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Electrospun poly(ethylene oxide) nanofibrous composites with enhanced ionic conductivity as flexible solid polymer electrolytes

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Abstract: Solid polymer electrolytes (SPEs) have great potential to address the safety issues of lithium (Li)-ion batteries when compared with conventional liquid electrolytes, which makes them a promising alternative for next-generation high-energy batteries. In this work, poly(ethylene oxide)-lithium perchlorate (PEO–LiClO₄) polymer electrolytes for Li-ion batteries were prepared using electrospinning. The crystallinity, ionic conductivity as well as mechanical properties were investigated. Ionic conductivities and mechanical properties of PEO–LiClO₄ based SPE have been obviously increased by incorporating modified TiO₂ nanofibres (TNFs) than TiO₂ nanoparticles (TNPs), due to that both TNFs and TNPs can decrease the crystalline phase concentration of PEO and increase segmental flexibility of PEO. The SPE with 3 wt% TNFs exhibits the highest conductivity of $5.308 \times 10^{-5} \text{ S cm}^{-1}$ at 20°C and higher tensile strength of 13.8 MPa. These results highlight the potential of utilising the electrospinning method to improve the ionic conductivity of SPEs.

1 Introduction

Lithium (Li) secondary battery using solid polymer electrolytes (SPEs) is an attractive energy source for portable devices. Recently, research and development of SPE has been paid more interesting as the Li-ion batteries are widely used in electric vehicles, mobile phones, computers and so on, regarding to the advantages with polymer such as flexibility, light weight, and most important is that the SPE can avoid the electrolyte leakage, thus it can improve the safety [1–4].

SPE makes the fabrication of safe batteries possible and permits the development of thin batteries. Conventional polymer electrolytes with poly(ethylene oxide) (PEO) are the most extensively studied due to its ability to form complexes with kinds of Li salts, and the charge carriers can easy to move in this system. PEO is a good polymer electrolyte, but suffer from bad ionic conductivity and poor mechanical strength [5]. These electrolytes exhibit very low ionic conductivity (order of $10^{-7} \text{ S cm}^{-1}$) at room temperature due to its high crystallinity [6]. Most researchers studied on PEO–LiX ($X = \text{ClO}_4^-$, PF_6^- , CF_3SO_3^- etc.) complexes [7–11]. Among them, lithium perchlorate (LiClO₄) is the most commonly used as electrolyte salts. However, the big problem is that PEO tend to crystallise at ambient temperatures with LiClO₄ electrolyte, while Li⁺ ion can only transfer in the amorphous state of polymer. Thus, the ionic conductivity would be decreased [12–16]. Although the incorporation of low molecular weight plasticisers offers high ionic conductivity, it adversely deteriorates the mechanical properties of the membranes. Generally, to enhance the ionic conductivity of polymer electrolyte, the most successful methods are to incorporate the inorganic nanofillers such as TiO₂, Al₂O₃ and SiO₂ into PEO

matrix. It is a good strategy for suppressing the crystallinity and enhancing the ionic conductivity. It not only leads to an increase on ionic conductivity, but also improves its mechanical strength [17–22]. The effects of TiO₂ on the ionic conductivity of PEO–LiClO₄ polymer electrolyte were studied, showing that ionic conductivity greatly enhanced due to the Li⁺ ions can easily transfer between the polymer chains [23]. However, there are no reports on the enhancement of electrical and mechanical properties of PEO based SPE films with TiO₂ nanofibres (TNFs) prepared by electrospinning.

In this work, TNFs were successfully prepared via electrospinning. The PEO–LiClO₄ solid polymer electrolytes for Li-ion batteries were also prepared using electrospinning. The effect of modified TiO₂ nanoparticles (mTNPs) and mTNFs on the electrical and mechanical properties of PEO–LiClO₄ polymer electrolyte was investigated. The PEO electrolyte containing 3 wt% mTNFs showed the best ionic conductivity enhancement at room temperature.

2 Experimental section

2.1 Materials

PEO with molecular weight of 6.0×10^5 was purchased from Aladdin Industrial Corporation. LiClO₄ with purity of 99.9% and anatase TiO₂ powder with diameter of 5–10 nm were also bought from Aladdin Industrial Corporation. Prior to use, PEO, LiClO₄ and TiO₂ were vacuum dried for 24 h at 50, 120 and 120°C, respectively. Tetra-n-butyl titanate (TNBT, purity > 98.5%) was purchased from Sinopharm Chemical Reagent CO., Ltd.

