Blending Poly(methyl methacrylate) and Poly(styrene-*co*-acrylonitrile) as Composite Polymer Electrolyte

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ABSTRACT: A blend of poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (PSAN) has been evaluated as a composite polymer electrolyte by means of differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, ac impedance measurements, and linear sweep voltammetry (LSV). The blends show an interaction with the Li^+ ions when complexed with lithium perchlorate ($LiClO_4$), which results in an increase in the glass-transition temperature (T_g) of the blends. The purpose of using PSAN as another component of the blend is to improve the poor mechanical properties of PMMA-based plasticized electrolytes. The mechanical property is further improved by introducing fumed silica as inert filler, and hence the liquid electrolyte uptake and ionic conductivity of the composite systems are increased. Room-temperature conductivity of the order of 10^{-4} S/cm has been achieved for one of the composite electrolytes made from a 1/1 blend of PSAN and PMMA containing 120% liquid electrolyte [$1M$ $LiClO_4$/propylene carbonate (PC)] and 10% fumed silica. These systems also showed good compatibility with Li electrodes and sufficient electrochemical stability for safe operation in Li batteries. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1319–1328, 2001

Key words: composite electrolyte; ionic conductivity; PMMA; PSAN; electrochemical stability

INTRODUCTION

Despite extensive research effort on polymer electrolytes,[1] the preparation of a polymer electrolyte having a combination of processability and physical properties of conventional thermoplastics with high ionic conductivity required for application in Li batteries is yet to be realized. For battery applications, high conductivity must be com-plemented by good dimensional stability because the polymer electrolyte will also function as a separator in the battery, providing electrical insulation between the anode and cathode. Of the many polymers, a polyethylene oxide (PEO)–based electrolyte is the earliest and is so far the most widely studied. The ionic conductivity of PEO lies in the range of 10^{-8} to 10^{-7} S/cm at ambient temperature, which is too low for application in Li batteries. The obstacle originates, first, from the high degree of crystallinity, which is unfavorable for the ionic mobility in the salt-doped PEOs and, second, the low solubility of salt in the amorphous phase. To improve the conductivity, modifications of the PEO system and evaluation of different plasticizers to PEOs have been

extensively studied.[2] The aim of the investigations for ionic conductivity of polymer electrolyte approaching those of their liquid counterparts (ca. 10^{-3} S/cm at room temperature) was to incorporate structural features in the electrolyte that increase the mobility and concentration of ionic charge carriers. The most striking advancement in the conductivity of polymer electrolytes has been achieved through the incorporation of substantial amounts of plasticizers. However, the effectiveness of plasticizers in PEO systems has not been achieved to a technically justified level of conductivity (ca. 10^{-3} S/cm at room temperature), without expending mechanical rigidity. Besides, the PEO-based gel electrolytes, polymers such as poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), poly(vinylidine fluoride) (PVdF), and poly(vinyl chloride) (PVC) were also tried as host matrices for gel electrolytes.[3–8]

The use of PMMA as a gel electrolyte was previously reported by Iijima et al.[9] and later by Bohnke et al.[6] They reported a conductivity of the order of 10^{-3} S/cm at 25°C for a homogeneous and transparent gel containing 15–20% of PMMA. The presence of high molecular weight PMMA imparts high macroscopic viscosity to the system without significantly diminishing the conductivity of the liquid electrolyte. Bohnke et al.[10,11] also reported in their later studies that the conductivity of the PMMA gel electrolytes decreases with an increase in PMMA content, varying in the range of 10^{-5} to 10^{-4} S/cm at room temperature. A change in the conduction path was reported at around 30–35 wt % of PMMA. Afterward, Appetecchi et al.[12] examined PMMA-based plasticized electrolytes in film form and reported conductivity of the order of 5×10^{-3} S/cm at 60°C. However, the plasticized PMMA electrolytes suffer from poor, gel-like mechanical properties; producing freestanding film is not possible at higher plasticizer concentration. Hence, an improvement in the mechanical property is required for successful application as a polymer electrolyte.

