Available online at www.sciencedirect.com

Polymer 46 (2005) 5702–5706

polymer

www.elsevier.com/locate/polymer

Nanocomposite polymer electrolyte comprising PEO/LiClO$_4$ and solid super acid: effect of sulphated-zirconia on the crystallization kinetics of PEO

Jingyu Xi[a], Xinping Qiu[a,*], Sixun Zheng[b], Xiaozhen Tang[b]

[a]Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China
[b]School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received 9 October 2004; received in revised form 5 May 2005; accepted 13 May 2005
Available online 8 June 2005

Abstract

A novel PEO-based nanocomposite polymer electrolyte is prepared by using solid super acid sulphated-zirconia ($SO_4^{2-}-ZrO_2$, SZ) as the filler. Polarized optical microscopy (POM) and differential scanning calorimeter (DSC) results show that part of SZ particles may act as the nucleus of PEO spherulites and thus increase the amount of PEO spherulites. On the other hand, other SZ particles, which do not act as the nucleus, can restrain the recrystallization tendency of PEO chains through Lewis acid–base interaction and hence decrease the growth speed of PEO spherulites. As a result, the PEO component in PEO–LiClO$_4$–SZ can maintain a high amorphous state for a long time. The room temperature ionic conductivity of PEO–LiClO$_4$–SZ is relative high and stable compared with pristine PEO–LiClO$_4$, indicating that it is promising for all solid-state rechargeable lithium ion batteries.

Keywords: Nanocomposite polymer electrolytes; Crystallization; Ionic conductivity

1. Introduction

PEO–LiX ($X = ClO_4^-$, BF_4^-, PF_6^- etc.) based solid polymer electrolytes (SPEs) have received extensive attentions [1–5], for their potential capability to replace traditional liquid electrolytes of rechargeable lithium ion batteries, since Wright et al. found that the complex of PEO and alkaline salts had the ability of ionic conductivity in 1973 [6]. Lithium polymer batteries (LPBs) may be one of the best choices for future electrochemical power source due to its high energy densities, good cyclability, reliability and safety [7,8].

General concepts of the transporting of Li^+ in PEO-based polymer electrolytes are coupled with the local relaxation and segmental motion of PEO chains [1], of which the conditions can only be obtained when PEO is in its amorphous state. However, due to its particular structure, PEO often shows much higher crystalline ratios at sub-ambient temperature region, and accordingly its ionic conductivity is lower than $10^{-7}\ S\ cm^{-1}$ [1,2]. Development of PEO-based electrolytes capable of combining high ionic conductivity with superior interfacial stability towards the lithium metal anode, and good mechanical properties is the key issue for the R&D of all solid-state lithium polymer batteries [1,7]. When the third component, i.e. inorganic fillers, was introduced into the PEO-based electrolytes to form the composite polymer electrolytes (CPE), all the above performances could be improved [1,9–15].

In previous work [16], we have found that solid super acid sulphated-zirconia ($SO_4^{2-}-ZrO_2$, denoted as SZ), due to its strong acidity [17–20], can obviously enhance the ionic conductivity and other electrochemical properties of PEO–LiClO$_4$ based electrolyte. In order to elucidate the enhancement mechanisms of SZ, the crystallization kinetics of PEO in both pristine PEO–LiClO$_4$ and PEO–LiClO$_4$–SZ nanocomposite polymer electrolyte are studied by polarized optical microscopy (POM) together with differential scanning calorimeter (DSC) techniques, and the experiment results are discussed in this paper. In addition, the relation between the crystallinity of PEO and its ionic conductivity is also studied.

---

* Corresponding author. Tel.: +86 10 62794235; fax: +86 10 62794234.
E-mail address: qiuxp@mail.tsinghua.edu.cn (X. Qiu).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.05.051

2. Experimental

The zirconia support was prepared by hydrolysis of zirconium oxychloride with ammonia, as already described [16]. The white precipitate zirconium hydroxide was then dried at 383 K for 24 h. Sulphation of this hydrous zirconia was done by percolating 1 N H_2SO_4 solution through it. The sulphated zirconium hydroxide was then calcined in air at 923 K for 3 h to obtain the final SZ. SEM image shows that the particle of SZ has average diameter of about 60–70 nm [16].

The nanocomposite polymer electrolyte was prepared by dispersing SZ and $LiClO_4$ in anhydrous acetonitrile, followed by addition of the PEO and a thorough mixing of the obtained slurry. The slurry was then cast onto a Teflon plate to let the solvent evaporate slowly. Finally, the obtained films were dried under vacuum at 50 °C for 24 h to get rid of the residue solvent [16].

