

A high-performance electrospun thermoplastic polyurethane/poly(vinylidene fluoride-co-hexafluoropropylene) gel polymer electrolyte for Li-ion batteries

Xiuxiang Peng¹ · Ling Zhou¹ · Bo Jing¹ · Qi Cao¹ · Xianyou Wang¹ · Xiaoli Tang¹ · Juan Zeng¹

Received: 9 June 2015 / Revised: 13 August 2015 / Accepted: 28 August 2015 / Published online: 10 September 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract Gel polymer electrolyte films based on thermoplastic polyurethane (TPU) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) (1/1, w/w) were prepared by electrospinning polymer. The highest ionic conductivity was $6.62 \times 10^{-3} \text{ S cm}^{-1}$ for 10 wt% electrolyte solution at room temperature. And, high value of tensile strength ($9.8 \pm 0.2 \text{ MPa}$) and elongation at break ($121.5 \pm 0.2 \%$) existed. The Li/PE/LiFePO₄ cell with the gel polymer electrolyte (GPE) delivered a high initial discharge capacity of $163.49 \text{ mAh g}^{-1}$ under 0.1 C rate and exhibited microscale attenuation (5.5 %) after 50 cycles. With the excellent characteristics, it is suitable for practical application in polymer lithium-ion batteries.

Keywords Thermoplastic polyurethane · Poly(vinylidene fluoride-co-hexafluoropropylene) · Gel polymer electrolyte · Electrospinning

Abbreviations

X_c	The crystallinity
ΔH	The fusion enthalpy of the membrane
ΔH_m	The fusion enthalpy of PVDF with 100 % crystallinity
Φ	The PVDF weight fraction in blend membrane
M_{wet}	The mass of the dry membrane

M_{dry}	The mass of the wet membrane
δ	The ionic conductivity
h	The thickness of polymer electrolyte
R_b	The bulk resistance of polymer electrolyte
S	The area of polymer electrolyte

Introduction

Many investigations have been devoted to gel polymer electrolytes (GPEs) in the rechargeable polymer lithium-ion battery, due to their high ionic conductivity, wide electrochemical window, and dramatic improvement of safety property [1–5]. There are many ways to get GPEs including electrospinning technique, phase inversion method, solvent casting technique, etc. In comparison to other membrane preparation techniques, electrospinning is simpler, rapider, and more inexpensive [6, 7]. It is clear that matrix is the most important factor affecting the performance of GPEs. Some polymer hosts have been developed and investigated such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polyvinyl chloride, polymethyl methacrylate, polyurethane, etc. Among these, PVDF-HFP has received much attention because of its high electrochemical stability and good affinity with liquid electrolyte [8, 9]. It comprises an amorphous and a crystalline phase [10–13]. The research of Saito et al. [14] implies that amorphous domain of microporous membrane influence the ionic conductivity and electrolyte reservation of corresponding polymer electrolyte. Therefore, PVDF-HFP has a high dielectric constant and electron withdrawing fluorine atoms in the backbone structure due to addition of an amorphous phase of HFP group into the main constituent VDF blocks.

However, the GPE membrane based on PVDF-HFP has poor mechanical strength. Blending is a simple and effective

✉ Bo Jing
jingboxtu@163.com
Qi Cao
wjcaoqi@163.com

¹ Key Laboratory of Environmentally Friendly Chemistry and Applications of Minister of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China

method to improve the properties of porous films. In recent years, some investigations on PVDF-HFP blend matrix for polymer electrolyte have been carried out. For example, Ding et al. [15] prepared PVDF-HFP/poly(methyl methacrylate) (PMMA) blend matrix and the ionic conductivity of corresponding polymer electrolyte exceeding $1.0 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. The value was more than the standard of practical application for lithium-ion batteries [16].

Thermoplastic polyurethane (TPU) is a linear segmented block copolymer composed of both hard segments and soft segments. The hard segments are interconnected by interchain hydrogen bonds to act as a mechanical support for the polymer matrix. While the soft segments dissolve alkali metal without formation of ionic cluster and help to capture large amount of liquid electrolytes.

We have done some research [17], which was the first trial of making TPU/PVDF-HFP fiber membranes. In comparison to pure TPU and pure PVDF-HFP films, the blend fibrous films show more noticeable electrochemical characteristic and mechanical performance. We would like to continue our efforts to develop TPU/PVDF-HFP porous fibrous films by electrospinning using different concentration polymer solutions. In order to investigate the influence of various polymer concentration stresses on the TPU/PVDF-HFP fiber membranes, membrane morphology, ionic conductivity, charge and discharge capacity, and mechanical properties will be examined systematically. In this study, we expect to provide a deep investigation and insight on the preparation of TPU/PVDF-HFP microporous fiber membranes with prominent electrochemical and mechanical performance.

