A Novel Electrospun TPU/PVdF Porous Fibrous Polymer Electrolyte for Lithium Ion Batteries

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ABSTRACT: Novel blend-based gel polymer electrolyte (GPE) films of thermoplastic polyurethane (TPU) and poly(vinylidene fluoride) (PVdF) (denoted as TPU/PVdF) have been prepared by electrospinning. The electrospun thermoplastic polyurethane-co-poly (vinylidene fluoride) membranes were activated with a $1M$ solution of $LiClO_4$ in EC/PC and showed a high ionic conductivity about 1.6 mS cm^{-1} at room temperature. The electrochemical stability is at 5.0 V versus Li$^+$/Li, making them suitable for practical applications in lithium cells. Cycling tests of Li/GPE/LiFePO4 cells showed the suitability of the electrospun membranes made of TPU/PVdF (80/20, w/w) for applications in lithium rechargeable batteries. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2556–2563, 2012

Key words: thermoplastic polyurethane (TPU); poly-(vinylidene fluoride) (PVdF); electrospun; gel polymer electrolyte; lithium batteries

INTRODUCTION

Since its birth, the gel polymer electrolytes (GPEs) with sufficient mechanical strength, high ionic conductivity at ambient temperature and good compatibility with lithium electrodes which could be used for rechargeable batteries have been investigated widely.[1,2] In general, GPEs are formed by adsorbing a certain amount of liquid electrolyte in a polymer framework. The polymer is the bone to maintain the physical strength and shape of the electrolyte, and it is also the main part of containing electrolyte for lithium ions through the membrane. Until now, some researches have been extended to understand the movement of ions through the structure of polymer backbone.[3] However, most of GPEs are less advantageous for their weak mechanical strength. The poor mechanical stability leads to leaking liquid and causes bad safety for lithium-ion batteries.

Thermoplastic polyurethane (TPU) has two-phase microstructure: the soft segments and the hard segments.[4,5] The soft segments can dissolve alkali metal without formation of ionic cluster, and the hard segments in glassy state are distributed or interconnected throughout the soft phase parts. So the hard segments play the role of reinforcing fillers and keeping the GPEs' dimensional stability. Therefore, this special structure is beneficial to the safety of lithium-ion batteries. So it makes TPU very useful as matrix materials for GPEs. There have been some reports on the use of the TPU-based electrolytes for battery applications.[6–9] In recent years, TPU with polyacrylonitrile (PAN) (denoted TPU/PAN)-based gel polymer electrolytes (GPEs) and TPU with linear poly (ethylene oxide) (PEO) (denoted TPU/PEO)-based gel polymer electrolytes (GPEs) for rechargeable lithium batteries have been reported.[10,11] Santhosh et al.[12] reported polyurethane/poly (vinylidene fluoride) (PU/PVdF)-based polymer electrolytes, where the polymer electrolytes films were prepared by solution casting technology. PVdF is a semicrystalline polymer and PVdF-based electrolytes are expected to have high anodic stabilities due to strong electron withdrawing functional groups.[13] Recently PVdF has been a favorable choice for polymer electrolyte. PVdF-based gel polymer electrolyte membranes show high ionic conductivity of $10^{-5} - 10^{-3}$ S cm^{-1} at room temperature in secondary batteries.[14]

Keeping the high ionic conductivity at room temperature, the blending of TPU and PVdF for GPEs will strengthen the mechanical strength of the

membrane. However, there is also no study on the formation of the TPU/PVdF blend membranes using electrospinning method so far. So we chose TPU and PVdF as electrospun matrixes for gel polymer electrolytes (GPEs). In this article, we investigated the cycle performances and the rate capabilities of electrospun TPU/PVdF-based fibrous membranes electrolyte for lithium ion polymer batteries.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (PVdF, Alfa Aesar) and thermoplastic polyurethane (TPU, yantaiwanhua,1190A) were dried under vacuum at 80°C for 24 h. $LiClO_4 \cdot 3H_2O$ (AR, Sinopharm Chemical Reagent) was dehydrated in vacuum oven at 140°C for 72 h. Liquid electrolyte was made by dissolving $1.0M$ $LiClO_4$ in ethylene carbonate (EC, Shenzhen capchem technology)/propylene carbonate (PC, Shenzhen capchem technology) (1/1,v/v). N,N-Dimethylformamide (DMF) and acetone were analytical purity and used as received without further treatment.

