



ELSEVIER

Journal of Power Sources 97–98 (2001) 628–631

JOURNAL OF
POWER
SOURCES

www.elsevier.com/locate/jpowersour

Ion diffusion mechanisms in the cross-linked poly(ether) doped with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$

Y. Aihara^{a,*}, K. Hayamizu^b, K. Sugimoto^b, T. Bando^a, T. Iguchi^a,
J. Kuratomi^a, T. Ono^a, K. Kuwana^a

^a5th Department, Advanced Technology Division, Yuasa Corporation, 4-5-1 Ohgi-cho, Odawara 250-0001, Japan

^bNational Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305-8565, Japan

Received 1 June 2000; received in revised form 16 October 2000; accepted 28 December 2000

Abstract

The cross-linked poly(ether) electrolytes were prepared by the polymerization of a macro-monomer (tri-acryloyl terminated ethyleneoxide-co-propyleneoxide (EO-PO)) containing $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ for the three different salt concentrations ($\text{O/Li} = 10/1, 20/1$ and $30/1$). The self-diffusion coefficients (D) of the anions (^{19}F NMR) measured by the pulsed gradient spin-echo (PGSE) NMR method showed the time dependency. The short-range anion diffusion is faster than the long-range diffusion. The accurate measurement of the diffusion for lithium (^7Li NMR) was difficult but the lithium diffusion seems slower than that of the anion. The fast hopping motion of lithium ions is correlated to the segment motion of the polymer. The ion conduction is closely related to the anion diffusion in the longer range. The transport number of the lithium ion can also be estimated from the electrochemical measurements. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolytes; Diffusion of anion; Hopping motion of lithium

1. Introduction

Many efforts to improve the ionic conductivity of the solvent-free solid polymer electrolytes have been reported; however, the application of polymer lithium batteries at ambient temperature is still not satisfactory enough due to their low ionic transport. Thus, clarification of the basic ionic conduction mechanism appears necessary for improving the characteristics and the design of these electrolytes. A number of studies, which were mainly focused on the diffusion phenomena and related ionic conduction in solid polymer electrolytes, have been reported; however, the present mechanism in these electrolytes is still not fully clarified [1–9].

We have reported the self-diffusion coefficients of the ions and the ionic conductivity for various liquid and gel electrolytes [10–13] and found that bulk structures (solvent and polymer structures) are very important for achieving the fast ion transport in the electrolytes. The degree of dissociation

in practical electrolytes could be derived from relations relating ionic conductivity and self-diffusion coefficient of both anions and cations. The applicability of our method was confirmed in the case of infinitesimal dilution electrolytes [14].

In the present work we have prepared and characterized cross-linked poly(ether) electrolytes which were obtained by the polymerization of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -dissolved macro-monomer of tri-acryloyl terminated ethyleneoxide-co-propyleneoxide (EO-PO) (molecular weight is about 8000) [15,16]. We have measured the self-diffusion coefficient of the anion (^{19}F NMR) and of the cation (^7Li NMR) in the solvent-free polymer electrolytes by using pulsed gradient spin-echo (PGSE) NMR method. The self-diffusion coefficients of the anion clearly depend on the measuring parameter “ Δ ”, i.e. the separation between first and second gradient pulse which is related to the diffusion distance. It was difficult to accurately measure lithium self-diffusion coefficients since the apparent diffusion coefficient of the lithium ion appeared smaller than that of the anion. The spin-lattice relaxation times of the anion, of the lithium and of the polymer were measured which allowed to clearly evidence that the fast hopping motions of the lithium is correlated to the polymer segment motions are clearly shown.

* Corresponding author. Tel.: +81-465-34-1111; fax: +81-465-35-5095.
E-mail address: yuichi.aihara@nifty.ne.jp (Y. Aihara).

¹ Present address: Department of Chemistry, University of Rome ‘La Sapienza’, Piazzale Aldo Moro 5, 00185 Rome, Italy.

2. Experimental procedure

2.1. Sample preparation

The macro-monomer precursor was obtained from Daiichi Kogyo Seiyaku, and the lithium salt ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) was purchased from Central Glass Co., Ltd. Since the precursor monomer was a viscous liquid at room temperature, the salt was dissolved and stirred at 333 K for 48 h. After the salt was completely dissolved, the solution was cast on a plate and irradiated with an electron beam (10 Mrad) under nitrogen. Three polymer electrolyte samples with different salt concentrations were prepared, i.e. O:Li = 10:1 (PL10TF1), 20:1 (PL20TF1) and 30:1 (PL30TF1). As a reference, a cross-linked polymer sample without salt (PL) was also prepared.

