sulfonyldiphenol) (PZS) microspheres as fillers were prepared. Electrochemical and thermal properties of PEO-based polymer electrolytes incorporated with PZS microspheres were studied. Differential scanning calorimetry (DSC) results showed there was a decrease in the glass transition temperature of the electrolytes and the crystallinity of the samples in the presence of the fillers. Maximum ionic conductivity values of 1.2×10^{-5} S cm^{-1} at ambient temperature and 7.5×10^{-4} S cm^{-1} at 80° were obtained and lithium ion transference number was 0.29. Compared with traditional ceramic fillers such as SiO_2, the addition of PZS microspheres increased the ionic conductivity of the electrolytes slightly and led to remarkable enhancement in the lithium ion transference number.

1 Introduction

Due to the potential applications in solid-state batteries [1–3], the development of polymer electrolytes with high ionic conductivity becomes one of the main goals in polymer research. The main advantage of polymer electrolytes is favorable mechanical properties, ease of fabrication of thin film of desirable size and an ability to form effective electrode-electrolyte contacts. Armand et al. [4] have claimed that the crystalline complexes formed from alkali-metal salts with polyethylene oxide (PEO) are capable of demonstrating significant ionic conductivity and have highlighted their possible application as battery electrolytes. In order to increase the low ionic conductivity and lithium ion transference number of solid polymer electrolytes at room temperature, studies have been made via various approaches such as incorporation of ceramic fillers into the polymer matrix [5]. The Lewis acid–base interaction plays a vital role in the enhancement of ionic conductivity, electrochemical stability and interfacial stability of solid composite polymer electrolytes. But the ceramic fillers are easy to aggregate because of the poor compatibility between polymer and fillers.

Hexachlorocyclotriphosphazene (HCCP) plays a crucial role in the development of new polymers because of the excellent tailoring property of the backbone and the unprecedented structural diversity [6, 7]. Recently, our group demonstrates for the first time the preparation of fully crosslinked poly (cyclotriphosphazene-co-4,4′-sulfonyldiphenol) (PZS) microspheres via precipitation polymerization [8]. It shows

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that HCCP possesses special potential in the fabrication of molecular-level inorganic–organic hybrid micro- and nano-scale materials [9]. The structure of PZS microspheres consist of alternating organic segments (benzene rings and C, O, H atoms) and inorganic segments (inorganic HCCP rings). Compared with traditional ceramic fillers which are easy to aggregate when highly loaded, PZS microspheres may have better compatibility with PEO chains due to the same elements as PEO on the hybrid inorganic–organic structure and it could combine the advantages of organic and inorganic fillers. Furthermore, the active groups such as hydroxyl groups can be retained selectively on PZS microspheres by controlling the ratio of the reactants. Together with the excellent tunability of the backbone, PZS microspheres may be a new class of fillers in the development of solid composite polymer electrolytes.
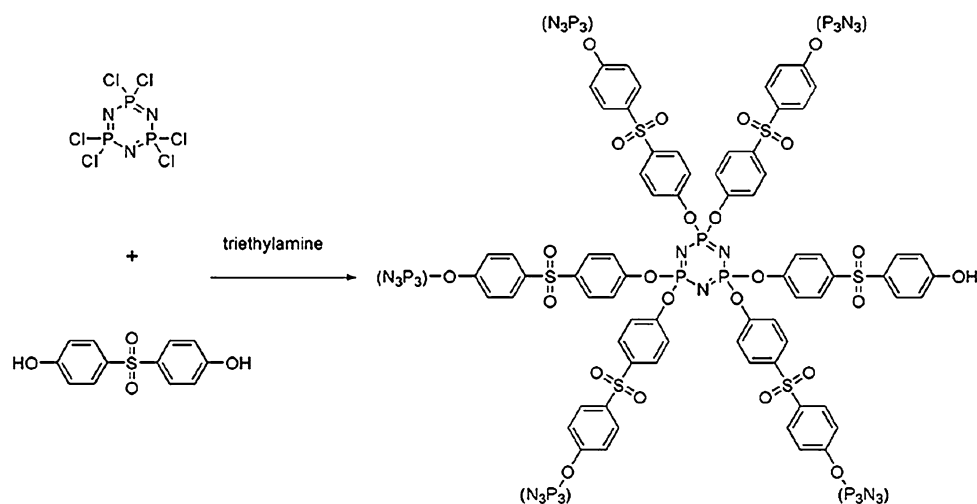
In this work, composite polymer electrolytes (CPE) based on poly(ethylene oxide) (PEO) with PZS microspheres as fillers were prepared by using $LiClO_4$ as doping salts in order to study the effects of PZS microspheres on performances of CPEs.