In this work, we report a blend system of PMMA with styrene–acrylonitrile copolymer (PSAN) as host and a solution of lithium perchlorate (LiClO$_4$) in propylene carbonate (PC) as liquid electrolyte, to overcome the poor mechanical property of the plasticized PMMA system. The presence of rigid polystyrene units in the copolymer imparts higher mechanical strength to the blend. A blend of PMMA with PVC was previously studied by Rhoo et al.,[13] who reported an increase

in conductivity with decreasing PVC/PMMA ratio and with increasing plasticizer content. In the present study, to enhance further the mechanical property of the blend system and hence to increase the liquid electrolyte uptake and ionic conductivity, fumed silica was introduced into the blend system. Electrolytes with good mechanical property up to 85°C and ionic conductivity of the order of 10^{-4} S/cm at room temperature are reported. The polymer electrolytes, made by complexing the blends with LiClO$_4$, are characterized by differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, and ac impedance measurements. The interfacial behavior and electrochemical stability of the corresponding cells using the composite gel electrolyte were also tested by time evolution ac impedance measurements and linear sweep voltammetry.

EXPERIMENTAL

Materials

Poly(styrene-*co*-acrylonitrile) (Aldrich, Milwaukee, WI) was used as received, having 25 wt % acrylonitrile and weight-average molecular weight 165,000. Methyl methacrylate (MMA; Aldrich) was alkali washed, dried, and distilled under reduced pressure before polymerization. LiClO$_4$ was dehydrated at 120°C under reduced pressure for 72 h. Fumed silica (Aldrich), with a surface area of 380 m^2/g, was heated at 150°C under vacuum for 48 h and then kept inside an argon-filled glove box (Vacuum Atmosphere Company) for several days before use. Propylene carbonate (PC; Aldrich) and tetrahydrofuran (THF; Tedia) were dehydrated overnight by using a molecular sieve before use.

Polymerization of MMA

Polymerization of MMA was carried out in a 250-ml volumetric flask at 60°C under N$_2$ atmosphere using azobisisobutyronitrile (AIBN) as initiator in a toluene medium. The distilled monomer, initiator, and the solvent were taken in the volumetric flask, deaerated by purging dry nitrogen gas for 10 min, stoppered, and polymerized at 60°C. After polymerization, the mixture was allowed to cool down to room temperature, after which the polymer was precipitated into excess methanol. It was purified by reprecipitating twice in methanol after dissolution in toluene, followed

by several washings with methanol and drying at 120°C for 72 h. The molecular weight of the synthesized polymer was determined by gel-permeation chromatography (Shimadzu, Japan). The molecular weight (M_W) and polydispersity index of the synthesized PMMA are 102,000 and 1.51, respectively.

Preparation of the Polymer Electrolytes

Both polymers were dissolved separately in THF to make 10 wt % solutions. The two solutions were mixed in different proportions to make blends of PSAN and PMMA. Films were cast on glass petri dishes for DSC experiments. For electrical measurements, the required amount of a liquid electrolyte ($1M$ LiClO$_4$ in PC) was mixed with the 10 wt % solutions of the individual polymers and the blends. The liquid electrolyte concentration was varied from 25 to 120 wt %, based on the weight of the polymers. The mixtures were stirred magnetically to make a homogeneous solution. At this stage, the required amount of fumed silica was added and stirred again. When the mixture was completely homogenized, films were cast in Teflon cuvettes. THF was allowed to evaporate slowly at room temperature for several days. The absence of THF was confirmed by ^{1}H–NMR. All the operations of preparing electrolytes were done in an argon-filled dry box (Vacuum Atmosphere Company). The composition of each of the samples is given in respective tables.

DSC Measurement

DSC measurements were carried out using a DSC 2010 differential scanning calorimeter (TA Instruments) over a temperature range of 0 to 150°C at a scan rate of 10°C/min. The dry samples were first annealed at 150°C for 10 min, cooled down to room temperature, and then scanned. For the plasticized samples, the annealing operation was not done, to avoid any loss of PC. All thermograms were baseline corrected and calibrated using Indium metal. Glass-transition temperature (T_g) was reported as the midpoint of the transition process.

FTIR Measurement

FTIR spectra were taken at ambient temperature using a Nicolet 550 equipment with a wave number resolution of 4 cm^{-1}. Samples for FTIR were prepared by casting films directly on KBr pellets from a 5 wt % solution and then drying at 120°C for 48 h. A total of 128 scans were signal averaged to increase the s/n ratio.

