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Electrochemical characterization of plasticized polymer electrolytes based on ABS/PMMA blends

Abstract Electrochemical characteristics of plasticized polymer electrolytes based on poly(acrylonitrile-butadene-styrene) and poly(methyl methacrylate) (abbreviated as ABS/PMMA) blends have been studied. The ionic conductivity of the polymer electrolyte with an ABS/PMMA ratio of 6/4 and a plasticizer content of 60% was highest when the $LiClO_4$ content was 4.8%. The transference numbers (T_+) of the polymer electrolytes were measured using the steady-state current method, and the T_+ values were found to be less than 0.5. The electrolyte system was found to have an electrochemical stability window up to 4.5 V. The properties of the electrode interface in contact with the polymer electrolyte were also investigated by impedance spectroscopy, and the evolution of these spectra as a function of storage time was explained and interpreted using a solid-polymer layer (SPL) model. The time evolution of the impedance parameters indicated that a passivation film grew rapidly on the lithium surface immediately after assembly of the cell.

Key words Polymer electrolytes · Lithium battery · Dual phase · Ionic conductivity · Interface

Introduction

Lithium batteries using polymer electrolytes have received increasing attention in the past two decades, owing to their design and manufacturing flexibility and outstanding performance [1, 2, 3]. The prerequisites for polymer electrolytes to be used in solid state lithium batteries are: (1) ionic conductivity higher than 10^{-3} S cm^{-1} at room temperature; (2) a wide electrochemical stability window up to 4.5 V vs. Li/Li$^+$; (3) a lithium transference number approaching unity; (4) chemical compatibility with electrode materials; and (5) sufficient dimensional stability to serve as separators in batteries [4]. Many attempts have been made to develop practical polymer electrolytes to meet the above requirements [5, 6, 7, 8]. The electrolytes based on a "simple" combination of high molecular weight polymer hosts and lithium salts (LiX) may be considered the first-generation electrolytes. They have conductivities in the order of 10^{-8} S cm^{-1} to 10^{-6} S cm^{-1} at ambient temperature [9, 10]. The second-generation polymer electrolytes are based on the combination of modified, comb-shaped poly(ethylene oxide) (PEO) structures with lithium salts, and have an improved conductivity of about 10^{-4} S cm^{-1} to 10^{-5} S cm^{-1} at room temperature [11]. More recently, third-generation electrolytes have been developed by adding plasticizers to "common" polymer-LiX complexes, or by trapping liquid electrolyte solutions of lithium salts in a gel matrix [12]. The third-generation electrolytes have conductivities as high as 10^{-3} S cm^{-1} at ambient and subambient temperatures [12, 13, 14]. However, such plasticized polymer electrolytes suffer from a gel-like mechanical property, making them unsuitable to serve as separators in batteries. One effective approach to this mechanical property problem is to use a polymer blend system consisting of two polymers [15]. Our recent studies on plasticized polymer electrolytes based on acrylonitrile-butadiene-styrene/poly(methyl methacrylate) (ABS/PMMA) blends have shown that the system has a much improved mechanical property and the same level of high ionic conductivity as the plasticized PMMA electrolyte system [16].

Our earlier studies were on the mechanical and thermal properties, the morphology and ionic conductivity of the ABS/PMMA-based plasticized polymer electrolyte system. In this work, the electrochemical characterization of the system will be reported. As mentioned above, the electrochemical behavior is an important criterion for a polymer electrolyte used in solid state lithium batteries. We will describe the ionic

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conductivities of the ABS/PMMA-based plasticized polymer electrolytes with different salt contents, and the interfacial behavior of the lithium electrode in contact with the polymer electrolyte. The lithium transference numbers and the electrochemical stability window of the electrolyte system have also been determined.

Experimental

Materials

ABS, with an average molecular weight of 1.8×10^5 and a polydispersity of 2.18, was obtained from Polyscience. PMMA of average molecular weight 1.2×10^5 and polydispersity 1.35 was obtained from Aldrich. Both the ABS and PMMA were precipitated with ethanol from tetrahydrofuran (THF) before use. High-purity (99%) ethylene carbonate (EC) and propylene carbonate (PC) were purchased from Fluka and were used after distillation under reduced pressure. $LiClO_4$ (purity > 97%) was obtained from Fluka and was dried at 150 °C under vacuum for 24 h before use. THF was purchased from J.T. Baker and distilled with sodium before use.

