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# Gel electrolytes based on poly(vinylidene fluoride-co-hexafluoropropylene)/thermoplastic polyurethane/poly(methyl methacrylate) with *in situ* SiO<sub>2</sub> for polymer lithium batteries

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Gel polymer electrolyte films based on poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), thermoplastic polyurethane (TPU) and poly(methyl methacrylate) (PMMA) with and without *in situ* SiO<sub>2</sub> fillers are prepared by electrospinning a polymer solution at room temperature. The electrospun PVDF-HFP/TPU/PMMA blending membrane with 2% *in situ* SiO<sub>2</sub> shows a highest ionic conductivity of  $8.5 \times 10^{-3} \text{ S cm}^{-1}$  with electrochemical stability up to 5.9 V *versus* Li<sup>+</sup>/Li at room temperature. In addition, it shows a first charge of 168.5 mA h g<sup>-1</sup>, which is about 99% of the theoretical capacity of LiFePO<sub>4</sub>; the tensile strength of the PVDF-HFP/TPU/PMMA membrane is 10.8 MPa with elongation-at-break at 86.4%. With the outstanding electrochemical and mechanical performance, it is very suitable for application in polymer lithium batteries.

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## 1. Introduction

Polymer lithium batteries are widely used in mass-produced digital devices and are gaining popularity in the electric vehicle market and energy storage systems because of their high energy density and long cycle life.<sup>1–5</sup> In recent years, polymer-based nanocomposites which are used in polymer lithium batteries have attracted considerable academic and industrial attention,<sup>6–10</sup> because polymer lithium batteries are safer than liquid lithium-ion batteries. Be that as it may, there is a long way to go in polymer lithium-ion battery large-scale application. A lot of techniques have been attempted to produce gel polymer electrolytes with excellent ionic transport properties and low crystallization, such as the phase inversion method, g-ray irradiation method, solvent casting technique, thermally induced phase separation (TIPS) technique, and electrospinning technique.<sup>11</sup>

Among these methods, by using electrospinning technique can be easily prepare porous polymer framework materials. Furthermore the choice of matrices for gel polymer electrolyte (GPE) is also very important. And a lot of work has been done.<sup>12–20</sup> Many investigations were devoted to copolymerize PVDF and its copolymers with other polymer for processing GPEs. Some article on based of coaggregant like PVDF/thermoplastic polyurethane (TPU) (PVDF/TPU), P(VDF-TrFE)/linear poly(ethylene oxide) (PEO) (P(VDF-TrFE)/PEO) and

polyurethane/poly(vinylidene fluoride) (PU-PVDF) as GPEs for rechargeable lithium batteries have been reported lately.<sup>21,22</sup> Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has been as the matrix of polymer electrolytes in lithium ion batteries. Making a comparison copolymers between PVDF and PVDF-HFP, the latter in the gel owns lower glass transition temperature, greater solubility for organic solvents and less crystallinity.<sup>23,24</sup> Accordingly, there are more amorphous domains in PVDF-HFP which could absorb greater amounts of liquid electrolytes, and enough mechanical integrity profiting from the crystalline regions is conducive to prepare free-standing membrane as well. Thermoplastic polyurethane (TPU) contains two-phase microstructure which are soft segments and hard segments.<sup>25,26</sup> The unfavorable interactions between the hard and soft segments make the system a micro-phase-separated one, which imparts elastomeric properties to polyurethane. The rubbery soft segments can dissolve alkali metal without formation of ionic cluster. On the other hand, the hard segment domains, which are in glassy state and are either distributed or interconnected throughout the rubbery phase, act as reinforcing filler and hence contribute to the dimensional stability of the GPEs. Because of this unique two-phase microstructure, the segmented polyurethanes find themselves very much useful as matrix materials for GPEs. Poly(methyl methacrylate) (PMMA) polymer matrixes have attracted much attention due to the advantages of excellent mechanical, chemical stability and considerable wettability.<sup>27–31</sup> Besides, the functional group (–CO) of PMMA could interact with lithium ions and liquid electrolytes such as ethylene carbonate (EC), dimethylformamide (DMF). Therefore, PVDF-HFP, TPU and PMMA

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are combined with electrolyte solution to create GPEs,<sup>32,33</sup> which had excellent performance in the lithium ion battery. Moreover doping ceramic fillers, such as TiO<sub>2</sub>, SnO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, is an effective way to improve the electrochemical and mechanical properties of GPE.

In this study, we choose poly(vinylidene fluoride-hexafluoro propylene) (PVDF-HFP)/thermoplastic polyurethane (TPU)/poly(methyl methacrylate) (PMMA) as electrospun matrix, PVDF-HFP/TPU/PMMA based gel polymer electrolyte with and without *in situ* SiO<sub>2</sub> fillers are prepared by electrospinning technique. The properties of electrospun membranes prepared with *in situ* SiO<sub>2</sub> fillers are observed to be comparatively better than the one prepared without *in situ* SiO<sub>2</sub> fillers. And the electrospun PVDF-HFP/TPU/PMMA blending membrane with 2% *in situ* SiO<sub>2</sub> has the most superior performance.

## 2. Experimental

### 2.1 Materials

Poly(vinylidene difluoride-co-hexafluoropropylene) (PVDF-HFP, Knyar Flex, LBG), thermoplastic polyurethane (TPU, Yantai Wanhua, 1190A) and poly(methyl methacrylate) (PMMA, Shanghai Chemical Reagents Co., China) 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 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 of analytical grade and used as received without further treatment.

