PVDF–PEO blends based microporous polymer electrolyte: Effect of PEO on pore configurations and ionic conductivity

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Abstract

A novel microporous polymer electrolyte based on poly(vinylidene fluoride) and poly(ethylene oxide) (PVDF–PEO) blends was prepared by a simple phase inversion technique, in which the addition of PEO can obviously improve the pore configuration, such as pore size, porosity, and pore connectivity of PVDF-based microporous membranes, and hence, the room temperature ionic conductivity was greatly enhanced. The highest porosity of about 84% and ionic conductivity of about 2 mS cm^{-1} can be obtained when the weight ratio of PEO to PVDF is 50%. This implies that PVDF–PEO blends based microporous polymer electrolyte can be used as candidate electrolyte and/or separator material for high-performance rechargeable lithium batteries.
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Keywords: Microporous polymer electrolyte; PVDF–PEO blends; Pore configuration; Ionic conductivity

1. Introduction

The rapid development of new technologies such as cell phones, notebook PC, and electric vehicles (EV) has promoted research aimed at improving battery performance with a special effort devoted to lithium batteries [1–3]. Rechargeable lithium batteries (RLBs) using polymer electrolytes instead of traditional liquid electrolytes are well adapted to various geometries and are cost competitive and safe compared with lithium ion batteries (LIBs) [1]. At present, polymer electrolytes mainly include three kinds [4–6]: solid polymer electrolytes (SPEs) [7–12], gel polymer electrolytes (GPEs) [13], and microporous polymer electrolytes (MPEs) [14–19]. From the aspect of industrialization, MPEs have significant advantages due to its high ionic conductivity and excellent mechanical properties [14,15].

In 1994, Bellcore developed the microporous membrane based on PVDF–HFP copolymer, which showed favorable ionic conductivity (∼1 mS cm^{-1}) at room temperature after soaking with liquid electrolyte [16]. However, the dibutyl phthalate (DBP) extraction step is inconvenient, since it increases the cost of the process and presents safety concerns related to handling of large volume of volatile solvents [16,17]. To overcome this shortcoming, the phase inversion method, for which a microporous polymer matrix can be prepared by casting a polymer solution and evaporating the solvent and non-solvent in turn, was developed and has been used successfully to prepare PVDF–HFP copolymer based microporous polymer electrolytes [17]. In this work, a novel MPE based on the blends of poly(vinylidene fluoride) and poly(ethylene oxide) (PVDF–PEO) was prepared by phase inversion technique, in which the addition of PEO can obviously improve the pore configuration, such as pore size, porosity, and pore connectivity of PVDF-based microporous membranes, and consequently, the room temperature ionic conductivity was greatly enhanced.

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2. Experimental

Chaput et al. have reported that PVDF and PEO performed immiscible polymer blends [20]. However, in our previous study [21], we found PEO, PVDF, and glycerin can form homogeneous solution in DMF at temperature higher than 70 °C. On the contrary, when temperature is lower than 70 °C, phase separation can be observed.

