



# A novel high-performance gel polymer electrolyte membrane basing on electrospinning technique for lithium rechargeable batteries

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## ABSTRACT

Nonwoven films of composites of thermoplastic polyurethane (TPU) with different proportion of poly(vinylidene fluoride) (PVdF) (80, 50 and 20%, w/w) are prepared by electrospinning 9 wt% polymer solution at room temperature. Then the gel polymer electrolytes (GPEs) are prepared by soaking the electrospun TPU–PVdF blending membranes in 1 M LiClO<sub>4</sub>/ethylene carbonate (EC)/propylene carbonate (PC) for 1 h. The gel polymer electrolyte (GPE) shows a maximum ionic conductivity of  $3.2 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature and electrochemical stability up to 5.0 V versus Li<sup>+</sup>/Li for the 50:50 blend ratio of TPU:PVdF system. At the first cycle, it shows a first charge–discharge capacity of 168.9 mAh g<sup>-1</sup> when the gel polymer electrolyte (GPE) is evaluated in a Li/PE/lithium iron phosphate (LiFePO<sub>4</sub>) cell at 0.1 C-rate at 25 °C. TPU–PVdF (50:50, w/w) based gel polymer electrolyte is observed much more suitable than the composite films with other ratios for high-performance lithium rechargeable batteries.

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## 1. Introduction

Over the past decades, gel polymer electrolytes (GPEs) have received extensive attention and been investigated widely in lithium-ion batteries [1–5]. GPEs are formed by adsorbing a certain amount of liquid electrolyte in a polymer framework. Several methods have been tried to get GPEs such as phase inversion method,  $\gamma$ -ray irradiation method, solvent casting technique, TIPS technique, and electrospinning technique. Among these methods, the polymer electrolytes prepared by electrospinning technique not only own good mechanical properties but also show high ionic conductivity [6–8]. Electrospinning is an alternative, simple and efficient process which is at least one or two order of magnitude smaller than the fibers produced from melt or solution spinning. When adopting electrospinning technique, many interconnected pores will be formed in the porous membrane, so enough liquid electrolytes were absorbed by the polymer membrane forming gelled polymer electrolytes.

Thermoplastic polyurethane (TPU) has two-phase microstructure: the soft segments and the hard segments [9,10]. The hard segments are interconnected throughout the soft phase parts, and play the role of keeping the GPEs' dimensional stability. While the soft segments dissolve alkali metal without formation of ionic cluster and offer the whole system with good ionic conductivity.

Many researchers also focus attention on the TPU copolymerized with other polymer hosts in the preparation of gel polymer electrolytes. There have been some reports on the use of thermoplastic polyurethane (TPU)/polyacrylonitrile (PAN) (TPU–PAN), thermoplastic polyurethane (TPU)/linear poly(ethylene oxide) (PEO) (TPU–PEO) and polyurethane/poly(vinylidene fluoride) (PU–PVDF) for rechargeable lithium batteries [11–13]. With high mechanical and anodically stability, poly(vinylidene fluoride), PVdF has been adopted as polymer electrolytes in lithium batteries [14,15,19]. The TPU-co-PVdF based GPEs not only have relatively high ionic conductivity, but also have good mechanical stability at room temperature. 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. Therefore, PVdF and TPU are miscible without any microphase separation as electrospun matrix for gel polymer electrolytes (GPEs).

In this paper, we prepare TPU–PVdF blending polymer electrolyte membranes by electrospinning using 9 wt% polymer solution with different weight ratio of TPU/PVdF. And then the nonwoven films are activated by immersing into 1 M LiClO<sub>4</sub>–EC/PC liquid electrolyte solution at room temperature in a glove box. We investigate the ionic conductivity and electrochemical properties, the cycle performances and the rate capabilities of these electrospun fibrous polymer electrolytes for lithium ion batteries. Primary results show that this kind of polymer electrolyte membrane has excellent enhancement in performance as GPE for lithium ion batteries.

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## 2. Experimental

### 2.1. Materials

Thermoplastic polyurethane (TPU, yantaiwanhua, 1190A) and poly(vinylidene fluoride) (PVdF, Alfa Aesar) were dried under vacuum at 80 °C for 24 h. LiClO<sub>4</sub>·3H<sub>2</sub>O (AR, Sinopharm Chemical Reagent Co. Ltd.) was dehydrated in vacuum oven at 120 °C for 72 h. 1.0 M liquid electrolyte was made by dissolving a certain quality of LiClO<sub>4</sub> in ethylene carbonate (EC, Shenzhen capchem technology Co. Ltd.)/propylene carbonate (PC, Shenzhen capchem Technology Co. Ltd.) (1/1, v/v). N,N-dimethylformamide (DMF) and acetone were analytical purity and used as received without further treatment.

