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Study the effect of a novel high-performance gel polymer electrolyte based on thermoplastic polyurethane/poly (vinylidene fluoride)/polystyren by electrospinning technique

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ABSTRACT:

In this paper, nanofibrous membranes based on poly(vinylidene fluoride) (PVDF) doped with thermoplastic polyurethane (TPU) and polystyrene(PS) are prepared by electrospinning technique and the corresponding composite gel polymer electrolytes(GPEs) are obtained after being activated in liquid electrolyte. Its morphology characteristics and electrochemical performance are systematically investigated by scanning electron microscopy (SEM), universal testing machines (UTM), thermal analysis (TGA), galvanostatic charge-discharge and electrochemical impedance spectroscopy. The GPE based on TPU/PVDF/PS shows a high ionic conductivity of 5.46 mS cm-1, the electrochemical stability window of 6.3 V, a first discharge capacity of 169.5 mAh g^{-1} which is about 99.9% theoretical capacity of $LiFePO_4$. The TPU/PVDF/PS films show a high tensile strength (12.8 ± 0.3 MPa) and elongation (99.4 ± 0.2%). With the help of excellent polyelectrolyte complexes, the prepared nanofibrous membranes present superior electrochemical and mechanical performance, which are very promising for application in polymer lithium ion batteries.

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1. Introduction

Lithium ion battery has been investigated widely and deeply in the energy sources rapid growth time, due to its high energy density, high working voltage, non-memory effect, etc.. Gel polymer electrolytes(GPEs) plays an important part in the comprehensive performance of lithium-ion battery by determining the interfacial structure, bulk resistance and so on, which have received considerable attention in recent years for application in polymer lithium-ion batteries.[1-5]

As the matrix for GPEs, the preparation and the composition of polymer membrane have significant impacts on the performance of the final obtained products.[6] Several methods for producing GPEs have been tried to improve the ionic conductivity, such as phase inversion method, γ-ray irradiation method, solvent casting technique, TIPS technique, and electrospinning technique.[7-9] Among these methods, electrospinning technique which made the solution of polymer into lots of uniform and slender nanofibers by high voltage is a simple, controllable and efficient approach.[10] Furthermore choosing appropriate original materials is also extremely significant for the property of GPEs.

Poly(vinylidene fluoride)(PVDF) is a semi-crystalline polymer. With anti-oxidation, superior thermal porosities, mechanical properties and interfacial stability with lithium metal.[11-13] Thermoplastic polyurethane(TPU) belongs to an elastomer class possessing high tensile strength, elasticity as well as low crystallinity. TPU has two-phase microstructure which is soft segments and hard segments. The hard and soft phases are thermodynamically incompatible, which promotes hydrogen bonding within the hard domain involving urethane C=O and N–H moieties on adjacent polymer chain segments. The whole system benefit from these two phases since that the hard part afford spatial stability and the soft phases are conducive to good ionic conductivity owing to the soft segments didn't form ionic cluster after being dissolved alkali metal.[14] Previous studies on based of coaggregant like thermoplastic polyurethane (TPU)/linear poly(ethylene oxide) (PEO) (TPU-PEO), thermoplastic polyurethane (TPU)/polyacrylonitrile (PAN) (TPU-PAN) and polyurethane/poly (vinylidene fluoride) (TPU-PVDF) as GPEs for rechargeable lithium batteries have been reported.[15-17] In addition, it is found that polystyrene (PS) polymers exhibit the merits of low price, low water absorption, good optic transparency, easy processing, high glass transition temperature, low dielectric loss and high dielectric breakdown field (about 500MV m^{-1}), which make these polymers attractive candidates as the polymer matrix for the development of polymer-based dielectric composites.[18] Therefore, the GPEs based on PVDF, TPU and PS possess high ionic conductivity and preeminent mechanical stability at ambient temperature.[10]

In this work, we explore for the first time on a novel electrospun membrane prepared from TPU-PVDF-PS mixture solution. In addition, we make TPU/PS, PVDF/PS and TPU/PVDF/PS mixture solution into three different membranes. Then the nonwoven films immerse into 1 M $LiClO_4$-EC/PC liquid electrolyte solution for being activated 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. The results of experiment demonstrates that the GPEs of TPU/PVDF/PS shows a high ionic conductivity of 5.46×10^{-3} S cm^{-1} ,with electrochemical stability up to 6.3 V versus Li+/Li and first charge capacity of 169.9 mAh g^{-1}, with $LiFePO_4$ as cathode material. The TPU/PVDF/PS film gets the longest elongation 99.4%, with the max breaking tensile strength 12.8 MPa. Both the tensile strength and elongation at break are excellent.

2. Experimental

2.1 Materials

Thermoplastic polyurethane (TPU, yantaiwanhua, 1190A), polystyrene(PS, yangzishihua) and poly(vinylidene fluoride) (PVDF, Alfa Aesar) were dried under vacuum at 80 ºC for 24 h. $LiClO_4 \cdot 3H_2O$ (AR, Sinopharm Chemical Reagent Co., Ltd.) was dehydrated in vacuum oven at 120 ºC for 72 h. 1.0 M Liquid electrolyte was made by dissolving a certain quality of $LiClO_4$ in ethylene carbonate (EC, Shenzhen capchem technology Co., Ltd.)/propylene carbonate (PC, Shenzhen capchem Technology Co. Ltd.) (1/1, v/v). N,N-dimethylforamide (DMF) and acetone were analytical purity and used as received without further treatment.