Preparation of TPU/PVdF and TPU porous fibrous membrane

Firstly a certain amount of TPU and PVdF powder (80/20, wt/wt) were homogeneously dissolved in the mixture of an acetone/N,N-dimethylacetamide (1 : 3, wt/wt) forming a 9 wt % solution. Totally, 9 wt % pure TPU solution was made by the same way. The solution was electrospun under high voltage of 24.5 kV and tip-to-collector distance of 15 cm at room temperature, respectively. Porous fibrous films were obtained on the collector plate. The electrospun porous fibrous films were finally dried under vacuum at 60°C for 12 h.

Preparation of gel polymer electrolytes

The dried porous fibrous films were activated by dipping in $1M$ $LiClO_4$–EC/PC liquid electrolyte solutions at room temperature in a glove box for 1 h. Then using filter papers wiped the surfaces of swelled membranes dry to get gel polymer electrolytes.

Membrane characterization

Scanning electron microscope (SEM, Hitachi S-3500N, Japan) was used to examine the morphology of films. The TPU/PVdF and pure TPU porous fibrous films were goldsprayed prior to SEM measurements.

The structure was investigated in the range of 450–4000 cm^{-1} on FTIR spectra (Spectrum One, PerkinElmer Instruments). The TPU/PVdF and pure

TPU porous fibrous films were observed directly without blending with KBr powder and the PVdF power samples was investigated blending with KBr powder.

The thermal stability of the films was monitored using thermogravimetric analysis (model TQAQ 50, TA company, USA). The TGA measurements were carried out under dry nitrogen atmosphere at a heating rate of 20°C min^{-1} from 30 to 900°C.

The differential scanning calorimeter (DSC) was carried out with a heating and cooling rate of 20°C/min on a DSC TA (DSC-7, Perkin-Elmer, USA) instrument. Samples were run under a nitrogen atmosphere over a temperature range of -90 to 230°C.

X-ray diffraction (XRD) measurements were performed in Rigaku D/Max 2500 diffractometer in the range of 2θ from10° to 60° at a scanning rate of 2° min^{-1}.

The percentage of electrolyte uptake was determined[6] by measuring the weight increase and calculated according to the following eq. (a): Uptake$(\%) = \frac{W-W_0}{W_0} \times 100\%$, Where W_0 is the weight of dried films [$W_0 = 0.0066$ g(TPU film) and 0.0134 g (TPU/PVdF (80/20, w/w) film)] and W is the weight of swelled films.

The ionic conductivity of the composite film was measured with a SS/PE/SS blocking cell by AC impedance measurement using a Zahner Zennium electrochemical analyzer with frequency range of 0.1 $\sim$ 1 MHz. The thin films were prepared about 100 μm in thickness and 2.24 cm^2 in area for impedance measurement. Thus, the ionic conductivity could be calculated from the following eq. (b): $\sigma = \frac{h}{RbS}$. In this equation, σ is the ionic conductivity, Rb is the bulk resistance, h and S are the thickness and area of the films, respectively.

Cell assembly and performance characteristics

Electrochemical stability was measured by a linear sweep voltammetry (LSV) of a Li/PE/SS cell using a Zahner Zennium electrochemical analyzer at a scan rate of 5 mV s^{-1}, with voltage from 2.5 to 6 V.

For charge–discharge cycling tests, the Li/PE/LiFePO$_4$ cell was assembled. The cell was subjected to electrochemical performance tests using an automatic charge–discharge unit, Neware battery testing system (model BTS-51, ShenZhen, China), between 2.5 and 4.2 V at 25°C, at a current density of 0.1 C.

RESULTS

Morphology and structure

The SEM photographs were taken for electrospun TPU and TPU/PVdF (80/20, w/w) based-polymer electrolytes films. It is clear to note from the SEM photographs that the membranes are made up of a
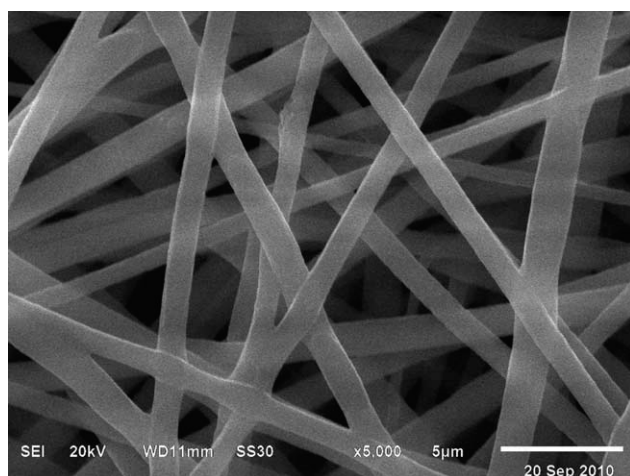
Figure 1 SEM image of electrospun pure TPU membrane.

