

P(DMS-co-EO)/P(EPI-co-EO) blend as a polymeric electrolyte

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Abstract

A new polymer electrolyte comprising the blend of poly(dimethylsiloxane-co-ethylene oxide) (P(DMS-co-EO)), and poly(epichlorohydrin-co-ethylene oxide) (P(EPI-co-EO)), with different concentrations of LiClO₄ is described. The polymer electrolyte was prepared by a solution-cast technique. The electrochemical properties were studied by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry techniques. The maximum ionic conductivity ($\sigma = 1.2 \times 10^{-4} \text{ S cm}^{-1}$) was obtained for the P(DMS-co-EO)/P(EPI-co-EO) 15/85 and 20/80 blends with 6 wt.% LiClO₄. These same films had a wide electrochemical stability, higher than 5 V at room temperature. A stable passive layer at the interface between the polymer electrolyte and lithium metal was formed within the first few days and maintained during the follow storage period. UV-Vis absorption spectra of the blends showed a transparent polymer electrolyte in the visible region. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolyte; Ionic conductivity; Blend; Copolymer; VTF equation

1. Introduction

The development of solid polymeric electrolytes has been the focus of numerous works since the discovery by Wright [1] and the suggestion by Armand et al. [2] that polymer ionic conductors could be used as electrolytes in lithium batteries. The main aim in these studies has been to produce polymeric systems with a high ionic conductivity applicable to electronic devices such as all solid-state rechargeable lithium batteries, electrochemical capacitors and electrochromic windows [3,4].

The polymer most studied has been poly(ethylene oxide) (PEO) containing inorganic salt dissolved in its matrix. However, the high degree of crystallinity of PEO restricts its use in a battery. Attempts to improve the low ionic conductivity of this material have included the use of blends and copolymers of the PEO [5–7], gel electrolytes [8–11] and hybrid electrolytes [12–14]. These new polymers have improved electrochemical and mechanical properties, including a wide electrochemical stability window, ionic conductivity at room temperature, higher electrochemical compatibility with electrode material, and thermal and dimensional stability. The blending process decreases the

degree of crystallinity of PEO and yields good mechanical stability in devices where high pressure is required.

In this report, we describe a system based on blends of poly(dimethylsiloxane-co-ethylene oxide) (P(DMS-co-EO)), and poly(epichlorohydrin-co-ethylene oxide) (P(EPI-co-EO)), with different concentrations of LiClO₄.

P(DMS-co-EO) and P(EPI-co-EO) are copolymers of PEO and were investigated since they show very different electrochemical and mechanical properties. P(DMS-co-EO) [15] has a high ionic conductivity ($\approx 1 \times 10^{-4} \text{ S cm}^{-1}$) and a wide electrochemical stability window, but has no mechanical support since it is a gel polymer electrolyte. In contrast, P(EPI-co-EO) [16] has a lower ionic conductivity than P(DMS-co-EO) ($\approx 1 \times 10^{-6} \text{ S cm}^{-1}$), an electrochemical stability window of 3.5 V, and good mechanical properties that make it an elastomeric polymer. We describe here a solid polymeric electrolyte with good electrochemical and mechanical properties formed by synergism between these two polymers.

2. Experimental

P(DMS-co-EO) was synthesized by a polycondensation reaction of dimethyldichlorosilane with monoethylene glycol [15]. P(EPI-co-EO) and LiClO₄ were purchased from Aldrich and used as received.

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The blends were prepared by dissolving the pure polymers and LiClO_4 in tetrahydrofuran. The solvent was evaporated and dried at high vacuum for 72 h. The P(DMS-co-EO)/P(EPI-co-EO) ratios used were: 10/90, 15/85 and 20/80 (w/w) and 2, 6 and 10 wt.% of LiClO_4 added in the blends.