2.2 Preparation of TPU/PS, PVDF/PS and TPU/PVDF/PS fibrous membrane

Firstly a certain amount of TPU, PVDF and PS powder (6/6/1, wt/wt/wt) were homogeneously dissolved in the mixture of an acetone/N,N-dimethylacetamide (3:1, wt/wt) forming a 10 wt % solution. Totally, 10 wt % PVDF/PS solution and 10 wt % TPU/PS solution were made by the same way, severally. 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 80 ºC for 12 h.

2.3 Preparation of gel polymer electrolytes

The thickness of the TPU/PVDF/PS nonwoven films used was ~100 μm. At room temperature, the dried TPU/PVDF/PS nonwoven films were activated by dipping in 1 M $LiClO_4$-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

Scanning electron microscope (SEM, Hitachi S-3500 N, Japan) was used to examine the morphology of films. 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 ºC min^{-1} from 30 to 900 ºC.

The mechanical strength of the polymer gel electrolyte films was measured by universal testing machines (UTM, Instron Instruments). There are some difficulties in surveying the "wet" films (with electrolyte), therefore the test was measured mechanical properties of the "dry" membrane (without electrolyte). The extension rate was kept at ~5 mm min^{-1}. The dimensions of the sheet used were 2 cm×5 cm × 150-250 μm (width × length × thickness). The porosity was investigated by immersing the membranes into n-butanol for 1 h and then calculated by using the following relation:

$$P = \frac{W_w - W_d}{\rho_b V_P} \times 100\% \quad \text{.. (A)}$$

Where W_w and W_d are the mass of the wet and dry membrane, respectively, ρ_b the density of n-butanol, and V_p the volume of the dry membrane.

The electrolyte uptake was determined by measuring the weight increase and calculated according to Eq. (B):

$$Uptake(\%) = \frac{W - W_0}{W_0} \times 100\% \text{ ....(B)}$$

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 100mm in thickness and 1.96 cm^2 in area for impedance measurement. Thus, the ionic conductivity could be calculated from the following equation:

$$\sigma = \frac{h}{R_b S} \text{ ....(C)}$$

In Eq.(C), σ is the ionic conductivity, R_b 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 electrochemical analyzer at a scan rate of 5 mV s^{-1}, with voltage from 2.5 V to 7 V. For charge-discharge cycling tests, the Li/PE/$LiFePO_4$ cell was assembled. The $LiFePO_4$ cathode was prepared as its blend with acetylene black and PVDF binder at a ratio of 80:10:10 by weight. 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 ºC, at different current densities.

3. Results and discussion

3.1 Morphology and structure

Fig. 1 shows the SEM images of the membranes prepared by electrospinning of polymer solution (TPU/PS, PVDF/PS, and TPU/PVDF/PS). It is clearly that the membranes are made up of a network of interlaid and nearly straightened tubular structure fibers. The fibers of TPU/PS (Fig. 1(a)) cross linked very stickily and unevenly, with the diameter distribution values range between 1 μm and 20μm, with an average fiber diameter of ~12 μm. As shown in Fig. 1(b), PVDF/PS nonwoven films (Fig. 1(b)) have many slim and oval beads, with the diameter distribution values range between 1 μm and 10 μm, with an average fiber diameter of ~8 μm. While the fibers of mix TPU, PVDF and PS (Fig. 1(c)) are relatively uniform and slender, with the diameter distribution values about 1.5 μm.

Due to rapid evaporation of solvent during electrospinning, all the membranes present network structure composed of fully interconnection with nanosized fibers. The parameters of influencing the morphology of electrospun fiber membranes contain the distance between the nozzle of the syringe and the collector, the applied voltage, dielectric constant of the solution and the concentration of the polymer solution. However, the only difference is the component of electrolyte. The diameter distribution values of the TPU/PVDF/PS membranes are smallest. Upon that we envisage the following reasons. The increased content of PVDF/PS have 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/PS composite solution and cause formation of fibers with lowest diameter.

