

Preparation and characterization of PVC/PMMA blend polymer electrolytes complexed with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$

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Abstract

Thin films of poly(vinylchloride) (PVC)/poly(methylmethacrylate) (PMMA) blend polymer electrolytes plasticized with a combination of ethylene carbonate (EC) and propylene carbonate (PC) and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ as salt have been prepared by solution casting technique. The prepared films were subjected to a.c. impedance measurements as a function of temperature ranging from -30 to 70 °C. Also, PVC/PMMA composite electrolytes were prepared using TiO_2 as inorganic filler. The effect of liquid plasticizer and inorganic filler on the interfacial stability of the blend polymer electrolytes was studied. The prepared films were also subjected to TG-DTA analysis and the results were discussed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymer electrolytes are extensively studied in the last two decades due to their potential applications in various electrochemical devices, such as high-energy density batteries, electrochromic devices and chemical sensors [1–3]. The poly(ethylene oxide) (PEO)-based electrolytes have been excluded from practical applications due to the high melting point of its crystalline phase and co-ordination of Li^+ ion with oxygen atom

in the PEO amorphous phase; these polymer electrolytes have low ionic conductivities in the order of 10^{-4} to 10^{-5} S cm^{-1} at room temperature [4]. Poly(acrylonitrile) (PAN) based gel electrolytes, on the other hand, are the most widely investigated gel electrolytes with appreciable conductivities in the order of 10^{-3} S cm^{-1} at 20 °C. Although PAN-based electrolytes exhibit exceptional properties like ionic conductivity, thermal stability and lithium transference number, its poor compatibility with lithium metal anode excludes it from practical applications [5,6]. Compared with PAN-based gels, the poly(methylmethacrylate) (PMMA) gels were found to have better interfacial properties towards the lithium electrodes [7,8] but its poor mechanical property remains as a problem area. Recent investigations on poly(vinyl-

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chloride) (PVC) electrolytes showed minimum percent capacity loss but this type of gels is more reactive towards lithium metal than PAN-based gels [9]. The importance of PVC/PMMA blend polymer electrolytes and their electrochemical properties have already been explored by us [10–13], in which PVC acts as a phase-separated mechanical rigid network that provides the desired mechanical strength to the polymer films.

Recently, with a view of making dimensionally stable with appreciable mechanical properties for lithium batteries, high surface area particle films such as ZrO_2 , TiO_2 , Al_2O_3 hydrophobic surface fumed silica and fiber glass were introduced into polymer matrices to obtain the so-called composite electrolytes. The general concept of adding ceramic powders to polymer electrolytes is not new. This procedure has been successfully employed from imposing mechanical and interfacial properties of the PEO-based electrolytes [14,15]. However, to the best of our knowledge, this procedure has never been used for the blend polymer electrolytes. In the present study, PVC-PMMA blend polymer electrolytes have been prepared with ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ as salt. Also, PVC/PMMA composite electrolytes were prepared with TiO_2 inorganic filler. An attempt has also been made to compare the effect of inorganic filler and liquid plasticizer in terms of compatibility towards lithium metal anode. (Table 1).

Table 1
Composition of polymer, plasticizer and lithium salt

Sample	Weight of polymer (g)		Weight of plasticizer (g)		Weight of salt (g)
	PVC	PMMA	EC	PC	$\text{LiN}(\text{CF}_3\text{SO}_2)_2$
S1	36.75	12.25	25	15	1
S2	36	12	30	20	2
S3	31.5	10.5	32	23	3
S4	27	9	35	25	4
S5	18.75	6.25	40	30	5
S6	0	35	35	25	5
S7	9	27	35	25	5
S8	17.5	17.5	35	25	5
S9	35	0	35	25	5
S10	40	35	10	10	5
S11	40	35	20 (TiO_2)		5

Plasticizer content = (Weight of plasticizer content / Weight of electrolyte) \times 100.