Polarized optical microscopy (POM) was performed using a LEICA-DMLP instrument equipped with a heating stage attached to a temperature controller. To study the recrystallization process of PEO, the sample was first annealed at 100 °C for 30 min and then quenched rapidly to a given temperature. The optical micrographs of recrystallized PEO spherulites were taken as a function of time after the initial appearance of spherulitic nucleus.

Differential scanning calorimeter (DSC) measurements were conducted on a Perkin–Elmer Pyris-1 analyzer. The measurements were carried out with a heating rate of 10 °C min^{-1} ranging from -60 to 100 °C in the heating scan. A flow of nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture.

Ionic conductivity of the nanocomposite polymer electrolyte films was determined by AC impedance spectroscopy. The electrolyte was sandwiched between two stainless steel (SS) blocking electrodes (with a diameter of 1 cm) to form a symmetrical SS/electrolyte/SS cell. The cell was placed into a self-designed oven coupled with a temperature controller. For each temperature, at least 60 min were waited before the impedance response was recorded. The impedance tests were carried out in the 1 MHz–1 Hz frequency range using a Solartron 1260 Impedance/Gain-Phase Analyzer coupled with a Solartron 1287 Electrochemical Interface.

3. Results and discussion

As has been found in previous work [16], SZ can obviously decrease the crystallinity of PEO, and hence improve the room temperature ionic conductivity of PEO–$LiClO_4$–SZ nanocomposite polymer electrolyte by more than two magnitudes. However, it is difficult to understand the effect of SZ on the crystallization kinetics of PEO only through the previous X-ray diffraction (XRD) and differential scanning calorimeter (DSC) results. Polarized optical microscopy (POM) is one of the most effective techniques to study the crystallization of PEO and other polymers [21–23]. Fig. 1 displays typical room temperature POM images of pristine PEO_{12}–$LiClO_4$ and PEO_{12}–$LiClO_4$–7%SZ nanocomposite polymer electrolyte.

It is well known that pure PEO spherulites have a Maltese cross-extinction pattern and a very fine spherulitic texture [21,22]. For PEO_{12}–$LiClO_4$ case (Fig. 1(a)), PEO exhibit a typical compact spherulitic morphology and its cross-extinction pattern can be observed clearly. However, the boundaries of the spherulites are smooth after impingement with adjacent spherulites, in agreement with the result in other papers [21,22]. In addition, only few spherulites with an average radius of about 100–200 μm can be observed. It is interesting to note that, with the addition of SZ filler (Fig. 1(b)), the amount of PEO spherulites increase and the average radius of spherulites decrease to about 20–30 μm, which are both beneficial for decreasing the crystallinity of PEO, in other word, increasing the ratio of amorphous PEO, as shown in Fig. 2.

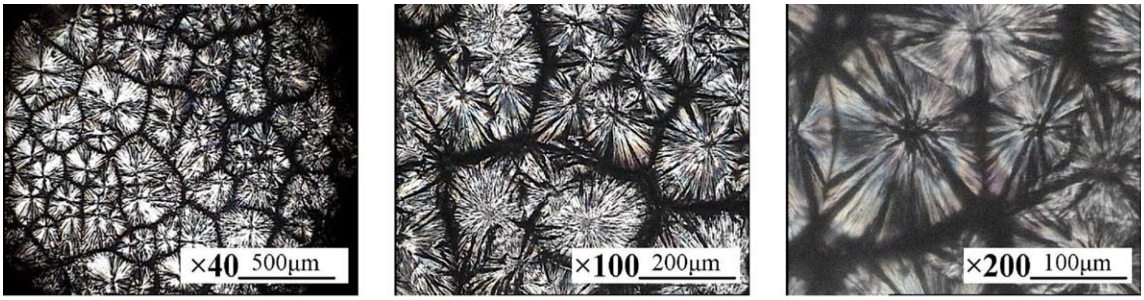
Thermal properties of PEO_{12}–$LiClO_4$ and PEO_{12}–$LiClO_4$–7%SZ obtained from DSC analysis are listed in Table 1. The relative percentage of crystalline PEO, X_c, can be calculated from the equation $X_c = \Delta H_m / \Delta H_m^*$, where ΔH_m^* is the melting enthalpy of a completely crystalline PEO sample [24]. It can be seen from Table 1 that both the melting temperature (T_m) and crystallinity (X_c) of PEO decrease obviously with the addition of SZ, which support the above model shown in Fig. 2. The glass transition temperature, T_g, of PEO also decreases with the addition of SZ. The decrease of T_g and X_c will increase the flexibility of the PEO chains and the ratio of amorphous PEO, respectively. Consequently, ionic conductivity should be enhanced at low temperature region [16]. In addition, compared with the continuous crystalline phase of PEO formed by the connections of adjacent large PEO spherulites in the case of PEO–$LiClO_4$ (Fig. 1(a) and left part of Fig. 2), there exist much more continuous amorphous phase of PEO in PEO–$LiClO_4$–SZ nanocomposite polymer electrolyte (Fig. 1(b) and right part of Fig. 2), which is very important for the transporting of Li^+.

