

Electrochemical Characteristics of the Blended Polymer Electrolytes Containing Lithium Salts

DONG-WON KIM,^{1,*} JUNG-KI PARK,^{1,†} JOON-SUNG BAE,² and SU-IL PYUN²

¹Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1, Kusung-Dong, Yusung-Gu, Daejeon, 305-701, Korea; ²Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1, Kusung-Dong, Yusung-Gu, Daejeon, 305-701, Korea

SYNOPSIS

Blend-based polymer electrolytes composed of poly(ethylene oxide), poly(oligo[oxyethylene]oxysebacoyl), and lithium salts have been prepared. These polymer electrolytes have been investigated in terms of ionic conductivity, transport number, and interfacial characteristics of the lithium electrode in contact with the polymer electrolyte. The influences of the blend composition, the salt used, and its concentration on the electrochemical behavior were studied. © 1996 John Wiley & Sons, Inc.

Keywords: a.c. impedance • ionic conductivity • passivation • polymer blend • polymer electrolytes • transport number

INTRODUCTION

Polymer electrolytes have received considerable attention as solid electrolyte materials in advanced applications such as high energy-density batteries.¹⁻⁴ 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. 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. In this respect, most of the research works have been directed to the synthesis and characterization of new polymer electrolytes that exhibit higher ionic conductivity at ambient temperature. The investigation conducted recently in our laboratory indicated that blending of PEO and poly(oligo[oxyethylene]oxysebacoyl) (PES) was one effective way to enhance the ambient temperature conductivity. Although the ionic conductivity of the

polymer electrolyte is of paramount importance, a high conductivity is not the sole requirement for the electrochemical applications. It is of also importance to understand the electrochemical behavior of lithium electrode in contact with the polymer electrolyte to guarantee the acceptable performance for a high-performance rechargeable battery. Nevertheless, relatively few research groups have devoted study to the lithium/polymer electrolyte interface,⁵⁻⁹ and even less to the interfacial behavior of the lithium electrode in the blended polymer electrolyte.

We have previously reported the preparation of a new blend-based polymeric electrolyte composed of poly(ethylene oxide), poly(oligo[oxyethylene]oxysebacoyl), and lithium perchlorate, and showed its high conductivity and good mechanical stability.¹⁰ It is thus worthy to study the electrochemical characteristics of these systems. In this work, we describe the interfacial behavior of the lithium electrode in the blended polymer electrolytes composed of PEO, PES, and lithium salts (LiClO₄, LiCF₃SO₃, LiBF₄) in terms of blend composition, salt species, and its concentration. To our knowledge, no systematic studies of this sort have been performed in the blend-based polymer electrolytes. The lithium transport number in these polymer electrolytes was also determined as a function of the salt species.

* Present address: Samsung Central Research Institute of Chemical Technology, 103-12, Moonji-Dong, Yusung-Gu, Daejeon, 305-380, Korea.

† To whom correspondence should be addressed.

EXPERIMENTAL

Materials

High molecular weight PEO (MW 5×10^6) was obtained from Aldrich and used without further purification. Poly(oligo[oxyethylene]oxysebacoyl), which will be abbreviated by PES in this article, was prepared by polycondensation reaction of sebacoyl chloride and poly(ethylene glycol) (PEG) (MW 1000) with a small amount of triethylamine as a catalyst, as previously described.^{11,12} The final product was a white waxy powder. PES was found to have the following structural formula $[-OC-(CH_2)_8COO(CH_2CH_2O)_{22}-]_n$ 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 54,000 with a polydispersity index of 2.1, using the monodisperse PEO of different molecular weight as standard. All the lithium salts were used after drying in a vacuum oven for 24 h at the temperature specified (LiClO₄: 150°C, LiCF₃SO₃: 100°C, LiBF₄: 90°C). Acetonitrile used in the preparation of polymer electrolyte was of the highest quality (HPLC grade), and was used as received. Ribbon-like metallic lithium was cut into disks, which were used as lithium electrodes.

Preparation of Polymer Electrolytes

Appropriate amounts of PES, PEO, and a lithium salt 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 flat container, 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 to avoid contamination in an argon-filled glove box with anhydrous P₂O₅. Throughout this report, abbreviations will be used to identify the different blend-based polymer electrolytes. In PES (X, Y, salt), X is the PES wt %, Y is the salt concentration ([Li]/[EO unit]). For example, PES (60, 0.10, LiClO₄) represents a blended polymer electrolyte containing 60 wt % PES and 40 wt % PEO with [LiClO₄]/[EO unit] of 0.10. In calculation of the salt concentration, all the [EO] units in the backbone of PEO and PES were considered.

Thermal Analysis and X-Ray Diffraction

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 crystallinity was estimated from the ratio of the experimentally determined ΔH_m to the value of 203 J/g reported in the literature¹³ for the enthalpy of melting of 100% crystalline PEO. X-ray diffraction patterns were obtained with a Rigaku X-ray diffractometer using a Ni-filtered Cu-K α ray in the range $2\theta = 5 \sim 45^\circ$ at room temperature. All samples were taken in the thin film form.

Electrical Measurements

Polymer electrolyte film was sandwiched between the two stainless steel electrodes (blocking nature) and assembled into a sample holder for measurement of ionic conductivity. In order to investigate the interfacial phenomena at the lithium electrode/polymer electrolyte interface, this sample was also sandwiched between the two lithium electrodes (non-blocking nature) with parallel stainless steel current collectors on each side, and assembled into a Teflon cell holder having stainless steel terminals under a high purity argon atmosphere in a glove box. The a.c. impedance measurement of the polymer electrolyte was then performed using a Solartron 1255 frequency response analyzer (FRA) coupled to an IBM PS/2 computer over a frequency range of 0.1 Hz \sim 10 MHz. Each sample was allowed to equilibrate for 2 h at any temperature before measurement. All the a.c. impedance results were fitted with the computer-fitting program in order to obtain the impedance parameters. The equivalent circuit utilized to elaborate the experimental data was based on the preferred interface model. The lithium transport number was evaluated in a cell of Li|polymer electrolyte|Li by the combination of the a.c. impedance and d.c. polarization measurements^{14,15} using a Solartron 1287 electrochemical interface coupled with the FRA at 40°C.