Thermal behavior of the polymer electrolytes was analyzed using a differential scanning calorimeter (DSC; NETZSCH DSC 204). The samples were placed in aluminum pans under a nitrogen atmosphere, heated to 150 °C, cooled to –100 °C and then heated to 250 °C. The thermograms were recorded at a rate of 10 °C min^{-1} . All DSC experiments were done in duplicate and the thermograms shown in the next section refer to the final heating.

The electrochemical experiments were done using an AUTOLAB-PGSTAT30 FRA. The ionic conductivity of the blends was investigated by electrochemical impedance spectroscopy (EIS) in the frequency range of 1–10⁵ Hz with an ac amplitude of 10 mV. To analyze the ionic conductivity of the blend at room temperature, the initial impedance spectra were obtained at room temperature. To analyze the ionic conducting mechanism and activation energy, the temperature was changed from 25 to 100 °C in steps of 10 °C. The impedance spectra were measured after 60 min of stabilization at the desired temperature.

The electrochemical stability window was evaluated by cyclic voltammetry at a scan rate of 10 mV s^{-1} using a Li/polymer electrolyte/stainless steel (SS) cell, in which lithium was used as the counter and reference electrodes. The Li/blend interface was also analyzed in the EIS experiments using a Li/polymer electrolyte/Li cell. All electrochemical experiments were carried out in a dry box under an argon atmosphere.

UV-Vis spectra were collected on a HP 8453 spectrophotometer. The background signals from the ITO glass substrate were considered as 0% absorbance.

3. Results and discussion

The films formed by casting of P(DMS-co-EO), P(EPI-co-EO), LiClO_4 and THF solution showed good mechanical support, flexibility, homogeneity and transparency.

The thermal behavior of the pure copolymers and of the P(DMS-co-EO)/P(EPI-co-EO) blends (10/90, 15/85 and 20/80 ratio) are shown in Fig. 1. P(EPI-co-EO) showed a well-defined phase transition at –42 °C which was attributed to the glass transition temperature (T_g) of P(EPI-co-EO). P(DMS-co-EO) presents a melting process located between –38.5 and 4 °C with a $T_m = -12.5$ °C, suggesting the presence of a crystalline phase, probably related to melting of the poly(dimethylsiloxane) block. The two-phase transition observed at –74.1 and –52.1 °C was related to the glass transition temperature of the poly(dimethylsiloxane) block and poly(ethylene oxide) block, respectively [17]. The decomposition of the material began at 120 °C.

To the blend with higher P(DMS-co-EO) ratio (20/80), a marked shift in the glass transition temperature of the P(DMS-co-EO) copolymer was observed. Two poorly defined phase transitions were observed at –69 and –41 °C and were related to the glass transition temperatures of the P(DMS-co-EO) and P(EPI-co-EO) blocks, respectively. The melting peak with a $T_m = -10.5$ °C was attributed to the crystalline phase of P(DMS-co-EO) with a $T_m = -12.5$ °C.

With the P(DMS-co-EO) ratio decreased, a gradual disappearance of the melting process ($T_m = -10.5$ °C) of the 15/85 and 10/90 blends, was observed. The glass transition temperature of these blends occurred at –41.7 and –42.2 °C, respectively, and was attributed to the P(EPI-co-EO) copolymer. Through these results, the 15/85 and 10/90 blend showed miscibility with amorphous material characteristics.

Decomposition processes of the blend began at 220 °C, with greater thermal stability being observed with P(DMS-co-EO).

To illustrate the P(DMS-co-EO)/P(EPI-co-EO) behavior with the addition of salt, the P(DMS-co-EO)/P(EPI-co-EO) blend 20/80 ratio containing 2, 6, 10 wt.% LiClO_4 was analyzed by DSC (Fig. 2). The absence of the crystalline phase for the 20/80 blends, was noted with increased salt concentration. This result has already been reported for P(EPI-co-EO) electrolytes [16] and is caused by ion complexation that acts as crosslinking nodes to decrease the degree of crystallinity. However, a high salt concentration induced the formation of a crystalline phase, as showed by the presence of a broad melting peak at $T_m = 125$ °C (Fig. 2). This crystalline phase was related to incomplete salt dissociation.

