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Enhanced ionic conductivity of poly(ethylene oxide) (PEO) electrolyte by adding mesoporous molecular sieve LiAlSBA

Abstract Mesoporous molecular sieve LiAlSBA was prepared via an ion exchange process with mesoporous AlSBA directly, which has a regular 2D hexagonal structure with pore size about 7 nm. It was added into poly(ethylene oxide) (PEO) solid electrolyte as filler. The characteristics of the composite polymer electrolyte were determined by XRD, DSC, TGA, FTIR, PLM and electrochemical methods. Compared with bare PEO electrolyte, the adding of dispersed LiAlSBA powder improved the ionic conductivity of PEO polymer electrolyte more than three orders. The reason for it is that mesoporous LiAlSBA powder acts as crystal cores in PEO composite electrolyte and fines the crystallites, decreases the crystallinity, which provides much more continuous amorphous domain for Li^+ moving easily in PEO electrolyte. Besides, lithium ions of the mesoporous molecular sieves can hop from one site to another along the surface of the mesoporous channels, this mechanism is absent in the case of common nano-ceramic fillers in PEO electrolyte.

Keywords LiAlSBA · Mesoporous molecular sieve · Composite polymer electrolyte · PEO · Ionic conductivity

Introduction

Polymer electrolytes have attracted great interest for the use in polymer lithium batteries with high energy density. However, usually polymer electrolytes exhibit conductivities in the range from 10^{-8} S cm^{-1} to 10^{-4} S cm^{-1} at temperatures between 30 °C and 100 °C. The low ionic conductivity excludes the practical application at ambient temperature. The research efforts have been devoted to improving ionic conductivity of solid polymer electrolyte (SPE) materials for the use in lithium ion batteries. It has been reported that the basic structure of the poly(ethylene oxide) (PEO)-LiX complexes involves the ether oxygen chains of PEO coiled around Li^+ cations with the counter anions located nearby for electroneutrality [1]. Studies in the late 1970s to early 1980s demonstrated that the chain dynamics plays a critical role in the conductivity mechanism and the ionic conduction was limited mainly to the amorphous polymer electrolytes above their glass transition temperature T_g. It has been reported that the conductivity in amorphous phase is two or three orders higher than that in crystalline phase [2]. This realization has been leading the research direction since that time.

Nowadays, it has been reported by many authors that the conductivity of the polymer electrolyte can be improved by adding micro or nano scale fillers such as SiO_2, Al_2O_3, TiO_2 and mesoporous silica SBA-15 [3–9]. The conductivity enhancement reflects the ability of the particles to inhibit crystallization of PEO and consequently to promote polymer section mobility, as well as to provide specific surface interactions with the electrolyte components.

Until now, most attention has been paid to nanosize ceramic materials as filler to enhance the conductivity of polymer electrolyte. In this work, we employed LiAlSBA, a kind of mesoporous molecular sieve containing lithium as filler added into PEO electrolyte. Compared with PEO/LiClO$_4$ and PEO/LiClO$_4$/nano-SiO$_2$ composite electrolytes, the conductivity is enhanced greatly by adding LiAlSBA. Crossed polarizers microscope measurement was employed to explain the mechanism on the conductivity enhancement of PEO/LiClO$_4$/LiAlSBA composite electrolyte besides XRD, FTIR and DSC methods.

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Experimental

Preparation of LiAlSBA mesoporous molecular sieve, composite PEO films

Mesoporous molecular sieve LiAlSBA was prepared via an ion exchange process from mesoporous AlSBA. The material AlSBA was synthesized by the similar method introduced by Yue et al. [10]. Briefly, aluminum tri-tert-butoxide 2 g was added into 18 ml acidic tetraethyl orthosilicate (TEOS) solution (pH 1.5) at the Si/Al ratio of 10, and then the solution was added into a second solution containing 8 g triblock poly(ethylene oxide)-poly(propylene oxide) ($EO_{20}PO_{70}EO_{20}$ Aldrich) at 40 °C. The mixture was stirred for 3 h and allowed to react at 100 °C for 48 h in high-pressure kettle. After being quickly cooled, filtered off, dried at 100 °C, and calcined at 500 °C for 3 h, the AlSBA powder was obtained. For the use for lithium ion battery, it is better to exchange the hydrogen ions in mesoporous AlSBA for lithium ions. The mesoporous LiAlSBA powder was prepared as follows: lithium perchlorate was dried at 120 °C for 24 h in vacuum box. One gram AlSBA and 0.7 g $LiClO_4$ were added into 100 ml H_2O under stirring for 72 h, then the solid was filtered out and dried at 200 °C for 12 h.