RESULTS AND DISCUSSION

Bulk Properties of the Blended Polymer Electrolytes

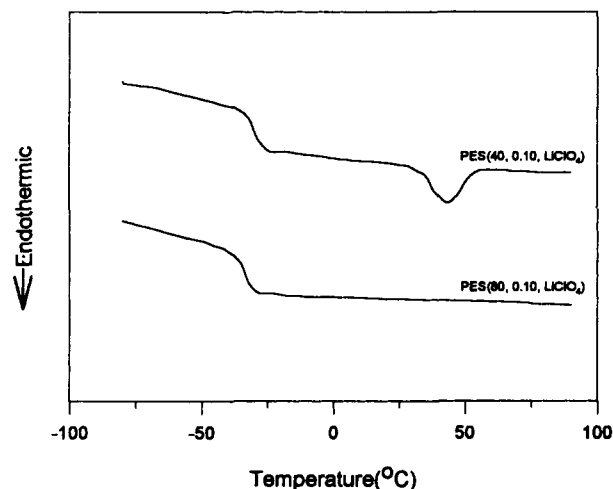
PES is a semicrystalline polymer with a crystallinity of 0.51, while that of pure PEO is 0.85. The presence of the interspersing oxysebacoyl groups in PES ap-

Table I. DSC Results of PES(X, 0.10, LiClO₄) Complexes as a Function of PES Composition

Polymer Electrolytes	T_g (°C)	T_m (°C)	ΔH_m (J/g)	Crystallinity
PES(0, 0.10, LiClO ₄)	-24.9	52.1	49.0	0.24
PES(20, 0.10, LiClO ₄)	-26.1	46.9	35.2	0.17
PES(40, 0.10, LiClO ₄)	-28.4	43.3	8.7	0.04
PES(60, 0.10, LiClO ₄)	-30.3	41.5	3.1	0.02
PES(80, 0.10, LiClO ₄)	-30.8	—	—	—
PES(100, 0.10, LiClO ₄)	-31.9	—	—	—

pears to reduce the crystallinity of the oligo-(oxyethylene) unit, as previously reported.¹¹ 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.¹¹

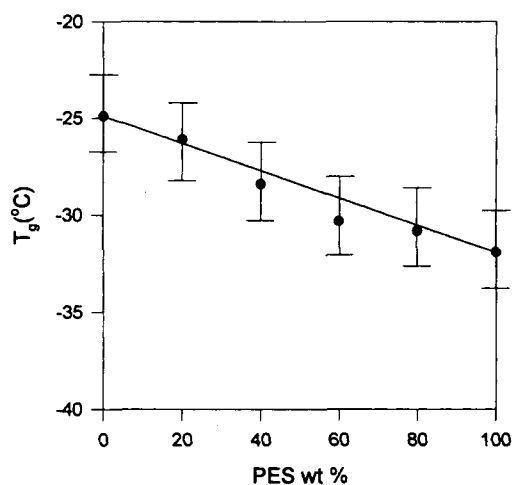
In order to investigate the effect of PES composition on the thermal properties and ionic conductivities of the blended polymer electrolytes, the salt concentration was fixed to be 0.10. The DSC results of the blended polymer electrolytes as a function of a PES composition are summarized in Table I, and the typical DSC thermograms for PES (40, 0.10, LiClO₄) and PES (80, 0.10, LiClO₄) are shown in Figure 1. The heat of fusion and the melting temperature are observed to be decreased as the amount of PES in the blended electrolytes increases, and the melting peak completely disappears when PES content is higher than 80 wt %. This result may be related to a decrease of perfect crystals imbedded in an amorphous matrix with an increase in the PES composition. Figure 2 shows the relationship between T_g and PES content represented in wt %. An


Figure 1. DSC thermograms of the PES (40, 0.10, LiClO₄) and PES (80, 0.10, LiClO₄) complexes.

experimental error is observed for the measurement of T_g at a variety of PES contents, as shown in Figure 2. From this figure, it can be said that the change in the T_g as a function of PES content seems to reasonably follow the Fox equation¹⁶ within the experimental error,

$$\frac{1}{T_g} = \frac{w_{PEO}}{T_{g,PEO}} + \frac{w_{PES}}{T_{g,PES}}$$

where $T_{g,PEO}$ and $T_{g,PES}$ represent the T_g s of PES (0, 0.10, LiClO₄) and PES (100, 0.10, LiClO₄), respectively, and w_{PEO} and w_{PES} are the weight fractions of each complex. This result suggests that homogeneous polymer electrolytes are formed over all the blend compositions. The addition of lithium perchlorate probably facilitates the 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 also


Figure 2. Relationship between T_g and PES content for PES (X, 0.10, LiClO₄) complexes. The symbols represent data points and the solid line is the fit of Fox equation.