Experimental

Materials

PVDF-HFP (Knyar Flex, LBG) and TPU (Yantai Wanhua, 1190A) were dehydrated in a vacuum drying oven at $80 \text{ }^\circ\text{C}$ for 24 h before using. $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (AR, Sinopharm Chemical Reagent Co., Ltd.) was dried in vacuum oven at $140 \text{ }^\circ\text{C}$ for 72 h. Liquid electrolyte (1.0 M) was made by dissolving a certain weights of LiClO_4 in ethylene carbonate (EC, Shenzhen Capchem Technology Co., Ltd)/propylene carbonate (PC, Shenzhen Capchem Technology Co., Ltd) (1/1, v/v). Acetone and *N,N*-dimethylformamide (DMF) were analytical purity and used without further purification.

Preparation of TPU/PVDF-HFP porous fibrous film

Appropriate amount of TPU and PVDF-HFP powder (1/1, wt/wt) were dissolved in the mixture of an acetone/*N,N*-dimethylacetamide (1/1, wt/wt). TPU/PVDF-HFP solutions of varying concentration from 6 to 14 wt% were then stirred

continuously. The solutions were electrospun under high voltage of 24.5 kV at room temperature. Porous fibrous film was obtained on the collector plate; then, it was removed under reduced pressure and dried at $80 \text{ }^\circ\text{C}$ for 12 h in a vacuum desiccator.

Preparation of gel polymer electrolyte

The dried porous fibrous film was soaked in 1 M LiClO_4 -EC/PC liquid electrolyte solution for 1 h in an Ar-filled glove box at room temperature. After activation, the membrane was removed from the electrolyte solution and excess electrolyte solution of swelled film was wiped with a filter paper.

Membrane characterization

The morphological examination of the films was made by scanning electron microscope (SEM, Hitachi S-3500N, Japan) after sputtering gold on one side of the films. The thermal characterization of membranes was measured by differential scanning calorimeter (DSC-7, Perkin-Elmer Co., USA) at a heating and cooling rate of $20 \text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere from 25 to $200 \text{ }^\circ\text{C}$. The crystallinity of the samples was calculated using the Eq. (1) from the DSC curves [18].

$$X_c(\%) = \frac{\Delta H}{\Delta H_m \varphi} \times 100 \quad (1)$$

where ΔH and ΔH_m represent the melting enthalpy of blend membrane and PVdF with 100 % crystallinity, respectively. The value of ΔH_m is 104.7 J/g [19]. φ is the measuring weight fraction of PVDF.

The electrolyte uptake was assessed by measuring the weight of the dried and wetted sample. Electrolyte uptake was calculated according to the following formula [20]:

$$\text{Uptake}(\%) = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100 \quad (2)$$

where M_{dry} and M_{wet} represent the weights of the dry and wet membrane, respectively.

The mechanical strength of the membrane was evaluated by universal testing machine (UTM, Instron Instruments) at a loading of $\sim 5 \text{ mm min}^{-1}$. The dimensions of the sheet used were $\sim 2 \text{ cm} \times 5 \text{ cm} \times \sim 150\text{--}250 \text{ } \mu\text{m}$ (width \times length \times thickness).

The ionic conductivity of the TPU/PVDF-HFP porous fibrous films were examined by the AC impedance method of the SS/PE/SS blocking cell, using Zahner Zennium electrochemical analyzer over a frequency range of 0.1–1 MHz. Thickness of $100 \text{ } \mu\text{m}$, an area of 1.96 cm^2 of the sample was prepared for impedance measurement. Thus, the ionic conductivity was calculated from the following Eq. (3):

$$\delta = \frac{h}{R_b S} \quad (3)$$

where δ is ionic conductivity, R_b is the bulk resistance, and h and S represent the thickness and area of film, respectively.

Cell assembly and performance characteristics

Charge–discharge cycling tests of Li/PE/LiFePO₄ cell were conducted using an automatic charge–discharge unit, Neware battery testing system (model BTS-51, ShenZhen, China), at a constant current density of 0.1 C and within the voltage range of 2.5–4.2 V at room temperature.

Results and discussion

Morphology and structure

Figure 1 shows SEM images of electrospun membranes prepared from 7 to 14 wt% polymer solutions. All of the films show network of interlaid and nearly straightened tubular structure fibers. It is important to note that the fibers have smooth surface, and there are no bead formation, which may be attributed to the hydrogen bonds' product between the strong electron-withdrawing functional group (-C-F) which is in the backbone structure of PVDF-HFP and amino group (-NH) which is in the hard segments of TPU. The average fiber diameters (AFDs) are 410, 400, 300, 250, 280, 350, 500, and 750 nm corresponding to Fig. 1 (7–14 %), respectively.

There are several factors contributing to the fiber morphology of electrospun film: the distance between the needle and the collection plate, properties of polymer and solvent, the voltage used for electrospinning, and the concentration of the polymer. In the present study, the first three factors in the above list were remained the same while electrospinning and hence cannot bring the morphological differences. Figure 1 (7 %) shows that the electrospun fiber film is very adhesive and uneven, which may be due to incomplete evaporation of the solvent and loose deposition of the fiber on the collector. With the increase of concentration, the situation will be better. However, as the concentration up to 11 %, the AFD increased with the increase of polymer solution concentration. It implied that the surface tension and viscosity of the solution increased with the polymer concentration increase; electrostatic stresses would not allow the droplets to elongate and be deposited uniform fibers. Kim et al. had reported that decreasing in AFDs can result in an increase in electrolyte uptake [21]. It is obviously seen that the fiber of 10 % is homogeneous and slender, so the film has prominent electrochemical properties and mechanical properties as followed.