The $PEO/LiClO_4$ electrolyte was fabricated by solvent-casting technique. High-molecular-weight (MW = 4×10^6 g/mol) PEO (Aldrich) was dried at 50 °C for 24 h in vacuum box. A composite solution at the mole ratio of PEO/Li = 8.2:1 was prepared by dissolving PEO and $LiClO_4$ in acetonitrile (AN). LiAlSBA is dispersed in acetonitrile under strong ultrasonic. Then, it was added into $PEO/LiClO_4$ composite solution. After stirring for 6 h, the slurry became homogeneous, and was kept in dry air until it became a gel. The gel was cast on a flat politetrafluoroethylene (PTFE) sheet to form a layer. The solvent evaporated gradually at room temperature in dry air for 24 h, and then the sheet was further dried at 80 °C under vacuum for 48 h. Finally the homogeneous and mechanically stable films with thickness range from 80 μm to 160 μm were obtained.

Physical and electrochemical characterization

The conductivity of the polymer electrolyte was measured by using Potentiostat/Galvanostat EG&G Model 273A frequency response analyzer over a frequency range from 100 kHz to 100 Hz. The electrolyte sample was placed in a two-electrode cell with the stainless steel electrode surface of 2 cm². The airproof cell was assembled in a dry air box. During the AC impedance measurement, the cell was kept in a dry desiccators, which contained P_2O_5 on the bottom in order to guarantee a very dry atmosphere. The electrochemical stability of the polymer electrolyte was determined by running linear-sweep voltammetry (LSV) carried out by a CHI660 Electrochemical Workstation at 80 °C in a two-electrode cell using stainless steel as the working electrode, lithium metal as both the counter and reference electrode, and the selected film sample as the electrolyte.

The morphologies of LiAlSBA were examined by a Japan JEOL JEM 2011 high-resolution transmission electron microscopy (TEM). X-ray powder diffraction (XRD) patterns of PEO composite electrolytes were determined using a Bruker D8 Advanced X-ray diffractometer with Cu Ka radiation at a scan rate of 4.5 °/min.

Differential scanning calorimetry (DSC) was carried out using a Perkin–Elmer DSC-141 with liquid N_2 as a coolant. Every sample weight was about 5 mg and was sealed in the reusable stainless steel high-pressure capsules. The polymer electrolyte samples were cooled to −70 °C and then heated to 110 °C at the heating rate of 10 °C/min. The glass-transition temperature (T_g) and the crystal melting transition temperature (T_m) were measured and the associated crystal melting transition enthalpy change (ΔH_m) was calculated. For the light micrographs, an Olympus BH-2 Research microscope was used and the images were taken under crossed polarizes.

Results and discussion

Structure and morphology of LiAlSBA

The N_2 adsorption–desorption isotherm indicates that LiAlSBA has a large BET surface area of 678 m² g^{-1} and mesoporous structure with the pore diameter of 7 nm. Transmission electron microscopy images in Fig. 1 present well-ordered hexagonal arrays of 1D mesoporous channels, which confirm that LiAlSBA material has a 2D hexagonal structure. Moreover, from TEM images we can estimate the distance between two consecutive centers of hexagonal pores is about 15 nm, and the pore diameter is about 7 nm, consistent with the N_2 adsorption result.