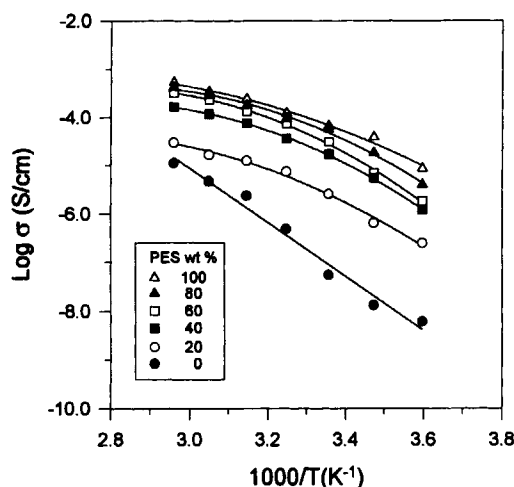


Figure 3. Temperature dependence of the ionic conductivities for the PES (X, 0.10, LiClO₄) complexes with different blend composition.

investigated earlier by other workers.^{17,18} Abraham et al. 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 %.^{19,20} In our study, PES has an advantage of being chemically almost identical to PEO, since PES is mainly composed of EO units with small amounts of oxysebacoyl groups. It is therefore expected that the compatibility of PES/PEO in the presence of LiClO₄ is more enhanced than that of MEEP/PEO blended electrolytes.

The ionic conductivity has been determined by a.c. impedance analysis, using the cells having blocking electrodes as described in the experimental section. Figure 3 shows the temperature dependence of the ionic conductivity for the blended polymer electrolytes with different blend composition. It is found that all of the blended electrolytes exhibit significantly higher conductivity than the pure PEO/

LiClO₄ complex, 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/LiClO₄ complex may be due to the higher degree of amorphous character stemming from the presence of PES, as given in Table I, since high conductivity is necessarily associated with an amorphous phase of the polymer.^{2,3} However, the blended polymer electrolytes containing a high amount of PES exhibited poor mechanical property. When the PES content is higher than 80 wt %, the samples were extremely difficult to handle, being very tacky and tending to stick to themselves, and they were unable to be pulled apart. Hence, the optimum PES content in the blended polymer electrolyte was thought to be 60 wt % considering both the mechanical stability and the ionic conductivity.

The DSC results for PES (60, Y, LiClO₄) complexes with change of the salt concentration are given Table II. 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 which correspond to the melting endotherms of PES and PEO can be observed. On the other hand, the only crystalline melting transition of PEO can be observed in the thermogram of PES (60, 0.10, LiClO₄), and the melting peaks completely disappear as the salt concentration is further increased. The reduction of crystallinity with an incorporation of LiClO₄ is attributed to the physical crosslinking arising from ion-polymer interactions. 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. The representative wide-angle X-ray diffraction patterns of PES (60, Y, LiClO₄) complexes are shown in Figure 4. From the X-ray diffraction pat-

Table II. DSC Results of PES(60, Y, LiClO₄) Complexes as a Function of Salt Concentration

Polymer Electrolytes	T_g (°C)	T_{m1} (°C) ^a	ΔH_{m1} (J/g) ^a	T_{m2} (°C) ^b	ΔH_{m2} (J/g) ^b
PES(60, 0, LiClO ₄)	—	42.0	45.3	70.8	51.6
PES(60, 0.01, LiClO ₄)	-48.7	42.7	31.2	68.2	45.1
PES(60, 0.02, LiClO ₄)	-47.0	41.3	28.6	63.7	32.3
PES(60, 0.05, LiClO ₄)	-41.4	31.0	7.0	57.3	25.3
PES(60, 0.10, LiClO ₄)	-30.3	—	—	41.5	3.1
PES(60, 0.20, LiClO ₄)	-23.9	—	—	—	—

^a Melting transition of crystalline PES.

^b Melting transition of crystalline PEO.

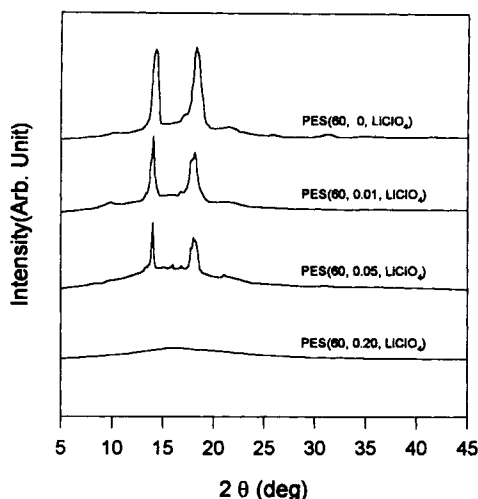


Figure 4. X-ray diffraction patterns of PES (60, Y, LiClO₄) complexes having a different salt concentration.

terns, it was found that there was a decrease in the relative intensities of the main peaks ($2\theta = 18.8, 23.0^\circ$) corresponding to the pure PES or PEO with an increase in the salt concentration, indicating that the amount of uncomplexed polymer present decreased with increasing the salt concentration. No X-ray diffraction patterns corresponding to crystalline complex were observed, suggesting that the complexation of LiClO₄ should occur in the amorphous phase of polymer. The temperature dependence of the ionic conductivities for PES (60, Y, LiClO₄) complexes having a different salt concentration is shown in Figure 5. The ionic conductivity increases with salt concentration and falls off with concentration at higher [LiClO₄]/[EO] ratio. The fall in conductivity observed at higher salt concentration is a consequence of increase in T_g , which reduces the ionic mobility. The electrolyte with [LiClO₄]/[EO] = 0.10 exhibited the highest conductivity at room temperature.

Figure 6 shows the temperature dependence of the ionic conductivities for PES (60, 0.10, salt) complexes containing the different lithium salts. For the LiCF₃SO₃ electrolyte, the lower conductivities were observed compared to those in LiClO₄ or LiBF₄ electrolyte over the temperature ranges studied. This result may be due to the lower degree of dissociation of the LiCF₃SO₃ salt. The degree of dissociation of the various lithium salts has been previously compared by various authors in liquid electrolytes.^{21,22} They reported that the association tendency of the anions with Li⁺ ions in nonaqueous aprotic solvents increases in the following order:

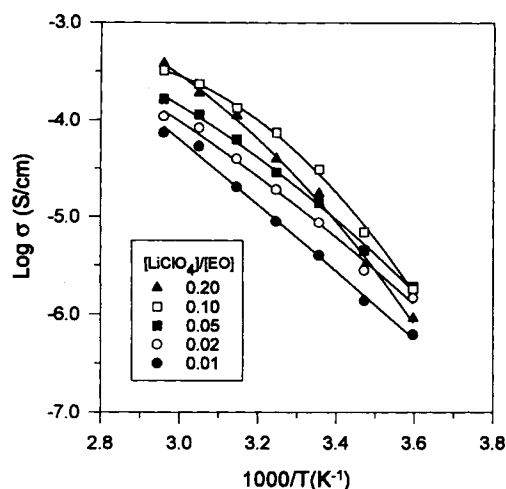
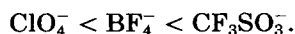


Figure 5. Temperature dependence of the ionic conductivities for the PES (60, Y, LiClO₄) complexes having a different salt concentration.

