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Conductivity and thermal studies of solid polymer electrolytes prepared by blending poly(ethylene oxide), poly(oligo[oxyethylene]oxysebacoyl) and lithium perchlorate

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Abstract

Blend-based polymer electrolytes composed of poly(ethylene oxide)(PEO), poly(oligo[oxyethylene]oxysebacoyl)(PES) and lithium perchlorate have been prepared. The characteristics of these polymer electrolytes were investigated in terms of blend composition and salt concentration. The addition of PEO to PES/$LiClO_4$ complex significantly improved the dimensional stability with a slight decrease in the latter's ionic conductivity. The PEO(40)/PES(60)/$LiClO_4$ electrolyte at $[LiClO_4]/[EO] = 0.10$ exhibited an ionic conductivity of 3×10^{-5} S/cm at 25°C, and was an elastomeric material with dimensional stability. The lithium transport number in this system was determined to be about 0.37 at 40°C.

Keywords: Ionic conductivity; Polymer electrolyte; Thermal property; Transport number

1. Introduction

Polymer electrolytes have received considerable attention as solid electrolyte materials in advanced electrochemical application such as high energy-density batteries [1,2]. A large number of studies to date have been carried out on polymer electrolytes based on poly(ethylene oxide)(PEO) containing the alkali metal salts. The mechanical strength, the chemical stability in contact with lithium metal, and the wide electrochemical stability window make them promising material for the solid state lithium batteries. However, these materials have a major drawback that the ionic conductivity of 10^{-4} S/cm, which is necessary for high-power applications, can only be reached at around 100°C, due to the high degree of crystallinity inherent in these complexes at room temperature. Because of the inherent drawback of PEO/alkali metal salt complexes, various attempts such as grafting [3–7], block copolymerization [8,9] and crosslinking [10–14] have been tried to incorporate PEO into a macromolecular sequence which inhibits crystallization, while maintaining a low value of the glass transition temperature. Although these novel approaches are promising, the fact that their preparation requires nontrivial synthetic processes is a serious drawback for practical application. There-

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fore, it is of considerable importance to develop easier method for preparing the polymer electrolytes with higher ionic conductivities and dimensional stability. In this regard, recent works on the preparation of polymer electrolytes by blending polymers are of interest [15–20]. The main advantages of these blend-based electrolytes are simplicity of preparation and easy control of physical properties by compositional change. Thus, the detailed studies of the blend based polymer electrolytes can furnish a valuable information on the relative importance of various factors which affect the electrical, thermal and mechanical properties of the polymer electrolytes.

We have previously reported the synthesis and properties of the new polymer electrolytes based on aliphatic polyester(poly(oligo[oxyethylene]oxysebacoyl)) containing a different number of ethylene oxide units, and showed their higher ionic conductivities at room temperature [21,22]. However, their poor mechanical property prevented the preparation of dimensionally stable thin films necessary for practical use in the electrochemical devices. In order to overcome this problem, we blended them with a high molecular weight PEO, enabling the fabrication of thin film with high ionic conductivity. In this paper, we present a detailed account of the ionic conductivity and thermal properties of the blend-based polymer electrolytes composed of PEO, poly(oligo-[oxyethylene]oxysebacoyl) and lithium perchlorate.

2. Experiment

2.1. Materials

PEO(MW:5×10^6) was obtained from Aldrich and used without further purification. Lithium perchlorate was dried in a vacuum oven for 24 h at 120°C prior to use. All the reagents were also supplied by Aldrich and were used without any purification. Poly(oligo(oxyethylene)oxysebacoyl) which will be abbreviated by PES in this paper was prepared by polycondensation reaction of sebacoyl chloride and PEG(poly(ethyleneglycol))(MW:1000) with a small amount of triethylamine as a catalyst, as previously described [22]. Final product was obtained as a white waxy powder. PES was found to have the following structural formula $[-OC(CH_2)_8-COO(CH_2CH_2O)_{22}-]_n$ by the analysis of ^1H NMR spectrum. From GPC analysis in DMF(0.05 M LiBr), its weight average molecular weight was determined to be 54000 with a polydispersity index of 2.1, using the monodisperse PEO of different molecular weight as standard.