Ionic conductivities

For conductivity measurements, we use two blocking electrodes to sandwich the polymer films. A series of impedance measurements at different temperatures were obtained from 30 °C to 80 °C. The Nyquist plots for $PEO/LiClO_4$ electrolyte at different temperatures are displayed in Fig. 2. Most curves present a semicircle with an oblique line. For electrochemical measurement cell, the corresponding equivalent circuit is presented in Fig. 3, where R_1 is the resistance of cell besides polymer film. R_m and C_m are the resistance and capacity of polymer electrolyte film. C_d is the interface capacity at stainless steel blocking electrodes. For blocking electrode, the electrochemical reaction resistance is very high and can be neglected in the equivalent circuit. The

semicircle in high frequency region reflects the properties of polymer electrolyte film, and the oblique line in low frequency region reflects both the behavior of C_d and the diffusion process. It can be seen that the diameters of semicircles drop fast with the increase of temperature. Meanwhile, the semicircle moves to higher frequency region. The value of R_m can be calculated from the diameter of the semicircle. In the case of 80 °C, the semicircle cannot be found because it may locate in the very high frequency region, which cannot reach in this experiment. Therefore, the R_m value can be calculated from the intercept on the real axis at the high frequency end. Figure 4 presents the Nyquist spectra of PEO/LiClO$_4$ electrolyte with 5% LiAlSBA at different temperatures. They are all oblique lines. For each curve, the value of R_m was obtained from the intercept point at the high frequency end. The conductivity of polymer electrolyte σ can be obtained using the relationship:

$$\sigma = L/R_m A \tag{1}$$

where L is the thickness of the electrolyte film, and A is the surface area of the film (2 cm^2).

Figure 5 presents the influence of temperature on the ionic conductivity for the composite electrolytes containing different amount of LiAlSBA. A linear relationship between $\log \sigma T^{1/2}$ and $1/(T-T_0)$ reflects that the behavior fits empirical Vogel–Tammann–Fulcher (VTF) equation:

$$\sigma = AT^{-1/2}\exp[-B/R(T - T_o)] \tag{2}$$

where A and B are constants related to the number of charge carriers and the activation energy of ion transport, respectively. T_o can be regarded as the temperature below which there is no further entropy loss due to configurational changes in the polymer. Here, T_o is taken as T_g-50 K, based on the Adam–Gibbs configurational entropy model [11]. The conductivities of composite electrolytes at 30 °C and 80 °C are summarized in Table 1. The conductivity for PEO/LiClO$_4$ SPE at 30 °C is as low as 5.2×10^{-9} S cm^{-1}, which is similar to that reported in the reference [3]. When 5% LiAlSBA is added, the conductivity on composite PEO electrolyte reaches to 3.4×10^{-5} S cm^{-1} at 30 °C, more than three orders than that of the electrolyte without filler. The conductivity at high temperature is improved as well.

On the other hand, the conductivity becomes lower when the content of filler increases to 8%. The reason is that when too much filler is introduced, the miscibility becomes worse and the separated phase will occur, where the filler aggregates together to form LiAlSBA-rich phase in PEO bulk, which limits the lithium ion mobility. Similar phenomenon was observed by Reddy and Chu [9].

Crystallinity of composite polymer electrolyte

X-ray diffraction measurements were made for PEO composite electrolyte to exam the probable influence on the crystallinity caused by adding LiAlSBA and the results are displayed in Fig. 6. No new brag peak is observed in Fig. 6b–d compared with the pure PEO/LiClO$_4$ sample (Fig. 6a), which indicates that no new crystalline phase is formed. However, all prominent crystalline peaks of PEO polymer electrolytes become weaker when LiAlSBA was added into the electrolyte. It suggests that by adding LiAlSBA the crystallinity decreases obviously, which benefits the performance of conductivity. The best amount of LiAlSBA is about 5 wt.%, with the lowest PEO peak intensity observed from XRD patterns.