PVDF–PEO blends microporous membranes were prepared by a phase inversion technique. PVDF ($M_w = 900,000$ obtained from Shanghai San Ai New Material Co., Ltd.) and PEO ($MB_{wB} = 1,000,000$ obtained from Shanghai Liansheng Chem. Tech. Co., Ltd.) were dissolved in a mixture of DMF (solvent) and glycerin (non-solvent) (v/v = 10/1). After strongly stirring for 3–4 h at 80 °C, the resulting homogeneous solution were cast onto a glass plate, and then placed in an oven at 120 °C for 24 h. In the drying process, solvent (DMF) and non-solvent (glycerin) evaporated in turn, and the location of glycerin formed micro-pores. Finally, we obtained white freestanding membranes with thickness ranging from 100 to 150 μm. TG analysis confirmed that both solvent and non-solvent evaporated completely during above preparing process. Elemental analysis results show that the microporous membrane has the same composition (PVDF and PEO) as the starting mixture. The blends microporous membranes used in this study was denoted as PVDF–x%PEO, in which the weight ratio of PEO to PVDF ranged from 10 to 80%.
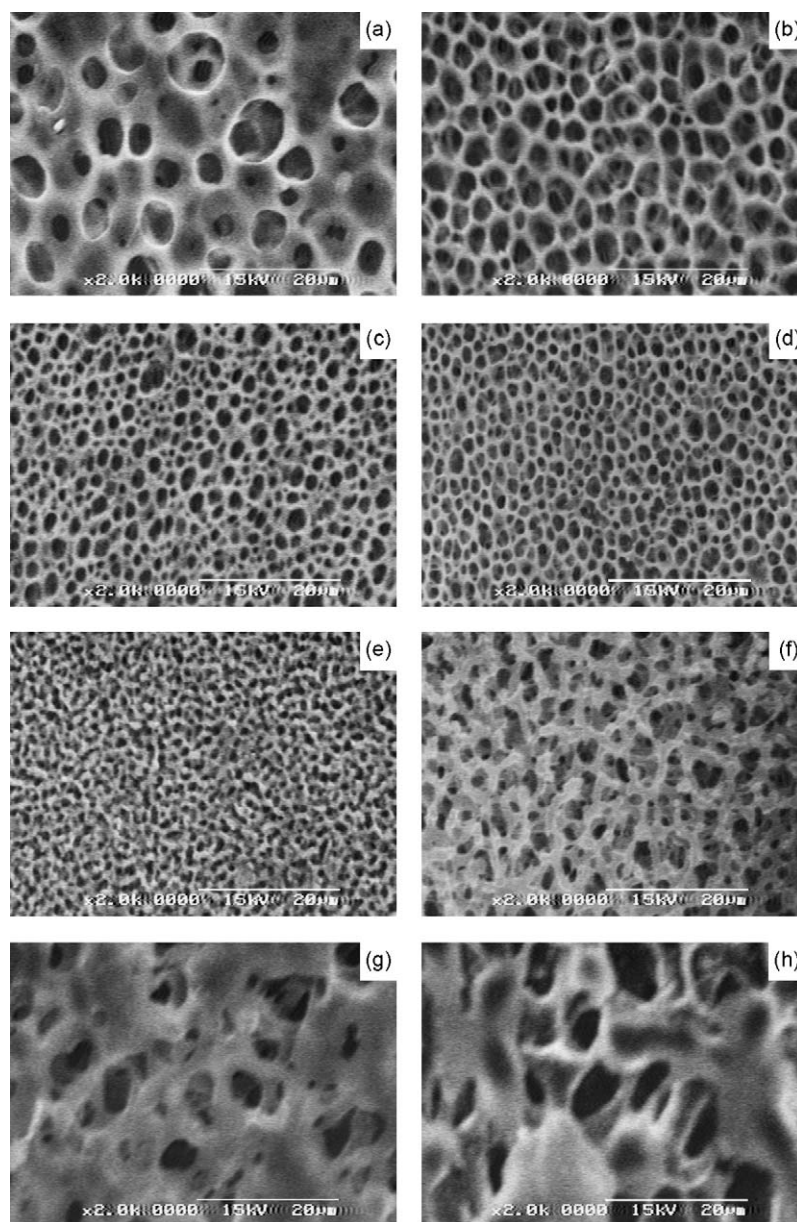

Fig. 1. Surface SEM images of pure PVDF (a) and PVDF–x%PEO blends membranes: (b) $x = 10$; (c) $x = 20$; (d) $x = 40$; (e) $x = 50$; (f) $x = 60$; (g) $x = 70$; (h) $x = 80$.

Pore distribution and pore structure in the surface and bulk of PVDF–x%PEO blends microporous membranes were studied by scanning electron microscopy (SEM) using Hitachi S-2150 instrument with gold sputtered coated films. To observe the cross-section of the samples, the PVDF–x%PEO blends microporous membranes were broken in liquid nitrogen.

The liquid electrolyte uptake of PVDF–x%PEO blends microporous membranes was measured as a function of dipping time in $1\,\mathrm{mol\,L^{-1}}$ LiClO$_4$/PC solution and calculated as follows:

$$\text{Weight uptake } (\%) = 100 \times \frac{w_\mathrm{t} - w_0}{w_0}$$

where w_t and w_0 are the weight of the wet and dry membrane, respectively.