Fig. 3 shows the glass transition temperature of all the blends as a function of salt concentration. A rise in T_g with increasing salt concentration was observed in all cases and resulted from the increased oxygen coordination of the chain with salt, as well as the incomplete salt dissociation. This in turn decreases the degree of chain movement and ionic

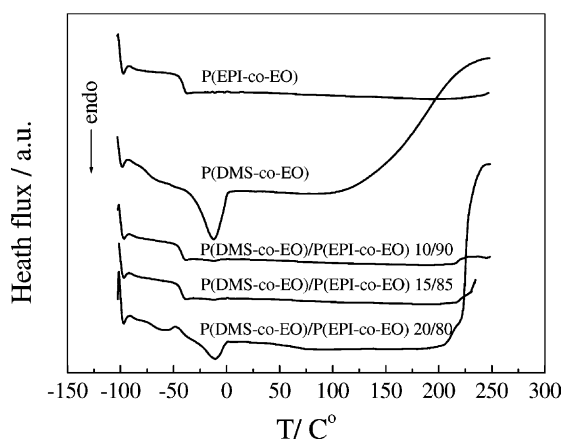


Fig. 1. DSC curves for P(EPI-co-EO), P(DMS-co-EO) and P(DMS-co-EO)/P(EPI-co-EO) blends (10/90, 15/85 and 20/80 ratio).

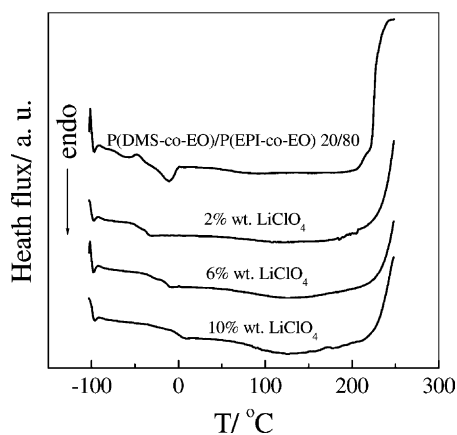


Fig. 2. DSC curves for P(DMS-co-EO)/P(EPI-co-EO) 20/80 blends containing different concentrations: 0, 2, 6, and 10 wt.% LiClO₄.

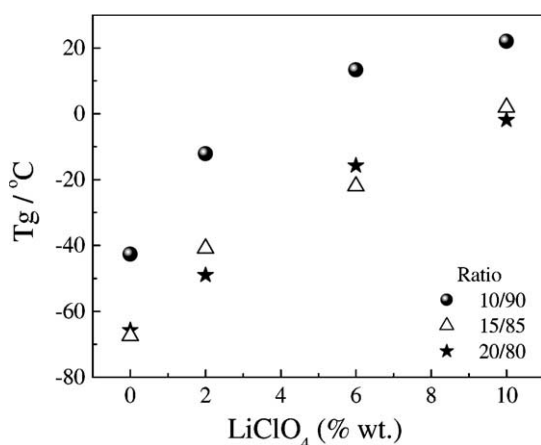


Fig. 3. Variation in the glass transition temperature (T_g) as a function of salt concentration P(DMS-co-EO)/P(EPI-co-EO) blends (10/90, 15/85 and 20/80).

conduction, the latter being measured by electrochemical impedance spectroscopy.