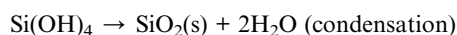
### 2.2 Preparation of PVDF-HFP/TPU/PMMA fibrous membrane

Four types of PVDF-HFP/TPU/PMMA fibrous membranes (a) without *in situ* SiO<sub>2</sub> fillers, (b) with 1% *in situ* SiO<sub>2</sub>, (c) with 2% *in situ* SiO<sub>2</sub> and (d) with 3% *in situ* SiO<sub>2</sub> were prepared by electrospinning the following solutions, respectively.

(a) A 11% solution of PVDF-HFP/TPU/PMMA (1 : 1 : 1, w/w/w) in DMF/acetone (3 : 1, w/w) was prepared by magnetic stirring for 12 h at room temperature.

(b) A 11% solution of PVDF-HFP/TPU/PMMA (1 : 1 : 1, w/w/w) in DMF/acetone (3 : 1, w/w) was prepared by magnetic stirring for 12 h at room temperature. For generating *in situ* SiO<sub>2</sub>, a small quantity of ammonium hydroxide (3–4 drops) was added to the polymer solution, which was followed by drop wise addition of the required quantity of TEOS under vigorous stirring. The stirring was continued at room temperature until forming a homogeneous solution.

The hydrolysis and condensation reactions of TEOS can be represented by the following equations:



Both (c) and (d) are the same with (b), their difference is only *in situ* SiO<sub>2</sub> content.

All of the solutions were electrospun under high voltage of 24.5 kV at room temperature, respectively. Nonwoven films were obtained on the collector plate and put on the table overnight to ensure the hydrolysis and condensation reactions fully completed. Then the electrospun nonwoven films were dried under vacuum at 80 °C for 12 h.

### 2.3 Preparation of gel polymer electrolytes

The thickness of the PVDF-HFP/TPU/PMMA films used were about 150 μm. At room temperature, the dried PVDF-HFP/TPU/PMMA films were activated by 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 the gel polymer electrolyte (GPE) was prepared.

### 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 TGAQ 50, TA Company, USA). Fourier transform infrared (FT-IR) spectra of the samples were recorded using FT-IR Tensor 37 (Bruker, German) in the range of 400–4000 cm<sup>-1</sup>. Differential scanning calorimetry (DSC) characterization was performed using Perkin Elmer DSC7 instrument (USA) under a nitrogen atmosphere from 20 to 200 °C at a scan rate of 10 °C min<sup>-1</sup>. Samples were run under a nitrogen atmosphere over a temperature range of -90 to 230 °C. The crystallinity ( $\chi_c$ ) was calculated based on eqn (1) from the DSC curves

$$\chi_c = \Delta H_f / \Delta H_f^* \phi \times 100\% \quad (1)$$

where  $\Delta H_f$  and  $\Delta H_f^*$  represent the fusion enthalpy of blend membrane and PVDF-HFP with 100% crystallinity, respectively. The value of  $\Delta H_f^*$  is 104.7 J g<sup>-1</sup>.  $\phi$  is the measuring weight fraction of PVDF-HFP.

The mechanical strength of the polymer gel films was measured by universal testing machines (UTM, Instron Instruments). The extension rate was kept at ~5 mm min<sup>-1</sup>. The dimensions of the sheet used were 2 cm × 5 cm × 100 μm (width × length × thickness).

The electrolyte uptake was determined by measuring the weight increase and calculated according to eqn (2):

$$\text{Uptake (\%)} = \frac{W - W_0}{W_0} \times 100\% \quad (2)$$

$W_0$  is the weight of dried films and  $W$  is the weight of swollen films.

The ionic conductivity of the composite film was measured with SS/PE/SS (SS means stainless steel plates) 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 1.65 cm<sup>2</sup> in area for impedance measurement. Thus, the ionic conductivity could be calculated from the following equation:



$$\sigma = \frac{h}{R_b S} \times 100\% \quad (3)$$

in eqn (3),  $\sigma$  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 (SS means stainless steel plates) cell using Zahner Zennium electrochemical analyzer at a sweep rate of  $5 \text{ mV s}^{-1}$ , with voltage from 2 V to 7 V. For charge-discharge cycling tests, the Li/PE/LiFePO<sub>4</sub> 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, CAPCHEM Technology China), between 2.0 and 4.5 V with different current densities at 25 °C.

# 3. Results and discussion

## 3.1 Morphology and structure

Fig. 1 shows the SEM images of the membranes prepared by electrospinning of polymer solution with and without *in situ* SiO<sub>2</sub> fillers. It can be seen that the electrospun nanofibers interlaced with each other randomly and formed a three-dimensional network structure. It is well known that TPU is a linear polymer material and the molecular structure is complicated. The duplicated carbamated-chain (–R–O–CO–NH–R–NH–CO–O–), which is in the hard segments of TPU, offers