Porosity of PVDF–x%PEO blends microporous membranes was tested as follows: after weighed, the membrane was immersed in 1-butanol for 2 h. Then, the surface of membrane was dried by filter paper and weighed again. Porosity was calculated using the following equation:

$$\text{Porosity } (\%) = 100 \times \frac{w_\mathrm{t} - w_0}{\rho V}$$

where w_t and w_0 are the weight of the wet and dry membrane, respectively. V is the apparent volume of the membrane. ρ is the density of 1-butanol.

Ionic conductivities of PVDF–x%PEO blends based microporous polymer electrolytes were measured by AC impedance spectroscopy carried out in the 1 MHz–1 Hz frequency range by using a Solartron 1260 Impedance/Gain-Phase Analyzer coupled with a Solartron 1287 Electrochemical Interface.

3. Results and discussion

Fig. 1 shows the surface SEM images of as-prepared PVDF–x%PEO blends microporous membranes. It can be seen that the pore distribution on surface of the membrane becomes denser (in other word, pore size decreases) with the increase of PEO content at first, and reaches the maximum when the weight ratio of PEO is about 50% (Fig. 1e), subsequently becomes sparser when PEO content increases further (Fig. 1f–h). The above phenomena is possibly due to the fact that PEO and glycerin (non-solvent) have stronger interactions through hydrogen bonds, therefore, glycerin is dis-
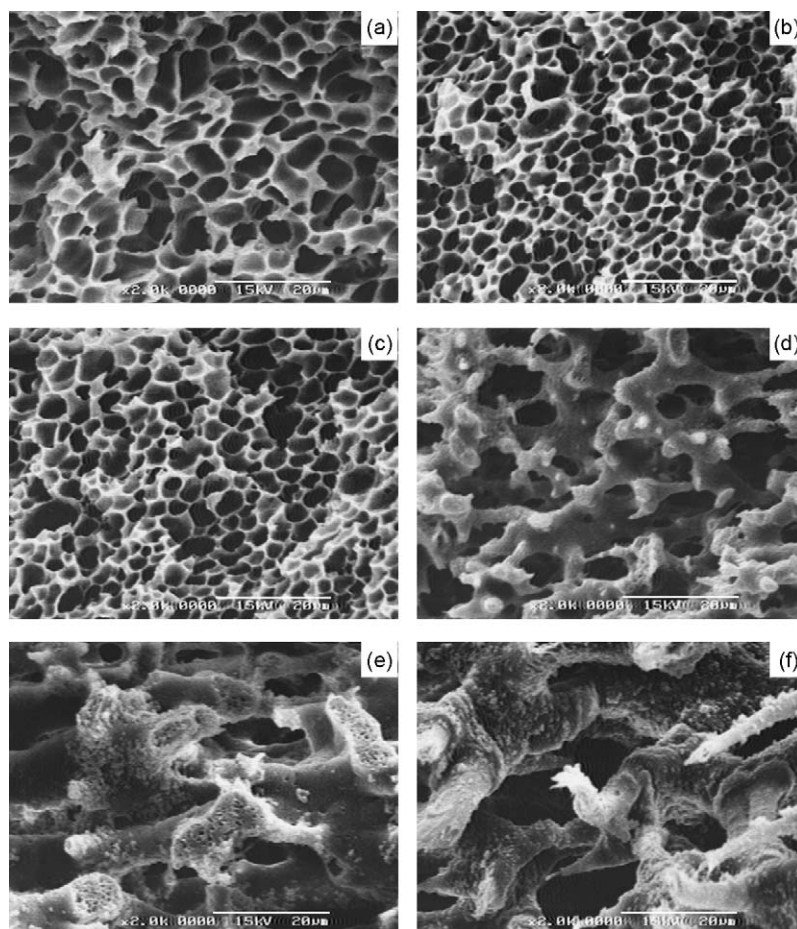

Fig. 2. Cross-section SEM images of pure PVDF (a) and PVDF–x%PEO blends membranes: (b) $x = 20$; (c) $x = 40$; (d) $x = 50$; (e) $x = 60$; (f) $x = 80$.

tributed better and the pore distribution becomes denser. Further increasing PEO content, the phase separation between PVDF and PEO happens and glycerin (non-solvent) gathers in PEO phase, thus the pore distribution becomes sparser.