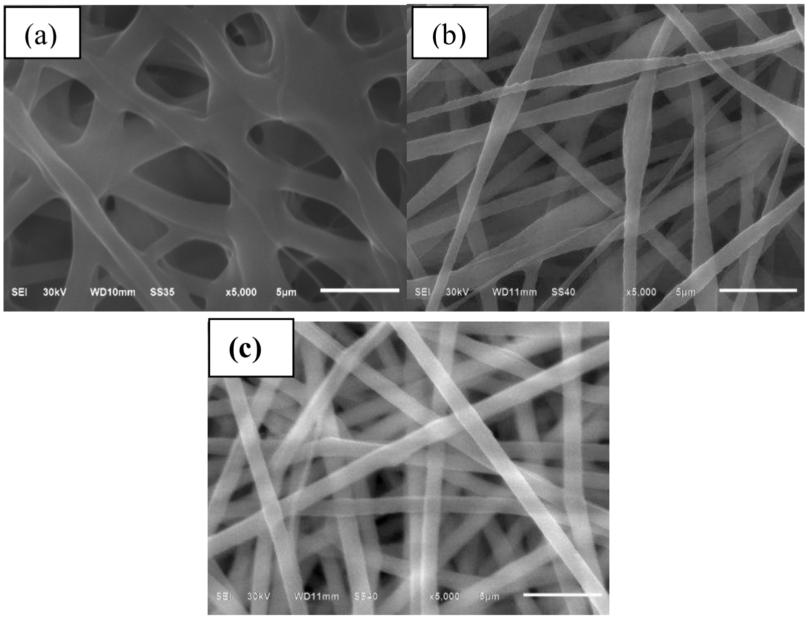

Fig.1. SEM images of electrospun membranes (a) TPU/PS (b)PVDF/PS (C) TPU/PVDF/PS

3.2 Thermal analysis

Thermograms of membranes with different compositions are shown in Fig. 2. The TPU/PS membranes and the TPU/PVDF/PS films both start to lose weight at about 300 ºC, and the TPU/PS membranes has 6% weight left at 530 ºC while the TPU/PVDF/PS films had lost 80% mass at 500 ºC. But the PVDF/PS diaphragm losses weight from 470 ºC to 530 ºC with 75% mass reduced. As is shown above, the TPU/PVDF/PS films are more stable. This may due to the strong interaction among the three polymer matrixes (TPU, PVDF and PS). The addition of PVDF/PS causes the interaction between its fluorine groups with carbonyl (C=O) and amino-group (-NH) in TPU. Thus the interaction of the three polymer chains would be stronger and the PVDF/PS chains would restrict the movement of the TPU chains during the glass transition. This enhances the compatibility of TPU/PVDF/PS.

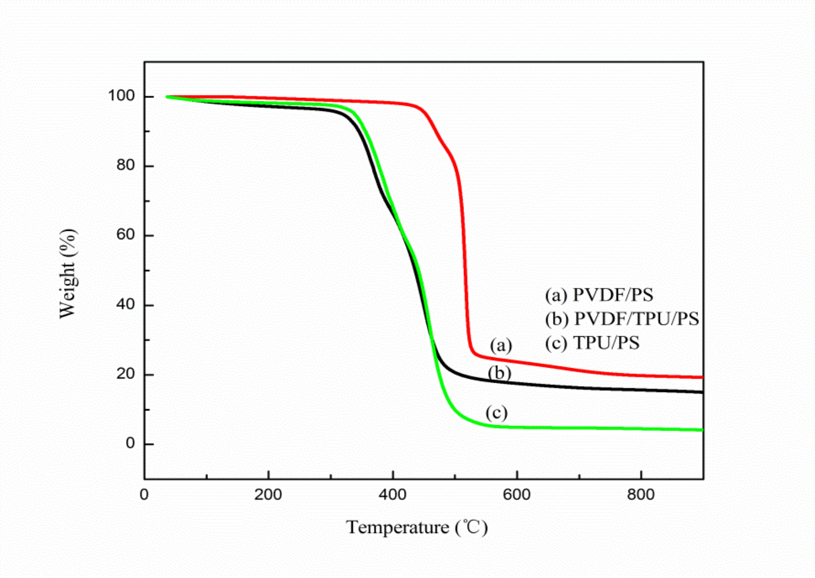

Fig.2. Thermograms of (a)TPU/PS (b)PVDF/PS (c)TPU/PVDF/PS films.

3.3 Porosity, electrolyte uptake and ionic conductivity

The porosity and wettability of the nanofibrous membrane are the important factors for the performance of polymer lithium-ion batteries (Table. 1). The results of porosity determination by n-butanol uptake method are presented in Table. 1. The porosity of TPU/PS membrane was about 48%. And the porosity of PVDF/PS membrane was 80%. Among all these membranes, TPU/PVDF/PS showed the highest porosity (87%).

Fig. 3 shows the uptake behavior of the electrospun fibrous membranes. The percentage of electrolyte uptake can be calculated according to Eq (A). The TPU/PS fibrous film shows an electrolyte uptake of about 120% within 2 min, while the PVDF/PS membrane is 275% and TPU/PVDF/PS film is 330%. The uptake of the electrolyte solution reaches up to 124% [TPU/PS], 341% [PVDF/PS] and 280% [TPU/PVDF/PS], respectively. After 15 min, it is found that when the electrolyte uptake of these three curves become stabile. The membrane with TPU/PVDF/PS always owns the highest electrolyte uptake percentage.

