

Boroxine ring containing polymer electrolytes

Mary Anne Mehta ^{a,*}, Tatsuo Fujinami ^a, Takayoshi Inoue ^b

^a Department of Materials Science, Faculty of Engineering, Shizuoka University, Hamamatsu, 432-8561 Japan

^b Genesis Research Institute, 4-1-35, Noritakeshinmachi, Nishiku, Nagoya 451-0051, Japan

Abstract

Anion trapping polymer electrolytes incorporating boroxine (B_3O_3) rings and oligoether side chains have been demonstrated to combine high Li^+ ion transference numbers, thermal stability and an electrochemical stability window in the region of 4.9 V. Ionic conductivities of up to $1.6 \times 10^{-5} S cm^{-1}$ at 30°C and which exhibit Volger–Tamman–Fulcher (VTF) behaviour have been observed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polymer electrolyte; Boroxine ring; Ionic conductivity

1. Introduction

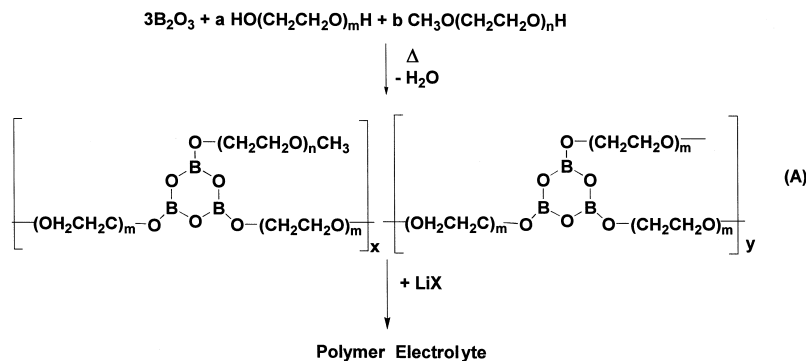
Since their initial discovery, solid polymer electrolytes have been attracting extensive attention due to their potential for application in a variety of all solid-state electrochemical devices. In particular, recent research has focused on the development of Li^+ ion-conducting electrolytes with high conductivity for use as the separator in lithium rechargeable batteries [1–6]. Most conventional solid polymer electrolytes are formed by the dissolution of a salt in a polymeric host and thus the conductivity contains contributions from both cation and anion motion. Since the report [7] that improved battery performance may be obtained by using electrolytes with high Li^+ ion transference numbers, many workers have focused on the development of single ion-conducting ‘polyelectrolytes’ which contain the anion immobilised onto the polymer backbone [8–11]. Such polyelectrolytes suffer from the problem of reduced ionic conductivity, typically at least 1–2 orders of magnitude less than bi-ion conductors. This may be ascribed to the reduced number of charge carriers combined with the effect of strong ion pairing between the cation and the bound anion. In addition, elaborate and costly synthetic techniques are often necessary for the preparation of these electrolytes.

In this laboratory, we have been developing the concept of anion trapping polymer electrolytes. We recently reported systems in which enhanced Li^+ ion transference numbers were achieved by the incorporation of anion trapping boroxine rings into the polymer host [12,13]. The polymer electrolytes were prepared by the very simple synthetic route illustrated in Scheme 1. Variation of the fraction of glycol in the system allowed control of the degree of cross-linking. Systems incorporating large proportions of glycol exhibited enhanced mechanical properties but a reduction in ionic conductivity was observed. Using a standard polymer host (defined as $a = 2.2$, $m = 4$, $b = 1.6$ and $n = 7.2$ in Scheme 1), optimum conductivity was observed for a $LiCF_3SO_3$:boroxine ring ratio of 0.5:1. In this paper, we report the electrochemical and thermal characteristics of these polymer electrolytes together with a discussion of the conductivity mechanism.