Preparation of the electrolytes

All the electrolytes were prepared by the solution casting technique. The solutions were prepared by dissolving appropriate amounts of ABS, PMMA, plasticizer (EC/PC = 1/1 by weight) and $LiClO_4$ together in anhydrous THF. The solutions were then poured into Teflon moulders and the solvent (THF) was allowed to evaporate at room temperature. Mechanically stable free-standing films (100–200 μm) were obtained after evaporation of the solvent. All the above operations were carried out in a dry box with a N_2 flow. The films were then further dried in a temperature-controlled vacuum oven at 50 °C for 24 h to remove any trace of THF. In this paper, the plasticizer content used is defined as plasticizer content (%) = (weight of the incorporated plasticizer/total weight of the composite) × 100%; the salt content is defined as salt content (%) = (weight of the incorporated salt/total weight of the composite) × 100%. For convenience, the composition of the plasticized polymer electrolytes is described as ABS/PMMA-(EC + PC)-$LiClO_4$.

Thermal analysis and X-ray diffraction patterns

Differential scanning calorimetry (DSC) measurements were carried out under a N_2 atmosphere with a 2200 thermal analyser (Dupont) over the temperature range of –150 °C to 150 °C at a heating rate of 10 °C min^{-1}. Samples were sealed in aluminium pans in a dry box filled with argon. During the measurements, samples were quenched by liquid nitrogen to –150 °C and then heated to 150 °C. The heat flow was recorded during the heating. The glass transition temperature (T_g) was taken as the temperature of the starting point of the baseline shift observed during the transition from a glassy to a rubbery state.

X-ray diffraction (XRD) patterns were obtained with a Siemens D5005 X-ray diffractometer using Cu-K_α radiation over the range $2\theta = 10$–$50°$ at room temperature. All X-ray samples were in the form of thin films.

Electrochemical measurements

An EG & G model 273A potentiostat/galvanostat was used to perform the a.c. impedance measurements and the d.c. polarization measurements, as well as the cyclic voltammetric (CV) experiments. All the cells for the electrochemical measurements were assembled in a dry box filled with argon. For ionic conductivity measurements, the specimens were prepared by sandwiching the polymer electrolyte with two stainless steel (SS) disc electrodes (blocking nature) of diameter 12.86 mm. Conductivity was calculated from the bulk resistance obtained from the impedance spectra. The impedance measurements for ionic conductivity were performed over a frequency range from 100 kHz to 1 Hz, using 5 mV a.c. amplitude. Each sample was equilibrated at the experimental temperature for 30 min before measurement. Cyclic voltammetry measurements of the polymer electrolytes were carried out with a stainless steel current collector using lithium both as the counter and the reference electrodes. A scan rate of 10 mV s^{-1} was adopted. The stability of the lithium/polymer electrolyte interface was investigated by monitoring the time dependence of the impedance of the cell prepared by sandwiching the polymer electrolyte between two lithium symmetric non-blocking electrodes, over the frequency range from 100 kHz to 10 mHz. The lithium transference numbers were evaluated in a Li|polymer electrolyte|Li cell by combination of a.c. impedance and d.c. polarization measurements [17, 18].

Results and discussion

Ionic conductivities with different salt contents

The ionic conductivity, σ, of an electrolyte is given by the product of the concentration of the ionic charge carriers and their mobility:

$$\sigma = \sum n_i z_i \mu_i \tag{1}$$

where z_i is the ionic charge, n_i the number of charge carriers and μ_i the ionic mobility. The ionic conductivity of an electrolyte can be increased if the ionic mobility and/or the number of ionic charge carriers are increased.