This result suggested that ion pairing took place to a lesser extent in the LiClO₄ or LiBF₄ electrolyte than in the LiCF₃SO₃ electrolyte. The DSC results of the blended polymer electrolytes containing the different salts are given in Table III. The T_g values increase with the decrease in the association tendency of the salt, which is due to the increase of the ion-polymer interaction. It is also found that there is a variation in the crystallinity with anion. Moreover, two melting peaks can be observed for the LiCF₃SO₃ electrolyte. They correspond to the melting endotherms of PES and PEO, respectively. These results indicate that the intermolecular crosslinking to destruct the crystalline structure is

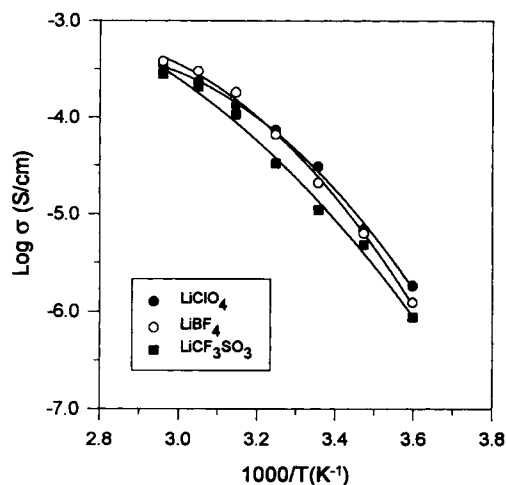


Figure 6. Temperature dependence of the ionic conductivities for the PES (60, 0.10, salt) complexes containing a different salt.

less effective as the association tendency of the anions with Li^+ ions increases. It is thus clear that the lower conductivity of the LiCF_3SO_3 electrolyte shown in Figure 6 is due to the lower concentration of charge carrier in the amorphous regions.

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 lithium transport number. In our study, we measured the lithium transport number by combination of a.c. impedance and d.c. polarization measurement. This technique has been proved to be applicable in circumstances where the proper correction for passivating layer is required. By a.c. impedance analysis of $\text{Li}|\text{PES}(60, 0.10, \text{salt})|\text{Li}$ cell, the initial interfacial resistance ($R_{i,0}$) was measured. A small d.c. polarization (ΔV) was applied to this cell, and the initial current (I_0) was measured. The current was monitored with time until the steady-state condition was established, and the steady-state current (I_s) was determined. The steady-state interfacial resistance of the cell ($R_{i,s}$) was again determined by a.c. impedance analysis. Following the treatment discussed by Evans et al.¹⁴ the cationic transport number is expressed as follows:

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

The values of t^+ obtained for the blended polymer electrolytes containing the different lithium salts are summarized in Table IV. The values of anionic radii are also given in Table IV. The values of lithium transport number were lower than 0.5, which 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 coordinated 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. Based on the previous reports,²² the radius of anion follows the order $\text{CF}_3\text{SO}_3^- > \text{ClO}_4^- > \text{BF}_4^-$. An examination of the lithium transport number and the anion radius given in Table IV reveals that the

Table IV. Lithium Transport Number at 40°C and Anion Radii

Polymer Electrolyte	t^+	Anion Radius (Å) ^a
PES(60, 0.10, LiClO_4)	0.37	2.37
PES(60, 0.10, LiBF_4)	0.34	2.29
PES(60, 0.10, LiCF_3SO_3)	0.46	2.70

^a From ref. 22.

lithium transport number shows a tendency to increase with increasing the radius of anion. It may be due to the fact that the anion mobility is more restricted in the polymer electrolytes as the size of anion increases, since the anions are floating in the polymer matrix.

Lithium Electrode/Polymer Electrolyte Interface

The lithium electrode/polymer electrolyte interface is a complicated interphase having different types of capacitive and resistive elements and, therefore, a.c. impedance technique is thought to be a useful tool for the study of lithium electrode in contact with the solid polymer electrolyte. A.C. impedance results can be analyzed on the basis of the regression of the observed response to the equivalent circuit model. Recently, various models such as homogeneous, composite, and stratified surface layers have been proposed for the interpretation of passivation layers formed on the lithium electrode during storage time. Thevenin and Muller proposed the polymer-electrolyte interphase (PEI) model to describe the homogeneous passivation layers growing on a lithium electrode in a propylene carbonate electrolyte.²³ Fauteux has also reported that the passive film formed at the lithium electrode in the polymer electrolytes could be best described by the PEI model.⁸ The PEI model describes the lithium passivated surface area as a compact mixture of polymeric and inorganic compounds, whose equivalent circuit is shown in Figure 7. Since the measurements were restricted to a relatively high-frequency range (10

Table III. DSC Results of the Blended Polymer Electrolytes Containing the Different Salts

Polymer Electrolyte	T_g (°C)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	Crystallinity
PES(60, 0.10, LiClO_4)	-30.3	—	—	41.5	3.1	0.02
PES(60, 0.10, LiBF_4)	-32.1	—	—	47.1	8.5	0.04
PES(60, 0.10, LiCF_3SO_3)	-38.3	23.3	6.8	56.5	10.3	0.08

