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# Polyethylene terephthalate/poly (vinylidene fluoride) composite separator for Li-ion battery

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#### Abstract

Electrospun nanofiber membranes have been proved to enhance performances of Li-ion batteries, but their poor mechanical strength hinders their industrial application. This paper combines meltblown polyethylene terephthalate (PET) nonwoven and electrospun poly (vinylidene fluoride) (PVDF) membrane together to improve the mechanical property via hot-pressing, wherein a dried 3 wt% PVDF solution coating on PET nonwoven is used as a binder. The hot-pressing temperature is optimized to be 145 °C and the composite PET/PVDF separator exhibits an excellent mechanical property, whose transverse and longitudinal tensile strength could reach 13.70 and 34.85 MPa respectively. Compared with a commercial PP separator, the hot-pressed PET/PVDF membrane separator shows better wettability, higher thermal shrinkage and improved electrochemical performance as well.

Keywords: PET nonwoven, electrospun PVDF membrane, hot-pressing, composite separator

(Some figures may appear in colour only in the online journal)

#### 1. Introduction

Rechargeable Li-ion batteries (LIBs) are in greatly growing demand in portable electronics (cell phones, cameras and laptops etc) and hybrid/all electric vehicles due to their high energy density, high operational voltage and long cycle life [1, 2]. As a critical component of LIBs, a separator greatly influences the specific discharge capacity, cycle life, safety performance of battery and so on [3]. It can not only keep the positive and negative electrodes apart to prevent electrical short circuits, but also allows rapid transport of the ionic charge carrier [4]. Currently, most commercial separators are generally based on polyethylene (PE), polypropylene (PP) and their composite PP/PE/PP, which are manufactured by stretching polymer film through a dry or wet process [5]. Such fabrication methods and the nonpolar and hydrophobic properties of polyolefin membranes have led to serious concerns, such as a low porosity of less than 50%, poor wettability in liquid electrolytes and weak thermal stability [6, 7]. In order to meet much more rigorous requirements in harsh application environments, tremendous attempts are being made to seek other novel techniques to develop porous polymeric separators to circumvent these limitations. Meanwhile numerous methods such as solvent casting [8], plasticizer extraction [9, 10], phase inversion [11], and electrospinning [12, 13] have been utilized to ameliorate the property of porous polymer membranes. Electrospinning is versatile and considered to be an ideal candidate method to fabricate porous nanofiber membranes. Until now, many polymeric materials including polyacryonitrile (PAN), polyimide (PI), polyvinylidene fluoride (PVDF), polyethylene terephthalate (PET) and so on have been electrospun to be used as separators for LIBs and the electrospun membranes are characterized as of high porosity, high ionic conductivity with electrolyte and excellent electrolyte uptake etc [14, 15]. In the midst of them, PVDF membrane has drawn researchers' attention because of its high dielectric constant, good electrochemical stabilities and excellent affinity to an electrolyte solution [7, 16]. However, its weak mechanical strength is still a challenge and hinders its practical applications. Ding et al [17] introduced a mixed solute of PVDF-HFP/PMMA for electrospinning a blend membrane and the mechanical strength could be improved from 6MPa to about 8.5MPa. Liang et al [16] verified that the preferred heat treatment temperature about 160 °C could enhance PVDF fibrous membrane's mechanical strength from about 3 to 9.2 MPa. Chen et al [18] prepared a bicomponent PVDF-HFP/PI membrane via a cross-electrospinning method. The mechanical property of the composite membrane could be strengthened from 2 to 7.5 MPa followed by thermal calendaring process.

In this paper, a bistratal composite membrane is introduced to improve the mechanical property, in which a meltblown PET nonwoven and an electrospun PVDF membrane are adhered together via hot-pressing. The PET nonwoven with excellent mechanical property is chosen as the structural support. Before hot-pressing, PET has been coated with PVDF under room temperature to solve the poor adhesion compatibility with PVDF membrane. Then the morphology, porosity, electrolyte uptake, wettability, thermal shrinkage and electrochemical performance of the composite PET/PVDF separator for LIBs are investigated. As a result, the composite membrane exhibits high mechanical property, thermal stability and superior battery performances compared with commercial PP or PE separator.