Figure 2 SEM image of electrospun TPU/PVdF membrane.

network of interlaid fibers. The presence of fully interconnected pores in the structure makes them suitable for application as a host matrix for the preparation of gel polymer electrolytes.

As shown in Figure 1, the diameters of the pure TPU fibers were ~ 1 μm and the TPU/PVdF (80/20, w/w) fibers in Figure 2 with an average fiber diameter (AFD) of ~ 0.4 μm. From Figure 2 we can see clearly that it appears to be uniform in composition without having any phase separated microstructure which is due to the miscibility of TPU and PVdF. However the good miscibility of TPU and PVdF dues to the special chemical structure of TPU.[15,16] Generally speaking, TPU is a linear polymer material. Its molecular structure is complicated, containing ether groups, ester groups and duplicated carbamated–chain (—R′—O—CO—NH—R—NH—CO—O—). The duplicated carbamated–chain (—R′—O—CO—NH—R—NH—CO—O—), which is in the hard segments of TPU, offers amino–group (—NH). So the strong electron-withdrawing functional group (—C—F) which is in the backbone structure of PVdF can form hydrogen bonds with amino–group (—NH). Therefore, PVdF and TPU are miscible without any microphase separation as electrospun matrix for gel polymer electrolytes (GPEs). The main parameters of influencing the morphology of electrospun fiber membranes, which are the distance between the nozzle of the syringe and the collector, the applied voltage, the concentration of the polymer solution, are kept as a constant while electrospinning. So the dielectric constant of the solution is the major reason for the morphological differences between Figures 1 and 2. Following the incorporation of PVdF into TPU solution, the electrospinning jets are more easily formed at the nozzle of the syringe for TPU/PVdF (80/20, w/w) mixed solution forming of fibers with lower diameter. Kim et al. had reported a decrease in AFD resulted in a
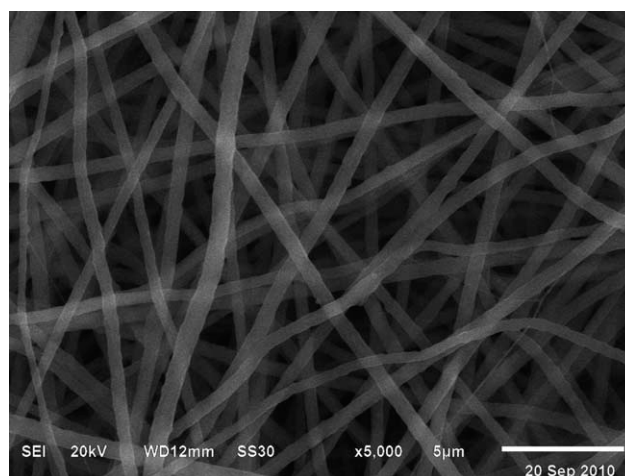
decrease in leakage rate.[17,18] This particular structure may result in high electrolyte uptake.

FTIR spectra of (a) TPU (b) the composite membrane of TPU/PVdF (80/20, w/w) (c) PVdF power are shown in Figure 3. The characteristic absorption peaks of TPU are clearly identified, i.e. 3308 cm^{-1} (stretching band of —NH in hard phase) and 1727 cm^{-1} (stretching band of C=O). The typical peaks of PVdF power are 1399 cm^{-1} (deformation vibration band of —CH$_2$—), 1073 cm^{-1} (stretching band of C—C in the β-phase) and 877 cm^{-1} (band for amorphous phase). In the case of the composite membrane of TPU/PVdF, the characteristic absorption peaks of TPU (3308 and 1727 cm^{-1}) and PVdF (1399, 1073, and 877 cm^{-1}) are present clearly, indicating that the composite membrane consists of two compounds: TPU and PVdF. And the strong electron-withdrawing functional group (—C—F) which is in the backbone structure of PVdF can form hydrogen bonds with amino–group (—NH) which is in the hard segments of TPU during to a little shift of
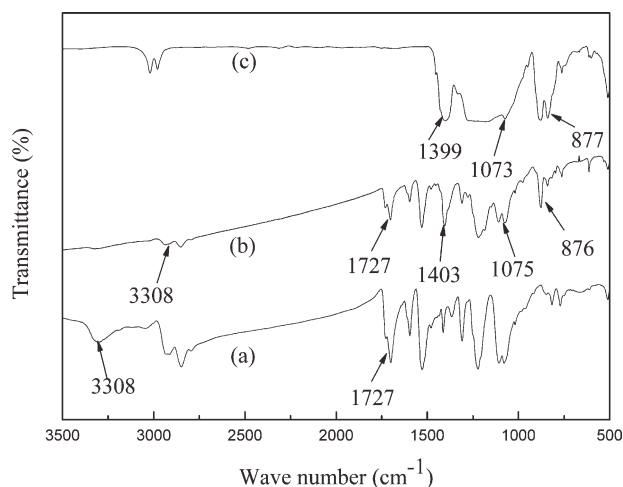

