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Ion conductivities and interfacial characteristics of the plasticized polymer electrolytes based on poly(methyl methacrylate-co-Li maleate)

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Abstract

The plasticized polymer electrolytes composed of poly(methyl methacrylate-co-Li maleate), lithium perchlorate, and ethylene carbonate as a plasticizer, were newly prepared. The ion conductivities of the plasticized polymer electrolytes based on the poly(methyl methacrylate-co-Li maleate) were found to be dependent on the ion content of the ionomer, poly(methyl methacrylate-co-Li maleate), in the polymer electrolyte, and the polymer electrolyte based on the ionomer with 8.5 mol% ion content showed the maximum ion conductivity.

The interfacial resistance at the polymer electrolyte/lithium interface and the cationic transference number were also investigated as a function of the ion content of the ionomer in the polymer electrolyte. The interfacial resistances as well as the cationic transference numbers of the polymer electrolytes were found to be also dependent on the ion content of the ionomer in the polymer electrolyte. Ion aggregations in the ionomer seemed to significantly influence the electrochemical behavior of the polymer electrolytes based on the ionomer. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ionomer; Polymer electrolyte; Ion aggregate; Ionic conductivity; Interfacial resistance

1. Introduction

Polymer electrolytes have received considerable attention as electrolyte materials in advanced applications such as high-energy density batteries [1]. Recently, the polymer electrolytes with high ionic conductivity in the neighborhood of 10^{-3} S cm⁻¹ at ambient temperature have been reported [2–4]. These polymer electrolytes were obtained by immobilizing solutions of Li salts in organic polymer matrices. The typical examples of such electrolytes were those based on polyacrylonitrile, poly(vinyl chloride), poly(methyl methacrylate), etc. Although, ion conductivity of polymer electrolyte is of paramount importance, a high conductivity is not the sole requirement for the electrochemical applications [5]. It is of importance also to understand the interfacial behavior between polymer electrolyte and electrode to guarantee the acceptable performance for high-energy density rechargeable batteries [6].

In this article, we report a new class of plasticized polymer electrolyte based on the ionomer, poly(methyl methacrylate-co-Li maleate), and its electrochemical behavior including the ion conductivity, interfacial resistance and cationic transport number.

The introduction of ionic units into matrix polymer for the plasticized polymer electrolytes is intended to induce the ionic interaction between the ionic moiety of the matrix polymer and the added salt. Such interaction was found to significantly influence the electrochemical behavior of the polymer electrolytes based on the ionomer.

2. Experimental

2.1. Preparation of poly(methyl methacrylate-co-maleic anhydride) and its ionomer

The methyl methacrylate-maleic anhydride copolymers were prepared by solution copolymerization of methyl methacrylate and maleic anhydride using AIBN as an initiator. To the reactor fitted with a mechanical stirrer,

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condenser, and nitrogen inlet and outlet, the mixed monomer and solvent (tetrahydrofuran) were added, and then the initiator (AIBN) was injected. The mixture was heated to 600°C with stirring for 24 h under nitrogen atmosphere. After the polymerization was completed, the product solution was precipitated in cold methanol, filtered, washed two times in methanol, and dried under vacuum at 150°C. Neutralization of the acid groups was accomplished in THF/methanol (90/10, v/v) solutions to which calculated amounts of standard solutions of the lithium hydroxide in methanol were added. The neutralized copolymers were then recovered by solvent casting in a hood and dried at 180°C under vacuum.

2.2. Preparation of polymer electrolytes

The appropriate amount of the ionomer, ethylene carbonate (EC), LiClO₄, and THF/methanol (50/50, v/v) as a cosolvent, were mixed well and heated to about 80°C until the ionomer and LiClO₄ were completely dissolved in the cosolvent. The viscous solutions were then placed on Teflon plates and preserved in a dried nitrogen atmosphere. After evaporation of the cosolvent, polymer electrolyte films were peeled from the plate. The thickness of the film was 25 ± 5 μm. The composition of the polymer electrolytes was 22.2/7.8/70 (ionomer/LiClO₄/EC, respectively) by weight percent.

