



Preparation of PVDF/PMMA blend microporous membranes for lithium ion batteries via thermally induced phase separation process

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ARTICLE INFO

Article history:

Received 31 January 2008

Accepted 24 April 2008

Available online 29 April 2008

Keywords:

Polymers

Thermally induced phase separation

Porosity

ABSTRACT

Thermally induced phase separation (TIPS) process was employed to prepare microporous poly (vinylidene fluoride)/poly (methyl methacrylate) (PVDF/PMMA) blend membranes using sulfolane as the diluent. Then they were immersed in liquid electrolyte to form polymer electrolytes. The effect of PMMA on the morphology and the crystallinity of blend membranes was studied. It was found that phase separation between PVDF and PMMA occurred when PMMA content was 40 wt.%. The addition of PMMA increased porosity and decreased the crystallinity, which in turn enhanced electrolyte uptake of blend membrane and the ionic conductivity of corresponding polymer electrolyte. The maximum ionic conductivity was $2.45 \times 10^{-3} \text{Scm}^{-1}$ at 20 °C.

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1. Introduction

PVDF has been widely used as the polymer matrix (or membrane) of polymer electrolyte in lithium ion batteries due to its appealing properties [1]. Polymer matrix is usually prepared by immersion precipitation process [2]. However, there are many factors influencing porous structure, which makes this process more difficult in controlling membrane structure. TIPS process is another method to prepare microporous membranes [3]. In this process, a polymer is dissolved in a diluent at high temperature, and then the solution is quenched to induce phase separation. Finally, the diluent is extracted to yield a microporous structure. Compared with immersion precipitation process, the main advantage of TIPS process is the ease of controlling membrane structure because of fewer factors influencing porous structure [4].

Ji et al. [5] have shown that TIPS process is a valid method to prepare PVDF matrix used as polymer electrolyte. However, in order to further increase conductivity, some measures should be taken. Blending with amorphous polymer is a good strategy for suppressing the crystallinity and enhancing the ionic conductivity [6]. Among them, PMMA is a suitable candidate when blended with PVDF. Ma et al. [7] have studied the effect of PMMA on crystallization behavior of PVDF/PMMA system. Rajendran et al. [8] have discussed the role of interaction between PVDF and PMMA on conductivity.

So far there have no studies on PVDF/PMMA blend membrane prepared via TIPS process. The main difficulty may be the choice of diluent. It has been suggested that sulfolane can be used as the diluent for PMMA [9] and PVDF [10], so sulfolane was chosen as the diluent to

prepare PVDF/PMMA blend membranes via TIPS process in this work. The effect of PMMA on the morphology and the crystallinity of blend membranes was studied. Ionic conductivity of corresponding polymer electrolytes was also investigated.

2. Experimental

Commercial PVDF ($M_w = 5.73 \times 10^5$, Solvay Silexis) and PMMA ($M_w = 1.04 \times 10^5$, Taiwan) were used as received. Sulfolane (chemical pure grade) was used as the diluent. Liquid electrolyte was made by dissolving 1 mol l^{-1} LiPF_6 in dimethyl carbonate/ethyl methyl carbonate/ethylene carbonate. (1/1/1, wt/wt/wt).

The total weight of PVDF and PMMA was kept at 25 wt.%, while the weight ratio of PVDF/PMMA was varied. PVDF, PMMA and sulfolane were mixed at 180 °C under nitrogen atmosphere for 4 h, and then quenched in liquid nitrogen to solidify the sample. The solidified sample was chopped in small pieces and compressed in a mold at 180 °C to form film, the mold was quenched in ice-water and then sulfolane in film was extracted with deionized water. The final blend

Table 1

Preparing condition and property parameters of blend membranes and polymer electrolytes

Code	Blend membrane					Polymer electrolyte
	PVDF/PMMA (wt/wt)	ΔH (J/g)	X_c (%)	ρ (%)	ΔW (%)	Code
M1	100/0	45.5	43.5	45.4	123.9	E1
M2	80/20	34.4	41.1	49.3	138.8	E2
M3	60/40	18.0	28.7	53.5	167.8	E3

