**Materials**

# Electrochemical behaviors of novel composite polymer electrolytes for lithium batteries

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(Received 2003-06-20)

**Abstract:** A novel composite polymer electrolyte was prepared by blending an appropriate amount of $LiClO_4$ and 10% (mass fraction) fumed $SiO_2$ with the block copolymer of poly (ethylene oxide) (PEO) synthesized by poly (ethylene glycol) (PEG) 400 and $CH_2Cl_2$. The ionic conductivity, electrochemical stability, interfacial characteristic and thermal behavior of the composite polymer electrolyte were studied by the measurements of AC impedance spectroscopy, linear sweep voltammetry and differential scanning calorimetry (DSC), respectively. The glass transition temperature acts as a function of salt concentration, which increases with the $LiClO_4$ content. Lewis acid-base model interaction mechanism was introduced to interpret the interactive relation between the filled fumed $SiO_2$ and the lithium salt in the composite polymer electrolyte. Over the salt concentration range and the measured temperature, the maximum ionic conductivity of the composite polymer electrolyte ($10^{-4.41}$ S/cm) appeared at EO/Li=25 (mole ratio) and 30°C, and the beginning oxidative degradation potential *versus* Li beyond 5 V.

**Key words:** composite polymer electrolyte; ionic conductivity; electrochemical stability; Lewis acid-base model interaction

## 1 Introduction

Polymer electrolytes have high potential applicability to advanced electrochemical devices such as high energy density batteries and electrochromic windows. The poly (ethylene oxide) (PEO)-based complexes acting as polymer electrolytes have been widely used [1-3]. However, there are several disadvantages in using PEO. The major drawback is that it is easy crystallization and the formation of crystalline complexes will result in a dramatic decrease in ionic conductivity. In order to solve this problem, many approaches have been carried out to reduce the crystallinity of PEO-based electrolytes and increase the segmental mobility of the host polymer. One of the most successful approaches relies on the preparation of polymer electrolyte nanocomposite. Nano-particles like $TiO_2$, $SiO_2$, $Al_2O_3$ and $LiAlO_2$ were incorporated in the polymer matrices to obtain the nano-composite polymer electrolytes [4-6]. These composite solid polymer electrolytes have potential advantages over conventional solid polymer complexes; for example, they exhibited better mechanical strength, higher ionic conductivity and better lithium anode and electrolyte interfacial stability. The large surface area of the solid oxide filler has prevented the local PEO chain reorganization, which leads to locking the local PEO chain in high degree of disorder and favors high ion transport.

In this paper, a compound polymer electrolyte was prepared by blending an appropriate amount of $LiClO_4$ and 10% (mass fraction) fumed $SiO_2$ with the block polymer of PEO synthesized by poly (ethylene glycol) (PEG) 400 and $CH_2Cl_2$. The composite polymer electrolyte had better processability, conductivity and electrochemical stability. This study interpreted the role of the filler in terms of Lewis acid-base model interaction [7, 8]. According to this model, Lewis acid-base interactions between the polar surface groups of the inorganic solid oxide filler and the electrolyte ionic species yield a greater degree of salt dissociation through the formation of ion-ceramic complex.

## 2 Experiment

### 2.1 Materials and measurements

PEG 400 and $LiClO_4$ were purchased from Aldrich Company Inc., USA. Fumed $SiO_2$ (self-prepared; particle size: 7-40 nm) was dehydrated for 24 h at 110°C under vacuum before use. Other analytical reagents were dried before use.

The ionic conductivities of polymer electrolytes were determined by AC impedance spectroscopy using a Solartron1280 B frequency response analyzer

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*J. Univ. Sci. Technol. Beijing, Vol.11, No.4, Aug 2004*

over a frequency range of 10 Hz to 20 kHz with an amplitude of 10 mV. The film of the polymer electrolyte was sandwiched between two stainless steel plates controlled by a Teflon spacer. The measurements were carried out after keeping the samples for 1 h at each temperature to attain thermal equilibration. The electrochemical stability of polymer electrolytes was evaluated by running a linear sweep voltammetry in three-electrode cells as Li/composite polymer electrolyte/stainless steel (SS), where lithium metal was used as a counter and reference electrode, SS as a working electrode. The interface resistance between the composite polymer electrolyte and the lithium metal electrode was evaluated by the impedance response of symmetric Li/electrolyte/Li cells. A Solatron 1280 B frequency analyzer measured the impedance over a 0.01 Hz to 20 kHz frequency range with an applied voltage of 10 mV.