DSC analysis

Figure 2 displays DSC curves, and the following observations were made. Firstly, all the blends with different TPU/PVDF-

HFP contents show almost similar melting temperatures, but the melting enthalpy of the electrospun TPU/PVDF-HFP (10 %) membrane is much lower than the others. Secondly, as shown in Table 1, the ΔH_f of electrospun TPU/PVDF-HFP (10 %) membrane is 15.11 J/g. According to the Eq. (1), the crystallinity of the membrane was 20.14 %. In the electrospinning process, a high electric power is applied (in the range of kilovolts) to overcome the surface tension of the polymer drops. The repulsion between molecules in the surface of the drops increases with increasing the concentration of the solution. The greater the force applied to the molecular chain, the more the molecular structure is destroyed. The regularity and symmetry of the molecular chains are destroyed, and the crystallinity is decreased. Therefore, the crystallinity decreased from 40.09 to 20.14 % as the polymer concentration increased from 6 to 10 %. However, as the concentration up to 11 %, surface tension and viscosity of the solution increases with the polymer concentration increase, it can prevent electrostatic stresses from elongating the droplets. The crystallinity increases with decrease of the external force on the molecular chain. Therefore, the crystallinity increased from 20.14 to 30.30 % as the polymer concentration increased from 10 to 14 %. What's more, growth of polymer crystallinity can decrease the free volume of amorphous region and hinder the migration of Li⁺ ions. Therefore, lower crystallinity of membrane can provide a favorable condition for higher conductivity enhancement. The results suggested that the electrospun TPU/PVDF-HFP (10 %) film may have the excellent ionic conductivity.