Ac Impedance Measurement

Impedance measurements of the polymer electrolytes were performed using thin films made by casting from solution and subsequent drying (as described earlier). Film thickness was maintained in the range of 200 to 250 μm and the area of contact was 0.785 cm^2. For measurement of ionic conductivity, the samples were sandwiched between two stainless steel electrodes, whereas for investigation of the interfacial phenomena, the samples were sandwiched between two Li electrodes. The electrodes were then fixed in an airtight double-wall glass cell, through the outer jacket of which thermostated water was circulated for measurements at different temperatures. Cell assembly was carried out in a dry argon atmosphere inside a glove box (Vacuum Atmosphere Company). Conductivity measurements were performed using a Autolab PGSTAT 30 equipment (Eco Chemie B.V., The Netherlands) with the help of Frequency Response Analysis system software under an oscillation potential of 10 mV. The interfacial behavior of the Li/PE/Li cell was studied by ac impedance measurements under open circuit potential (OCP) condition.

Linear Sweep Voltammetry

Three electrode-laminated cells were assembled inside a glove box for LSV experiments. Stainless steel (SS) was used as the working electrode and lithium metal was used both as a counter and as a reference electrode. LSV measurements were carried out using Autolab PGSTAT 30 potentiostat/galvanostat equipment (Eco Chemie B.V.).

RESULTS AND DISCUSSION

Interaction of Li$^+$ Ions with the Polymers

The thermal behavior of PSAN, PMMA, and their three blends is shown in Figure 1 and the T_g values are summarized in Table I. All the blend films appeared transparent and show only one glass-transition temperature resulting from the miscibility of PMMA and PSAN. The T_g for PSAN is about 79°C and that of PMMA is about 122°C.
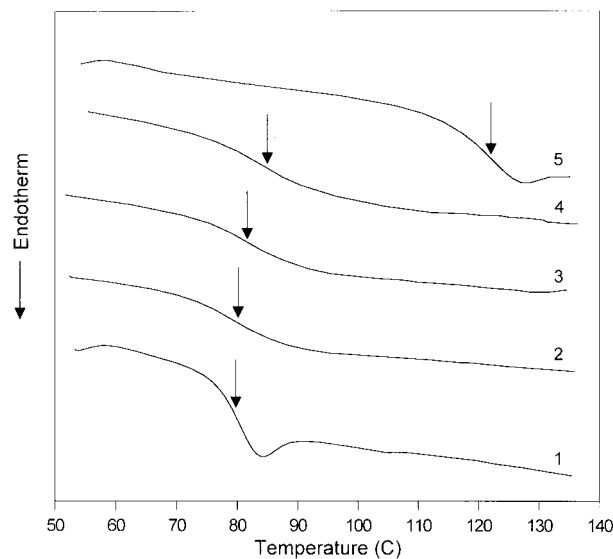
Figure 1 Thermal-transition temperatures of (1) sample 1, (2) sample 2, (3) sample 3, (4) sample 4, and (5) sample 5.

Table II Thermal Behavior of Sample 3 Containing Different Amounts of Liquid Electrolyte (1M LiClO$_4$/PC)

Sample	3	6	7	8
Liquid electrolyte (wt %)	0	25	50	75
$T_g{}^a$ (°C)	81.52	52.81	29.28	23.16

[a] The results are as available from the instrument; accuracy is ±1°C.

The three blends show T_g values in between the T_g's of PSAN and PMMA, and the T_g values are found to increase with the increase in PMMA content in the blends. To see the effect of liquid electrolyte on the thermal behavior, different concentrations of liquid electrolyte were mixed with sample 3, the data of which are presented in Table II. As expected, the T_g of the plasticized electrolytes was found to decrease with an increase in liquid electrolyte concentration. This may be attributed to the increase in segmental motion of the polymer chains in the presence of the plasticizer. The lowering of T_g is well observed in plasticized polymer electrolytes,[14] in which the plasticizers increase the distance between the polymer chains and, hence, reduce the possibility of formation of crosslinks among the polymer chains through Li$^+$ ions.

To understand the role of the Li salt on the thermal behavior of the blends, sample 3 was complexed with three different concentrations of LiClO$_4$, close to the LiClO$_4$ concentration of samples 6, 7, and 8, respectively, and then the organic solvent (THF) was removed by evacuation. The DSC results of these three samples are shown in Table III. All three plasticizer-free samples show a single T_g, indicating the absence of phase separation in the presence of LiClO$_4$. The presence of Li$^+$ ions does not lead to any change in the macroscopic phase structure of the blend. The DSC results reveal that there is an increase in the blend T_g with increasing salt concentration. Such an increase in T_g of the Li salt–polymer complexes is well known,[1a] and results from the interaction of Li$^+$ ions with the electron-rich coordinating sites (—NH, $\rangle$C=O, —O—, —CN, etc.), leading to the formation of transient crosslinks. In our blend system, the presence of —CN groups in PSAN and —C(O)O groups in PMMA are also very likely to undergo such a type of coordination with the Li$^+$ ions. To investigate further the interaction of Li$^+$ ions with the —CN and —C(O)O groups of the blend system, IR spectral features of the undoped and doped blends were analyzed.