### 2.2. Preparation of TPU–PVdF fibrous membrane

A certain amount of TPU and PVdF powder as a unit with different weight ratio (80:20; 50:50 and 20:80) were dissolved in N,N-dimethylacetamide (DMF)/acetone (3:1, w/w) forming a 9 wt% solution, separately. The solution was electrospun under high voltage of 24.5 kV at room temperature, respectively. Nonwoven films were obtained on the collector plate. The TPU–PVdF electrospun nonwoven films were dried under vacuum at 80 °C for 12 h.

### 2.3. Preparation of gel polymer electrolytes

The thickness of the TPU–PVdF nonwoven films used were ~100 μm. At room temperature, the dried TPU–PVdF nonwoven films were activated by dipping in 1 M LiClO<sub>4</sub>–EC/PC liquid electrolyte solutions for 1 h in a glove box filled with argon. Wipe the surface of swelled membranes by filter paper and then get gel polymer electrolytes.

### 2.4. Membrane characterization

The morphology of films was examined by Scanning electron microscope (SEM, Hitachi S-3500N, Japan). The thermal stability of the films was monitored using thermogravimetric analysis (model TGAQ 50, TA Company, USA). The TGA measurements were carried out under dry nitrogen atmosphere at a heating rate of 20 °C min<sup>-1</sup> from 30 to 900 °C.

The porosity was investigated by immersing the membranes into *n*-butanol for 1 h and then calculated by using the following relation:  $P = (W_w - W_d / \rho_b V_p) \times 100\%$ , where  $W_w$  and  $W_d$  are the mass of the wet and dry membrane, respectively,  $\rho_b$  the density of *n*-butanol, and  $V_p$  the volume of the dry membrane.

The electrolyte uptake was determined [16] by measuring the weight increase and calculated according to the following Eq. (A):  $Uptake (\%) = (W - W_0 / W_0) \times 100\%$ , where  $W_0$  is the weight of dried films and  $W$  is the weight of swelled films.

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

### 2.5. Cell assembly and performance characteristics

Electrochemical stability was measured by a linear sweep voltammetry (LSV) of a Li/PE/SS cell using Zahner Zennium elec-

trochemical analyzer at a scan rate of 5 mV s<sup>-1</sup>, with voltage from 2.5V–6V. For charge–discharge cycling tests, the Li/PE/LiFePO<sub>4</sub> cell was assembled. The LiFePO<sub>4</sub> cathode was prepared as its blend with acetylene black and PVdF binder at a ratio of 85:10:5 by weight. A certain amount of these three powers were mixed together in N-methylpyrrolidone (NMP) solvent to get homogeneous slurry which was cast on the shell of the cell and dried under vacuum at 80 °C for 24 h. 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 densities of 0.1 C.