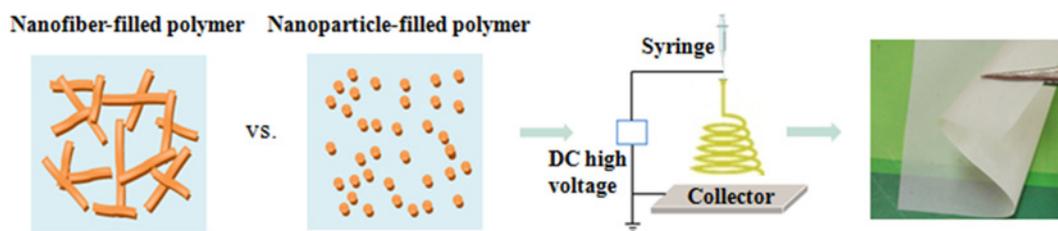


Fig. 1 Schematic illustration for the preparation of SPE films filled with mTNFs and mTNPs by electrospinning

(3-aminopropyl)triethoxysilane (KH-550) were bought from Alfa Aesar CO., Ltd. Polyvinylpyrrolidone (PVP, Mw ~1,300,000) was obtained from Aladdin Industrial Corporation.

2.2 Preparation of the TNFs

First, absolute ethyl alcohol was mixed with PVP in a beaker followed by magnetic stirring for ~2 h, and then the acetic acid glacial and TNBT were added. Second, the mixture was immediately loaded into a plastic syringe after stirring for 0.5 h. The spinning voltage, spinning rate, deposition distance and cylinder speed were, respectively, set at 14.5 kV, 0.008 mm/min, 12 cm and 1000 r/min. The fibre membrane was kept in an open environment for 24 h to allow the TNBT in the nanofibres to completely hydrolyse and turn into three-dimensional (3D) network (gel). Finally, the fibre membrane was calcinated in the muffle furnace with the heating rate of 1°C/min and kept at 600°C for 3 h. Then the TNFs were successfully prepared.

2.3 Preparation of the SPE with TNFs

Prior to use, the TNFs were modified with KH-550. The preparation process of SPE films with mTNFs is shown in Fig. 1. First, the PEO and LiClO₄ were dissolved in anhydrous acetonitrile and mechanically stirred for 2 h. Second, the required amount of mTNFs (0, 3, 5 and 8 wt%) was added to the mixture with ultrasonic dispersion for 1 h and mechanically stirred for 12 h. Then, the mixture was immediately loaded into a plastic syringe for electrospinning. The spinning voltage, spinning rate, deposition distance and cylinder speed were, respectively, set at 16 kV, 0.01 mm/min, 12 cm and 800 r/min. Finally, the electrospun films were dried in a vacuum oven at 50°C for 24 h to completely remove the residual solvent and moisture, and the homogeneous polymer electrolyte films with an average thickness of 80–100 μm were obtained. For comparison, the SPE films filled with mTNPs were also prepared following the same process.

2.4 Characterisation

The morphologies of the electrospun nanofibrous films were observed by scanning electron microscope (SEM, HITACHI S4700, Japan) and transmission electron microscope (TEM, H800, Japan). The crystal structures of TNFs were characterised by X-ray diffraction (XRD, SmartLab, Japan) with Cu Kα radiation in the range of 10°–90°. The structures of polymer electrolytes were investigated by Fourier transform infrared spectrometer (FTIR, Nicolet 560-IR, America). The crystallinity of the polymer electrolytes was evaluated by differential scanning calorimeter (DSC, Japan) under the nitrogen atmosphere in the temperature range of 30–100°C. The heating and cooling rates were set as 10°C min⁻¹. The crystallinity (X_c) was calculated according to the following equation

$$X_c = \frac{\Delta H_f / \phi}{\Delta H_f^*} \times 100\% \quad (1)$$

where ΔH_f is the enthalpy of fusion of nanofibrous films, ΔH_f^* is the fusion enthalpy of 104.7 J·g⁻¹ for PEO at the state of totally

crystallinity. Φ is the concentration of PEO. The ionic conductivities of composite films were measured by using electrochemical analyser in the frequency range of 0.1–1 MHz. For impedance measurement, the films with the thickness of 90 μm and the area of 0.785 cm² were prepared. Then, the ionic conductivity can be obtained from the following equation [24, 25]

$$\sigma = \frac{d}{R_b S} \quad (2)$$

where σ is the conductivity, d is the thickness of the films, S is the area of the films and R_b is the bulk resistance.