Table 1
Thermal properties of PEO_{12}–$LiClO_4$ and PEO_{12}–$LiClO_4$–7%SZ nanocomposite polymer electrolyte

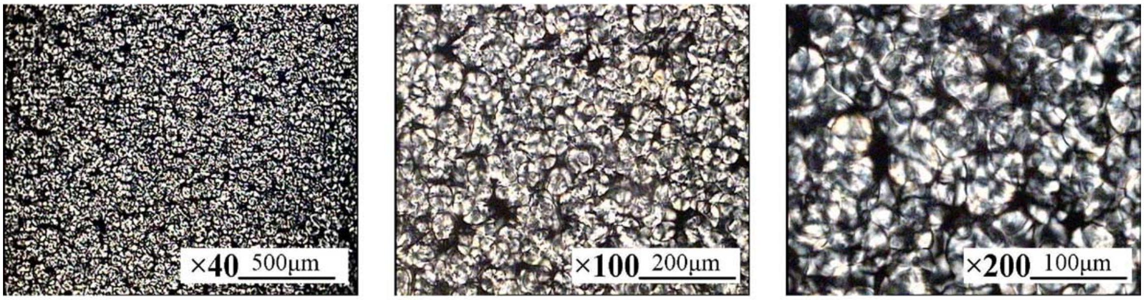
Sample[a]	Glass point T_g (°C)	Melting point T_m (°C)	Melting enthalpy ΔH_m (J g^{-1})	Crystallinity X_c[b] (%)
PEO_{12}–$LiClO_4$	-32.8	54.4	83.4	39.0
PEO_{12}–$LiClO_4$–7%SZ	-45.7	48.5	40.4	18.9

[a] All samples have the same thermal history like those samples used for room temperature POM analysis.

[b] $X_c = (\Delta H_m / \Delta H_m^*) \times 100$, $\Delta H_m^* = 213.7$ (J g^{-1}).



(a) PEO$_{12}$-LiClO$_4$



(b) PEO$_{12}$-LiClO$_4$-7%SZ

Fig. 1. Polarized optical microscopy (POM) images recorded at room temperature (25 °C). All samples have the same thermal history before POM analysis.

The effect of SZ on the crystallization kinetics of PEO are studied by monitoring the recrystallization process of PEO spherulites in PEO$_{12}$–LiClO$_4$ and PEO$_{12}$–LiClO$_4$–7%SZ sample, and the obtained in situ POM images are compared in Fig. 3. In the case of PEO$_{12}$–LiClO$_4$, it can be seen from Fig. 3(a) that the PEO spherulites grows rapidly within few minutes and only one spherulites can be observed at one time even when its radius reach to more than 200 μm. This phenomenon suggests that PEO chains are hard to form effective nucleus of the spherulites only through spontaneous arrangement in PEO$_{12}$–LiClO$_4$ system. However, these few nucleuses begin to grow rapidly as soon as they are formed due to the regular structure of PEO chains.

PEO spherulites in PEO$_{12}$–LiClO$_4$–7%SZ show completely different crystallization kinetics compared with the case of pristine PEO$_{12}$–LiClO$_4$, as shown in Fig. 3(b). With the addition of nano-filler SZ, the amount of PEO spherulites increases and about 40–60 spherulites can be observed at one time. On the other hand, the growth speed of these spherulites decreases obviously and the average radius of these spherulites is only 20–30 μm after 10 min. Because part of the nano-size SZ particles may act as the nucleus for the growth of PEO spherulites, the amount of PEO spherulites increase evidently. However, other SZ particles, which do not act as nucleus, can restrain the recrystallization tendency of PEO chains through the well-known Lewis acid–base interaction [1,14] because of its strong Lewis acidity [17], thus the spherulites growth speed is reduced. It is worthy to note that the isothermal crystallization result agrees well with Fig. 1 and the proposed schematic shown in Fig. 2, which supports the above discussion.