Fig. 1 Transmission electron micrographs for mesoporous LiAlSBA. In the direction of the pore axis (a), in the direction perpendicular (b), and diffraction image (c)
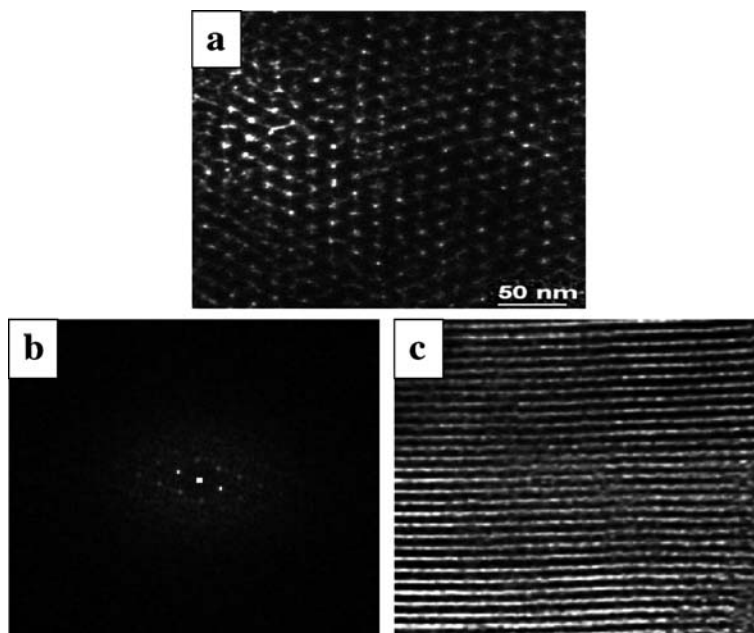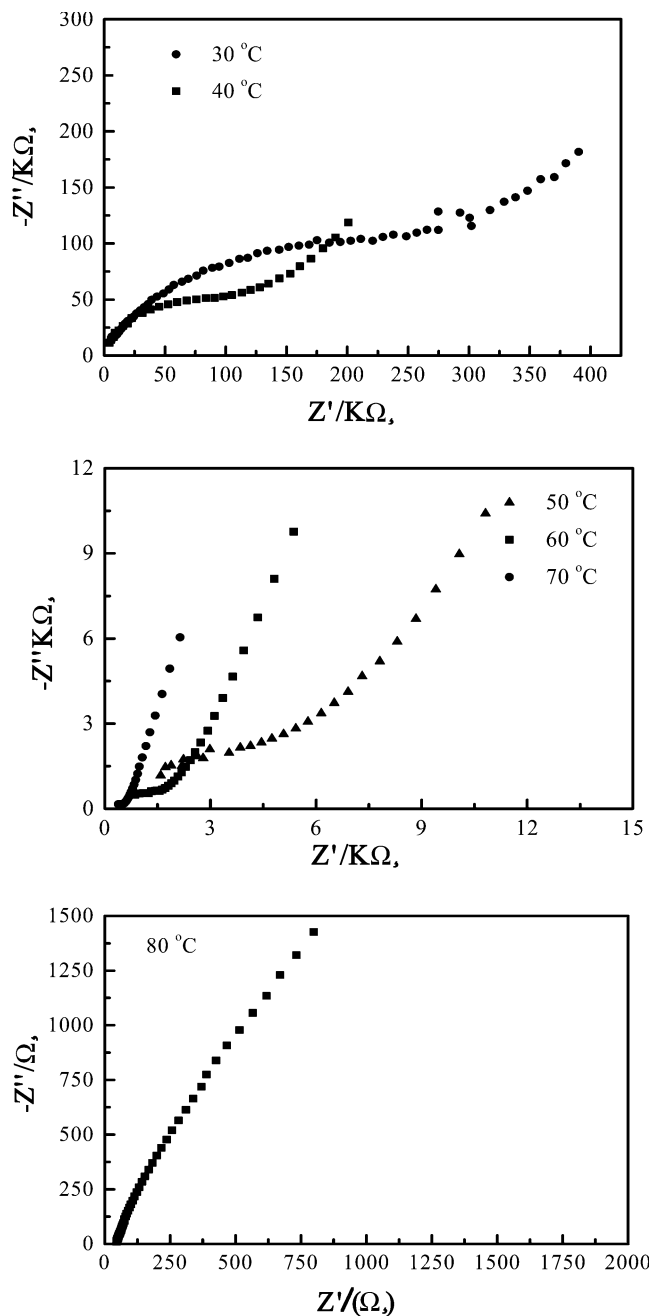
Fig. 2 Nyquist spectra of PEO/LiClO$_4$ electrolyte at different temperature

From the FTIR spectra of PEO composite electrolyte (shown in Fig. 7), there is no peak around 2,500 cm^{-1} (related to the –C ≡ N stretching), which rules out that
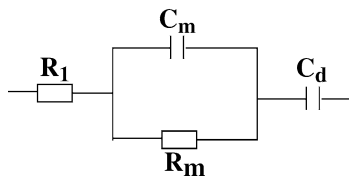