amino-group (–NH). The amino-group (–NH) can form hydrogen bonds with the strong electron-withdrawing functional group (–C–F) and (–CO). The functional group (–C–F) is in the backbone structure of PVDF–HFP, and the functional group (–CO) is in the backbone structure of PMMA. Therefore, PVDF–HFP, TPU and PMMA are miscible without any microphase separation as electrospun matrix. A network of interlaid and nearly straightened tubular structure fibers are found in the membrane without *in situ* ceramic fillers (Fig. 1(a)) and the surface of the membrane have no *in situ* silica films, moreover, there are a lot of the pore network structure. While the surface of the membrane with *in situ* silica films are found in the membrane with *in situ* gel polymer electrolyte films based on poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP), thermoplastic polyurethane (TPU) and poly(methyl methacrylate) (PMMA) with and without *in situ* SiO<sub>2</sub> fillers are prepared by electrospinning a polymer solution at room temperature. SiO<sub>2</sub> (Fig. 1(b)–(d)), the differences of the three membranes are thickness and cover area of the *in situ* silica films. And as shown in Fig. 1(a)–(c), the nanofibers are very homogeneous and tenuous, however, the nanofibers of the membrane with 3% *in situ* SiO<sub>2</sub> are unevenly distributed (Fig. 1(d)), this maybe added amount too much *in situ* SiO<sub>2</sub> into the solution.

From the preparation steps of fibrous membrane, we can found that the hydrolysis and condensation reactions took place for generating *in situ* SiO<sub>2</sub> fillers. The hydrolyzed precursor molecules Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> moved slowly because of the viscous polymer solution and the steric hindrance. So the probability of the resulting sol nuclei Si(OH)<sub>4</sub> meeting together

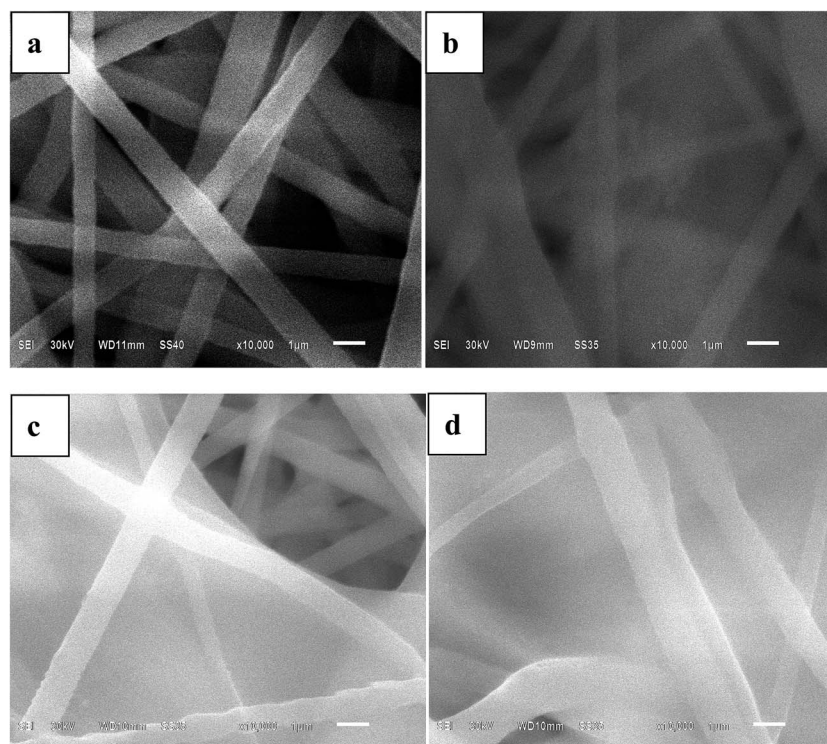


Fig. 1 SEM images of electrospun PVDF–HFP/TPU/PMMA membranes (a) without *in situ* SiO<sub>2</sub> (b) with 1% *in situ* SiO<sub>2</sub> (c) with 2% *in situ* SiO<sub>2</sub> (d) with 3% *in situ* SiO<sub>2</sub>.





and growing into extended structure or large  $\text{SiO}_2$  particles is greatly reduced. As we know *in situ*  $\text{SiO}_2$  is conducive to the absorption of the electrolyte. Predicting the membrane with *in situ*  $\text{SiO}_2$  will have a higher electrolyte uptake.

### 3.2 FT-IR spectra analysis

FT-IR spectra of (a) TPU, (b) PVDF-HFP, (c) PMMA and (d) the composite membrane of PVDF-HFP/TPU/PMMA with *in situ*  $\text{SiO}_2$  are shown in Fig. 2. The characteristic absorption peaks of TPU are clearly identified, *i.e.*  $2939\text{ cm}^{-1}$  (stretching band of  $-\text{NH}$  in hard phase) and  $1700\text{ cm}^{-1}$  (stretching band of  $\text{C}=\text{O}$ ). The typical peaks of PVDF-HFP are  $1399\text{ cm}^{-1}$  (deformation vibration band of  $-\text{CH}_2-$ ),  $1073\text{ cm}^{-1}$  (stretching band of  $\text{C}-\text{C}$  in the  $\beta$ -phase) and  $873\text{ cm}^{-1}$  (band for amorphous phase). The vibrational peaks of PMMA are  $1392\text{ cm}^{-1}$  ( $\text{C}-\text{CH}_3$  stretching),  $1115\text{ cm}^{-1}$  ( $\text{C}-\text{C}-\text{O}$  bending vibrations). As we can see, the characteristic absorption peaks are shifted to ( $2922$  and  $1699\text{ cm}^{-1}$ ), ( $1399$  and  $1073\text{ cm}^{-1}$ ) and ( $1120\text{ cm}^{-1}$ ) in the complexes, respectively. And the strong electron-withdrawing functional group ( $-\text{C}-\text{F}$ ) which is in the backbone structure of PVDF-HFP and functional group ( $-\text{C}-\text{C}-\text{O}$ ) which is in the backbone structure of PMMA can form hydrogen bonds with amino-group ( $-\text{NH}$ ) which is in the hard segments of TPU during to a shift of absorption bands ( $2922\text{ cm}^{-1}$ ,  $1699\text{ cm}^{-1}$  and  $1120\text{ cm}^{-1}$ ) in the characteristic absorption peaks of the PVDF-HFP/TPU/PMMA based membrane.