2.2. Electrochemical measurements

The impedance of SS/electrolyte/SS and of Li/electrolyte/Li cells was determined using the AC method. The value of the ionic conductivity was then calculated from the cell constant and the bulk resistance. The lithium ion transport number was determined by DC polarization/AC impedance combination method [17]. A constant polarization potential of 10 mV was applied between the cell. Hence the transport number of the lithium was calculated by the relation

$$T_{\text{Li}} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (1)$$

where the I_i and I_s are the current at the initial and steady-states, respectively, R_i and R_s the passivating layer resistances at initial and steady-state, respectively.

2.3. Thermal analysis

The Differential Scanning Calorimetry (DSC) measurements were performed using a DSC220C differential scanning calorimeter (Seiko Electronics). The electrolyte samples were sealed in aluminum pans and scanned from 373 to 123 K with a scanning rate of 10 K min^{-1} . The glass transition temperature (T_g) was determined from the midpoint of the heat capacity changes.

2.4. NMR measurements

The T_1 and T_2 measurements were performed by using the inversion recovery ($180^\circ - \tau - 90^\circ - \text{Acq.}$) and Hahn spin-echo ($90^\circ - \tau - 180^\circ - \text{Acq.}$) sequences, respectively. To measure the self-diffusion coefficients, a modified Hahn spin-echo sequence containing a rectangular magnetic field gradient pulse of duration δ and magnitude g was used. In all cases, echo signal attenuation, E , versus the square of the gradient duration was well-described by a single exponential which is consistent with free diffusion. The equation relating the echo signal attenuation to the diffusion coefficient is

given by [18–20]

$$E = \frac{S(g)}{S(g=0)} = \exp\left(-\gamma^2 g^2 \delta^2 D \left(\Delta - \frac{\delta}{3}\right)\right) \quad (2)$$

where γ is the gyromagnetic ratio and Δ is the separation between the leading edges of the gradient pulses that defines the time-scale over which the diffusion is measured.

3. Results

3.1. Thermal properties of the solvent-free polymer electrolytes

All DSC curves clearly indicated that the heat capacity changes at the glass transition. Although the endothermic or exothermic peaks observed for PL and PL30TF1 are attributed to the crystalline or melt structures arising from the partially existent block copolymer in the random structure, no crystallizing or melting behavior was observed in the PL10TF1 system. This suggests close interactions between lithium ions and oxygen of the matrix polymer. Due to their increasing population in the polymer matrix, lithium ions induced macroscopically homogeneous structures. The glass transition temperature (T_g) of the polymer electrolyte increases with the salt concentration, such as 212, 221, 227 and 238 K for PL, PL30TF1, PL20TF1, and PL10TF1, respectively.

3.2. Ionic conductivity of the solvent-free polymer electrolytes

Arrhenius plots of the ionic conductivity, σ , of the solvent-free solid polymer electrolytes are given in Fig. 1. The plots can be fitted by the VTF equation, viz.

$$\sigma(T) = AT^{-1/2} \exp\left(\frac{-B}{T - T_0}\right) \quad (3)$$

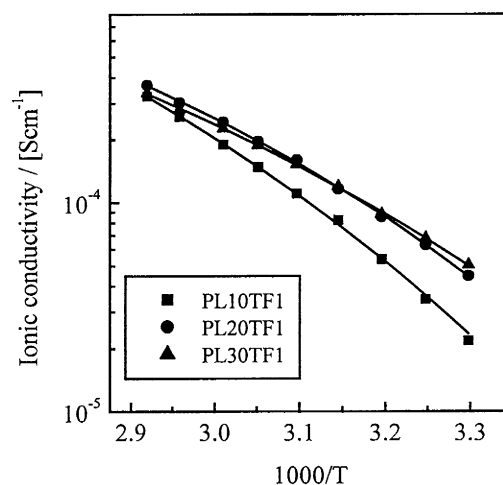


Fig. 1. Arrhenius plots of the ionic conductivity for the electrolytes at various salt concentrations. The solid lines are the results of regressing the VTF equation onto the ionic conductivity data.