2 Experimental

2.1 Materials

Poly(ethylene oxide), PEO, $M_w = 200,000$ (Shanghai Chemical Reagent Company) and $LiClO_4$, A.R. (Shanghai Chemical Reagent Company), were vacuum dried for 24 h at 50 and 120 °C, respectively. The vacuum pressure is <400 Pa. The vacuum was obtained by a rotary vane vacuum pump (2XZ(S)-4 type, Shanghai Deying Vacuum and Lighting Equipment Co. LTD) and the vacuum was applied through a vacuum drying oven (DZF-3 type, Shanghai Deying Vacuum and Lighting Equipment Co. LTD). Acetonitrile, A.R. (Shanghai Chemical Reagent Company), dehydrate by 4 A molecular sieves before use.

HCCP (synthesized as described in the literature [10]) was recrystallized from dry hexane followed by two times subli-mation. The melting point of purified HCCP was 113–114 °C.

4,4'-Sulfonyldiphenol (BPS), triethylamine (TEA) and SiO_2 (average diameter 500 nm) were purchased from Shanghai Chemical Reagent Company and used without further purification.

2.2 Preparation of PZS microspheres (PZSMS) via a self-template approach

The facile preparation of PZS microspheres (PZSMS) was carried out as follows (Scheme 1) [9]: TEA (0.87 g, 8.64 mmol) was added to a solution of HCCP (0.50 g, 1.44 mmol) and BPS (1.08 g, 4.32 mmol) in acetone (100 mL). The reaction mixtures were stirred at 30 °C in an ultrasonic bath (100 W, 80 kHz) for about 4 h. The resultant particles were obtained by centrifugation and then washed three times respectively using tetrahydrofuran and deionized water. Finally, the product was dried under vacuum to yield PZS microspheres as a white powder (0.99 g, yield 87%, calculated from HCCP).

2.3 The preparation of CPEs

The preparation of CPEs involved first the dispersion of the fillers and $LiClO_4$ by ultrasonication using an ultrasonic cleaner in anhydrous acetonitrile at room temperature and the addition of the PEO/acetonitrile solution. The resulting slurry was cast onto a Teflon plate and then the plate was put under air sweeping in order to let the solvent evaporate. Finally, the result films were dried under vacuum at 50 °C for 24 h to remove the residue solvent. These procedures yielded transparent homogenous films. All the CPE films were stored in an argon atmosphere glove box before test.

The CPE samples used in this study were denoted as PEO_{10}–$LiClO_4$/x% filler, in which the EO/Li ratio was

Scheme 1 Synthetic route and chemical structure of PZS microspheres

fixed to 10 for all samples and the content of filler, x, ranged from 0 to 30 wt% of the PEO weight.

2.4 Characterization and instruments

SEM images of the surface of CPEs were observed on a JEOL JSM-7401F field emission SEM instrument with gold sputtered-coated films.

Differential scanning calorimeter (DSC) measurements were carried out on a Perkin-Elmer Pyris-1 analyzer. The measurements were carried out at a heating rate of 10 °C min^{-1} from −60 to 100 °C in the heating cycle and from 100 to −20 °C in the cooling cycle.

