Electrical properties of the plasticized polymer electrolytes based on acrylonitrile-methyl methacrylate copolymers

Dong-Won Kim[a,*], Young-Roak Kim[a], Jung-Ki Park[b], Seong-In Moon[c]

[a]*Polymer Materials Laboratory, Samsung Advanced Institute of Technology, 103-12, Moonji-Dong, Yusung-Gu, Daejon, 305-380, South Korea*
[b]*Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1, Kusung-Dong, Yusung-Gu, Daejon, 305-701, South Korea*
[c]*Battery Technology Team, Korea Electrotechnology, Research Institute, Changwon, 641-600, South Korea*

Abstract

The plasticized polymer electrolytes composed of acrylonitrile (AN)-methyl methacrylate (MMA) copolymer and liquid electrolyte solution have been prepared. The electrochemical characteristics of these polymer electrolytes were investigated in terms of copolymer composition and content of liquid electrolyte. The relative molar ratio of AN-MMA in the copolymer proved to play a critical role in determining the ionic conductivity and capacity to retain electrolyte solution. The ionic conductivities of these systems reached an order of 10^{-3} S/cm in the presence of 80 wt.% of liquid electrolyte solution at room temperature, giving homogeneous films which exhibited good mechanical properties. The encapsulation of liquid electrolyte in the matrix polymer was found to diminish the passivation of lithium electrodes. The polymer electrolytes studied in this work displayed a sufficient electrochemical stability to allow safe operation in rechargeable lithium polymer batteries.

1. Introduction

A large number of studies to date have been carried out on the solid-state batteries utilizing the gel polymer electrolytes in which the liquid electrolyte solution has been immobilized by incorporation into a matrix polymer, such as poly(acrylonitrile) (PAN) [1–3], poly(vinylidene fluoride) (PVdF) [4,5] and poly(vinyl chloride)(PVC) [6,7]. These plasticized polymer electrolytes combine the best features of both liquid and solid electrolytes. Among them, the PAN based polymer electrolytes plasticized by liquid electrolyte solution showed the relatively high ionic conductivity of 10^{-3} S/cm at room temperature. However these systems require a processing at elevated temperature at which PAN becomes soluble. And the poor compatibility towards lithium electrode and the solvent exudation which might lead to cell leakage still remain a crucial problem for their successful application in the rechargeable lithium batteries [2,8]. One of the prospective ways of

*Corresponding author. Tel.: + 82 42 865 4074; fax: + 82 42 865 4075; e-mail: dwkim@saitgw.sait.samsung.co.kr

solving these problems is an employment of statistical copolymer as a matrix polymer. This approach allows to optimize the physico-chemical properties such as ionic conductivity, mechanical properties, compatibility with plasticizing electrolyte solution, and stability towards lithium electrode.

In this paper, we report the synthesis and some of the electrical properties of plasticized polymer electrolytes composed of acrylonitrile-methyl methacrylate copolymer as a matrix polymer and plasticizing liquid solution.

2. Experimental

2.1. Polymer synthesis

High purity acrylonitrile (AN) and methyl methacrylate (MMA) were purchased from Aldrich and used without further purification. Poly(acrylonitrile-co-methyl methacrylate)(P(AN-co-MMA)) copolymer was synthesized via the emulsion polymerization with distilled water at 60°C in a glass reactor equipped with a nitrogen inlet, a reflux condenser, an additional funnel and a mechanical stirrer. The molar ratio of co-monomers in the reaction feed was varied as given in Table 1, with a total monomer concentration of 1 mol/l. Potassium persulfate ($K_2S_2O_8$) was used as a free-radical water-soluble initiator, and sodium lauryl sulfate was used as a emulsifier. The copolymerization was continued for 5 h with vigorous agitation. The polymer was isolated by filtration

and washed successively with distilled water at 80°C to remove any impurities such as residual monomer and initiator. The product was then dried in a vacuum oven at 80°C for 24 h. The white powder was obtained as a product.