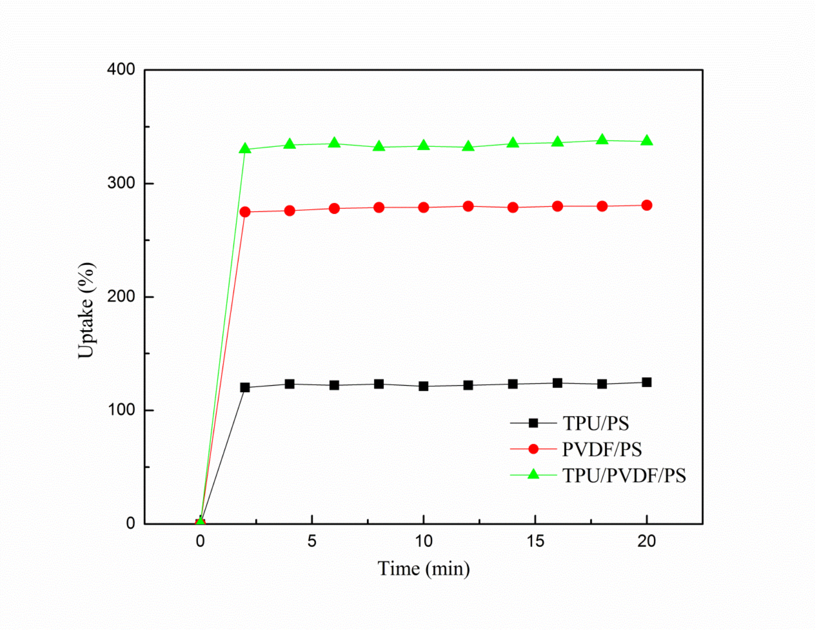

Fig.3. The uptake behavior of the electrospun fibrous films.

Fig. 4 shows the impedance spectra of TPU/PVDF/PS based fibrous polymer electrolyte. It is typical AC impedance for gel polymer electrolyte. From the morphology of the prepared porous electrospun TPU/PVDF/PS membranes in Fig. 1, it is known that there are many interconnected pores in the porous membranes, so enough liquid electrolytes were absorbed by the polymer membrane to form gelled polymer electrolyte. Being improved with ionic conductivity, there are three phases in the prepared GPEs, such as PVDF solid state, gel state and the absorbed liquid electrolyte state. Due to high crystalline character of PVDF polymer chains prevents the diffusion of lithium ions in the electric field, ion conduction mainly occurs mainly through the entrapped liquid electrolyte and the swelling gel layer.[19] In addition, 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 Li^+ ions are in gelled polymer electrolyte. According to all known 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 conductivity is mainly the result of ion conduction.[20] It can be observed clearly from Fig. 4 that the bulk resistance (R_b) of the TPU/PS fibrous polymer electrolyte is 11.7 Ω. And in Fig. 4 the PVDF/PS has a bulk resistance of 3.01 Ω. However, in Fig. 4 the bulk resistance (R_b) of the TPU/PVDF/PS fibrous polymer electrolyte is only 1.18 Ω. 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 Li^+ in the same volume, leads to a lower bulk resistance (R_b). Though the data in Table 1, the ionic conductivity could be calculated with Eq.(C). The ionic conductivity of TPU/PS and PVDF/PS fibrous polymer electrolyte is 4.78×10^{-4} S cm^{-1} and 2.03×10^{-3} S cm^{-1}, respectively. However the TPU/PVDF/PS fibrous polymer electrolyte film has an ionic conductivity of 5.46×10^{-3} S cm^{-1}. 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). The formability and rigidity of PS are excellent. Its molecular structure contains conjugate benzene,while it avails to the migration of lithium-ion. Therefore, the ionic conductivity of TPU/PVDF/PS fibrous polymer electrolyte film is the most superior.

In addition, the main parameters of influencing the porosity, electrolyte uptake and ionic conductivity of electrospun fiber membranes are the average fiber diameters and ions carriers. Kim et al. had reported decreasing in average fiber diameters can result in a decrease in leakage rate.[21] This particular structure may result in high electrolyte uptake, porosity, ionic conductivity. The presence of fully interconnected pores in the structure makes them appropriate as a host matrix for the preparation of gel polymer electrolytes.

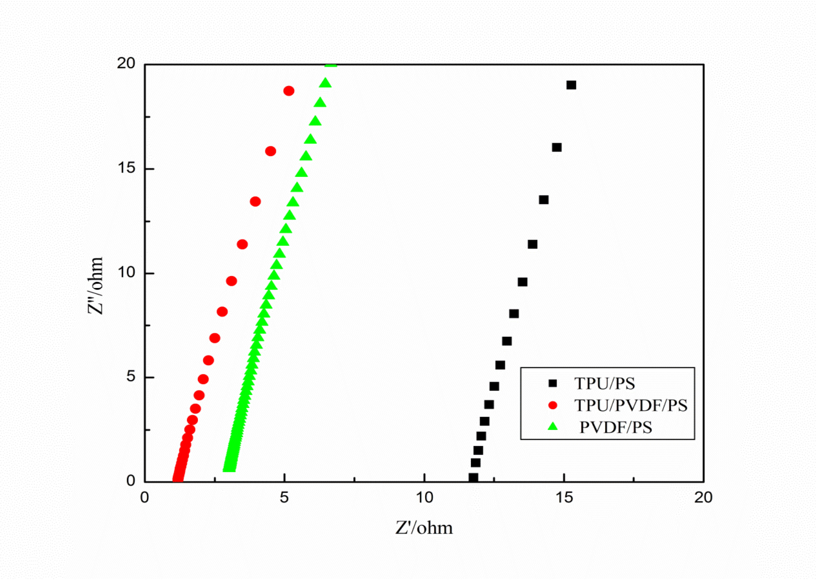

Fig.4. Impedance spectra of gel polymer electrolytes

Table 1. Surface area, height and porosity of fibrous membranes.

