Ionic Conductivity and Interfacial Properties of Polymer Electrolytes Based on PEO and Boroxine Ring Polymer

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ABSTRACT: Blended polymer electrolytes based on poly(ethylene oxide) (PEO) and boroxine ring polymer (BP) solvated with lithium triflate were formulated and evaluated. Compared to PEO–salt polymer electrolyte, ionic conductivities of blended polymer electrolytes were two orders of magnitude higher in a low-temperature range; as well, lithium transference numbers were increased to ~ 0.4. These were due to the increased mobility and anion trapping of boroxine rings. BP also exhibited the stabilizing effect on lithium–polymer electrolyte interface, and a reduced interfacial resistance between lithium metal and the polymer electrolyte was found with increasing of BP content. Polymer electrolytes based on PEO and BP are suitable for use in lithium secondary battery. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 17–21, 2002; DOI 10.1002/app.10090

Key words: blends; conducting polymers; interfaces

INTRODUCTION

During the past 3 decades, polymer electrolyte has been a heated topic for its potential application in high-energy-density batteries, and other electrochemical devices. Poly(ethylene oxide) (PEO) has been widely studied as a host polymer in polymer electrolytes, due to its chemical and electrochemical stability good mechanical properties;[1] however, some shortages, such as insufficient ionic conductivities (for the PEO–salt system, $\sigma < 10^{-8}$ S/cm at ambient temperature, and $\sigma \sim 10^{-5}$ S/cm at 100°C[2]), a relative low-lithium ionic transference number (for the PEO–salt sys-

tem, typically in the range of 0.2–0.3[3]), prevent it from practical use.

Some approaches to increasing ionic conductivities of PEO-based polymer electrolytes have been reported, such as a plasticizer,[4,5] nanometer size ceramic filler,[6,7] blended polymer electrolytes,[8,9] and so on. Polymer electrolytes for a lithium secondary battery should have the combination of high ionic conductivity, good electrochemical and thermal stability, as well as good mechanical properties. Whereas these desirable properties usually cannot be achieved by using a single polymer, blending polymers with the required characteristics is an important approach to modifying the characteristics of the system. Several of the authors have previously reported[10–13] that polymer electrolytes incorporating boroxine ring systems exhibit moderately high ionic conductivity, good electrochemical and thermal stability, as well as exceptionally high Li$^+$ transference numbers; however, it was difficult to concurrently

$$3 \, B_2O_3 \quad + \quad 1.6 \, HO(CH_2CH_2O)_4H \quad + \quad 2.8 \, CH_3O(CH_2CH_2O)_{7\cdot2}H$$
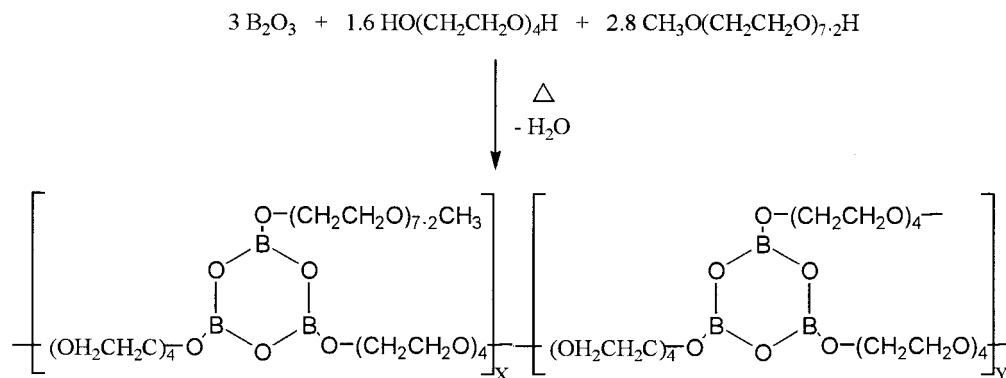
Scheme 1 Synthesis of anion trapping polymer containing boroxine rings.

EXPERIMENTAL

The oligoethers poly(ethylene glycol) monomethylether (M_w 350) and tetraethyleneglycol (TEG) (all Aldrich Chemical Co.) were dried by dry nitrogen bubbling under partial vacuum at 30–50°C for at least 24 h and were stored over molecular sieves. Boric oxide (Merck) was used as supplied. Poly(ethylene oxide) (PEO, Aldrich, M_w 5,000,000), lithium triflate, and solvents were rigorously dried before use. All manipulations were carried out on a dry nitrogen/vacuum line, and intermediates and final products were transferred to an argon filled glove box prior to use.