## 3. Results and discussion

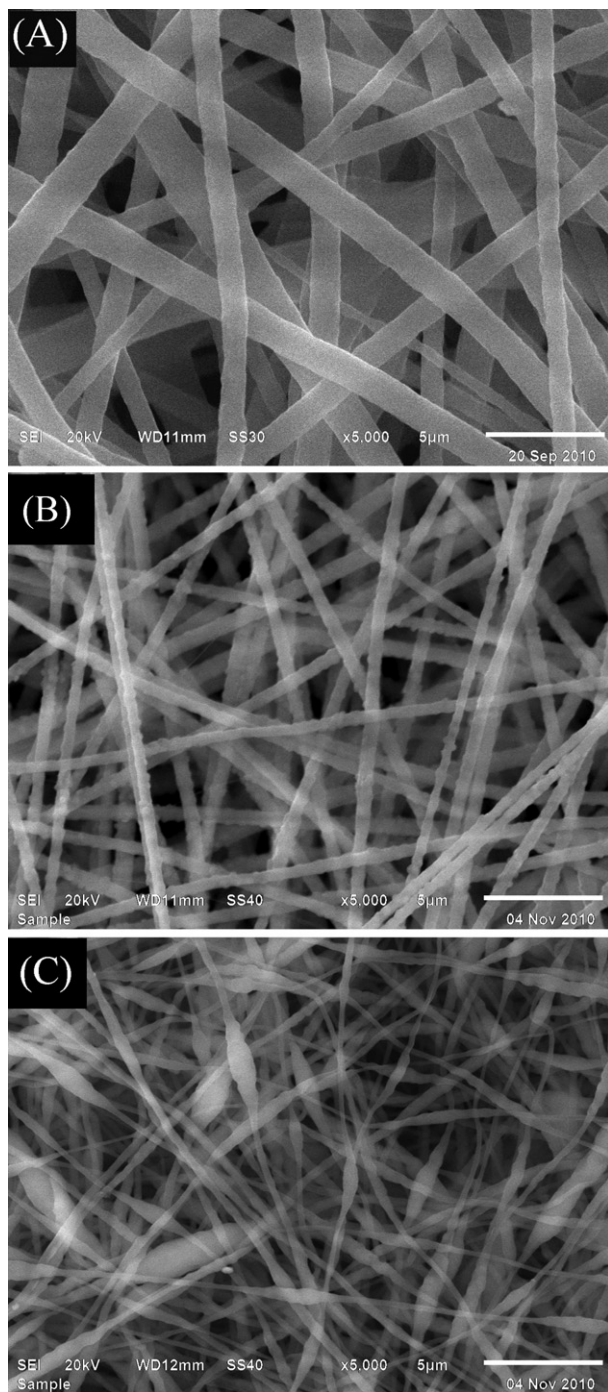
### 3.1. Morphology and structure

Fig. 1 shows the morphology of the prepared porous electrospun TPU/PVdF membranes with different weight ratio. It is clearly that the membranes are made up of a network of interlaid and nearly straightened tubular structure fibers. Electrospun TPU/PVdF fibrous membrane with 20 wt% of PVdF in the composite (Fig. 1A) has a structure with an average fiber diameter (AFD) of ~1.2 μm. As shown in Fig. 1B, TPU/PVdF (50:50, w/w) nonwoven film (Fig. 1B) has interconnected multifibrous layers with ultrafine porous structure. The AFDs of TPU/PVdF (50:50, w/w) nonwoven films are much more uniformly about ~0.57 μm, which is half size of the fiber diameters in TPU/PVdF (80:20, w/w) membrane. Although TPU/PVdF (20:80, w/w) membrane in Fig. 1C has a narrowest fiber diameter range, there are many beads in the fiber membrane.

All of the fibers mentioned above appear to be uniform in composition without having any microphase separation which due to the miscibility of TPU and PVdF. However the good miscibility of TPU and PVdF dues to the special chemical structure of TPU [17,18]. 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).

It is well known that the parameters of influencing the morphology of electrospun fiber membranes are the distance between the nozzle of the syringe and the collector, the applied voltage, the concentration of the polymer solution and dielectric constant of the solution. In this study, the first three factors in the above list were kept as a constant while electrospinning. So they cannot be the reasons for the morphological differences. Upon that we envisage the following reasons. The increased content of PVdF has been attributed to increasing dielectric constant of the medium for electrospinning. Electrospun jets are easily formed at the nozzle of the syringe for TPU–PVdF composite solution and cause formation of fibers with lower diameter. However the incorporation of PVdF increases, the viscosity and surface tension of the solution decreases. The droplets of the solution have got to the collector before the solvent evaporates completely. This is the reason for the formation of beads structure in Fig. 1C.

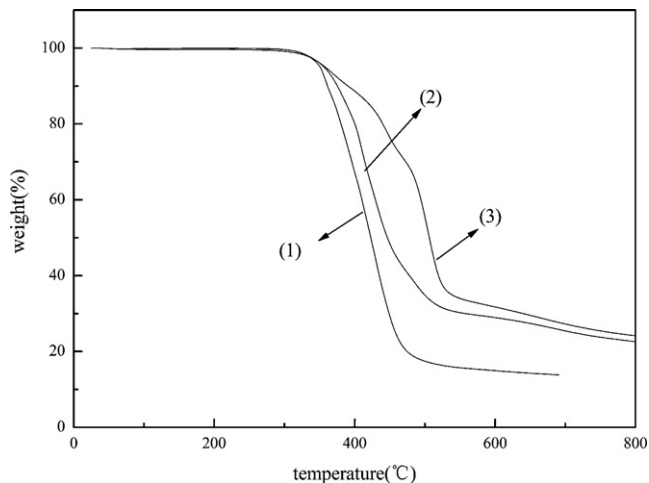
Kim et al. had reported decreasing in average fiber diameters can result in a decrease in leakage rate [19,20]. This particular structure may result in high electrolyte uptake. The presence of fully interconnected pores in the structure makes them suitable as a host matrix for the preparation of gel polymer electrolytes.



**Fig. 1.** SEM images of electrospun TPU-co-PVdF membranes (A) 80:20 ratio (w/w) blend of TPU/PVdF, (B) 50:50 ratio (w/w) blend of TPU/PVdF and (C) 20:80 ratio (w/w) blend of TPU/PVdF.