2.2. Characterization

^{1}H NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 solvent on a Bruker-DRX-400 NMR spectrometer with tetramethylsilane (TMS) as an internal standard. DSC thermal analysis was carried out to measure the thermal properties with a heating rate of 10°C/min from -100 to 100°C. Samples were loaded in crimped aluminum pans and measurements were always taken under the dry helium atmosphere during thermal scans. The recorded T_g was taken as the inflection point.

2.3. Preparation of polymer electrolytes

Attempts were initially made to cast the copolymer as film from easily managed solvents such as acetone, chloroform, tetrahydrofuran and acetonitrile at reasonable ambient conditions. Among a variety of organic solvents, THF was selected as the co-solvent on the basis of its efficacy for dissolution of copolymer and excellent film formability. The P(AN-co-MMA) copolymer was first dissolved in anhydrous THF. After the polymer has completely dissolved, a predetermined amount of liquid electrolyte solution, 1 M $LiClO_4$ in EC/PC (1:1 by volume, Mitsubishi Chemical, battery grade) was added and the solution was further stirred. The added amount of electrolyte solution was changed from 20 to 80 wt.% based on the total weight of the polymer electrolyte composed of matrix polymer and liquid electrolyte. When the complete homogenization of mixture had occurred, the resulting viscous solution was cast with a doctor blade apparatus onto a release paper, then left to evaporate the solvent slowly at room temperature. After evaporation of THF, the film was separated from a release paper. The resulting films were transparent, and the thickness of cast films was in the range 60–200 μm. The polymer electrolyte was confirmed to be free of co-solvent by means of ^{1}H NMR.

Table 1
Molar composition and glass transition temperatures of PMMA, P(AN-co-MMA) copolymers and PAN

Polymer	Composition of AN (mol.%)		T_g (°C)
	In feed	In copolymer	
AN0[a]	0	0	127.0
AN26	25	26.0	109.4
AN47	50	46.8	101.4
AN56	75	56.4	97.5
AN100[b]	100	100	96.4

[a] Pure PMMA.
[b] Pure PAN.

2.4. Electrical measurements

Polymer electrolyte film was cut into 4 cm^2 squares and sandwiched between the two stainless-steel (SS) electrodes. In order to investigate the interfacial phenomena at the lithium electrode–polymer electrolyte interface, this sample was also sandwiched between the two lithium electrodes (Cyprus Foote Mineral, 50 μm thick). The sandwich was vacuum-packed in an aluminized polyethylene bag in order to avoid contamination. The a.c. impedance measurement was then performed using a Zahner Elektrik IM6 impedance analyzer over a frequency range of 0.1 Hz–1 MHz with an amplitude of 10 mV. Each sample was allowed to equilibrate for 1 h at any temperature before measurement. The cyclic voltammetry experiment was carried out on a stainless-steel working electrode with lithium electrodes as the counter and reference electrode in the potential range of −1.0 to 4.5 V vs. Li at a scanning rate of 5 mV/s.

3. Results and discussion

The composition of the copolymer was determined by ^{1}H NMR spectrum, an example of which is shown in Fig. 1. In the ^{1}H NMR spectrum of P(AN-co-MMA) copolymer, the methoxy proton of
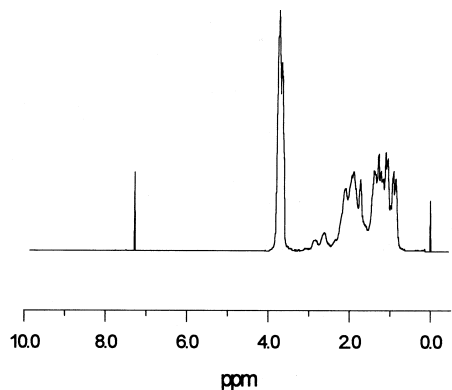

Fig. 1. ^{1}H NMR spectrum of P(AN-co-MMA) copolymer in CDCl$_3$ at 25°C.