Ionic conductivity of the CPEs was determined by ac impedance spectroscopy. The film was sandwiched between two stainless steel (SS) blocking electrodes (with a diameter of 1 cm) to form a symmetrical SS/CPE/SS cell. The impedance tests were carried out in the 1 MHz to 1 Hz frequency range using a Solartron 1260 Impedance/Gain-Phase Analyzer coupled with a Solartron 1287 Electrochemical Interface.

Lithium ion transference number, t_{Li}^+, was evaluated using the method of ac impedance combined with steady-state current technique, proposed by Vincent and Bruce [11–14]. The CPE was sandwiched between two lithium-unblocking electrodes to form a symmetrical Li/CPE/Li cell. The cell was assembled and sealed in an argon-filled UNILAB glove box ($O_2 < 0.1$ ppm; $H_2O < 0.1$ ppm).

Electrochemical stability window of the CPEs were determined by running a linear sweep voltammetry in three electrode cells using stainless steel as the blocking working electrode, lithium as both the counter and the reference electrode and the CPE film as the electrolyte. A Solartron 1287 Electrochemical Interface was used to run the voltammetry at a scan rate of 1 mV s^{-1}.

3 Results and discussion

3.1 Surface morphology

Figure 1 shows the SEM microphotograph of PZS microspheres. It can be seen from the SEM images that the average diameter of PZS microspheres is about 0.38 μm.

SEM micrographs of various CPEs are presented in Fig. 2. It can be seen from Fig. 2a that PEO$_{10}$–LiClO$_4$ film shows a rough surface. After blended with PZS microspheres, the PEO surface morphology changes from rough to smooth (Fig. 2b). This may be related to the reduction of PEO crystallinity upon blending with PZS microspheres, and the inorganic–organic hybrid structure of PZS microspheres making good compatibility between PEO polymer matrix and PZSMS. The morphology of the electrolytes
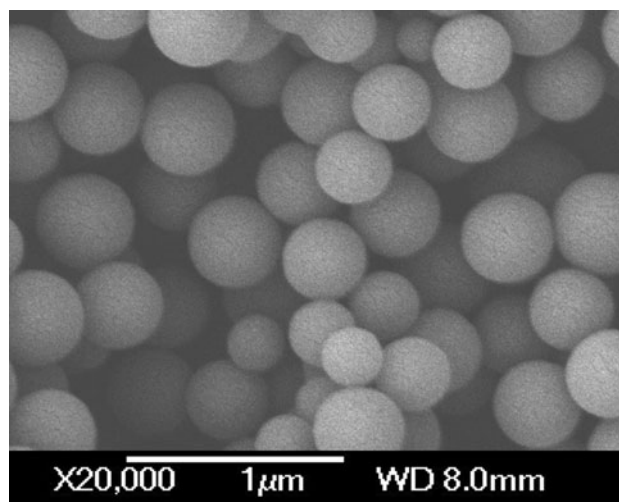

Fig. 1 SEM image of PZS microspheres

becomes rough when the content of PZSMS at high loading content (Fig. 2c), but compared with inorganic fillers the aggregation of PZSMS is much slighter due to the good compatibility of PZSMS.

3.2 Thermal analysis of composite polymer electrolytes

Detailed thermal properties of PEO$_{10}$–LiClO$_4$/x% PZSMS composite polymer electrolytes obtained from DSC analysis are summarized in Table 1. Figure 3 shows a direct view of the tendency. It can be seen from Table 1 and Fig. 3 that both the melting temperature (T_m) and the crystallinity of PEO (X_c) decrease obviously when PZS microspheres are added in PEO$_{10}$–LiClO$_4$ complex. T_m of PEO$_{10}$–LiClO$_4$/x% PZSMS decreases from 60.5 to 54.9 °C when the content of PZS microspheres increases from 0 to 20 wt%. At the same time, X_c of PEO$_{10}$–LiClO$_4$/x% PZSMS decreases from 44.0 to 28.7%. In addition, PZS microspheres can also decrease the T_g of PEO from −34.9 to −45.6 °C with increasing content of PZS microspheres.

