Single-Ion Conduction and Lithium Battery Application for Ionomeric Cross-Linking Polymer

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SYNOPSIS

The single-Li^+ conduction of the cross-linking poly[oligo(oxyethylene) methacrylate-co-lithium methacryloyl hexylsulfonate]s was studied, and an Li^+ ionic transport number of 0.994 estimated from the isothermal transient ionic current (ITIC), in which an ion-blocking platinum electrode was used. The results show that Li^+-ionic conduction can be reasonably described by Vogel–Tammann–Fulcher (VTF) equation, suggesting that there is close correlation between ionic migration and segmental motion in these polymers. The battery composed of lithium/this copolymer film/polyaniline supplied a constant short circuit current (J_{SC}) of 45 $\mu A/cm^2$ and an open circuit potential (V_{OC}) of 3.6 V at 25°C. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric solid electrolytes (PSE) have recently received extensive attention for their potential application in solid electrochemical devices, especially in lithium batteries with Li^+-inserted compounds as cathodic materials. The emphasis mainly has been on improving the conductive and mechanical properties of PSEs, and hence a principle that amorphous domain of PSEs functions as an ionic conduction host. That there is a close correlation between ion conduction and segmental motion of matrix polymer has guided the achievement of these objectives.[1] Although great progress had been made, in addition to ionic conductivity the cationic transport feature also plays an important role in the performance of lithium batteries, which therefore initiates the study of single-ion conductors with opposite anions fixed covalently in the macromolecular chain.[2-8] Unfortunately, single-ion conductors possess far lower conductivity (ca. 10^{-7}–10^{-8} s/cm at room temperature if no liquid additives are used) than the corresponding bi-ion conductors since only cations can act as the charge carrier. Thus, increasing conduc-

tivity has become a key to the study of single-ion conductors, which to some extent can be realized by means of blending,[2] copolymerizing,[3,4] cross-linking,[5] and controlling the length of side-chains in comb-like polyethers[6-8] even if no plasticizers are used. In this paper we report Li^+-ionic conduction of the cross-linking poly[oligo(oxyethylene) methacrylate-co-lithium methacryloyl hexylsulfonate]s and their application to the solid-state polyaniline/lithium (PAn/Li) battery. Meanwhile, the VTF empirical equation and Adam–Gibbs configurational entropy model will be used to analyze conductivity data.
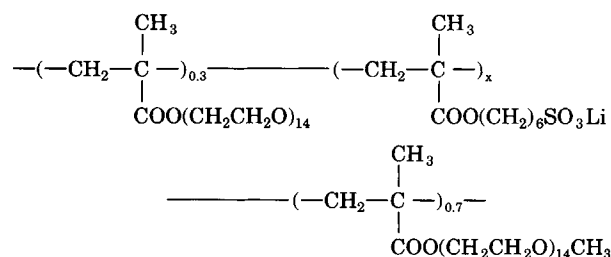
EXPERIMENTAL

Materials

Oligo(oxyethylene) methacrylate (MEO_n, $n = 14$) was previously prepared by esterification of monomethoxyl oligo(oxyethylene) (MePEG) with methacryloyl chloride at room temperature with triethylamine as catalyst, in which a well-defined MePEG had conveniently been made by means of ring-opening polymerization of oxirane with potassium monomethoxyl di(oxyethylene) glycol ether as initiator under near normal pressure.[5] The structure of resultant MEO_n was checked by IR, ^1H-

NMR, and analysis of Cl-element. The GPC results gave an M_w/M_n value of 1.05, confirming that MEO_n has a narrow molecular weight distribution. Similarly, the esterification of oligo(oxyethylene) glycol and methacryloyl chloride produced oligo(oxyethylene) dimethacrylate ($DMEO_n$, $n = 14$), a cross-linking reagent used in this work.