### 3.2. Thermal analysis

Thermograms of TPU–PVdF membranes with different mass ratio are shown in Fig. 2. The decomposition of the first two films [Fig. 2(1) and (2)] follow a similar pattern in thermograms. TPU–PVdF membrane with  $m_{\text{TPU}}/m_{\text{PVdF}}$  equal to 80:20 [Fig. 2(1)] has a weight loss starting at about 334 °C with 19% weight left at 506 °C. The TPU–PVdF [50:50, w/w, Fig. 2(2)] membrane starts losing weight at 329 °C with a drastic fall in weight thereafter. At 528 °C, TPU–PVdF [50:50, w/w, Fig. 2(2)] membrane has 31% residual mass. But TPU–PVdF [20:80, w/w, in Fig. 2(3)] has three-stage



**Fig. 2.** Thermograms of TPU–PVdF films (1) TPU/PVdF (80:20, w/w), (2) TPU/PVdF (50:50, w/w) and (3) TPU/PVdF (20:80, w/w).

weight losses starting at 326 °C with 84% weight left at 426 °C. The first-stage weight loss is the decomposition of the hard segments in TPU. The second-stage weight loss is the decomposition of the soft segments in TPU starting at 426 °C with 68% mass left at 480 °C. After 480 °C there is a sharply fall in weight which due to PVdF decomposing. Finally TPU–PVdF [20:80, w/w, Fig. 2(3)] has 33% residual mass at 558 °C. For the second stage, the picture shows that the decomposition temperature of TPU–PVdF [20:80, w/w, Fig. 2(3)] is the highest. And the decomposition temperature of our TPU–PVdF composites film is higher than the value ~300 °C reported by Kuo et al. [11] for TPU–PAN composite polymer electrolyte films system. This implies that TPU–PVdF composite polymer electrolyte film has a better thermal stability.

With the content of PVdF increasing, the film becomes more and more stable. This may due to the strong interaction between the two polymer matrixes (TPU and PVdF). The addition of PVdF causes the interaction between its fluorine groups with carbonyl (C=O) and amino-group (–NH) in TPU. Thus the interaction of the two polymer chains would be stronger and the PVdF chains would restrict the movement of the TPU chains during the glass transition. This enhances the compatibility of TPU and PVdF.

The final decomposition temperatures are higher than 500 °C for all of these three TPU–PVdF composites films prove that the TPU–PVdF film is suitable for considering as GPEs in lithium rechargeable batteries.

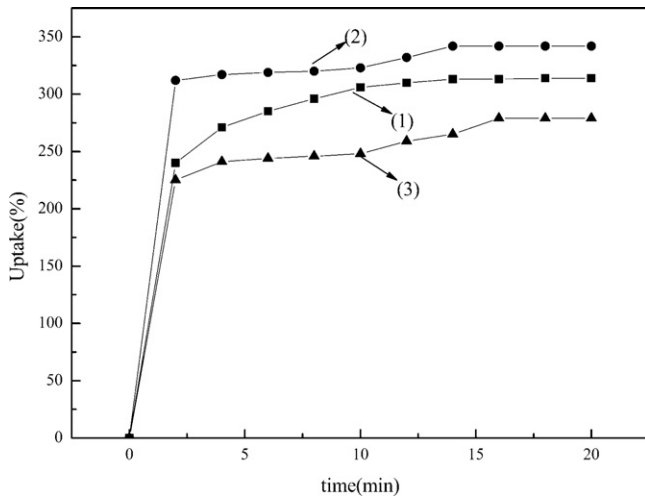
### 3.3. Porosity, electrolyte uptake and ionic conductivity

The results of porosity determination by *n*-butanol uptake method are presented in Table 1. As shown, the porosity of TPU/PVdF (80:20, w/w) membrane was about 82%. And the porosity of TPU/PVdF (20:80, w/w) membrane was 18%. Among all these TPU/PVdF blending electrospun membranes, TPU/PVdF (50:50, w/w) showed the highest porosity (86%).

Fig. 3 shows the uptake behavior of the electrospun TPU–PVdF fibrous membranes. The percentage of electrolyte uptake can be calculated according to Eq (A). The TPU/PVdF fibrous film with

**Table 1**  
Surface area data and porosity of TPU/PVdF membranes.

Samples	Surface area (cm <sup>2</sup> )	Porosity (%)
TPU/PVdF (80:20, w/w)	2.997	82
TPU/PVdF (50:50, w/w)	2.716	86
TPU/PVdF (20:80, w/w)	2.060	18

