

Dual-Phase Polymer Electrolytes Based on Blending Poly(MMA-g-NBR) and PMMA

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ABSTRACT: A new type dual-phase polymer electrolyte (DPE) based on poly(MMA-g-NBR) and poly(methyl methacrylate) (PMMA) was prepared by film-casting method. In the DPE, PMMA phase is selectively impregnated with the lithium salt solution, forming an ion-conducting network, while poly(MMA-g-NBR) phase maintains mechanical strength in the system. With grafting effect, the compatibility of two phases (PMMA/poly(MMA-g-NBR)) can be enhanced obviously. The chemical and physical characteristics, morphology and ionic conductivity behavior of DPEs,

and their interfacial stability between lithium metal electrode were characterized by using of FTIR, ¹HMR, DSC, SEM, optical microscopic images, AC impedance, and linear sweep voltammetry. A new type DPE with good mechanics and high electrochemistry properties is obtained at an optimum proportion of two blending polymers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3084–3090, 2007

Key words: thin films; blends; electrochemistry; compatibility

INTRODUCTION

There are considerable interests in polymer electrolyte because of the potentially wide range of application in variant area such as lithium-ion polymer battery, electrochromic devices, and sensors.^{1–3} Among them, gel-polymer electrolyte (GPE) is thought as the most possible candidate to be used in practice. This category of GPE is characterized by a higher ambient ionic conductivity but poorer mechanical property, and it is usually obtained by incorporating a larger quantity of liquid plasticizer and/or solvent(s) to a polymer matrix that is capable of forming a stable gel.⁴ To date, several types of GPEs have been developed and characterized, such as those based on poly(ethylene oxide) (PEO),⁵ poly(acrylonitrile) (PAN),^{6,7} poly(methyl methacrylate) (PMMA),^{8,9} poly(vinyl chloride) (PVC),¹⁰ and poly(vinylidene fluoride) (PVdF).^{11,12} The use of PMMA as a GPE was previously reported by Iijima et al.⁸ and Bohnke et al.⁹ The GPE exhibit homogeneous and transparent, and the conductivity reached the order of 10^{-3} S cm⁻¹. In this GPE, the organic solvent plays the role of the ion-supporting carrier and plasticizer of polymer matrix. However, the

plasticized polymer electrolytes suffer from poor, gel-like mechanical property; producing freestanding film is not possible at higher plasticizer concentration. Hence, an improvement in the mechanical property is required for the successful application as a GPE.

In 1990s, Ichino et al. proposed a concept: dual-phase polymer electrolyte (DPE),^{13–16} in which a comparatively highly polar polymer (nitrile butadiene rubber (NBR)) is impregnated with a lithium salt solution and formed continuous ion-conductive channels, while a lowly polar polymer (styrene-butadiene rubber (SBR)) produced good mechanical strength. GPE with rubber has low glass transition temperature (T_g), soft elastomer characteristics at room temperature, and good elasticity. However, the polarity difference of the blending polymers would then bring out compatibility problem. The interface between two polymers is frangible, and the prepared thin films are mechanically too weak to be used in practice.

In this article, we tried to prepare a new type DPE with enhanced phase compatibility. First, PMMA was grafted onto NBR chains, and then the DPE films based on PMMA/poly(MMA-g-NBR) were impregnated with a lithium salt solution to activate. The grafted PMMA is thought to act as a compatibilizer between the NBR and PMMA phases. With this effect, the comparatively lowly polar

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polymer NBR can be blended well with the highly polar polymer PMMA. The prepared DPE films show uniform and transparent. Their ionic conductivities are at 10^{-3} S cm^{-1} magnitude at room temperature and their electrochemistry stability window reaches 5.0 V vs. Li/Li⁺, which make them an ideal potential candidate as electrolyte for devices. We varied the two blending polymers with weight ratio of 1 : 1, 1 : 2, and 1 : 4, and studied the performance of the different DPE to find out the best weight ratio.