MMA unit separately appears at $\delta = 3.73$ ppm, whereas peaks of the methylene and methyl protons in MMA observed at higher field are overlapped with peaks of the methylene and methine protons in AN. The relative intensities of the methylene and methyl protons in MMA could be calculated by multiplying the intensity of the methoxy protons by 5/3. The intensities of the methylene and methine protons in AN are determined by subtracting the calculated intensities of the methylene and methyl protons in MMA from the total intensities of peaks superimposed at $\delta = 0.61$–3.20 ppm. The mole fraction of each co-monomer unit can thus be estimated by the total intensity of the corresponding monomer unit. The mole fraction of AN in the P(AN-co-MMA) copolymer was determined to be 0.47 from the ^{1}H NMR spectrum shown in Fig. 1. The compositions of the copolymers synthesized are listed in Table 1. For brevity, the P(AN-co-MMA) copolymers synthesized are designated as ANx, where x indicates a mole% of AN unit in the copolymer. The copolymer with a higher AN content could not be synthesized, which is caused by the comparatively poor reactivity of AN for copolymerization. The DSC results of PMMA, P(AN-co-MMA) and PAN are also given in Table 1. The T_g value of PMMA is 127.0°C, while that of PAN is 96.4°C. Only one glass transition for each P(AN-co-MMA) is observed in the temperature range of 96.4 to 127.0°C, and the T_g value is found to be decreased with AN content in the copolymer, which is a typical behavior of glass transition observed in the random copolymer [9,10].

Fig. 2 shows the a.c. impedance spectra of the SS–SPE–SS (SPE:solid polymer electrolyte) cells as a change of content of liquid electrolyte at 25°C. The matrix polymer used for preparing the polymer electrolyte is AN47. The intercept on the real axis gives the electrolyte resistance (R_e). The electrolyte resistance decreases with the amount of electrolyte solution in the polymer electrolyte. The improved ionic conductivity is due to the enhancement of the ionic mobility and number of carrier ions, as the many previous workers have already reported [11]. It is noted that the semicircle observed at high frequency gradually fades away as the content of liquid electrolyte increases, and completely disappears in the polymer electrolytes with electrolyte solution
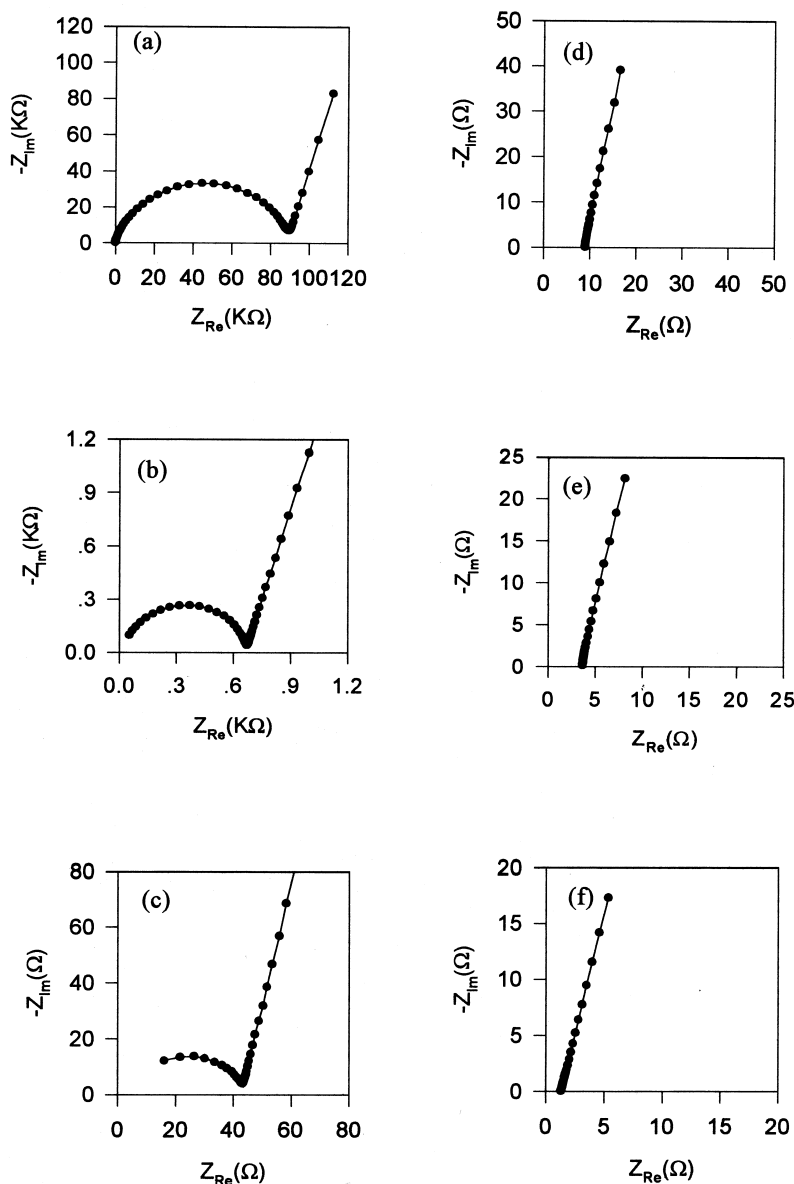
Fig. 2. A.C. impedance spectra of the SS–SPE–SS cells with the liquid electrolyte content at 25°C: (a) 30 wt.%, (b) 40 wt.%, (c) 50 wt.%, (d) 60 wt.%, (e) 70 wt.%, and (f) 80 wt.%.