The mechanical properties of the nanofibrous films were tested by electronic tensile machine (Shimadzu, Model AG-IC, Japan) with the tension rate of 10 mm min⁻¹ at room temperature. The standard of mechanical measurement was adopted according to ASTM D638. Five specimens for each sample were tested to manifest the repeatability of mechanical properties.

3 Results and discussion

3.1 Microstructure of the TNFs

SEM images of as-spun and calcined TNFs prepared by electrospinning and subsequent calcination process are shown in Fig. 2. It can be seen that the diameters of as-spun TNFs are in the range of 230–240 nm as shown in Fig. 2a. Fig. 2b shows the SEM images of the calcined TNFs. It can be seen that TNFs transform systematically from cylindrical nanofibres to wrinkled nanofibres after calcination at 500°C, and a little break appeared. Transmission electron microscopy (TEM) image of the calcined TNFs is shown in Fig. 2c. It can also be clearly illustrated that the surface became rough after calcination at 500°C. Fig. 2d shows the X-ray diffraction (XRD) patterns of the calcined TNFs. The peaks were observed at 25.31, 37.81, 48.01, 53.91, 62.71 and 68.81, corresponding to the (101), (004), (200), (105), (204), and (116) planes of anatase TiO₂ phases (JCPDS No. 841286), which implies successful formation of anatase TiO₂ phases.

3.2 FTIR spectra of the pristine and modified TiO₂

Fig. 3 shows the FTIR spectra of pristine TiO₂ (TNPs and TNFs) and the modified TiO₂ (mTNPs and mTNFs), respectively. It can be seen that the peak shape of infrared spectra changed obviously after modification. The stretching vibration absorption peak of hydroxyl groups on the surface of TiO₂ are at about 1642 and 3000–3600 cm⁻¹, and the two peaks weakened after modification in the infrared spectra. This is mainly because that part of hydroxyl was occupied by silanol after grafting, thus the hydroxyl content reduced. The new peaks at about 2953 cm⁻¹ are the stretching vibration absorption band of coupling agent KH-550. The appearance of Si–O–Si absorption peak at about 1050 cm⁻¹ proved that condensation reaction had occurred between TiO₂ and KH-550 as well [26, 27]. Moreover, the characteristic absorption peaks of KH-550 are clearly presented, indicating that the modification is successful.