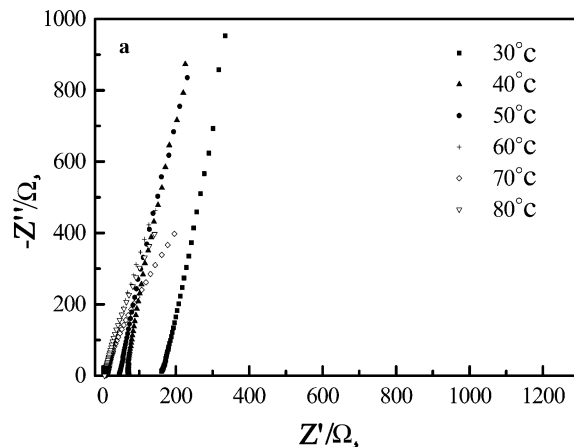**Fig. 3** Equivalent circuit for the system in impedance measurement

Fig. 4 Nyquist spectra of PEO/LiClO$_4$ electrolyte with 5%LiAl-SBA at different temperature
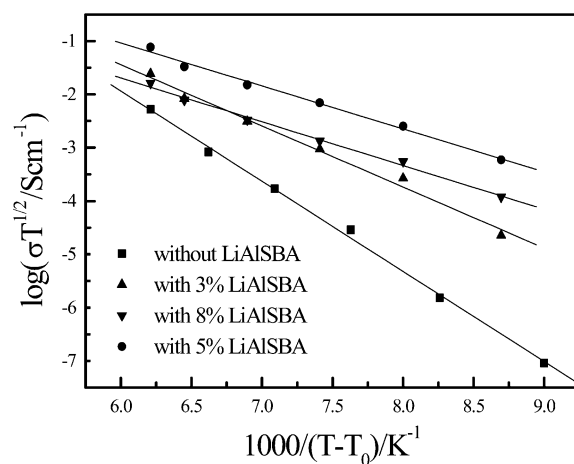

Fig. 5 VTF relationships for PEO/LiClO$_4$ electrolytes with different amount of LiAlSBA

the conductivity enhancement in the PEO composite electrolyte could not relate to the excess liquid adsorbed on mesoporous LiAlSBA. The peak at 1,343 cm^{-1} corresponds to the crystal phase in PEO composite electrolyte, and that at 1,349 cm^{-1} is attributed to the amorphous phase. As shown in Fig. 6, the corresponding amorphous peak at 1,349 cm^{-1} (curve b) for PEO/LiAlSBA composite electrolyte almost replace the crystal peak at 1,343 cm^{-1} for PEO electrolyte without

Table 1 Conductivity of composite polymer electrolytes

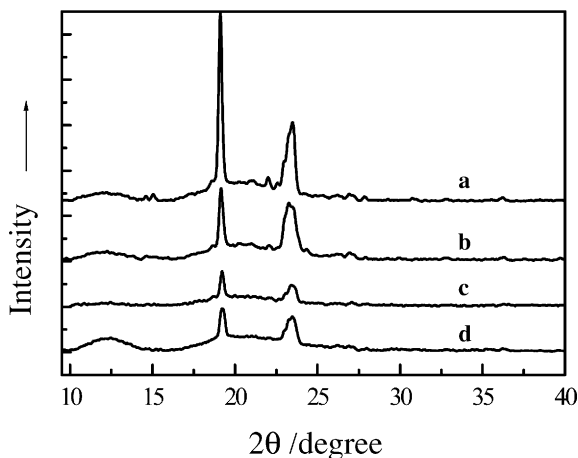| LiAlSBA to PEO/LiClO$_4$ (wt.%)	Conductivity (S cm^{-1})	
	At 303 K	At 353 K
0%	5.2×10^{-9}	2.8×10^{-4}
3%	1.3×10^{-6}	1.3×10^{-3}
5%	3.4×10^{-5}	4.1×10^{-3}
8%	6.8×10^{-6}	8.6×10^{-4}

Fig. 6 XRD patterns of PEO/LiClO$_4$ electrolytes with LiAlSBA at different weight ratios: **a** 0%, **b** 3%, **c** 5% and **d** 8%

Fig. 8 DSC thermograms of PEO/LiClO$_4$ solid electrolytes without filler; with 5% LiAlSBA; and with 5% nano-SiO$_2$

LiAlSBA (curve a). It indicates that the fraction of the crystal phase decreases greatly by adding LiAlSBA to PEO polymer electrolyte. That changes for the crystallinity of the polymer electrolyte as a function of the addition of LiAlSBA.