Figure 3 FTIR spectra of the electrospun membranes (a) TPU (b) TPU/PVdF (80/20, w/w) (c) PVdF power.
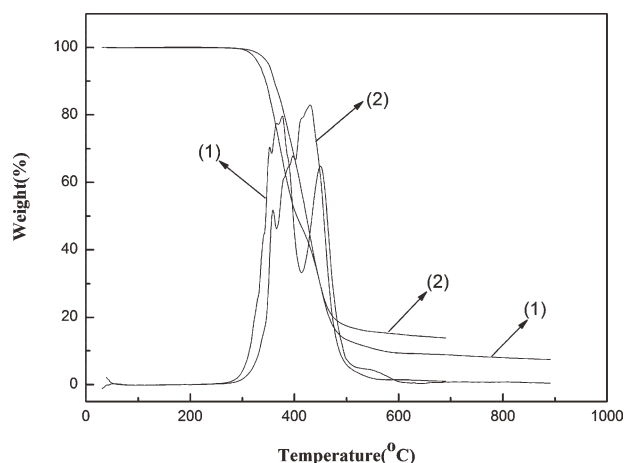
Figure 4 Thermograms of (1) pure TPU (2) TPU/PVdF composite.

Figure 5 DSC curves of the samples(a) eletrospun TPU (b) TPU/PVdF (c) PVdF power (d) Non-eletrospun TPU

absorption bands(1403, 1075, and 876 cm^{-1}) in the characteristic absorption peaks of the TPU/PVdF-based membrane.

Thermal analysis

Thermograms of TPU and TPU/PVdF (80/20, w/w) composites are shown in Figure 4. TPU has a two-stage weight losses starting at about 320°C with 14% weight left at 495°C. The decomposition of TPU/PVdF composites followed a similar pattern in thermogram as that of pure TPU. The first weight loss of TPU/PVdF composites was at 345°C and 19% residual mass at 506°C. For the second stage, the picture shows the decomposition temperature of TPU/PVdF (506°C) is higher than TPU (495°C). All these results suggest that TPU/PVdF membrane has better thermal stability than TPU film. This may be due to the strong interaction between the two polymers. The addition of PVdF causes the interaction between its fluorine groups (-F) with carbonyl (C=O) and amino–group (-NH) in TPU.[19] This enhances the
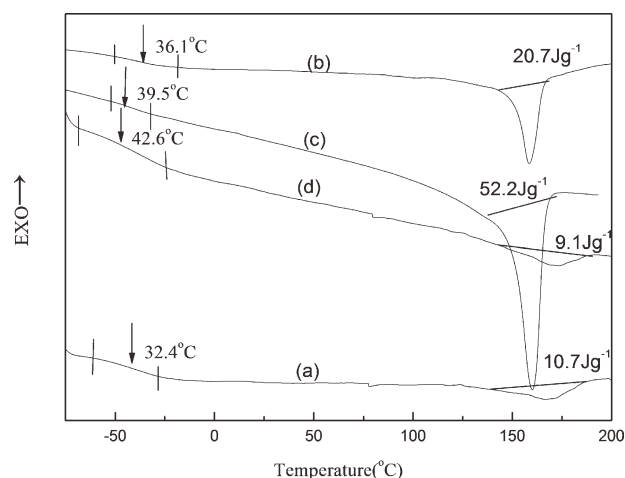
compatibility of TPU and PVdF. The decomposition temperature is higher than 300°C for TPU/PVdF composites proves that the TPU/PVdF film is suitable for considering the PE composite in lithium rechargeable batteries.

Figure 5 displays DSC curves and the following observations were made. First, the heating curve of electrospun TPU/PVdF [80 : 20, w/w] membrane((a) in Fig. 5] showed a melting peak at temperature of 146.7°C. Compared with the pure TPU membrane, although the melting temperatures of these two samples are nearly the same, the melting enthalpy (ΔH_m) of the electrospun TPU/PVdF (80 : 20, w/w) membrane is much higher than that of the pure TPU membrane.