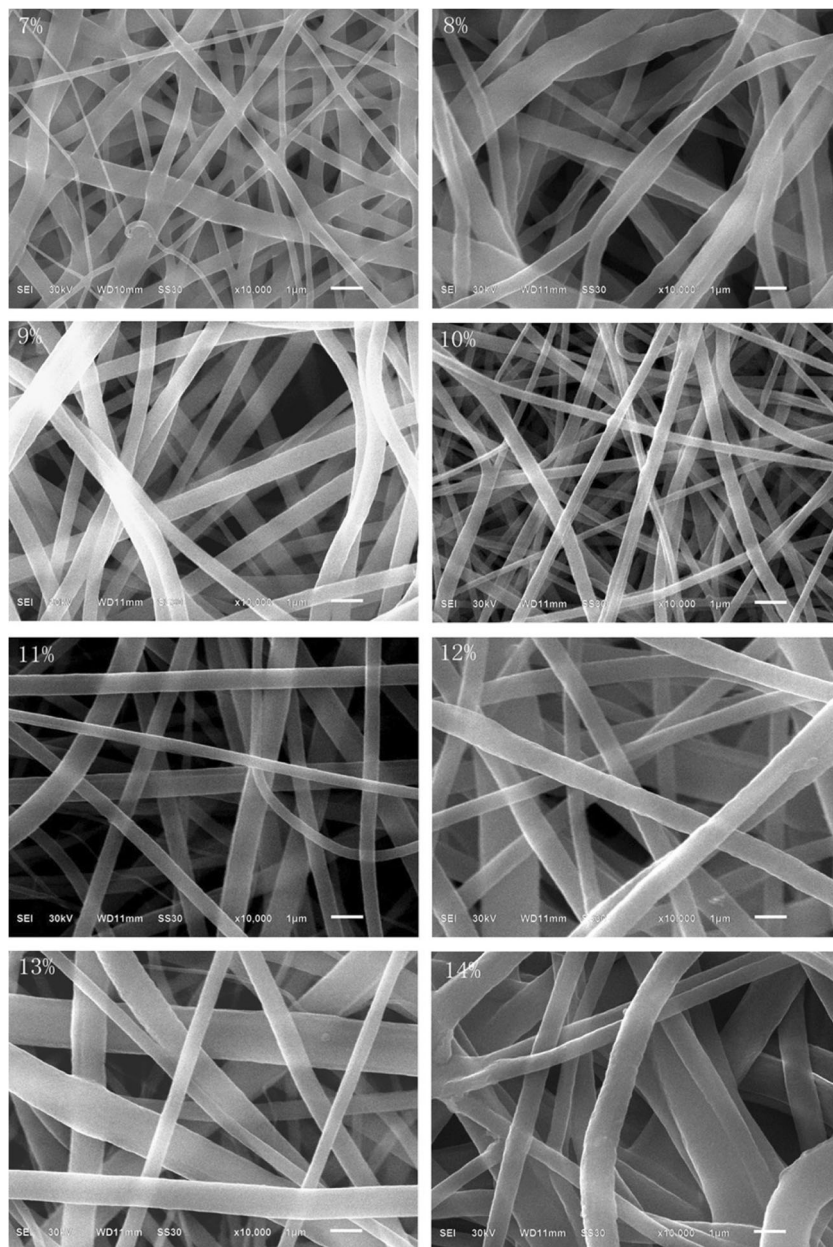
Mechanical properties

Figure 3 presents the stress–strain curves of polymer membranes. As our previous investigation [18], pure TPU is ductile elastomer, which can improve both elongation at break and tensile strength in TPU/PVDF-HFP blends. The mechanical test dates of the membranes are also summarized in Table 2. The results of mechanical strength test show that both the membrane (10 %) and membrane (13 %) possessed the highest stress of 9.8 MPa, but the latter corresponding value of elongation at break was smaller. These marked enhancements in the mechanical properties are due to finer morphology, good compatibility, and stronger interfacial adhesion between PVDF-HFP and TPU. Comprehensive comparison, the membrane (10 %) is more suitable for gel polymer electrolyte material of lithium-ion battery.

Electrolyte uptake

The variations of the uptake behavior of the TPU/PVDF-HFP membranes were presented in Fig. 4. The percentage of electrolyte uptake can be calculated according to Eq. (2). The fibrous film (10 %) shows an electrolyte uptake of about

Fig. 1 SEM images of electrospun membranes based on TPU/PVDF-HFP (1/1, w/w)



345 % within 2 min. After 14 min, it is found that the electrolyte uptake of these eight curves become stable and the sample with 10 % TPU/PVDF-HFP owns the highest electrolyte uptake percentage.

The absorption of large quantities of liquid electrolyte by the composite membranes mainly results from the high porosity of the membranes and the high amorphous content of the polymer. The AFD significantly affected the physical properties of the fibrous membranes such as their porosity, pore size and specific surface area, and so on. In the certain volume, the pores will increase when the AFD decreases. Saito et al. [14] studied the influence of electrolyte uptake by pore structure. They found that electrolyte uptake improved with an increase

in the number of pore. Compared with the other concentration solutions, the 10 % fibers display significantly thin AFDs; in addition, its size distributions are much narrower, so it always has the higher electrolyte uptake percentage.

Ionic conductivity

Figure 5 illustrates the impedance spectra of TPU/PVDF-HFP-based fibrous polymer electrolyte with different concentrations. It is a typical AC impedance for gel polymer electrolyte. According to the Eq. (3) $\delta = h/R_b S$, the conductivity of membranes was calculated and given in Table 3. It can be seen that ionic conductivity increased from $0.84 \times 10^{-3} \text{ S cm}^{-1}$ to

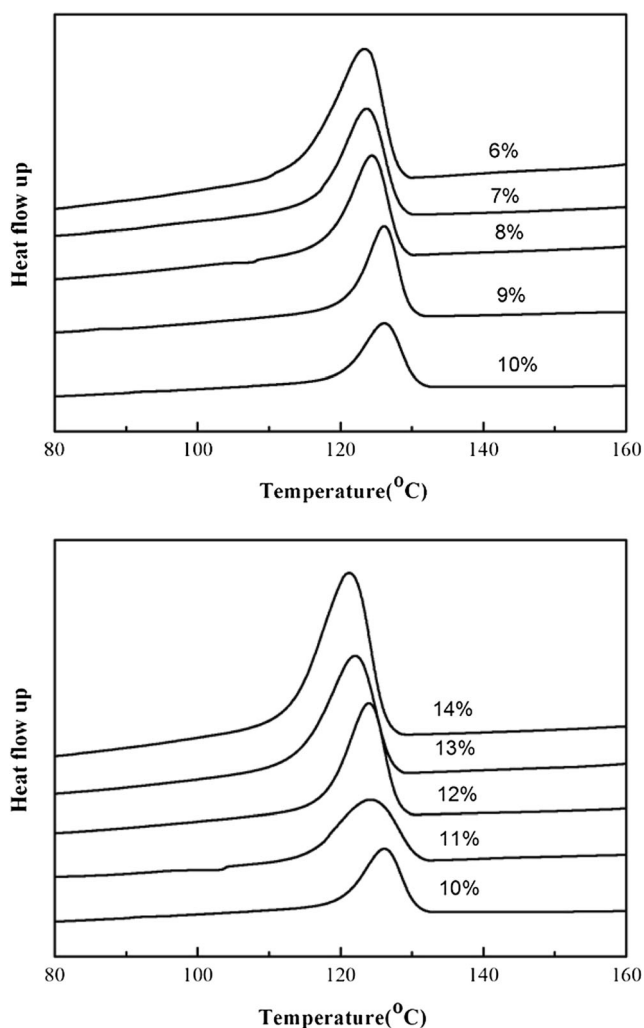


Fig. 2 DSC curves of TPU/PVDF-HFP films

the maximum $6.62 \times 10^{-3} \text{ S cm}^{-1}$ as polymer concentration increase from 6 to 10 %. However, the ionic conductivity decreased from $6.62 \times 10^{-3} \text{ S cm}^{-1}$ to $0.21 \times 10^{-3} \text{ S cm}^{-1}$ as the polymer concentration increase from 10 to 15 %. The TPU/PVDF-HFP (10 %) fibrous polymer electrolyte film has an ionic conductivity of $6.62 \times 10^{-3} \text{ S cm}^{-1}$. It is much