### 3.3 Thermal and DSC analysis

Fig. 3 presents the thermograms of membranes with and without *in situ*  $\text{SiO}_2$ . The thermograms curve (a) of the membranes without *in situ*  $\text{SiO}_2$  illustrates three main weight loss processes: the initial weight loss occurring in the temperature range from  $380\text{ }^\circ\text{C}$  to  $420\text{ }^\circ\text{C}$  is also attributed to the PMMA; the weight loss in the phase two from  $430\text{ }^\circ\text{C}$  to  $470\text{ }^\circ\text{C}$  can be assigned to thermal decomposition reaction of TPU; the final perpendicular weight loss occurring in the temperature

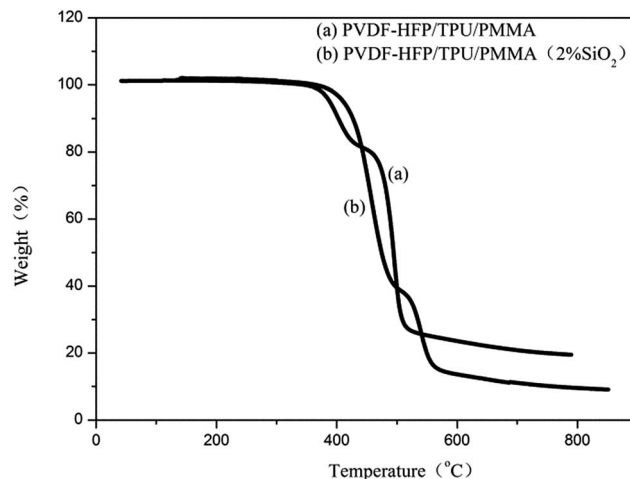


Fig. 3 Thermograms of electrospun PVDF-HFP/TPU/PMMA membranes (a) without *in situ*  $\text{SiO}_2$  (b) with 2% *in situ*  $\text{SiO}_2$ .

range from  $480\text{ }^\circ\text{C}$  to  $510\text{ }^\circ\text{C}$  is aroused from thermal collapse of PVDF-HFP. The thermograms curve (b) of the membranes with 2% *in situ*  $\text{SiO}_2$  also illustrates that there are three weight loss processes: the initial weight loss occurring in the temperature range from  $400\text{ }^\circ\text{C}$  to  $500\text{ }^\circ\text{C}$  is attributed to the removal of PMMA due to decomposition reaction of carbonyl, the loss occurring temperature is higher than the membranes without *in situ*  $\text{SiO}_2$ , the weight loss in the second stage from  $510\text{ }^\circ\text{C}$  to  $530\text{ }^\circ\text{C}$  must be associated with the thermal decomposition reaction of TPU; the final perpendicular weight loss occurring in the temperature range from  $530\text{ }^\circ\text{C}$  to  $580\text{ }^\circ\text{C}$  is aroused from thermal collapse of PVDF-HFP. The higher the temperature of the weight loss, meaning that, its thermal stability is better. The results suggested that the membrane with *in situ*  $\text{SiO}_2$  have the excellent thermal stability.

Fig. 4 displays DSC curves and the following observations were made. As shown in Fig. 4, firstly, the heating curve of

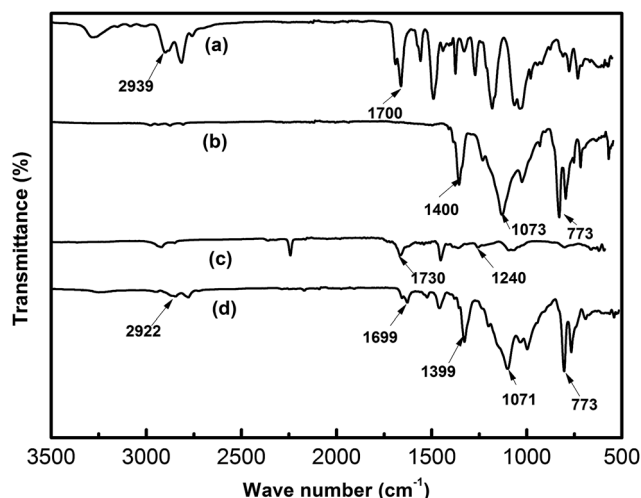


Fig. 2 FTIR spectra of the electrospun membranes (a) TPU (b) PVDF-HFP (c) PMMA (d) PVDF-HFP/TPU/PMMA membranes with *in situ*  $\text{SiO}_2$ .