The degree of miscibility of TPU and PVdF in TPU/PVdF membrane was also determined by using DSC analysis. We had carried three repeated DSC experiments to get the average values of the glass transition temperatures (T_g), melting enthalpies (ΔH_m) and melting points (T_m) and they were shown in Table I. As shown in Table I, the electrospun

TABLE I
The Differential Scanning Calorimeter (DSC) Data of the Samples(a) Eletrospun TPU (b) TPU/PVdF (c) PVdF power (d) Noneletrospun TPU

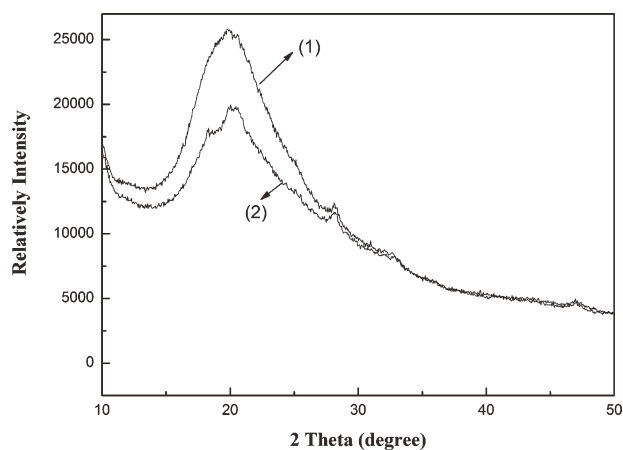| Samples	Glass transition temperature T_g (°C)		Melting enthalpy ΔH_m (J g^{-1})		Melting point T_m (°C)	
	Test data	Average	Test data	Average	Test data	Average
Eletrospun TPU	−31.9		9.5		146.7	
	−34.2	−32.4	12.3	10.7	148.6	146.7
	−31.1		10.3		144.8	
TPU/PVdF(80/20, w/w)	−35.7		19.9		151.8	
	−35.9	−36.1	21.1	20.7	148.9	150.2
	−36.7		21.1		149.9	
PVdF power	−38.7		51.9		163.0	
	−39.9	−39.5	53.0	52.2	164.6	163.9
	−39.9		51.7		164.1	
Noneletrospun TPU	−41.8		10.2		125.9	
	−43.0	−42.6	8.4	9.1	126.0	126.3
	−43.0		8.7		127	

Figure 6 XRD patterns of the electrospun membranes (1) pure TPU film (2) TPU/PVdF film.

TPU, nonelectrospun TPU and PVdF power shows a average glass transition temperature at −32.4, −42.6, and −39.5°C, respectively. while the TPU/PVdF membrane shows a average glass transition temperature at −36.1°C . The addition of PVdF into the TPU matrix shifts the T_g to higher temperature. These changes in T_g inform that there might be interactions between the groups present in TPU and PVdF. Several researchers reported on the phase-mixed state of PU as a result of interactions between hard (C=O and —NH groups) and soft (C (O) —O—C) segments through hydrogen bonding.[12,19]

XRD studies

XRD patterns of TPU film and TPU/PVdF film are shown in Figure 6. It can be seen that the plots of two samples were almost the same: there existed two obvious diffraction peaks at 2θ = 20° and 26°. From the diffraction patterns, peaks were observed at 2θ = 18.2°, 20°, 26° for TPU/PVdF film. The peaks at 2θ = 18.2°, 20° corresponded to (020) and (110) crystalline peaks of PVdF α crystalline phase, respectively.[20,21] By comparing the XRD characteristics with those of PVdF, the same diffraction peaks indicated the crystalline in the TPU/PVdF film was generated from vinylidene fluoride (VdF) segments and appeared α phase crystalline. Moreover, compare with the TPU film, the relative intensity of the peaks of the TPU/PVdF film decreased. The polymers apparently undergo structural reorganization when TPU blended with PVdF. We can presume that the blending of TPU and PVdF decreased the crystallinity of the film while did not change the crystalline phase.

Electrolyte uptake and ionic conductivity

Figure 7 shows the uptake behavior of the electrospun TPU/PVdF fibrous film and TPU membrane.

The percentage of electrolyte uptake can be calculated according to eq. (a). The TPU fibrous film shows an electrolyte uptake of about 196% within 2 min, while that of the TPU/PVdF membrane is 240%. It was found that when the electrolyte uptake of these two curves became stabile, TPU/PVdF membrane was always higher than TPU membrane. The fully interconnected pore structure makes fast penetration of the liquid into the membrane possible, and hence the uptake process is stabilized within the initial 15 min. The decrease in the AFD from 1.0 μm to 0.4 μm also leads to the increase in the absorption ratio of the electrolyte solution from 196 to 240%. Because the porosity of the film will increase when the average fiber diameters decrease. The increasing of surface area of the pore wall causes the elevation of the electrolyte uptake. This leads TPU/PVdF composites film to have a higher ionic conductivity than pure TPU fibrous membrane.