Table 1 Melting enthalpy and crystallinity of membranes

Samples	$\Delta H (\text{J g}^{-1})$	$X_c (\%)$
TPU/P(VDF-HFP) (6 %)	21.05	40.09
TPU/P(VDF-HFP) (7 %)	18.93	25.24
TPU/P(VDF-HFP) (8 %)	18.80	25.06
TPU/P(VDF-HFP) (9 %)	16.57	22.09
TPU/P(VDF-HFP) (10 %)	15.11	20.14
TPU/P(VDF-HFP) (11 %)	16.72	22.29
TPU/P(VDF-HFP) (12 %)	17.47	23.29
TPU/P(VDF-HFP) (13 %)	18.76	25.01
TPU/P(VDF-HFP) (14 %)	22.73	30.30

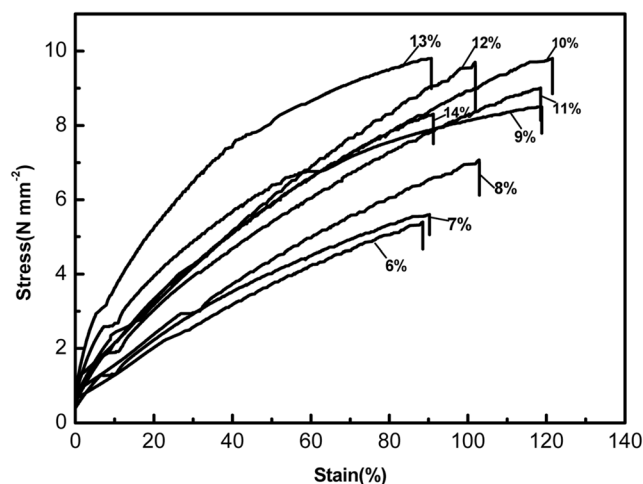


Fig. 3 Stress–strain curves of the electrospun TPU/PVDF-HFP membranes

higher than the value $1 \times 10^{-4} \text{ S cm}^{-1}$ reported by Kuo et al. [22] for TPU–PAN incorporating LiClO_4 /propylene carbonate (PC) gel polymer electrolyte system and the value $3.2 \times 10^{-3} \text{ S cm}^{-1}$ reported by Wu et al. [23] for TPU–PVDF/ LiClO_4 (9 wt%) soaked by EC/PC of 0.1 M LiClO_4 polymer electrolyte system.

The formation of stable LiF restricts the use of PVDF-HFP-based polymer electrolytes. However, the addition of TPU causes the hydrogen bond generation between the two polymer matrixes. Therefore, Li^+ ions in the blend membrane can freely migrate to improve the ionic conductivity. It was reported that the electrolyte solution introduced in the polymer was trapped in the pores and then penetrated into the polymer chains for swelling the polymer network [14]. The content of carrier ions and their mobility domain contributed to the ionic conductivity. The ionic conductivity increased with the decrease in AFD, which resulted from the higher electrolyte uptake. Therefore, the high ionic conductivity for 10 % sample is attributed to arise from the combined influence of higher content of electrolyte (>400 %) incorporated into the pores of the membrane and augmented lithium ion mobility in the gelled state. Moreover, low crystallinity can increase the mobility of lithium ion to result higher conductivity of electrolyte.

Evaluation in Li/LiFePO₄ cell

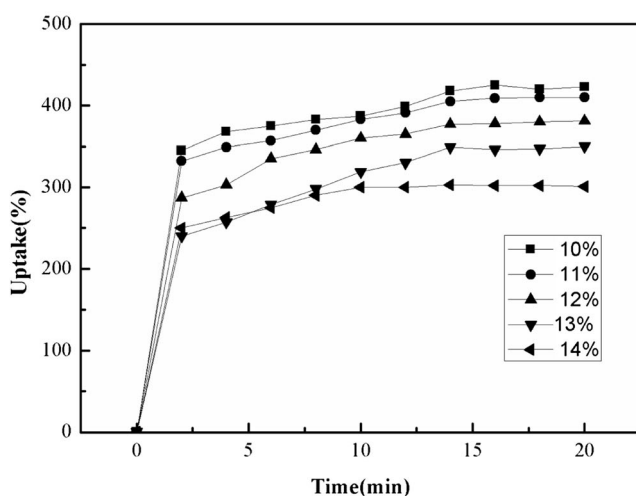
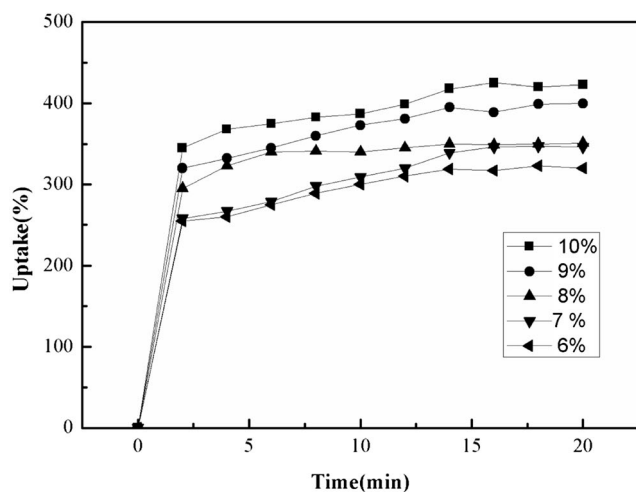
In the following study, the cell prototypes were assembled in sequence of the three components, i.e., the lithium anode, electrospun TPU/PVDF-HFP membrane as the electrolyte, and the LiFePO_4 as cathode. The performance was assessed under 0.1 C rate at room temperature.