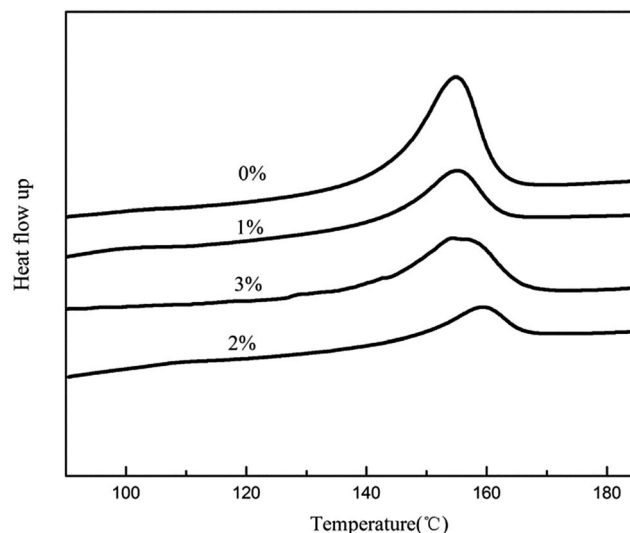


Fig. 4 DSC curves of the electrospun PVDF-HFP/TPU/PMMA membranes with and without *in situ*  $\text{SiO}_2$ .



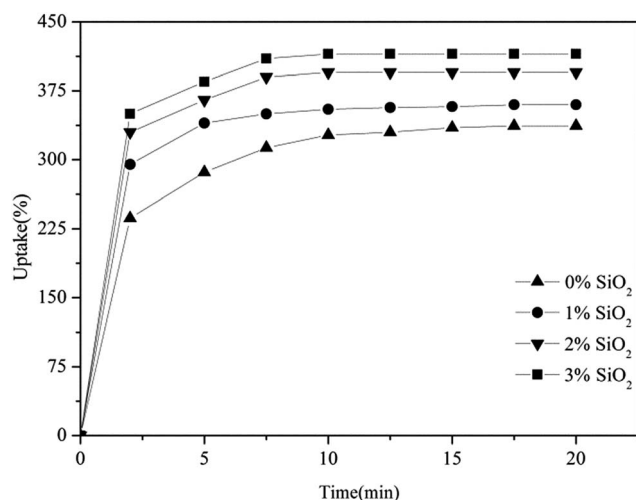
electrospun PVDF-HFP/TPU/PMMA membranes without *in situ* SiO<sub>2</sub> membrane showed a melting peak at temperature of 155.8 °C, while the membrane with 2% *in situ* SiO<sub>2</sub> has the highest melting temperature which is 160.3 °C. As shown in Table 1, the melting enthalpy ( $\Delta H_f$ ) of the electrospun membranes with *in situ* SiO<sub>2</sub> is much lower than that of the membrane without *in situ* SiO<sub>2</sub>. According to eqn (1), the percentage of crystallinity values of the membrane is 21.30% (without *in situ* SiO<sub>2</sub>), 17.49% (with 1% *in situ* SiO<sub>2</sub>), 14.73% (with 2% *in situ* SiO<sub>2</sub>), 16.78% (with 3% *in situ* SiO<sub>2</sub>), respectively. Low crystallinity of membrane can supply a beneficial condition for conductivity enhancement. The results suggested that the membrane with 2% *in situ* SiO<sub>2</sub> based gel polymer electrolyte may have the excellent ionic conductivity.

### 3.4 Electrolyte uptake and ionic conductivity

Fig. 5 shows the uptake behavior of the electrospun PVDF-HFP/TPU/PMMA fibrous membranes. The percentage of electrolyte uptake can be calculated according to eqn (2). The fibrous film without *in situ* SiO<sub>2</sub> has liquid electrolyte uptake up to 236 wt% within 2 min, in the meantime, the membranes with 1% *in situ* SiO<sub>2</sub> is 295%, the membrane with 2% *in situ* SiO<sub>2</sub> is 330% and the membrane with 3% *in situ* SiO<sub>2</sub> is 350%. In order to reach up to the maximum uptake, the electrospun fibrous membrane were immersed into liquid electrolyte 15 min, it is found that the uptake of the electrolyte solution reaches up to 337% (the

**Table 1** Crystallinity ( $\chi_c$ ) of the electrospun PVDF-HFP/TPU/PMMA membranes with and without *in situ* SiO<sub>2</sub>

Materials (SiO <sub>2</sub> )	$\Delta H_f$ (J g <sup>-1</sup> )	Crystallinity $\chi_c$ (%)
0%	22.30	21.30
1%	18.32	17.49
2%	15.43	14.73
3%	17.57	16.78



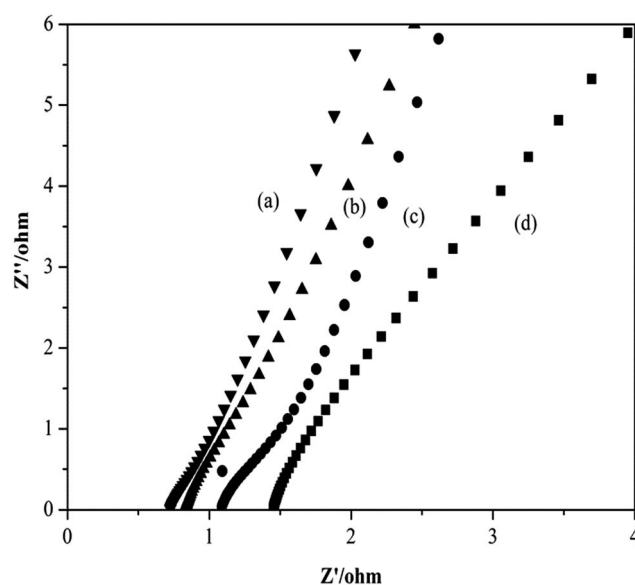
**Fig. 5** The uptake behavior of electrospun PVDF-HFP/TPU/PMMA membranes with and without *in situ* SiO<sub>2</sub>.