Figures 8 and 9 show the impedance spectra based on the TPU and TPU/PVdF-based fibrous polymer electrolyte, respectively. Ions are the current carriers. This may be the reason for the high frequency semicircular disappearing in the impedance spectra. And this leads to a further conclusion that the total conductivity is mainly the result of ion conduction.[22] It can be observed clearly in Figure 8 that the bulk resistance (Rb) of the pure TPU fibrous polymer electrolyte is 27.7 ohm. However, in Figure 9 the bulk resistance (Rb) of the TPU/PVdF fibrous polymer electrolyte is only 2.2 ohm.

The AFD decrease of film causes the increasing of membranes electrolyte uptake. TPU/PVdF membranes' electrolyte uptake increasing leads to its lower bulk resistance (Rb). The ionic conductivity could be calculated using eq. (b). The ionic conductivity of pure TPU fibrous polymer electrolyte is 1.87
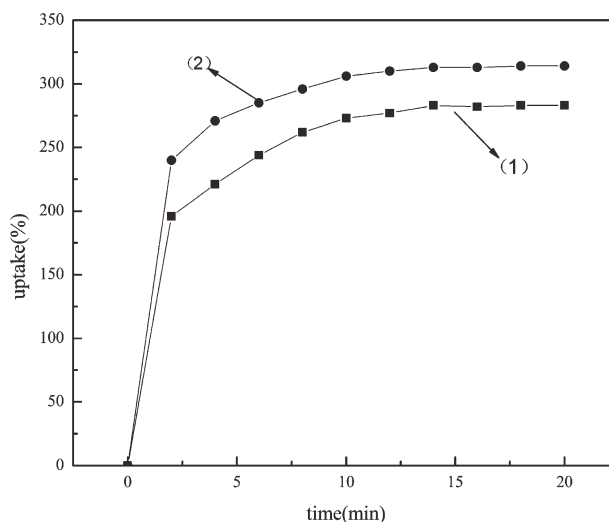

Figure 7 The uptake behavior of the electrospun membranes (1) pure TPU film (2) TPU/PVdF film.
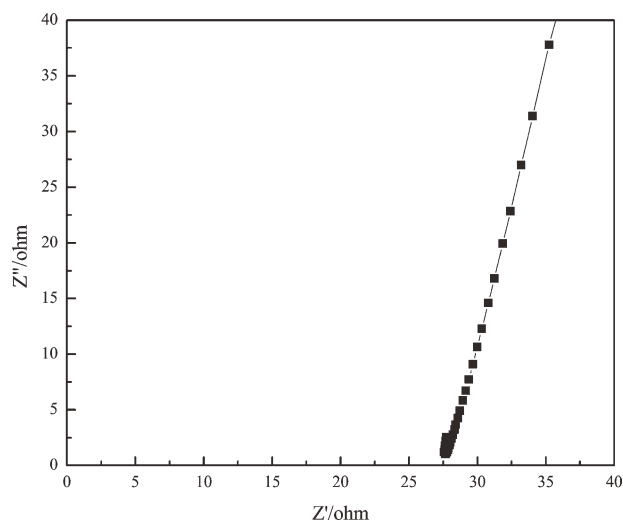
Figure 8 Impedance spectra of TPU film at 25°C.

Figure 10 The variation of ionic conductivity with temperature of electrospun TPU/PVdF-based fibrous membranes.

$\times 10^{-4}$ S cm^{-1}. And the TPU/PVdF fibrous polymer electrolyte film has an ionic conductivity of 1.6×10^{-3} S cm^{-1}. It is higher than the value $\sim 0.32 \times 10^{-4}$ S cm^{-1} reported by Santhosh et al.[12] for PU/PVdF incorporating LiClO$_4$ polymer electrolyte system, the value $\sim 1.8 \times 10^{-4}$ S cm^{-1} reported by Shen et al.[23] for PVdF/LiClO$_4$ (5 wt%) wetted by EC/PC of 0.1M LiClO$_4$ polymer electrolyte system and the value $\sim 1 \times 10^{-4}$ S cm^{-1} reported by Kuo et al.[10] for TPU-PAN incorporating LiClO$_4$/propylene carbonate (PC) gel polymer electrolyte system.