2.3. DSC measurement

Thermal behavior of the ionomers and their electrolyte films was studied by means of differential scanning calorimetry using a Du Pont 9900 instrument. Samples were loaded in hermetically sealed aluminum pans, and measurements were taken within an appropriate temperature range at a heating rate of 10°C min⁻¹ under nitrogen atmosphere.

2.4. FT-IR measurement

The samples were cast onto the Krs-5 window for the FT-IR measurement. The FT-IR spectra were recorded in transmission on the Bomem 450 with the resolution of 4 cm⁻¹ in the vibrational frequency range of 400–4000 cm⁻¹.

2.5. Conductivity measurement

Polymer electrolyte film was sandwiched between the two stainless steel electrodes with blocking nature and assembled into a sample holder for measurement of ion conductivity. In order to investigate the interfacial phenomena at the lithium electrode/polymer electrolyte interface, the polymer electrolyte film was 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 ac

impedance measurement of the polymer electrolyte was then performed using a Solatron 1225 frequency response analyzer (FRA) coupled to an IBM computer over a frequency range of 0.1 Hz–10 MHz. Each cell was allowed to equilibrate for 2 h at a given temperature before measurement. The lithium transference number was evaluated with a cell of Li | polymer electrolyte | Li by the combination of the ac impedance and dc polarization measurements.

3. Results and discussion

3.1. Structure characterization

By comparing the FT-IR spectra for the unneutralized copolymer of methyl methacrylate and maleic anhydride, and the corresponding lithium-metal ionomer, it is possible to ascertain the chemical structure of the ionomer. The expanded FT-IR spectra for the unneutralized copolymer and the corresponding ionomer are shown in Fig. 1. The peak at 1790 cm⁻¹ in Fig. 1(a) corresponds to the stretching mode of the carbonyl group of anhydride ring in the unneutralized copolymer. For the ionomer, new peaks for the carbonyl stretching band did appear in the region of 1550–1650 cm⁻¹ as shown in Fig. 1(b). These new peaks are reported to arise from the asymmetric stretching mode of carboxylate anion of the maleate ionomer [7,8]. The disappearance of the peak at 1790 cm⁻¹ for the ionomer as shown in Fig. 1(b) reconfirms that the transformation of the anhydride into the Li maleate has occurred. The strong peak centered at 1740 cm⁻¹ is assigned to the carbonyl stretching of the ester group in methyl methacrylate unit.

3.2. Ion conductivities of the polymer electrolytes

Fig. 2 shows the ion conductivities of the polymer electrolytes based on the Li maleate ionomer, EC, and the salt,

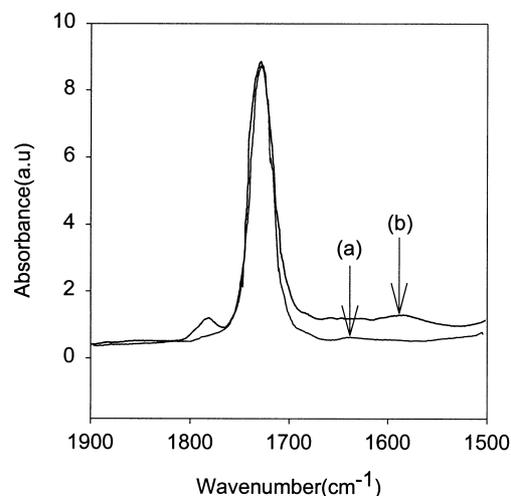


Fig. 1. Expanded FT-IR spectra for the unneutralized copolymer and its lithium metal ionomer.