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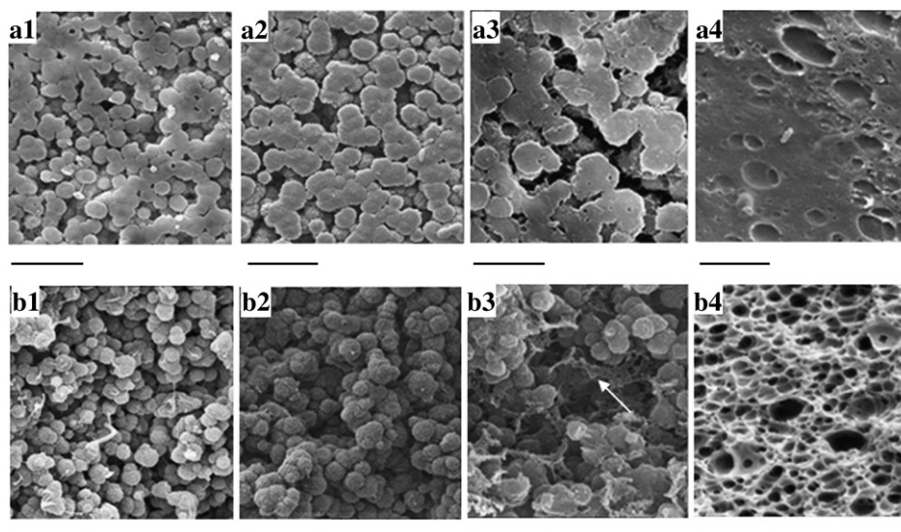


Fig. 1. SEM photographs of blend membranes (a) surface section; (b) cross section. 1, 2, 3, 4 represented M1, M2, M3 and PMMA membrane. The bar is 5 μm .

membranes were dried under vacuum at 50 $^{\circ}\text{C}$ for 24 h. Polymer electrolytes were obtained by immersing blend membranes in liquid electrolyte for 4 h. The composition of blend membranes and corresponding polymer electrolytes were listed in Table 1.

The morphology of blend membranes was observed by SEM (Sirion-100). The crystallinity (X_c) of blend membranes was studied using DSC (Perkin-Elmer DSC-7) and calculated from $X_c = (\Delta H / \Delta H_m \phi) \times 100\%$. Here, ΔH and ΔH_m (104.7 J/g [5]) represent the fusion enthalpy of blend membrane and PVDF with 100% crystallinity, respectively, ϕ is the weight fraction of PVDF. Porosity (ρ) of blend membrane was evaluated using a mercury porosimeter (Auto Pore IV9500, Micromeritics). Electrolyte uptake (ΔW) was calculated from $\Delta W = (W_i - W_o) / W_i \times 100\%$. Here, W_o and W_i is the weight of blend membrane and corresponding polymer electrolyte, respectively. The ionic conductivity (σ) was measured by sandwiching polymer electrolyte between two stainless steel (SS) electrodes and calculated from the AC impedance, using a Solartron SI 1255B frequency response analyzer combined with an SI 1287 electrochemical interface. The frequency range is 1 ~ 100 kHz.

3. Results and discussion

Fig. 1 shows the morphology of blend membranes. For pure PVDF microporous membrane (M1), it can be seen that there were pores on surface layer. Spherulites formed

by PVDF crystallization were observed from the cross section, which is the typical structure formed by solid–liquid phase separation. For pure PMMA microporous membrane, only cellular structure, a typical structure formed by liquid–liquid phase separation, was observed. For blend membrane containing 20 wt.% PMMA (M2), only spherulites were detected. This suggests that no discernable phase separation occurred. However, as PMMA content increased to 40 wt.% (M3), non-spherulitic PMMA phase (as shown with arrow) was found between PVDF spherulites. This indicates that phase separation between PVDF and PMMA occurred. This is because during TIPS process, PVDF crystallizes from the PVDF/PMMA/sulfolane system. Generally, amorphous PMMA will be excluded by PVDF crystallization. However, when PMMA content is low (M2), the miscibility between PVDF and PMMA is relative good, which results PMMA possibly resides between lamellae, fibrils, spherulites of PVDF crystallization or their combinations [7], and thus no other structure but PVDF spherulites can be found. When PMMA content is high (M3), the miscibility between PVDF and PMMA depresses and part of PMMA is excluded.

Fig. 2 shows that the endotherm peak became broad and shifted towards lower temperature with PMMA content increasing. This suggests that crystal growth of PVDF is affected by the interaction between PVDF and PMMA. This interaction will in turn decrease the crystallinity. As shown in Table 1, the crystallinity was 43.5%, 41.1% and 28.7% respectively when PMMA content was 0, 20 and 40 wt.%.

Fig. 3 shows the temperature dependence of the ionic conductivity of polymer electrolyte over the temperature range of 0 ~ 80 $^{\circ}\text{C}$. The conductivity at 20 $^{\circ}\text{C}$ was 1.69×10^{-3} , 1.98×10^{-3} and $2.45 \times 10^{-3} \text{Scm}^{-1}$ respectively as PMMA content was 0, 20 and 40 wt.%. The conductivity value of E1 ($1.69 \times 10^{-3} \text{Scm}^{-1}$) presented in this work is much higher than the value of $0.72 \times 10^{-3} \text{Scm}^{-1}$ [11] for PVDF matrix prepared by immersion precipitation process. The higher conductivity is most likely from the following sources. (1) Pores formed between spherulites are well-interconnected. (2) Porosity and amorphous domain (composing excluded PMMA and amorphous section of PVDF) increase with PMMA content increasing.