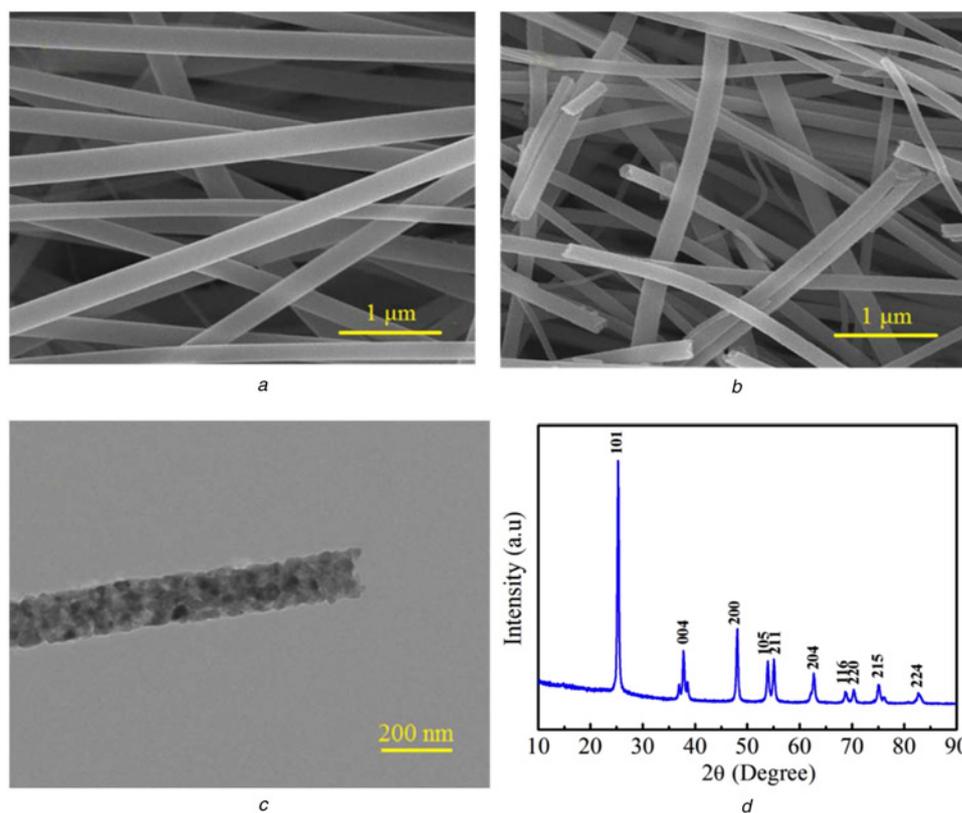


Fig. 2 SEM images of TNFs

- a Before
- b After calcination
- c TEM image
- d XRD pattern of TNFs after calcinations

3.3 Microstructure of polymer electrolytes

Figs. 4 and 5 show the SEM images of the $(\text{PEO})_8\text{LiClO}_4$ polymer electrolytes filled with mTNPs and mTNFs, respectively. It can be seen that the nanofibrous films has the 3D network structure with a large number of holes. The fibre diameters are relatively uniform. It proves that the polymer electrolytes are miscible and homogeneous. Compared with the electrolyte films filled with mTNPs, the average diameter of the electrolyte film filled with mTNFs decreases relatively so that the specific surface areas increase. Thus, the contact areas between fibres increase. This is also contributed to the improvement of the tensile strength of polymer electrolyte films.

3.4 FTIR spectra of polymer electrolytes

Fig. 6 shows the FTIR spectra of the $(\text{PEO})_8\text{LiClO}_4$ polymer electrolytes filled with mTNPs and mTNFs. FTIR spectroscopy is used to study polymer structure and interactions between PEO and LiClO_4 , which can make changes in the vibrational modes of the atoms or molecules in the material. It can be seen that the peak shape of infrared spectra changed obviously after adding mTNPs and mTNFs. The infrared spectra show the complexation of LiClO_4 with PEO. The FTIR spectra are obtained in the range of $2000\text{--}800\text{ cm}^{-1}$ at room temperature. According to the previous studies, the vibration of C–O–C in PEO centralised at 1114 cm^{-1} [28–30]. It can be seen that the wavenumber of C–O–C absorption