membrane without *in situ* SiO<sub>2</sub>), 360% (the membrane with 1% *in situ* SiO<sub>2</sub>), 395% (the membrane with 2% *in situ* SiO<sub>2</sub>) and 415% (the membrane with 3% *in situ* SiO<sub>2</sub>), respectively. After 15 min, it is found that when the electrolyte uptake curves stable, the membrane with *in situ* SiO<sub>2</sub> (2% and 3%) show higher 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 storage protection of *in situ* SiO<sub>2</sub>. From the SEM images of the membranes, we can find that 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. Because *in situ* SiO<sub>2</sub> form a layer of film on the surface of fibrous membranes, which is good to help the absorption of the electrolyte storage, so it has the higher electrolyte uptake percentage, which means more Li/Li<sup>+</sup> exchanging in the same volume. This leads it to have a high ionic conductivity.

Fig. 6 shows the interfacial resistance of the gel polymer electrolytes with and without *in situ* SiO<sub>2</sub>. It can be observed clearly from Fig. 6(a) that the bulk resistance ( $R_b$ ) of the gel polymer electrolytes with 2% *in situ* SiO<sub>2</sub> is 0.71  $\Omega$ . And in Fig. 6(b) the electrolyte with 1% *in situ* SiO<sub>2</sub> has a bulk resistance of 0.88  $\Omega$ . The electrolyte with 3% *in situ* SiO<sub>2</sub> has a bulk resistance of 1.10  $\Omega$  in Fig. 6(c). However, in Fig. 6(d) the electrolyte without *in situ* SiO<sub>2</sub> has a bulk resistance of 1.46  $\Omega$ . We could calculate ionic conductivity by eqn (3), the gel polymer electrolyte film has an ionic conductivity of  $4.2 \times 10^{-3}$  S cm<sup>-1</sup> (GPE without *in situ* SiO<sub>2</sub>),  $6.8 \times 10^{-3}$  S cm<sup>-1</sup> (GPE with 1% *in situ* SiO<sub>2</sub>),  $8.5 \times 10^{-3}$  S cm<sup>-1</sup> (GPE with 2% *in situ* SiO<sub>2</sub>),  $5.5 \times 10^{-3}$  S cm<sup>-1</sup> (GPE with 3% *in situ* SiO<sub>2</sub>), respectively.

From the morphology of the prepared porous electrospun membranes in Fig. 1, it can be seen that there are many interconnected pores in the porous membranes, which help polymer



**Fig. 6** Impedance spectra of gel polymer electrolytes (a) with 2% *in situ* SiO<sub>2</sub> (b) with 1% *in situ* SiO<sub>2</sub> (c) with 3% *in situ* SiO<sub>2</sub> (d) without *in situ* SiO<sub>2</sub>.



membrane absorbs large quantity of liquid electrolyte, then they form a gelled polymer electrolyte together. What's more, 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. And the more uptake of liquid electrolyte, the more  $\text{Li}^+$  in the same volume. As *in situ*  $\text{SiO}_2$  is semi-conductor inorganic nano ions, itself exists body resistance, so a balanced amount of *in situ*  $\text{SiO}_2$  adding can increase absorption of liquid electrolyte and improve the ionic conductivity. So the GPE with 2% *in situ*  $\text{SiO}_2$  has the highest ionic conductivity.

### 3.5 Electrochemical stability

Fig. 7 shows the LSV curves of the gel polymer electrolytes. It is seen that the electrochemical stability of gel polymer electrolyte without *in situ*  $\text{SiO}_2$  is at 5.4 V. With the addition of the *in situ*  $\text{SiO}_2$  fillers, the stability of the gel polymer electrolytes are further enhanced. The gel polymer electrolyte delivers a electrochemical stability of 5.8 V (GPE with 1% *in situ*  $\text{SiO}_2$ ), 5.9 V (GPE with 1% *in situ*  $\text{SiO}_2$ ), 5.6 V (GPE with 3% *in situ*  $\text{SiO}_2$ ). As we can see that the PVDF-HFP/TPU/PMMA gel polymer electrolyte with 2% *in situ*  $\text{SiO}_2$  is shows the best electrochemical stability up to 5.9 V, which is much higher than the requirements of practical applications, rendering it suitable for most of the common cathode materials used in lithium ion batteries. Besides, a decomposition process, which is associated with electrode/electrolyte, results 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 V to 5.9 V for PVDF-HFP/TPU/PMMA gel polymer electrolyte with 2% *in situ*  $\text{SiO}_2$ . The beginning of current flow at 5.9 V represents the decomposition of the lithium electrode. A considerable current began to flow along with further increase of the cell voltage, indicating the onset of electrolyte decomposition process.