higher than 60 wt.%. This result suggests that only the resistive component of polymer electrolyte can be considered, when the amount of plasticizing electrolyte solution is high. The polymer electrolytes with lower solvent content can be considered as one homogeneous phase of the polymer plasticized by aprotic solvent. In this case, the migration of ions may occur through the free volume of matrix polymer, which can be represented by a resistor. The immobile polymer chains become polarized in the alternating field, which can be represented by a capacitor. The ionic migration and bulk polarization are physically in parallel, and, therefore, the semicircle at high frequency can be observed. As the

amount of liquid electrolyte increases, it is possible to construct a local effective pathway in liquid phase for ionic conduction. As a result, ions can transport quickly in the liquid phase as the electric potential alternates between positive electrode and negative electrode in an a.c. field. Therefore no capacitance effect was occurred in the polymer electrolytes with higher content of electrolyte solution.

Fig. 3 shows the change of ionic conductivity with content of liquid electrolyte, which is determined from the a.c. impedance spectra in Fig. 2. It should be noted that the plot can be divided into two straight lines with different slopes above and below the inflection point located at 50–60 wt.% electrolyte solution. This result may be related to the conducting pathway in the polymer electrolytes, as explained above. When the amount of electrolyte solution exceeds about 55%, the added electrolyte solution can form a local solvent channel for ionic conduction, which is major medium governing the ionic conductivity. From these results, it can be said that local path of liquid electrolyte can be constructed in these polymer electrolytes with liquid electrolyte solution higher than 55 wt.%. However an addition of electrolyte solution beyond 80 wt.% caused the poor mechanical strength. The poor mechanical property prevented the preparation of dimensionally stable films necessary for practical use. Therefore,
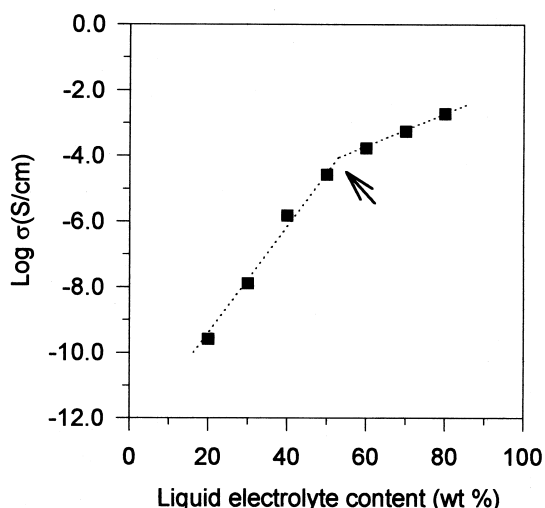
the amount of electrolyte solution is maintained below 80 wt.% to ensure the acceptable mechanical properties.