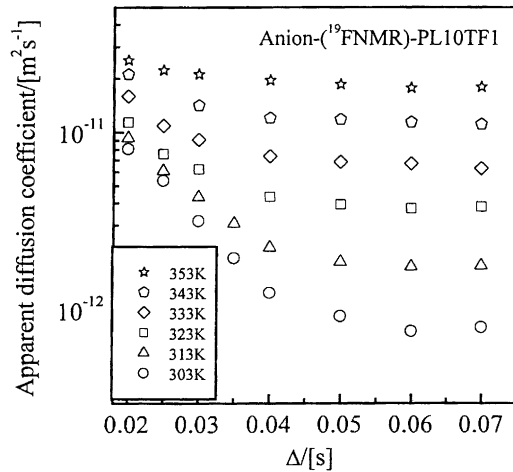


Fig. 2. Apparent self-diffusion coefficients of the anion versus time interval Δ for PL10TF1 electrolyte.

where A and B are fitting constants and T_0 is thought to be related to T_g . The temperature dependence of the ionic conductivity suggests that PL20TF1 shows good performance in the measured temperature range. PL10TF1, although having a high ionic conductivity at 353 K, at lower temperatures, shows a significant decay.

3.3. NMR spin-lattice relaxation measurements

Since the temperature dependent T_1 showed a minimum for the lithium and the polymer, the correlation times were calculated by the Bloembergen, Purcell and Pound (BPP) equation [21]. The results are shown in Fig. 3 for all the electrolytes that were examined. The temperature dependence of the correlation times was well described by a single exponential process in agreement with the fact that the activation energies obtained from the Arrhenius relationship are similar in all the three cases.

3.4. Measurements of self-diffusion coefficients

While the diffusion plots of the anion (^{19}F NMR) (following Eq. (2)) were straight as expected on the bases of normal

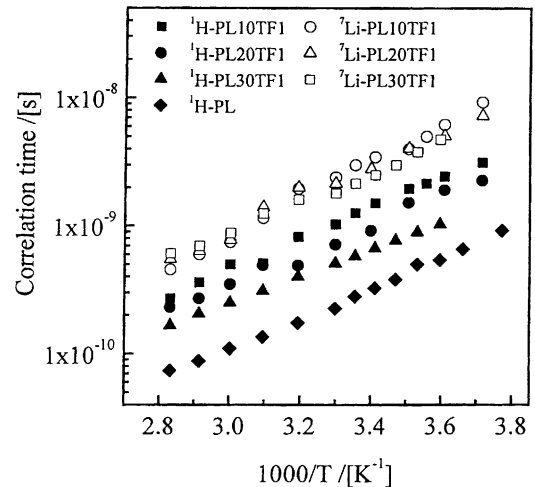


Fig. 3. The temperature dependences of the reorientational correlation times (τ_c) for the lithium and the polymer.

isotropic diffusion, the calculated self-diffusion coefficients resulted time (Δ) dependent. Fig. 3 shows the apparent self-diffusion coefficients of anions plotted versus Δ at various temperatures for the case of the PL10TF1 electrolyte. The apparent self-diffusion coefficients are faster at shorter Δ , and decrease with the longer Δ at every temperature. The degree of the time dependency of apparent self-diffusion coefficients became significantly larger at lower temperatures and at larger salt concentrations.

3.5. Lithium ion transport number

The electrochemically determined transport numbers of the electrolytes, calculated from Eq. (1) are reported in Table 1. The dc polarization first promoted reciprocal anion and cation movements to the current decay, which finally reached a value, associated to the cation transport only. The steady-state current of the PL10TF1, PL20TF1 and PL30TF1 was approximately 5, 12 and 14 μA , respectively. The apparent transport numbers so determined appears to decrease with salt concentration. In the case of the PL10TF1 electrolyte, almost the entire transport appears to be due to anion motion.

Table 1
The calculation of the transport number from ac/dc combination method

Sample	dV (mV)	Polarization time (h)	R_0 (Ω)	R_s (Ω)	I_0 (μA)	I_s (μA)	$t_{ac/dc}^+$
PL30TF1	10	40	6.4	6.5	111	14	0.12
	10	12	6.2	6.0	111	14	0.12
	10	12	5.9	5.9	103	14	0.13
PL20TF1	10	40	4.8	4.4	99	12	0.12
	10	12	5.6	9.0	112	13	0.11
	10	12	6.2	5.8	102	12	0.11
PL10TF1	10	40	25.6	20.6	84	5	0.05
	10	12	20.6	18.7	92	6	0.05
	10	12	18.8	21.7	88	5	0.05

4. Discussion

4.1. The ion diffusion mechanism and correlation to ionic conduction

The correlation times of the pure polymer are in the order of nanoseconds in the temperature range of 273 and 353 K (see Fig. 2), which corresponds to the fast segmental motions of the CH₂CH₂O moiety. After salt addition the segmental motion became slower depending on salt concentration. The lithium correlation times are slightly longer than those of the polymers. Since the activation energies of the polymer and of the lithium are almost the same, the lithium motions are clearly activated by the polymer segmental motions. The hopping motion of the lithium ions is in the order of 10⁻⁸ s, i.e. very fast in the temperature range examined here.