EXPERIMENTAL

Preparation of the DPEs

Commercially purchased PMMA ($M_n \sim 10^5$) was first dissolved in acetone and then extracted with methanol to purify. NBR (polybutadiene contents of the NBR was 60%) was first plasticated at room temperature before being used. Both PMMA and NBR were dehydrated under reduced pressure at 60°C for 48 h. Methyl methacrylate (MMA) (Sinopharm Chemical) was distilled under reduced pressure before use and THF (Sinopharm Chemical) was dehydrated using 4 Å molecular sieve.

The experiment was conducted in a batch reactor comprising three-neck, with an argon inlet, an outlet, a condenser, and a thermocouple connected to a temperature controller. Weighed amount of NBR was dissolved in THF and stirred overnight until it became homogeneous. Then, BPO dissolved MMA was added to the above and the weight of MMA was equal to NBR. The mixtures were polymerized in argon atmosphere at 75°C for 24 h. MMA monomer was assumed to react with each other or grafted onto NBR chains under heat, forming crosslinker between the adjacent NBR polymer chains. The above system was then heated above 110°C to get the unreacted monomer and the residual solvent out. To separate the PMMA homopolymer, the prepared poly(MMA-g-NBR) was then subsequently extracted with petroleum ether/acetone (1 : 1) for 6 h and dried in a vacuum oven at 60°C for about 24 h.

To prepare DPE films, weighed amount of PMMA and poly(MMA-g-NBR) were mixed in anhydrous THF and stirred overnight, and then the solution was poured into the Teflon plate. And then, THF was allowed to evaporate slowly at room temperature in a dry box full of nitrogen gas to get the blending films. After being dried under vacuum at 50°C for 48 h, the resultant films were transferred to a glove box. They were immersed in the calculated organic liquid electrolyte (DMC : DEC : EC = 1 : 1 : 1 (w/w) LiPF₆ 1 mol/L, Guotai-Huarong Chemical) to activate.

FTIR measurement

FTIR measurement was carried out on BRUKER VECTOR-22 spectrometer at room temperature. Samples for FTIR were prepared by casting films directly on KBr pellets.

¹H NMR measurement

¹H NMR measurement was conducted in Varian Mercury 300 Plus 300 MHz spectrometer (solvent : CDCl₃; internal standard: tetramethylsilane).

DSC measurement

Differential scanning calorimetry (DSC) measurement was carried out using a DSC Q100 (TA Instruments) over a temperature range of 173–423 K at a scan rate of 10 K/min. Samples were sealed in aluminum pans in a dry box. Glass transition temperature (T_g) was taken as the temperature of starting point of the baseline shift observed during the transition from glassy to rubbery state. The dry sample was first annealed at 393 K for 5 min, cooled down to 173 K, and then scanned.

SEM measurement

The cross-sectional morphology of the blending polymer film was observed by scanning electron microscopy (SEM) (SIRION, FEI) under vacuum after sputtering with gold at 10 mA for 10 min.

AC-impedance measurement

The ionic conductivity (σ) of gel films was determined by AC-impedance spectroscopy (EG and G Model 273A potentiostat). Sample films were sandwiched between two parallel stainless steel (SUS) discs (Φ : 1 cm). During the measurement, the polymer electrolyte film was mounted in a sealed coin cell to prevent from contaminating the sample. The frequency ranged from 100 KHz to 10 Hz at a perturbation voltage of 5 mV. The ionic conductivity (σ) was then calculated from the electrolyte resistance (R_b) obtained from the intercept of the Nyquist plot with the real axis, the film thickness (l), and the electrode area (A) according to the equation $\sigma = l/AR_b$.

Linear sweep voltammetry

Three electrode-laminated cells were assembled inside a glove box for linear sweep voltammetry (LSV) experiments. Stainless steel (SS) was used as working electrode and lithium metal was used both as a counter and as a reference electrode. LSV measurements were carried out using CHI660A (CH Instruments).

