Polymer Electrolytes for the Lithium Secondary Polymer Batteries

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1. Introduction

Solid polymer electrolytes, formed by dissolving salts in a polymer matrix, have long received extensive attention because of their potential for achieving high ionic conductivities. Among their many direct applications are high energy-density batteries, electrochromic display devices(ECD), and fuel cells.[1,2,3] Poly(ethylene glycol)(PEG) of low molecular weight has the advantage of having relatively high ambient ionic conductivity (10^{-4}S/cm) when complexed with alkali-metal salts, however, their poor mechanical stability cannot satisfy the requirement for solid-state processing. Various attempts have been made to prepare the solid polymer electrolytes with the improved ionic conductivities and dimensional stability at ambient temperature.[4,5,6]

The aim of the present work is to obtain the high ion-conducting and mechanically stable solid polymer electrolytes. For this purpose, we prepared the polymer electrolytes based on the mixture of poly(methyl methacrylate-co-lithium methacrylate) (P(MMA-co-LiMA)), low molecular weight PEG, and $LiCF_3SO_3$. The effect of ion content in the ionomer on the ionic conductivities of the polymer electrolytes was also thoroughly investigated.

2. Experimental

Preparation of Polymer Electrolytes

To obtain the poly(methyl methacrylate-co-methacrylic acid) P(MMA-co-MAA) copolymer, the mixture of MMA, MAA and AIBN was added to THF under nitrogen atmosphere and the polymerization was carried out at 65℃ for 16 h. The P(MMA-co-LiMA) ionomer was made by neutralizing the P(MMA-co-MAA) in THF with the stoichiometric amount of lithium hydroxide. The ion content of the P(MMA-co-LiMA) ionomer was controlled by the feed composition of monomers, and was calculated from the titration method. In order to prepare the polymer electrolytes, the mixtures of the P(MMA-co-LiMA)ionomer/PEG/$LiCF_3SO_3$ were dissolved in THF or methanol. The solutions were cast onto a Teflon substrate, and the solvent was evaporated slowly in a hood for 24 h. The resulting polymer electrolytes were dried at 60℃ in vacuum for 24 h. The salt concentration in all the polymer electrolytes was set to be constant($[O]/[Li^+]=15$) and the PEG content was defined as follows : wt% = (wt of PEG/wt of the ionomer) x 100.

Conductivity and Dielectric loss Measurements

The ionic conductivities of the polymer electrolyte films were measured by complex impedance analysis using a Solartron 1255 frequency response analyzer coupled to an IBM PS/2 computer over a frequency range of 100Hz - 10MHz. 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. Impedance data were also converted to the real, or storage(ε'), and imaginary, or loss(ε''), components of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, at each tested frequency.

Thermal Analysis

The differential scanning calorimetry(DSC) studies were carried out to determine the glass transition temperatures(T_g) or melting temperatures(T_m) of the samples using a Du-Pont 9900 instrument. The measurements were taken over a temperature range of -100 to 250℃ at a heating rate of 10℃ min^{-1} under nitrogen atmosphere.

Infrared Measurements

The samples used for FTIR studies were prepared by casting the THF solution of the mixture of the P(MMA-co-LiMA), PEG, $LiCF_3SO_3$ on the Krs-5 window. FTIR spectra were recorded in the absorption mode on a Bomem MB 102 FTIR spectrometer covering a range from 400 to $4000cm^{-1}$. The resolution for all spectra was $4cm^{-1}$.