2. Experimental

The oligoethers poly(ethylene glycol) monomethylether (MW 350), (PEGMME 350) and tetraethyleneglycol (TEG), (Aldrich Chemical), lithium salts and all solvents were rigorously dried before use. Lithium aluminium hydride (1 M solution in tetrahydrofuran (THF), Aldrich Chemical) was used as supplied. Unless otherwise stated, all manipulations were carried out on a dry nitrogen/vacuum line. Host polymers were prepared according to

* Corresponding author. Tel.: +81-53-478-1176; Fax: +81-53-478-1176; E-mail: tcmehta@eng.shizuoka.ac.jp



Scheme 1. Synthesis of polymer electrolytes containing boroxine rings.

Scheme 1 as previously reported [12,13]. Polymer electrolyte yields in excess of 95% were routinely achieved. Intermediates and final products were transferred to an argon-filled dry box prior to use.

Solid state ^{11}B -NMR spectra of samples were obtained using a JEOL Ex270 NMR spectrometer operating at 86.68 MHz. Samples were packed into sealed zirconia sample tubes under dry argon and all resonances were externally referenced to the ^{11}B -NMR spectra of solid NaBH_4 (-61.0 ppm with $\text{B}(\text{OCH}_3)_3$ defined as 0.0 ppm).

Ionic conductivities were determined by AC impedance measurement of samples sandwiched between blocking stainless steel electrodes using a Solartron 1260 frequency response analyser and 1287 electrochemical interface. (Signal amplitude 10 mV, frequency range typically 1 MHz– 1 Hz). Cationic transference numbers were determined using the combined AC/DC polarization method of Evans et al. [14].

Cyclic voltammetry of samples using a Pt working electrode ($A = 0.30$ cm 2) and Pt pseudo reference electrode was performed using a Solartron 1287 electrochemical interface under the control of Corrware electrochemical software [15].

Differential scanning calorimetry (DSC) of samples, sealed into aluminium 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 $10^\circ\text{C}/\text{min}$. Glass transition temperatures (T_g) were reported as the onset temperature for the transition observed on the second heating cycle.

3. Results and discussion

The thermal and electrochemical characteristics for standard polymer electrolytes with a Li salt:boroxine ring ratio of $0.5:1$ are illustrated in Table 1. Maximum conductivity was observed for the system containing $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. DSC measurements indicated that the electrolytes were thermally stable (the majority to in excess of

250°C) and completely amorphous. The ionic conductivity (σ) of amorphous polymer electrolytes is often observed to obey the Volger–Tamman–Fulcher (VTF) equation:

$$\sigma = AT^{-1/2} \exp[-B/(T - T_0)]$$

where A and B are constants related to the number of charge carriers and the activation energy for ion conduction, respectively. The standard temperature, T_0 , is the temperature below which there is no further entropy loss resulting from configuration changes of the polymer. VTF plots for standard polymer electrolytes containing a variety of lithium salts are illustrated in Fig. 1. Since it is often observed that T_0 falls approximately 50 K below T_g [16], T_0 was taken as $T_g - 50$ K. The linearity of these plots suggests that the ionic conductivity can be well described by the VTF equation and that therefore, ion transport is facilitated by the segmental motion of the oligoether chains.

The effect of varying the Li^+ :boroxine ring ratio on the ionic conductivity and thermal properties was investigated for the system containing LiCF_3SO_3 . Examination of the conductivity isotherms (at 30° , 60° , 80° and 100°C) illustrated in Fig. 2 shows that at each temperature there is a tendency to pass through a maximum as the salt concentration is increased. This is a common phenomenon observed in polymer electrolytes and can be ascribed to the compet-

Table 1
Electrochemical and thermal characteristics of polymer electrolytes

Salt	σ (at $30^\circ\text{C}/\text{S cm}^{-1}$)	T_+	T_g ($^\circ\text{C}$)	Decomposition ($^\circ\text{C}$)
$\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$	1.6×10^{-5}	–	-41	189
LiCF_3SO_3	7.2×10^{-6}	0.75	-40	251
LiBF_4	4.8×10^{-6}	0.75	-40	> 250
LiClO_4	2.9×10^{-6}	–	–	218
LiBr	9.5×10^{-7}	0.62	-45	> 250
LiCl	6.6×10^{-7}	0.88	-56	> 250
LiPF_6	1.6×10^{-7}	–	–	> 250
None	2.5×10^{-9}	–	-72	> 250