For analysis of the FTIR spectra of the dry samples, two regions, which are most likely to be affected by coordination with the Li$^+$ ions (i.e., the —CN and the $\rangle$C=O region), were considered. The FTIR spectra of the —CN and $\rangle$C=O region for the undoped and the three doped samples are

Table I Thermal-Transition Temperatures of PSAN, PMMA, and Their Blends

Sample	1	2	3	4	5
Composition (PSAN/PMMA)	100/0	70/30	50/50	30/70	0/100
$T_g{}^a$ (°C)	79.07	80.41	81.52	86.08	122.08

[a] The results are as available from the instrument; accuracy is ±1°C.

Table III   Thermal Behavior of Sample 3 Containing Different Concentrations of LiClO$_4$

Sample	3	9	10	11
LiClO$_4$ conc. (mmol/g)	0.0	0.5	1.0	1.5
T_g[a] (°C)	81.52	103.17	106.97	112.34

[a] The results are as available from the instrument; accuracy is ±1°C.

presented in Figure 2(a) and (b). The variation of the peak positions with salt concentration is given in Table IV. As is evident from Table IV, the $\rangle$C=O peak is shifted to a lower frequency with an increase in salt concentration, whereas there is no change in the peak position for the —CN group. Shifting of the $\rangle$C=O absorption peak to a lower frequency may be considered as the evidence of coordination of Li$^+$ ions with the $\rangle$C=O groups. Coordination of Li$^+$ ions with the electron-rich oxygen atoms of the $\rangle$C=O groups may lead to weakening of the C=O bond, resulting in a shifting of the peak to a lower frequency.

The observation that the —CN stretching vibration remains unchanged with salt concentration is in line with results of Wang et al.[15] for a polyacrylonitrile system. However, they observed a shoulder in the region of 2270 cm^{-1} when the concentration of Li salt is high enough ($\sim$ 25%).

They assigned this shoulder to an associate of —CN groups and the Li$^+$ ions, which is formed by the interaction of an unbound electron pair in the N atom of —CN groups with the electron-deficient Li$^+$ ions. The absence of the shoulder at 2270 cm^{-1} in our case may be the result of the lower concentration of LiClO$_4$ (max 10%) used. Another possible explanation might be the competition of $\rangle$C=O and —CN groups to be coordinated by the Li$^+$ ions. As the C≡N bond is much stronger than the C=O bond, interaction of Li$^+$ ions with —CN groups may result in negligible effect compared to that with $\rangle$C=O groups. Based on this discussion, it is reasonable to mention that PSAN competes with PMMA to interact with Li$^+$ ions and hence increases the ability of the blend to solvate more Li salts. Moreover, the presence of polystyrene units in PSAN imparts more rigidity to the blend system, which improves the gel-like mechanical property of PMMA-based plasticized electrolytes.

Conduction Behavior

To study the conduction behavior of the charge carriers in the plasticized blends, we measured the ionic conductivity of the polymer electrolytes placed in between two stainless steel electrodes at different temperatures, by varying the blend composition, liquid electrolyte concentration, Li salt concentration, and the inert filler (fumed silica) loading. In the first instance, the effect of blend
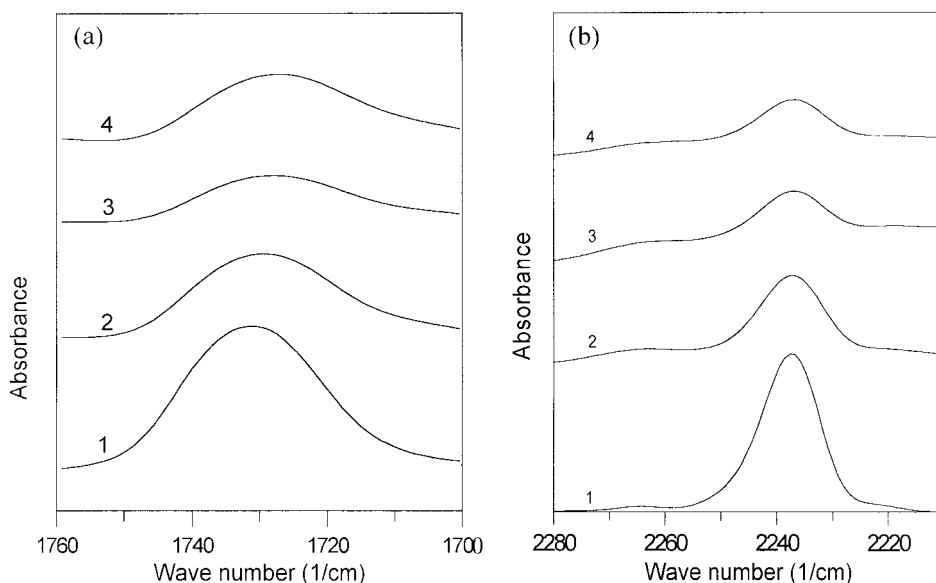