The decrease of T_g and X_c indicates the increase of flexibility of PEO chains and the ratio of amorphous state PEO. It may be because of the good compatibility between PZSMS and PEO chains, and the coordination between the ether O atoms of PEO chains and Li$^+$ cations.

3.3 Electrochemical behaviors

Figure 4a shows the temperature dependence of ionic conductivity for PEO$_{10}$–LiClO$_4$/x% PZSMS composite electrolytes and Fig. 4b shows the ionic conductivity of PEO$_{10}$–LiClO$_4$/x% PZSMS composite polymer electrolytes as a function of PZSMS concentration at different temperatures. As seen in Fig. 4, the conductivity increases with
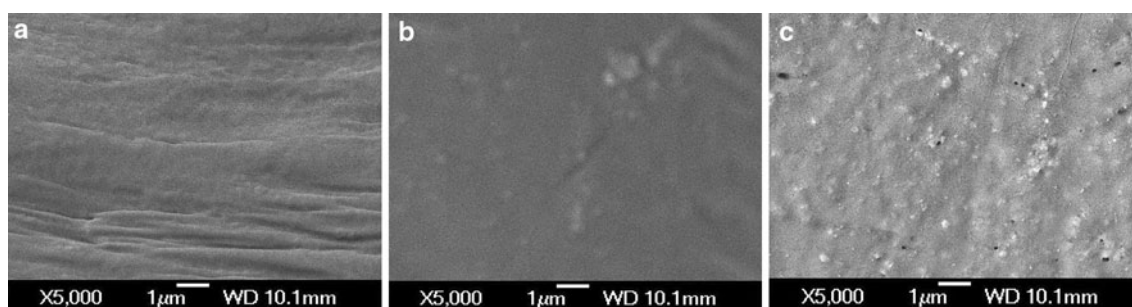
Fig. 2 Surface SEM images of **a** PEO_{10}–$LiClO_4$, **b** PEO_{10}–$LiClO_4$/10% PZSMS, **c** PEO_{10}–$LiClO_4$/30% PZSMS composite polymer electrolytes

Table 1 Thermal properties of PEO_{10}–$LiClO_4$ and PEO_{10}–$LiClO_4$/x% PZSMS composite polymer electrolytes obtained from DSC analysis

Sample	Glass point T_g (°C)	Melting point T_m (°C)	Melting enthalpy[a] ΔH_m (J g^{-1})	Crystallinity[b] X_c (%)
PEO_{10}–$LiClO_4$	−34.9	60.5	94.0	44.0
PEO_{10}–$LiClO_4$/5% PZSMS	−38.4	58.7	79.7	37.3
PEO_{10}–$LiClO_4$/10% PZSMS	−42.9	57.8	67.3	31.5
PEO_{10}–$LiClO_4$/15% PZSMS	−45.4	56.5	63.7	29.8
PEO_{10}–$LiClO_4$/20% PZSMS	−45.6	54.9	61.3	28.7

[a] The data have been normalized to the weight of the PEO matrix

[b] $X_c = (\Delta H_m^{sample}/\Delta H_m^*) \times 100$, where $\Delta H_m^* = 213.7$ J g^{-1}

the increase of PZSMS content and then attains a maximum value when PZSMS concentration is about 10 wt%. Then the conductivity decreases with further increasing PZSMS content. One reason for the enhancement in ionic conductivity with the addition of PZSMS fillers is due to the existence of a highly conducting layer at the electrolyte/filler interface [15–20]. This interface layer could be an amorphous polymer layer surrounding PZSMS and a space-charge layer [21, 22]. At low PZSMS loadings, the increase of conductivity with PZSMS content is basically due to the increasing amount of the conductive layers. The inorganic–organic hybrid surface of PZSMS may act as the special conducting pathway of the charge carriers. On the other hand, when the content of PZSMS is too high, the blocking effect on the transporting of charge carriers resulting from the aggregation of the PZS microspheres may decrease the ionic conductivity of the composite polymer electrolyte [11].