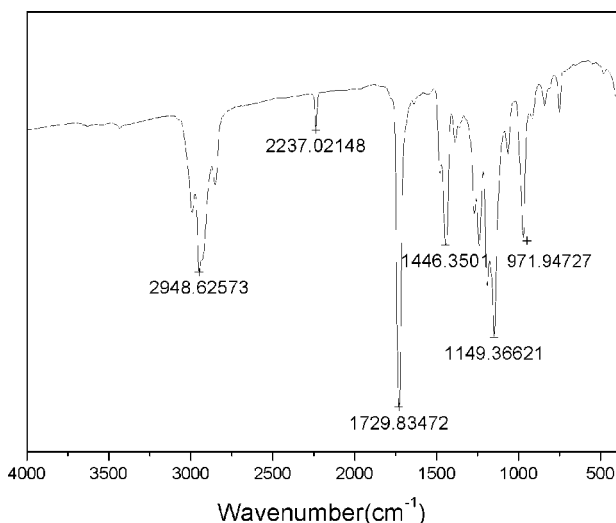


Figure 1 FTIR spectrum of polymer blend (PMMA/poly(MMA-g-NBR) = 1 : 2).

RESULTS AND DISCUSSION

FTIR and ^1H NMR spectra

Figure 1 shows the FTIR spectrum of poly(MMA-g-NBR). Characteristic absorptions (cm^{-1}) of 2948 ($\nu_{\text{C-H}}$), 2237 (ν_{CN}), 1730 ($\nu_{\text{C=O}}$), 1446 ($\delta_{\text{as,C-CN}}$), and 1149 ($\delta_{\text{as,C-O-C}}$) are observed in the IR spectrum and the disappearance of absorption peak 1630 cm^{-1} indicates no MMA monomer and C=C double bonds in the production.

The complexes interaction of Li^+ ion in different coordination sites of polymer hosts is investigated in the article, and polymer blend (PMMA/poly(MMA-g-NBR) = 1 : 2) was blent with LiClO_4 (2 mmol/g to blending polymers).

Figure 2(a,b) show the characteristic absorptions of the cyano group ($2200\text{--}2300\text{ cm}^{-1}$) and that at 1700--

1750 cm^{-1} , wavebands for carbonyl group, which are most likely to be affected by complexation with Li^+ cations. In Figure 2(a), line 2 shows a shoulder at around 2260 cm^{-1} as a result of interaction between the Li^+ cations and C≡N groups.^{17,18} This is attributed to the formation of an associate involving the pair of unbonded electron on the nitrogen atom of the C≡N groups and the Li^+ cations. In Figure 2(b), line 2 shows that the absorbance band of the carbonyl oxygen shifts to a lower frequency, and the change in the stretching region of the carbonyl oxygen may be expected because of the coordination of the Li^+ ions to the unbonded electrons of the oxygen and the existence of ClO_4^- , which may lead to the weakening of the C=O bond as Li^+ complex with ether oxygen, which has been reported in other studies.^{19–21}

The mole composition of the copolymer is investigated by ^1H NMR spectrum. The protons in the unit of $-\text{CH}-\text{CN}$ and the methoxy protons of the poly(MMA-g-NBR) unit are at around $\delta = 2.6\text{ ppm}$ and $\delta = 3.6\text{ ppm}$, respectively. The peaks of the methine, methylene, and methyl protons in NBR and PMMA units observed at a higher filed were overlapped one another. The molar composition of the PMMA to NBR units can thus be estimated from the total intensity of the corresponding monomer. According to the method described in Ref. 22, the molar proportion (M_c) of MMA and AN was deduced to be 1 : 2.96, and the graft degree (M_g) of PMMA side chain in the system was then calculated to be 25.5 wt %.