2.2. Preparation of polymer electrolytes

Appropriate amounts of PES, PEO and $LiClO_4$ were dissolved together in anhydrous acetonitrile in order to prepare a blend-based polymer electrolyte. The solution was stirred well and cast on a Teflon plate, then left to evaporate the solvent slowly at room temperature. The resulting films were then dried in a vacuum oven at 60°C for at least 24 h. The dried samples were stored in an argon filled glove box with anhydrous P_2O_5.

2.3. Characterization

X-ray diffraction patterns were obtained with a Rigaku X-ray diffractometer using Ni-filtered Cu Kα X-rays in the range $2\theta = 5–50°$. DSC thermal analysis was carried out to measure the T_g, T_m, ΔH_m values with a heating rate of 10°C/min from -100 to 100°C. Samples were loaded in hermetically-sealed aluminum pans and measurements were always taken under the dry nitrogen atmosphere during the thermal scans. The recorded T_g was taken as the inflection point and T_m was given as the peak of the melting endotherm. The spherulitic structure in the blends was observed on thin films prepared by solution casting from acetonitrile with a Leiz Orholux polarizing microscope at room temperature.

2.4. Conductivity measurements

Polymer electrolyte film was sandwiched between the two stainless steel electrodes and assembled into a sample holder for measurement of ionic conductivity. The ionic conductivity of the polymer electrolyte was then measured by complex impedance analysis using a Solatron 1255 frequency response analyzer (FRA) coupled to an IBM PS/2 computer over a frequency range of 10 Hz–10 MHz. Each sample was allowed to equilibrate for 1 h at any temperature before measurement. The real and imaginary parts of

the complex impedance were plotted, and the ionic conductivity (σ) could be obtained from the bulk resistance (R_b) found in complex impedance diagram. The cationic transport number was evaluated in a cell of Li | polymer electrolyte | Li by the combination of ac impedance and dc polarization measurements [23,24] using a Solartron 1287 electrochemical interface coupled with a FRA at 40°C. Throughout this report, abbreviations will be used to identify the different blend-based polymer electrolytes. For example, PES (60, 0.10) indicates a blended polymer electrolyte containing 60 wt% PES and 40 wt% PEO with [$LiClO_4$]/[EO unit] of 0.10. For the salt concentration calculation, all the [EO] units in the chains of PEO and PES were considered.

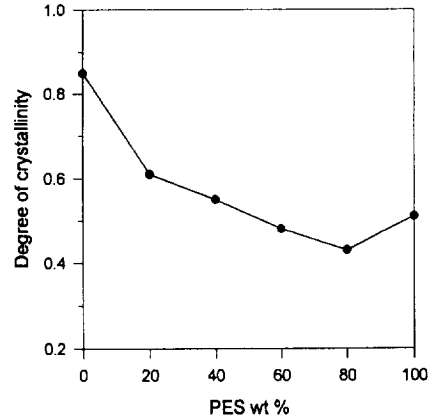

Fig. 2. Degree of crystallinity for the PEO/PES blend as a function of the PES content.

3. Results and discussion

3.1. PEO / PES blends without $LiClO_4$

Free standing and dimensionally stable thin films (thickness: 50–200 μm) could be prepared by solution blending PES with high molecular weight PEO when the amount of PES in the blend was less than 80 wt%. Their physical properties depended on the blend composition. When the PES content has exceeded 80 wt%, the blends were sticky and glutinous materials, and thus were difficult to handle.

The thermal behavior of PEO/PES blends without $LiClO_4$ was characterized by DSC measurements. Fig. 1 shows the DSC traces of the blends as a function of blend composition. An endothermic peak due to the melting of crystalline PES is observed at 41°C with a fusion heat of 104 J/g. This value is much lower than the fusion heat (176 J/g) of melting transition observed at 74°C for the crystalline PEO. The presence of the interpersing oxysebacoyl group in PES appears to reduce the crystallinity of the oligo(oxyethylene) unit, as previously reported [22]. The crystal structure of PES was, however, proved to be almost the same as that of PEO by analyzing the X-ray diffraction patterns, indicating similar short-range structure within the crystalline unit cell. The crystallinity was estimated from the ratio of the experimentally determined $\Delta H_m(\Delta H_{m,PES} + \Delta H_{m,PEO})$ to the value of 203 J/g reported in the literature [25] for the enthalpy of melting of 100% crystalline PEO. Fig. 2 shows the degree of crystallinity of the blend as a function of PES composition. It is found that the degree of crystallinity of the blend decreases with an increase in the PES composition up to 80 wt%, and then increases as the PES content further increases. The decrease in degree of crystallinity with increasing PES content up to 80 wt% may be attributed to the formation of less perfect crystalline lamellae, resulting from the dispersion of PES having the crystal defects in the blend. An increase in the degree of crystallinity for the pure PES may be due to the absence of a certain amount of disorder caused in the system by mixing two polymer components. The reduction of crystallinity in these blends is thus expected to increase the ionic conductivity of the

