J Appl Electrochem (2008) 38:109–114
DOI 10.1007/s10800-007-9407-0

ORIGINAL PAPER

P(VDF-HFP)-based micro-porous composite polymer electrolyte prepared by in situ hydrolysis of titanium tetrabutoxide

Z. H. Li · H. P. Zhang · P. Zhang · Y. P. Wu

Received: 17 April 2007 / Revised: 19 July 2007 / Accepted: 23 August 2007 / Published online: 7 September 2007

Abstract A micro-porous composite polymer electrolyte (MCPE) was prepared in situ by adding TiO_2 nanoparticles from the hydrolysis of titanium tetrabutoxide to a solution of poly(vinylidenefluoride-co-hexafluoropropylene) [P(VDF-HFP)] copolymer. The prepared microporous polymer films (MCPFs) were characterized by scanning electronic microscopy, X-ray diffraction, thermogravimetric analysis, FT-IR and electrochemical interface resistance. After the addition of TiO_2 nanoparticles the polarity of CF_2 groups in the polymer chains and the crystallinity of the MCPFs decreased. When the composite polymer film contained 8.5 wt% of TiO_2 nanoparticles the MCPE exhibited excellent electrochemical properties such as high ionic conductivity, up to 2.40×10^{-3} S cm^{-1} at room temperature.

Keywords Polymer electrolyte · Nanoparticles · Ionic conductivity · Titanium tetrabutoxide · In situ hydrolysis

1 Introduction

Polymer lithium ion batteries (PLIBs), using polymer electrolyte as separator as well as carrier of ions, have been used as power sources for portable electronic equipment due to their high energy density. Polymer electrolytes can be categorized as true solid-state and gel types. Gel polymer electrolytes (GPEs) are widely used because of their high ionic conductivity. Recently, a porous polymer electrolyte based on poly(vinylidenefluoride-co-hexafluoropropylene) [P(VDF-HFP)] copolymer has attracted much attention since its first reporting in 1994 [1–3]. Since this kind of copolymer membrane swells only in organic solvents such as propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC), which are usually used as solvents in non-aqueous electrolytes for lithium ion batteries, it acts as a separator with good mechanical strength in PLIBs to avoid short-circuit during cycling. It has been found that addition of inorganic nanoparticles such as Al_2O_3, SiO_2 and TiO_2 improves the mechanic strength and the ionic conductivity of the gel polymer electrolyte [4–7]. However, aggregation of nanoparticles is very difficult to avoid due to the high specific surface energy of the nanoparticles. In order to overcome the problem of aggregation a series of composite polymers have been prepared by in situ hydrolysis of the precursor of the inorganic compound in polymer solution or in situ polymerization of polymer units on the surface of the nanoparticles [8–12].

Here we report a method of adding TiO_2 nanoparticles by hydrolysis of the precursor, titanium tetrabutoxide [$Ti(OC_4H_9)_4$], to a solution of P(VDF-HFP) copolymer in N-methyl pyrrolidone (NMP). The resulting microporous polymer films display good electrochemical properties.

2 Experimental

2.1 Materials

P(VDF-HFP) copolymer (KnyarFlex®2801, containing 12% HFP unit) from Atofina Chem., *N*-methyl pyrrolidone (NMP)

Z. H. Li · H. P. Zhang · P. Zhang · Y. P. Wu (✉)
Department of Chemistry & Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China
e-mail: wuyp@fudan.edu.cn

Z. H. Li
College of Chemistry, Xiangtan University, Hunan 411105, China

Z. H. Li · H. P. Zhang · P. Zhang · Y. P. Wu
Fudan University-Tongxiang R & D Center for Power Batteries, Tongxiang, Zhejiang, China

and titanium tetrabutoxide (TTB) obtained from Shanghai Chemical Reactants Plant were used as received without further treatment. 1.0 M $LiPF_6$ solution in ethylene carbonate/diethyl carbonate (EC/DEC, v/v = 1:1) was purchased from Merck Co. and also used without further treatment.