Another reason is the increase of the ratio of the amorphous phase of PEO and more free Li$^+$. The hybrid inorganic–organic structure of PZSMS increases the ratios of the amorphous phase of PEO, which is beneficial for the transport of Li$^+$ cations. The oxygen atoms, nitrogen atoms and sulfur atoms on the surface of PZSMS coordinating with Li$^+$ cations can enhance the dissolvability of LiClO$_4$ in PEO matrix and lead to more free Li$^+$ [16]. The weakening of the polymer-cation association and Li$^+$–ClO$_4^-$ contact-ion

pairs induced by PZS microspheres is also very important for ionic conduction.

Figure 5 shows the conductivity of PEO_{10}–$LiClO_4$, PEO_{10}–$LiClO_4$/10% SiO_2 and PEO_{10}–$LiClO_4$/10% PZSMS as a function of temperature. It can be seen that in the temperature range studied the conductivity of PEO_{10}–$LiClO_4$/10% PZSMS is higher than PEO_{10}–$LiClO_4$/10% SiO_2. As SiO_2 and PZSMS used in this study have similar diameter, the reason for the enhancement of conductivity is attributed to the different surface chemical structure of the two fillers. The chemical elements of PZS microspheres surface includes S, O and N atoms which can interact with Li$^+$ ions and enhance the dissolvability of LiClO$_4$ in PEO matrix more efficiently than SiO_2. And then the conductivity is increased more by PZSMS than SiO_2.

3.4 Lithium ion transference number

Lithium ion transference number, t_{Li}^+, is very important in the development of rechargeable lithium ion batteries in order to eliminating the concentration gradients within the batteries and ensuring the battery operation at high current density [5, 23]. t_{Li}^+ of PEO_{10}–$LiClO_4$ before and after the addition of PZSMS fillers are compared in Table 2 and it can be seen that t_{Li+} of the composite polymer electrolytes can be obviously increased by the addition of PZS microspheres.
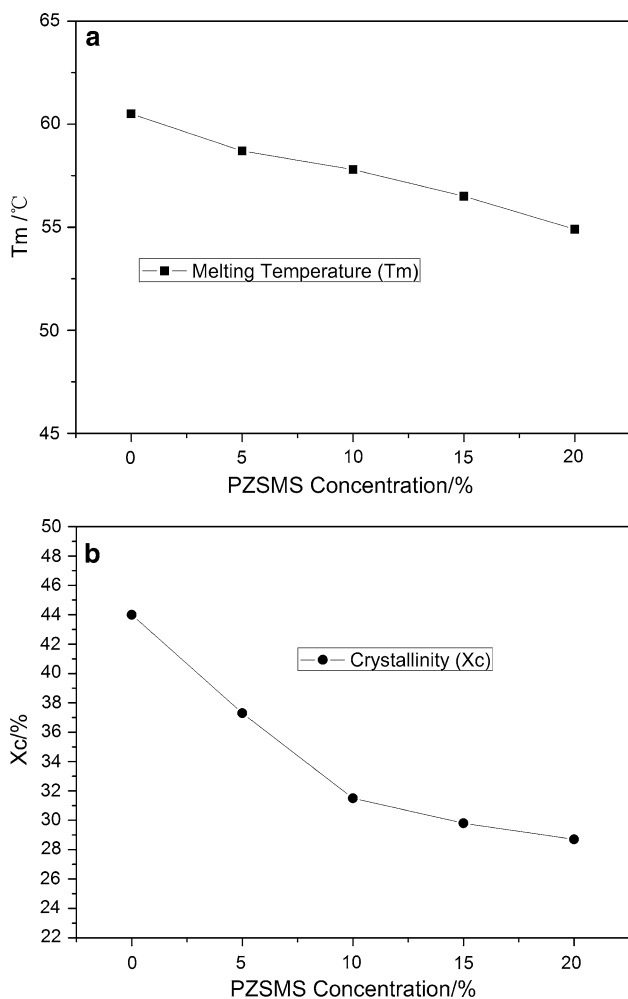
Fig. 3 **a** Melting temperature (T_m) of PEO_{10}–$LiClO_4$/x% PZSMS composite polymer electrolytes and **b** crystallinity (X_c) of PEO_{10}–$LiClO_4$/x% PZSMS composite polymer electrolytes