The anion time-dependent self-diffusion coefficients can be interpreted phenomenologically assuming that the anions move different at diffusion distances at a specific time that they diffuse faster in shorter distances. At a constant Δ , the Arrhenius plot of the apparent ion diffusion coefficients is straight and the calculated activation energies for the anion are time dependent. In fact, for shorter Δ , the activation energy decreases to reach average values only at the longer Δ , when they agree with those obtained from the ionic conduction measurements (see Fig. 1).

5. Conclusion

In the present study we have shown that the ionic conductivity of systems are formed by dissolving in cross-linked poly(EO/PO). The apparent, temperature dependent ionic conductivity is closely correlated with the anion long-range diffusion in the systems. The self-diffusion coefficients of the anions have a Δ dependency. These ions apparently diffuse faster in the shorter range, to finally approach the equilibrium values. The lithium ions diffusion is slower compared to that of the anions, since the fast hopping motions of the former are activated from the segmental motions of the polymer.

In addition, the occurrence of strong ion–ion interactions is assumed in the systems here investigated. New theories to interpret the ion conduction mechanisms are under already for elaborating accurate transport models.

Acknowledgements

This research was supported by New Energy and Industrial Technology Development Organization (NEDO).

References

- [1] W. Gorecki, R. Andreani, C. Berthier, M. Armand, M. Mali, J. Roos, D. Brinkmann, *Solid State Ionics* 18/19 (1986) 295.
- [2] W. Gorecki, B. Belorizky, C. Berthier, P. Donoso, M. Armand, *Electrochim. Acta* 37 (1992) 1685.
- [3] J. Shi, C.A. Vincent, *Solid State Ionics* 60 (1992) 11.
- [4] S. Arumugam, J. Shi, D.P. Tunstall, C.A. Vincent, *J. Phys. B* 5 (1993) 153.
- [5] W. Gorecki, M. Jeannin, B. Belorizky, C. Roux, M. Armand, *J. Phys.: Condens. Matter* 8 (1995) 6823.
- [6] C.A. Vincent, *Electrochim. Acta* 40 (1995) 2035.
- [7] C. Roux, W. Gorecki, J.-Y. Sanchez, M. Jeannin, E. Belorizky, *J. Phys.: Condens. Matter* 8 (1996) 7005.
- [8] C. Roux, W. Gorecki, J.-Y. Sanchez, E. Belorizky, *Electrochim. Acta* 43 (1998) 1575.
- [9] J.-Y. Sanchez, F. Alloin, *Electrochim. Acta* 43 (2000) 1255.
- [10] K. Hayamizu, Y. Aihara, S. Arai, W.S. Price, *Solid State Ionics* 107 (1998) 1.
- [11] Y. Aihara, S. Arai, K. Hayamizu, *Electrochim. Acta* 45 (2000) 1321.
- [12] K. Hayamizu, Y. Aihara, S. Arai, W.S. Price, *Electrochim. Acta* 45 (2000) 1313.
- [13] K. Hayamizu, Y. Aihara, S. Arai, C.G. Martinez, *J. Phys. Chem.* 103 (1999) 519.
- [14] Y. Aihara, K. Sugimoto, W.S. Price, K. Hayamizu, *J. Chem. Phys.* 113 (2000) 1981.
- [15] M. Watanabe, A. Nishimoto, *Solid State Ionics* 79 (1995) 306.
- [16] M. Kono, E. Hayashi, M. Watanabe, *Electrochem. Soc.* 145 (5) (1998) 1521.
- [17] J. Evance, C.A. Vincent, P.G. Bruce, *Polymer* 28 (1987) 2324.
- [18] E.O. Stejskal, J.E. Tanner, *J. Chem. Phys.* 42 (1965) 288.
- [19] W.S. Price, *Concepts Magn. Reson.* 9 (1997) 299.
- [20] W.S. Price, *Concepts Magn. Reson.* 10 (1998) 197.
- [21] N. Bloembergen, E.M. Purcell, R.V. Pound, *Phys. Rev.* 73 (1948) 679.