2.2 Preparation of microporous polymer films (MCPFs)

P(VDF-HFP) (2 g) was dissolved in NMP (8 g, containing 0.8 g of dibutyl phthalate, (DBP)) to form a viscous solution. After adding 0.5 mL concentrated hydrochloric acid some TTB was added to the polymer solution and stirred to avoid drastic hydrolysis. After complete hydrolysis to yield TiO_2, the mixed solution was cast on a clean glass plate at room temperature and kept in the vapor bath at 80 °C for 12 h to form a polymer film. The TiO_2 nanoparticles formed by hydrolysis were dispersed in the polymer matrix. After cooling in air the polymer film was peeled off the glass plate and placed in ether for 2 h to extract the remaining NMP and DBP. The MCPFs were obtained after finally drying at 30 °C under vacuum for 2 h.

2.3 Characterization of MCPFs

The amount of TiO_2 particles in MCPF was determined by thermogravimetric analysis (TGA) on a WRT-3P microthermo-balance (Shanghai Balance Instrument Factory) in an oxygen atmosphere. MCPFs containing different amounts of TiO_2 were dried under vacuum at 80 °C for 48 h at first, and then their thermal properties were measured with a Perkin Elmer DSCQ10 instrument under nitrogen atmosphere at a heating rate of 10 °C/min. The infrared spectra were recorded under nitrogen on a Perkin Elmer FTIR 1710 spectrometer, covering a range of 450–4,000 cm^{-1} with a resolution of 1 cm^{-1}. X-ray diffraction (XRD) patterns were taken using a Rigaku D/Max2500 diffractometer in the range 2θ from 5° to 45°. Scanning electron micrographs (SEM) were obtained by means of a Philips XL30 D6716 digital scanning electron microscope.

The porosity of the polymer film was measured as follows. The film was immersed in *n*-butanol for 1 h and the mass was weighed before and after the absorption of *n*-butanol. The porosity *p* of the polymer film was calculated based on the Eq. 1.

$$p = \frac{m_a/\rho_a}{m_a/\rho_a + m_p/\rho_p} \tag{1}$$

where m_a, m_p are the mass of the wet film and the dry film and ρ_a, ρ_p are the densities of butanol and the polymer, respectively. The absorbed ratio of electrolyte to the net weight of MCPF (φ) was obtained by weighing the mass difference before and after impregnating in 1 mol L^{-1} solution of $LiPF_6$/EC-DEC for 2 h.

2.4 Electrochemical measurement of the MCPEs

The resulting MCPFs were punched into circular pieces with a diameter of 12 mm and stored in a dry glove box for 48 h. They were then immersed into 1 mol L^{-1} solution of $LiPF_6$/EC-DEC for 24 h to produce microporous composite polymer electrolytes (MCPEs). The MCPEs were sandwiched between two symmetrical lithium electrodes and sealed in a module cell, and AC impedance spectra of the assembly were measured using an EG&G Potentiostat/Golvannostat M273 in conjunction with M5210 Lock-in amplifier electrochemical analysis system in the frequency range 0.1 Hz to 100 kHz. The ionic conductivity of MCPE was determined from the resulting complex impedance spectra using the Eq. 2.

$$\sigma = d/(R_b S) \tag{2}$$

where σ is the ionic conductivity, R_b the bulk resistance, d the thickness of the MCPF, and S the area of the symmetrical electrode.

3 Results and discussion

3.1 Micrograph of MCPFs

Typical scanning electron micrographs (SEM) of MCPFs containing different amounts of TiO_2 particles are presented in Fig. 1. The MCPFs have a porous structure within a polymer matrix for all of polymer films. DBP did not evaporate away from the polymer matrix due to its high boiling temperature (340 °C). After extraction of DBP from the polymer film with ether, a large number of pores were left in the polymer film, forming a porous network structure as shown in Fig. 1a. The number of pores increased with the amount of TiO_2 particles added (Fig. 1b). When the amount of TiO_2 particles was 8.5 wt% the polymer film showed a very uniform distribution of pores with 2.0 μm in diameter (Fig. 1c), which act as the sites to store non-aqueous electrolyte. The interconnected structure facilitates the migration of lithium ions. Excessive addition of TiO_2 particles results in a decrease in the number of pores and the degree of interconnection as shown in Fig. 1d. These phenomena can be further confirmed by measuring porosity.