The changes of the polymer electrolyte crystallinity can be further revealed by DSC plots. Figure 8 shows the characteristic DSC behavior of PEO/LiClO$_4$ solid electrolytes without or with 5% LiAlSBA. To compare the difference between LiAlSBA and nano-SiO$_2$ (size of 20–30 nm), the DSC plot for PEO/LiClO$_4$ composite electrolyte containing 5% SiO$_2$ as filler is also displayed in Fig. 8. The glass-transition temperature (T_g), crystal-melting temperature (T_m), and the heat of crystal fusion (ΔH_m) for various composite materials obtained from DSC measurements, as well as the ionic conductivity (σ) at ambient temperature are summarized in Table 2.

For PEO/LiClO$_4$/LiAlSBA electrolyte, T_g is about −35 °C, slightly lower than that of PEO/LiClO$_4$ electrolyte, which indicates the enhancement of the chains
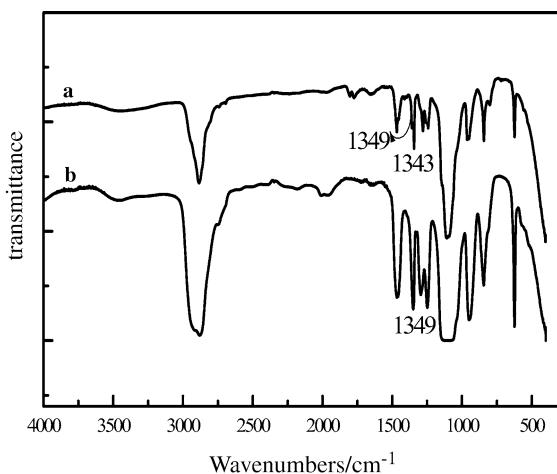
mobility. Compare with pure solid PEO/LiClO$_4$ electrolyte, T_m decreases from 47 °C to 40.8 °C. It reflects that the crystals in PEO/LiClO$_4$/LiAlSBA electrolyte can melt to amorphous structure under lower temperature. The heat of crystal fusion ΔH_m, as a value proportional to the weight fractions of crystalline PEO [12, 13], are 41.34 J/g and 18.9 J/g for polymer electrolytes without and with LiAlSBA, respectively. Therefore, we can calculate that the crystallinity of the latter is about 0.46 times of the former, providing further evidence of suppressed crystallization. For PEO/LiClO$_4$/SiO$_2$ electrolyte, T_g, T_m, and ΔH_m are a little lower than those of PEO/LiClO$_4$ electrolyte, but higher than those for PEO/LiClO$_4$/LiAlSBA electrolyte.

The pictures of the electrolyte films taken by crossed polarizers microscope (PLM) are displayed in Fig. 9. The magnifying multiple for both pictures is 250 times. Figure 9a shows there are large spherulites with the diameter about 175 μm in PEO/LiClO$_4$ electrolyte. In addition, the crystal boundaries connect closely with each other. Only a little continuous amorphous phase among the crystal domain is observed. However, in Fig. 8b, when the sample containing 5% LiAlSBA the spherulites become much smaller with the diameter about 25 μm, and the fraction of amorphous phase increases greatly. In addition, all the amorphous domains form a continuous pathway, where Li$^+$ cation can move freely and quickly with the motion of the polymer sec-

Fig. 7 FTIR spectra of PEO composite electrolytes, **a** filler free **b** with LiAlSBA

Table 2 T_g, T_m, ΔH_m of composite electrolytes obtained from DSC plots, and σ measured at 303 K

Composite PEO/LiClO$_4$	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})	σ (S cm^{-1}) at 303 K
Filler free	−31.0	47	41.3	5.2×10^{-9}
With 5% SiO$_2$	−31.2	42.4	37.4	1.5×10^{-6}
With 5% LiAlSBA	−35.6	40.8	18.9	3.4×10^{-5}