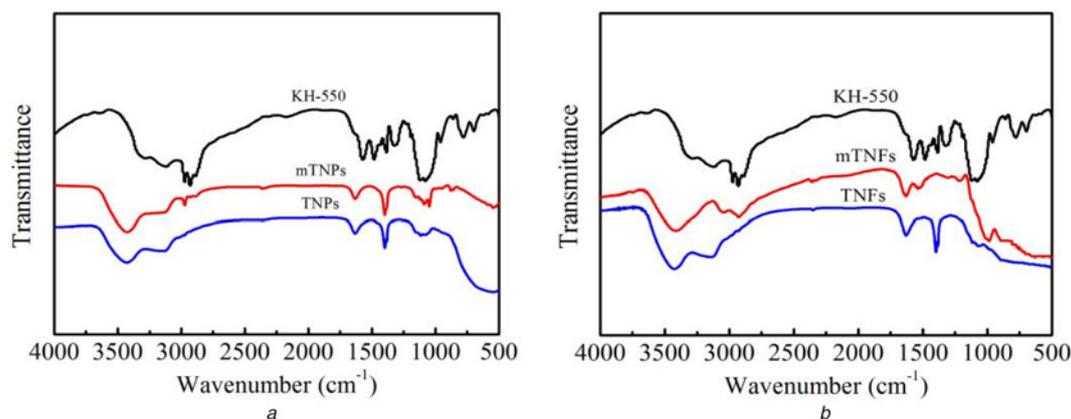


Fig. 3 FTIR spectra of

- a KH-550, TNPs, mTNPs
- b KH-550, TNFs, mTNFs

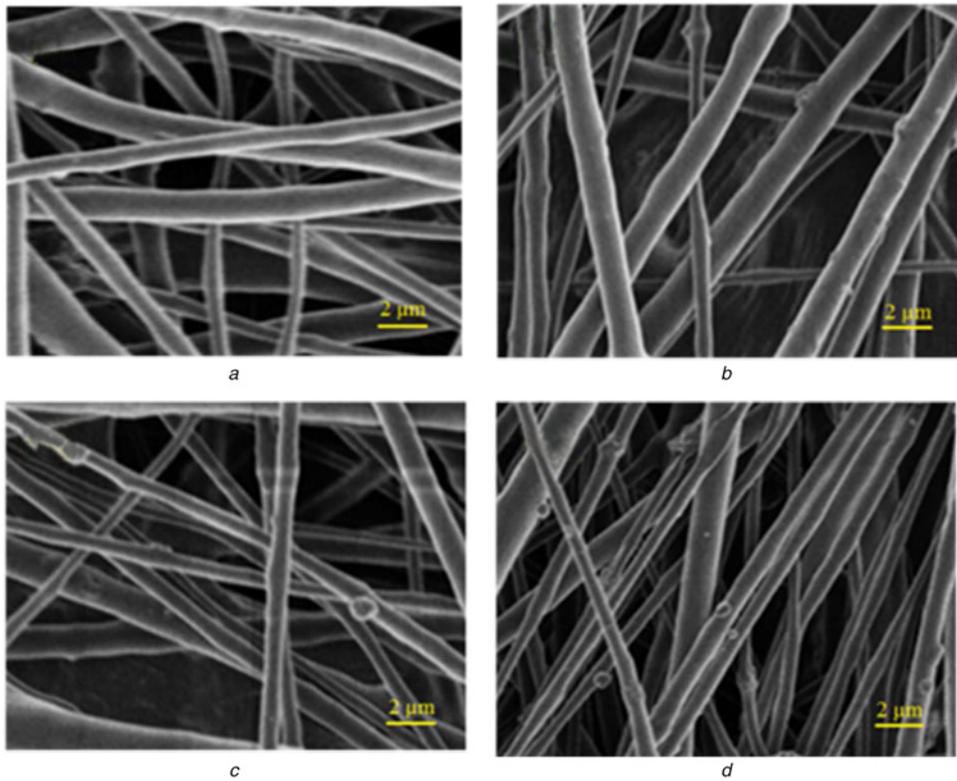


Fig. 4 SEM images of the $(PEO)_8LiClO_4$ polymer electrolytes filled with mTNPs
 a 0 wt%
 b 3 wt%
 c 5 wt%
 d 8 wt%, respectively

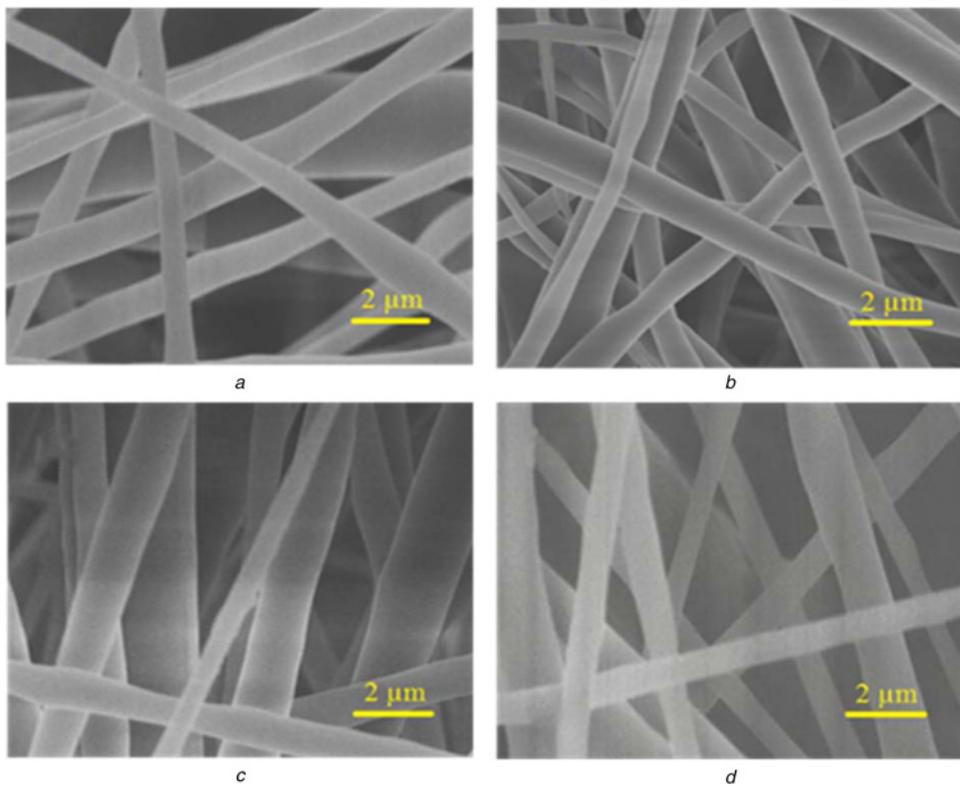


Fig. 5 SEM images of the $(PEO)_8LiClO_4$ polymer electrolytes filled with mTNFs
 a 0 wt%
 b 3 wt%
 c 5 wt%
 d 8 wt%, respectively