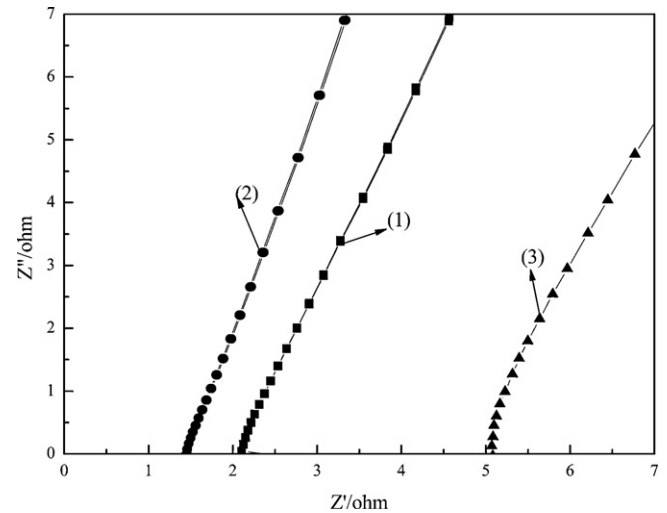


**Fig. 3.** The uptake behavior of the electrospun TPU–PVdF fibrous films (1) TPU/PVdF (80:20, w/w), (2) TPU/PVdF (50:50, w/w) and (3) TPU/PVdF (20:80, w/w).

$m_{\text{TPU}}/m_{\text{PVdF}} = 80:20$  [Fig. 3(1)] shows an electrolyte uptake of about 240% within 2 min, while the TPU/PVdF [50:50, w/w, Fig. 3(2)] membrane is 312% and TPU/PVdF [20:80, w/w, Fig. 3(3)] film is 225%. The uptake of the electrolyte solution reaches up to 314% [TPU/PVdF = 80:20, w/w, Fig. 3(1)], 342% [TPU/PVdF = 50:50, w/w, Fig. 3(2)] and 279% [TPU/PVdF = 20:80, w/w, Fig. 3(3)], respectively. After 15 min, it is found that when the electrolyte uptake of these three curves become stable, TPU/PVdF membrane with  $m_{\text{TPU}}/m_{\text{PVdF}} = 50:50$  [Fig. 3(2)] always owns the highest electrolyte uptake percentage.

The absorption of large quantities of liquid electrolyte by the composite membranes results from the high porosity of the membranes and the high amorphous content of the polymer. The fully interconnected pore structure makes fast penetration of the liquid into the membrane possible, and hence the uptake process is stable within the initial 15 min. TPU/PVdF [50:50, w/w] membrane owns the highest porosity, so it always has the highest electrolyte uptake percentage. Furthermore the decreasing of the average fiber diameters from  $1.2 \mu\text{m}$  [TPU/PVdF = 80:20, w/w] to  $0.57 \mu\text{m}$  [TPU/PVdF = 50:50, w/w] also leads to the increasing in the absorption ratio of the electrolyte solution from 279 to 342%. Because the porosity and the surface area of the pore wall of the film will increase when the average fiber diameters decrease. The increasing of surface area of the pore wall and more pores result in a higher uptake of the liquid electrolyte, which means more  $\text{Li}^+$  in the same volume. This leads TPU–PVdF polymer electrolyte to have a high ionic conductivity.

Fig. 4 shows the impedance spectra of TPU–PVdF based fibrous polymer electrolyte with different mass ratio of TPU/PVdF. It is a typical AC impedance for gel polymer electrolyte. From the morphology of the prepared porous electrospun TPU/PVdF membranes in Fig. 1, it is known that there are many interconnected pores in the porous membranes, so enough liquid electrolyte was absorbed by the polymer membrane to form gelled polymer electrolyte. The pores are also interconnected by the sub-micron windows, which offer channels for the migration of ions and are small enough to well retain the electrolyte solution in the membrane. Obviously, the higher electrolyte-solution uptake is, the more  $\text{Li}^+$  ions are in gelled polymer electrolyte. As we all know 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 [21]. It can be observed clearly from Fig. 4(1) that the bulk resistance ( $R_b$ ) of the TPU/PVdF [80:20, w/w] fibrous

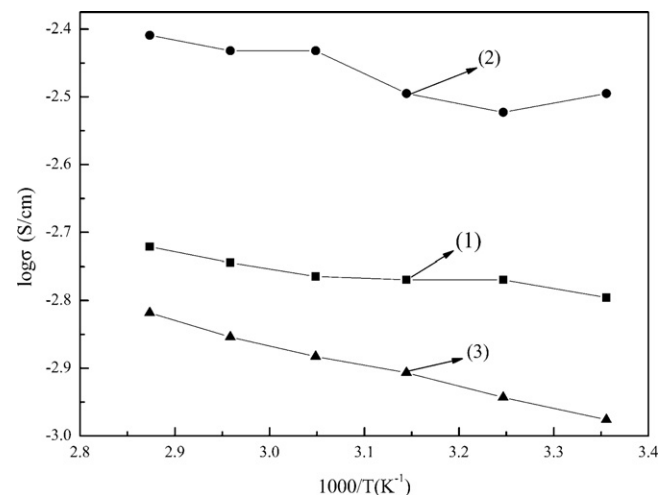


**Fig. 4.** Impedance spectra of TPU–PVdF films at 25 °C (1) TPU/PVdF (80:20, w/w), (2) TPU/PVdF (50:50, w/w) and (3) TPU/PVdF (20:80, w/w).

polymer electrolyte is  $2.1 \Omega$ . And in Fig. 4(3) the TPU/PVdF with  $m_{\text{TPU}}/m_{\text{PVdF}}$  equal to 20/80 has a bulk resistance of  $5.1 \Omega$ . However, in Fig. 4(2) the bulk resistance ( $R_b$ ) of the TPU/PVdF [50:50, w/w] fibrous polymer electrolyte is only  $1.4 \Omega$ .