#### 2. Experimental

#### 2.1. Preparation of PET/PVDF composite separator

PVDF (Mw ~ 500000, Sensure, Shanghai) was respectively dissolved into a binary solvent system with N, N-Dimethylformamide (DMF) and acetone at equal volume ratio and a simplex solvent of DMF. The former solution with 16% concentration was used for electrospinning PVDF nanofibers and the latter with 3% concentration was used as a binder solution. PET nonwoven was from Foshan Jinhui Co., Ltd.

As depicted in figure 1, the electrospinning setup includes a high voltage power supply (GAMMA, USA), a precision pump (Harvard, USA), a syringe (2 mL) and a grounded collector attached to XY moving platform (Googol, Shenzhen, China). The solution rate, working distance and the bias voltage were set to be  $100 \mu L Hr^{-1}$ , 10 cm and 10 kV respectively to obtain PVDF nanofibers with uniformity diameter. During the electrospinning process, the moving platform moved back and forth at a speed of 40 cm min<sup>-1</sup> in the X-axial direction with a moving displacement of 12 cm and moved



Figure 1. Schematic diagram of electrospinning setup.

periodically 16 cm in the *Y*-axial direction for better distribution uniformity of nanofibers.

PET was coated with a thin layer of 3% PVDF solution using a slicker and then dried under room temperature. And finally these two membranes were attached together through two heat rollers at a speed of  $2 \text{ mm s}^{-1}$  as illustrated in figure 2.

#### 2.2. Characterization

The morphologies of PET nonwoven and PVDF nanofiber membrane before and after hot-pressing were investigated by scanning electron microscopy (SEM 1530, Germany; S-4800, Hitachi, Japan) after sputtering a thin layer of gold. The cross sectional views of the hot-pressed PET/PVDF membranes were prepared by a sharp knife. The mechanical properties of the membranes were operated on a universal testing machine (UTM 4000, SUNS, Shenzhen). The adhesion strength tests were conducted on tensile testing machine (SHIMADZU, Japan). The contact angle of the membrane's surface was performed on JC2000C1 (Powereach, Shanghai). The dimensional stability of the membranes was determined by thermal shrinkage tests at different temperatures 150 °C for 30 min in the incubator.

The ionic conductivity was measured by an ac impedance spectroscopy using electrochemical workstation (AUT84892, Metrohm) to estimate the influence of separator on internal resistance of batteries. To investigate electrochemical properties of battery with PET/PVDF separator, CR2016 coin cell, Li/separator and electrode/LiMn<sub>2</sub>O<sub>4</sub> were employed and assembled in glove box. The electrolyte LB-303, consisting of EC/DEC/DMC 1:1:1 (v/v/v) and 1 mol L<sup>-1</sup> LiPF<sub>6</sub>, was purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. (Jiangsu, China). The positive electrode consisting of 90 wt% LiMn<sub>2</sub>O<sub>4</sub>, 5 wt% acetylene black and 5 wt% PVDF were coated on aluminum foils, and lithium metal played the role of the counter electrode. And then the cycling performance at 0.5 C rate and rate capacity of the cells were conducted in the LAND multi-channel battery tester (Wuhan, China).



Figure 2. Schematic diagram of hot-pressing.



**Figure 3.** Fiber diameter distributions and their SEM images before hot-pressing. (a) original meltblown PET nonwoven and (b) electrospun PVDF nanofibers.



Figure 4. SEM image of PET coated with dried PVDF binder.