Fig. 4 represents the variation of T_g for polymer electrolytes prepared with AN47, as a function of content of liquid electrolyte. There is a decrease in value of T_g with increasing the content of liquid electrolyte up to 50 wt.%, since the matrix polymer is plasticized by aprotic solvent. An addition of more liquid electrolyte is found to be a little effect for decreasing the glass transition temperature of polymer electrolytes. This result may be due to the fact that the electrolyte solution added is contributed to the formation of effective local pathway for ionic conduction, instead of plasticizing the matrix polymer.

Fig. 5 shows the conductivity variation of the polymer electrolytes containing liquid electrolyte solution higher than 60 wt.%, as a function of the AN content in the copolymer at 25°C. The mechanical state of polymer electrolytes was found to be dependent on both the content of liquid electrolyte and the copolymer composition in P(AN-co-MMA) copolymer. With decreasing the AN content in the copolymer, the addition of electrolyte solution rendered the polymer electrolyte to be more flexible. The polymer electrolytes prepared with AN0 containing liquid solution higher than 70 wt.% and AN

Fig. 3. Ionic conductivities of AN47-based polymer electrolytes as a function of liquid electrolyte content.
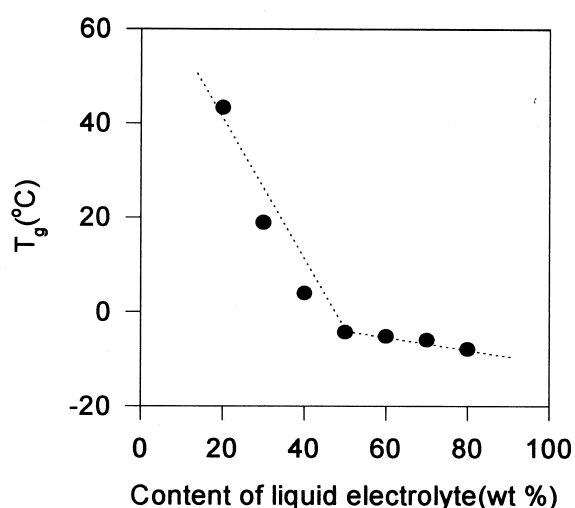
Fig. 4. Glass transition temperatures for the AN47-based polymer electrolytes as a function of liquid electrolyte content.
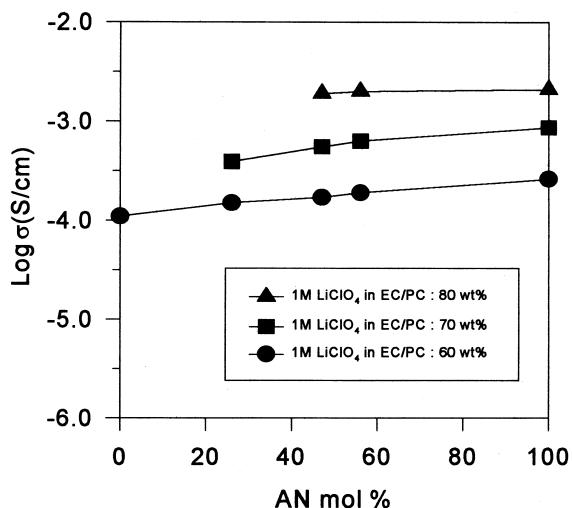
Fig. 5. Ionic conductivities of P(AN-co-MMA) copolymer-based electrolytes as a function of AN content at room temperature.