The DSC (differential scanning calorimetry) measurement of samples, sealed into aluminum pans under an argon atmosphere, was performed using a Perkin-Elmer Pyris 7 differential scanning calorimeter. Heat-cool reheat cycles were performed at a rate of 10°C per minute from −70 to 200°C. The glass transition temperature of polymer electrolytes was reported for the second heating cycle.

## 2.2 Synthesis of the block PEO-based copolymer

PEG 400 and $CH_2Cl_2$ were polycondensated to form a soft main chain block polymer [9, 10].

## 2.3 Film preparation of composite polymer electrolytes

The block PEO polymer/$LiClO_4$ electrolytes with different (EO/Li) mole ratios were dissolved in acetonitrile, the acetonitrile solution with evenly dispersed $SiO_2$ powder was dropped into the solution above. Decanted the solution into the mold made of polytetera-fluoroethylene, then evaporated the solvent to form the film under drying atmosphere. Being vacuum drying at 70°C for 72 h, then placed into a drying cabinet with Ar protection for a week prior to use.

# 3 Results and discussion

## 3.1 Thermal properties of the compound polymer electrolyte

Figure 1 shows the DSC thermograms of 10% (mass fraction) $SiO_2$ composite polymer/$LiClO_4$ electrolytes with various $LiClO_4$ concentrations. The glass transition temperature $(T_g)$ acts as a function of salt concentrations. The thermogram of the composite electrolyte with salt EO/Li=31 shows an exothermic peak at −20°C and an endothermic peak at 10°C, cor-

responding to the recrystallization and melting of the block PEO polymer, respectively. The glass transition temperature of this composite electrolyte can also be found approximately at −53°C. The $T_g$ of the composite polymer electrolytes increases with the increasing of $LiClO_4$ concentration, and no recrystallization exotherm and melt endotherm can be found. This phenomenon can be interpreted as the Lewis base-acid type interactions among polymer matrix containing lithium cation and corresponding anion [11]. The increasing of $T_g$ with the incorporation of $LiClO_4$ can be attributed to the formation of transient cross-linking between the salt and the polyether phase.
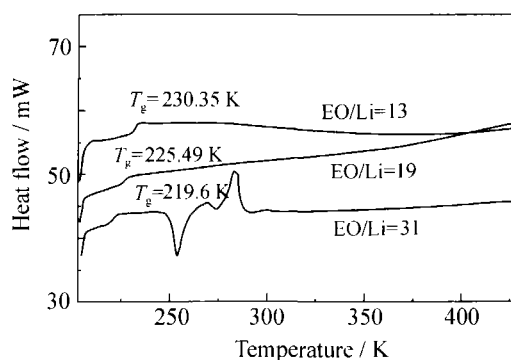


**Figure 1 DSC thermograms of composite polymer electrolytes with different salt concentrations.**

## 3.2 Effect of fumed $SiO_2$ on the block copolymer electrolyte film

Though the number average molecular mass of the PEG-based polymer reaches $10^5$ in this paper, the polymer main chain composed of soft −C−C−O− segments is difficult to form a self-standed film. The mechanical property and processability of the polymer matrix were enhanced when proper quantity fumed $SiO_2$ was adulterated into the polymer. Meanwhile the conductivity was also increased. **Table 1** shows that the effect of $SiO_2$ quantity on the processability and conductivity of the electrolyte. When the content of the fumed $SiO_2$ in the electrolyte was more than 10% the film would get brittle, there was fracture on the surface of the film, and the conductivity decreased. On the contrary, the conductivity was better when the content of the fumed $SiO_2$ in the electrolyte was less than 10%, while the processability was not enhanced and the self-supported film could not be formed.

## 3.3 Conductivity

The ionic conductivity of all polymer electrolytes was determined by means of impedance spectroscopy. From the $Z''$ versus $Z'$ plot, the ionic conductivity values were calculated at each temperature from the intercept of the curve with real axis. **Figure 2** shows the Arrhenius plots of the conductivity of optimum 10%

(mass fraction) $SiO_2$-added (table 1) and free-$SiO_2$ composite block PEO/$LiClO_4$ electrolytes. The figure clearly shows that in this electrolyte, the presence of the $SiO_2$-added induces the enhancement of the conductivity. As already pointed out, the role of $SiO_2$ can not be limited to the sole action of preventing the crystallization of block polymer chains, it also may extend to specific interactions induced by Lewis acid-base reactions between the filler's surface and the polymer segments. In fact, the Lewis-base groups of the added $SiO_2$ (*e.g.*, –OH groups on the $SiO_2$ surface) may quite likely compete with the Lewis-acid lithium cation for the formation of complexes with the polymer chains. Thus, these surface groups may provide cross-linking centers for the polymer segments, lowering the polymer chain reorganization tendency and promoting a structure modification, which induces $Li^+$ conducting pathways on the $SiO_2$ surface.