Boroxine ring polymer (henceforth denoted as BP) was prepared as shown in Scheme 1. Solutions in toluene of the glycol and PEGMME (350) were added to a 1–2% excess of boric oxide. After prolonged heating at 130–140°C (typically, 6 h under nitrogen flow, 6 h under vacuum) to remove water and toluene, a viscous yellow liquid was obtained. The structure of this polymer was confirmed with IR, and no peaks associated with remained alcohol were found.

BP and a calculated amount of PEO were dissolved in dry acetonitrile containing the calculated amount of lithium triflate to give a boroxine ring (Bx) : Li$^+$ ratio of 1 : 1. The solution was stirred until becoming homogeneous. Removal of the solvent under reduced pressure gave polymer electrolytes.

Ionic conductivities and interfacial resistances were performed by AC impedance measurement using a Solartron 1260 frequency response analyzer and 1287 electrochemical interface. Polymer electrolyte films of a thickness of 0.4 mm (controlled using a Teflon spacer) were prepared by the hot-pressing method at 60°C for 1 h, and were sandwiched between blocking stainless steel electrodes for conductivity measurements, and symmetrical nonblocking lithium–electrode cells were used to investigate interfacial phenomena. Before conductivity measurement, all samples were heated at 90°C for 2 h, then cooled to room temperature over about 2.5 h to get good electrode–electrolyte contact. All interfacial resistance measurements were carried out 12 h after preparation of the cells. A 10 mV AC amplitude was applied, and the data were collected over a frequency range from 1 MHz–0.1 Hz in conductivity measurements, and from 1 MHz–0.0001 Hz in interfacial resistance measurements. Bulk electrolyte resistances were determined from the width of the semicircle appearing at high frequency in the Cole–Cole plot, and interfacial electrolyte resistances were determined from the width of the semicircle appearing at an intermediate frequency. Cationic transference numbers of samples sandwiched between nonblocking lithium electrodes were determined using the combined AC impedance/DC polarization method Evans modified by Abraham.[14,15]

Differential scanning calorimetry (DSC) of samples, sealed into aluminum pans under an argon atmosphere, was performed using a Perkin-Elmer Pyris 1 differential scanning calorimeter.

Heat-cool reheat cycles were performed at a rate of 10°C per minute from −100 to 200°C. Glass transition temperatures (T_g) of polymer electrolytes were reported for the second heating cycle.

RESULTS AND DISCUSSION

Boroxine ring polymers (BP) exhibit high Li$^+$ transference numbers, good electrochemical and thermal stability; however, it was found to be difficult to concurrently achieve electrolyte films with good mechanical properties and high ionic conductivity; on the other hand, polymer electrolytes based on PEO exhibit good electrochemical stability and mechanical properties, but insufficient ionic conductivity and lithium ionic transference number. Blended polymer electrolytes based on PEO and BP solvated with lithium triflate with various compositions were prepared. Polymer electrolytes with lower than 30% PEO content showed inadequate mechanical properties at room temperature. Visible phase separation was found for blended polymer electrolyte consisting of 50% PEO and 50% BP.

Figure 1 shows the ionic conductivities of these polymer electrolytes. It can be seen that an increase in ionic conductivity of the polymer electrolytes was observed with increasing BP content in the polymer electrolyte, especially in the low temperature range. At temperatures lower than the melting point of PEO, ionic conductivity decreased with an increase of PEO content, and this could be ascribed to the crystallization of PEO (polymer electrolyte containing 50% PEO exhibited a lower ionic conductivity than that containing 60 and 70% PEO at low temperatures, and this should be associated with the visible phase separation occurring at this composition); however, at temperatures above the melting point of PEO, the polymer electrolyte with 70% PEO exhibited the highest ionic conductivities. This was because the PEO is amorphous, and can facilitate ion transport at temperatures above its melting point. The salt content in the polymer electrolyte decreased with an increase of PEO content, and thus even if at high temperatures, ionic conductivities of polymer electrolyte with very high PEO contents, and consequently low salt contents, were low.