The decrease in the average fiber diameters leads to the increase in the absorption ratio of the electrolyte solution. And a higher uptake of the liquid electrolyte, which means more  $\text{Li}^+$  in the same volume, leads to a lower bulk resistance ( $R_b$ ). The ionic conductivity could be calculated with Eq. (B). The ionic conductivity of TPU/PVdF [80:20, w/w] and [20:80, w/w] fibrous polymer electrolyte is  $1.7 \times 10^{-3} \text{ S cm}^{-1}$  and  $1.1 \times 10^{-3} \text{ S cm}^{-1}$ , respectively. However the TPU–PVdF [50:50, w/w] fibrous polymer electrolyte film has an ionic conductivity of  $3.2 \times 10^{-3} \text{ S cm}^{-1}$ . It is much higher than the value  $\sim 1.8 \times 10^{-4} \text{ S cm}^{-1}$  reported by Shen et al. [22] for PVdF/LiClO<sub>4</sub> (5 wt%) wetted by EC/PC of 0.1 M LiClO<sub>4</sub> polymer electrolyte system and the value  $\sim 1 \times 10^{-4} \text{ S cm}^{-1}$  reported by Kuo et al. [11] for TPU–PAN incorporating LiClO<sub>4</sub>/propylene carbonate (PC) gel polymer electrolyte system.

Fig. 5 shows the ionic conductivity of the TPU–PVdF fibrous gel polymer electrolyte against the reciprocal absolute temperature.



**Fig. 5.** The variation of ionic conductivity with temperature of electrospun TPU–PVdF based fibrous membranes (1) TPU/PVdF (80:20, w/w), (2) TPU/PVdF (50:50, w/w) and (3) TPU/PVdF (20:80, w/w).

The  $\log \delta \sim 1/T$  curve suggests that its conductive behavior obeys to Arrhenius equation  $\delta = \delta_0 \exp(-E_a/RT)$ , where  $R$  is the gas constant,  $\delta$  is the conductivity of polymer electrolyte,  $\delta_0$  is the pre-exponential index and  $T$  is the testing absolute temperature.

This phenomenon indicates that the charge carriers are decoupled from the segmental motion of the polymer chain and transport occurs via coupling mechanism. At low temperature, the presence of lithium salt leads to salt–polymer or cations–dipole interactions. 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 temperatures, the dissociation of salts would be improved, which increased ionic conductivity. With the temperature increasing, the chain segmental thermal movements of polymer electrolyte also enhance. 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.

From the picture it is known clearly that the ionic conductivity of electrospun TPU/PVdF [50:50, w/w, Fig. 5(2)] based fibrous membrane is always higher than the other two electrospun TPU–PVdF with  $m_{\text{TPU}}/m_{\text{PVdF}}$  equal to 80:20 and 20:80 based fibrous films. One of the reason is the average fiber diameters decreasing resulted in a increase in electrolyte uptake rate, so electrospun TPU/PVdF [50:50, w/w, Fig. 5(2)] fibrous membrane displays the highest ionic conductivity at room temperature,  $3.2 \times 10^{-3} \text{ S cm}^{-1}$ . But with the content of PVdF increasing, the crystalline domains in PVdF hinder migration of lithium ions and lower the ionic conductivity. It is well known that the migration of ions can be prevented by the increase of the crystallinity of the polymer matrix. So the ionic conductivity of electrospun TPU/PVdF [20:80, w/w, Fig. 5(3)] fibrous membrane is the lowest.

### 3.4. Electrochemical stability

The electrochemical stability window of the electrolytes is analyzed using the linear sweep voltammetry (LSV) and the linear sweep voltammetry plot of gel polymer electrolyte films is shown in Fig. 6. Some studies have reported that PU–PVdF based electrolyte has high electrochemical stability for battery applications [13]. In our research, the electrochemical stability is at 4.8 V for TPU/PVdF [80:20, w/w, Fig. 6(1)]. There is no electrochemical reaction in the potential range from 3.0 V to 4.8 V. The onset of current flow at 4.8 V is related with the decomposition of the electrolyte.