#### 3. Results and discussions

#### 3.1. Morphology

From the SEM images of PET and PVDF in figure 3, it can be found that the average diameter of meltblown PET fiber is about  $17.71 \,\mu$ m, which is much larger than  $356.9 \,\text{nm}$  in diameter of electrospun PVDF nanofiber. The large diameter and meltblown process lead to great mechanical performance. But the large interstices of PET as seen in inset figure 3(a) may cause a short circuit between electrodes in LIB. This is the reason why PET is unsuitable to be the separator of LIB in spite of its robust mechanical performance. On the contrary, the distribution and porosities of PVDF membrane are more uniform than that of PET as described in figure 3(b). So the combination of PET and PVDF via roll compacting can admirably remedy shortcomings of each other.

Figure 4 shows that the dried PVDF binder attaches to PET fibers and especially many large fragments of residual PVDF binder lie in the large micropores of PET. Furthermore, there also are many mini pores in the PVDF binder. The introduction of PVDF binder helps to not only modify pore-size distribution of PET, but also boosts the adhesion strength between PET and PVDF membranes after hot-pressing.

Based on our previous work and reference 16, hotpressing temperature greatly affects the morphology of PVDF nanofibers. Only when the temperature is raised up



**Figure 5.** SEM images of PET/PVDF membranes after hot-pressing treatment under different temperature. (a), (d) and (g) are the contact surface morphologies of PET; (b), (e) and (h) are the surface morphologies of PVDF membranes; (c), (f) and (i) are the cross-section views. The numbers of 140, 150 and 160  $^{\circ}$ C are the corresponding treatment temperatures respectively.



**Figure 6.** SEM images of the composite membrane after hotpressing treatment. (a) PVDF surface; (b) cross sectional view. The treatment temperature is 145 °C.

to 140 °C, could the PET/PVDF possibly exhibit a good mechanical performance. But the heating temperature over 170 °C makes PVDF nanofibers melt together and most



**Figure 7.** Transverse and longitudinal tensile strength of original PET, hot-pressed PVDF and hot-pressed PET/PVDF in 145 °C. The thickness of PET, PVDF and PET/PVDF are 36, 12 and  $42 \,\mu$ m respectively.

micropores disappear. The electrolyte uptake of PVDF membrane will sharply decrease. If the membrane forms a pore-free layer, it will lose its function of free ionic transport. Thus the hot-pressing was performed in three different temperatures including 140, 150 and 160 °C. When the hot-pressing temperature was 140 °C, the adhesion between



Figure 8. Contact angle of separator's interface: (a) PP; (b) PVDF; (c) PET/PVDF.

PET and PVDF membranes was very weak and they could be separated easily. It can be seen in figures 5(a)-(b) that PVDF membrane surface appears only pressing brands of superficial PET fibers and there is almost no residual PVDF binder. In many places separation between PVDF and PET membranes can be observed from the cross-section view in figure 5(c). Therefore the hot-pressing temperature of 140 °C is not high enough to bond them. While the temperature was increased to 150 °C, PET and PVDF membranes could be adhered together tightly and PVDF binder begins to melt and collapse in the partial regions as seen in figures 5(d)-(f). Even in some regions, micropores are closed down under the pressure of thermal calendaring process. Figures 5(g)-(i) show that more obvious phenomenon can be found when the temperature is 160 °C. Then the hot-pressing temperature is chosen to be  $145 \,^{\circ}$ C. Figure 6(a) depicts that some PVDF binder has been transferred to PVDF membrane and the PET and PVDF membranes cling to each other from the cross sectional image in figure 6(b). It is believed that they might be tightly adhered together and the adhesion strength of 64.7 kPa proves it. Therefore hot-pressing temperature is set to 145 °C in the following study.

#### 3.2. Mechanical property

Mechanical property is very important in separator applications. The excellent mechanical property can enhance the separator's capacity of resistance to the puncture from lithium dendrites. As seen in figure 7, the mechanical strength of PVDF and PET/PVDF membrane are greatly enhanced by the hot-pressing process in 145 °C. And the process causes tensile strength difference between that along and perpendicular to the hot-pressing direction (that is, longitudinal and transverse). It makes the longitudinal tensile strength higher than the transverse tensile strength. In addition, the composite membrane can respectively achieve 13.70 and 34.85 MPa in transverse and longitudinal directions. It profits from the robust PET and the bonding structure formed between the adjacent layers. The mechanical property is considered to be sufficient to use in LIB [19].