26 containing solution of 80 wt.% were very sticky, and, therefore, the ionic conductivities of these systems could not be measured. From the figure, it is found that the ionic conductivity increases as the AN content increases. The difference in ionic conductivity may be caused by degree of interaction between matrix polymer and aprotic solvent. Since the MMA unit has a carbonyl group (-COO-) in the side chain, it can be presumed that the MMA unit is more compatible with the carbonate-based electrolyte as compared to AN unit. The above speculation is confirmed by measuring the evaporation rate of aprotic solvent under open-atmosphere condition. With increasing the AN content in the copolymer, the weight loss of plasticizing solvent is found to be increased. This result suggests that there is a strong specific interaction between MMA unit and aprotic solvent, which makes the plasticizer difficult to phase-separate from a matrix polymer. The polymer electrolytes with lower AN content are thus a homogeneous mixture of the polymer and liquid electrolyte. As a result, the conduction pathway is mainly a free volume of matrix polymer, which results in a delayed motion of ions. On the contrary, the polymer electrolytes prepared with the copolymer having higher AN content are composed of two phases. One is the liquid electrolyte rich phase, and the other is the gel polymer phase plasticized by

aprotic solvent. The second phase is similar to the homogeneous state of polymer electrolytes prepared with copolymer having lower AN content. Since the ionic motion is faster in the liquid electrolyte rich phase, the ionic conductivity is increased with AN content, as shown in Fig. 5. However, it should be noted that the capacity to retain electrolyte solution is decreased with AN content in the copolymer, because the plasticizing solvent is thought to be present almost exclusively in the MMA unit. Therefore, it is expected that the relative ratio of the two phases, which is controlled by the AN-MMA molar ratio, plays a critical role in determining the ionic conductivity and the capacity to retain electrolyte solution. The copolymer comprising about 47–56% by mole AN is thought be desirable; this ensures high ionic conductivity and enables the retention of the liquid electrolyte. With a 60–80 wt.% liquid electrolyte solution, the polymer electrolytes exhibited an ionic conductivity between 10^{-4} and 10^{-3} S/cm, as shown in Fig. 5.

Fig. 6 shows the Arrhenius plot of ionic conductivities for the polymer electrolytes containing 80 wt.% liquid electrolyte. For the AN47-based polymer electrolyte, the ionic conductivity reaches an order of 4.2×10^{-3} S/cm at 55°C, and the conductivity
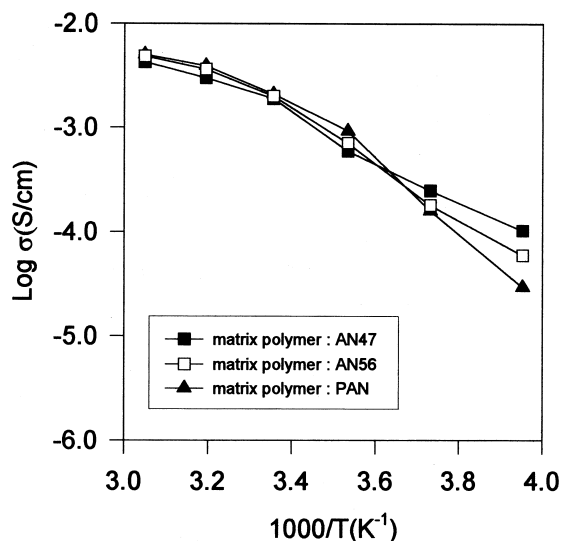

Fig. 6. Temperature dependence of ionic conductivity for the P(AN-co-MMA) copolymer-based electrolytes containing 80 wt.% of liquid electrolyte.

remains at quite a high value $(1.0 \times 10^{-4}$ S/cm), even at $-20°C$. The ionic conductivities at low temperatures were found to decrease with AN content. It is well known that an abrupt decrease in ionic conductivity observed at low temperatures in the plasticized polymer electrolyte is related to the crystallization of plasticizing solvent [3]. Since the relative fraction of liquid phase which does not interact with a matrix polymer increases with AN content, the crystallization of the plasticizing solvent would be easier with a higher AN content. It could lead to a decrease of ionic conductivity to a larger extent at low temperatures.