To increase conductivity of polymer electrolytes, much attention has been paid to synthesize low T_g polymer electrolytes.[16] The dependence of T_g against the composition of polymer electro-
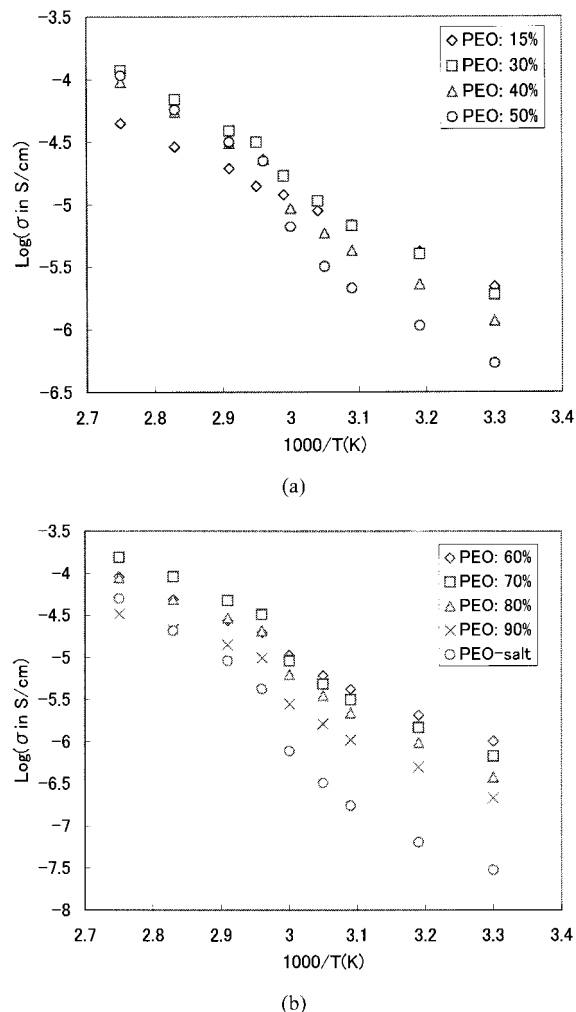

(a)

(b)

Figure 1   Ionic conductivities of polymer electrolytes based on PEO and BP solvated with lithium triflate (Bx : Li$^+$ = 1 : 1 (mol); BP% = (100 − PEO)%) (PEO-Salt : PEO–lithium triflate; EO : Li$^+$ = 16 : 1).

lytes is shown in Figure 2. Even if phase separation was observed, DSC curves for the blended polymer electrolytes exhibited a single glass transition temperature (T_g), because of the little difference between T_gs of PEO and BP. Blended polymer electrolytes exhibited much lower T_g compared to PEO–lithium salt polymer electrolyte;[17] at the same time, T_gs of polymer electrolytes slightly decreased with increasing BP content in the polymer electrolyte; therefore, mobility of PEO polymer electrolyte was increased upon blended with BP, and this gave higher ionic conductivity.

Compared with PEO–lithium salt polymer electrolytes,[3] blended polymer electrolytes containing BP exhibited higher lithium ionic trans-
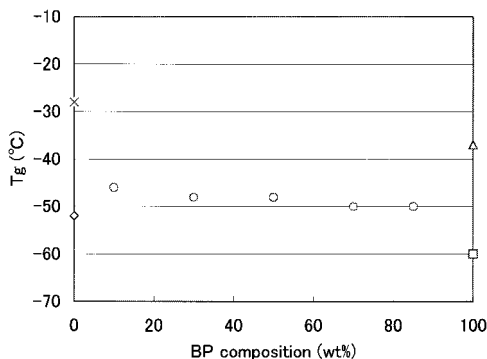
Figure 2 T_g against compositions of polymer electrolytes. Diamond: pure PEO; cross: PEO–lithium triflate (EO : Li$^+$ = 16 : 1 (mol)); triangle: BP–lithium triflate (Bx : Li$^+$ = 1 : 1 (mol)); square: pure BP; circle: blended polymer electrolytes (PEO% = (100 − BP)%; Bx : Li$^+$ = 1 : 1 (mol)).

ference number values (T^+) (T^+ of 70% PEO–30% BP (Bx : LiCF$_3$SO$_3$ = 1 : 1) is 0.38 at 70°C, and T^+ of 40% PEO–60% BP (Bx : LiCF$_3$SO$_3$ = 1 : 1) is 0.40 at 70°C). The increase of lithium transport number was ascribed to the interaction between anion and anion trapping boroxine rings. Solid state ^{11}B-NMR data[10,11] have demonstrated that there are strong interaction between boroxine rings and some anions (Scheme 2), such as CF$_3$SO$_3^-$, I$^-$. However, T^+s of blended polymer electrolytes were much lower than that of BP–lithium triflate polymer electrolyte[10,11] or polymer electrolytes based on PMMA and boroxine ring compounds.[13] The reason for this is unclear at present, but we suggest this should be connected with that PMMA polymer exhibits inadequate polarity to disassociate lithium salt and provides no conducting pathway itself. In BP–lithium triflate polymer electrolyte or polymer electrolytes based on PMMA and boroxine ring compounds, lithium salt is disassociated only by ether oligomers on BP, and transports via segmental motion of ether oligomers on BP.