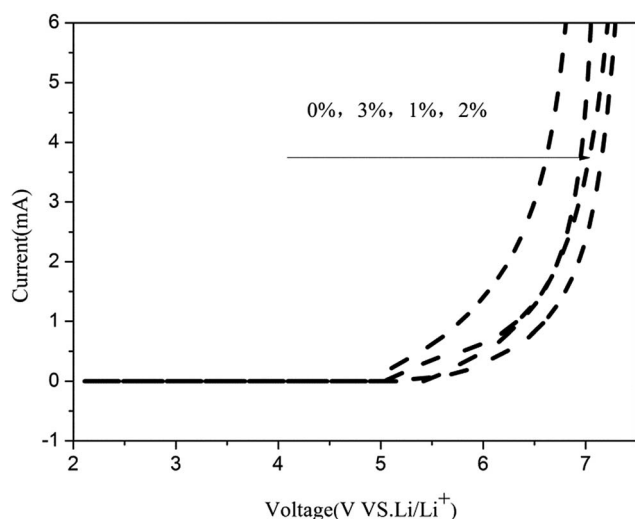


Fig. 7 Linear sweep voltammograms of the gel polymer electrolytes with and without *in situ*  $\text{SiO}_2$ .

Hence, the partial swelling of the *in situ*  $\text{SiO}_2$  membrane with a large surface area significantly contributed to the increase in the stability of the electrolyte solution under electrochemical environments, although the ionic conduction occurred mainly through the entrapped liquid electrolyte in the pore structure. The swollen phase of the membrane probably includes the complex compounds such as associated VDF- $\text{Li}^+$  groups. This complex formation with lithium ion and VDF groups of PVDF-HFP enhances the electrochemical stability of GPEs. The electrochemical stability was also influenced by the high porosity, large and fully interconnected pores. So the gel polymer electrolyte with 2% *in situ*  $\text{SiO}_2$  shows the best electrochemical stability.

The high stability of these polymer electrolytes indicate that they are very suitable for applications in lithium-ion battery.

### 3.6 Mechanical property

Fig. 8 shows the stress-strain curves of the polymer membranes. The test results show that the mechanical properties of membranes are improved with *in situ*  $\text{SiO}_2$  fillers. The PVDF-HFP/PMMA membrane without *in situ*  $\text{SiO}_2$  extended only 62% with a poor breaking tensile strength 6.10 MPa. Referring to the PVDF-HFP/PMMA film with 2% *in situ*  $\text{SiO}_2$  fillers, the membrane has 86.4% elongation and was broken under the 10.8 MPa tensile strength. Both the tensile strength and elongation at break were enhanced. From the SEM images, we can see clearly that there is a *in situ* silica film on the surface of the polymer membrane. Thus 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.

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

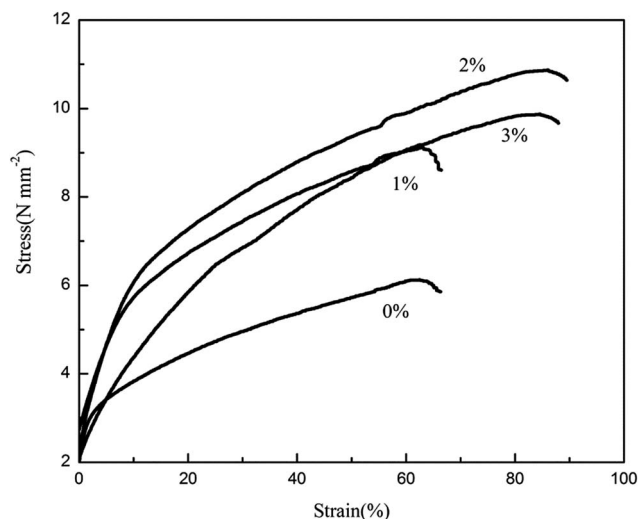


Fig. 8 Stress-strain curves of electrospun PVDF-HFP/TPU/PMMA membranes with and without *in situ*  $\text{SiO}_2$ .



suggests that the membrane with *in situ* SiO<sub>2</sub> fillers is more suitable for application in polymer lithium ion batteries.

### 3.7 Evaluation in Li/LiFePO<sub>4</sub> cell

As active materials LiFePO<sub>4</sub> as cathode has high theoretical capacity 170 mA h g<sup>-1</sup>, the practical applicability of the electrospun fibrous membrane polymer electrolyte is tested in Li/CPE/LiFePO<sub>4</sub> cell. Fig. 9 shows the first charge–discharge capacity curves of Li/GPE/LiFePO<sub>4</sub>. The gel polymer electrolyte film (GPE without *in situ* SiO<sub>2</sub>) delivers a charge capacity of 164.84 mA h g<sup>-1</sup> and discharge capacity of 162.15 mA h g<sup>-1</sup>, while the gel polymer electrolyte film with *in situ* SiO<sub>2</sub> delivers a charge capacity of 166.80 mA h g<sup>-1</sup> (GPE with 1% *in situ* SiO<sub>2</sub>), 168.23 mA h g<sup>-1</sup> (GPE with 2% *in situ* SiO<sub>2</sub>), 166.50 mA h g<sup>-1</sup> (GPE with 3% *in situ* SiO<sub>2</sub>), and discharge capacity of 164.98 mA h g<sup>-1</sup> (GPE with 1% *in situ* SiO<sub>2</sub>), 166.58 mA h g<sup>-1</sup> (GPE with 2% *in situ* SiO<sub>2</sub>), 164.38 mA h g<sup>-1</sup> (GPE with 3% *in situ* SiO<sub>2</sub>), respectively. We can find that the gel polymer electrolyte film with 2% *in situ* SiO<sub>2</sub> own the best charge–discharge capacity, and its first charge–discharge efficiency up to 99% of the theoretical capacity, which means that the cycle efficiency is very high. On the one hand, this may be the result of the compatibility of PVDF–HFP, TPU and PMMA in polymer matrix. At the same time, the membranes with *in situ* SiO<sub>2</sub> have a stable structure, a large number of pores for Li<sup>+</sup> exchanging and high specific surface area in contacting with electrode also make outstanding electrochemical performance.