Fig. 4 shows the ionic conductivity of polymer electrolyte P(DMS-co-EO)/P(EPI-co-EO)/LiClO₄ with copolymer ratio of 10/90, 15/85 and 20/80 and 0, 2, 6 and 10 wt.% LiClO₄ at room temperature. The ac impedance spectra of P(DMS-co-EO)/P(EPI-co-EO) blend 15/85 with 2 wt.% LiClO₄ at room temperature (inset in Fig. 4) is shown as representative of the impedance spectra behavior of all the polymer electrolytes at room temperature. A typical impedance plot for a polymeric electrolyte was observed for all polymer electrolyte compositions, where a depressed semicircle at high frequency was observed, followed by a straight line in the low frequency region. This semicircle was related to relaxation processes in the bulk electrolyte, whereas the straight line contains information regarding the electrode/electrolyte interface. With ideally blocking (inert) electrodes, the inclination of the straight line should be 90°, but some variation in this inclination was observed as a result of surface adsorption or even unexpected electrochemical reactions at the interface. The electrolyte resistance was obtained by

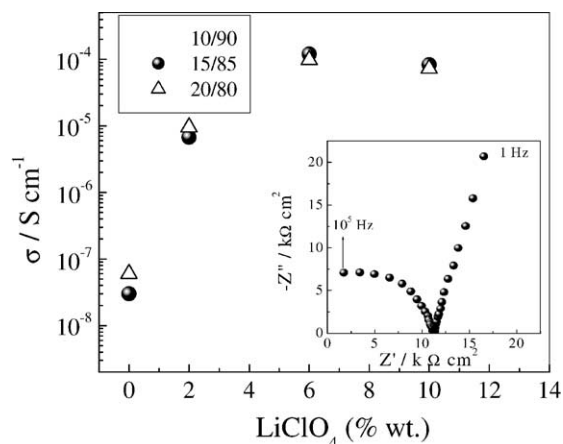


Fig. 4. Ionic conductivity all of the polymer electrolytes studied at room temperature. The inset shows the impedance spectra for the P(DMS-co-EO)/P(EPI-co-EO) blend 15/85 with 2 wt.% LiClO₄.

extrapolating the spike to the point of intersection with the x-axis. The electrolyte conductivity was obtained from the equation $\sigma = L/(RA)$, where L is the thickness, R the resistance obtained and A is the electrode area. With increasing salt concentration for all blends, the semicircle tended to disappear and shift to a lower resistance value, increasing the ionic conductivity.

The maximum ionic conductivity ($\sigma = 1.2 \times 10^{-4} \text{ S cm}^{-1}$) was obtained for the P(DMS-co-EO)/P(EPI-co-EO) 15/85 and 20/80 blends with 6 wt.% LiClO₄. This value was one order of magnitude higher than P(EPI-co-EO) electrolyte [16] and was the same magnitude as that of the P(DMS-co-EO) gel electrolyte [15]. The decrease in ionic conductivity beyond the maximum can be due to several factors such as: presence of a crystalline phase, increase in the macromolecular rigidity of the amorphous phase and the appearance of ion pairs.

The mechanism of ionic transport in the P(DMS-co-EO)/P(EPI-co-EO)/LiClO₄ polymer electrolyte was analyzed using ionic conductivity measurements based on impedance spectroscopy of all the polymer electrolytes at several temperatures. Fig. 5 shows an example of impedance spectra

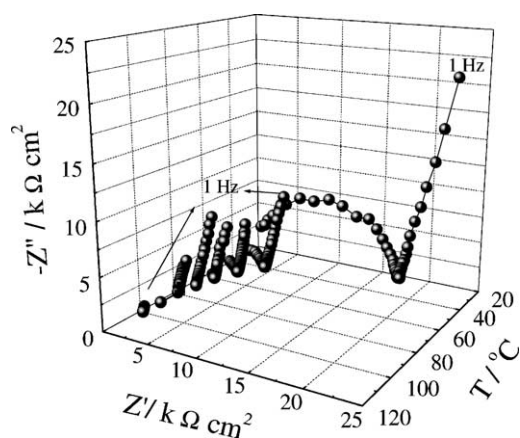


Fig. 5. Impedance spectra for P(DMS-co-EO)/P(EPI-co-EO) 15/85 with 6 wt.% LiClO₄ at various temperatures.