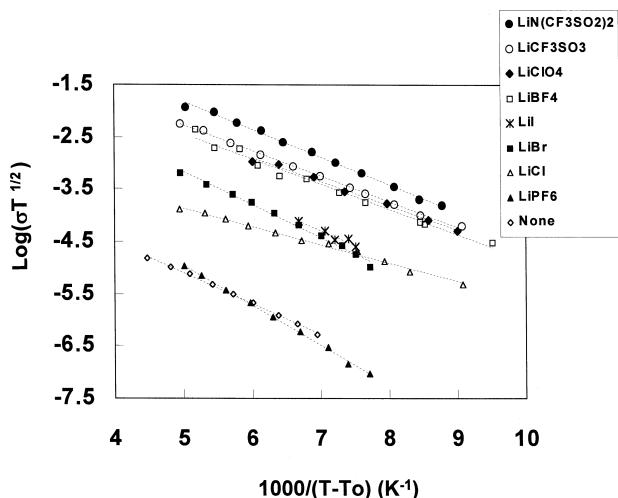


Fig. 1. Ionic conductivity (σ) of polymer electrolytes containing a variety of lithium salts. Dashed lines have been fitted to the VTF equation taking $T_0 = T_g - 50$ K.

ing effects of increasing charge carrier density with increasing ion pairing and decreasing polymer segmental motion. This latter effect is a result of the increase in intra-chain stiffening accompanying solvation which is also apparent in the variation of T_g with concentration as illustrated in Fig. 3. While optimum conductivity is observed for the sample containing a LiCF_3SO_3 :boroxine ring ratio in the region of 0.5:1 at room temperature, as the temperature is raised, and therefore, the polymer segmental motion increases, there is a slight tendency for the peak maximum to shift towards higher concentration.

Solid-state ^{11}B -NMR measurements of the standard polymer host exhibited a single broad peak which was ascribed to the resonance of tri-coordinate boron in the

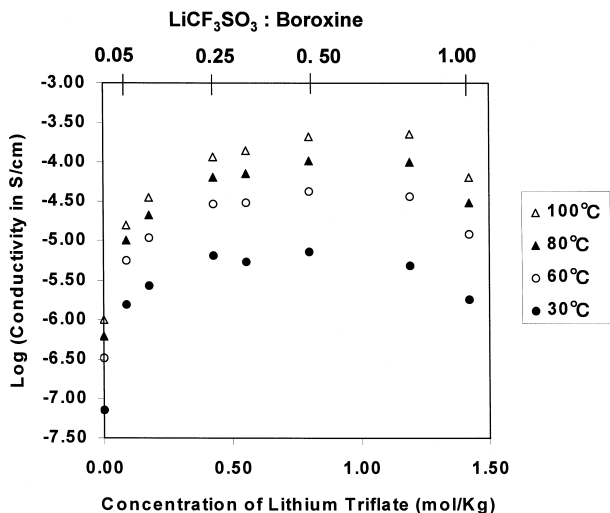


Fig. 2. Conductivity isotherms for polymer electrolytes containing LiCF_3SO_3 .

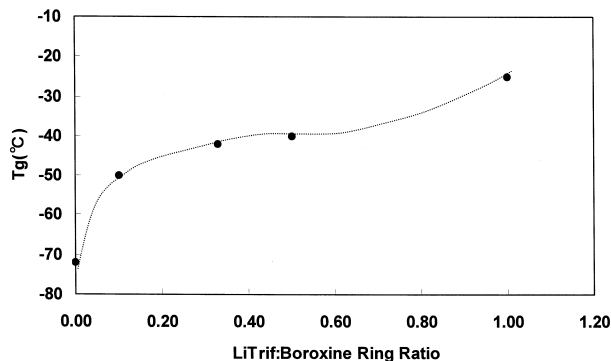


Fig. 3. Glass transition temperatures (T_g) for polymer electrolytes containing LiCF_3SO_3 .