Samples	Surface area (cm^{-2})	Height (cm)	Porosity (%)
TPU/PS	1.988	0.014	48
PVDF/PS	1.962	0.012	80
TPU/PVDF/PS	1.861	0.012	87

3.4 Evaluation in Li/LiFePO$_4$ cell

Fig. 5(a) shows the first charge-discharge capacity curves of the cells with GPEs of TPU/PVDF/PS. 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/PS based GPEs. The GPEs with TPU/PS delivers a charge capacity of 136.5 mAh g^{-1} and discharge capacity of 135.6 mAh g^{-1} , only 80% of the theoretical capacity of $LiFePO_4$. PVDF/PS gel polymer electrolyte delivers a charge capacity of 155.6 mAh g^{-1} and discharge capacity of 153.6 mAh g^{-1}. The TPU/PVDF composite polymer electrolyte shows a charge capacity of 169.9 mAh g^{-1} and discharge capacity of 169.5 mAh g^{-1}, which is about 99.9% of the theoretical capacity. The charge-discharge capacities of lithium-ion batteries always depend on the electrode material, electrolyte, and separator. In this work, the difference is only the polymer electrolytes. From the results, we can find the TPU/PVDF/PS based GPEs delivers a discharge capacity of 169.5 mAh g^{-1}. The increased lithium-ion diffusion ability from the ion-complex may be the reason why the initial capacity of lithium battery can be improved. As to detailed reasons, further study is under way.

Upon that we studied the charge-discharge capacity of the cell with GPEs of TPU/PVDF/PS at different current rates, the results can be seen from Fig. 5(b). It is noted that the charge and discharge capacities of $LiFePO_4$ are 169.9 and 169.5 mAh g^{-1} at 0.1 C. Although the discharge capacities decrease with the increasing current rates due to the higher polarization at higher current densities, the anode material still exhibits high discharge capacities of 166.8, 161.9 and 160.1 m Ah g^{-1} at relatively smaller current rates of 0.2, 0.5 and 1 C. The Li cell with GPEs has been evaluated for cycle ability property under the 0.1 C rate at 25 ºC and the cycling performances of batteries with three kinds of GPEs are shown in Fig. 6(a). The batteries used different kinds of GPEs show relatively stable performance with capacity fading. Compared to the cells with GPEs containing TPU/PS and PVdF/PS in Fig. 6(a), the cell with

TPU/PVDF/PS based GPEs in Fig. 6(a) has a highest discharge capacity in the whole 50 cycles and exhibits the significantly improved cycle performance. After 50 cycles, the battery with GPEs based on TPU/PVDF/PS retains 97% of initial discharge capacity, while the batteries with GPEs based on TPU/PS and PVDF/PS nanofibrous membranes delivers 85% and 90% of the initial discharge capacity. There is no evident capacity fading of the cell with TPU/PVDF/PS based GPEs after a few cycles. This suggests that the cell exhibits a better reversibility. May be it results from a better stabilization of the system as a whole. This study shows that electrospun TPU/PVDF/PS based GPEs is very suitable for Li/$LiFePO_4$ cells under low current densities (0.1 C) at room temperature.

At the same time, the cycle performance of cell with GPEs of TPU/PVDF/PS at different current rates from 0.1 to 1 C illustrated in Fig. 6(b). At lower current rates (0.2 C), the capacity retentions are close to 96% after 50 cycles. Even at high-rate of 1 C, the capacity retention is as high as 93% and the cell still remains a discharge capacity of 146 mAh g^{-1} after 50 cycles. The outstanding electrochemical performance of GPEs is attributed to the particular morphology and structure of TPU/PVDF/PS that the nanofibers, high porosity and no microphase separation of mingling among TPU, PVDF and PS.

The results of evaluation in Li/$LiFePO_4$ cell indicate the electrochemical performance of composite gel polymer electrolytes is further enhanced with the interacting of TPU/PVDF/PS. This may due to the strong interaction among the polymer matrixes (TPU, PVDF and PS). The molecular structure of PS contains olefin-chain(R–C=C) and benzene (p-π) chain. Thus the interaction of the polymer chains would be stronger. Perhaps for two reasons：First， the PVDF chains would restrict the movement of the TPU chains during the glass transition， and second, the interaction between the PS chains and the hard segments of TPU make the whole system better and better.