Upon that we studied the cycle performance of cell with 2% *in situ* SiO<sub>2</sub> at different current rates from 0.1 to 10C illustrated in Fig. 10. At lower current rates (0.1C), the capacity retention is 99.5% after 50 cycles. Even at high-rate of 10C, the capacity retention is as high as 91% and the cell still remains a discharge capacity of 125.03 mA h g<sup>-1</sup> after 50 cycles, which clearly demonstrates high capacity retention of the cells.

The results of evaluation in Li/LiFePO<sub>4</sub> cell indicate the electrochemical performance of composite gel polymer electrolytes with *in situ* SiO<sub>2</sub> is further enhanced. The outstanding

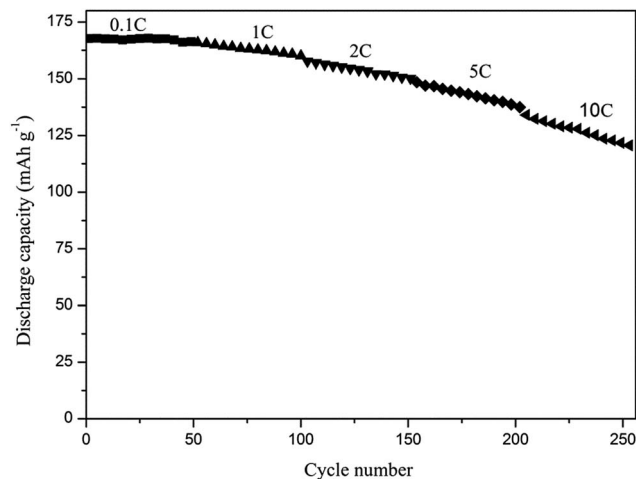


Fig. 10 The cycle performance of cell with 2% *in situ* SiO<sub>2</sub> at different current rates (1C = 170 mA h g<sup>-1</sup>).

electrochemical performance of the cell with *in situ* SiO<sub>2</sub> are attributed to a fairly high liquid electrolyte uptake of fibrous membrane, a high ionic conductivity and no microphase separation of mingling among PVDF–HFP, TPU and PMMA. Beyond that, good electrode/electrolyte interface contact and stable structure also have contributed to excellent cell performance.

## 4. Conclusions

PVDF–HFP/TPU/PMMA based gel polymer electrolytes with and without *in situ* SiO<sub>2</sub> blend/composite membranes were prepared by electrospinning the 11 wt% polymer solution in DMF/acetone (3 : 1, w/w) at room temperature. The gel polymer electrolytes were prepared by activating the dried electrospun nonwoven films in 1 M LiClO<sub>4</sub>–EC/PC liquid electrolyte solutions.

The gel polymer electrolyte with *in situ* 2% SiO<sub>2</sub> has a high ionic conductivity of  $8.5 \times 10^{-3}$  S cm<sup>-1</sup> with electrochemical stability up to 5.9 V versus Li<sup>+</sup>/Li at room temperature. And the first charge–discharge capacity of PVDF–HFP/TPU/PMMA based gel polymer electrolyte with *in situ* 2% SiO<sub>2</sub> lithium battery is 168.5 mA h g<sup>-1</sup>, which is about 99% of the theoretical capacity of LiFePO<sub>4</sub>. The cell shows a very stable charge–discharge behavior and little capacity loss under current constant voltage condition after 50 cycles at the 0.1C-rate at 25 °C, and exhibiting a good compatibility with lithium electrodes. And it has a perfect mechanical stability with high tensile strength (10.8 MPa) and elongation at break (86.4%). Both tensile strength and elongation allow safe operation in rechargeable lithium ion polymer batteries. These results indicated that incorporation of *in situ* generated 2% SiO<sub>2</sub> is more efficient in improving the properties of gel polymer electrolyte for practical application.

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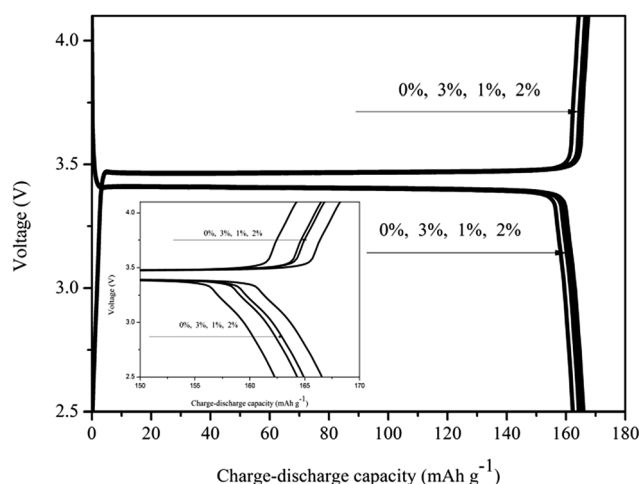


Fig. 9 First charge–discharge capacities of GPEs based on electrospun membrane with and without *in situ* SiO<sub>2</sub>.





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