The porosity (p) for MCPFs is shown in Table 1. The added nanoparticles at first increase the porosity. After the

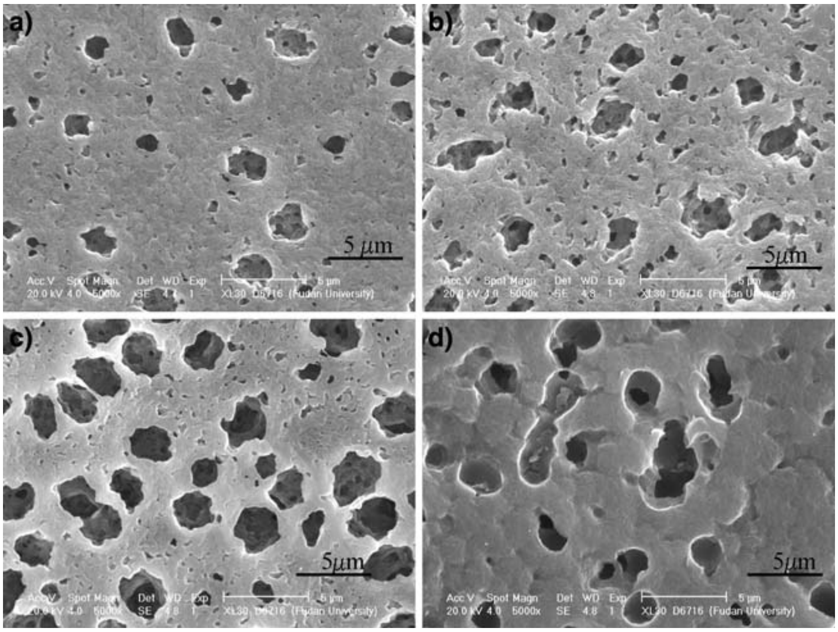

Fig. 1 SEM micrographs of a polymer film containing different amounts of TiO_2 (**a**) 0, (**b**) 6.3, (**c**) 8.5, (**d**) 16.5 wt% (scale bar: 5 μm)

Table 1 Some data of MCPE filled with various amounts of TiO_2 nanoparticles

TiO_2/wt%	ρ/%	X_c/%	φ/%	$\sigma/10^{-3}$ S cm^{-1}	E_a kJ mol^{-1}
0	63	44.6	125	0.93	29
6.3	71	44.2	140	1.31	29
8.5	83	42.0	189	2.40	23
10.0	79	37.7	176	1.42	26
13.0	69	34.4	131	1.21	26
16.5	53	29.6	110	0.66	29

porosity reaches a maximum (83%) at 8.5 wt% TiO_2 nanoparticles, it decreases with further addition.

3.2 Characterization of MCPFs

Figure 2 presents that the characteristic XRD diffraction peaks of P(VDF-HFP), which are situated at 18.3 (020, β), 20.0 (110, β), and 26.8 (021, α), respectively [13, 14]. The positions of these peaks scarcely vary, indicating that the crystal structure of the polymer matrix does not change.

Figure 3 shows the DSC curves of MCPFs containing different amounts of TiO_2 particles. It suggests that the melting temperature (T_m) of the MCPFs is about 2 °C lower than that of the pure polymer film because of the interaction between TiO_2 particles and polymer chains. However, the amount of TiO_2 in the MCPFs has little effect on their T_m. The crystallinity (X_c) can be calculated from the equation:

$$X_c = (\Delta H_m/\Delta H_m^{\emptyset}) \times 100\% \quad (3)$$

where $\Delta H_m^{\emptyset}$ is the heat of melting of pure α-PVDF crystalline, 104.7 J g^{-1} [15] and ΔH_m the heat of fusion of MCPFs. ΔH_m can be calculated from the integral area of the DSC curves. The values of X_c are summarized in Table 1.

The crystallinity of MCPFs decreases slightly with increase in the amount of TiO_2 nanoparticles in the polymer matrix. The reorganization of polymer chains may be hindered by the cross-linking sites from the Lewis acid groups (–OH) on the surface of nanoparticles, which react with the polar F atoms of the polymer chains. As a result, the degree of crystallization of polymer matrix decreases with the amount of nanoparticles.