(a)

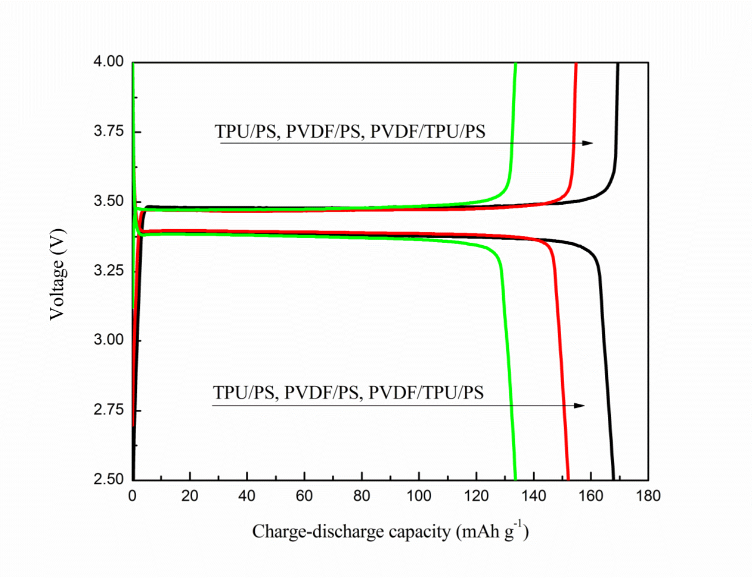

Fig.5.(a) First charge-discharge capacities of GPEs based on electrospun TPU/PVDF/PS membrane

(b)

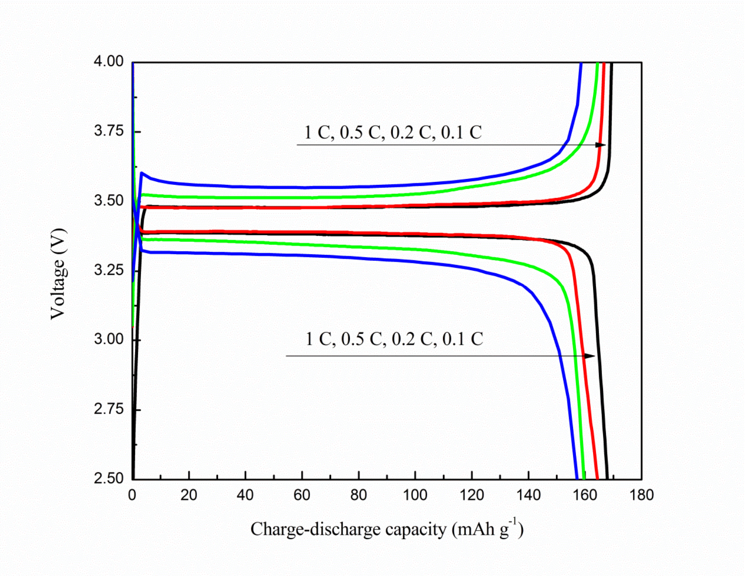

Fig.5.(b) First charge-discharge capacities of GPEs based on electrospun TPU/PVDF/PS membrane at different capacity rate (1 C = 170 mAh g^{-1})

(a)

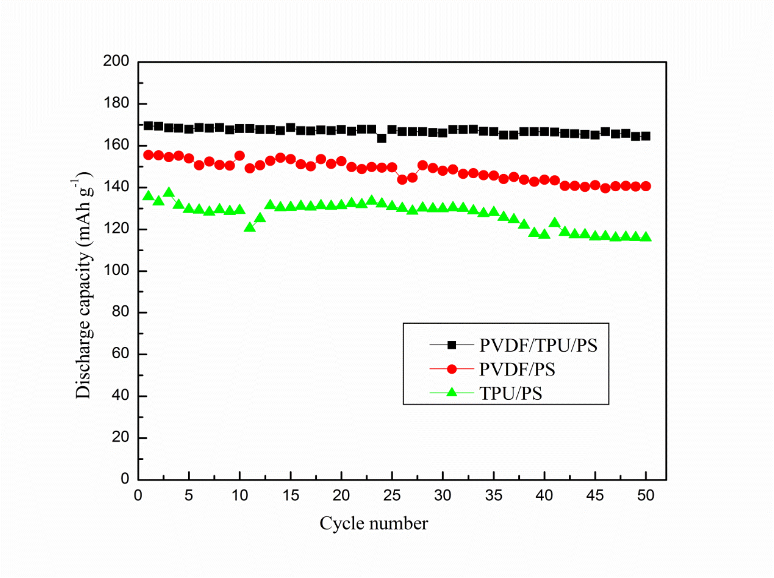

Fig.6.(a) The Cycle performance (discharge capacities) of GPE based on electrospun TPU/PVDF/PS membranes

(b)

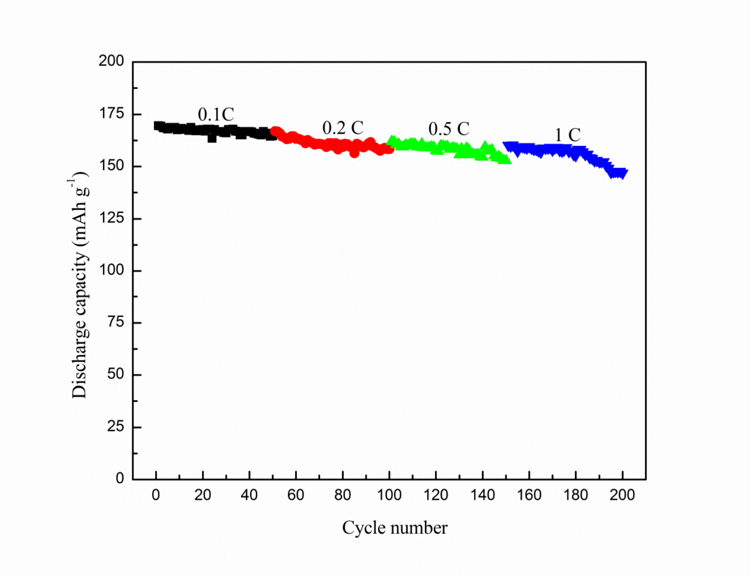

Fig.6.(b) The Cycle performance (discharge capacities) of GPE based on electrospun TPU/PVDF/PS membranes at different capacity rate