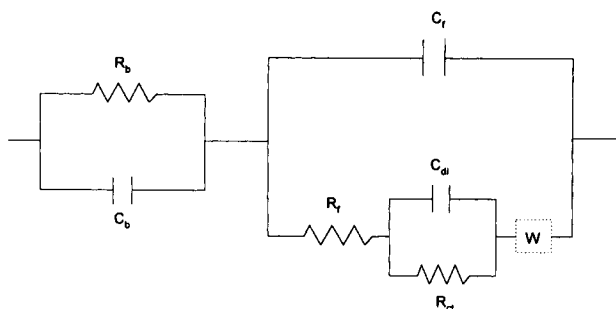


Figure 7. Equivalent circuit of a polymer-electrolyte interphase (PEI) model. R_b : electrolyte resistance, C_b : electrolyte capacitance, R_f : resistance of passivation film, C_f : capacitance of passivation film, R_{ct} : charge transfer resistance, C_{dl} : double layer capacitance, W : Warburg impedance.

MHz \sim 0.1 Hz), the Warburg impedance, which is associated with ionic diffusion arising from the presence of concentration gradients within the polymer electrolyte, was excluded from our equivalent circuit model. The equivalent circuit is determined by three types of impedances: (i) conduction impedance defined by the bulk resistance (R_b) and the bulk capacitance (C_b); (ii) transport of the lithium ions across the passivation film which is controlled by the resistance of the film (R_f) and to which is associated a capacitance of the film (C_f); (iii) charge transfer impedance represented by the charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}).

Figure 8 shows the time evolution of the a.c. complex impedance response of a Li|PES (60, 0.10, LiClO₄)|Li cell at 40°C. In order to confirm the validity of the assumed equivalent circuit, the a.c. impedance results were compared to the data obtained by fitting with equivalent circuit shown in Figure 7. As demonstrated in this figure, the fitted results follow in a very satisfactory fashion the experimentally obtained a.c. response. It is found that two arcs corresponding the conduction of Li⁺ ion in the passive layer and the charge transfer are not well separated, and are mixed to form a single distorted arc. It is also clearly seen that the low-frequency arc increases with increasing time. The expansion of the low-frequency arc is attributed to the increase of the interfacial resistances, which indicates the growth of a passivation layer on the lithium electrode surface. By the numerical fitting based on the equivalent circuit of PEI model, it is possible to evaluate the time evolution of the resistive components (R_b , R_f , R_{ct}). This result is shown in Figure 9. It should be noted that R_b is associated with the bulk property of the polymer electrolyte, and R_f and

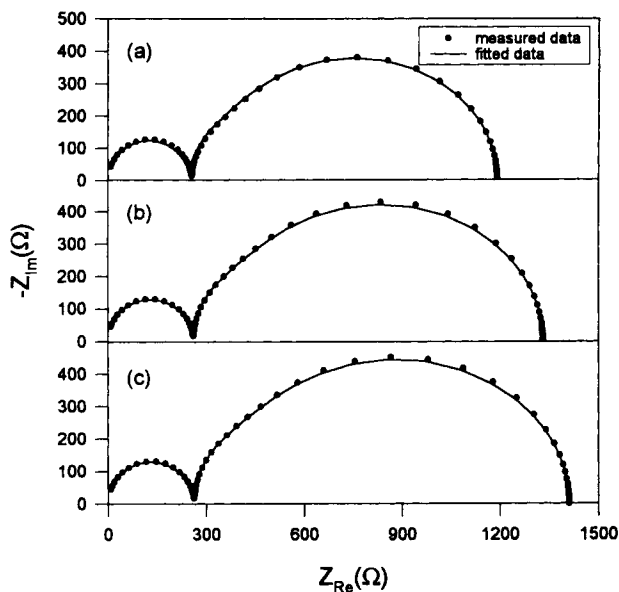


Figure 8. The a.c. impedance spectra of a Li|PES (60, 0.10, LiClO₄)|Li cell as a function of storage time at 40°C. (a) at 0 h, (b) after 24 h, (c) after 48 h.

R_{ct} can be ascribed to the electrode/electrolyte interface. It is found that the bulk resistance (R_b) of the polymer electrolyte is almost constant over the times measured, while the interfacial resistances (R_{ct} , R_f) are slightly increased up to the stable values with time. Since the value of R_f^{-1} represents the ionic conductivity of the passive film, an increase of R_f with time may be related to the increase in the passivating film thickness. The increase of the charge transfer resistance according to the increase of R_f with time also indicates that the charge transfer reaction is limited by the formation of a passivating film at the lithium electrode. The increase of R_{ct}

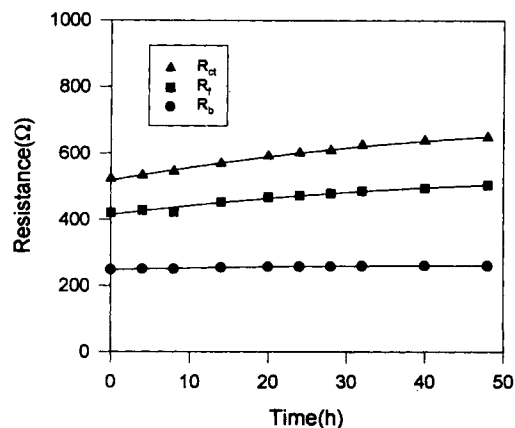


Figure 9. Variation of R_b , R_f , and R_{ct} with storage time in the Li|PES (60, 0.10, LiClO₄)|Li cell at 40°C.