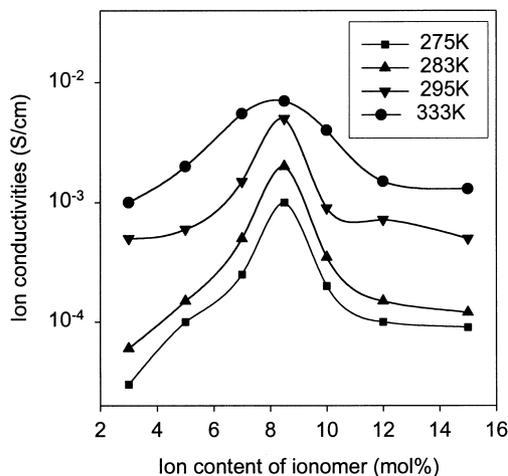


Fig. 2. The ion conductivities of the maleate ionomer based plasticized polymer electrolytes as a function of the ion content of the ionomer in the polymer electrolyte.

LiClO_4 , as a function of the ion content of the Li maleate ionomer. The ion conductivities of the plasticized polymer electrolytes are found to initially increase to reach a maximum and then decrease with the ion content of the ionomer in the polymer electrolyte. It is expected that the initial increase of the ion conductivity of the polymer electrolyte with the ion content of the ionomer is attributed to the two factors, the mobility and the number of the charge carrier. The mobility would be related to the compatibility of the ionomer with the plasticizer, EC. With the increase of the ion content of the ionomer, the compatibility between the ionomer and EC would be enhanced resulting in the generation of larger free volume in the polymer electrolytes, and consequently leading to the increase of the mobility of the charge carrier. Another factor for the initial increase of ion conductivity is associated with the increase of the charge carrier concentration by the increase of the ion content of the ionomer. Since the lithium cation from the ionomer can also contribute to the ionic conduction as well as the charge carriers from lithium perchlorate, the total concentration of the charge carrier should increase with the increase of the ion content of the ionomer. However, the increase in the compatibility between the ionomer and the plasticizer seems to mainly contribute to the initial increase of the ion conductivity, because the contribution of the lithium cation in the ionomer to the charge carrier concentration is quite small compared to that of the added salt. The relative amount of the charge carrier increment with the increase of the ion content of the ionomer from 3 to 8.5 mol% to the charge carrier concentration from the incorporated LiClO_4 is ca. 0.22, which is too small to be a significant factor for the 10-fold increase of the ionic conductivity.

With the increase of the ion content of the ionomer above 8.5 mol% in the ionomer, the ion conductivity is shown to decrease. We expect that this decrease of the ion conductivity at higher ion content of the ionomer is associated with the formation of the ion aggregates within the polymer

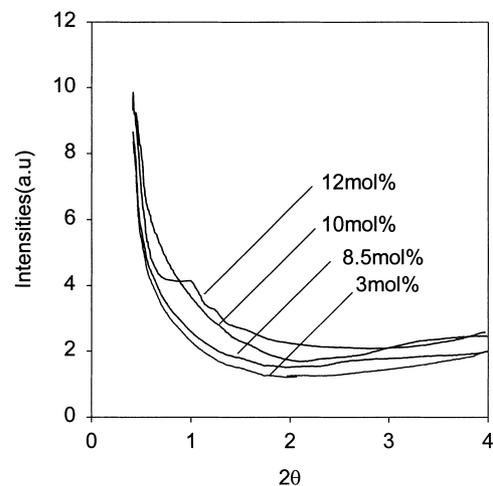


Fig. 3. X-ray scattering profiles for the plasticized polymer electrolytes based on the Li maleate ionomer.

electrolytes. Fig. 3 shows X-ray scattering profile for the polymer electrolytes based on the ionomer with different ion content. The peak corresponding to the formation of ion aggregates is clearly observed near the scattering angle $2\theta = 0.90^\circ$ (scattering vector $q = 0.032 \text{ \AA}^{-1}$) for the plasticized polymer electrolytes containing the ionomer with the ion content greater than 10 mol%. The ion aggregates in the Li maleate based plasticized polymer electrolytes will cause a decrease in the ion conductivity.