Figure 2   FTIR spectra of the (a) $\rangle$C=O and (b) —CN stretching region of (1) sample 3, (2) sample 9, (3) sample 10, and (4) sample 11.

Table IV   Variation of $\rangle$C$=$O and —CN Stretching Vibrations of Sample 3 with LiClO$_4$ Concentration

Sample	LiClO$_4$ Conc. (mmol/g)	$\rangle$C$=$O Stretching (cm^{-1})	—CN Stretching (cm^{-1})
3	0.0	1731	2237
9	0.5	1729	2237
10	1.0	1727	2237
11	1.5	1726	2237

composition on the ionic conductivity was studied at different temperatures and two different concentrations of liquid electrolyte. Variation of the ionic conductivity data for two different liquid electrolyte concentrations at 85°C with blend composition is presented in Figure 3. It is evident from the figure that, for a particular concentration of liquid electrolyte, conductivity is increased with increased concentration of PSAN, to a maximum at 50 to 60 wt % of PSAN. This may be explained on the basis of stronger interaction of PC with the PMMA units compared to that with the PSAN units.[16] At a lower concentration of PSAN, the plasticized electrolyte can be considered as a homogeneous mixture of all the components. As a result, the movement of the ions will be dependent mainly on the free volume of the matrix polymer. On the other hand, at a higher PSAN concentration, the blend electrolyte may contain two phases resulting from significantly different interactions of PC with PSAN and PMMA.[16] One of the two phases is the liquid electrolyte–rich phase and the other is the gel–polymer phase. Since the mobility of the ions is higher in the liquid electrolyte–rich phase, the ionic conductivity is increased with an increase in

PSAN concentration (up to 50 to 60 wt %). When the concentration of PSAN is increased further (beyond 60 wt %), conductivity was found to decrease slightly. At this stage, a part of the charge carriers may also migrate through the gel–polymer phase, in which the mobility of the charge carriers may also migrate through the gel–polymer phase, in which the mobility of the charge carriers is relatively slow and hence the conductivity is decreased. It is to be noted that with increasing PMMA content in the blends, addition of liquid electrolyte makes the blend more flexible. Hence, for higher ionic conductivity and optimum mechanical property, the blend composition of PSAN/PMMA is maintained at 1/1 (50 wt % PSAN) for further experiments.