during the passivation process may be caused by a decrease in the electrochemically active surface area, or the change in the nature of the passivating film, whose structure and composition are of such nature to block the charge transfer reaction. Time constants (τ_f) for the ionic conduction across the passive film and those (τ_{ct}) for the charge transfer reaction at the lithium electrode are presented in Figure 10. The values of time constants (τ_f and τ_{ct}) were calculated from the product of the resistances (R_f and R_{ct}) by the capacitances (C_f and C_{dl}). The values of τ_f are found to be almost constant with storage time, which indicates that the increase in R_f with time is mainly due to the increase in the thickness of passive film. On the other hand, the values of τ_{ct} gradually increase with time, which means that the nature of the passive film near the lithium electrode is being changed to impede the charge transfer reaction. Hence, it can be said that the increase in R_{ct} with storage time shown in Figure 9 is mainly due to the change in the nature of the passive film during storage. A similar conclusion has been also drawn by Croce et al.⁹ The passive layers 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.^{5,6} Since a reactive impurity in the polymer electrolyte is mainly water, the formation of LiOH and Li₂O may be expected. LiCl can be also formed by the decomposition of LiClO₄ in the presence of lithium.²⁴

Figure 11 shows the temperature dependence of R_f for the PES (60, 0.10, LiClO₄) electrolyte. To avoid the time dependence error arising from the increase of the resistance with time, a.c. impedance

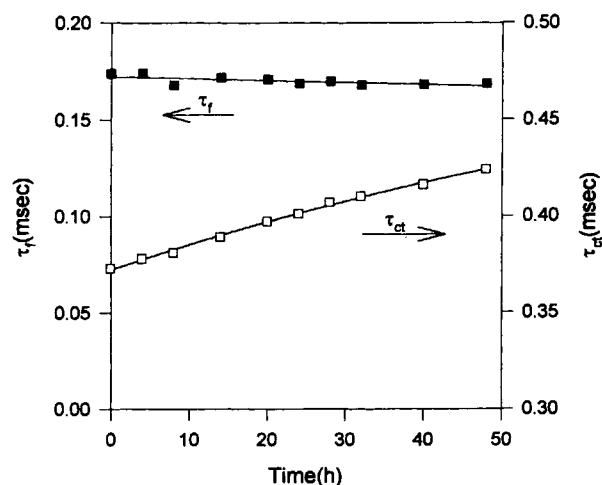


Figure 10. Variation of τ_f and τ_{ct} with storage time in the Li|PES (60, 0.10, LiClO₄)|Li cell at 40°C.

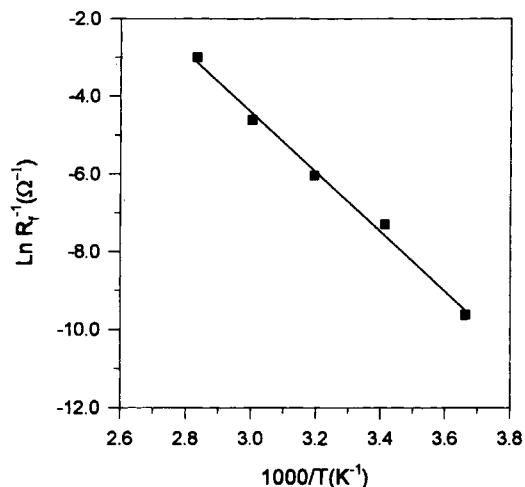


Figure 11. Temperature dependence of R_f in the Li|PES (60, 0.10, LiClO₄)|Li cell at $t = 0$ h.

measurements taken at $t = 0$ h are employed. A linear dependence of $\ln(R_f^{-1})$ as a function of temperature was observed. It is characteristic of the ionic conduction process in the solid electrolyte, which can be interpreted as being representative of the formation of a solid passive film at the interface. Based on the linear dependence of $\ln(R_f^{-1})$ vs. $1/T$, the apparent activation energy associated with the ionic transport through the passivating film was determined to 0.66 eV. An activation energy value of 0.65 eV for the ionic transport of lithium through the LiOH or Li₂O passivating film has been reported by Radman for the lithium electrodes in liquid electrolytes containing small amounts of water.²⁵ Thus, the passivating film in our system would consist mostly of an inorganic salt such as LiOH or Li₂O based on the comparison of the activation energy. As mentioned earlier, trace water in polymer electrolytes may react with the lithium electrode. Direct reduction forms LiOH, which can be further reduced to Li₂O.

In order to investigate the effect of matrix polymer on the passivation phenomena of the lithium electrode, the a.c. impedance measurements were performed as a function of blend composition in the blended polymer electrolytes. Of particular interest in this investigation is a variation of the R_f value, from which the information on the kinetics of passivation can be derived. Figure 12 shows the time dependence of R_f value in the polymer electrolytes having different blend composition at 40°C. In Figure 12, the resistance of passive film is seen to increase with increasing time in all the blended polymer electrolytes examined. However, the kinetics of passivation seems to vary from one electrolyte to