DSC thermograms

DSC measurement was used to elucidate the effect of PMMA grafting on NBR chains and the complex

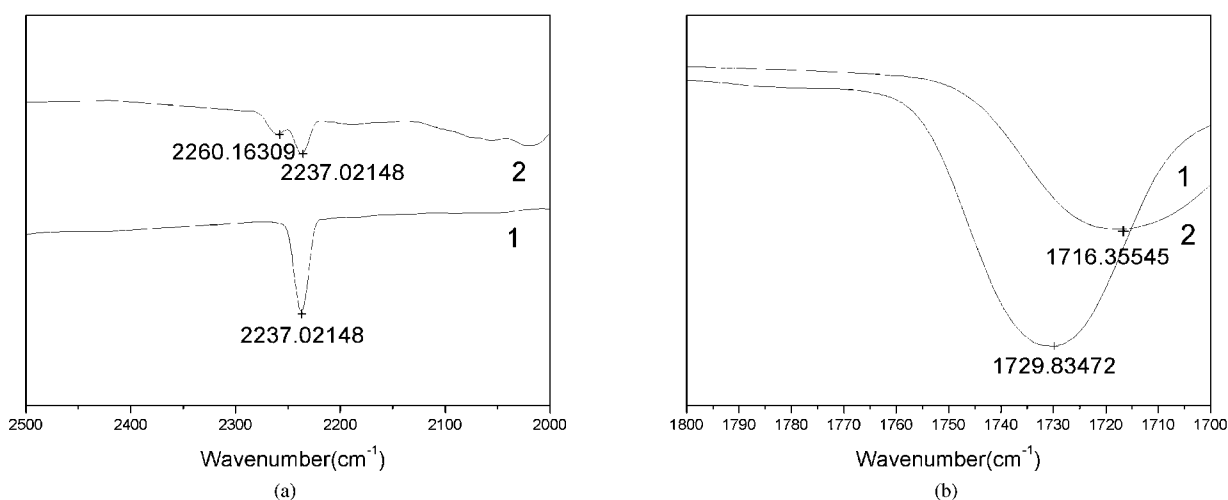


Figure 2 FTIR spectra for (a) cyano group composite with LiClO_4 and (b) carbonyl group composite with LiClO_4 .

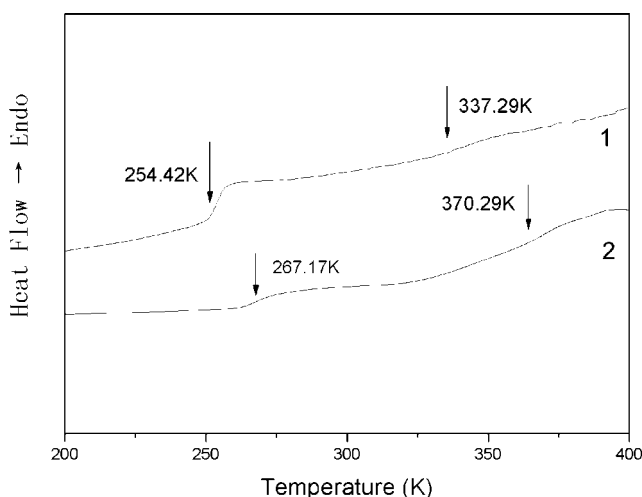


Figure 3 DSC thermograms of polymer blend (PMMA/poly(MMA-g-NBR) = 1 : 2) with and without LiClO₄.

interaction effect of LiClO₄ on the blending films on thermal behavior.