The FTIR spectra of MCPFs are shown in Fig. 4. The absorption peaks at 2,980 and 3,018 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibration of CH_2 groups, respectively [16]. The peaks at 510 and 475 cm^{-1} can be assigned to the deformation vibration of CF_2 groups, belonging to the characteristic peaks of the crystal phase of P(VDF-HFP) copolymer [17]. The integral area of these four peaks decreases with increase in the amount of TiO_2 nanoparticles. The weakening of the wide stretching vibration peak of the CF_2 group at about 1,200 cm^{-1} with the amount of TiO_2 nanoparticles further suggests that there is an interaction between the polymer chains and nanoparticles. The

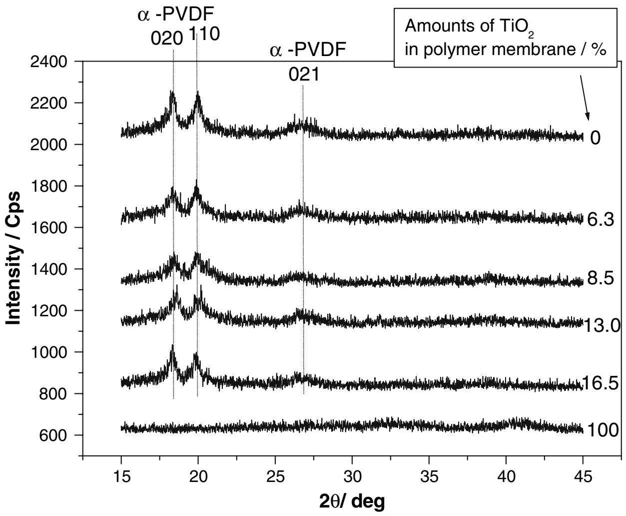

Fig. 2 XRD patterns of MCPF

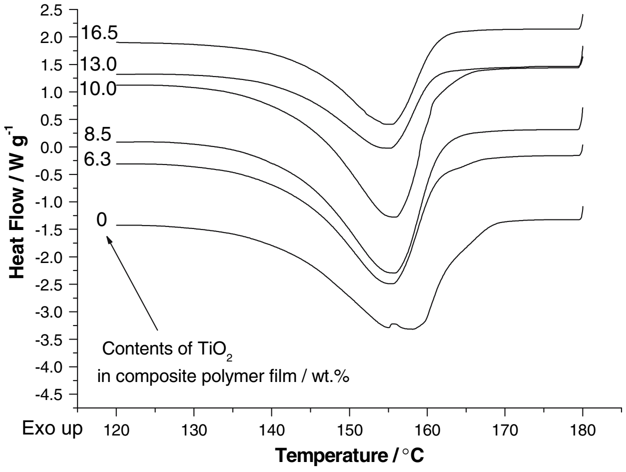

Fig. 3 DSC curves of MCPFs

new absorption peak at 1,640 cm^{-1} can be assigned to the bending vibration of –OH groups on the surface of nanoparticles. Because the vibration position of the CH_2 groups does not change, there are no hydrogen bonds between these groups in the polymer chains and the added nanoparticles. Nevertheless, the Lewis-acid effect of nanoparticles decreases the polarity of CF_2 groups, thus weakening the interaction between Li^+ ions and polymer chains in MCPEs.

3.3 Conductivity of MCPE

The bulk resistance of MCPE measured by EIS can be obtained from Fig. 5. In the Nyquist plots, the left intercept of the semicircle represents the bulk resistance of MCPE, while the right intercept represents the total resistance of the cell, which includes the interfacial resistance of Li/MCPE. The ionic conductivity of MCPEs calculated according to Eq. 2 is shown in Table 1.