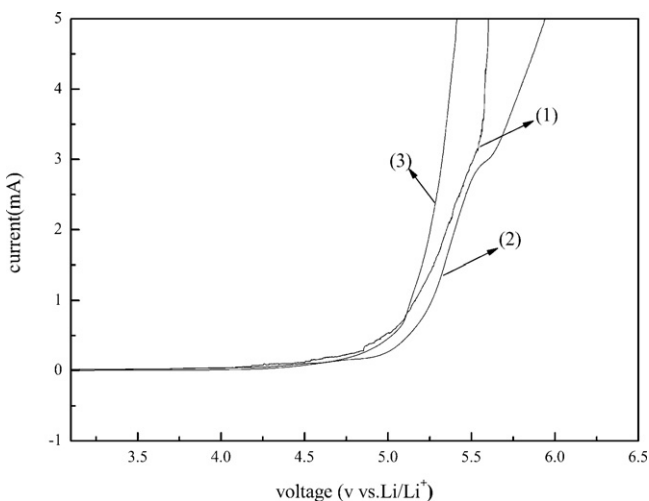


Fig. 6. Linear sweep voltammograms of (1) TPU/PVdF (80:20, w/w), (2) TPU/PVdF (50:50, w/w) and (3) TPU/PVdF (20:80, w/w).

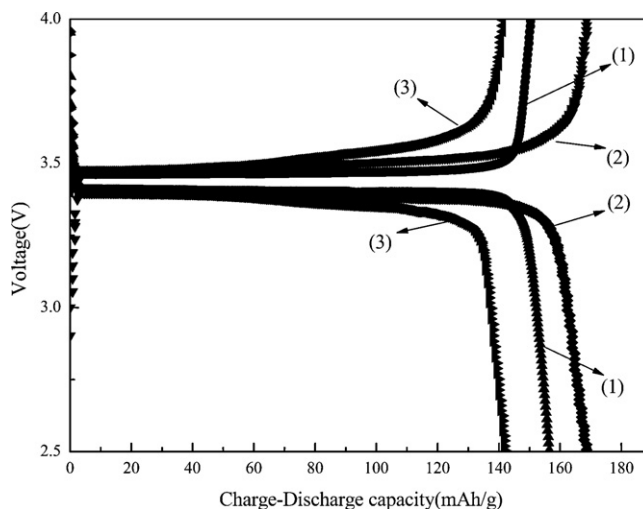


Fig. 7. First charge–discharge capacities of GPEs based on electrospun TPU–PVdF membrane activated with 1.0 M  $\text{LiClO}_4$  in EC/PC ( $v/v = 1:1$ ) (1) TPU/PVdF (80:20, w/w), (2) TPU/PVdF (50:50, w/w) and (3) TPU/PVdF (20:80, w/w).

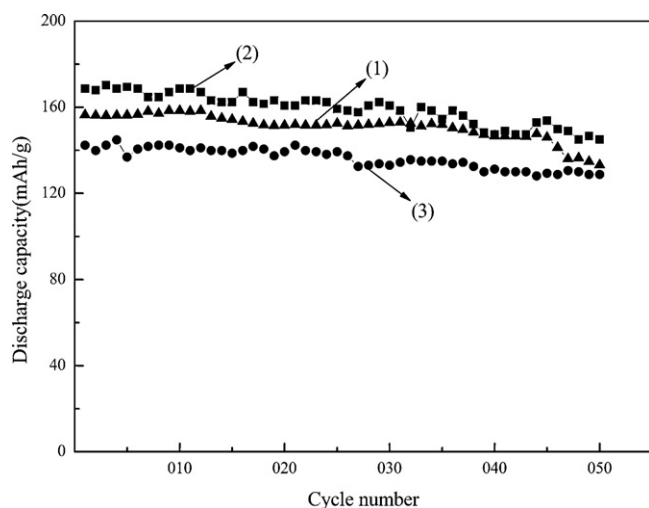
The decomposition current above 4.8 V was found to decrease with the increasing PVdF content from  $m_{\text{TPU}}/m_{\text{PVdF}} = 80:20$  to 50:50. But it increases again when PVdF content increases up to the proportion of 80%. So the electrochemical stability for TPU/PVdF [50:50, w/w, Fig. 6(2)] is at 5.0 V and 4.8 V for TPU/PVdF [20:80, w/w, Fig. 6(3)]. From these results, the TPU–PVdF composite polymer electrolyte is thought to be acceptable for applications in lithium-ion battery.

### 3.5. Evaluation in Li/LiFePO<sub>4</sub> cell

In the following study, the cells consisting of lithium as anode,  $\text{LiFePO}_4$  as cathode and electrospun TPU/PVdF nonwoven membrane as the electrolyte were constructed and the performance was evaluated under 0.1 C-rate at room temperature.