In Figure 3, line 1 corresponds to polymer blends (PMMA/poly(MMA-g-NBR) = 1 : 2) in the range of 200–400 K, it displays that there are two distinguished T_g s in the amorphous regions of polymer blends. T_{g1} (254.42 K) is substantially higher than that of pure NBR (the polybutadiene contents of the NBR was 60%) (247 K) and T_{g2} (337.29 K) is lower than that of pure PMMA (378 K). These results indicate that the blend polymers have a certain degree of NBR and PMMA segment mixing because of PMMA grafted onto NBR chains. And it is seen from line 2 that T_g for poly(MMA-g-NBR) increased to 267.17 K and T_g of PMMA increased to 370.29 K when incorporating LiClO₄ into the polymer blends. Such increase in T_g of the LiClO₄ adulterated poly-

mer blends results from the interaction of Li⁺ ions with the electron-rich coordinating sites (—NH, >C=O, —O—, —CN, etc.), which leads to the formation of transient crosslinks, thus will cause an increase in the T_g .^{22,23}

Morphology and conduction behavior

The phase interface figures were observed directly by optical microscope (Olympus BX51). Optical microscopic images of the PMMA/NBR = 1 : 1 and PMMA/poly(MMA-g-NBR) = 1 : 1 are shown in Figure 4(a,b), respectively.

Because of the different polarity of NBR and PMMA and the different composition of two polymer chains, it is seen from Figure 4(a) that the interface between two phases is obvious. This will then bring out the compatibility problem; the prepared thin films are mechanically too weak to be used in practice. While it is seen from Figure 4(b) that with PMMA grafting effect, the two polymer chains are tended to entangle with each other, and the interface between two polymer phases becomes blurry and the entire film shows transparent and homogeneous.

Figure 5 shows the SEM of the surface of polymer blends (PMMA/poly(MMA-g-NBR) = 1 : 1). It is very flat and no wrinkles with phase separation are found (the granule is thought to be the impurity). Grafting effect can enhance the compatibility of two polymer phases, and the grafted PMMA is considered as compatibilizer. So, the dual-phase polymer blends with enhanced compatibility can be prepared by film casting method.

The DPE comprises two polymers; one has a very good affinity for polar solvent to facilitate electrolyte swelling and the other has poor affinity so that structural integrity and mechanical strength can be maintained. An experiment was conducted to

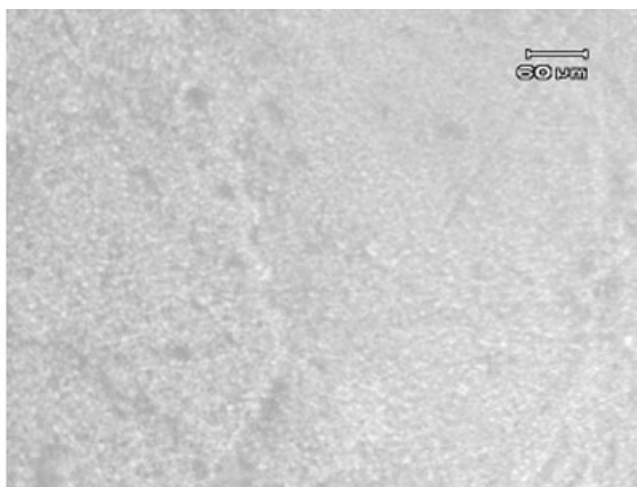
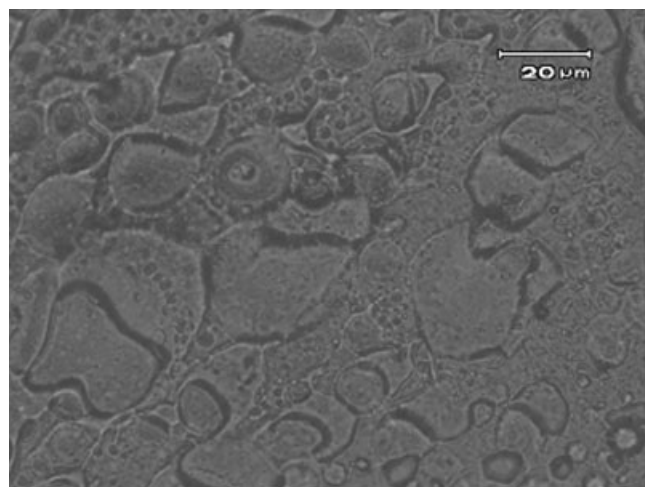


Figure 4 Optical microscopic images of (a) PMMA/NBR = 1 : 1 and (b) PMMA/poly(MMA-g-NBR) = 1 : 1.