High conductivity is not sufficient to make an electrolyte useful in practical terms. The compatibility of an electrolyte with the lithium electrode is also an essential parameter to guarantee the acceptable performance in rechargeable lithium batteries, and, therefore, we tried to investigate the interfacial behavior of the lithium electrode in contact with the polymer electrolyte under a prolonged timescale. Fig. 7 shows the time evolution of the a.c. complex impedance response of a Li–polymer electrolyte–Li cell under open-circuit potential conditions at 25°C. From these impedance spectra, it is possible to represent the time evolution of electrolyte resistance (R_e) and interfacial resistance (R_i), as shown in Fig. 8. It is found that the resistance of the polymer

Fig. 8. Variation of R_e and R_i with storage time in the Li–SPE–Li cell at 25°C, where SPE consists of AN47 (20 wt.%) and 1 M LiClO$_4$ in EC/PC (80 wt.%).

electrolyte maintains a constant value, irrespective of time. This result suggests that the encapsulated liquid electrolyte in the polymer matrix was not lost due to the good compatibility between the P(AN-co-MMA) copolymer and the aprotic solvent such as EC and PC in the closed Li–SPE–Li cell. The interfacial resistance increased initially, and eventually stabilized at a constant value of about 50 Ω. An initial increase can be attributed to the formation of a passive layer due to the reactivity of the lithium electrode and the polymer electrolyte. Given the intrinsic stability of the polymer backbone, one might speculate that lithium electrode reacts with carbonate-based electrolytes. Aprotic solvents such as EC and PC have been well known to form a passivating layer on the lithium metal [12–14]. In contrast, the final steady-state value of R_i indicates no further growth of the passive film. Similar results have also been observed in the blended polymer electrolytes by us [15]. For comparative purpose, we tried to measure the interfacial resistance of lithium electrode in contact with the polymer electrolyte composed of PAN and 1 M LiClO$_4$–EC/PC. Fig. 9 shows the results obtained with PAN-based polymer electrolytes containing 80 wt.% liquid electrolyte. In the PAN-based cell, the passivation occurs with a continuous growth, which was not observed in the
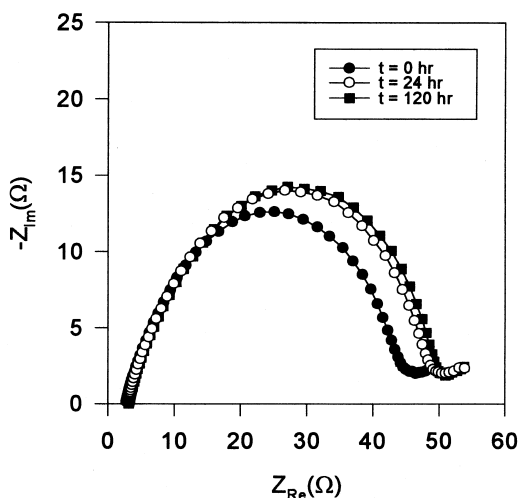

Fig. 7. A.C. impedance spectra of a Li–SPE–Li cell as a function of storage time at 25°C, where SPE consists of AN47 (20 wt.%) and 1 M LiClO$_4$ in EC/PC (80 wt.%).
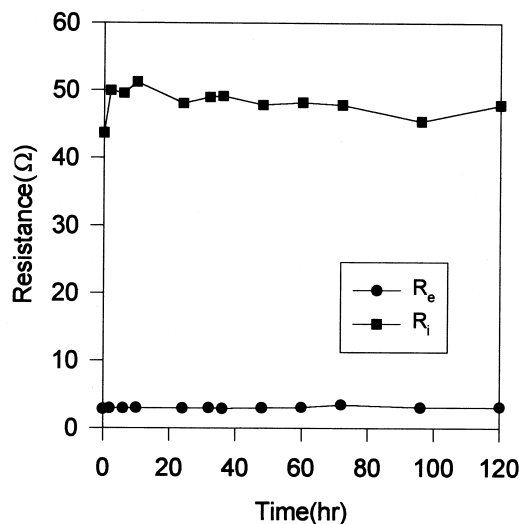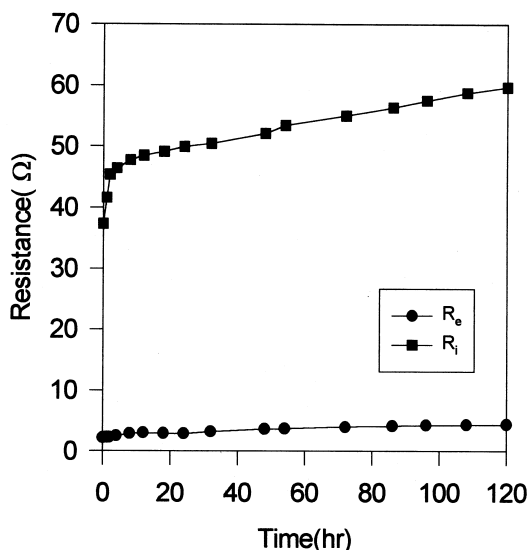
Fig. 9. Variation of R_e and R_i with storage time in the Li–SPE–Li cell at 25°C, where SPE consists of PAN (20 wt.%) and 1 M LiClO$_4$ in EC/PC (80 wt.%).

