Electrochemical Characteristics of the PAN Ionomer based Polymer Electrolytes

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1. Introduction

Special interest today is focused on polymer systems having high ionic conductivity at ambient and subambient temperatures, since they may find unique applications such as rechargeable lithium batteries, separators, and fuel cell[1,2]. Among the most promising examples are plasticized polymer electrolytes obtained by the immobilizaiton of liquid solutions of lithium salts in a polymer matrix. The transport properties of these electrolytes are quite exceptional, because they have an ionic conductivity of the order of 10^{-3} S/cm, good dimensional stability, and an electrochemical stability window exceeding 4.5V[3,4]. However, these favorable properties are somewhat contrasted by a poor compatibility towards the lithium metal electrode. The previous results have clearly demonstrated that the interfacial resistance of the PAN based polymer electrolyte with lithium electrode increases with time[5,6]. The uncontrolled interfacial stability affects the cyclability of the rechargeable lithium battery and thus, puts restriction on the application of the PAN based polymer electrolytes to the lithium polymer batteries.

These considerations motivated us to develop the plasticized polymer electrolytes based on the modified PAN with both the high ion conductivities and the interfacial stability. In this work, the polymer electrolytes composed of the poly(acrylonitrile-co-Li methacrylate)(P(AN-co-LiMA), PAN ionomer), EC, and $LiClO_4$ were prepared. The ion conductivities and the interfacial behavior of the PAN ionomer based plasticized polymer electrolytes were also investigated and compared with those of the PAN based plasticized polymer electrolytes.

2. Experimental

Preparation of the P(AN-co-MAA) and Its Ionomer

The poly(acrylonitrile-co-methacrylic acid)(P(AN-co-MAA)) copolymers were prepared by copolymerization of acrylonitrile(AN) and methacrylic acid(MAA). The P(AN-co-LiMA) ionomers were made by neutralizing the P(AN-co-MAA). For brevity, the P(AN-co-LiMA) copolymers synthesized are designated as PANx, where x indicates a mol% of LiMA unit in the copolymer.

Preparation of Polymer Electrolytes

The appropriate amount of the P(AN-co-LiMA), EC, and $LiClO_4$ were well mixed and heated until the ionomer, EC, and $LiClO_4$ were completely dissolved in the cosolvent. The viscous solutions were then placed on Teflon plates, and the cosolvent was evaporated.

Electrical Measurements

Polymer electrolyte films were sandwiched between the two stainless steel(SS) electrodes for measurement of ion conductivities. In order to investigate the interfacial phenomena at the lithium electrode/polymer electrolyte interface, polymer electrolyte films were sandwiched between the two lithium electrodes (2x2 cm^2). The ion conductivities and interfacial resistances of the polymer electrolyte films were measured by complex impedance analysis using a Solartron 1255 frequency response analyzer.

3. Results and Discussion

Ion conductivities of the PAN and PAN Ionomer based Polymer Electrolytes

The ion conductivities of the polymer electrolytes as a function of ion content in the ionomer are shown in Fig. 1. It is found that the ion conductivities of the polymer electrolytes increase, reach a maximum and then decrease as the ion content in the PAN ionomer increases. The reason for the initial increase of the ion conductivities with the ion content is related to the fact that the ion groups in the ionomer prevent EC from crystallization. In Fig. 2, the DSC thermograms for the polymer electrolytes with different ion content are represented. As seen from Fig. 2, the melting endothermic peak around 15°C which is corresponding to the melting transition of the EC crystal is observed for the polymer electrolyte based on PAN. This endothermic peak becomes weaker for the polymer electrolyte based on the PAN4 ionomer, and eventually disappears for the polymer electrolytes based on the PAN7 and PAN11 ionomers. This suppression of the EC crystallization is expected to result from the strong ion-dipole interaction between the ion groups in the ionomer and the polar groups of EC. Since the crystalline phase of EC cannot transport the charge carrier and hinder the motion of the charge carrier[7,8], the disruption of the EC crystal is expected to be a main factor for the initial increase in the ion conductivities with the increase of the ion content.

However, the increase of the ion conductivities by the disruption of the EC crystal is offset by the decrease in the mobility of the charge carrier at the higher ion content. The decrease in the mobility of the charge carrier with the increase of the ion content is attributed to the increased microscopic viscosity of the EC phase owing to the ion-dipole interaction between the polymer matrix(ion groups in the ionomer) and the plasticizer(the polar groups in the EC). This presumption is supported by our DSC results on the glass transition temperatures of the polymer electrolytes. In Fig. 2, the glass transition temperature is found to increase as the ion content in the PAN ionomer increases, indicating that the mobility of the charge carrier decreases as the ion content in the PAN ionomer increases.