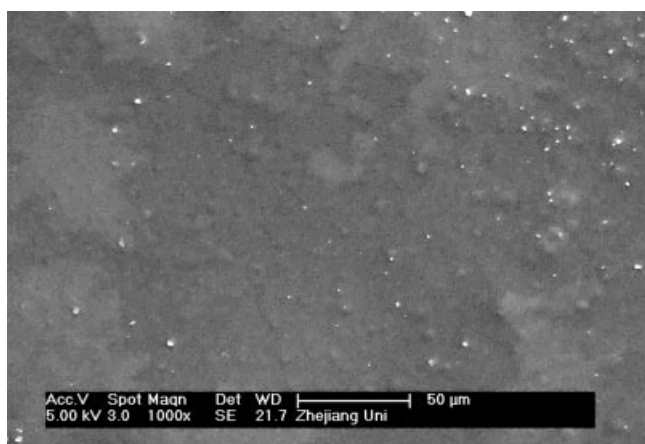


Figure 5 Scanning electron micrograph of PMMA/poly(MMA-g-NBR) = 1 : 1.

examine the swelling ability of the two blending polymers. PMMA and poly(MMA-g-NBR) were dipped into the liquid electrolyte for 30 min, respectively, and then the dry and the wet film were weighed to calculate the absorbed electrolyte. The liquid electrolyte was absorbed with the polymers rather than freely existed to form a new phase because of the strong affinity between the polymers and the salt solution. The experimental results indicated that for liquid electrolyte, the maximum solution content of PMMA and NBR were 80 and 35%, respectively, since the poly(MMA-g-NBR) less polar CN groups and the serious crosslinks also prevented the poly(MMA-g-NBR) from absorbing the solution. The highly polar PMMA and chemical construction resemblance between MMA group and the plasticizer (EC, PC) bring out a high affinity for liquid electrolytes. In summary, the affinity between the PMMA and the liquid electrolyte is stronger than the affinity between NBR. Because of the strong entanglement of macromolecule chains and particularly the self-crosslinks of poly(MMA-g-NBR) in the solid PMMA/poly(MMA-g-NBR) films, the progress of impregnating the PMMA/poly(MMA-g-NBR) in the salt solution should not destroy the original distribution of PMMA and poly(MMA-g-NBR) in the films. It is thus not surprised that the majority of the absorbed solution is mainly present in more polar PMMA

phase; poly(MMA-g-NBR) phase supports polymer matrix whereas PMMA phase forms continuous ion-conductivity channels.

Table I shows the appearance and ionic-conductivity property of the PMMA/NBR and PMMA/poly(MMA-g-NBR), respectively. The absorbed liquid electrolyte was fixed in 50 wt % (according to polymer blends) to get the best ion conductivity of DPE without demolishing their mechanics performance. The ion-conductivity mechanism of DPE with high solution content ($> \sim 40\%$ w/w) is similar to that of "free" lithium salt solution.²⁴

Because of the reasons discussed earlier, the PMMA and NBR-blending polymer films are a little brittle, and the GPEs are too soft to be handled. Only, when the ratio of two polymers is 1 : 4, the film can be a little tough and its ionic conductivity is $1.02 \times 10^{-3} \text{ S cm}^{-1}$. When PMMA is grafted onto NBR chains, the prepared polymer films present transparent and homogeneous, they all can be a free standing film after absorbing the liquid electrolyte, and the ionic conductivity reaches $1.5 \times 10^{-3} \text{ S cm}^{-1}$, which can be used in practice.

Taking DPE (PMMA/poly(MMA-g-NBR) = 1 : 1) as an example, the AC-impedance spectra of it at various temperatures are presented in Figure 6; the bulk resistance is the intercept of the straight line with Z_{re} axis.