3.3. Interfacial resistance

Fig. 4 shows the initial and steady state interfacial resistances between the Li maleate ionomer based electrolytes and the lithium surface at room temperature. The initial interfacial resistance was measured at time $t = 0$, and the steady state interfacial resistance was determined when no

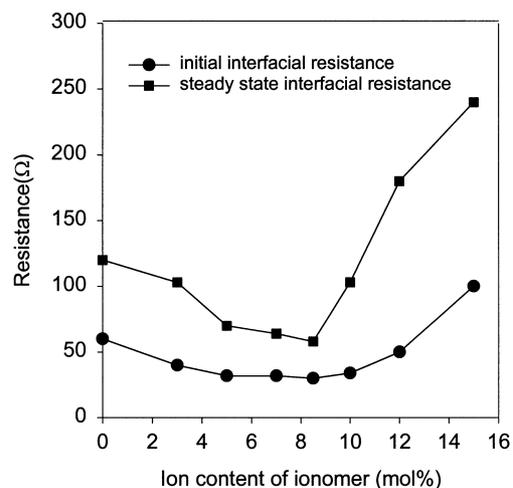


Fig. 4. The initial and steady state resistance of the interface between the lithium metal and the ionomer based plasticized polymer electrolytes with the ion content of the ionomer (cell dimension: 2 cm × 2 cm).

further increase in the interfacial resistance with time was observed. With the increase of ion content in the ionomer in the polymer electrolyte, the interfacial resistance initially decreased and reached a minimum at 8.5 mol% of the ion content in the ionomer and then increased. The initial decrease in the interfacial resistance for the polymer electrolytes based on the ionomer with lower ion content seems to be driven by the enhanced interfacial adhesion between the polymer electrolyte and the lithium metal. It is interesting to note that the interfacial resistance values of the polymer electrolytes based on the ionomer with rather low ion content are lower than those of the polymer electrolytes based on the pure poly(methyl methacrylate) (PMMA). This can be caused by the difference in compatibility of the PMMA and ionomer with EC. When the compatibility of plasticizer and polymer is poor, the polymer chains would shrink and thus a resistance for the charge transport from the polymer electrolyte to lithium metal surface may increase. When the ion content of the ionomer is high, it seems that the ionic units of the ionomer aggregate to form a physical crosslinking which can lead to the poor interfacial adhesion and thus act as an obstacle for the transport of the charge carriers at the interface.

3.4. Effect of ion content of the ionomer on the cationic yield

One of the most important parameters in designing the polymer electrolytes is a cationic yield which represents the proportion of the current which is carried by the cation. It is related to concentration polarization of anions which significantly influences cell performance under dc condition. The lithium transference number could be determined by combination of ac complex impedance and dc polarization measurement [10,11].

Fig. 5 illustrates the ac impedance response of a Li|6 mol% ionomer electrolytes|Li cell at room temperature

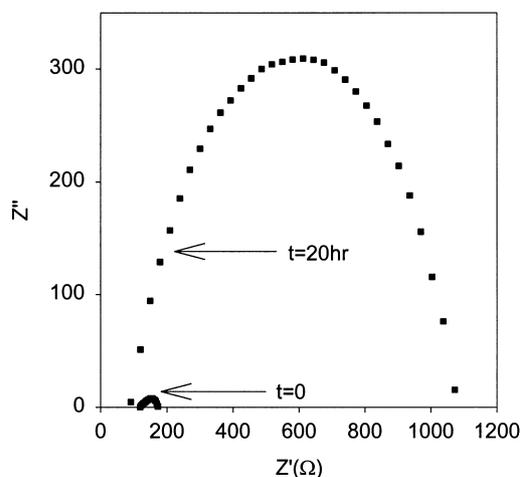


Fig. 5. The ac impedance response of Li|6 mol% ionomer based plasticized polymer electrolyte|Li cell at room temperature before and after dc polarization.