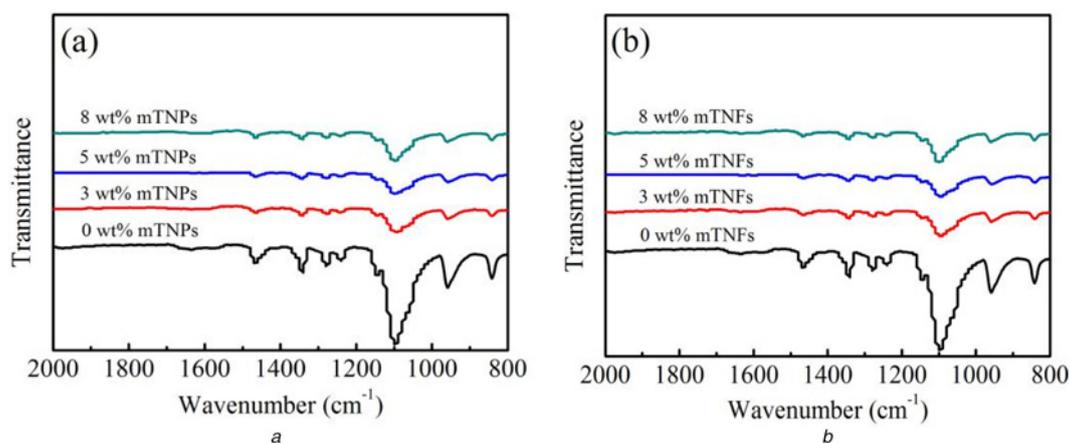


Fig. 6 FTIR spectra of the $(\text{PEO})_8\text{LiClO}_4$ polymer electrolytes filled with *a* mTNPs *b* mTNFs, respectively

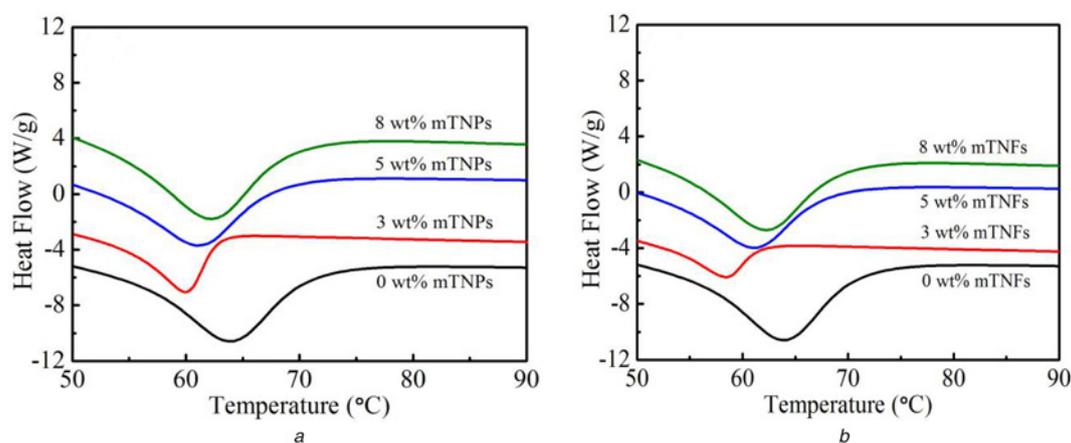


Fig. 7 DSC curves of the $(\text{PEO})_8\text{LiClO}_4$ polymer electrolytes filled with *a* mTNPs *b* mTNFs, respectively

peak decreased to 1090 cm^{-1} after incorporation with LiClO_4 in the PEO-based polymer electrolytes. It proves that the chemical environment of C–O–C has changed and the energy increased when C–O–C vibrate. That directly indicates the complexation of LiClO_4 with PEO. The wavenumber of C–O–C absorption peak increased to 1100 cm^{-1} after the addition of mTNPs and mTNFs. This may be due to that the hydroxyl groups on the surface of TiO_2 were interacted with C–O–C of the PEO, which weakened the complexation of Li^+ with PEO. Therefore, it promoted the transmission of Li^+ along the PEO polymer chain segment.