From the cross-section SEM images (Fig. 2), we can find that the pores in the bulk of the membranes are not interconnected when PEO content is low. However, the pores become well interconnected when the weight ratio of PEO exceeds 50% (Fig. 2d–f). Here, we can propose one possibility to explain this result. In the solution of PVDF/DMF/glycerin, with the evaporation of DMF (solvent), the phase separation between PVDF and glycerin (non-solvent) happens, resulting in very poor pore connectivity. However, when PEO is added into the above solution, in present good affinity with glycerin through hydrogen bond and improves the compatibility. Accordingly, the connectivity of pores can be improved markedly with the increase of PEO content. The further mechanism is still under studying.

Fig. 3a displays the liquid electrolyte up-take plots of PVDF–x%PEO blends microporous membranes. It can be seen that PEO content has great influence on both the rate (Fig. 3a) and the ratio (Fig. 3b) of liquid electrolyte up-take of PVDF–x%PEO blends microporous membranes. Pure PVDF microporous membrane reaches saturation after about 8 min
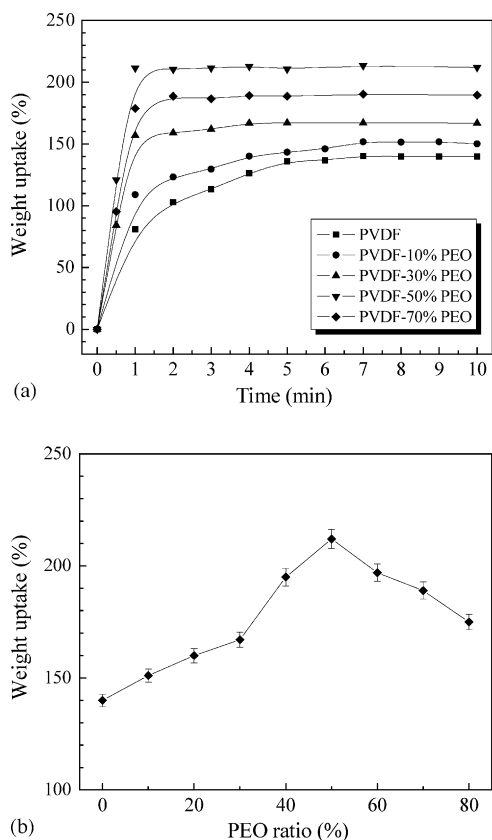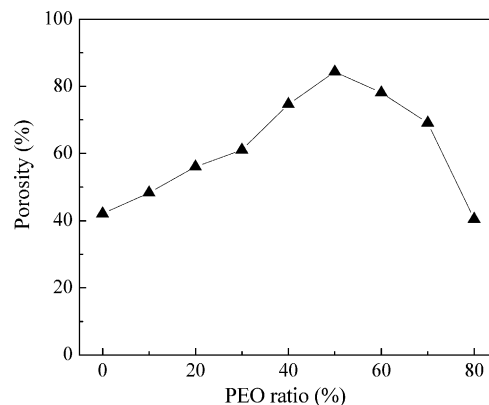

Fig. 4. Porosity of PVDF–x%PEO blends microporous membranes as a function of PEO ratio.

with a weight up-take ratio of 130%. With the addition of PEO, both the liquid electrolyte up-take rate and weight up-take ratio increase, which should be attributed to the novel pore connectivity and high pore density of PVDF–x%PEO blends microporous membranes, as respectively shown in Figs. 1 and 2. The sample PVDF–50%PEO reaches saturation only after 1–2 min with a maximum weight up-take ratio of 210%.

Fig. 4 shows the porosity of PVDF–x%PEO blends microporous membranes as a function of PEO content. As can be seen from Fig. 4, the porosity of PVDF–x%PEO blends microporous membranes first increases with PEO content, and reaches the maximum (84%) when the weight ratio of PEO is 50%, and then decreases when PEO content further increases. This trend agrees well with the change of pore configuration observed from SEM images, as shown in Figs. 1 and 2. The change tendency of porosity also agrees with the liquid electrolyte up-take rate (Fig. 3b), suggesting that PVDF–x%PEO blends microporous membranes can store more liquid electrolyte when its porosity increases.