boroxine ring. Incorporation of salts into the polymer host resulted in a shift to high field as illustrated in Table 2. Venkatasubramanian et al. [17] has reported that the resonance of tetra-coordinate boron in borate anions occurs to high field of that due to tri-coordinate boron in the boroxine ring. As we reported previously [13], the occurrence of a single ^{11}B resonance indicates that all of the B atoms are in an identical environment and this combined with the shift to high field suggests that there is fast exchange on the NMR timescale of anions between B sites on the boroxine ring. The Li^+ ion transference numbers obtained when salts are dissolved in polyether hosts are typically observed to fall in the range 0.15–0.45 [14,18–23]. As illustrated in Table 1, Li^+ ion transference numbers in the range of 0.62–0.88 were obtained for the present system. These enhanced values are clearly the result of the suppression of anion mobility due to anion interaction with the Lewis acid boron sites in the boroxine ring.

Using the electrolyte $(\text{B}_3\text{O}_3)_2(\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{7.2})_6$ LiCF_3SO_3 as a model compound, the electrochemical stability window was investigated. Initially, a stability window in the region of 4.9 V was obtained as shown in Fig. 4a. However, upon repeated cycling, peaks gradually appeared in the region between the oxidation and reduction limits as illustrated in Fig. 4b. IR spectra of these electrolytes exhibited a very small peak due to residual $-\text{OH}$. After reaction of the model compound with small amounts of LiAlH_4 , to remove residual $-\text{OH}$ (typically 0.02–0.05 mol equivalents compared to the boroxine ring), the cyclic

Table 2
 ^{11}B -NMR chemical shifts at RT

Salt	δ (ppm)
LiCF_3SO_3	–19.0
LiI	–18.2
LiCl	–17.9
No salt	–16.3

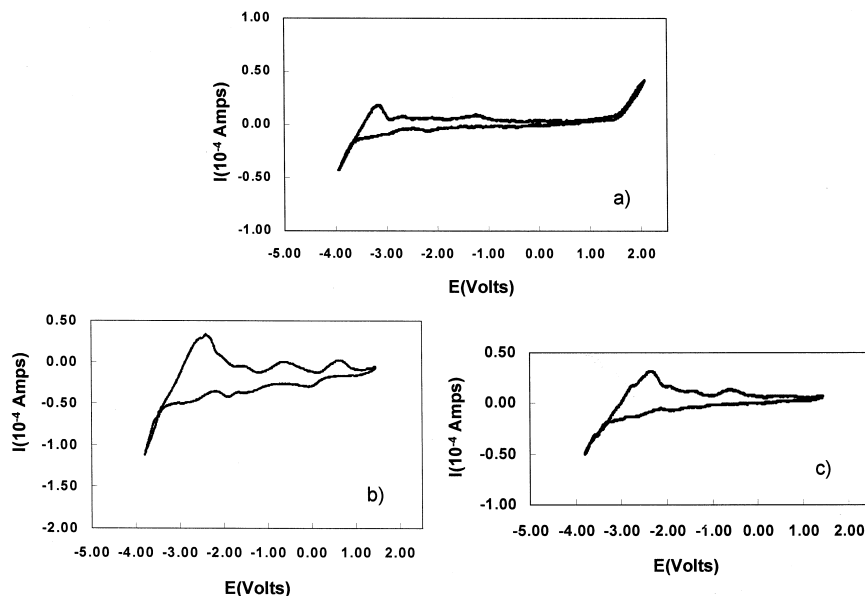


Fig. 4. Cyclic voltammograms for the model compound $(\text{B}_3\text{O}_3)[(\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{7.2}]_3 \cdot 0.5 \text{LiCF}_3\text{SO}_3$. (a and b) Before treatment with LiAlH_4 . (c) After treatment with LiAlH_4 [Pt working, counter and pseudo reference electrodes, sweep rate 20 mV/s, (b and c) 10th cycle illustrated].

voltammogram in Fig. 4c was obtained and improved cyclability was observed.