Figure 1 shows the influence of $LiClO_4$ content on the conductivity of the polymer electrolytes with a fixed plasticizer content of 60%. It was found that at all temperatures the ionic conductivity increased until a salt content of about 4.8% was reached. Further addition of salt led to a decrease in conductivity. It is reasonable to suggest that the decrease is due to the formation of cation-anion associates, because the average distance between the cation and anion is significantly reduced at high salt content [7, 8, 19, 20]. These associates may be electrically neutral, which will be non-conducting, or charged aggregates, such as $[M_2X]^+$ or $[MX_2]^-$, which will have low ionic mobility (compared to the ionic mobility of the free ions such as M^+ or X^-). Furthermore, the associates may form some kind of physical cross-linking which will hinder the transport of ions. As has been reported [16], the present plasticized polymer electrolyte system is a dual-phase system comprising a plasticizer-rich phase and an ABS-rich phase. The plasticizer-rich phase acts as a tunnel for ionic transport while the ABS-rich phase acts as mechanical support. When the salt content exceeds the maximum solvability of the plasticizer-rich phase, some form of physical cross-linking may form, which will result in blockage to the tunnel in the plasticizer-rich phase (i.e. a fragmentary plasticizer-rich phase may be formed). In addition, the physical cross-linking will also result in an increase
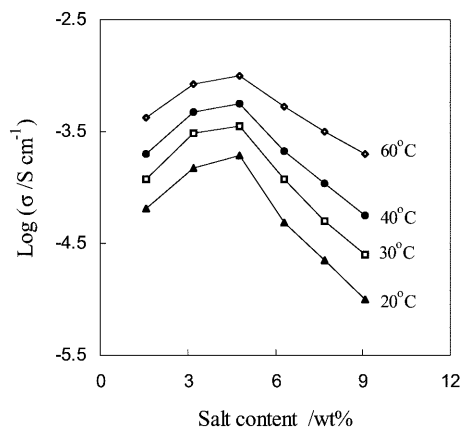
Fig. 1 The effect of LiClO$_4$ content on the ionic conductivity of the plasticized polymer electrolytes; ABS/PMMA = 6/4, 60% (EC + PC). The points are for the following LiClO$_4$ content: 1.6%, 3.2%, 4.8%, 6.3%, 7.7%, 9.1%

Fig. 2a, b XRD patterns of the polymer electrolytes with different LiClO$_4$ content; ABS/PMMA = 6/4, 60% (EC + PC)

of T_g of the polymer electrolyte system, because of interactions between the salt and polymer matrix [21], as shown in Table 1.
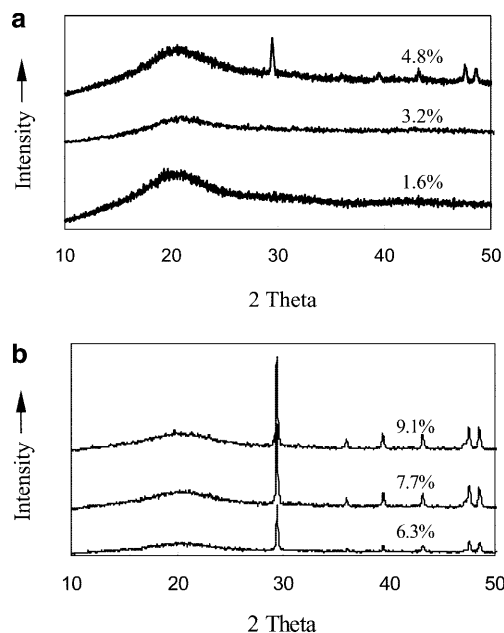
It is also noted that the salt content has a stronger effect on the conductivity at lower temperatures than at higher temperatures. It seems reasonable to assign this phenomenon to two reasons: (1) a decrease of ionic association with increasing temperature, and (2) an increase of the thermal mobility of the polymer chains that makes the plasticizer-rich phase more liquid-like.

The above explanation of the effect of salt content on the ionic conductivity of the polymer electrolyte finds support with evidence from the XRD patterns in Fig. 2. It can be seen clearly from Fig. 2 that:

1. The relative intensities of peaks at $2\theta = 29.4$, 35.9, 39.4, 43.1, 47.5 and 48.5 increase progressively with increasing salt content, indicating the existence of some form of salt crystal. On the other hand, the electrolytes with salt content below 4.8% are in an amorphous state, as shown in Fig. 2a.
2. When the salt content is less than 3.2%, there are relatively small numbers of salt ions in the polymer matrix to provide enough charge carriers and hence the polymer electrolytes (with less than 3.2% salt content) have low ionic conductivity. When the salt content is between 3.2% and 4.8%, the salt can be
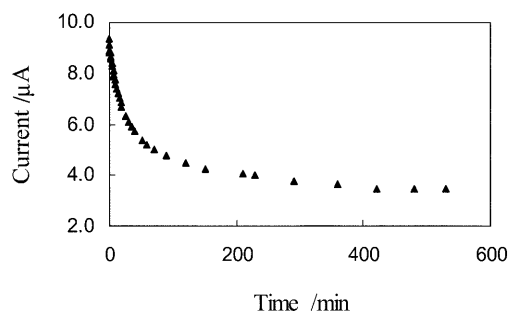
dissolved in the polymer electrolyte system completely, giving the electrolytes high ionic conductivity. Thus, for the polymer electrolytes with a fixed plasticizer content of 60%, the optimal salt content in terms of ionic conductivity is 3.2–4.8%.

Transference number

In the electrochemical characterization of polymer electrolytes, it is important to know not only the ionic conductivity but also the values of the lithium transference number. Therefore, the lithium transference numbers of the electrolytes were determined by a combination of a.c. impedance and d.c. polarization measurements. This technique has been proved to be applicable in circumstances where proper correction for a passivation layer is required [17]. The initial interfacial resistance ($R_{i,0}$) of a symmetrical Li|polymer electrolyte|Li cell was measured by a.c. impedance analysis. A small d.c. polarization ($\Delta V = 10$ mV) was applied to this cell, and the initial current (I_0) was measured. The current was monitored as a function of time until the steady-state condition was established, and the steady-state current (I_s) was determined. The steady-state interfacial resistance of the cell ($R_{i,s}$) was again determined by a.c. impedance analysis. Figure 3 shows the typical current change with time for the cell studied during polarization.

Following the treatment discussed by Evans et al. [17], the cation transference number can be expressed as:

$$T_+ = \left[I_s\left(\Delta V - I_0 R_{i,0}\right)\right] / \left[I_0\left(\Delta V - I_s R_{s,0}\right)\right] \qquad (2)$$

Table 1 Glass transition temperatures (T_g) of the polymer electrolytes with different salt contents

Composition of the electrolytes	Glass transition temperature (°C)
38.4%ABS/PMMA(6/4)-60%(EC + PC)-1.6%LiClO$_4$	18.0
36.8%ABS/PMMA(6/4)-60%(EC + PC)-3.2%LiClO$_4$	18.1
35.2%ABS/PMMA(6/4)-60%(EC + PC)-4.8%LiClO$_4$	18.8
33.7%ABS/PMMA(6/4)-60%(EC + PC)-6.3%LiClO$_4$	21.5
32.3%ABS/PMMA(6/4)-60%(EC + PC)-7.7%LiClO$_4$	24.2
30.9%ABS/PMMA(6/4)-60%(EC + PC)-9.1%LiClO$_4$	27.8

Fig. 3 Variation of current with time during polarization of a Li|ABS/PMMA(6/4)-60%(EC + PC)-1.6%LiClO$_4$|Li cell at 25 °C, with a total applied potential difference of 10 mV

The values of T_+ obtained for the polymer electrolytes containing different amounts of LiClO$_4$ are shown in Table 2. It is clear that the values of the lithium transference number compare well with those reported for PEO-based electrolytes, whose values, depending upon composition, vary from 0.2 to 0.5 [7]. Furthermore, they are all lower than 0.5. This means that the mobility of the cation is relatively lower than that of the anion. This is probably because the cation interacts relatively strongly with the polymer and plasticizer, while the anion is loosely associated with them and therefore can be displaced more readily under an electric field [22, 23].