It is seen from Figure 6 that there are no semi-circles observed at high frequency. This result suggests that only the resistive component of polymer electrolyte could be considered when the amount of plasticizing solution is high. It is possible to construct a local effective pathway in the absorbed liquid phase for ionic conduction. As a result, ions can transport quickly in the absorbed liquid phase as the electric potential alternates between positive electrode and negative electrode in an AC field. Therefore, no capacitance effect is occurred in the polymer electrolytes with higher content of plasticizing solution. In addition, it is clear that increasing temperature results in the expansion of the material, which produced the local empty space, and expends the free volume. It promoted the polymer segments and ionic carriers to move. Hence, as the temperature increased, the R_b decreases.

TABLE I
Morphology and Conduction Behavior of DPEs

Composition	Dry polymer film	Gel polymer film	Ionic conductivity (σ^*) [($10^{-3} \text{ S cm}^{-1}$)/303 K]
PMMA/NBR = 1 : 1	Brittle	Gel (hard to handle)	–
PMMA/NBR = 1 : 2	A little brittle	Gel (hard to handle)	–
PMMA/NBR = 1 : 4	A little tough	Gel (free-standing film)	1.02
PMMA/poly(MMA-g-NBR)=1 : 1	A little tough	Gel (free-standing film)	1.6
PMMA/poly(MMA-g-NBR)=1 : 2	Tough	Gel (free-standing film)	1.5
PMMA/poly(MMA-g-NBR)=1 : 4	Tough	Gel (free-standing film)	1.45

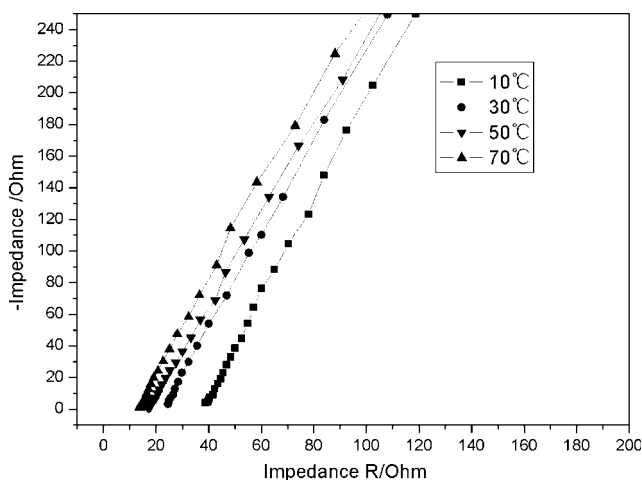


Figure 6 The AC impedance spectra of SS/DPE/SS cell with DPE (PMMA/poly(MMA-g-NBR) = 1 : 1).

The ionic conductivity of the electrolyte samples against the reciprocal absolute temperature is shown in Figure 7. A linear relationship confirms that the variation in conductivity with temperature follows an Arrhenius relationship, $\sigma = A \exp(-E/k_B T)$. This phenomenon indicates that the charge carriers are decoupled from the segmental motion of the polymer chain and transport occurs via the liquid electrolyte rather than polymeric chain in GPEs. This behavior is typically observed in liquid electrolytes and gel-type polymer electrolytes. It is also seen from Figure 7 that ion conductivity increases with the content of PMMA at the same temperature, and this phenomenon may be explained by widening the ion-conductive pathway by increasing the proportion of PMMA in DPE systems. However, this effect is not distinct at the same content of absorbed liquid electrolyte. The conduction mechanism of GPE has been recognized to comprise two conduction paths