2. Experimental procedure

Both PVC (mol. wt. 1.5×10^5) and PMMA (mol. wt. 3.5×10^5) (Aldrich, USA) were used in the present study. As plasticizers, ethylene carbonate (EC) and propylene carbonate (PC) (Merck, Germany) were used without further purification. The lithium salt, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, was dried at 70 °C and kept under vacuum for 48 h before use. All electrolytes were prepared by forming a slurry with the appropriate amounts of polymers, plasticizers and salt in anhydrous tetrahydrofuran (THF) and casting as films using a doctor blade method as reported in our earlier reports [10–13]. After evaporation of THF, the films were further dried in a temperature-controlled oven at 50 °C for 8 h to remove traces of THF. All operations were carried out under argon atmosphere in a glove box and stored in a desiccator. The composite polymer electrolytes were also prepared as described elsewhere [14,15]. The prepared films were subjected to a.c. impedance measurements at different temperatures ranging from –30 to 70 °C using an impedance analyzer (EG and G Princeton Electrochemical analyzer, Model 6310A USA). The films were also subjected to TG/DTA (Rigaku TG101D, Japan) analysis and are discussed.

3. Results and discussion

3.1. Ionic conductivity

Fig. 1 shows the temperature dependence of ionic conductivity for different plasticizer content of ethylene carbonate and propylene carbonate for fixed PVC/PMMA (25:75) blend ratio. In ionic conductivity measurements, the effect of 2% residual water on $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ has not been taken in to account. It is evident from figure that the ionic conductivity increases with the increase of salt concentration, to a level, i.e. up to 60% of the plasticizer content, and then decreases. The same trend was observed for all the temperatures studied from –30 to 70 °C. The maximum on the conductivity–salt concentration curve may be explained as follows. Up to the concentration level, corresponding to the conductivity plateau, more and more number of ions are made available for electrolytic conduction. At higher con-

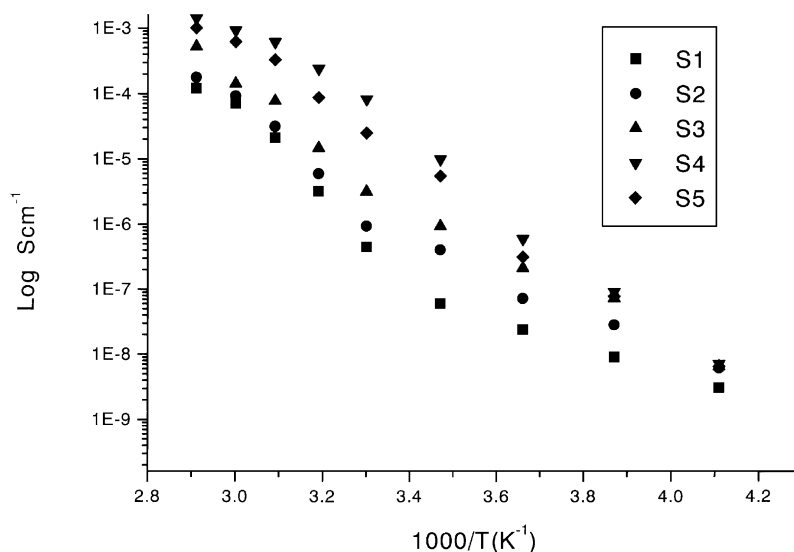
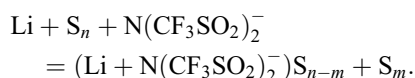
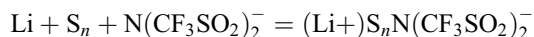


Fig. 1. Temperature dependence of ionic conductivity for the films with different plasticizer content.

centration in low dielectric media, essentially two types of ion pairs and solvated ion pairs are present [16].

These may be represented by the equilibria:



Where S represents the solvating species. Re-dissociation of such ion pairs can occur due to long-range coulombic forces giving rise to free ions, which contribute to conductance. At higher concentrations, short-range ion–solvent interactions take over and therefore, even though the number of ions dissolved in the electrolyte medium is higher, the effective number of charged species available for charge transport gets reduced.

In order to find the role of PVC/PMMA blend ratio on ionic conductivity, samples S4, S6, S7, S8 and S9 are considered with fixed plasticizer content. Fig. 2 depicts the temperature dependence on ionic conductivity for different PMMA content in the blend for the fixed plasticizer (60%) and salt content. The sample S4 with the blend ratio of PVC/PMMA 75:25 is considered for comparison. Although it contains 4%

salt, it exhibited maximum conductivity. The conductivity at any particular temperature increases with increasing PMMA content in the film. Film containing little or no PMMA shows the lowest conductivities. On the other hand, 100% PMMA film (i.e. film 0% PVC) has the highest conductivity but no mechanical stability. However, films with intermediate blend ratios 50:50 and 75:25 possess good mechanical properties with reasonable conductivity. Thus, it is necessary to add PVC to obtain a good free-standing film. But the films with 100% PVC shows the lowest conductivity. This is quite expected, as PVC is necessary to give mechanical support to the inter-connected plasticizer rich-phase through which ionic transport is believed to take place. The mechanically strong PVC rich-phase is a solidlike medium through which penetration is found to be difficult.