Electrochemical stability

For a lithium battery, the anodic reaction occurs in the vicinity of 0 V vs. Li/Li$^+$, while the cathodic potentials can approach as high as 4.5 V, implying that the electrochemical stability is also an important parameter regarding cycling reversibility. To evaluate the electrochemical stability of the ABS/PMMA-based electrolytes, a three-electrode cell with stainless steel as the working electrode and lithium as the counter and reference electrodes was assembled and its cyclic voltammetry measured. Figure 4 illustrates the cyclic current-potential curves of the plasticized polymer electrolyte studied. With the decomposition potential being defined as the potential at which the current density approaches 0.1 mA cm^{-2} [24], Fig. 4a indicates that the plasticized polymer electrolyte based on ABS/PMMA is electrochemically stable up to 4.5 V. Furthermore, a peak at 1.15 V vs. Li/Li$^+$ can be clearly observed in Fig. 4b. Although the peak is prominent in the first scan, its in-

Table 2 Transference number values of the polymer electrolytes with different salt contents

| Composition of the electrolytes	Transference number
38.4%ABS/PMMA(6/4)-60%(EC + PC)-1.6%LiClO$_4$	0.41
36.8%ABS/PMMA(6/4)-60%(EC + PC)-3.2%LiClO$_4$	0.41
35.2%ABS/PMMA(6/4)-60%(EC + PC)-4.8%LiClO$_4$	0.40
33.7%ABS/PMMA(6/4)-60%(EC + PC)-6.3%LiClO$_4$	0.38
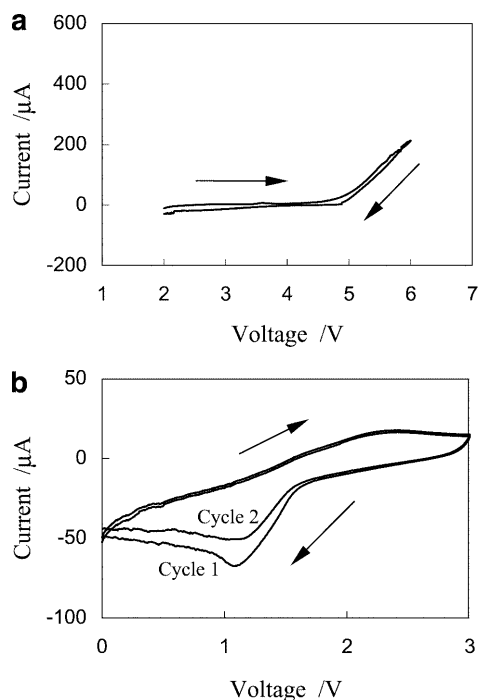
Fig. 4 Cyclic voltammograms for ABS/PMMA(6/4)-60%(EC + PC)-4.8%LiClO$_4$ at 10 mV s^{-1} and 25 °C on a stainless steel working electrode vs. lithium: **a** 2.0–6.0 V; **b** 0–3.0 V

tensity weakens in the second scan. This peak is the result of the reduction of trace water on the stainless steel electrode [25]. The above results illustrate that the electrolytes have good electrochemical stability and are thus compatible with high-voltage electrode couples such as Li-V$_6$O$_{13}$ or Li$_x$C$_6$-LiMO$_2$ (M = Co or Ni) couples.