Fig. 7 shows the first charge–discharge capacity curves of the cells with GPEs containing different mass ratio of TPU/PVdF. The charge–discharge curves are similar to what is observed in lithium ion batteries in general, which ensures a good contact between the electrodes and TPU–PVdF based GPEs. The GPEs with  $m_{\text{TPU}}/m_{\text{PVdF}}$  equal to 80:20 [Fig. 7(1)] delivers a charge capacity of  $150.8 \text{ mAh g}^{-1}$  and discharge capacity of  $155.9 \text{ mAh g}^{-1}$ . TPU/PVdF [50:50, w/w, Fig. 7(2)] gel polymer electrolyte delivers a charge capacity of  $168.9 \text{ mAh g}^{-1}$  and discharge capacity of  $168.9 \text{ mAh g}^{-1}$ , which is about 99% of the theoretical capacity of  $\text{LiFePO}_4$ . The TPU/PVdF [20:80, w/w, Fig. 7(3)] composite polymer electrolyte shows a charge capacity of  $141.5 \text{ mAh g}^{-1}$  and discharge capacity of  $142.6 \text{ mAh g}^{-1}$ , only 83% of the theoretical capacity. This could be the result of reduced the compatibility of TPU and PVdF in polymer matrix. As to detailed reasons, further study is under way. From the results, we can find the TPU/PVdF [50:50, w/w, Fig. 7(2)] based GPEs delivers a charge–discharge capacity of  $168.9 \text{ mAh g}^{-1}$ . This is a remarkable enhancement of performance since the GPEs are able to serve for lithium ion polymer batteries.

The Li cell with GPEs incorporating EC/PC has been evaluated for cycleability property under the 0.1 C rate at 25 °C and the results are shown in Fig. 8. Compared to the cells with GPEs containing TPU/PVdF [80:20, w/w] in Fig. 8(1) and TPU/PVdF [20:80, w/w] in Fig. 8(2), the cell with TPU/PVdF [50:50, w/w] based GPEs in Fig. 8(3) has a highest discharge capacities in the whole 50 cycles and exhibits the significantly improved cycle performance. In the first 40 cycles, there is little difference between the cells with



**Fig. 8.** The cycle performance (discharge capacities) of GPE based on electrospun TPU–PVdF membranes activated with 1.0 M LiClO<sub>4</sub> in EC/PC (v/v = 1:1) (1) TPU/PVdF [80:20, w/w], (2) TPU/PVdF [50:50, w/w] and (3) TPU/PVdF [20:80, w/w].

GPEs containing different TPU/PVdF mass ratio. However, after 40 cycles, the capacity fading of the cell with TPU/PVdF [50:50, w/w, Fig. 8(2)] based GPEs is heavily retarded, while the capacities of the other cell with TPU/PVdF [80:20, w/w, Fig. 8(1)] based GPEs continue to drop with increasing cycle number. The capacity retention after 50 cycles is found to be 86% for the TPU/PVdF [50:50, w/w, Fig. 8(2)] based GPEs, 84% and 87% for the TPU/PVdF [80:20, w/w, Fig. 8(1)] and TPU/PVdF [20:80, w/w, Fig. 8(3)] based GPEs, respectively. There is no evident capacity fading of the cell with TPU/PVdF [50:50, w/w, Fig. 8(2)] based GPEs after a few cycles. This suggests that the cell exhibits a better reversibility. Maybe it results from a better stabilization of the system as a whole. This study shows that electrospun TPU–PVdF [50:50, w/w] based GPEs is very suitable for Li/LiFePO<sub>4</sub> cells under low current densities (0.1 C) at room temperature.

#### 4. Conclusions

GPEs based on fibrous TPU/PVdF blend/composite membranes were prepared by electrospinning the 9 wt% polymer solution in DMF/acetone (3:1, w/w) at room temperature. The optimum blend composition has been observed for the electrolyte with 50:50

weight ratio of TPU:PVdF. TPU/PVdF [50:50, w/w] based gel polymer electrolyte has a high ionic conductivity of  $3.2 \times 10^{-3} \text{ S cm}^{-1}$  and better interfacial property. The electrochemical stability is up to 5.0 V versus Li/Li<sup>+</sup>. The first charge–discharge capacity of TPU/PVdF [50:50, w/w] based gel polymer electrolyte lithium battery is about  $168.9 \text{ mAh g}^{-1}$ , which is about 99% of the theoretical capacity of LiFePO<sub>4</sub>. This is a remarkable enhancement in performance since the GPEs are able to serve for lithium ion polymer batteries. The cell exhibits good compatibility with lithium electrodes. After 50 cycles the cell shows a very stable charge–discharge behavior and little capacity loss under current constant voltage conditions, at the 0.1 C-rate of 25 °C. The above results indicate that the cell with TPU/PVdF [50:50, w/w] based gel polymer electrolyte displays a superior potential and is very suitable for rechargeable lithium batteries.

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