The dependence of ionic conductivity of PEs on temperature is shown in Figure 10 (The temperature ranges from 25 to 75°C). The log$\sigma \sim 1/T$ curve of the TPU/PVdF-based fibrous polymer electrolyte suggests that its conductive behavior generally obeys to Arrhenius equation $\sigma = \sigma_0 \exp(-E_a/RT)$, where R is the gas constant, σ is the conductivity of polymer
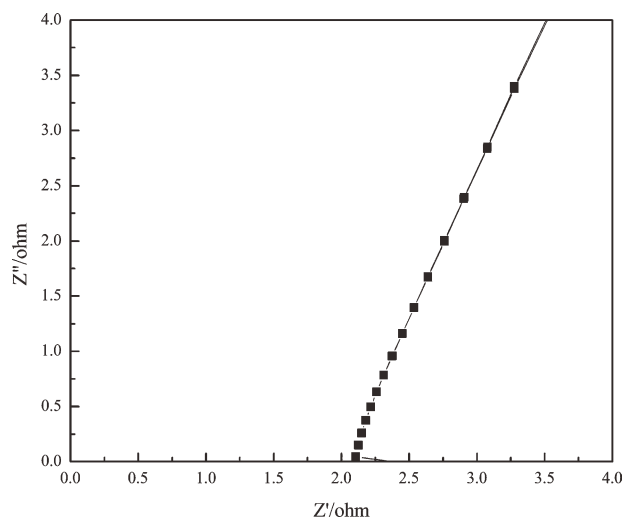

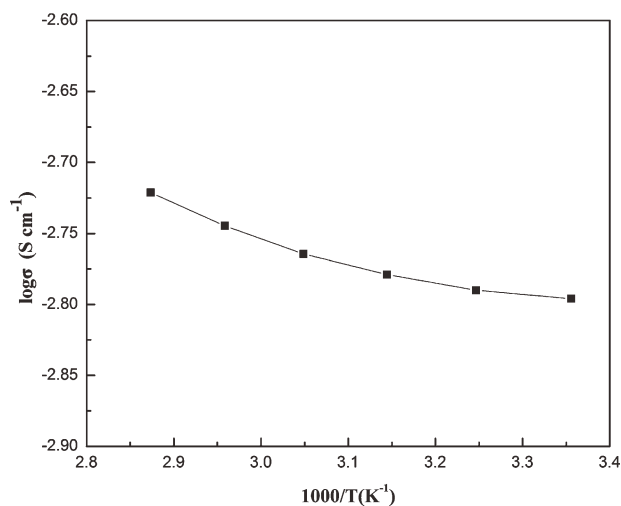**Figure 9** Impedance spectra of TPU/PVdF membrane at 25°C.

electrolyte, σ_0 is the pre-exponential index and T is the testing absolute temperature.

At low temperature, the presence of lithium salt leads to salt-polymer or cations–dipole interactions.[10,11] This increases the cohesive energy of polymer networks. So the free volume was decreased and polymer segmental motion and ionic mobility were hindered, then the ionic conductivity decreased. At higher temperature, the dissociation of salts would be improved, which increased ionic conductivity. With the temperature increasing, the chain segmental thermal movements of polymer electrolyte also enhances. This leads thermo-kinetic energy of ions to increase. All of these changes are beneficial for ionic movement. So the ionic conductivity gets higher with the temperature increasing.

Electrochemical stability

The linear sweep voltammetry plot of gel polymer electrolyte films is shown in Figure 11. There have been some reports on PU/PVdF-based electrolytes having high electrochemical stability for battery applications.[12,24,25] In our study, the electrochemical stability is at 4.6 V for TPU and 5.0 V for TPU/PVdF, respectively. The electrochemical stability of TPU/PVdF-based gel electrolytes is higher than that of PU/PVdF-based electrolytes which have been reported.[12,24,25] The results suggest that the TPU/PVdF composite polymer electrolyte is very suitable for applications in lithium-ion battery.

Evaluation in Li/LiFePO$_4$ cell

In the following study, the suitability of TPU/PVdF-based GPE for a Li/LiFePO$_4$ cell has been studied under varying 0.1C-rate at room temperature.
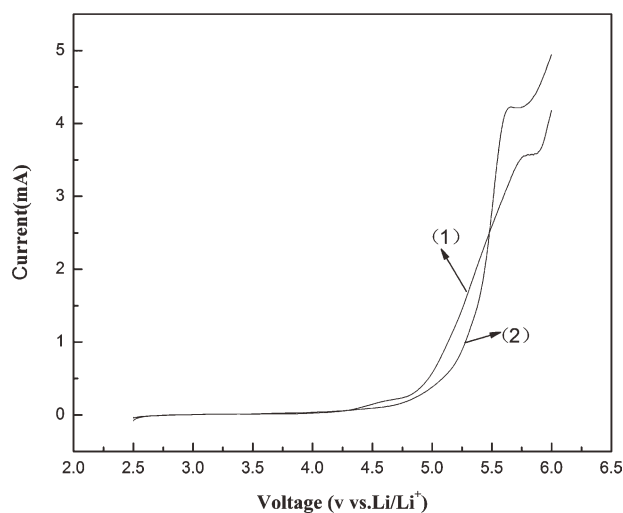
Figure 11 Linear sweep voltammograms of (1) TPU and (2) TPU/PVdF.