Lithium methacryloyl hexylsulfonate (SHMLi) was synthesized by the reaction of lithium 6-hydroxyhexane sulfonate with methacrylic acid in the presence of hydroquinone at reflux temperature. The experimental procedure has been described in detail previously.[2,4,5]

Copolymerization of SHMLi, MEO_n, and $DMEO_n$ ($n = 14$) was carried out in absolute methanol solution with 2,2'-azobisisobutyronotrile as initiator at 60°C for 24 h as described elsewhere.[2,4,5] The resulting polymers were precipitated, washed with ethyl ether, and finally dried at 80°C under reduced pressure for at least 24 h. The salt concentration of resultant copolymers was expressed in terms of O/Li and the cross-linking degree was defined as the molar ratio of $DMEO_n$ to the total EO-containing monomers. In this paper the cross-linking degree of all the copolymers is 30 mol %: in other words, the copolymers may be abbreviated as P(0.7 MEO_{14}-0.3 $DMEO_{14}$-SHMLi) whose structural formula is illustrated as follow:

$$-(-CH_2-\underset{\underset{COO(CH_2CH_2O)_{14}}{|}}{\overset{\overset{CH_3}{|}}{C}}-)_{0.3}-------(-CH_2-\underset{\underset{COO(CH_2)_6SO_3Li}{|}}{\overset{\overset{CH_3}{|}}{C}}-)_x$$

$$-------(-CH_2-\underset{\underset{COO(CH_2CH_2O)_{14}CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-)_{0.7}-$$

Polyaniline (PAn) was synthesized according to the Chiang and Macdiarmid method.[9] The obtained product doped by an appropriate amount of $HClO_4$ is a blue-black power with conductivity ranging between 10^{-1} and 10^{-2} s/cm at ambient temperature.

Measurements

All measurements were conducted in a glove box filled with dry nitrogen.

Ac conductivity was determined by using an ac conductometer (1.10 kHz) as described elsewhere.[2] The sample that was sandwiched between Pt electrodes was allowed to equilibrate thermally for 1 h at each temperature before a measurement was made following each incremental rise. The same cell was used to measure the isothermal transient ionic current (ITIC) by using 173 model potentiostat/galvanostat apparatus, from which the Li$^+$-ionic transport number was estimated. The procedure outlined by Watanabe et al. was followed.[10] Using the same apparatus the measurement of J-V characteristic and discharging process for the battery (Li/PSE/PAn) was performed by recording current at different time intervals.

Glass transition temperature (T_g) of the cross-linking copolymers was evaluated with a Perkin-Elmer 7 Series Thermal Analyzer. The T_g was taken as the midpoint temperature of the base-line shift observed during the transition from the glass to the rubber-like state. The scanning rate was 10°C/min.

RESULTS AND DISCUSSION

Conduction Mechanism of Lithium Ions in Polymer Matrix

Conductivities of the cross-linking copolymers have two maximum values at O/Li value of ca. 24 and 72, respectively, as well as a minimum value at O/Li of ca. 36, as illustrated by the previous work.[5] Conductivities of these three samples were therefore typically determined from 25–90°C, which are plotted against reciprocal absolute temperature in Figure 1. The plots of log σ vs. $1/T$ is a curved line rather than linear line, suggesting that lithium transport occurs in amorphous regions and segmental motion plays an important role in ion conduction. Thus the
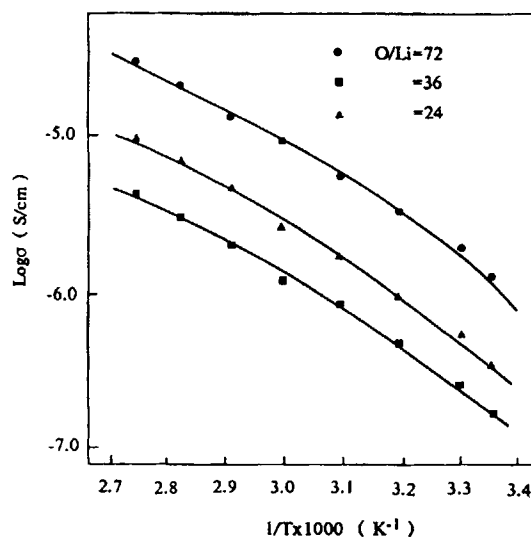

Figure 1 Li$^+$-ionic conductivity as temperature function for the P(MEO_{14}-$DMEO_{14}$-SHMLi).