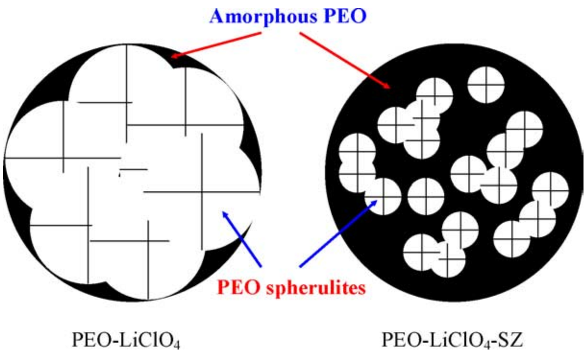
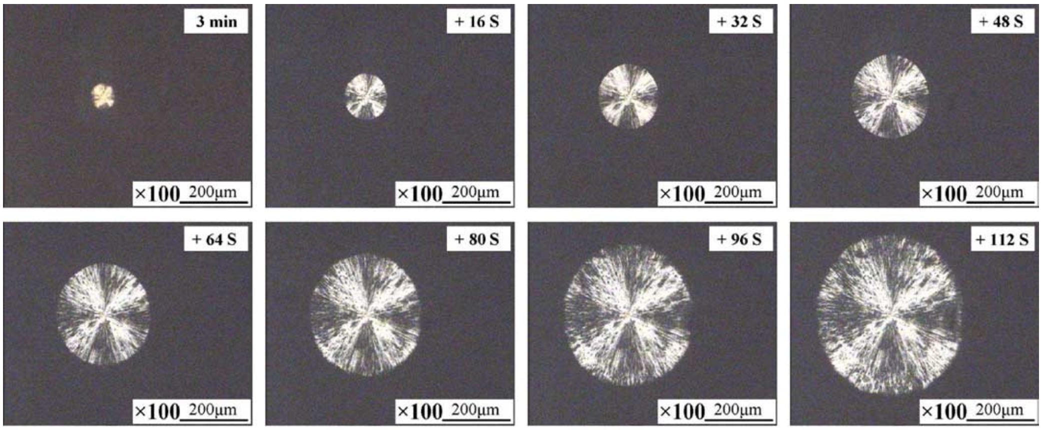


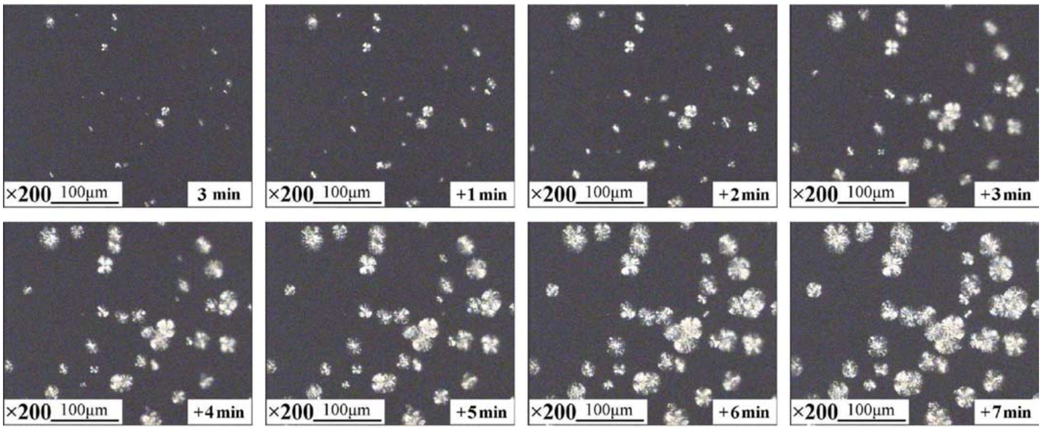
Fig. 2. Schematic representation of the morphology of PEO spherulites grows from pristine PEO–LiClO$_4$ and nanocomposite polymer electrolyte PEO–LiClO$_4$–SZ.

Fig. 4(a) shows the DSC plots of PEO$_{12}$–LiClO$_4$ and PEO$_{12}$–LiClO$_4$–7%SZ stored for different time. All samples used for DSC test have the same thermal history as those used for POM analysis. The endothermic peak between 20 and 70 °C corresponds to the melting of the crystalline PEO. For PEO$_{12}$–LiClO$_4$ sample, it can be seen from Fig. 4(a) that the area of the melting peak increases fast during the whole experiment time. However, no obviously change for this peak can be observed in the case of PEO$_{12}$–LiClO$_4$–7%SZ.