#### 3.3. Porosity, wettability and electrolyte uptake

The porosity (P) of a separator is a key parameter because it affects the electrolyte uptake and ionic conductivity [13]. The



**Figure 9.** Photographs of PP, PVDF and composite PET/PVDF membrane (a) before and (b) after exposure to 150 °C for 30 min.

n-butanol uptake method is used to analyze the porosity and it is calculated as [20]:

$$P(\%) = M_{\rm BuOH} / (\rho_{\rm BuOH} \times (M_{\rm BuOH} / \rho_{\rm BuOH} + M_{\rm p} / \rho_{\rm p})) \times 100\%$$
(1)

where  $M_{\text{BuOH}}$  and  $M_{\text{P}}$  represent the mass of the absorbed n-butanol and polymer, respectively, while  $\rho_{\text{BuOH}}$  and  $\rho_{\text{P}}$  represent the densities of n-butanol and polymer, respectively. Then the porosity of the membrane was tested to be about 51.4%, which is higher than 40–45% of commercial separators.

The excellent wettability can retain the electrolyte enduring and facilitate an electrolyte to diffuse smoothly in the LIB [3]. The contact angle of the separator is used to characterize the separator's wettability in electrolyte. The angle was measured at three seconds after a drop of electrolyte contacted the interface of separator. Figure 8 shows that the contact angle of PP is 28.2° and the contact angles of PVDF and PET/PVDF are zero because the electrolyte has been soaked completely into PVDF and PET/PVDF membranes. It can be concluded that PVDF and PET/PVDF membranes are easier to absorb the electrolyte than PP separator. The phenomenon benefits from the inherent excellent affinity to electrolyte solutions of PVDF polymers. Thus, it can be concluded that PET/PVDF composite membrane possesses a good wettability, which can accelerate the infiltration of electrolyte.



**Figure 10.** (a) The holding devices for ionic conductivities test of separators; ac impedance spectroscopy of PP (b) and PET/PVDF (c) at room temperature. The thickness of PP and PET/PVDF separators are 16 and  $42 \mu m$  and the diameter of copper is 16 mm.



**Figure 11.** The cycling performance of CR2016 Li/LiMn<sub>2</sub>O<sub>4</sub> coin cells containing commercial PP membrane and hot-pressed ( $145 \,^{\circ}$ C) PET/PVDF composite membrane. The charging/discharging current is 0.5 C and the electrolyte is LB-303.

The electrolyte uptake (EU) can be computed as:

$$EU(\%) = (W - W_0)/W_0 \times 100\%$$
(2)

where  $W_0$  and W represent the mass of the dry membrane and wet electrolyte-absorbed membrane, respectively. Three samples were tested and the average electrolyte uptake was 124%.

#### 3.4. Thermal shrinkage

Many microporous membranes often cannot resist shrinkage at elevated temperature, which may generate a serious safety concern when it has been applied in LIB. Only little thermal shrinkage, less than about 2%, is permitted to prevent internal short circuit under corresponding running temperature. Figure 9 compares the photographs of PP membrane, PET and composite PET/PVDF membrane before and after thermal exposure at 150 °C for 30 min. The traditional PP membrane melts down with the color change from white to transparent and shrinks greatly. And the PVDF membrane shrinks about 15% due to its low melting point (about 170 °C). But the PET/PVDF membrane is able to maintain its shape (only shrinks about 1.1%), revealing excellent heat resistance due to the adoption of high temperature tolerant PET. Obviously, the commercial PP separator can not maintain its original morphology when the temperature is 150 °C while PET/PVDF membrane can maintain its mechanical integrity at the same temperature for better thermal stability due to the higher melting temperatures of PVDF and PET.