T_g glass transition temperature, T_m crystal melting temperature, ΔH_m heat of crystal fusion, σ conductivity
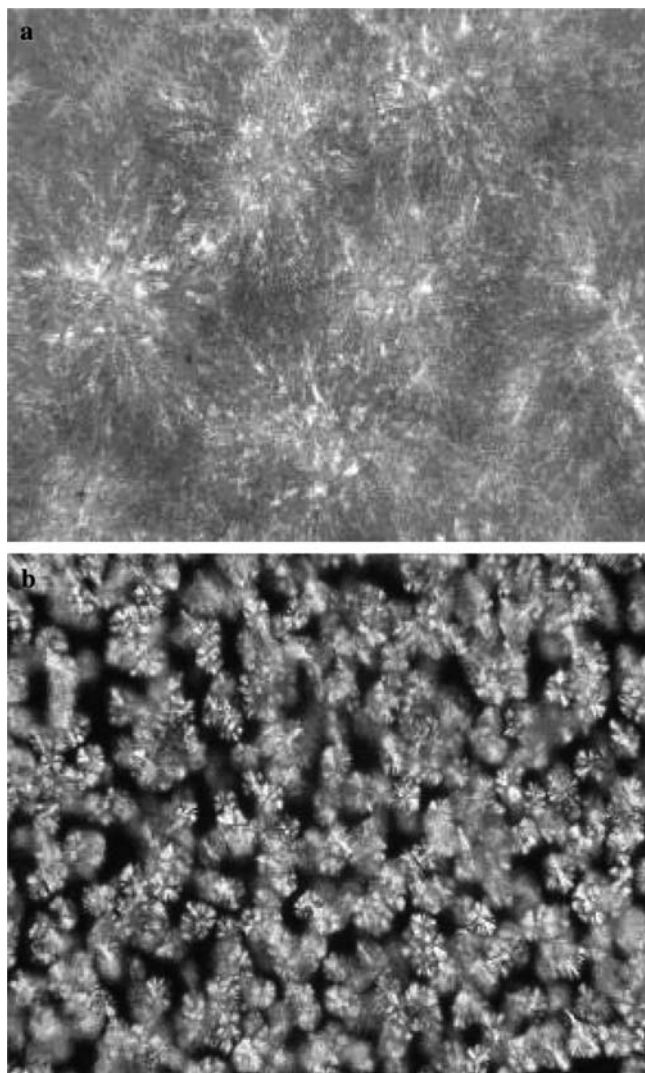
Fig. 9 PLM images of PEO/LiClO$_4$ electrolytes samples: **a** without LiAlSBA, **b** with 5% LiAlSBA, Magnifying ×250

tion. It will be benefit for increasing conductivity of polymer electrolyte.

Stability of PEO films

An important parameter in the characterization of polymer electrolyte used in lithium ion batteries is the electrochemical stability window, which is measured by linear sweep voltammetry. A stainless steel electrode was used as the working electrode and lithium foil was used as both the counter and reference electrode. The voltammograms at 80 °C are shown in Fig. 10. The stable potential window in positive direction for PEO/LiClO$_4$/LiAlSBA composite electrolyte is above 5.0 V, which is higher than that of the PEO/LiClO$_4$ electrolyte. The reason may be that the interaction of PEO chains with the interior and exterior surface of LiAlSBA channels changes the microstates of PEO chains, therefore, improves its electrochemical stability.
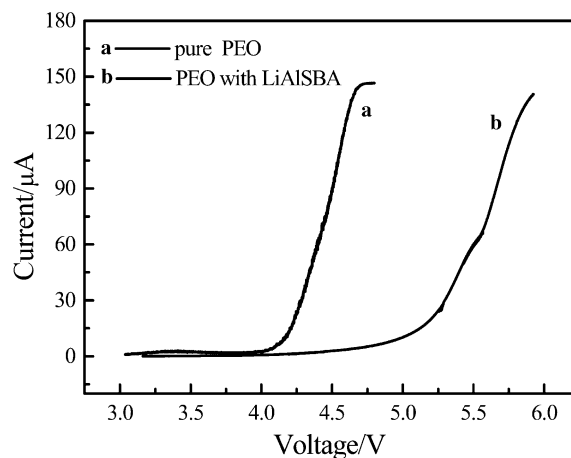

Fig. 10 Linear-sweep voltammertry for PEO electrolyte with and without LiAlSBA at 80 °C

Discussion about the conductivity mechanism of PEO/LiClO$_4$/LiAlSBA composite electrolyte

The XRD, DSC and crossed polarizers microscope results indicate that the addition of LiAlSBA decreases the crystallinity of the composite PEO electrolyte and promotes the mobility of polymer chains. Since the critical size of the crystal cores usually is very small, some of the crystal facets of the finely dispersed LiAlSBA in polymer electrolyte may act as crystal cores to fine the crystal grains, hence, decreases the crystallinity and increases the fraction of amorphous phase. As the ion transport mainly happens in the amorphous domain, the increase of amorphous phase domain will favor the enhancement of ionic conductivity.