Time evolution of the X_c of PEO in PEO$_{12}$–LiClO$_4$ and PEO$_{12}$–LiClO$_4$–7%SZ are shown in Fig. 4(b). The initial X_c of PEO in the case of PEO$_{12}$–LiClO$_4$ (25.8%) is much higher than that in the case of PEO$_{12}$–LiClO$_4$–7%SZ (11.4%). In addition, the X_c of PEO in PEO$_{12}$–LiClO$_4$ increased very fast during the first month and then



(a) PEO_{12}-$LiClO_4$



(b) PEO_{12}-$LiClO_4$-7%SZ

Fig. 3. In situ POM images documenting the growth of PEO spherulites from different samples with isothermal condition (45 °C).

maintained at about 45%. On the contrary, the X_c of PEO in PEO_{12}–$LiClO_4$–7%SZ increased very slowly during the whole experiment time and then maintained a relative low value of about 19.1% after 1 month. The DSC results further prove that the filler SZ can prevent the recrystallization of PEO effectively, which agrees with the POM analysis (Fig. 3).

The crystallinity of PEO has great effect on the room temperature ionic conductivity of PEO-based polymer electrolyte [1,2]. Fig. 5 shows the time evolution of the room temperature (25 °C) conductivity of the polymer electrolytes. Prior to test, all samples were vacuum annealed at 100 °C for 5 h, to ensure that the PEO chains could organize freely. Then the test is conducted after the temperature reached given point. As can be seen from Fig. 5, the initial conductivity of PEO_{12}–$LiClO_4$ after annealing (4.0×10^{-7} S cm^{-1}) is two times higher than that without any treatment (1.5×10^{-7} S cm^{-1}). However, this electrolyte tends to recrystallize and, consequently, its conductivity decreases very fast and then maintains at 1.0×10^{-7} S cm^{-1} after 5 days. PEO_{12}–$LiClO_4$–7%SZ shows an initial conductivity about two magnitudes higher than that of the pristine PEO_{12}–$LiClO_4$, and only a small decrease of conductivity could be detected during the first 2 days, and then the conductivity stays stable in all experimental times. The final conductivity of PEO_{12}–$LiClO_4$–7%SZ is about 85% compared with its initial value, which strongly suggests that SZ could restrain the recrystallization of PEO.

4. Conclusions

A novel PEO-based all solid-state nanocomposite polymer electrolyte is prepared by using solid super acid sulphated-zirconia ($SO_4^{2-}-ZrO_2$, SZ) as the filler. POM and DSC results show that part of SZ particles may act as the nucleus of PEO spherulites and thus increase the amount of PEO spherulites. On the other hand, other SZ particles, which do not act as the nucleus, can restrain the recrystallization tendency of PEO chains through Lewis acid–base interaction and hence decrease the growth speed of PEO spherulites. As a result, the PEO component in

PEO–$LiClO_4$–SZ can maintain a high amorphous state for a long time. In addition, compared with the continuous crystalline phase of PEO formed by the connections of adjacent large PEO spherulites in the case of PEO–$LiClO_4$, there exist much more continuous amorphous phase of PEO in PEO–$LiClO_4$–SZ nanocomposite polymer electrolyte, which is very important for the transporting of Li^+ ions. A relative high and stable room temperature ionic conductivity indicates that PEO–$LiClO_4$–SZ is promising for all solid-state rechargeable lithium ion batteries.