Fig. 4 **a** Temperature dependence of ionic conductivity for $PEO_{10}4_4$/x% PZSMS composite polymer electrolytes and **b** ionic conductivity of PEO_{10}–$LiClO_4$/x% PZSMS composite polymer electrolytes as a function of PZSMS concentration at different temperatures

In PEO_{10}–$LiClO_4$ complex, Li^+ can coordinate not only with the ether O in PEO chains but also with the O atoms in ClO_4^-, and then its transport ability is restricted, resulting in a very low t_{Li}^+ value. After the addition of PZSMS, t_{Li}^+ can be increased. The O, N, S atoms on the surface of PZSMS can interact with Li^+ and hence weaken the interactions between Li^+ and the O atoms of PEO chains and ClO_4^-, and enhance the dissolvability of $LiClO_4$ to free more Li^+. On the other hand, the interface between the inorganic–organic hybrid framework of PZSMS and PEO chains may provide novel conducting pathway for Li^+. And as a result, more free Li^+ ions are released and t_{Li}^+ is enhanced.

Another important reason for the increased transference number is the entrapment of ClO_4^- anion by the rigid hybrid structure of PZSMS, similar to what is observed in boron-based systems and additives [24–27]. The rigid
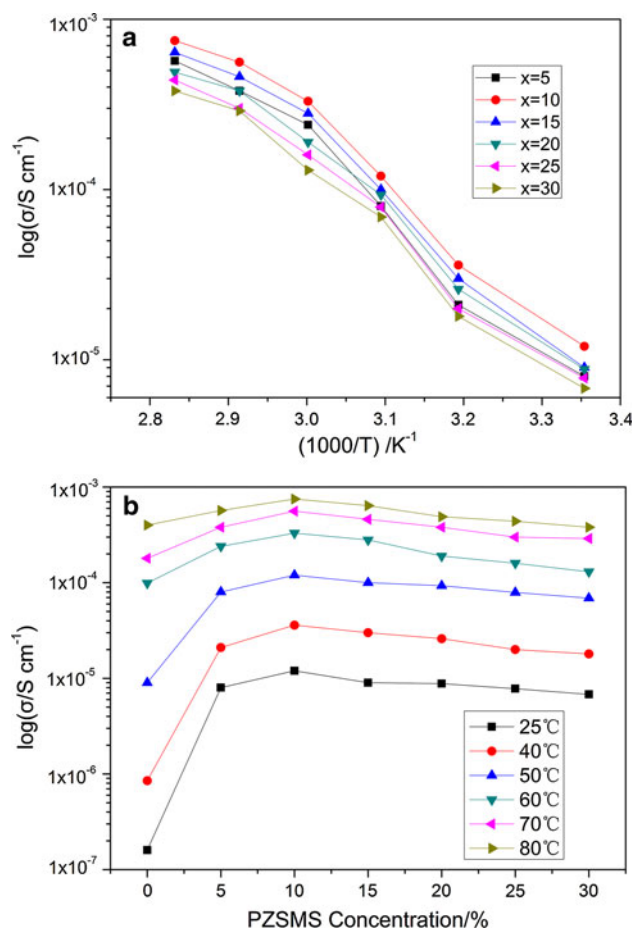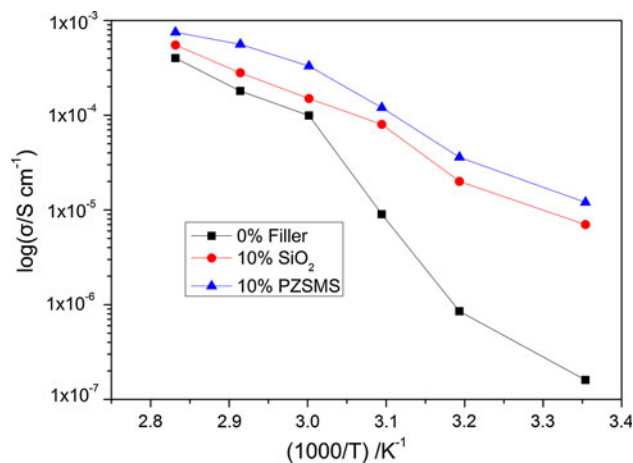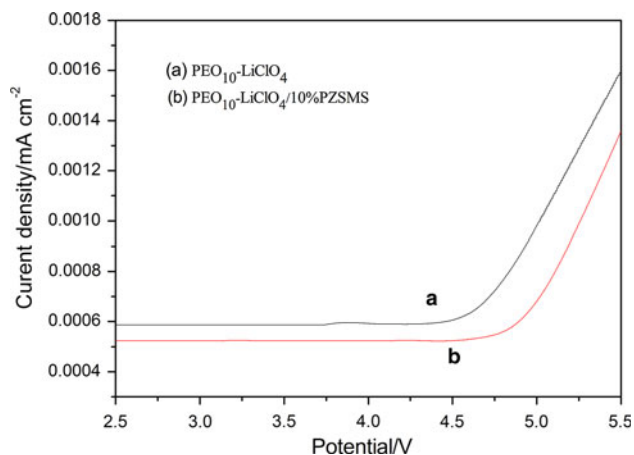