Table I   VTF Parameters for P(MEO$_{14}$-DMEO$_{14}$-SHMLi) Together With Heat Capacity and Activation Energy Values

O/Li	T_g (K)	A	B	T_o (K)	$(T_g - T_o)$ (K)	ΔC_p (J/K · mol)	$\Delta\mu$ (kJ/mol)
72	222	0.214	1166	173	49	25.6	55.3
36	227	0.027	1110	178	49	28.7	58.6
24	228	0.093	1166	178	50	27.1	58.4

Vogel–Tammann–Fulcher (VTF) equation was adequately used to analyze the obtained conductivity data usually used to describe the behavior of mass transport in amorphous polymers[11]:

$$\sigma = AT^{-1/2}\exp\left(\frac{-B}{T - T_o}\right) \qquad (1)$$

where T is the absolute temperature (K); A and B are empirical constants related to the number of charge carriers and conduction activation energy, respectively; and T_o is the thermodynamically limited glass transition temperature, below which there is no further entropy loss caused by configurational changes in the polymer. According to the configurational entropy model of Gibbs et al. the T_o is predicted to be approximately 50 K lower than T_g. The constant B can be expressed as a function [eq. (2)] of ΔC_p, the change in heat capacity at temperature T as the polymer transfers from the glass to the

$$B = \frac{T_o S_c^* \Delta\mu}{\kappa \Delta C_p T} \qquad (2)$$

rubber-like state; $\Delta\mu$, the molar free energy barrier of segmental rearrangement; and ΔS^*, the minimum configurational entropy required for such a segmental rearrangement. A reasonable approximation for S_c^* is $\kappa \ln 2$ where κ is the Boltzmann constant.

A nonlinear least squares analysis of the data yields the values of A, B, and T_o as listed in Table I and then the $\Delta\mu$ values are calculated through eq. (2) from the ΔC_p and the derived T_o values where the values of ΔC_p expressed in terms of kJ/mol of ethylene oxide are determined from DSC traces. When these constants are substituted for eq. (1), all give good linear plots for the different polymers (Fig. 2). The $(T_g - T_o)$ values ranging over 49–50 K for these three cross-linking copolymers are well coincided with the theoretical value. This suggests that the configurational entropy theory might have some validity in our system. In other words, the conduction of lithium ions in these network poly-

mers is mainly influenced by segmental motion of matrix polymer.

The $\Delta\mu$ values remain almost at a constant of ca. 58 kJ/mol, implying that there should be near-activation energies of segmental arrangement for these polymers since the Adam–Gibbs theory suggests that $\Delta\mu$ represents the activation energy of spatial rearrangement of the segments. They are found to be very close to those observed in the complexes of cross-linking polyether with lithium perchlorate.[12] This may be caused by the similar effect of cross-linking reagent on the segmental motion, which then influences the activation energy of ionic conduction.