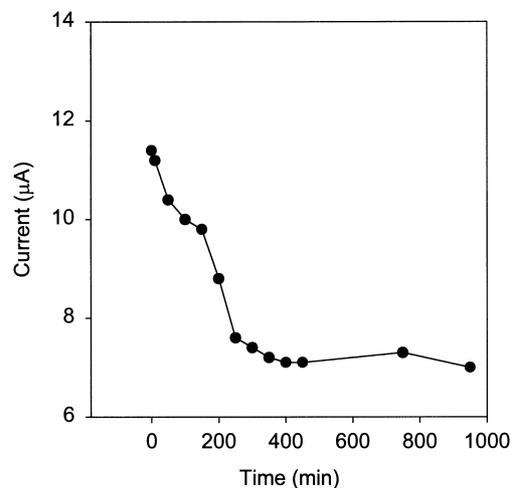


Fig. 6. The measured current during dc polarization with time for the Li|6 mol% ionomer based plasticized polymer electrolyte|Li cell (cell dimension: 2 cm × 2 cm).

before polarization ($t = 0$ h) and after a steady state current has been reached under dc polarization experiment ($t = 20$ h). It is clearly seen that the low-frequency semi-circle becomes significantly larger in 20 h. This semicircle is associated with the lithium electrode/polymer electrolyte interface, and the passivation of lithium may grow at the interfaces with time. After ac impedance measurement at $t = 0$ h, a constant dc potential of 20 mV was applied to this cell, and the current was monitored as a function of time as shown in Fig. 6. Following the treatment discussed by Evans et al. [9], the cationic transference number can be calculated as follows:

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

where ΔV is the potential applied across the cell, I_0 and I_s the initial and steady state currents, and $R_{i,0}$ and $R_{i,s}$ the initial and steady state resistances associated with lithium electrode/polymer electrolyte interface, respectively. The lithium transference numbers for the various polymer electrolytes are shown in Fig. 7. The values of the cation transference numbers are found to initially increase with the ion content of the ionomer and finally saturate to a certain value. It should be noticed that all the transference numbers obtained from the polymer electrolytes based on Li maleate ionomers are higher than those obtained from the polymer electrolyte based on PMMA. This may imply that a substantial amount of anions lose their mobility by the introduction of ionic units into the matrix polymer chain. It is expected that the anion of the salt, ClO_4^- , becomes complexed with the ionic units of the ionomer via interionic interaction between the anion of the salt and ionic units of the ionomer. The exposed cation, a counter cation of the ionomer, would hold the anion of the salts, resulting in the increase of the transference number of the polymer electrolytes. When the ion content of the ionomer is high enough

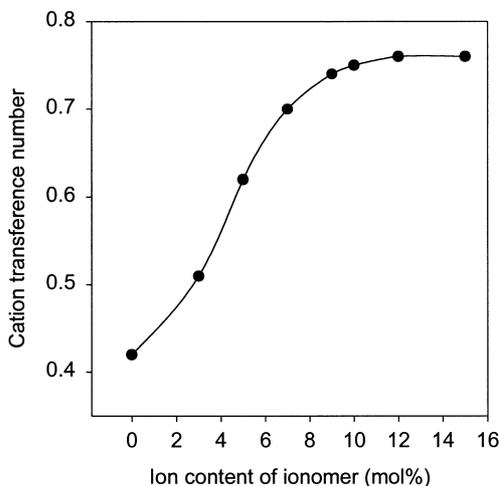


Fig. 7. The cationic transference number of the ionomer based plasticized polymer electrolytes with the ion content of the ionomer at room temperature.

for the formation of the ion aggregates in the ionomer electrolytes, the ionic unit of the ionomer is no more effective to capture the anion of the salts added.

3.5. Effect of temperature on the cationic yield

It is expected that the ionic interaction occurring in the polymer electrolytes is influenced by temperature, since the interionic interaction can be dependent upon temperature. Fig. 8 shows a plot of the lithium transference numbers of the polymer electrolytes based on the Li maleate ionomer as a function of temperature. The lithium transference number of the polymer electrolytes based on the ionomer containing the ion content less than 8.5 mol% is found to decrease with temperature, while the cationic transference numbers for the polymer electrolytes based on the ionomer with higher ion