3. Results and Discussion

In order to investigate the effect of the ion content in the ionomer on the miscibility between the MMA units in the ionomer and PEG, the glass transition temperatures of the polymer electrolytes were determined and the results are given in Table I. For the case of PMMA/PEG/$LiCF_3SO_3$ blend system, the T_g of the PEG phase in the blend remains nearly unchanged with the PEG content. The T_g of the PEG phase in the P(MMA-co-LiMA)/PEG/$LiCF_3SO_3$ system shifts however to the higher temperature as the PEG content decreases. It means that the miscibility between the ionomer and the PEG is better than that between the PMMA and the PEG. In the case of the ionomer blend system, the T_g is found to increase as the ion content in the ionomer increases, which indicates that the degree of miscibility between the MMA units in the ionomer and PEG enhances with the increase of the ion content in the ionomer. It was expected that this enhanced miscibility results from the ion-dipole interaction between the ion groups in the ionomer and the oxygens in PEG. To confirm this conclusion, we investigated the molecular interactions occurring between the P(MMA-co-LiMA) and the PEG by means of FTIR spectroscopy. Fig. 1 shows the FTIR spectra of the P(MMA-co-LiMA) ionomer/PEG blends in the range 1550-1650cm^{-1}, which corresponds to the region of the asymmetric stretching vibration of the carboxylate ion(COO^-). It is recognized from Fig. 1 that the asymmetric stretching vibration frequency of the carboxylate ion increases as the content of PEG in the Li ionomer/PEG blend is increased. It is well known that the increase in COO^- asymmetric stretching vibration frequency with adding PEG to the ionomer originates from the ion-dipole interaction between the cation in the ionomer and ether groups in PEO.[7,8,9] It is thus concluded that the ion groups in the ionomer enhance the miscibility between the Li ionomer and the PEG through the ion-dipole interaction, and consequently the degree of miscibility increases as the ion content in the ionomer increases.

The ambient ion conductivities of the polymer electrolytes as a function of ion content in the ionomer are shown in Fig. 2. It is found that as the ion content in the

P(MMA-co-LiMA) ionomer increases, the ion conductivities of the polymer electrolytes increase, reach a maximum and then decrease at higher ion content. This behavior is attributed to the two opposite effects of the ion groups on the ion conductivity. One is related to the pathway of charge carrier. The other is related to the number and mobility of the charge carrier. The initial increase of ion conductivities with the ion content can be expected for the reason that the ion groups in the ionomer make the MMA units and PEG miscible : As is seen from the above DSC results, the ion groups in the ionomer enhance the miscibility between the MMA units and PEG phase, which is an important factor for increasing the ion conductivities. In the blend of PMMA with PEG/$LiCF_3SO_3$, the two components, e.g., the PMMA and PEG components are immiscible and thus phase-separated. Since the ion cannot be transported through the PMMA phase, the presence of hard PMMA phase which is caused by the phase separation may be energetic barriers for ion transport, and consequently brings about the tortuous pathway. As the ion content increases, the components in these blend systems become more miscible and the pathway for ion transport becomes less tortuous and thus the ion conductivities increase.

In order to prove our presumption that the pathway is less tortuous as the ion content increases at the lower ion content range, the dielectric relaxation studies of the blend system were carried out. In Fig. 3 the dielectric loss (ε'') versus frequency($f = \omega / 2\pi$) plots are illustrated for the blends with the different ion content. According to Mauritz et al.,[10,11,12] the tortuosity of the ion motion can be characterized by the absolute value(n) of the slope of the dielectric loss versus the frequency plot : the larger n, the less tortuous pathway. In Fig 4, the values of n calculated from the slope of dielectric loss versus frequency plot(Fig. 3) are presented as a function of ion content in the ionomer for the blend with the different PEG content. It is observed that the value of n increases with increasing the ion content. This result means that the ion-conducting pathway becomes less tortuous as the ion content increases, which is consistent with our presumption.

However, the increase of the ion conductivities by the improvement of miscibility between the MMA units and the PEG is offset at the higher ion content by the following two reasons : The first reason is that the mobility of the charge carrier decreases with the increase of the ion content due to the reduction in the segmental motion of the PEG, which results from the ion-dipole interaction of the ions in the ionomer with the oxygens in the ether group and also from clustering of COO^-Li^+ ion pairs in the ionomer. This conclusion is supported by our DSC results on the glass transition temperatures of the polymer electrolytes. In Table I, the glass transition temperature is observed to increase as the ion content in the ionomer increases at the given PEC content. This increase in T_g of the PEG phase in the blend with the ion content is expected to originate from the ion-dipole interaction of the ions in the ionomer with the oxygens in ether group and also from clustering of COO^-Li^+ ion pairs in the ionomer, which leads to the decrease in ion conductivity at higher ion content.