ITIC

Figure 3 shows the dependence of ITIC upon time, during which a constant voltage of 3.0 V dc is applied for 1 h across the polymer P(MEO$_{14}$-DMEO$_{14}$-SHMLi) (σ = 1.1 × 10^{-6} s/cm at 25°C) film and then voltage polarity is reversed for another 6 h. For the initial period of 3.0 V dc polarization the ITIC decreases steeply and then attains a negligible level, which makes us conclude that ionic migration dom-
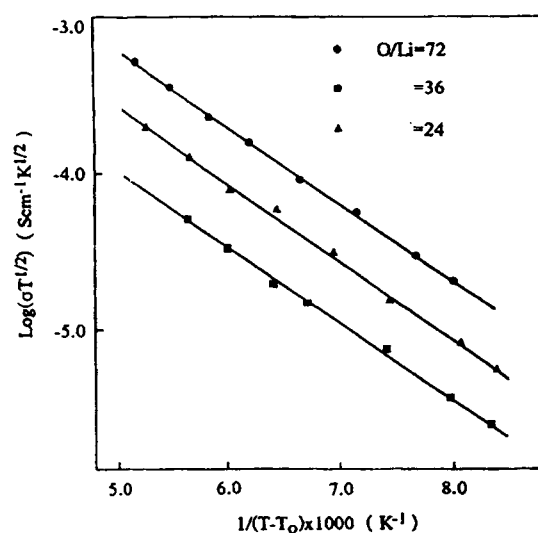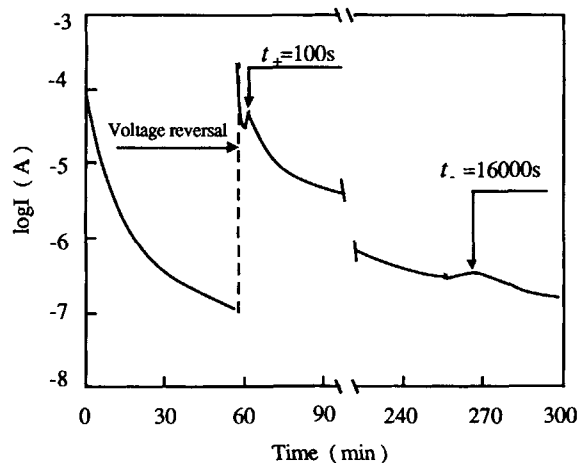

Figure 2 VTF plots of the P(MEO$_{14}$-DMEO$_{14}$-SHMLi).

Figure 3   ITIC curve of 3.0 V dc for P(MEO$_{14}$-DMEO$_{14}$-SHMLi) at 25°C. The sample size: diameter, 12 mm; thickness, 200 μm.

inates the conductivity of the polymer. In this period the rapid decrease of ITIC is mainly caused by the decrease in the number of carrier ions in the bulk since an ion-blacking platinum electrode provides no carrier ions when lithium ions migrate toward the anode and accumulate in the vicinity of the anode. After the polarity of the applied voltage is reversed, the ITIC jumps to a certain level, and then yields two ITIC peaks at particular time of 100 s and 16000 s, respectively (Fig. 3). This is similar to the observance for poly(ethylene succinate)/LiSCN system by Watanabe et al.[10] The position of ITIC peaks should be of great concern with the dominant carrier ionic species and its mobility since ITIC probably results from the release of the accumulated carrier ions from the corresponding electrodes. Therefore, two ITIC peaks observed may be attributed to lithium ions and anions, respectively. The initial peak should be ascribed to lithium ion caused mainly by its smaller volume and larger charge density, both of which leads to a greater mobility. Theoretically ionic mobility (μ) may be written by the following formula[10]:

$$\mu = \frac{d^2}{tV^*(t)} \qquad (3)$$

where d is the thickness of the sample; t, time corresponding to the maximum ITIC, is the time-of-flight taken for carrier ions to reach one electrode from another electrode of the cell; $V^*(t)$ is an effective voltage across the sample. The $V^*(t)$ should be the same for both cations and anions, hence lithium ionic transport number can be calculated from eq. (4)

$$t_{Li^+} = \frac{1/t_+}{1/t_+ + 1/t_-}. \qquad (4)$$

The t_{Li^+} of the P(MEO$_{14}$-DMEO$_{14}$-SHMLi) is found to be 0.994, verifying the single-ion conduction of this ionomeric cross-linking polymer.