4. Conclusion

A series of anion trapping polymer electrolytes have been simply prepared by dissolution of lithium salts in a polymer host incorporating boroxine rings and oligoether side chains. The majority of the electrolytes were thermally stable to in excess of 250°C and all were completely amorphous. Ionic conductivity was observed to exhibit VTF behaviour indicating that ion motion was facilitated by the segmental motion of the polymer chains. Evidence for significant interaction with the B atoms in the boroxine rings was obtained from the shift to high field of the ^{11}B resonance upon incorporation of salt into the polymer host. The large Li^+ ion transference numbers observed in these electrolytes was therefore ascribed to the anion trapping nature of the boroxine rings. After removal of the small amounts of residual $-\text{OH}$ by reaction with LiAlH_4 , an electrochemical stability window in the region of 4.9 V was observed by cyclic voltammetry and improved cyclability was observed. Anion trapping polymer electrolytes incorporating boroxine rings thus combine high Li^+ ion transference numbers, electrochemical and thermal stability as well as exhibiting significant ionic conductivity. While the conductivity is presently insufficient for application to battery use, these materials show great promise for the future.

References

- [1] Y. Matsuda, M. Morita, H. Tsutsumi, *Polym. Adv. Tech.* 4 (1992) 209.
- [2] T. Osaka, T. Momma, K. Nishimura, S. Kakuda, T. Ishii, *J. Electrochem. Soc.* 141 (1994) 1994.
- [3] D. Fauteux, A. Massucco, M. McLin, M. Van Buren, J. Shi, *Electrochim. Acta* 40 (1995) 2185.
- [4] G. Nagasubramanian, D.H. Shen, S. Surampudi, Q. Wang, G.R. Syrya Prakash, *Electrochim. Acta* 40 (1995) 2277.
- [5] M. Gauthier, A. Belanger, P. Bouchard, B. Kapfer, S. Ricard, G. Vassort, M. Armand, J.Y. Sanchez, L. Krause, *J. Power Sources* 54 (1995) 163.
- [6] A. Noda, A. Nishimoto, M. Watanabe, 11th International Conference on Solid State Ionics, Honolulu, USA, November 1997, Abstract B17.
- [7] M. Doyle, T.F. Fuller, J. Newman, *J. Electrochim. Acta* 39 (1994) 2073.
- [8] D. Benrabah, S. Sylla, J.Y. Sanchez, M. Armand, *J. Power Sources* 54 (1995) 456.
- [9] T. Fujinami, A. Tokimune, M.A. Mehta, D.F. Shriver, G.C. Rawsky, *Chem. Mater.* 9 (1997) 2236.
- [10] K. Onishi, M. Matsumoto, K. Shigehara, *Chem. Mater.* 10 (1998) 927.
- [11] T. Fujinami, K. Sugie, K. Mori, M.A. Mehta, *Chem. Lett.* 7 (1998) 619.
- [12] M.A. Mehta, T. Fujinami, *Chem. Lett.* 9 (1997) 915.
- [13] M.A. Mehta, T. Fujinami, 11th International Conference on Solid State Ionics, Honolulu, USA, November 1997, Abstract B14.
- [14] J. Evans, C.A. Vincent, P.G. Bruce, *Polymer* 28 (1987) 2234.
- [15] *CorrWare for Windows*, Version 1.4, Scribner Associates.
- [16] M.A. Ratner, in: J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews 1*, Elsevier, London, 1987.
- [17] N. Venkatasubramanian, B. Wade, P. Desai, A.S. Abhiraman, L.T. Gelbaum, *J. Non-Cryst. Solids* 130 (1991) 144.
- [18] W. Gorecki, R. Andreani, C. Berthier, M.B. Armand, M. Mali, J. Ross, D. Brinkman, *Solid State Ionics* 18–19 (1985) 295.

- [19] M. LeVeque, J.F. LeNest, A. Gandini, H. Cheradame, *J. Power Sources* 14 (1986) 23.
- [20] A. Bouridah, F. Dalard, D. Deroo, M.B. Armand, *Solid State Ionics* 18–19 (1986) 287.
- [21] J.E. Weston, B.C.H. Steele, *Solid State Ionics* 7 (1982) 81.
- [22] P. Ferloni, G. Giodelli, A. Magistris, M. Sanesi, *Solid State Ionics* 18–19 (1986) 265.
- [23] M. LeVeque, J.F. LeNest, A. Gandini, H. Cheradame, *Makromolekulare Chemie Rapid Communications* 4 (1983) 497.