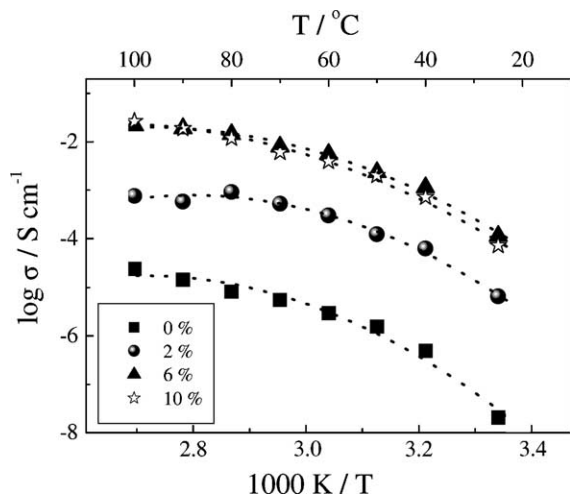


Fig. 6. Ionic conductivity as a function of temperature for P(DMS-co-EO)/P(EPI-co-EO) 15/85 with 6 wt.% LiClO₄.

behavior for P(DMS-co-EO)/P(EPI-co-EO) 15/85 with 6 wt.% LiClO₄. The size of the semicircle related to ionic resistance decreased with increasing temperatures.

Fig. 6 shows the ionic conductivity of the P(DMS-co-EO)/P(EPI-co-EO) 15/85 with 6 wt.% LiClO₄ as a function of temperature calculated from the previous impedance spectra. The same behavior was observed for the other polymer electrolyte compositions. Initially, the Arrhenius equation was used to adjust these curves, but the equation that best fitted the ionic conductivity versus temperature curve was the Vogel–Tamman–Fulcher (VTF) equation [18]:

$$\sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right)$$

In this equation, σ_0 is a pre-exponential factor proportional to the number of charge carriers, B the pseudoactivation energy for ionic conductivity and T_0 is the quasi-equilibrium glass transition of the electrolyte, where T_0 is generally estimated to be about 50 °C below T_g . The fact that the curves were fitted using the VTF equation implies that ionic conduction is related to segmental movements of the polymeric matrix. These movements were characterized by a glass transition temperature, below which the chain segments are essentially immobile and above this temperature, the vibrational energy of the segments is sufficient to push against the hydrostatic pressure imposed by its neighbor segments, thereby creating a small amount of space surrounding its own volume in which vibrational motion can occur. This extra space is known as the free volume per segment, and is where ionic conduction occurs.

The activation energy of the blends shown in Fig. 7 was obtained by VTF fitting. An energy minimum was observed for all blends with 6 wt.% LiClO₄, but the lowest values were observed in blends with a high P(DMS-co-EO) ratio (blends 15/85 and 20/80). In these cases, the activation energy was lower than the pure P(EPI-co-EO)/LiClO₄ system, indicating that the addition of P(DMS-co-EO)

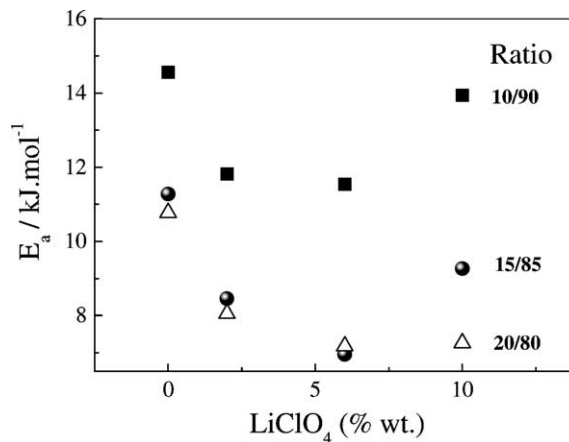


Fig. 7. Activation energy as a function of salt concentration for the P(DMS-co-EO)/P(EPI-co-EO) blends (10/90, 15/85 and 20/80 ratio).

increased the segmental movement and flexibility of the blend. The higher glass transition temperature observed with the P(DMS-co-EO)/P(EPI-co-EO) 10/90 blend could be an indication of a lower flexibility of the conducting phase which is related to the ionic mobility.