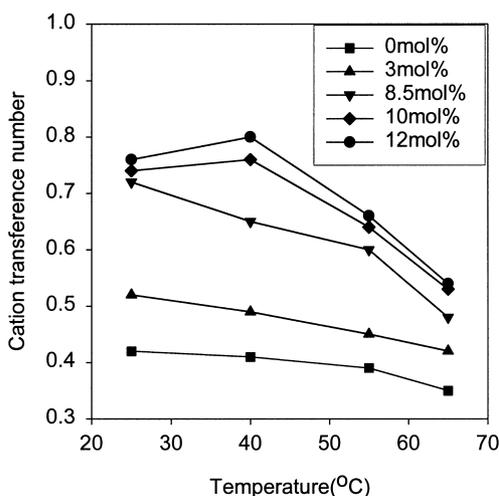


Fig. 8. The cationic transference number of the various ionomer based plasticized polymer electrolytes with temperature: (■) 0 mol%; (▲) 3 mol%; (▼) 8.5 mol%; (◆) 10 mol%; (●) 12 mol%.

content (10, 12 mol%) initially increase up to 40 °C and then decrease. The monotonous decrease in the lithium transference number for the polymer electrolytes based on the ionomer with the ion content less than 8.5 mol% might be due to the loosening of the ionic interaction between the anion of the salts and ionic sites of the ionomer with increase in temperature. The anions of the salts at lower temperatures are supposed to be bound to the ionic sites of the ionomer through the ionic interaction. Such ionic interaction becomes weaker with increase in the temperature, and the bound anions will be more mobile. The increase in the mobility as well as in the number of charge carriers of the anion will thus lead to a decrease in the cationic transference number in the polymer electrolytes.

For the polymer electrolytes based on the ionomer with 10, 12 mol%, there is a clear evidence for the presence of the ion aggregates within the polymer electrolytes. Fig. 9 typically shows the small angle X-ray scattering patterns for the polymer electrolytes based on the ionomer with the ion content of 12 mol% at various temperatures. It seems that the ion aggregates in the polymer electrolytes are loosened or disrupted at higher temperature. Due to destruction of the ion aggregates, the cationic transference numbers for the polymer electrolytes based on the ionomer with 10, 12 mol% ion contents increase initially with temperature. The ion aggregates formed in the polymer electrolytes would contain a substantial amount of ions dissociated from the added salts. The destruction of the ion aggregates makes the engaged cations and anions move, and the cation might move faster than the corresponding anion since the ionic units of the ionomer forces the anion to be captured at the ionic sites. The cationic transference number is thus found to initially increase with temperature. Further increase in temperature would weaken the binding of anion to the ionic sites of the ionomer, and bring about a decrease in the cationic transference number of the polymer electrolytes.

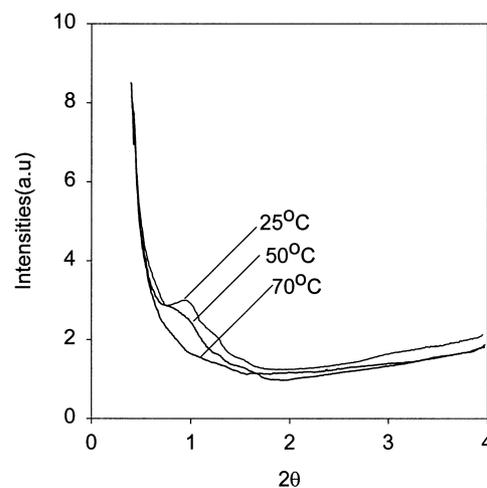


Fig. 9. X-ray scattering profiles for the plasticized polymer electrolyte based on the Li maleate ionomer with 12 mol% of ion content at different temperatures.

4. Conclusion

The new plasticized polymer electrolytes based on poly-(methyl methacrylate-co-Li maleate) were prepared. The maximum ion conductivities of these polymer electrolytes were found at 8.5 mol% of the ion content of the ionomer in the polymer electrolyte, which seems to be caused by the change in the mobility, charge carrier concentration, and degree of ion aggregation with the ion content of the ionomer. The change of interfacial resistance with the ion content of the ionomer in the polymer electrolyte, which is largely influenced by the interfacial adhesion, was shown to be similar to ion conductivities. The lithium transference number of the polymer electrolyte initially increased with the ion content of the ionomer and was eventually saturated. It was found to be significantly dependent on temperature.

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