Fig. 5 displays the room temperature impedance plots of PVDF–x%PEO blends based microporous polymer electrolyte. After soaking with liquid electrolyte (1 mol L^{-1} LiClO$_4$/PC solution), room temperature ionic conductivity of the resulting PVDF–x%PEO blends microporous polymer electrolyte (Fig. 6) shows the same trend as the case of porosity (Fig. 4) as a function of PEO content. It is worth to note that when the weight ratio of PEO increases from 40 to 50%, ionic conductivity increases more than one magnitude (from 0.15 to 1.96 mS cm^{-1}), despite the very small change of porosity (from 75 to 84%), suggesting that porosity is not the only factor that affects ionic conductivity of microporous polymer electrolyte. Another factor may be due to the obviously improved pore connectivity, which is very important for the transporting of charge carriers in microporous polymer electrolyte, when the weight ratio of PEO increases from 40 to 50%, as shown in the inset of Fig. 6 (also see Fig. 2c and d). In addition, PVDF–60%PEO has conductivity of 0.97 mS cm^{-1}, about five times higher than PVDF–40%PEO, although their electrolyte up-take is nearly
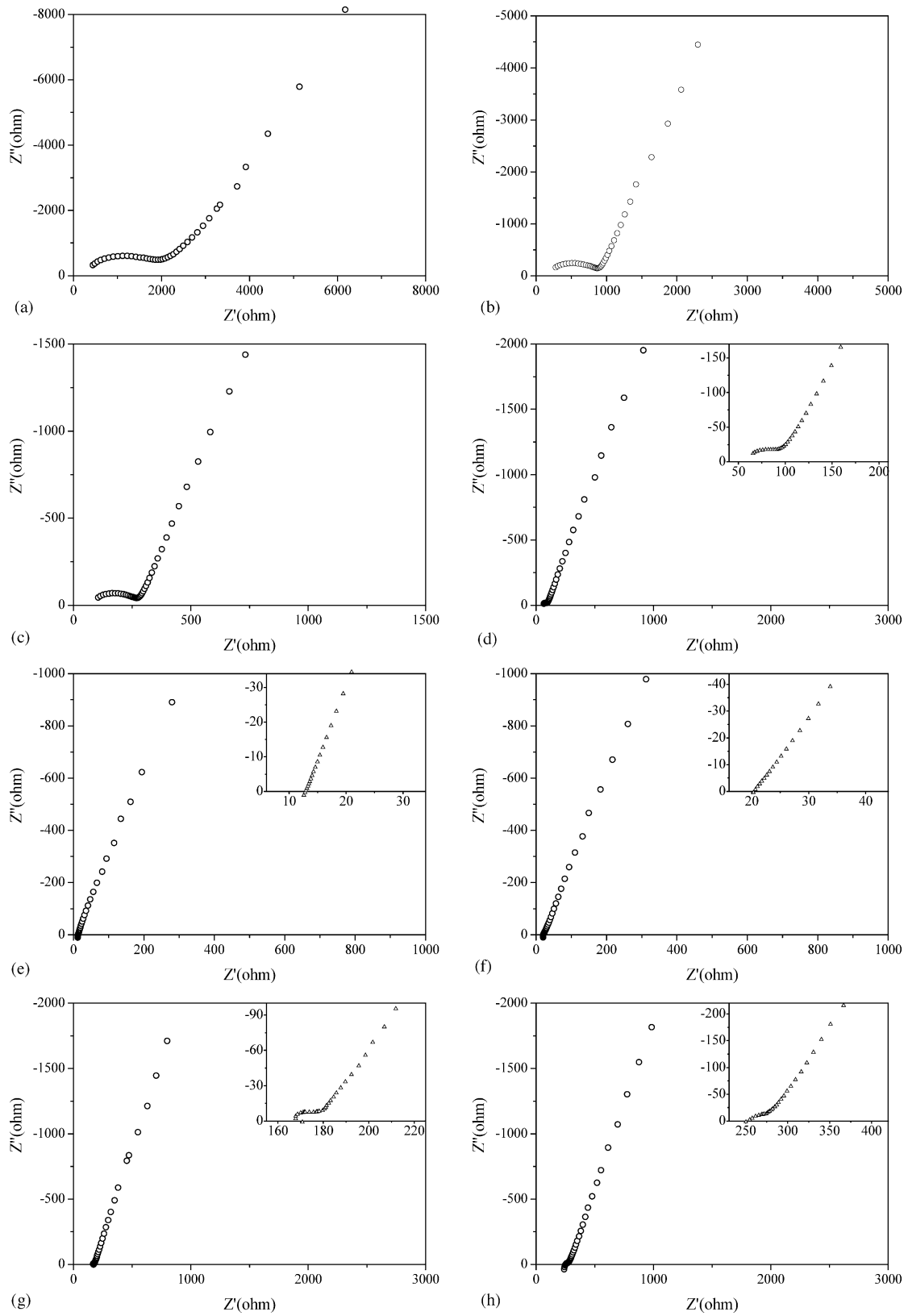