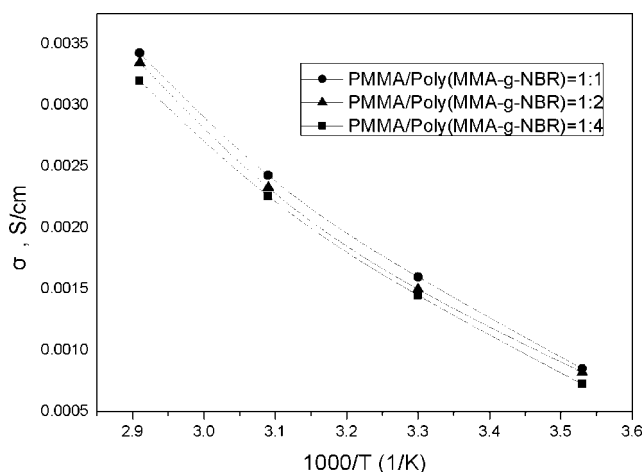


Figure 7 Dependence of conductivity on the reciprocal of temperature for different proportion of blend polymer (weight percentage).

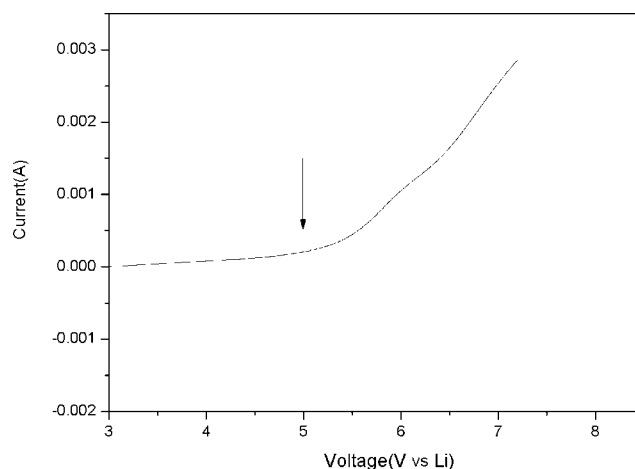


Figure 8 Electrochemical stability window of the DPE (PMMA/poly(MMA-g-NBR) = 1 : 1).

through liquid and gel phase.²⁵ The Li^+ ionic transport in liquid phase is by far faster and easier than the gel phase.¹ The content of absorbed liquid electrolyte plays an important role in ion conductivity in GPE.

Electrochemistry stability

For a lithium-ion polymer battery, the cell potential can approach as high as 4.5 V vs. Li/Li^+ , implying that the polymer electrolyte should be electrochemically stable up to at least 4.5 V.²⁶ To ascertain the electrochemical stability of the DPE, linear sweep voltammogram of the laminated three-electrode cells were performed at ambient temperature. Figure 8 shows the LSV curve of one of the DPE films (PMMA/poly(MMA-g-NBR) = 1 : 1). The working electrode potential of the cell was varied from 3.0 to 8.0 V (versus Li) at sweep rate of 0.05 V/s. It is evident from the figure that there is no electrochemical reaction in the potential range 3.0 to 5.0 V. The onset of current flow at 5.0 V is associated with the decomposition of the electrolyte. The anodic stability limit of the electrolyte is 5.0 V versus that of Li/Li^+ , which is sufficiently high for the lithium oxide cathodes LiCoO_2 and $\text{Li}_2\text{Mn}_2\text{O}_4$. The liquid electrolyte can be absorbed in the polymer blends efficiently and there is no separate electrolyte in the system, which will reduce the reaction possibility between liquid electrolyte and Li, and so the electrochemical stability is high in DPE system.

CONCLUSIONS

With the effect of PMMA grafting on NBR chains, the prepared DPE based on PMMA/poly(MMA-g-NBR) showed high phase compatibility and the

liquid electrolyte can be absorbed well in the blending films. The conductivity of the prepared DPE (PMMA/poly(MMA-*g*-NBR) = 1 : 1) was measured to be $1.5 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature and the electrochemistry stability window reaches 5.0 V vs. Li/Li⁺. It displayed a high ionic conductivity and electrochemical stability, exhibiting no solvent leakage. And the use of this DPE in practice is promising. Further investigations in application are in progress.

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