3.5 Electrochemical stability

The results of electrochemical stability tests of the gel polymer electrolytes by LSV are shown in Fig. 7. The electrochemical stability of TPU/PS and PVDF/PS fibrous polymer electrolyte is at 4.7 V and 5.6 V. While the stability of the TPU/PVDF/PS gel polymer electrolyte is further enhancing. Their electrochemical stability follows the order: membrane of TPU/PS (4.7 V) < PVDF/PS (5.6 V) < TPU/PVDF/PS (6.3 V). From Fig. 7, we can see obviously that the gel polymer electrolyte of TPU/PVDF/PS shows the best electrochemical stability. The decomposition process, which is associated with electrode/electrolyte, result in the onset of current flow in the high voltage range. And this onset voltage is the upper limit of the electrolyte stability range. There is almost no electrochemical reaction in the potential range from 2.5 V to 6.3 V for TPU/PVDF/PS gel polymer electrolyte. The better electrochemical stability maybe due to better compatibility between liquid electrolyte and nanofirbrous membranes with less leakage of liquid electrolyte. Therefore, the swollen phase of the membrane probably includes the complex compounds such as associated VdF-Li^+ groups. This complex formation with lithium ion and VdF groups of PVdF enhances the electrochemical stability of GPEs. The electrochemical stability was also influenced by the large and fully interconnected pores, high porosity, higher specific surface area, uniform morphology of membranes and the AFDs. The oxidation stability of the GPE increased with the decreasing of AFDs. So the gel polymer electrolyte of TPU/PVDF/PS shows the best electrochemical stability. These polymer electrolytes should render them very suitable for applications in lithium-ion battery because of the high anodic stability.[14,22]

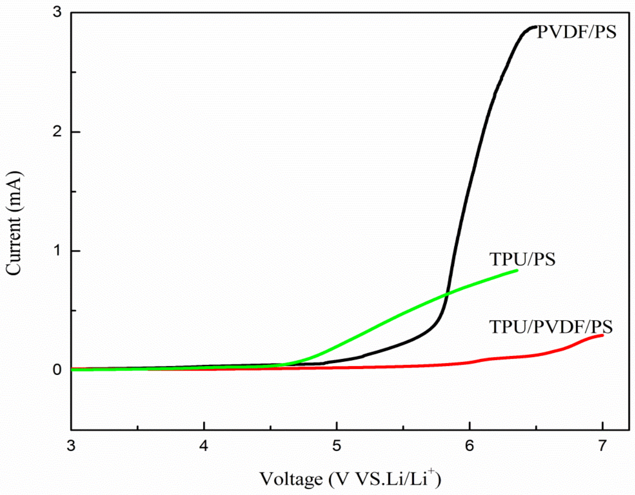

Fig. 7. Linear sweep voltammograms of the gel polymer electrolytes

3.6 Mechanical property

Fig. 8 shows the stress-strain curves of the polymer membranes. The results of mechanical strength test show that the hybrid fillers improved the mechanical performance of membranes. The PVdF/PS membrane extended only 68.8% with the max breaking tensile strength 6.44 MPa. Referring to the TPU/PS film, the membrane has 86.8% elongation and been broken under the 9.83 MPa tensile strength. While the mixed film owes the longest elongation 99.4%, it can bear the tensile strength below 12.8 MPa. Both the tensile strength and elongation of the mixed films at break were enhanced. The reasons are as below. The copolymers fabricate by TPU, PVDF and PS are homogeneous and symphysic. There is no microphase separation of miscibling among TPU, PVDF and PS as electrospun films and in consequence it has a great contact area with the polymeric matrix. When the material is struck, the more microcracking will absorb more impact energy. So the further expansion of the cracks is blocked.

As we all know, elongation at break often reflects the impact performance of material and the impact resistance is shown by the material toughness. The higher toughness in mechanical properties will reduce the risk of the collapse of the membrane, which is suggests that the membrane prepared through polymers TPU, PVDF and PS is more suitable for application in polymer lithium ion batteries.