For the purpose of optimization of liquid electrolyte concentration on the conductivity of the blends, four plasticized electrolytes were prepared by mixing 25, 50, 75, and 100 wt % (with respect to the weight of the polymers) of liquid electrolyte with the blend polymer (sample 3). The temperature dependence of ionic conductivity of the first three plasticized electrolytes is presented in Figure 4. The fourth one, containing 100 wt % of liquid electrolyte, becomes much too flexible and sticky, and hence conductivity of this electrolyte could not be measured. An examination of Figure 4 indicates that the ionic conductivity of the plasticized electrolytes can be explained with the help of the Vogel–Tamman–Fulcher (VTF) equation. As is evident from the figure, the activation energy is decreased as the conductivity of the samples is increased. Regarding the relation of conductivity with the concentration of liquid electrolyte in the measured range of temperature and up to a liquid electrolyte concentration of 75 wt %, conductivity was found to increase with an increase in liquid electrolyte concentration. The reason for such increase in conductivity with liquid electrolyte concentration is
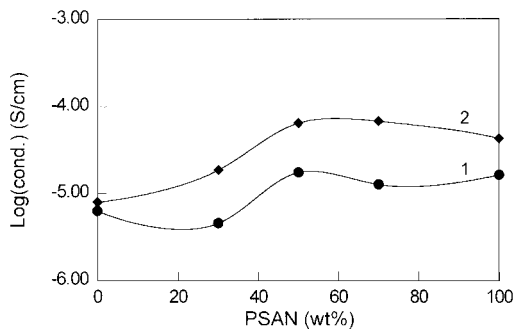
Figure 3 Variation of conductivity of the blend electrolytes at 85°C with composition, containing (1) 50% and (2) 75% liquid electrolyte.
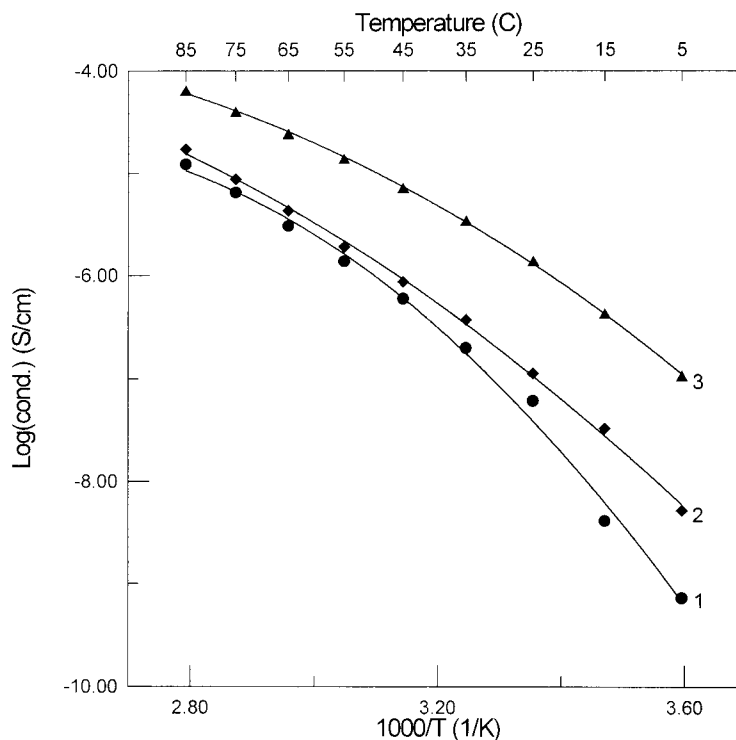
Figure 4 Temperature dependence of conductivity of sample 3 containing different amounts of $1M$ Li-perchlorate/PC: (1) 25%, (2) 50%, and (3) 75%.

the increased number of charge carriers and higher mobility at higher liquid electrolyte concentration.

Because the conductivity of the electrolytes is not high enough (ca. 10^{-4} S/cm at 85°C), an attempt was made to see whether conductivity can be increased by increasing the salt concentration, while maintaining good mechanical strength by keeping the plasticizer concentration constant at 75 wt %. Figure 5 presents the variation of conductivity with $LiClO_4$ content at two different temperatures (5 and 85°C). It was found that the conductivity is increased with an increase in $LiClO_4$ concentration to a maximum value when the salt concentration is 1.0 mmol/g of the blend, and then decreased with an increase in salt concentration. The reason for the increase in conductivity with salt concentration (up to 1.0 mmol/g) is the increase in the number of charge carriers. The decrease in conductivity at a salt concentration higher than 1.0 mmol/g of the blend may be the result of the formation of charge-neutral contact ion pairs[17,18] at higher salt concentration. Being neutral in nature, the ion pairs do not contribute to the conductivity and hence the electrolytes

having a higher concentration of $LiClO_4$ show lower conductivity.

It is quite well known that addition of inorganic fillers leads to an improvement in the me-
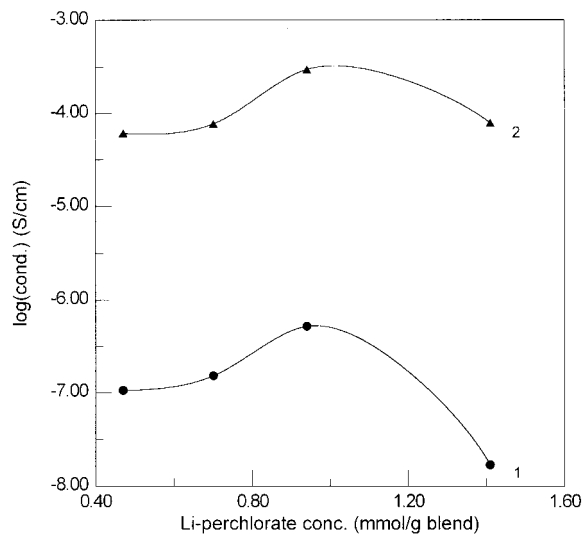