Table 1    Effect of fumed $SiO_2$ on the conductivity and processability for the polymer electrolyte (EO/Li = 25)

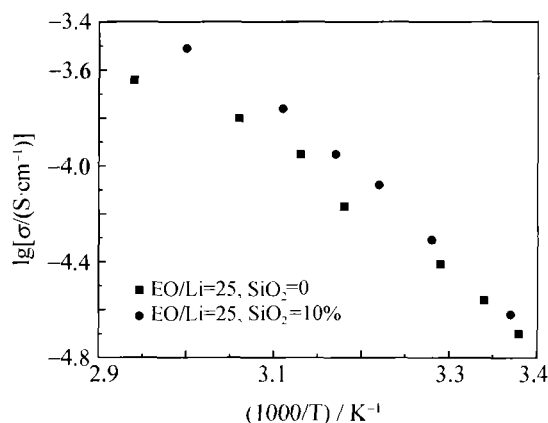| $SiO_2$ | Film apparent | $\sigma$ / ($10^{-5}$ S·cm$^{-1}$) |
|---|---|---|
| 0 | Sofer | 2.40 |
| 5% | Sofer | 2.45 |
| 10% | Good | 2.63 |
| 15% | Few flaws | 1.78 |
| 20% | Many flaws | 1.22 |



Figure 2    Temperature dependence of the conductivity of block PEO polymer/$LiClO_4$ with 0% and 10% $SiO_2$.

The dependence of the ionic conductivity on temperature for $SiO_2$ complexes with different $LiClO_4$ concentrations, $\lg\sigma$ is plotted against reciprocal absolute temperature in **figure 3**. The ionic conductivity increased with increasing the temperature, a maximum conductivity was obtained at the concentration of [EO]/[Li]=25. As the $LiClO_4$ concentration increases, the changes in free volume, electrostatic interactions, and transient coordination bond significantly affect the conductivity. From the conductivity data (figure 3), it is clear that these ion-transport behaviors [12] can not be explained by only the effect of the ionic mobility or

the number of carrier ions but are affected by the combination of these two effects. Over the salt concentration range, the maximum conductivity $\sigma=10^{-4.41}$ S/cm is found to be at EO/Li=25 and 30°C, $\sigma=10^{-3.40}$ S/cm at 66°C.
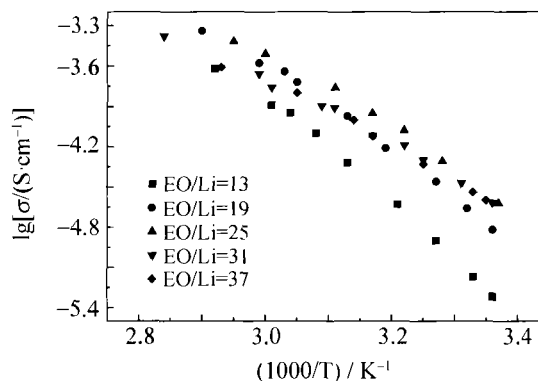


Figure 3    Dependence of the conductivity on temperature for composite electrolytes with different salt concentrations.