The lithium metal–polymer electrolyte interfacial resistance (R_i) can be calculated from the
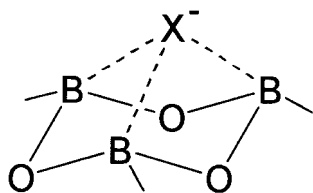
Scheme 2 Interaction between anion trapper boroxine ring and anion.
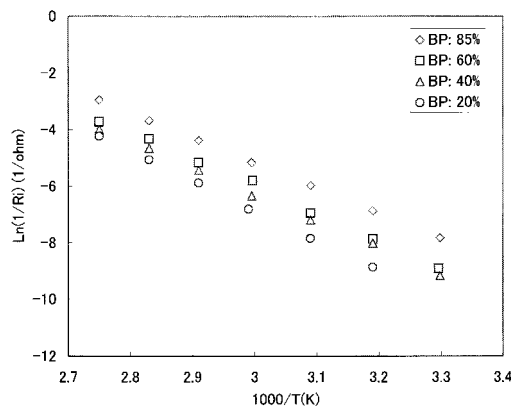

Figure 3 Temperature dependence of the reciprocal of the R_i of polymer electrolytes as a function of inverse temperature (PEO% = (100 − BP) %; Bx : Li$^+$ = 1 : 1 (mol)).

width of the semicircles arising in the intermediate frequency region of the ac impedance plot. Zhang et al.[18] reported the stabilizing effect of boric acid esters of glycols on lithium–liquid electrolyte interface, and they proposed that this was due to the formation of a protective amorphous LiBO$_2$ single ion conducting film on the lithium surface. The same effect was found on lithium-blended polymer electrolyte interface containing the boroxine ring polymer. Figure 3 shows interfacial resistances were reduced by incorporation of BP content into polymer electrolytes.

The inverse of R_i represents the rate of the charge transfer reaction at the interface;[19] therefore, introduction of BP into polymer electrolyte is beneficial for improving the rate of the charge transfer reaction at the interface between lithium metal and the polymer electrolyte. The temperature dependence of R_i can be described by an Arrhenius-type dependence eq. (1) for each electrolyte composition.[19]

$$R_i^{-1} = A \, \exp\left(\frac{-E_a}{k_B T}\right) \qquad (1)$$

Here, A is a preexponential factor, E_a is activation energy, and k_B is the Boltzmann constant. The temperature dependence of the reciprocal of the R_i as a function of inverse temperature is shown in Figure 3, and values of activation energy calculated on the basis of eq. (1) are shown in Figure 4. The activation energies decreased with increasing BP content in the polymer electrolytes. Further study of polymer and morphology on
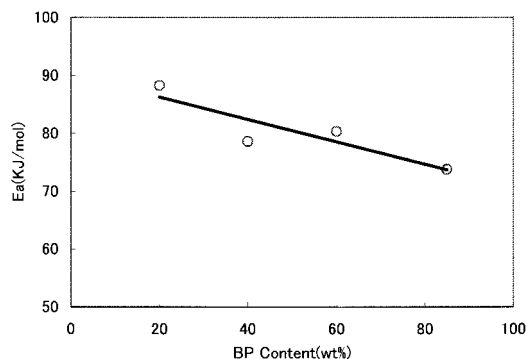
Figure 4 Activation energy of different polymer electrolytes calculated on the basis of eq. (1) (PEO% = (100 − BP)%; Bx : Li$^+$ = 1 : 1 (mol)). Line is drawn as a guide to the eye.

ionic conductivities as well as electrochemical characterization of polymer electrolytes will be described in subsequent articles.

CONCLUSIONS

Blended polymer electrolytes based on PEO and an anion trapping boroxine ring polymer exhibited higher ionic conductivity, higher lithium ion transference number, and reduced interfacial resistance; therefore, it was promising to get polymer electrolytes beyond shortages of PEO in this way.

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