Figure 5 Variation of conductivity of sample 3 plasticized with 75% PC against Li-perchlorate concentration at (1) 5°C and (2) 85°C.
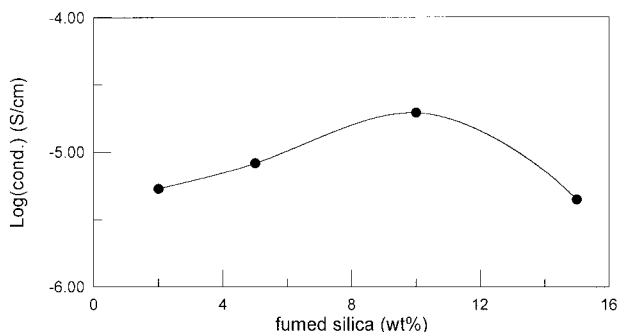
Figure 6 Variation of conductivity of sample 3, plasticized with 100% liquid electrolyte, with silica content at 25°C.

chanical and electrochemical characteristics of polymer electrolytes.[19-22] To enhance the mechanical property of the gelled electrolytes and, hence, to increase the concentration of liquid electrolyte in the host composite, fumed silica was added in different ratios to the blend system. The effect of fumed silica on the conductivity of the electrolytes is shown in Figure 6. It is evident from the figure that conductivity is maximum at about 10 wt % (with respect to the weight of the polymers) of silica. Beyond that, conductivity is decreased with an increase in silica concentration. The increase in conductivity with an increase in silica concentration (up to 10 wt % level) is associated with the increase in ability of the composite to hold the liquid electrolyte, because it has a high adsorption capability resulting from the very high surface area (380 m^2/g). Further addition of fumed silica may lead to the formation of aggregates, which restrict the movement of the ions, resulting in a decrease in ionic conductivity.[23] At a concentration of about 10 wt %, the finely divided silica particles remain homogeneously dispersed in the liquid electrolyte and form a three-dimensional network, thus increasing the mechanical strength of the electrolyte.

Introduction of 10 wt % fumed silica increases the ability of the blend to retain liquid electrolyte higher than 100 wt %, where the composite electrolytes are obtained in the form of freestanding film with reasonably good mechanical property. Beyond 100 wt % liquid electrolytes, the composites become soft and hence difficult to handle. The conductivity variation of one of the polymer-fumed silica composites containing 120 wt % liquid electrolyte against reciprocal temperature is shown in Figure 7. It is to be noted that conduc-

tivity of the order of 10^{-4} S/cm at room temperature is achieved for the composite electrolyte based on a 1 : 1 blend of PSAN and PMMA, 10 wt % of fumed silica, and 120 wt % of liquid electrolyte.

Interfacial Behavior and Electrochemical Stability

After attaining acceptable ionic conductivity and mechanical properties of the composite electrolytes, we attempted to investigate the interfacial behavior of the electrolyte in contact with Li electrodes under prolonged exposure, to check their compatibility with Li metal. For successful performance of a polymer electrolyte in Li batteries, good compatibility of the electrolyte with Li metal is essential. For this purpose ac impedance of Li/polymer electrolyte (PE)/Li cell under open circuit potential conditions at 25°C was measured at different time intervals. Figure 8 presents the time-evolution response of ac impedance of one of the composite electrolytes containing 10 wt % fumed silica and 100 wt % liquid electrolyte at ambient temperature. From these ac impedance spectra, the electrolyte resistance (R_e) and the interfacial resistance (R_i) were calculated and plotted against time in Figure 9. It is evident from Figure 9 that the electrolyte resistance remains
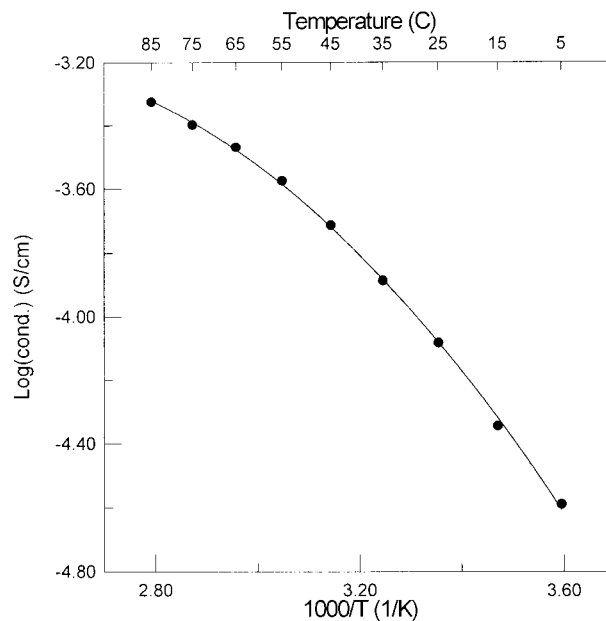