Fig. 5 Temperature dependence of ionic conductivity for PEO_{10}–$LiClO_4$, PEO_{10}–$LiClO_4$/10% SiO_2, PEO_{10}–$LiClO_4$/10% PZSMS composite polymer electrolytes

Table 2 Lithium ion transference numbers of pristine PEO_{10}–$LiClO_4$ and PEO_{10}–$LiClO_4$/10% filler composite polymer electrolytes

Sample	PEO_{10}–$LiClO_4$	PEO_{10}–$LiClO_4$/10% SiO_2	PEO_{10}–$LiClO_4$/10% PZSMS
t_{Li+}	0.19	0.24	0.29

Fig. 6 Current–voltage response of (*a*) PEO_{10}–$LiClO_4$ and (*b*) PEO_{10}–$LiClO_4$/10% PZSMS composite polymer electrolytes at 80 °C on stainless steel working electrode at a scanning rate of 1 mV s^{-1}

hybrid structure of PZSMS could act as anion receptors and form the complex with anions, causing a decrease in the share of ion pairs and immobilization of anions, resulting in an increase in the lithium ion transference number [28–31].

3.5 Electrochemical stability window

Electrochemical stability window of the polymer electrolyte can be obtained by the method of linear voltage sweep. Figure 6 displays the linear voltage sweep curves of pristine PEO_{10}–$LiClO_4$ and PEO_{10}–$LiClO_4$/10% PZSMS composite polymer electrolyte at 80 °C. The irreversible onset of the current determines the electrolyte breakdown voltage. The maximum working voltage (V_{max}) of PEO_{10}–$LiClO_4$ only extends to about 4.5 V versus Li and the addition of PZSMS widens the electrochemical stability window. The V_{max} of PEO_{10}–$LiClO_4$/10% PZSMS exceeds to 4.8 V, indicating that PZSMS obviously improves the electrochemical stability.

4 Conclusions

Novel PEO-based all solid-state composite polymer electrolytes by using inorganic–organic hybrid PZS microspheres as fillers are obtained. Compared with traditional ceramic fillers such as SiO_2, PZSMS in PEO-based polymer electrolytes leads to higher enhancement in ionic conductivity. PZS microspheres can also enhance other electrochemical properties such as lithium ion transference number, electrochemical stability window of the composite polymer electrolyte. The excellent electrochemical properties such as high room temperature ionic conductivity and lithium ion transference number combined with wide electrochemical stability window ensures the use of PEO_{10}–$LiClO_4$/PZSMS composite polymer electrolytes as candidate electrolyte materials for all solid-state rechargeable lithium polymer batteries.

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