Although the 15/85 and 20/80 blends with 6 wt.% LiClO₄ had the same ionic conductivity and activation energy, the P(DMS-co-EO)/P(EPI-co-EO) 15/85 blend with 6 wt.% LiClO₄ was chosen for characterization of the electrochemical stability window, UV-Vis spectroscopy and Li/electrolyte interface analysis, because of its better mechanical performance.

Electrochemical stability with a wide potential range is necessary for electrochemical devices such as batteries, electrochemical capacitors, and electrochromic devices. The electrochemical stability window of the Li/P(DMS-co-EO)/P(EPI-co-EO) 15/85 blend with 6 wt.% LiClO₄ was evaluated with a stainless steel blocking electrode. Fig. 8 shows the current–voltage response obtained at a

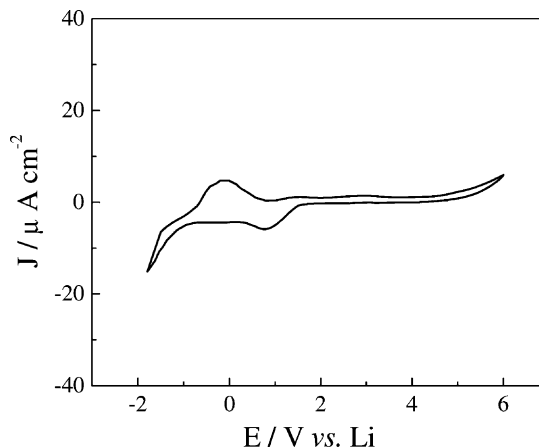


Fig. 8. Electrochemical stability windows for the P(DMS-co-EO)/P(EPI-co-EO) blend 15/85 ratio with 6 wt.% LiClO₄.

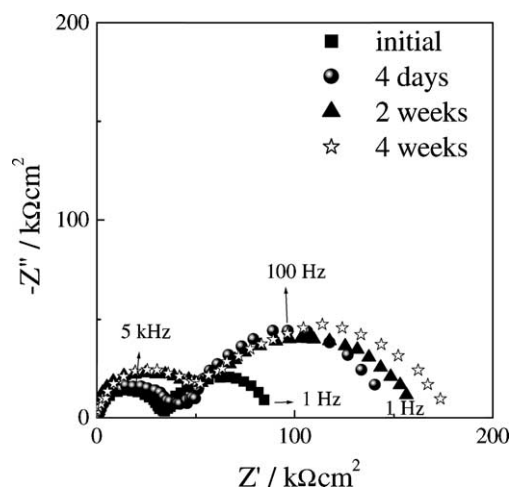


Fig. 9. The ac impedance spectrum of a Li/P(DMS-co-EO)/P(EPI-co-EO) 15/85 blend with 6 wt.% LiClO₄/Li system as a function of time at room temperature.

sweep rate of 10 mV s⁻¹. The voltammetric profile observed was consistent with those reported for the PEO polymer electrolyte [2,19]. Wide electrochemical stability was observed at room temperature. A defined cathodic peak was verified between 1.5 and -0.5 V and was possibly related to impurities present in the blend. Plating of lithium occurs at a lower potential and the related process of lithium stripping was observed at a potential greater than 0 V. On the anodic side, a high anodic potential limit higher than 5 V was observed. This finding implied that the P(DMS-co-EO)/P(EPI-co-EO) 15/85 blend with 6 wt.% LiClO₄ could be used compatible with the lithium metal oxide materials normally used as a cathode in high potential batteries.