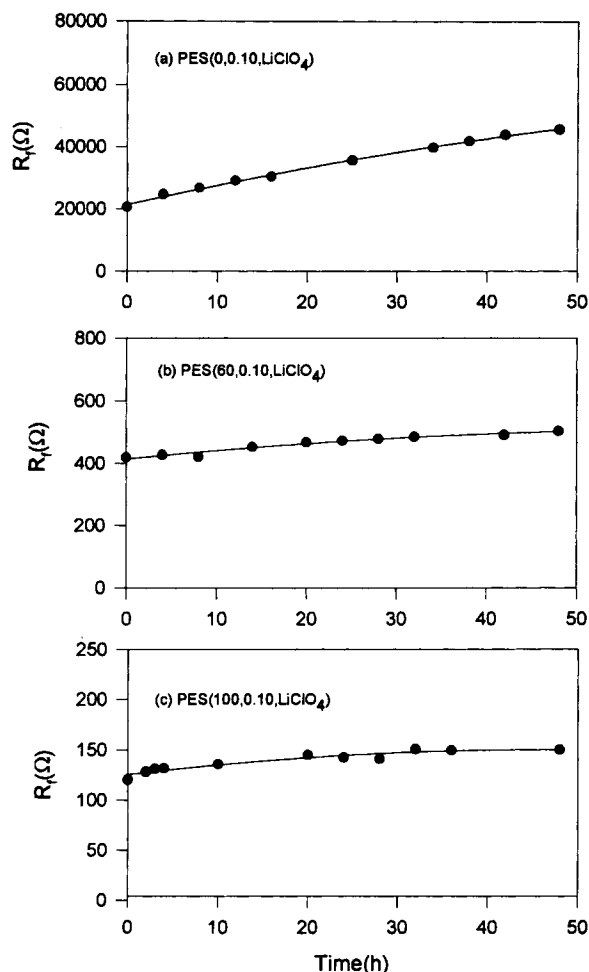


Figure 12. Variation of R_f with storage time in the Li|PES (X , 0.10, LiClO₄)|Li cell having different blend composition at 40°C.

another. The variation of the R_f value may be related to the effect of the trace water, as discussed above. Even in the driest polymer electrolytes, they may contain water at the ppm level. The water content is thought to be sufficient to influence the kinetics of the formation of passivation film, as previously suggested by Fauteux.⁶ Water diffuses through the polymer matrix to the lithium surface and reacts there to form LiOH or Li₂O. Water content is supposed to be richer as the content of PEO increases, because PEO is more polar and hygroscopic than PES, and therefore there is an efficient passivation against water reaction in PES (0, 0.10, LiClO₄). The growth of the passivating film may be also related to the reactivity of the polymer itself with lithium metal. This presumption has not yet been confirmed at this stage. The influence of the polymer blend composition on the charge transfer resistance is also shown in Figure 13. It is found that the value of R_{ct}

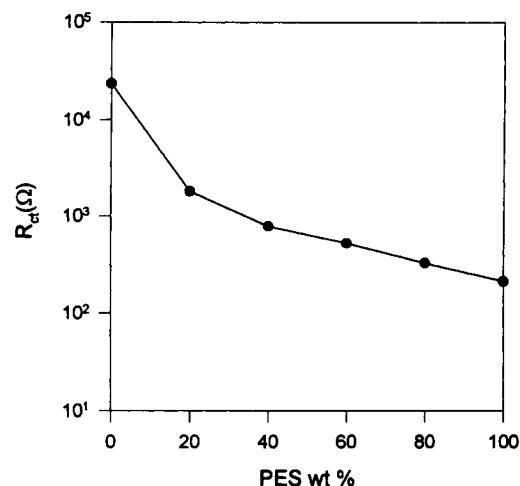


Figure 13. Charge transfer resistance as a function of a blend composition in Li|PES (X , 0.10, LiClO₄)|Li cell at 40°C.

decreases with the PES content. The difference in R_{ct} may be mainly related to the effective electrode area, since the degree of electrode/electrolyte contact will be dependent on the physical stiffness of the polymer electrolytes. If a marked change occurs in the contact area between the lithium electrode and the polymer electrolyte as a change of PES content, a decrease in R_{ct} can be expected as a result of better wetting of the lithium electrode by the matrix polymer, as the PES content in the blend increases. It is also plausible that the existence of the crystallites affects the charge transfer reaction, because the interface between the lithium electrode and the crystalline polymer may function as a barrier for the electrochemical reaction of lithium.

The interfacial resistances derived from the impedance spectra obtained for the LiClO₄, LiBF₄, and LiCF₃SO₃ electrolytes are summarized in Table V. It is noted that the interfacial resistance is calculated by adding R_{ct} and R_f . Initial values of R_i are found to be about the same irrespective of salt type,

Table V. Interfacial Resistances Obtained for the LiClO₄, LiBF₄, and LiCF₃SO₃ Electrolytes at 40°C ([Li]/[EO] = 0.10)

Polymer Electrolyte	$R_{i,0}$ (Ω) ^a	$R_{i,48}$ (Ω) ^b	$R_{i,48}/R_{i,0}$ (Ω)
PES(60, 0.10, LiClO ₄)	943	1152	1.22
PES(60, 0.10, LiBF ₄)	1002	2962	2.96
PES(60, 0.10, LiCF ₃ SO ₃)	965	1110	1.15

^a Interfacial resistance at $t = 0$ h.

^b Interfacial resistance after 48 h.

but the interfacial resistance in LiBF_4 electrolyte is much higher than in LiClO_4 or LiCF_3SO_3 electrolyte after 48 h. This result indicates the involvement of salt reduction processes in the build-up of passive films and reflects the different degree of reactivity of the various salts with the lithium electrode. Since the PES (60, 0.10, LiBF_4) system has the largest transport number for the anion, as in given Table IV, it is thought that the large increase of R_i with time in the LiBF_4 electrolyte may arise from a chemical reaction associated with the BF_4^- anion reached easily at the electrode surface. The chemical instability of the BF_4^- anion may give rise to LiF and other decomposition products in the electrode surface. These results are consistent with the previous observations on the lithium electrode in propylene carbonate solutions.²⁶ From the comparison of the $R_{i,48}/R_{i,0}$ values, it can be said that the LiCF_3SO_3 salt is most stable to the lithium electrode among the electrolytes studied; however, its main disadvantage is the low conductivity, as shown in Figure 6. Thus, it is proposed that the LiClO_4 electrolyte is the best system on the basis of minimizing R_i and ΔR_i .

Figure 14 shows the dependence of R_i on storage time for PES (60, Y, LiClO_4) complexes of different salt concentration. The value of R_i is found to be higher and its dependence on storage time seems to be steeper as the salt concentration increases. This is due to the fact that the possibility of the reduction of anion in the presence of lithium electrode is much higher in the electrolyte of higher salt concentration. For high salt concentration electrolyte, an electrochemical reaction of LiClO_4 leads to the formation of LiCl in addition to the formation of LiOH or Li_2O . LiCl is hardly soluble in polymer and will therefore remain at the interface between the lithium electrode and the polymer electrolyte. On the other hand, for low salt concentration electrolyte, the residual impurities may determine the nature of the passivating film, in which case it would consist of an inorganic salts such as Li_2O or LiOH , as suggested earlier.