Figure 7 Temperature dependence of conductivity of sample 3 containing 120% liquid electrolyte and 10% fumed silica.
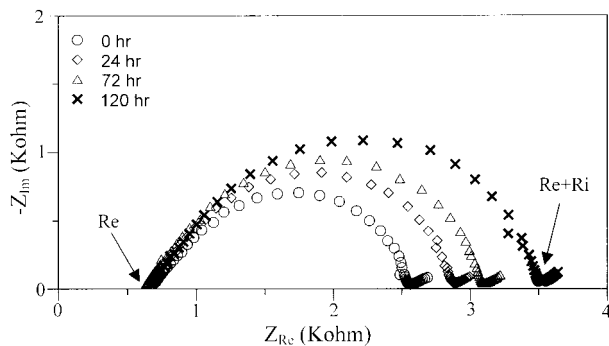
Figure 8 Time evolution ac impedance spectra of a Li/PE/Li cell at 25°C; the PE consists of sample 3, 100% liquid electrolyte, and 10% fumed silica.

Figure 10 Electrochemical stability window of the PE by LSV method; the PE consists of sample 3, 100% liquid electrolyte, and 10% fumed silica.

unaltered with time. This indicates good compatibility of the liquid electrolyte with the polymer blend, which prevents loss of any liquid electrolyte with time. The interfacial resistance of the Li/PE/Li cell is found to increase with time. However, the rate of increase is appreciably decreased with time. The initial increase in R_i may be attributed to the formation of a passive layer resulting from the reaction of Li with the composite electrolyte. The composite electrolyte contains an aprotic solvent (PC), which reacts with Li metal[24,25] and consequently passivates the Li electrode. The decrease in the rate of increase of R_i with time indicates very slow growth of the passivating layer and hence the stability of the interface.

To ascertain the electrochemical stability of the composite electrolyte, LSV of the laminated three electrode cells were performed at ambient temperature. The linear sweep voltammogram of one of the composite electrolytes is presented in Figure 10. The working electrode potential of the cell
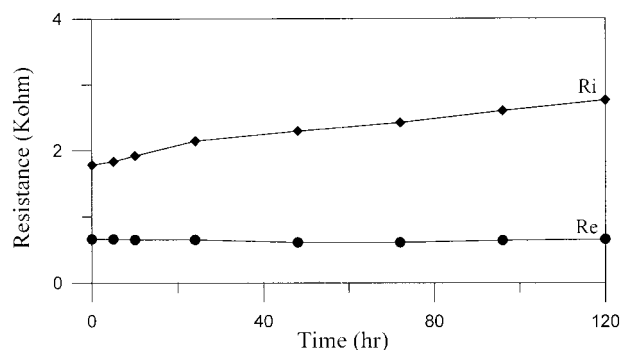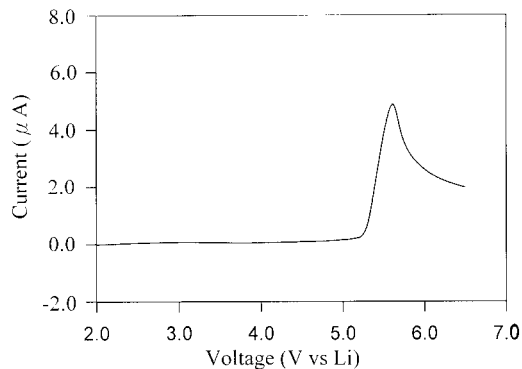
was varied from 2.0 to 8.0 V (versus Li) at a sweep rate of 5 mV/s. It is evident from Figure 10 that there is no electrochemical reaction in the potential range 2.0 to 5.3 V. The onset of current flow at 5.3 V is associated with the decomposition of the electrolyte. The anodic stability limit of the electrolyte is 5.3 V versus that of Li. Hence it may be concluded that the polymer blend (PSAN/PMMA) does not have any effect on the electrochemical stability of the electrolyte. This can be safely used as a composite polymer electrolyte in rechargeable lithium batteries.

Figure 9 Variation of R_e and R_i of the Li/PE/Li cell with storage time at 25°C.

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