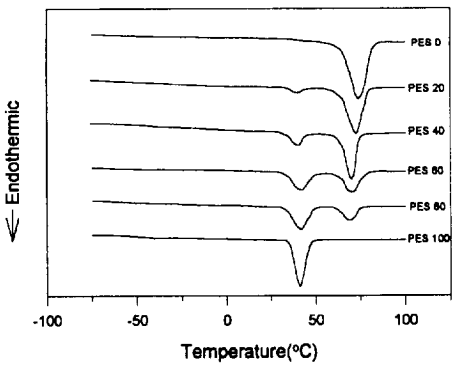

Fig. 1. DSC thermograms of the PEO/PES blends without $LiClO_4$ as a change of the blend composition.

polymer electrolyte prepared with the blend, as compared to that prepared with PEO only, since it is generally known that high conductivity is necessarily associated with an amorphous phase of the polymer [1,2].

The crystalline morphology of the blended film was studied on the optical microscope between the cross-polarizers. The typical micrographs of spherulitic texture of the blends are shown in Fig. 3. The spherulites for PES (20, 0) display a maltese cross pattern which is typical in crystalline polymers with flexible chains. It is however seen that the regularity of spherulite is disrupted with increasing the PES content in the polymer blend. Especially, for the blend containing 80 wt% PES, the maltese cross texture can hardly be observed. The coarseness of the crystalline lamellae may be due to the crystal defect introduced by the presence of PES in the interlamella regions.

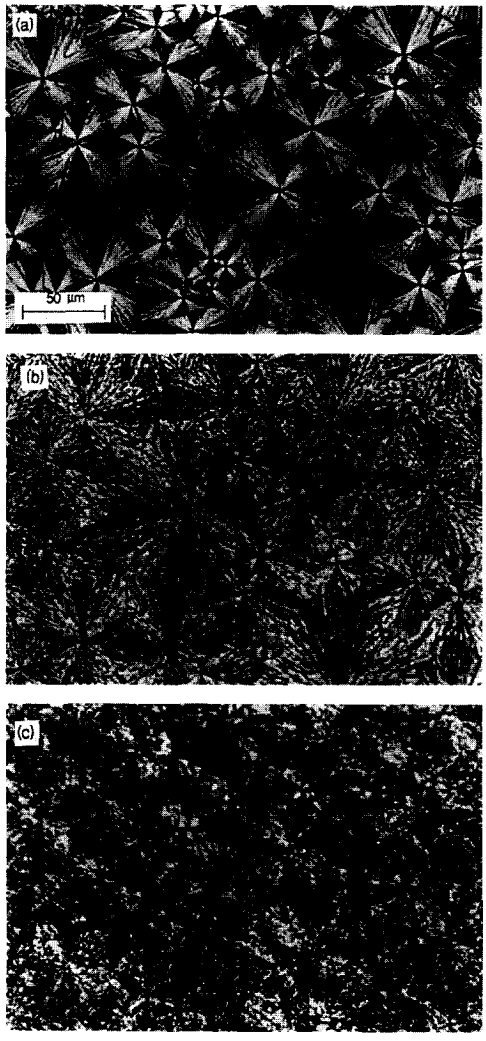

Fig. 3. Optical micrographs of the spherulitic texture viewed between the crossed polarizers for the PEO/PES blends without $LiClO_4$: (a) PES 20; (b) PES 60; (c) PES 80.