#### 3.5. Ionic conductivity and battery performance

The ionic conductivity of separator with electrolyte at room temperature was measured by the ac impedance spectroscopy over the frequency ranging from 10<sup>5</sup> to 1 Hz with 5 mV of ac amplitude. As shown in figure 10(a), a sandwiched copper/ separator/copper structure was employed during the measurements. The figures 10(b) and (c) present the Nyquist curves of the liquid electrolyte-soaked PP and PET/PVDF separator. The resistance of a separator saturated with an electrolyte can be obtained from the intercept of Z' axis. For comparison, impedance spectroscopy intercept of PP separator and the composite separator are 2.2 and 2.5 Ohm respectively. But the ionic conductivity of the PET/PVDF composite separator with electrolyte can be improved to  $8.36 \,\mathrm{mS \, cm^{-1}}$ , which is higher than that of the PP separator  $(3.62 \,\mathrm{mS \, cm^{-1}})$ . The results manifest that the relatively higher ionic conductivity of the composite membrane with electrolyte depends on fully interconnected pore structure of PET and PVDF membranes, and the PVDF excellent affinity to electrolyte solutions.

Additionally, CR2016 coin cell using hot-pressed PET/ PVDF membrane as separator was assembled and evaluated in order to investigate the feasibility of the composite membranes in lithium ion battery. Cell with commercial PP membrane was also tested for comparison. The positive electrode composed of  $90\,wt\%\,LiMn_2O_4, 5\,wt\%$  acetylene black and  $5\,wt\%\,PVDF\,cov$ ered on aluminum foil. The counter electrode was lithium metal and the electrolyte LB-303 consisted of EC/DEC/DMC 1:1:1 (v/v/v) and  $1 \mod L^{-1} \operatorname{LiPF_6}$ . The cell cycling performance was measured in 100 cycles at 0.5 C rates. As shown in figure 11, the initial capacity of PP membrane is  $110.51 \text{ mAh g}^{-1}$  and the value for PET/PVDF membrane is  $112.55 \text{ mAh g}^{-1}$ . At the end of 100 cycles, the capacity retentions of cells containing commercial PP membrane and PET/PVDF composite membrane are 93.56 and 96.94% respectively. The improvement in the cycling performance of the composite membranes may be partially ascribed to its better wettability in electrolyte and higher ionic conductivity. The rate capacity was also characterized by charging the cells to 4.2V and discharging them at different current rate ranging from 0.2 to 4C of 6 cycles each to 3.6V in



**Figure 12.** The rate performance of the Li/  $LiMn_2O_4$  cells with hotpressed PET/PVDF composite membrane and PP membrane. The electrolyte is LB-303.

sequence. Figure 12 shows that the cell with PET/PVDF membrane has higher average discharge capacity of 114.63 mAh g<sup>-1</sup> at 0.2 C than 112.61 mAh g<sup>-1</sup> from the cell with the PP separator. When the current rate was changed to 4 C, the discharge capacity retention ratio of the cells with PET/PVDF and PP separator is 87.4% and 86.7% respectively. Furthermore, the cell with the PET/PVDF membrane has higher discharge capacity than those of cells using the PP separators in all tests.

#### 4. Conclusion

A bistratal composite membrane composed of PET nonwoven and PVDF nanofibrous membrane was adhered successfully by hot-pressing treatment at 145 °C, using PVDF coating on PET nonwoven as binder. The morphology, mechanical property, wettability, thermal shrinkage, ionic conductivity and battery performance of the composite membrane was tested. The results exhibit that the mechanical property of PET/ PVDF composite membrane could be enhanced dramatically by the hot-pressing treatment. Specially, transverse and longitudinal tensile strength of PET/PVDF could reach 13.70 and 34.85 MPa respectively. In addition, compared with commercial PP separator, better wettability, higher thermal property, prominent ionic conductivity and improved electrochemical performance were achieved. Therefore, PET/PVDF composite membrane can be a promising candidate for separators of LIBs.

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