The other reason for the decrease of ion conductivities at the higher ion content is that the number of charge carrier decreases with the increase of ion content. The change of charge carrier number with the ion content was investigated through the FTIR spectroscopy. Spectra for the blend of P(MMA-co-LiMA)/PEG/$LiCF_3SO_3$ with various ion contents are shown in Fig. 5. It shows only the region of symmetric stretching band of the anion SO_3^- . It is well known that the peak at 1030cm^{-1} is due to vibrations of free $CF_3SO_3^-$ anions and another peak at 1040cm^{-1} due to the ion pairs of $Li^+CF_3SO_3^-$.[13,14,15] As can be seen from Fig. 5, the relative peak intensity of the ion pairs of the $Li^+CF_3SO_3^-$ with the ion content in the ionomer for the blend increases at the given PEG content. This increase in the fraction of the ion pairs of the $Li^+CF_3SO_3^-$with the ion content is expected to be another reason for the decrease of ion conductivity at higher ion content. This increase in the relative fraction of the ion pairs of the $Li^+CF_3SO_3^-$ with the ion content may result from the following origin : It is well known that the ion groups in ionomers are generally aggregated to form cluster or multiplets.[16] In the P(MMA-co-LiMA)/PEG/salts blends, the salt may interact not only with the oxygens in PEG, but also with the ion groups in the ionomer. The ion groups in the ionomer may aggregate to form cluster or multiplets together with salts and thus the salts can exist as a form of ion pairs or ion aggregates. However, the first reason, i. e., the rise in T_g with the increase of the ion content, might mainly attributed to the decrease of the ion conductivity at the higher ion content since the ion pair fraction is probably still quite small relative to the free ions even though the ion pairs of the $LiCF_3SO_3$ increase with the increase in the ion content of the ionomer.

Table I also shows the mechanical state of the polymer electrolyte with the ion content in the ionomer. Most of the films are free standing except for the ones with the lower ion content(3mol%). The presence of cluster or multiplets in the P(MMA-co-LiMA)/PEG/ $LiCF_3SO_3$ blends contributes to the improvement of mechanical stability of the polymer electrolyte film, acting as a physical crosslinking. The ion-dipole interaction between the Li ionomer and the PEG in the blend is also expected to improve the mechanical stability.

4. References

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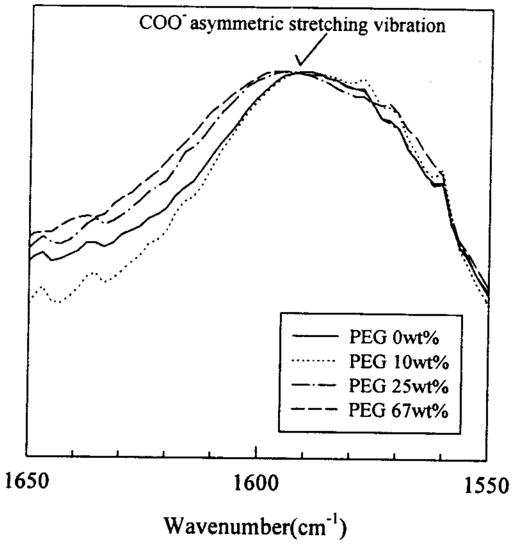

Fig. 1. The FTIR spectra of the COO$^-$ asymmetric stretching vibration for the P(MMA-co-LiMA)(13mol%) and PEG blend

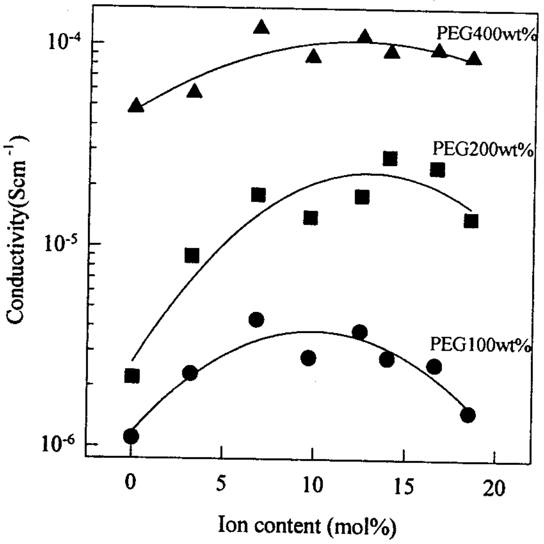

Fig. 2. The ion conductivities of the polymer electrolytes as a function of ion content in the ionomer (at 25°C)