Table 1
DSC results of PEO/PES/$LiClO_4$([$LiClO_4$]/[EO] = 0.10) complexes as a function of PES composition

Polymer electrolytes	T_g (°C)	T_m (°C)	ΔH_m (J/g)
PES (0, 0.10)	−24.9	52.1	49.0
PES (20, 0.10)	−26.1	46.9	35.2
PES (40, 0.10)	−28.4	43.3	8.7
PES (60, 0.10)	−30.3	41.5	3.1
PES (80, 0.10)	−30.8	–	–
PES (100, 0.10)	−31.9	–	–

3.2. PEO / PES / $LiClO_4$ blend-based polymer electrolytes

We have already reported [22] that the ionic conductivities of the PES/$LiClO_4$ complexes reach maximum values at [$LiClO_4$]/[EO] ratios between 0.05 and 0.10. In order to investigate the effect of PES composition on the ionic conductivity and thermal properties of the blended electrolytes, the salt concentration was fixed to be constant ([$LiClO_4$]/[EO] = 0.10). The DSC results of the blended polymer electrolytes as a change of a PES composition are summarized in Table 1, and the typical DSC thermograms for PES (40, 0.10) and PES (80, 0.10) are shown in Fig. 4. Most of the blended polymer electrolytes have relatively low T_g(−32 ~ −25°C) and the values seem to decrease with the PES content. As shown in Fig. 4, the only single melting endotherm can be observed for PES (40, 0.10) in spite of the presence of two melting transitions in the blend without $LiClO_4$. The melting endotherm around 43°C may correspond to the melting of crystalline PEO. Table 1 shows that, as the amount of PES in the blended electrolytes increases, both the heat of fusion and the melting temperature decrease, and the melting peak completely disappears when PES content is higher that 80 wt%. All the samples were very

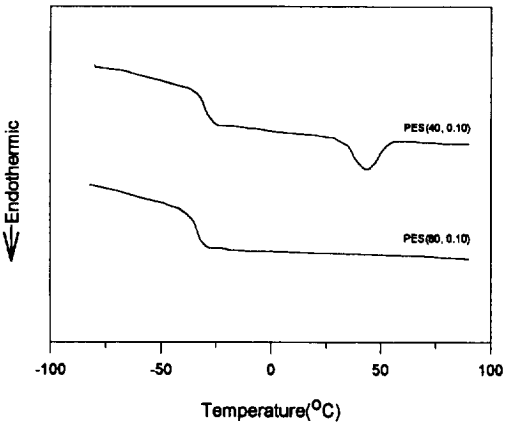

Fig. 4. DSC thermograms of the PES (40, 0.10) and PES (80, 0.10) complexes.

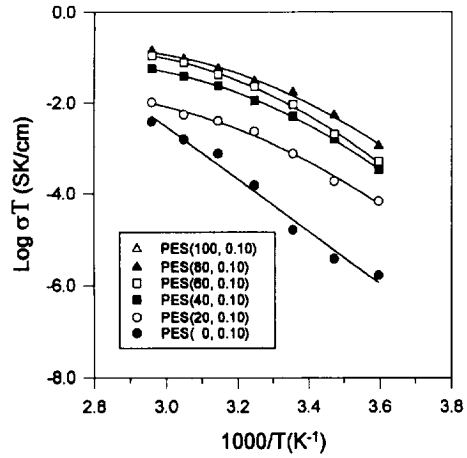

Fig. 5. Temperature dependence of the ionic conductivity for the PEO/PES/$LiClO_4$([$LiClO_4$]/[EO] = 0.10) complexes having different PES content.

stable with time and did not phase aggregate, which suggests that homogeneous polymer electrolytes are formed over all the blend compositions. The addition of lithium perchlorate probably facilitates uniform film formation, because the lithium cation simultaneously interacts with the oxygen atoms of PEO and the ether oxygens or ester group of PES. The role of the salt in compatibilizing the polymer pair was investigated earlier by other workers [19,20]. Abraham et al. [15,18] have reported that homogeneous polymer electrolyte films were formed only for MEEP(poly[bis-(methoxyethoxy ethoxide) phosphazene])/PEO blends in which MEEP content was less than 70 wt%. In our study, PES has an advantage of being chemically almost identical to PEO, since PES is mainly composed of EO units with small amount of oxysebacoyl group. It is therefore expected that the compatibility of PES/PEO in the presence of $LiClO_4$ is more enhanced than that of MEEP/PEO blended electrolytes.