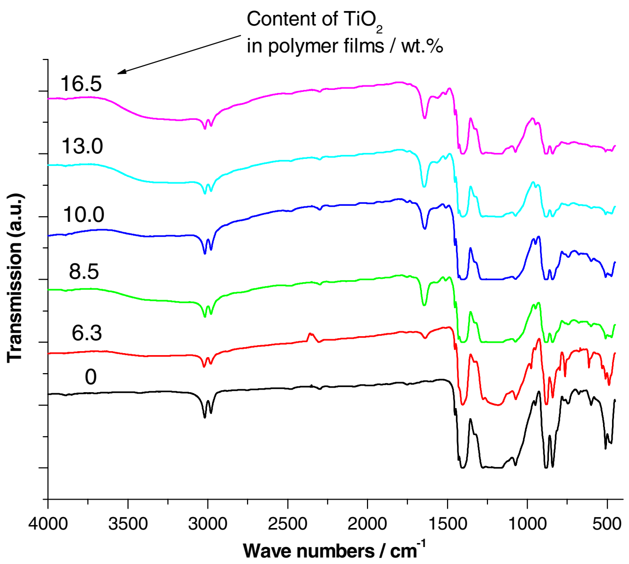

Fig. 4 FTIR spectra of MCPF

The ionic conductivity of MCPE with no addition of nanoparticles is 0.93 × 10^{-3} S cm^{-1}, lower than that of MCPE filled with TiO_2 (<3.0 wt%). When the amount of TiO_2 in MCPFs was 8.5 wt%, the ionic conductivity at 25 °C reaches a maximum, 2.40 × 10^{-3} S cm^{-1}. Further addition of TiO_2 decreases the conductivity. It is well known that the MCPE possesses three phases: solid polymer matrix, gel polymer and liquid trapped in the micropores [18]. Moreover, lithium ions move faster in liquid than in gel polymer. Consequently, the increase in porosity of the polymer film enhances the amount of absorbed non-aqueous electrolyte as shown in Table 1, facilitating the migration of lithium ions, and increasing the ionic conductivity.

The dependence of ionic conductivity on temperature for MCPE is shown in Fig. 6. These curves are linear, indicating that their conductive behavior follows the Arrhenius equation $\sigma = \sigma_0 exp(-E_a/RT)$ in the measuring temperature range 25–55 °C. In this range, the pores in the polymer membrane absorb “free” electrolyte solution and Li^+ ions migrate in the liquid phase. If the pores interconnect with each other very well, the conductive behavior is similar to that of liquid electrolyte. The apparent activation energy for lithium ion transfer, E_a, can be calculated from the log σ–$1/T$ curves, listed in Table 1. MCPE containing 8.5 wt% TiO_2 particles has the minimum value of apparent activation energy for lithium ion transfer, 23 kJ mol^{-1}.