Interfacial Characteristics of the PAN and PAN Ionomer based Polymer Electrolytes

The lithium/plasticized polymer electrolyte interfacial resistance and its stability over time were investigated by impedance spectroscopy. The PAN7 based polymer electrolyte was typically chosen for observing the interfacial characteristics of the PAN ionomer based polymer electrolytes. A plot of the interfacial resistance(R_i) for the PAN and PAN7 based polymer electrolytes against lithium electrodes is shown in Fig. 3. The PAN based polymer electrolyte did not attain a stable interface with lithium as indicated by the continuous increase in R_i with time. However, the PAN7 based polymer electrolyte exhibited a stable interface with R_i of about 70Ω, indicating that the ion groups in the PAN ionomer have made a significant influence on the interfacial response. This different interfacial response between the two polymer electrolytes based on the different polymer matrices is expected to result from the leakage behavior of the plasticizer.

The leakage behavior of the plasticizer from the polymer electrolyte with time can be well shown by the optical microscopy. Fig. 4 shows the surface of the polymer electrolyte films based on the PAN and PAN7 ionomer after 3 days of storage time. For the PAN based polymer electrolyte the drops which result from the leakage of plasticizer are observed on the surface of the polymer electrolyte film while any drops are not observed for the PAN7 based polymer electrolyte. The plasticizer excluded from the polymer matrix might be the origin of the continuous growth of the passivation layer through the reaction with the lithium. The leaked plasticizer from the PAN based polymer electrolyte will diffuse toward the lithium surface, react there with lithium metal to form the passivation layer and thus, the interfacial resistance continuously increases with time. The amount of the plasticizer leaked from the PAN7 based polymer electrolyte would be much smaller than that from the PAN based polymer electrolyte, and thus the formed passivation layer is expected to be thinner. As mentioned above, the interaction between the polymer matrix and the plasticizer in the PAN7 based polymer electrolyte contributes to the reduction in the amount of the leaked plasticizer from the polymer electrolyte with time.

The other reason for the different behavior of the interfacial resistance between the two types of polymer electrolytes might be associated with the change of contact area between the polymer electrolyte and lithium electrode with time. The change of contact area with time could also be generated from the plasticizer leakage. In the PAN based polymer electrolyte, the larger leakage of the plasticizer from the polymer electrolyte may cause the increase in the stiffness of the polymer electrolyte, especially the polymer electrolyte surface that is in contact with the lithium electrode. Since the contact between the polymer electrolyte and the lithium electrode is poorer as the polymer electrolyte becomes stiffer, it results in the reduction in the contact area accompanied by the void formation at the interface between the polymer electrolyte and the lithium electrode. A detailed study on the change of contact area with time is now in progress.

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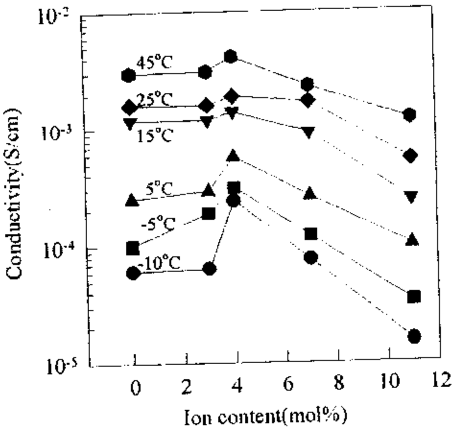


Fig. 1. The ion conductivities of the polymer electrolytes as a function of ion content

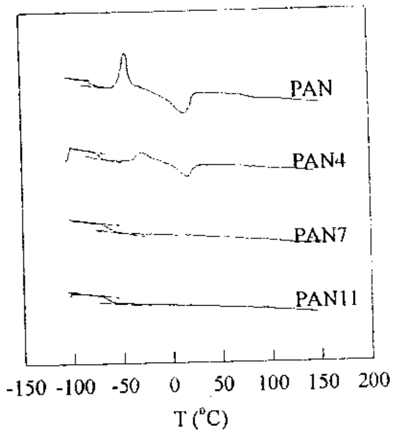


Fig. 2. DSC thermograms of the polymer electrolytes as a function of ion content

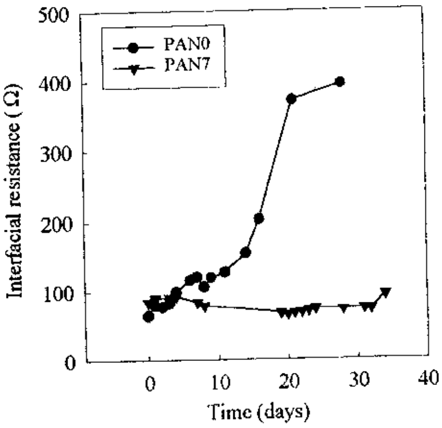
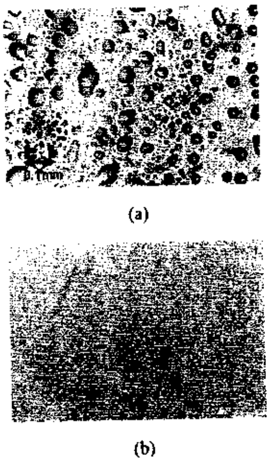


Fig. 3. Time evolution of the interfacial resistance of the PAN and PAN7 based polymer electrolytes at 25°C


(a)

(b)

Fig. 4. Optical microscopy of the surface of (a) PAN and (b) PAN7 based polymer electrolytes after 3 days of storage time