Lithium electrode/polymer electrolyte interface

The lithium electrode/polymer electrolyte interface is a complicated interface, having different types of capacitive and resistive elements. The a.c. impedance technique is the usual tool to study the lithium/electrolyte compatibility. The impedance spectra of a Li|ABS/PMMA(6/4)-(EC + PC)-LiClO$_4$|Li cell at various times under open circuit conditions at room temperature are given in Fig. 5. It can be seen that the overall a.c. impedance response is composed of a distorted semicircle in the high-frequency range, which can be related to a charge transfer process [26, 27], and a spur in the low-frequency region, which is characteristic of a diffusion process. Figure 6 gives the bulk resistance values of the SS|ABS/PMMA(6/4)-(EC + PC)-LiClO$_4$|SS cell at different times under the same conditions. The curve in Fig. 6 shows that there is no apparent ageing of the cell over the same period of storage time. The increase of the semicircles in the high-frequency range with storage time (see Fig. 5) indicates, therefore, that there are changes in the properties of the interface in between the lithium electrode/polymer electrolyte [28, 29]. It has been rec-
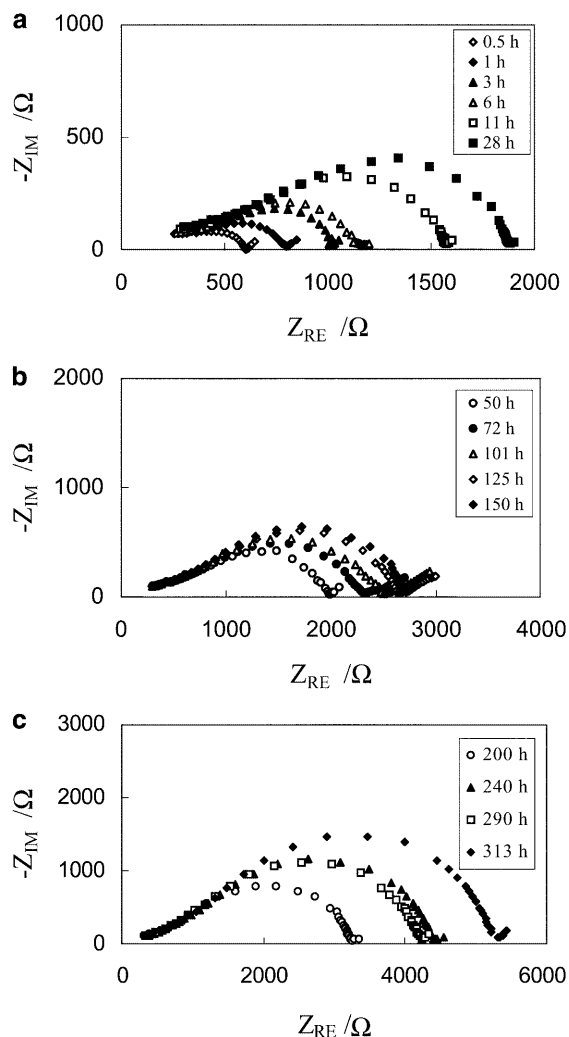
Fig. 5a–c Impedance spectra of a Li|ABS/PMMA(6/4)-60%(EC + PC)-4.8%LiClO$_4$|Li cell at different storage times at 25 °C under open circuit conditions
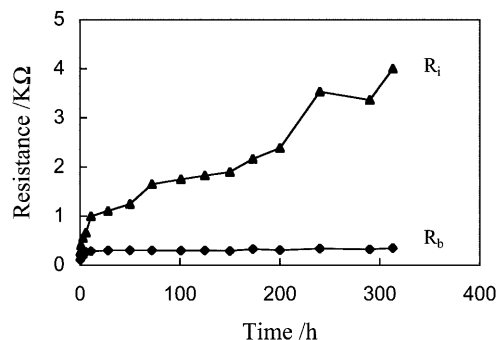
ognized [30, 31] that a passivation layer forms from the products of the corrosion reactions between the lithium electrode and the electrolyte medium [28, 32].
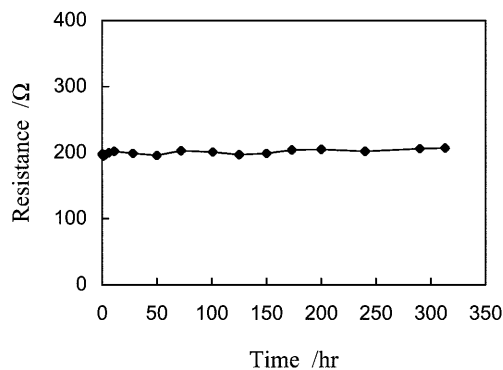
One may notice that the expansion of the semicircles, and thus the growth of the resistive layer, does not follow a regular trend. Considering the composition and characteristics of the polymer electrolyte being studied, the a.c. impedance results can be analysed using an equivalent circuit model, namely the solid-polymer layer (SPL) model proposed by Thevenin and Muller [32], in which the passivation layer is assumed to consist of solid compounds dispersed in a polymer electrolyte. Therefore, it is possible to separate the various impedance parameters that contribute to determine the responses illustrated in Fig. 5. It should be noted that, even if a given model fits the experimental data satisfactorily, it does not necessarily prove its absolute validity. However, a good fit may still be a valid support for using the model to gain some insight into the electrochemical processes occurring at the interface. Bearing this in mind and using the SPL equivalent, we determined the time evolution of the circuit parameters, as shown in Fig. 7, in which R_i represents the lithium electrode/electrolyte interfacial resistance and R_b represents the bulk resistance of the electrolyte. It is clear that the values of R_i increase dramatically within the initial 10 h after the assembly of the lithium cell. The increase then becomes slower and with irregular fluctuations. This phenomenon can be explained in terms of the reactivity of the electrolyte towards the lithium electrode [28, 33, 34, 35]. As soon as the cell is assembled, a series of reactions between the electrolyte and lithium electrode take place which include the chemical decomposition of propylene carbonate in the presence of lithium, the decomposition of LiClO$_4$, and the reaction of trace water with lithium [32, 34, 35]. These reactions will result in a passivation layer between the lithium electrode and the electrolyte, which will hinder the ion transport and lead to a rapid increase of the resistance of the passivation layer. The thickness and morphology of the passivation layer vary with time, and in response to such variations the R_i values increase in a corresponding way, as can be seen in Fig. 7.