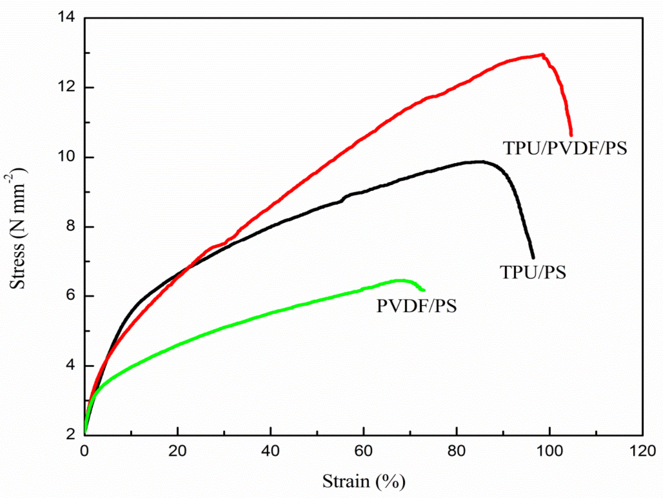

Fig.8. Stress–strain curves of the electrospun TPU/PVDF/PS membranes

4. Conclusions

GPEs based on fibrous TPU/PVDF/PS composite membranes were prepared by electrospinning the 10 wt% polymer solution in DMF/acetone (3:1, w/w) at room temperature. The optimum blend composition has been observed for the electrolyte TPU/PVDF/PS. PS is a kind of outstanding polymers which is benefical to the migration of ions. With the addition of the PS, the performances of polymer electrolyte membranes have been improved obviously. The GPEs based on TPU/PVDF/PS have a high ionic conductivity of 5.46×10^{-3} S cm^{-1}, with electrochemical stability up to 6.3 V versus Li^{+}/Li at room temperature. The first discharge capacity of TPU/PVDF/PS based gel polymer electrolyte lithium battery is about 169.5 mAh g^{-1}, which is relatively close to the theoretical capacity of $LiFePO_4$. This is a remarkable enhancement in performance since the GPEs are able to serve for lithium ion polymer batteries. 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 ºC. The TPU/PVDF/PS mixed films owes the longest elongation 99.4%, and it can bear the tensile strength below 12.8 MPa. As is shown above, the cell with TPU/PVDF/PS based gel polymer electrolyte displays a superior potential and is very suitable for rechargeable lithium batteries.

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References

[1] J. Y. Song, Y. Y. Wang, C. C. Wan, *J. Power Sources.,* 1999, 77, 183-197.

[2] H. P. Zhang, P. Zhang, Z. H. Li, M. Sun, Y. P. Wu, H. Q. Wu, *Electrochem. Commun*., 2007, **9,** 1700-1703.

[3] X. J. Wang, J. J. Kang, Y. P. Wu, S. B. Fang, *Electrochem. Commun*., 2003, **5,** 1025-1029.

[4] L. Z. Fan, J. Maier, *Electrochem. Commun*., 2006, **8,** 1753-1756.

[5] F. Croce, L. Settimin, B. Scrosati, *Electrochem. Commun*., 2006, **8,** 364-368.

[6] W. L. Li, Y. J. Xing, Y. H. Wu, J. W. Wang, L. Z. Chen, G. Yang, B. Z. Tang. *Electrochimica Acta*., 2015, **151,** 289-296.

[7] C. R. Yang, Z. D. Jia, Z. C. Guan, L. M. Wang, *J. Power Sources*., 2009, **189,** 716-720.

[8] P. Raghavan, J. W. Choi, J. H. Ahn, G. Cheruvally, G. S. Chauhana, H. J. Ahn, C. Nah, *J. Power Sources.*, 2008, **184,** 437-443.

[9] R. Prasanth, N. Shubha, H. H. Hng, M. Srinivasan, *J. Power Sources.*, 2014, **245,** 283-291.

[10] N. Wu, Q. Cao, X. Y. Wang, X. Y. Li, H. Y. Deng, *J. Power Sources.*, 2011, **196,** 8638-8643.

[11] W. W. Cui, D. Y. Tang, Z. L. Gong, *J. Power Sources.*, 2013, **223,** 206-213.

[12] Y. S. Zhu, S. Y. Xiao, Y. Shi, Y. Q. Yang, Y. P. Wu, *J. Mater. Chem. A.,* 2013, **1,** 7790-7797.

[13] L. Zhou, N. Wu, Q. Cao, B. Jing, X.Y. Wang, Q. Wang, H. Kuang, *Solid State Ionics.,* 2013, **249-250,** 93-97.

[14] L. Zhou, Q. Cao, B. Jing, X. Y. Wang, X. L. Tang, N. Wu, *J. Power Sources.,* 2014, **263,** 118-124.

[15] H. H. Kuo, W. C. Chen, T. C. Wen, A. Gopalan, *J. Power Sources.,* 2002, **110,** 27-33.

[16] Y. L. Du, T. C. Wen, *Mater. Chem. Phys.*, 2001, **71,** 62-69.

[17] P. Santhosh, T. Vasudevan, A. Gopalan, K. -P. Lee, *Mater. Sci. Eng. B.,* 2006, **135,** 65-73.

[18] C. Yang, Y. H. Lin, C. W. Nan, *Carbon.,* 2009, **47,** 1096-1101.

[19] W. Wieczorek, J. R. Stevens, Z. Florjahczyk, *Solid State Ionics.,* 1996, **85,** 67-72.

[20] M. Jacob, S. Prabaharan, S. Radhakrishna, *Solid State Ionics.,* 1997, **104,** 267-276.

[21] J. R. Kim, S. W. Choi, S. M. Jo, W. S. Lee, B. C. Kim, *Electrochimica. Acta.,* 2004, **50,** 69-75.

[22] N. Wu, Q. Cao, X. Y. Wang, S. Li, X. Li, H. Deng, *J. Power Sources.,* 2011, **196,** 9751-9756.