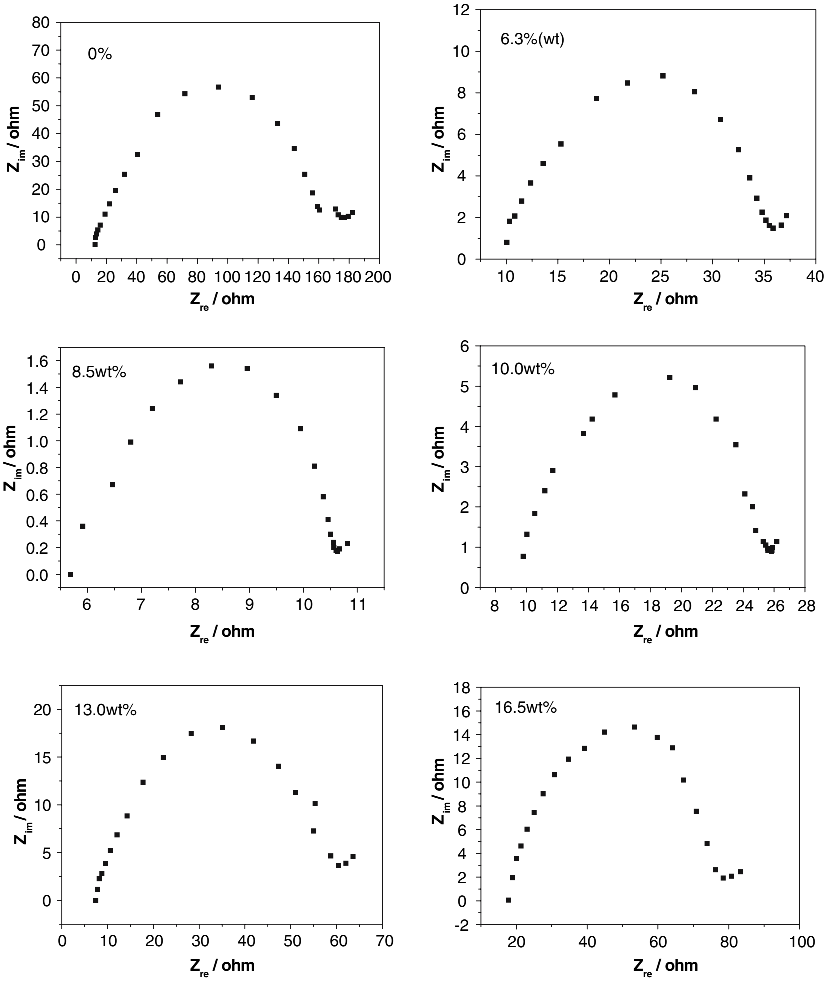

Fig. 5 AC impedance spectra for MCPE

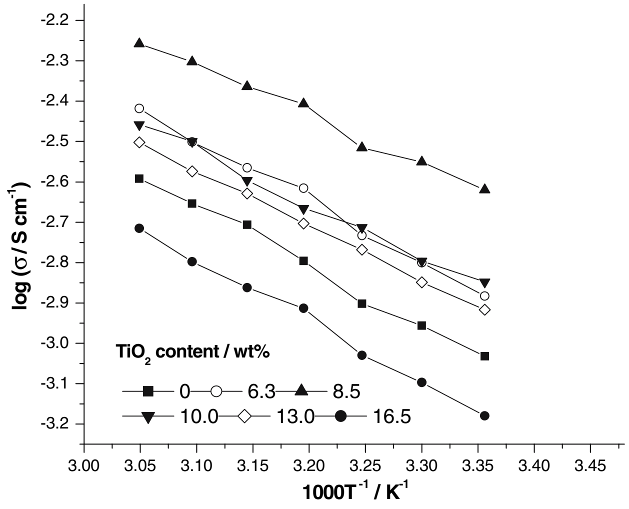

Fig. 6 logσ–1/T curves of MCPE

4 Conclusion

Micro-porous P(VDF-HFP)-based polymer electrolytes containing different amount of TiO_2 nanoparticles were prepared by hydrolysis of TTB in situ, which ensured the uniform dispersion of nanoparticles in the polymer film. The crystallinity of the polymer matrix decreased slightly with increase in the amount of TiO_2 nanoparticles due to the Lewis-acid interaction between the nanoparticles and F atoms. The added TiO_2 nanopartilces weakened the polarity of CF_2 groups in the polymer molecular chains. The optimal amount of TiO_2 nanoparticles in the polymer matrix is 8.5 wt%, at which the ionic conductivity of the MCPE is up to 2.40×10^{-3} S cm^{-1}.

Acknowledgement Support from National Basic Research Program of China (973 Program No: 2007CB209700), Chinese Postdoctoral Science fund (20060400618), the Open Fund from State Key Laboratory of Chemical Engineering in East China University of Science and Technology (HF06008), and the Doctoral Starting Fund from Xiangtan University (05QDZ18) is greatly appreciated.

References

1. Gozdz AS, Schmutz CN, Tarascon JM (1994) US Patent 5,296,138
2. Huang H, Wunder SL (2001) J Power Sources 97–98:649

3. Magistris A, Quartarone E, Mustarelli P, Saito Y, Kataoka H (2002) Solid State Ionics 152–153:347
4. Kim KM, Park N, Ryu KS, Chang SH (2002) Polymer 43:3951
5. Caillon-Caravanier M, Claude-Montigny B, Lemordant D, Bosser G (2002) J Power Sources 107:12
6. Wang BB, Gu LX (2002) Mater Lett 57:361
7. Li ZH, Su GY, Gao DS, Wang XY, Li XP (2004) Electrochim Acta 494:633
8. Liu Y, Lee JY, Hong L (2004) J Power Sources 129:303
9. Mallick K, Witcomb MJ, Dinsmore A, Scurrell MS (2005) Langmuir 21:7964
10. Grohn F, Kim G, Bauer BJ, Amis EJ (2001) Macromolecules 34:2179
11. Wang JY, Chen W, Liu AH, Lu G, Zhang G, Zhang JH, Yang B (2002) J Am Chem Soc 124:13358
12. Palkovits R, Althues H, Rumplecker A, Tesche B, Dreier A, Holle U, Fink G, Cheng CH, Shantz DF, Kaskel S (2005) Langmuir 21:6048
13. Martin S, Stephan S, Ralf BW, Gosele U, Wendorff JH (2003) Macromolecules 36:3646
14. Saikia D, Kumar A (2004) Electrochim Acta 49:2581
15. Teyssedre G, Bernes A, Lacabanne C (1993) J Polym Sci (B) 31:2027
16. Salimi A, Yousefi AA (2003) Polym Testing 22:699
17. Rajendran S, Mahendran O, Mahalingam T (2002) Eur Polym J 38:49
18. Zhang SS, Xu K, Foster DL, Ervin MH, Jow TR (2004) J Power Sources 125:114