In addition, the interaction of mesoporous LiAlSBA with PEO bulk can be described by Lewis acid–base reactions model, which is widely employed in PEO-based composite solid polymer electrolyte [14, 15]. In the present system, there is a great deal of –O–Li$^+$ group on the surface of the channels (including interior and exterior) of mesoporous LiAlSBA. Both the oxygen atoms in polymer PEO and LiAlSBA serve as the Lewis base centers and the Li$^+$ cation acts as Lewis acid. When an electric field is applied on the system, Li$^+$ of LiClO$_4$ cannot only move along the amorphous PEO chains, but also hop from one site to another on the surface of mesoporous interior and exterior channels as supported in reference [9, 16]. Moreover, Li$^+$ of mesoporous LiAlSBA itself can also move along PEO amorphous chains or replace the vacancy on LiAlSBA surface, which is another source of transfer charge.

Conclusions

The study has demonstrated the enhancement of ionic conductivity for PEO/LiClO$_4$ electrolyte by adding mesoporous molecular sieve LiAlSBA. The ionic conductivity of composite solid polymer electrolyte can

reach 3.4×10^{-5} S cm^{-1} at ambient temperature, which is more than three orders than that of PEO/LiClO$_4$ electrolyte. The conductivity enhancement is mainly due to the increase of continuous amorphous domain and the decrease of crystallinity, detected by XRD, DSC, TGA, FTIR and PLM methods. The improvement of Li$^+$ transport along the surface of mesoporous LiAlSBA may also benefit the enhanced conductivity of composite polymer electrolyte. Additionally, the electrochemical stability of polymer electrolyte was improved by adding small amount LiAlSBA. Therefore, it is an effective way to enhance the ionic conductivity of PEO solid polymer electrolyte, and may be used for solid electrolyte lithium ion battery.

References

1. Berthier C, Gorecki W, Minier M, Armand MB, Chabagno JM, Rigaud P (1983) Solid State Ionics 11:91
2. Oslen I, Koksbang R, Shou E (1995) Electrochim Acta 40:1701
3. Croce F, Appetecchi GB, Persi L, Scrosati B (1998) Nature 394:456
4. Liu Y, Jim YL, Hong L (2003) J Appl Polym Sci 89:2815
5. Sun HY, Sohn HJ, Yamamoto O, Takeda Y (1999) J Electrochem Soc 146:1672
6. Sun HY, Takeda Y, Imanishi N, Yamamoto O, Sohn HJ (2000) J Electrochem Soc 147:2462
7. Walls HJ, Peter SF, Thomas AZ Jr, Saad AK (2003) J Electrochem Soc 150:E165
8. Binod K, Stanley JR, Lawrence GS (2001) J Electrochem Soc 148:A1191
9. Reddy MJ, Chu PP (2004) J Power Sources 135:1–8
10. Yue Yh, Gedeon A, Bonardet JL, Melosh N, Baptiste J, Fraissard J (1999) Chem Commun 1967
11. Ding LM, Shi J, Yang CZ (1997) Synthet Metal 87:157
12. Mo ZS, Lee KB, Moon YB, Kobayashi M, Heeger AJ, Wudl F (1985) Macromolecules 18:1972
13. Jiang S, Yu D, Ji X, Au L, Jiang B (2000) Polymer 41:2041
14. Croce F, Curini R, Martinelli A, Persi L, Ronci F, Scrosati B (1999) J Phys Chem B 103:10632
15. Wieczorek W, Florjancyk Z, Stevens JR (1995) Electrochim Acta 40:2251
16. Chu PP, Reddy MJ, Kao HM (2003) Solid State Ionics 156:141