Figure 6 shows the first charge–discharge curves of Li/GPE/LiFePO₄ cells. The membrane (10 %) delivers a

Table 2 Tensile strength and elongation at break of membranes

Samples	Tensile strength (MPa)	Elongation at break (%)
TPU/P(VDF-HFP) (6 %)	5.4±0.2	88.5±0.2
TPU/P(VDF-HFP) (7 %)	5.6±0.2	90.2±0.2
TPU/P(VDF-HFP) (8 %)	7.1±0.2	102.9±0.2
TPU/P(VDF-HFP) (9 %)	8.5±0.2	118.8±0.2
TPU/P(VDF-HFP) (10 %)	9.8±0.2	121.5±0.2
TPU/P(VDF-HFP) (11 %)	9.0±0.2	118.6±0.2
TPU/P(VDF-HFP) (12 %)	9.7±0.2	101.9±0.2
TPU/P(VDF-HFP) (13 %)	9.8±0.2	90.5±0.2
TPU/P(VDF-HFP) (14 %)	8.3±0.2	91.2±0.2

charge capacity of 167.23 mAh g⁻¹, which is about 98.37 % of the theoretical capacity of LiFePO₄. The charge and discharge capacity of the cells increased from

**Fig. 4** The uptake behavior of the electrospun fibrous films

152.65 and 151.73 to 167.23 and 163.49 mAh g⁻¹ as polymer solution concentration increased from 6 to 10 %, then decreased to 159.99 and 157.46 mAh g⁻¹ as the polymer solution concentration further increased to 14 %. The charge capacity was influenced by uniform morphology of membranes, AFDs, higher electrolyte uptake, and fully interconnected pores.

The Li cell with GPEs incorporating EC/PC has been evaluated for cycleability character under the 0.1 C rate at 25 °C, and the results are shown in Fig. 7. The membrane (10 %) has highest discharge capacities in the whole 50 cycles. The GPE with 10 % TPU/PVDF-HFP achieves a discharge capacity of 163.49 mAh g⁻¹; after 50 cycles, its residual capacity is 154.41 mAh g⁻¹. In other words, there is no evident capacity fading of the cell-based GPEs after 50 cycles. It suggests that all the cells exhibit a better reversibility. This study

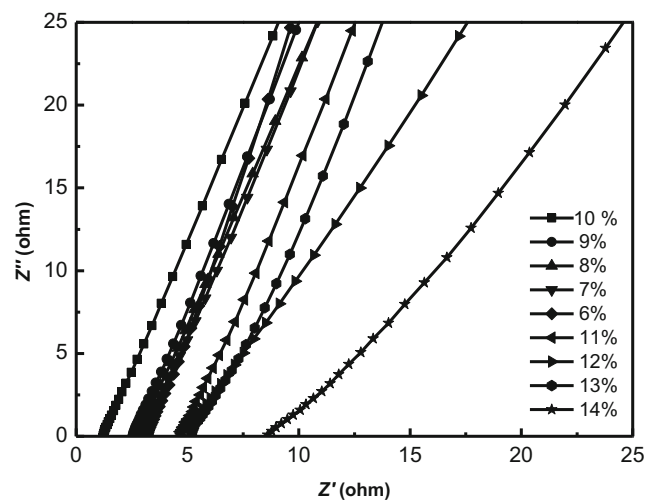
**Fig. 5** Impedance spectra of gel polymer electrolytes

Table 3 Bulk resistance, thickness, surface area, and ionic conductivity of polymer electrolytes

Materials	R_b (Ω)	h (cm)	S (cm^2)	δ ($10^{-3} \text{ S cm}^{-1}$)
6 %	3.17	0.012	2.00	1.89
7 %	2.92	0.014	1.96	2.44
8 %	2.78	0.014	2.02	2.49
9 %	2.52	0.014	2.04	2.72
10 %	1.19	0.016	2.03	6.62
11 %	4.72	0.014	1.97	1.51
12 %	5.01	0.014	1.98	1.41
13 %	5.19	0.014	2.10	1.28
14 %	8.61	0.014	2.00	0.81

displays that electrospun TPU/PVDF-HFP membrane (10 %) based GPE is more suitable for Li/LiFePO₄ cells under 0.1 C rate at 25 °C.