CONCLUSION

The electrochemical characteristics of the blend-based polymer electrolytes composed of poly(ethylene oxide), poly(oligo[oxyethylene]oxysebacoyl), and lithium salts were investigated in terms of the blend composition, the salt used, and its concentration. From the consideration of the mechanical stability and the ionic conductivity as a function of a blend composition, the optimum PES compo-

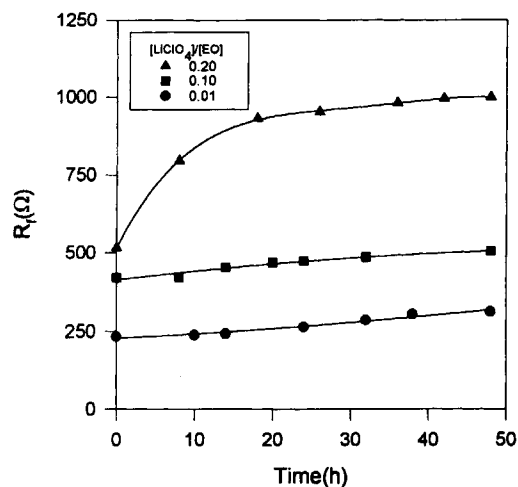


Figure 14. Variation of R_i with storage time in $\text{Li}|\text{PES}(60, Y, \text{LiClO}_4)|\text{Li}$ cell at 40°C .

sition in the blended polymer electrolyte was determined to be 60 wt %. The lithium passivation appeared to take place in all the blended-based polymer electrolytes studied. Based on the activation energy of the ionic conduction process in the passivating layer, LiOH and Li_2O are thought to be the major components in the passivating film. The kinetics and the degree of passivation varied as a function of blend composition, the salt used, and its concentration, and eventually the PES (60, 0.10, LiClO_4) electrolyte system was proved to be the most satisfactory system to maximize the ionic conductivity and to assure acceptable stability of the lithium electrode in the polymer electrolytes. The lithium transport number in this system was determined to be 0.37.

This work has been supported by the Korea Science and Engineering Foundation (KOSEF) in 1995.

REFERENCES AND NOTES

1. M. B. Armand, J. M. Chabagno and M. Duclot, *Extended Abstracts of Second International Meeting on Solid Electrolytes*, St Andrews, Scotland, Sept., 1978.
2. J. R. MacCallum and C. A. Vincent, Eds., *Polymer Electrolyte Reviews, Vol. 1 and 2*, Elsevier Applied Science, London, 1987 and 1989.
3. J. S. Tonge and D. F. Shriver, in *Polymers for Electronic Applications*, J. H. Lai, Ed., CRC Press, Inc., Boca Raton, FL, 1989, Chap. 5.
4. R. J. Neat, in *Modern Battery Technology*, C. D. S. Tuck, Ed., Ellis Horwood Limited, New York, 1991.
5. D. Fauteux, *Solid State Ionics*, **17**, 133 (1985).
6. D. Fauteux, *J. Electrochem. Soc.*, **135**, 2231 (1988).

7. B. Scrosati, *Br. Polym. J.*, **20**, 219 (1988).
8. D. Fauteux, *Electrochim. Acta*, **38**, 1199 (1993).
9. F. Croce and B. Scrosati, *J. Power Sources*, **43-44**, 9 (1993).
10. D. W. Kim, J. K. Park, and H. W. Rhee, *Solid State Ionics*, in press (1996).
11. D. W. Kim, J. K. Park, and M. S. Gong, *J. Polym. Sci. Part B: Polym. Phys.*, **33**, 1323 (1995).
12. J. K. Park, D. W. Kim, and J. S. Song, *Extended Abstract of Fourth International Symposium on Polymer Electrolytes*, New Port, RI, June, 1994, p. 120.
13. B. Wunderlich, *Macromolecular Physics*, Vol. 3, Academic Press, New York, 1980, p. 67.
14. J. Evans, C. A. Vincent, and P. G. Bruce, *Polymer*, **28**, 2324 (1987).
15. P. G. Bruce and C. A. Vincent, *J. Electroanal. Chem.*, **225**, 1 (1987).
16. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
17. R. Mani, T. Mani, and J. R. Stevens, *J. Polym. Sci. Part A: Polym. Chem.*, **30**, 2025 (1992).
18. J. Li and I. M. Khan, *Macromolecules*, **26**, 4544 (1993).
19. K. M. Abraham, M. Alamgir, and R. K. Reynolds, *J. Electrochem. Soc.*, **136**, 3576 (1989).
20. K. M. Abraham, M. Alamgir, and R. D. Moulton, *J. Electrochem. Soc.*, **138**, 921 (1991).
21. A. Webber, *J. Electrochem. Soc.*, **138**, 2586 (1991).
22. M. Ue, *J. Electrochem. Soc.*, **141**, 3336 (1994).
23. J. G. Thevenin and R. H. Muller, *J. Electrochem. Soc.*, **134**, 273 (1987).
24. D. Aurbach and A. Zaban, *J. Electroanal. Chem.*, **348**, 155 (1993).
25. D. M. Radman, *Abstract 125, The Electrochemical Society Extended Abstracts*, Vol. 84-2, New Orleans, LA, Oct., 1984, p. 188.
26. D. Aurbach, I. Weissman, A. Zaban, and O. Chusid, *Electrochim. Acta*, **39**, 51 (1994).

Received June 30, 1995

Revised April 11, 1996

Accepted April 18, 1996