Ostrovskii et al. [36] reported the characterization of molecular interactions and interfacial resistance in two

Fig. 6 Variation of the resistance values of the polymer electrolyte with storage time in a SS|ABS/PMMA(6/4)-60%(EC + PC)-4.8%LiClO$_4$|SS cell stored and tested at 25 °C

Fig. 7 Time evolution of the bulk resistance (R_b) of the electrolyte and the interface resistance (R_i) of a Li|ABS/PMMA(6/4)-60%(EC + PC)-4.8%LiClO$_4$|Li cell stored at 25 °C under open circuit conditions

different plasticized (gel-type) polymer electrolytes based on polyacrylonitrile (PAN) and PMMA, respectively. They showed that PMMA was much more stable than PAN in contact with electrolyte solutions, and therefore stable in contact with the lithium electrode. Compared with their results, the interfacial stability of our ABS/PMMA-based polymer electrolyte is better than that based on PAN, but not as good as the one based on PMMA. This can be explained in view of the dual-phase structure of our electrolyte system in which the plasticizer-rich phase formed by the compatibility of PMMA with plasticizer provides the ion path, and the ABS-rich phase with less plasticizer provides the mechanical support. The plasticizer-rich phase, containing mainly PMMA and plasticizer, is less reactive towards the lithium electrode, just like the PMMA-based electrolyte in which the liquid electrolyte solutions are embedded in a "passive" host polymer. On the other hand, the ABS-rich phase, containing the acrylonitrile group, shows some characteristics of the PAN-based system with strong polymer-liquid electrolyte interactions, which makes the polymer matrix groups the species reacting with the lithium electrode [21, 36]. The ABS-rich phase reduces, therefore, the overall compatibility of the ABS/PMMA-based electrolyte with lithium electrodes compared with the pure PMMA-based system.

The reaction between the electrolyte and lithium electrodes may also affect the morphology of the bulk electrolyte, because of the coordination of lithium ions to the acrylonitrile group in ABS [21, 23, 36]. This would lead then to a slight increase in its resistance (R_b) during the first few hours after the assembly of the cell, as can be seen from Fig. 7.

Figure 8 illustrates the impedance spectra at different temperatures for a lithium symmetric cell with a plasticized polymer electrolyte based on ABS/PMMA. The cell had been stored in a dry box at 25 °C under open circuit conditions for two weeks prior to measurement. The decrease of the semicircle in the high-frequency range with increasing temperature indicates the decrease of the R_b and R_i values with temperature. This observation is consistent with the fact that the ionic conductivity of the polymer electrolyte increases with increasing temperature. It also could be deduced that the passivation film would become more ion conductive with an increase of temperature. At the same time, the frequency of the maximum of the semicircle for the interface shifts towards a higher frequency as the temperature increases.