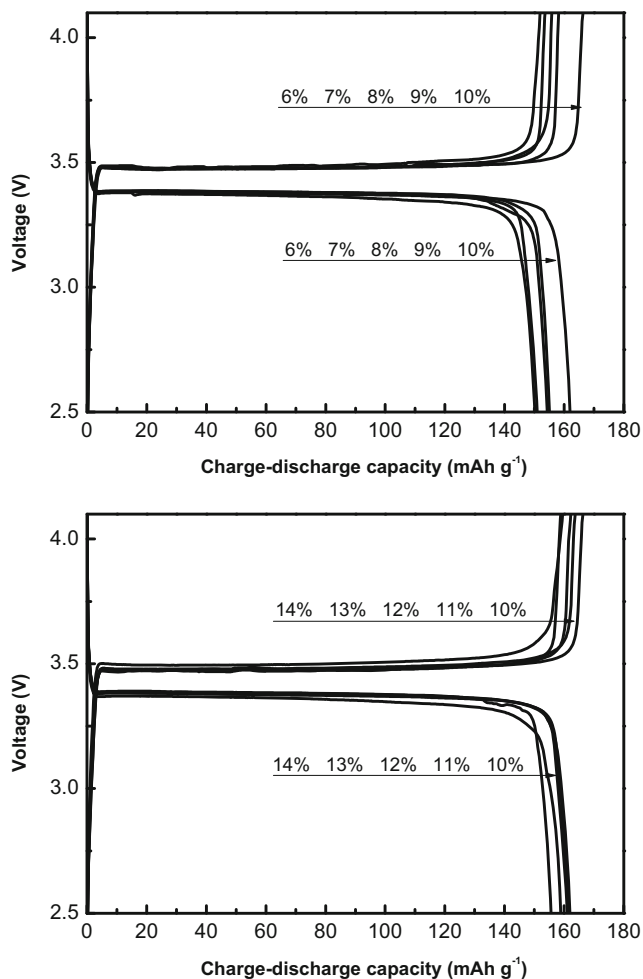


Fig. 6 First charge–discharge capacities of GPEs based on electrospun TPU/PVDF-HFP membrane

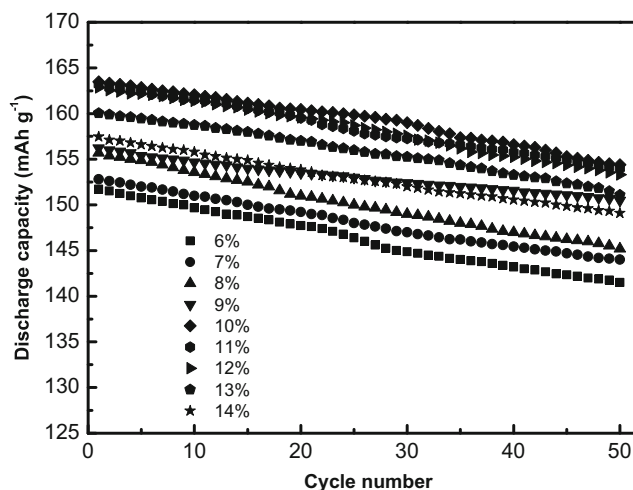


Fig. 7 The cycle performance (discharge capacities) of GPE based on electrospun TPU/PVDF-HFP membranes

Conclusions

GPEs based on fibrous TPU/PVDF-HFP blend membranes were prepared by electrospinning the 6–14 % polymer solutions in DMF/acetone (1:1, wt/wt) at room temperature. The optimum blend composition has been observed for the electrolyte with 10 % of TPU/PVDF-HFP (1:1, wt/wt). Firstly, TPU/PVDF-HFP (10 %) based gel polymer electrolyte has a high ionic conductivity of $6.62 \times 10^{-3} \text{ S cm}^{-1}$. Besides, the GPE has good mechanical stability and strength to allow safe operation in rechargeable lithium polymer batteries. What’s more, after 50 cycles, the cell shows a very stable discharge behavior and little capacity loss under current constant voltage conditions, at the 0.1 C rate of 25 °C. Considering these results, the cell with 10 % TPU/PVDF-HFP-based gel polymer electrolyte appears as a promising candidate for rechargeable lithium-ion batteries.

Acknowledgments The workers gratefully appreciate the financial supports from the Youth Project of National Nature Science Foundation of China (Grant No. 51203131).