The first charge–discharge capacity curves of the cells show in Figure 12. Form the crave, we can find the GPE delivers a charge capacity of 155.7 mAh g^{-1} and discharge capacity of 156.5 mAh g^{-1} . This charge–discharge capacity is about 91–92% of the theoretical capacity of LiFePO$_4$. This is a remarkable enhancement of performance since the GPE is able to serve for lithium ion polymer batteries.

The Li cell with GPE incorporating EC/PC has been evaluated for cycleability property at the 0.1C rate at $25°C$ and the results are shown in Figure 13. After 30 cycles, the cell still shows a charge–discharge capacity of 154.5 mAh g^{-1}, which is about 98% of the first cycle. The cell exhibits a better reversibility after a few cycles. Maybe it results from a better stabilization of the system as a whole. This
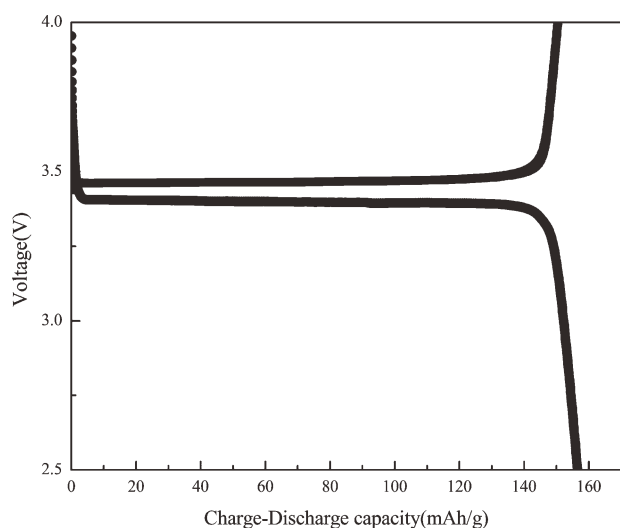

Figure 12 First charge-discharge capacities of GPE based on electrospun TPU/PVdF membrane activated with 1.0 M LiClO$_4$ in EC/PC (v/v = 1 : 1).
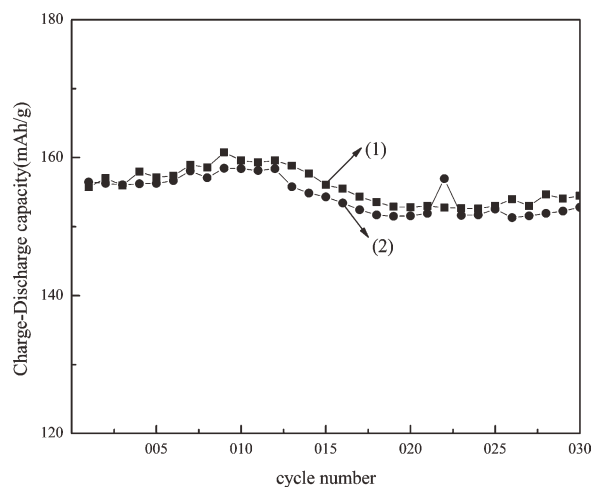

Figure 13 The Cycle performance (charge and discharge capacities) of GPE based on electrospun TPU/PVdF membrane activated with 1.0M LiClO$_4$ in EC/PC(v/v=1 : 1) (1) charge capacity (2) discharge capacity.

study shows that using electrospun TPU/PVdF-based GPE is very suitable for Li/LiFePO$_4$ cells at room temperature and low current densities (0.1C).

CONCLUSIONS

An electrospun TPU/PVdF membrane has been activated by 1.0M LiClO$_4$ in EC/PC (v/v = 1 : 1) to prepare novel composites GPE. Because of the special structure (two-phase microstructure-the soft segments and the hard segments) of electrospun TPU, TPU/PVdF-based gel polymer electrolyte has a high ionic conductivity of 1.6 mS cm^{-1} and better stabilization. The electrochemical stability is up to 5.0 V versus Li/Li$^+$. The first charge–discharge capacity of TPU/PVdF-based gel polymer electrolyte lithium battery is about 156.5 mAh g^{-1}, which is about 91–92% of the theoretical capacity of LiFePO$_4$. The cell exhibits a better reversibility after a few cycles. All these outstanding performances of the cell prove that TPU/PVdF gel polymer electrolyte is very suitable for lithium ion batteries.

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