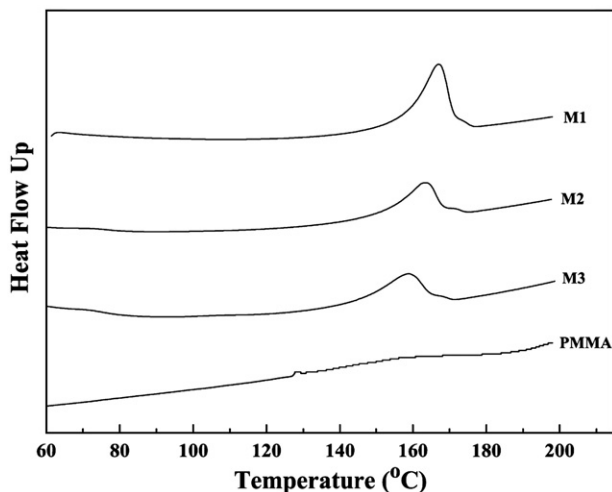


Fig. 2. DSC curves of blend membranes.

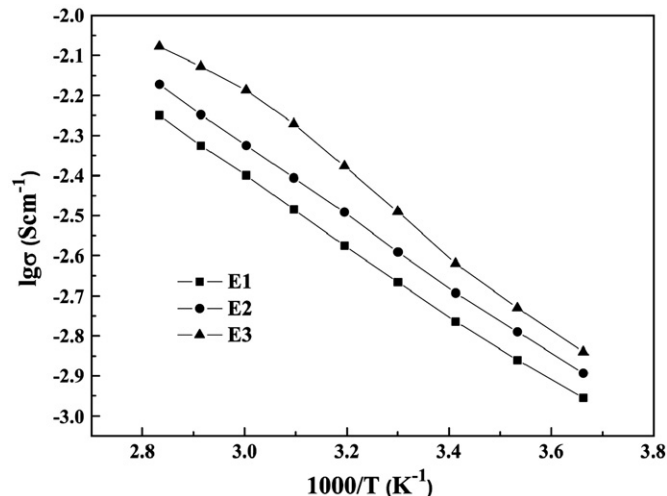


Fig. 3. Temperature dependence of the ionic conductivity for polymer electrolytes.

Generally, ionic conductivity is governed by the content of carrier ions and their mobility. A mechanism for the ionic conduction in the polymer electrolytes along pores filled with liquid electrolyte and a swelled amorphous polymer phase has been postulated [2]. Well-interconnected pores formed between spherulites are good for fast transport of Li^+ when pores are filled by liquid electrolyte. The increase of porosity (from 45.4% to 53.6%, as shown in Table 1) and amorphous domain enhances electrolyte uptake (from 123.9% to 167.8%, as shown in Table 1), and thus increases the content of carrier ions, which in turn increases ionic conductivity.

Ionic conductivity increased as temperature increased. This is a typical behavior of lithium polymer electrolyte. Moreover, two kinds of pattern were shown in plot. (1) For polymer electrolyte containing no or low PMMA content, i.e., E1 and E2, the $\lg\sigma \sim 1/T$ showed a linear variation and followed Arrhenius-type behavior. (2) For polymer electrolyte containing high PMMA content, i.e., E3, a slightly curved relation was observed, which indicates that the temperature dependence of ionic conductivity could be described by the VTF (Vogel–Tammann–Fulcher) equation. This can be ascribed to the influence of excluded PMMA, because PMMA will form plasticizer-rich phase after being swelled by liquid electrolyte. The ion transport mechanism in plasticizer-rich phase is governed by the free-volume. The contribution of free-volume to ionic conductivity leads to curved relation between $\lg\sigma$ and $1/T$ [8].

4. Conclusions

PVDF/PMMA blend membranes were prepared via TIPS process. Phase separation between PVDF and PMMA occurred when PMMA content reached 40 wt.%. The addition of PMMA increased porosity

and increased the crystallinity, which in turn enhanced electrolyte uptake and the ionic conductivity. The plot of $\lg\sigma \sim 1/T$ showed that an ion transport changed from Arrhenius-type to VTF-type with PMMA content increasing.

Acknowledgements

This work is supported by the National Nature Foundation of China (No. 50433010).

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