3.5 DSC analysis

Fig. 7 shows DSC curves of $(\text{PEO})_8\text{LiClO}_4$ polymer electrolytes. The detailed thermal properties of $(\text{PEO})_8\text{LiClO}_4$ polymer electrolytes obtained from DSC analysis are summarised in Table 1. It can be seen from Fig. 7 and Table 1 that both the melting temperature (T_m) and the crystallinity (X_c) of PEO decrease obviously when TiO_2 were added in $(\text{PEO})_8\text{LiClO}_4$ complex. The T_m of $(\text{PEO})_8\text{LiClO}_4$ -mTNPs decreased from 64 to 60°C when the content of mTNPs increased from 0 to 8 wt%. The T_m of $(\text{PEO})_8\text{LiClO}_4$ -mTNFs decreased from 64 to 59°C when the content of mTNFs increased from 0 to 8 wt%. The X_c of $(\text{PEO})_8\text{LiClO}_4$ -mTNPs decreased from 48.50 to 16.35%, while the X_c of $(\text{PEO})_8\text{LiClO}_4$ -mTNFs decreased from 48.50 to 10.45% when the content of TiO_2 increased from 0 to 8 wt%. The crystallinity degree follows the order: 3 wt% mTNFs (10.45%) < 3 wt% mTNPs (16.35%) < 0 wt% TiO_2 (48.50%).

This may be due to that the interactions between the fillers and polymer chains which inhibit the crystallisation process [31–34]. The lower crystalline phase and improved segmental flexibility will lead to the enhanced conductivity. DSC studies confirm that the polymer electrolyte with 3 wt% mTNFs has the minimum volume fraction of crystalline phase.

3.6 Electrochemical impedance spectrum analysis

Fig. 8 shows the typical AC impedance spectra of the $(\text{PEO})_8\text{LiClO}_4$ polymer electrolytes filled with mTNPs and mTNFs. Insets are the impedance spectra of the SPE films with 3 wt% TiO_2 . It can be observed clearly from Table 2 that the R_b of PEO electrolyte without the fillers loading is $10^4\ \Omega$ and has a non-ideal ionic

Table 1 Thermal parameters obtained for various compositions of the polymer electrolyte system

mTNPs, X wt%	$T_m, ^\circ\text{C}$	$\Delta H_f, \text{J}\cdot\text{g}^{-1}$	$X_c, \%$
0	64	-53.74	48.50
3	60	-17.75	16.35
5	62	-37.02	34.60
8	63	-42.16	40.28
mTNFs, X wt%	$T_m, ^\circ\text{C}$	$\Delta H_f, \text{J}\cdot\text{g}^{-1}$	$X_c, \%$
0	64	-53.74	48.50
3	59	-11.34	10.45
5	61	-32.89	30.74
8	62	-37.16	35.50

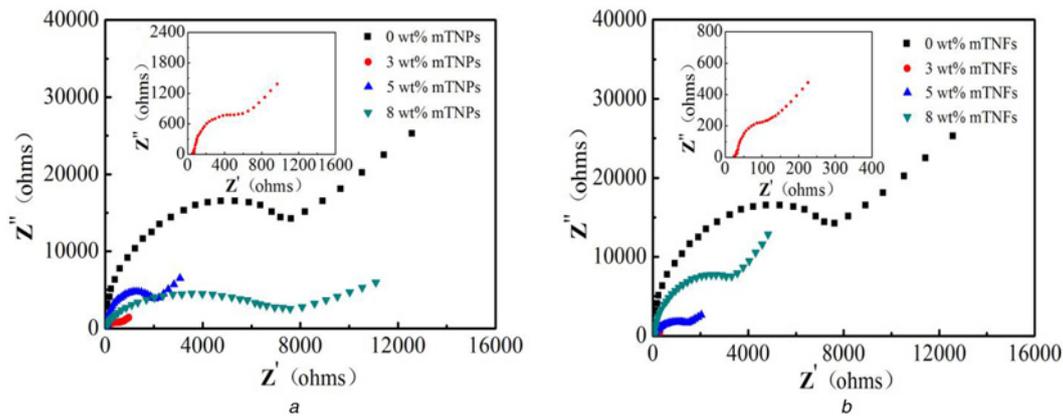


Fig. 8 Impedance spectra of the $(\text{PEO})_8\text{LiClO}_4$ polymer electrolytes filled with *a* mTNPs *b* mTNFs, respectively