Fig. 5 shows the temperature dependence of the ionic conductivity for our blended polymer electrolytes with different blend compositions. All of the Arrhenius plots except for PES (0, 0.10) show a slightly positive curvature, indicating the high degree of amorphous character. It is found that all of the blended electrolytes exhibit significantly higher conductivity than the pure PEO/$LiClO_4$ complex (i.e., PES (0, 01)), especially at lower temperatures, and the ionic conductivity continuously increases with increasing the PES content. The higher ionic conductivities of the blended electrolytes compared to PEO/$LiClO_4$ complex may be attributed to their higher degree of amorphous character stemming from the presence of PES, as given in Table 1. The ionic conductivities of the blended electrolytes are found to become closer to those for PES (100, 0.10) when the amount of PES is higher than 40 wt%. The ionic conductivities and mechanical states at room temperature for the blended electrolytes are given for a comparative purpose in Table 2. From the data in Table 2, it is found that the room temperature conductivities of the blended electrolytes are greater than 1.7×10^{-5} S/cm when PES content is above 40 wt%. However, the blended electrolytes containing high amount of PES exhibited poor mechanical property. Hence, it seems that PES (60, 0.10) is an optimum blended polymer electrolyte system in con-

Table 2
Room temperature ionic conductivities and mechanical states of the PEO/PES/$LiClO_4$([$LiClO_4$]/[EO] = 0.10) complexes

Polymer electrolytes	σ_{RT} (S/cm)	Mechanical states
PES (0, 0.10)	5.5×10^{-8}	free standing film
PES (20, 0.10)	2.6×10^{-6}	free standing film
PES (40, 0.10)	1.7×10^{-5}	free standing film
PES (60, 0.10)	3.1×10^{-5}	rubbery elastomer
PES (80, 0.10)	5.8×10^{-5}	sticky solid
PES (100, 0.10)	6.6×10^{-5}	sticky solid

sideration of both the mechanical stability and the ionic conductivity. The ionic conductivity of PES (60, 0.10) complex at room temperature was about 3.1×10^{-5} S/cm, which is quite a high value for the solid polymer electrolytes without any additives. It is rubbery elastomer with dimensional stability.

The DSC results for PES 60/$LiClO_4$ complexes with change of the salt concentration are given in Table 3. The value of T_g increases with salt concentration, which is similar to the results observed on the other polymer electrolyte systems. When the salt concentration is lower than 0.05, two melting peaks can be observed, which correspond to the melting endotherms of PES and PEO respectively. On the other hand, the crystalline melting transition of PEO can be only observed in the thermogram of PES (60, 0.10), and the melting peaks completely disappear as the salt concentration is further increased. The salt concentration effect on the reduction of crystallinity is attributed to the physical crosslinking arising from ion–polymer interactions. From the data in Table 3, it is found that $d\Delta H_m/dC$ (the derivative of fusion heat with respect to salt concentration) for the melting of the crystalline PES is about -720 J/g, whereas that of the crystalline PEO is around -459 J/g. The larger decrease in the heat of fusion with salt concentration for the PES melting suggests that the reduction or elimination of crystallinity by ion–polymer interaction is much more effective in PES phase due to its less perfect crystal structure.

Several ionic conductivity isotherms of PES(60)/$LiClO_4$ complexes as a function of salt concentration are shown in Fig. 6. The ionic conductivity increases with salt concentration, reaches a maximum and falls off with concentration at higher $[LiClO_4]/[EO]$ ratios. The fall in conductivity observed at higher salt concentration is a consequence of increase in T_g which reduces ionic mobility. The electrolyte with $[LiClO_4]/[EO] = 0.10$ exhibited the highest conductivity at room temperature. As the temperature increases, the salt concentration for a maximum conductivity moves to a higher salt concentration, which is due to the easier diffusion of charge carrier at higher temperature.

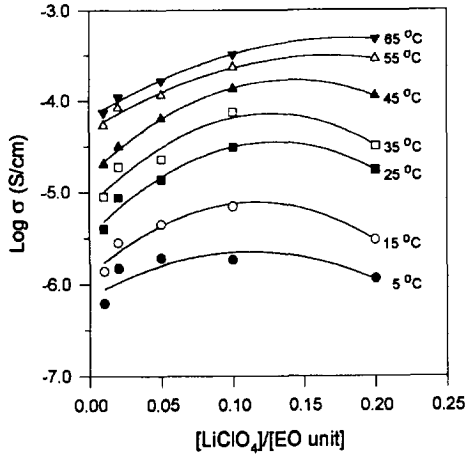

Fig. 6. Isothermal variation of the ionic conductivity with $LiClO_4$ concentration for the PEO(40)/PES(60)/$LiClO_4$ complexes.