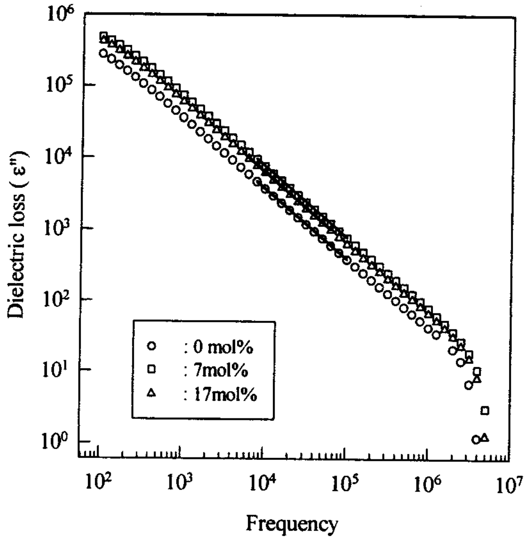

Fig. 3. Dielectric loss spectra for the polymer electrolytes containing 400wt% of PEG

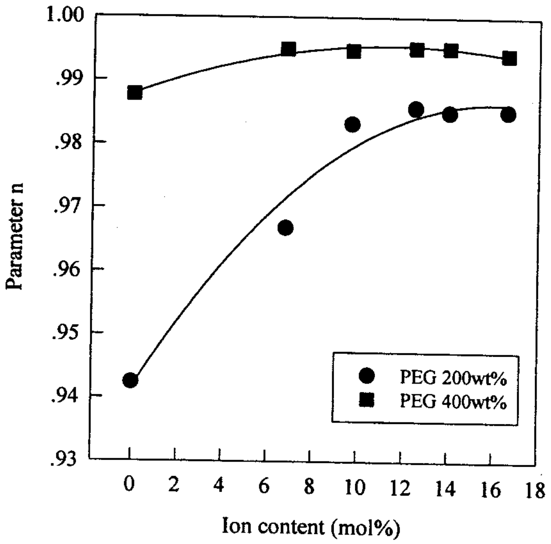

Fig. 4. The values of n parameter for the polymer electrolytes as a function of ion content in the ionomer

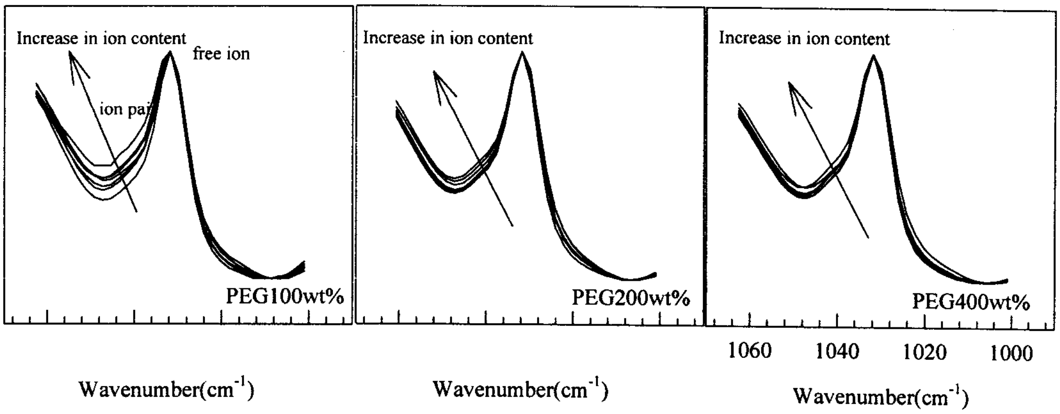

Fig. 5. The FTIR spectra of the SO_3^- symmetric vibration for the polymer electrolytes with the different ion content

Table I. Glass transition temperatures, optical transparencies and mechanical state of the blends of P(MMA-co-LiMA)/PEG/$LiCF_3SO_3$

PEG content (wt%)	Ion content(mol%)									
	0		3		7		10		13	
	T_g	appear/ mecha. state	T_g	appear/ mecha. state	T_g	appear/ mecha. state	T_g	appear/ mecha. state	T_g	appear/ mecha. state
100	-54.7	cloud/ *l&s	-51.2	cloud/ free stand	-40.2	cloud/ free stand	-35.6	clear/ free stand	-32.3	clear/ free stand
200	-53.8	cloud/ l&s	-53.1	cloud/ l&s	-48.1	cloud/ free stand	-48.3	clear/ free stand	-48.5	clear/ free stand
400	-53.0	cloud/ l&s	-53.7	cloud/ l&s	-50.1	cloud/ waxy	-50.5	cloud/ free stand	-48.9	clear/ free stand

*l&s = liquid and solid state