### 3.4 Electrochemical stability

The cyclic voltammogram of composite electrolytes is shown in **figure 4** for Li/composite electrolytes/SS cell at 40°C. Significant oxidative degradation of the composite electrolyte is not observed until a potential of 5 V (*versus* Li) is reached. Voltammograms show peaks associated to the oxidation process on the anodic site and the reduction on the cathodic site [13, 14]. These peaks might also be caused by the contaminated impurities in composite electrolytes. Thus, our polymer electrolytes could have sufficient electrochemical stability to allow safe operation in the rechargeable lithium battery.
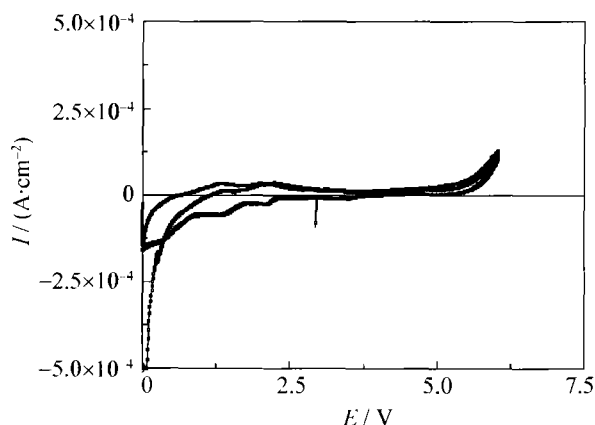


Figure 4    Cyclic voltammogram of composite electrolytes obtained at 40°C (the scan rate is 10 mV/s).

### 3.5 Interface properties with lithium

The performance of the interface between the lithium electrode and the composite polymer electrolyte was evaluated by measuring the AC impedance response of a Li/polymer electrolyte/Li cell stored at 60°C under the open-circuit potential conditions is

shown in **figure 5**. The changes in the bulk resistance ($R_b$) and the interfacial resistance ($R_e$) as a function of the storage time are shown in **figure 6**. The value of $R_b$ changes little during the experiment. On the other hand, $R_e$ increases rapidly initially, at a longer time, the resistance increases slowly, and after 8 days, it reaches an almost steady value. The initial increase in $R_e$ may be explained by the formation of a passivation film on the surface of the lithium electrode due to the residual impurities in the composite polymer electrolyte. Previous studies [15, 16] suggested that the interfacial resistance of the pure Li/PEO-LiClO$_4$/Li system was higher, and still increased after 8 days. The formation of a passivation film on the surface of the lithium electrode may be mainly due to the absorbed water in the pure Li/PEO-LiClO$_4$/Li system. The fine SiO$_2$ fillers are effective as a scavenger of water in the electrolyte. Therefore, the addition of SiO$_2$ was quite effective to reduce the interfacial resistance.
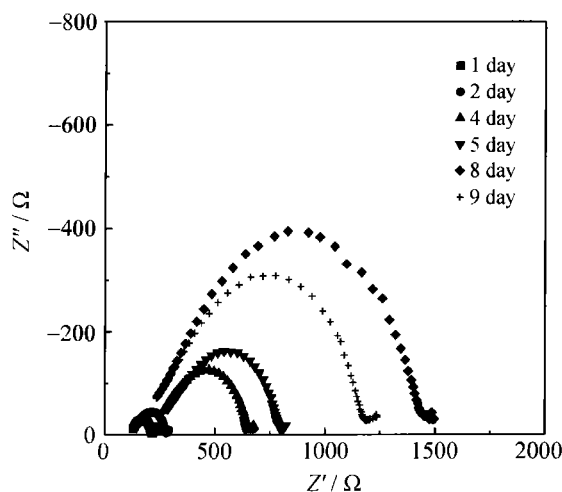


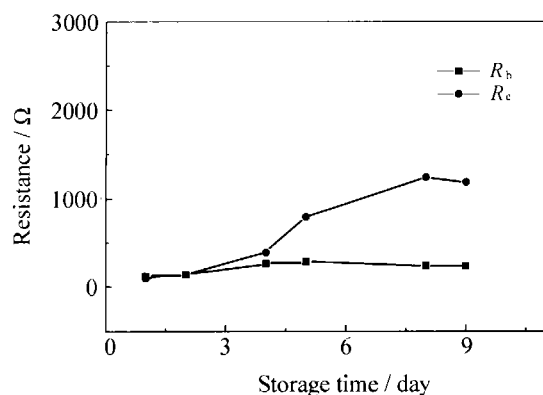**Figure 5**    **Niquist plots of composite eletrolyte at 60°C.**



**Figure 6**    **Variations of the bulk and interfacial resistance with the storage time.**

## 4 Conclusions

( 1) The addition of 10% (mass fraction) fumed SiO$_2$ to the block PEO/LiClO$_4$ electrolyte system forms a composite polymer electrolyte with a high conductiv-

ity film of $10^{-4.41}$ S/cm at room temperature. The ion-transporting behaviors can be explained not only by the effect of the ionic mobility or the number of carrier ions separately but also by the combination of these two effects.