3.3. Estimation of lithium transport number

In the characterization of the polymer electrolytes, it is important not only to measure the ionic conductivity but also to determine the value of the cationic transport number. In our study, we measured the lithium transport number by combination of ac complex impedance and dc polarization measurements which was proposed by Vincent et al. [23,24]. This technique has been proved to be applied in a straightforward manner, even in circumstances where the electrode kinetics is slow, or where the proper

Table 3
DSC results of PEO(40)/PES(60)/$LiClO_4$ complexes as a function of salt concentration

Polymer electrolytes	T_g (°C)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)
PES (60, 0)		42.0	45.3	70.8	51.6
PES (60, 0.01)	−48.7	42.7	31.2	68.2	45.1
PES (60, 0.02)	−47.0	41.3	28.6	63.7	32.3
PES (60, 0.05)	−41.4	31.0	7.0	57.3	25.3
PES (60, 0.10)	−30.3	–	–	41.5	3.1
PES (60, 0.20)	−23.9	–	–		–

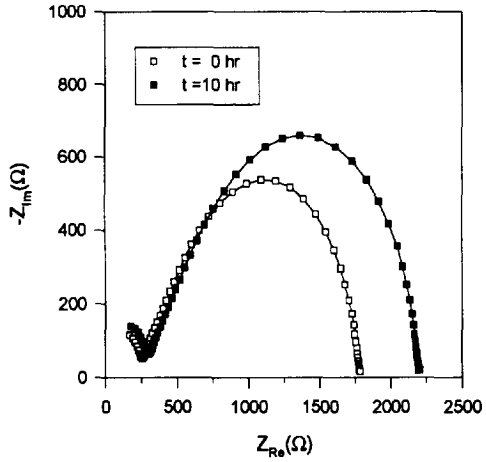

Fig. 7. ac Impedance spectra of a Li|PES(60, 0.10)|Li cell at 40°C before ($t = 0$ h) and after polarization ($t = 10$ h) with total applied potential difference of 20 mV.

correction for passivating layer is required. By ac impedance analysis of a Li|PES(60, 0.10)|Li cell as shown in Fig. 7, the initial interfacial resistance ($R_{i,0}$) was measured. A constant voltage of 20 mV was then applied to the cell and the current was monitored as a function of time until the steady-state was attained. This result is given in Fig. 8. From the plot shown in this figure, the initial(I_0) and steady-state current(I_s) were determined. After the steady-state condition was reached, the interfacial resistance of the cell($R_{i,s}$) was again measured by ac impedance analysis. As shown in Fig. 7, a progressive extension of the low-frequency semicircle can be easily noticed, indicating an increase of the interfacial resistance, which in turn must be associated with the growth of a passivation layer on the lithium electrode, as the previous authors suggested [26,27]. The passive layer of the lithium electrode may contain the product of the corrosion reaction between the lithium electrode and the polymer, the salt, the residual solvent and other impurities. The steady state current observed in Fig. 8 is thus considered to result from the establishment of a concentration polarization of the anion and the growth of passivating layers. From the cited values, the cationic transport number was estimated by the following equation:

$$t^+ = \frac{I_s(\Delta V - I_0 R_{i,0})}{I_0(\Delta V - I_s R_{i,s})}. \quad (1)$$

The lithium transport number of 0.37 was obtained in this electrolyte by using Eq. (1). The transport number lower than 0.5 means that the mobility of the cation is relatively lower than that of the anion. As many workers suggested, it is thought that the cation is strongly solvated by the polyether chains, while the anion is loosely associated to the polymer segments and can consequently be displaced more readily under an electric field. More detailed studies on the lithium ion transport number for other systems and under various conditions are in progress and will be reported in the near future.

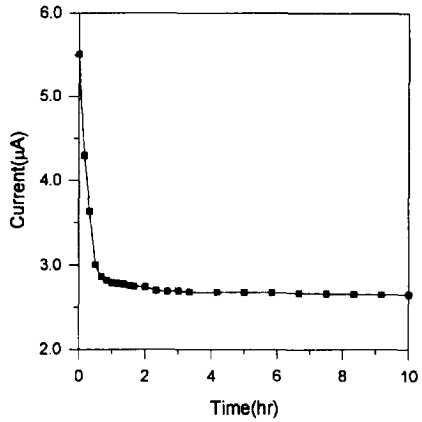

Fig. 8. Variation of the current with time during polarization of a Li|PES(60, 0.10)|Li cell at 40°C, with an applied potential difference of 20 mV.

Acknowledgements

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