These results have already been substantiated using SEM analysis in our earlier studies [13] for the films containing LiCF_3SO_3 and LiBF_4 . It should be noted from the figures that the Arrhenius relation holds well at low plasticizer contents and at high temperatures, while the VTF relation is obeyed higher plasticizer levels and low temperatures. At high levels of plasticizer, transport of ions may be expected to take place along the plasticizer-rich phase. From these results, it is suggested that in electrolyte films containing both

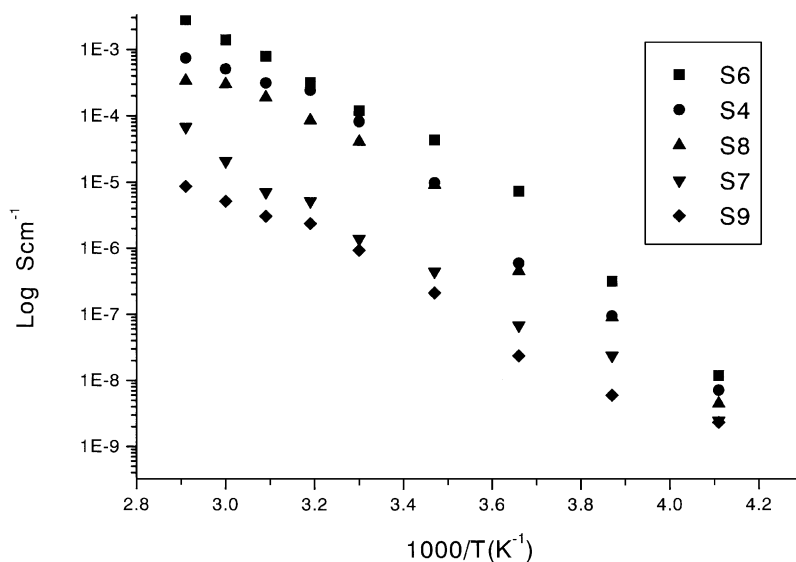


Fig. 2. Temperature dependence of ionic conductivity for the films with different PVC/PMMA blend ratio (plasticizer content 60%).

PVC and PMMA, the PVC rich-phase acts as a mechanical support and the plasticizer rich-phase acts as tunnel for ionic transport. Since the PVC-rich phase is a solidlike medium, it is very difficult for ions to penetrate this phase [10–13]. The transport of ions must occur via indirect motion along a convoluted path restricted to the plasticizer-phase, which is responsible for low conductivity at a high PVC content. A homogeneous conducting medium exists in the 100% PMMA film (sample S6), which results in the direct drift of the ion. This is the reason for the relatively high ionic conductivity [10–13].

3.2. Compatibility

That charge–discharge performance of a cell is influenced by the characteristics of the interface between the lithium anode and the electrolyte is well known. Interfacial characteristics have been sought to be influenced by use of electrolyte. It is believed that the chemical properties of the interface play a dominant role on the efficiency with which lithium is cycled across the interface. In order to determine the stability of lithium metal with the polymer electrolyte over time, an impedance analysis of a symmetric cell of the type Li/polymer electrolyte/Li was assembled and tested under open-circuit condition at room tem-

perature. Fig. 3 displays the variation of interfacial resistance “*R_i*” as a function of time for polymer electrolytes containing different blend ratios (samples S6, S7 and S9). The increase in “*R_i*” may generally be attributed due to a resistive layer continuously growing on the lithium electrode surface. It is evident from the figure that the growth of resistive layer does not follow a regular pattern. After 200 h, the “*R_i*” values remain unchanged. This goes to show that the morphology of the passivation film keeps changing with time until it finally acquires a noncompact and possibly porous structure. It may be seen from the figure that the value of “*R_i*” are a minimum for films with 100% PMMA and a maximum for the films with 100% PVC. Predictably, in the case of PVC/PMMA blend polymer electrolytes, the values of “*R_i*” were intermediate and consistent with the fact that PMMA is compatible with lithium. In fact, increase in PMMA composition led to reduced “*R_i*” values. One possibility that can explain the reduced interfacial resistance with PMMA-based electrolytes is the reaction of lithium with the ester groups of PMMA, resulting in the formation of a protective layer at the electrode–electrolyte interface. This layer could protect lithium from impurities present in the electrolyte. In order to compare the effect of inorganic fillers in terms of compatibility on the PVC/PMMA blend electrolytes,