Table 2 Thickness, bulk resistance, contact area and ionic conductivity of the SPE films

mTNPs, X wt%	<i>d</i> , cm	R_b , Ω	<i>S</i> , cm^2	σ , $\text{S}\cdot\text{cm}^{-1}$
0	0.0100	10000	0.785	1.274×10^{-6}
3	0.0085	900	0.785	1.203×10^{-5}
5	0.0080	2600	0.785	3.920×10^{-6}
8	0.0090	7000	0.785	1.638×10^{-6}
mTNFs, X wt%	<i>d</i> , cm	R_b , Ω	<i>S</i> , cm^2	σ , $\text{S}\cdot\text{cm}^{-1}$
0	0.0100	10000	0.785	1.274×10^{-6}
3	0.0075	180	0.785	5.308×10^{-5}
5	0.0080	2200	0.785	4.632×10^{-6}
8	0.0085	5000	0.785	2.166×10^{-6}

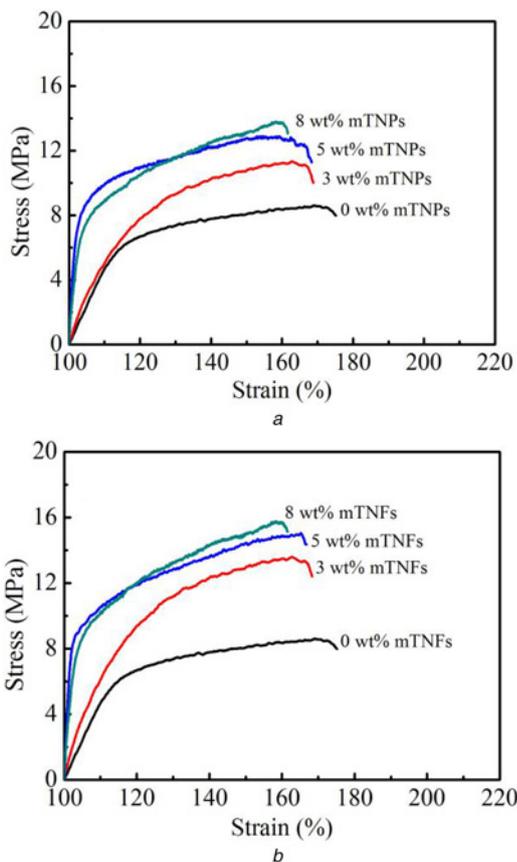


Fig. 9 Stress-strain curves of the SPE films with the addition of *a* mTNPs *b* mTNFs, respectively

conductivity of $1.274 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 20°C . After the modification, the lowest R_b of the PEO electrolyte with mTNPs fillers is 900Ω and has an ionic conductivity of $1.203 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 20°C . Moreover, the lowest bulk resistance of the polymer electrolyte with mTNFs fillers is 180Ω and has an ionic conductivity of $5.308 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 20°C . The enhancement of ionic conductivity may be attributed to the reduced crystallinity by the addition of mTNPs and mTNFs as shown in Table 1.

3.7 Mechanical properties

Fig. 9 shows the stress-strain curves of the $(\text{PEO})_8\text{LiClO}_4$ polymer electrolytes filled with mTNPs and mTNFs. It can be seen that both additives improve the mechanical properties of the SPE films. The tensile strength of the SPE films increases from 8.6 to 13.5 MPa with an addition of 8 wt% mTNPs in the polymer matrix, whereas it increases from 8.6 to 15.9 MPa with an addition of 8 wt% mTNFs. Thus, the mechanical strength of SPE films with mTNFs is higher than that of the SPE films with the same content of mTNPs. This is due to that the polar groups on the surface of TiO_2 are attracted with the oxygen atoms of PEO polymer chain segment, which have the effect of physical crosslinking. Meanwhile, the mTNFs have a better physical crosslinking with PEO fibres.

4 Conclusions

Novel PEO-based all solid-state polymer electrolytes filled with the mTNFs or mTNPs were prepared by electrospinning. Compared with mTNPs, 3 wt% mTNFs in PEO-based polymer electrolytes leads to higher enhancement in ionic conductivity of $5.308 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 20°C and mechanical properties. The enhanced conductivity is ascribed to the incorporation of mTNFs leading to increase the amorphous phase content which is beneficial for Li^+ ion transportation. Therefore, this work opens up a new path to fabricating SPE with the optimised conductivity in the Li battery application.

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