Fig. 10. Cyclic voltammogram of the Li–SPE–SS cell at 25°C (scan rate: 5 mV/s), where SPE consists of AN47 (20 wt.%) and 1 M LiClO$_4$ in EC/PC (80 wt.%).

P(AN-co-MMA)-based cell. The variation of R_i value may be related to the exudation of liquid electrolyte. The carbonate-based aprotic solvents such as EC and PC exude from the matrix polymer and diffuse toward the lithium surface, and react there with the lithium metal. A change of R_e with time is also shown in Fig. 9. It is seen that the electrolyte resistance continuously increases as the passivation occurs. This result suggests that there is a progressive loss of aprotic solvent due to the reaction of the solvent with the lithium electrode. From these results, it can be said that the encapsulation of liquid electrolyte in the matrix polymer could, at least in part, diminish the passivation of the lithium electrode.

The cyclic voltammogram for the Li–polymer electrolyte–SS cell at room temperature is given in Fig. 10. On sweeping the electrode cathodically, the cathodic peak is observed at around − 0.52 V, which corresponds to the plating of lithium onto the stainless-steel electrode. On the reverse scan, stripping of lithium is observed at around 0.39 V. The voltammograms ascribed to the lithium deposition/dissolution are highly reversible, since the integrated charges in the cathodic and anodic processes are equal. The peak current tends to decrease with
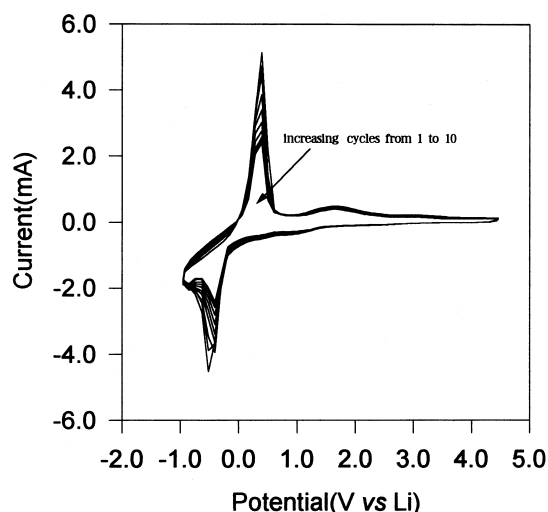
cycling and stabilizes after a few cycles. This phenomenon may result from the formation of a passivating layer on the stainless-steel electrode. On further sweeping the electrode to 4.5 V, there are no more oxidation peaks related to the decomposition of polymer electrolyte. Thus, our polymer electrolytes could have sufficient electrochemical stability to allow safe operation in the rechargeable lithium battery. More detailed studies on the electrical performances of the Li–polymer electrolyte–LiMn$_2$O$_4$ solid-state cell employing these polymer electrolyte systems are in progress and will be reported in the near future.

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