References

1. Manuel Stephan A (2006) Review on gel polymer electrolytes for lithium batteries. *Eur Polym J* 42:21–42
2. Zhang HP, Zhang P, Li ZH, Sun M, Wu YP, Wu HQ (2007) A novel sandwiched membrane as polymer electrolyte for lithium ion battery. *Electrochem Commu* 9:1700–1703
3. Hwang YJ, Nahm KS, Kumar TP, Stephan AM (2008) Poly(vinylidene fluoride- hexafluoropropylene)-based membranes for lithium batteries. *J Membr Sci* 310:349–355
4. Muniyandi N, Kalaiselvi N, Periyasamy P, Thirunakaran R, Babu BR, Gopukumar S, Premkumar T, Renganathan NG, Raghavan M

- (2001) Optimisation of PVdF-based polymer electrolytes. *J Power Sources* 96:14–19
5. Idris NH, Rahman MM, Wang JZ, Liu HK (2012) Microporous gel polymer electrolytes for lithium rechargeable battery application. *J Power Sources* 201:294–300
 6. Matabola KP, Moutloali RM (2013) The influence of electrospinning parameters on the morphology and diameter of poly(vinylidene fluoride) nanofibers—effect of sodium chloride. *J Mater Sci* 48:5475–5482
 7. De Vrieze S, Van Camp T, Nelvig A et al (2009) The effect of temperature and humidity on electrospinning. *J Mater Sci* 44:1357–1362
 8. Shi L, Wang R, Cao Y, Feng C, Liang DT, Tay JH (2007) Fabrication of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) asymmetric microporous hollow fiber membranes. *J Membr Sci* 305:215–225
 9. Khayet M, Cojocar C, Garcia-Payo MC (2010) Experimental design and optimization of asymmetric flat-sheet membranes prepared for direct contact membrane distillation. *J Membr Sci* 351:234–245
 10. Xiao Q, Wang X, Li W, Li Z, Zhang T, Zhang H (2009) Macroporous polymer electrolytes based on PVDF/PEO-*b*-PMMA block copolymer blends for rechargeable lithium ion battery. *J Membr Sci* 334:117–122
 11. Saikia D, Wu HY, Pan YC, Lin CP, Huang KP, Chen KN, Fey GTK, Kao HM (2011) Highly conductive and electrochemically stable plasticized blend polymer electrolytes based on PVdF-HFP and triblock copolymer PPG-PEG-PPG diamine for Li-ion batteries. *J Power Sources* 196:2826–2834
 12. Ferrari S, Quartarone E, Mustarelli P, Magistris A, Fagnoni M, Protti S, Gerbaldi C, Spinella A (2010) Lithium ion conducting PVdF-HFP composite gel electrolytes based on *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide ionic liquid. *J Power Sources* 195:559–566
 13. Ren Z, Liu Y, Sun K, Zhou X, Zhang N (2009) A microporous gel electrolyte based on poly(vinylidene fluoride-co-hexafluoropropylene)/fully cyanoethylated cellulose derivative blend for lithium-ion battery. *Electrochim Acta* 54:1888–1892
 14. Saito Y, Kataoka H, Quartarone E, Mustarelli P (2002) Carrier migration mechanism of physically cross-linked polymer gel electrolytes based on PVDF membranes. *J Phys Chem B* 106:7200–7204
 15. Ding YH, Zhang P, Long ZL, Jiang Y, Xu F, Di W (2009) The ionic conductivity and mechanical property of electrospun P(VdF-HFP)/PMMA membranes for lithium ion batteries. *J Membr Sci* 329:56–59
 16. Wu CG, Lu MI, Chuang HJ (2005) PVdF-HFP/P123 hybrid with mesopores: a new matrix for high-conducting, low-leakage porous polymer electrolyte. *Polymer* 46:5929–5938
 17. Zhou L, Cao Q, Jing B, Wang XY, Tang XL, Wu N (2014) Study of a novel porous gel polymer electrolyte based on thermoplastic. *J Power Sources* 263:118–124
 18. Ma W, Zhang J, Wang X, Wang S (2007) Effect of PMMA on crystallization behavior and hydrophilicity of poly(vinylidene fluoride)/poly(methyl methacrylate) blend prepared in semi-dilute solutions. *Appl Surf Sci* 253:8377–8388
 19. Ji GL, Zhu BK, Cui ZY, Zhang CF, Xu YY (2007) Effect of PMMA on crystallization behavior and hydrophilicity of poly(vinylidene fluoride)/poly(methyl methacrylate) blend prepared in semi-dilute solutions. *Polymer* 48:6415–6425
 20. Raghavan P, Zhao X, Kim JK, Manuel J, Chauhan GS, Ahn JH, Nah CW (2008) PVDF porous matrix with controlled microstructure prepared by TIPS process as polymer electrolyte for lithium ion battery. *Electrochim Acta* 54:228–234
 21. Kim JR, Choi SW, Jo SM, Lee WS, Kim BC (2004) Ionic conductivity and electrochemical properties of nanocomposite polymer electrolytes based on electrospun poly(vinylidene fluoride-co-hexafluoropropylene) with nano-sized ceramic fillers. *Electrochim Acta* 50:69–75
 22. Kuo HH, Chen WC, Wen TC, Gopalan A (2002) Electrospun PVdF-based fibrous polymer electrolytes for lithium ion polymer batteries. *J Power Sources* 110:27–33
 23. Wu N, Cao Q, Wang X, Li X, Deng H (2011) A novel high-performance gel polymer electrolyte membrane basing on electrospinning technique for lithium rechargeable batteries. *J Power Sources* 196:8638–8643