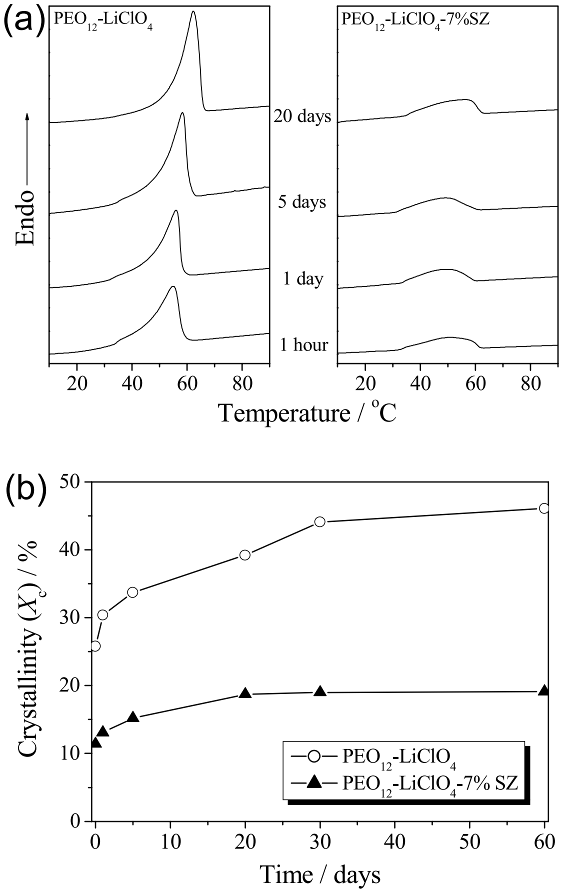


Fig. 4. (a) DSC curves of PEO_{12}–$LiClO_4$ and PEO_{12}–$LiClO_4$–7%SZ stored for different time; (b) Time evolution of the crystallinity (X_c) of PEO in PEO_{12}–$LiClO_4$ and PEO_{12}–$LiClO_4$–7%SZ.

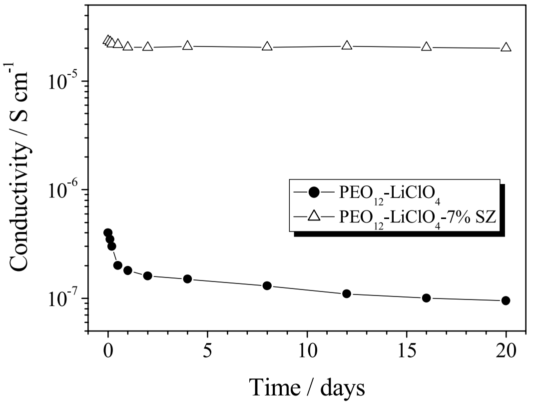


Fig. 5. Time evolution of room temperature (25 °C) ionic conductivity of PEO_{12}–$LiClO_4$ and PEO_{12}–$LiClO_4$–7%SZ nanocomposite polymer electrolyte.

Acknowledgements

This work was supported by the State Key Basic Research Program of China (2002CB211803) and Key Science and Technology Project of Shanghai (02dz11002).

References

[1] Croce F, Appetecchi G, Persi L, Scrosati B. Nature 1998;394:456.
[2] Meyer W. Adv Mater 1998;10:439.
[3] Chandrasekhar V. Adv Polym Sci 1998;135:139.
[4] Gray F. Polymer electrolytes. Cambridge: Royal Society of Chemistry; 1997.
[5] Gadjourova Z, Andreev Y, Tunstall D, Bruce P. Nature 2001;412:520.
[6] Fenton D, Parker J, Wright P. Polymer 1973;14:589.
[7] Tarascon J, Armand M. Nature 2001;414:359.
[8] Scrosati B, Croce F, Panero S. J Power Sources 2001;100:93.
[9] Zhou J, Fedkiw P. Solid State Ionics 2004;166:275.
[10] Quartarone E, Mustarelli P, Magistris A. Solid State Ionics 1998; 110:1.
[11] Nan C, Fan L, Lin Y, Cai Q. Phys Rev Lett 2003;91:266104.
[12] Xi J, Ma X, Cui M, Huang X, Zheng Z, Tang X. Chin Sci Bull 2004; 49:785.
[13] Xi J, Miao S, Tang X. Macromolecules 2004;37:8592.
[14] Croce F, Curini R, Martinelli A, Persi L, Ronci F, Scrosati B. J Phys Chem B 1999;103:10632.
[15] Wieczorek W, Raducha D, Zalewska A, Stevens J. J Phys Chem B 1998;102:8725.
[16] Xi J, Tang X. Chem Phys Lett 2004;393:271.
[17] Corma A. Chem Rev 1995;95:559.
[18] Ecormier M, Wilson K, Lee A. J Catal 2003;215:57.
[19] Sun Y, Ma S, Du Y, Yuan L, Wang S, Yang J, et al. J Phys Chem B 2005;109:2567.
[20] Mishra H, Parida K. Appl Catal A 2002;224:179.
[21] Choi B. Solid State Ionics 2004;168:123.
[22] Choi B, Kim Y. Electrochim Acta 2004;49:2307.
[23] Ziabicki A, Misztal-Faraj B. Polymer 2005;46:2395.
[24] Li X, Hsu S. J Polym Sci, Polym Phys Ed 1984;22:1331.