Using the SPL model and its equivalent circuit, the values of R_b and R_i of the cell at different temperatures can be obtained from the impedance spectra. The results are shown in Fig. 9. A linear relationship of log$R$ versus reciprocal temperature is observed for both the resistances. This is characteristic of ionic conduction behavior in solid electrolytes, indicating that a solid passivation film has formed between the lithium electrode and the electrolyte. The linear relationship of log$R$ vs. T^{-1} also suggests that the ionic conduction in the bulk electrolyte and across the interface of the lithium/passivation film/
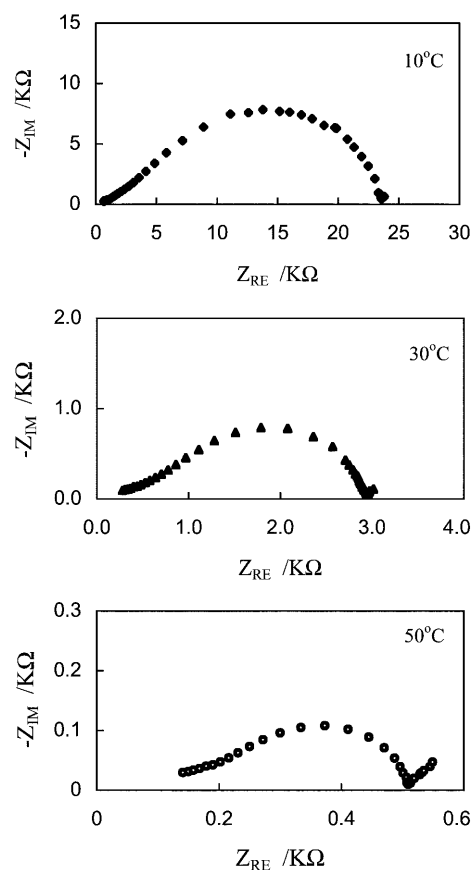
Fig. 8 The impedance responses at different temperatures of a Li|ABS/PMMA(6/4)-(60%)(EC + PC)-4.8%LiClO$_4$|Li cell stored at 25 °C under open circuit conditions for two weeks prior to measurements
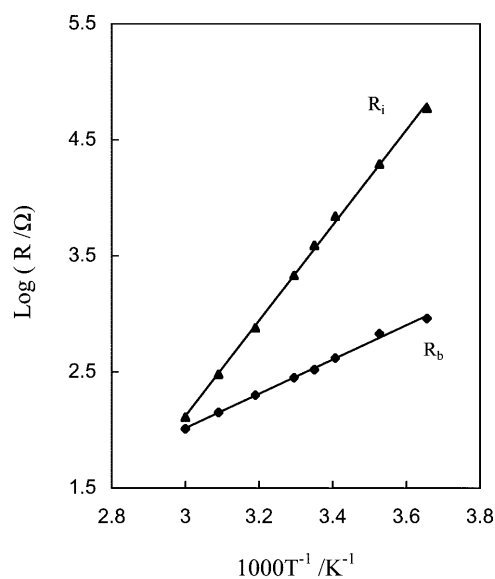
Fig. 9 Temperature dependence of the resistances (R_b, R_i) of a Li|ABS/PMMA(6/4)-60%(EC + PC)-4.8%LiClO$_4$|Li cell stored at 25 °C under open circuit conditions for two weeks

electrolyte all followed Arrhenius behavior in the temperature range of the experiment. Based on this linear relationship, the apparent activation energy associated with the ionic transport through the passivation film (E_a) was determined as 0.36 eV. It compares well with those reported for PEO-PPO/PMMA blend-based electrolytes, whose values vary within 0.3–0.6 eV according to the composition of the electrolytes and the storage time of the cell [37]. However, it is smaller than the activation energy of 0.65 eV for lithium transport through LiOH and/or Li_2O passivation films reported by Radman [38] for lithium electrodes in liquid electrolytes containing a small amount of water. Therefore, it is reasonably to say that the passivation film in our system would be different in composition from the LiOH and/or Li_2O passivation films.

Conclusions

The highest conductivity value of the dual-phase plasticized polymer electrolytes based on ABS/PMMA blends was obtained when the salt content was 4.8%. The transference numbers of the polymer electrolytes were determined by the steady-state current method and the T_+ values of the electrolytes were around 0.40 when the $LiClO_4$ content was 1.6–6.3%. The electrolyte system had a stable electrochemical stability window up to 4.5 V. An interfacial stability study showed a passivation phenomenon, which could be described using the SPL model. The time evolution of the impedance responses showed a fast growth of a passivation film during the initial period after assembly of the cell, followed by a slower growth with irregular fluctuations. The interfacial stability of the plasticized ABS/PMMA-based electrolytes was better than that based on PAN but not as good as the one based on PMMA. The temperature dependence of R_b and R_i indicated that the ionic conduction in the bulk electrolyte and across the interface of the lithium/passivation film/electrolyte all followed Arrhenius behavior.

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