(2) The DSC results indicate that the glass transition temperature of the composite polymer electrolyte increases with LiClO$_4$ concentration and no recrystallization exotherm and melt endotherm peaks can be found at high salt concentration.

(3) The composite electrolyte displays a sufficient electrochemical stability, and it's oxidative degradation potential is beyond 5 V (*versus* Li).

(4) Composite polymer electrolyte reacts with the lithium electrode to form passivation layer, which causes the interfacial resistance to increase slowly over the stored time and reach a steady value after 8 days.

## References

[1]   W. Huang and F. Frech, Dependence of ionic association on polymer chain length in poly (ethylene oxide)-lithium triflate complexes [J], *Polymer*, 35(1994), No.2, p. 235.

[2]   J. Koo and D. Kim, Poly (ethylene glycol) electrolyte gels prepared by condensation reaction [J], *J. Appl. Polym. Sci.*, 86(2002), p.948.

[3]   J.Y. Kim and H.K. Seong, Ionic conduction behavior of network polymer electrolytes based on phosphate and polyether copolymers [J], *Solid State Ionics*, 124(1999), p. 91.

[4]   K.M. Abraham, V.R. Koch, and T.J. Blakley, Inorganic-organic composite solid polymer electrolytes [J], *J. Electrochem. Soc.*, 147(2000), No.4, p. 1251.

[5]   C.Y.Y. Whie, H.C. Chen, F.J. Lin, C.W. Liao, and T.L. Chen, Preparation and conductivity of the composite polymer electrolytes based on poly [bis(methoxyeth-oxyethoxy) phosphazene], LiClO$_4$ and a-Al$_2$O$_3$ [J], *Solid State Ionics*, 156(2003), p.383.

[6]   H.W. Chen, C.Y. Chiu, H.D Wu, I.W. Shen, and F.C. Chang, Solid-state electrolyte nanocomposites based on poly (ethylene oxide), poly (oxypropylene) diamine, mineral clay and lithium perchlorate [J], *Polymer*, 43(2002), p. 5011.

[7]   B. Scrosati, F. Croce, and L. Persi, Impedance spectroscopy study of PEO-based nanocomposite polymer electrolytes [J], *J. Electrochem. Soc.*, 147(2000), No.5, p.1718.

[8]   D. Golodnitsky, G. Ardel, and E. Peled, ion-transport phenomena in concentrated PEO-based composite polymer electrolytes [J], *Solid State Ionics*, 147(2002), p.141.

[9]   G.R. Chen, P.F. Shi, Y.P. Bai, and T.B. Fan, Research on synthesis of liner PEO block polymer [J], *Polym. Mater. Sci. Eng.* (in Chinese), 19(2003), No.2, p.101.

[10]   G.R. Chen, P.F. Shi, Y.P. Bai, and T.B. Fan, Synthesis of amorphous PEO-polymer and study on its conductivity [J], *J. Functional Mater.* (in Chinese), 34(2003), No.2, p.176.

[11]   T. Fujinami, M.A. Mehta, K. Sugie, and K. Mori, Mo-

lecular design of inorganic-organic hybrid polyelectrolytes to enhance lithium ion conductivity [J], *Electrochim. Acta,* 45(2000), p.1181.

[12] A. Nishimoto, M. Watanabe, Y. Ikeda, and S. Kohjiya, High ionic conductivity of new polymer electrolytes based on high molecular weight polyether comb polymers [J], *Electrochim. Acta,* 43(1998), No.10-11, p.1177.

[13] E. Morales and J.L. Acosta, Synthesis and characterization of poly (methylalkoxysiloxane) solid polymer electrolytes incorporating different lithium salts [J], *Electrochim. Acta,* 45(1999), p.1049.

[14] D.W. Kim, Y.R. Kim, J.K. Park, and S.I. Moon, Electrical

properties of the plasticized polymer electrolytes based on acrylonitrile-methyl methacrylate copolymers [J], *Solid State Ionics,* 106(1998), p.329.

[15] Q. Li, H.Y. Sun, Y. Takeda, N. Imanishi, J. Yang, and O. Yamamoto, Interface properties between a lithium metal electrode and a poly (ethylene oxide) based composite polymer electrolyte [J], *J. Power Sources,* 94(2001), p.201.

[16] P.P. Prosini and S. Passerini, A lithium battery electrolyte based on gelled polyethylene oxide [J], *Solid State Ionics,* 146(2002), p.65.