To investigate the properties of the Li/electrolyte interface over time (days), impedance spectra of the Li/P(DMS-co-EO)/P(EPI-co-EO) 15/85 blend, 6 wt.% LiClO₄/Li cell were monitored (Fig. 9). This interface corresponds to the compatibility of the polymer electrolyte with the electrode material and is an important factor in the use of a polymer electrolyte in electrochemical devices. Two different frequency regions were observed: the semicircle seen at high frequency was related to ionic conduction and the second semicircle at low frequency was associated with the charge transfer process. The spectra were fitted using equivalent circuit software and the circuit is shown in Fig. 10. This circuit has been proposed for analysis of the lithium interface in several polymer electrolytes [20,21]. The R_b value is

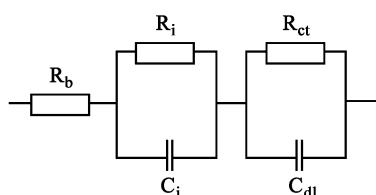


Fig. 10. Equivalent circuit used to fit the impedance spectra.

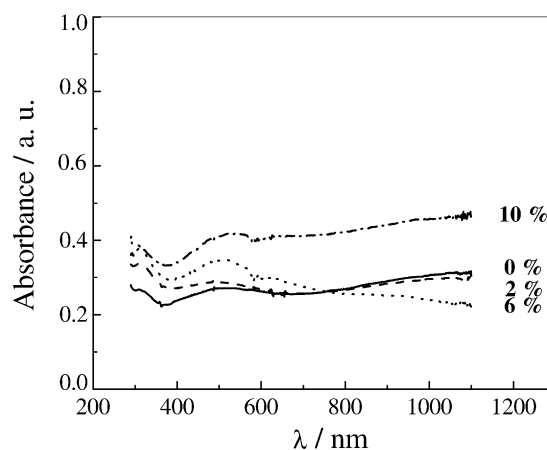


Fig. 11. UV-Vis spectra for the P(DMS-co-EO)/P(EPI-co-EO) blend 20/80 at different concentration of LiClO₄.

related to the bulk resistance of the polymeric electrolyte, an increase of 25 kΩ cm² was observed in the first two weeks and remained practically constant thereafter, indicating that there was no degradation of the polymeric chain. Initially, an increase in the R_i value was observed, stabilizing after 2 weeks. This initial increase resulted from a corrosion process caused by reduction of the salt in the build up of the passivation layer. A similar finding has been reported by others [22]. The R_{ct} values varied by 50 kΩ cm² in the first four days, but then became constant after 2 weeks. The steady R_i and R_{ct} values indicated that a stable passive layer at the interface between the polymer electrolyte and lithium metal had formed within the first few days and was maintained during the follow storage period.

A transparent polymer electrolyte is an important requisite for electrochromic applications and the addition of salt to the polymer electrolyte can result in formation of a non-transparent polymer, because of incomplete salt dissociation. As shown by the UV-Vis absorption spectra of the blends, there was no significant absorption in the visible region at the salt concentration investigated (Fig. 11).

4. Conclusion

This work showed that it is possible to produce a polymeric electrolyte by mixing two copolymers with very different mechanical and electrochemical properties. The addition of P(DMS-co-EO) to P(EPI-co-EO) significantly affected the electrochemical properties; whilst the flexibility of the polymer electrolyte film (characteristic of P(EPI-co-EO)) was maintained. The increase in ionic conductivity and the electrochemical stability window is a result of the increase of segmental motion of polymeric chain and the flexibility of polymer blend with the addition of the P(DMS-co-EO). These results indicate that the blends with P(DMS-EO)/P(EPI-EO) can be used

as solid-state polymeric electrolytes. This work will continue with the application of polymer electrolytes in high potential batteries.

Acknowledgements

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