Fig. 3. (a) Liquid electrolyte (1 mol L^{-1} LiClO$_4$/PC solution) weight up-take vs. time for PVDF–x%PEO blends microporous membranes. (b) Liquid electrolyte (1 mol L^{-1} LiClO$_4$/PC solution) weight up-take of PVDF–x%PEO blends microporous membranes as a function of PEO ratio.

Fig. 5. Room temperature (25 °C) impedance plots of PVDF–x%PEO blends microporous membranes (soaking with 1 mol L^{-1} LiClO$_4$/PC solution): (a) $x = 0$; (b) $x = 10$; (c) $x = 20$; (d) $x = 40$; (e) $x = 50$; (f) $x = 60$; (g) $x = 70$; (h) $x = 80$.
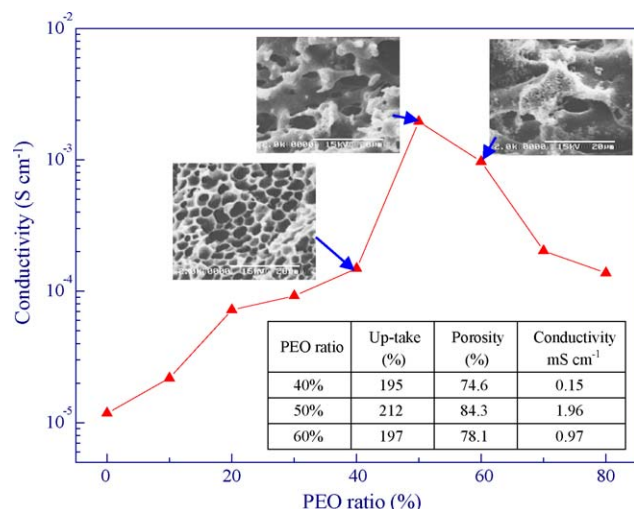
Fig. 6. Room temperature (25 °C) ionic conductivity of PVDF–*x*%PEO blends microporous membranes (soaking with 1 mol L^{-1} LiClO$_4$/PC solution) as a function of PEO ratio. Inset shows cross-sectional SEM images of the samples.

connectivity. As a result, room temperature ionic conductivity was greatly enhanced. This implies that PVDF–PEO blends microporous polymer electrolyte can be used as candidate electrolyte and/or separator material for high-performance rechargeable lithium batteries.

the same (195 and 197%, respectively). This is because that the connectivity of each pore in PVDF–60%PEO is better than that in PVDF–40%PEO, as shown in the inset of Fig. 6 (also see Fig. 2c and e), which further confirms that, compared with electrolyte up-take, pore connectivity is more important for increasing the conductivity of microporous polymer electrolyte.

It should be indicated that the mechanical strength of PVDF–*x*%PEO blends is lower than pure PVDF. The tensile modulus decreased from ∼85 MPa of pure PVDF to ∼30 MPa of PVDF–50%PEO. However, this value is still comparable with the mechanical strength of traditional PVDF–HFP copolymer based microporous polymer electrolytes [14,22] and may be further increased by the addition of inorganic fillers.

4. Conclusion

In summary, a novel microporous polymer electrolyte based on PVDF–PEO blends was prepared by a simple phase inversion technique, in which the addition of PEO can obviously improve the pore configuration of PVDF-based microporous membranes, such as pore size, porosity, and pore

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