Properties of Rechargeable Batteries Using Polymeric Electrolyte

In order to compare the merit of the single-ion conductor to the bi-ion conductor film with lithium ion transport number of 0.3–0.5, PMEO$_{14}$/LiClO$_4$, the P(MEO$_{14}$-DMEO$_{14}$-SHMLi) film (ca. 200 μm) is also used to assemble the solid lithium battery in the structure of ($-$)lithium/PSE/polyaniline(+). The discharge curves of these two batteries under short-circuit condition are indicated in Figure 4. The short circuit current (J_{SC}) of the battery (I) containing single-Li$^+$ conductor slightly rises at first period, then reaches a constant value of ca. 45 μA/cm^2 at 25°C and supplies current continuously for longer than 3 h, which reflects a stable dc conductivity of this film. While the J_{SC} of the battery (II) containing bi-ionic conductor (PMEO$_{14}$/LiClO$_4$ complex possessing an ac conductivity of 1.4 $\times$ 10^{-5} s/cm at 25°C) decays rapidly upon discharge time, which might be ascribed to the decrease in dc conductivity resulting from anionic migration toward the cathode. The J-V characteristic of the battery (I) is obtained by monitoring the current density under the controlled potential as illustrated in Figure 5. From the intercept of J-V curve an open circuit potential (V_{OC}) of 3.6 V and a J_{SC} of 44 μA/cm^2 at 25°C are estimated for this battery. These two values
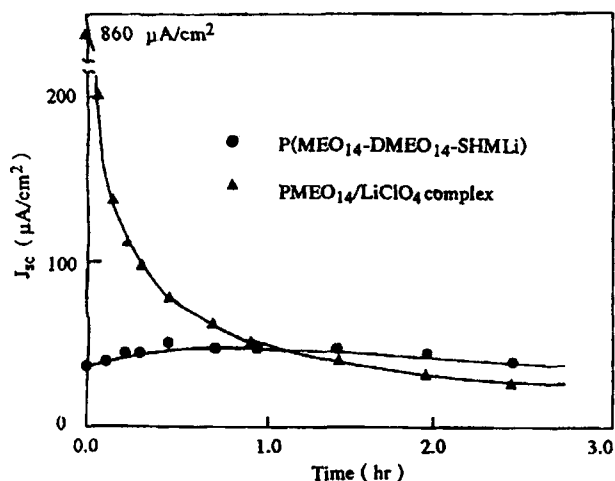

Figure 4   Time dependence of short-circuit current for the Li/polymeric electrolyte/PAn battery at 25°C.
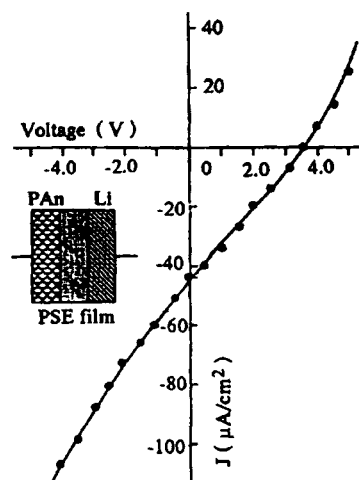
Figure 5 J-V characteristic of Li/P(MEO$_{14}$-DMEO$_{14}$-SHMLi)/PAn battery at 25°C. Electrolyte film thickness: 200 μm.

coincide with (E'_{Li} − E'_{PAn}) value and with the σ_{dc} value of the ionomeric cross-linking polymer used here.

CONCLUSION

Crosslinked poly[oligo(oxyethylene) methacrylate-co-lithium methacryloyl hexylsulfonate] possesses a conductivity as high as 1.1×10^{-6} s/cm at 25°C and an Li$^+$-ionic transport number of 0.994. Temperature dependence of Li$^+$-ionic conductivity exhibits non-Arrhenius behavior and the data can be well analyzed by the VTF empirical equation and the Adam–Gibbs configurational entropy model. The battery composed of Li/this film/PAn provides a constant J_{SC} of 45 μA/cm^2 for more than 3 h and an open circuit potential (V_{OC}) of 3.6 V at 25°C.

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