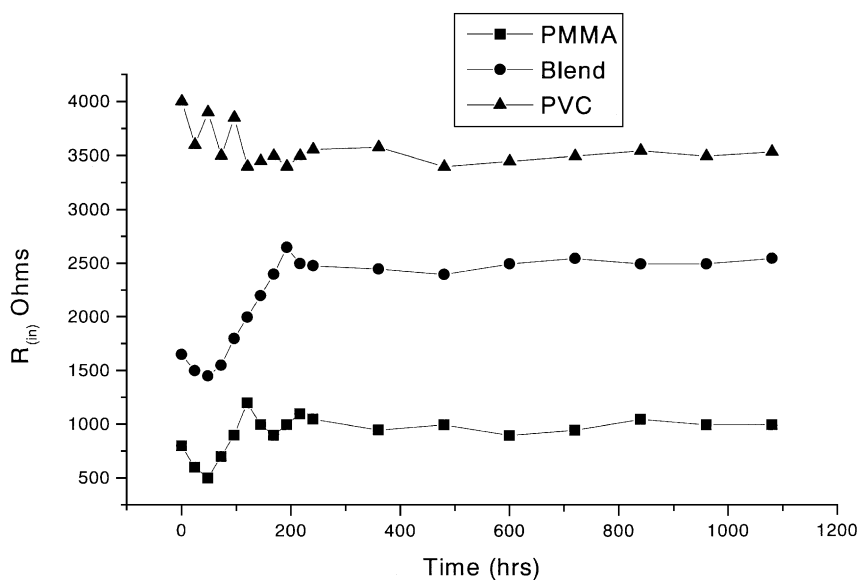


Fig. 3. Time evolution of interfacial resistance “ R_i ” for Li/polymer electrolyte/Li cell under open circuit condition at 25 °C.

composite electrolytes were prepared for the same amount of plasticizers (sample S10 and S11). Fig. 4 compares the growth of interfacial resistance for the films prepared with EC-PC as plasticizers and that of

the films having the same amount of inorganic filler TiO_2 . It is seen that the film containing inorganic filler is more compatible than the films containing EC and PC. This study implies that the presence of PC

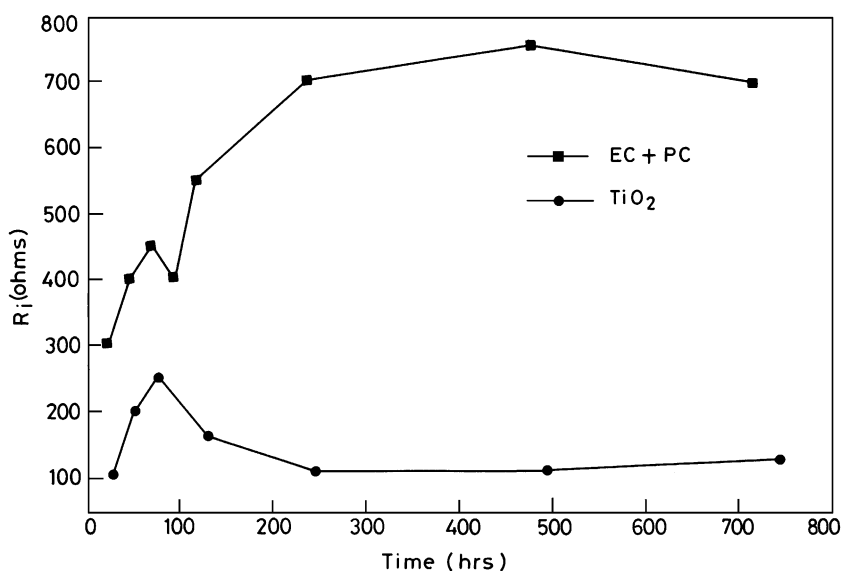


Fig. 4. Time evolution of interfacial resistance “ R_i ” for Li/polymer, composite electrolyte/Li cells under open circuit condition at 25 °C.

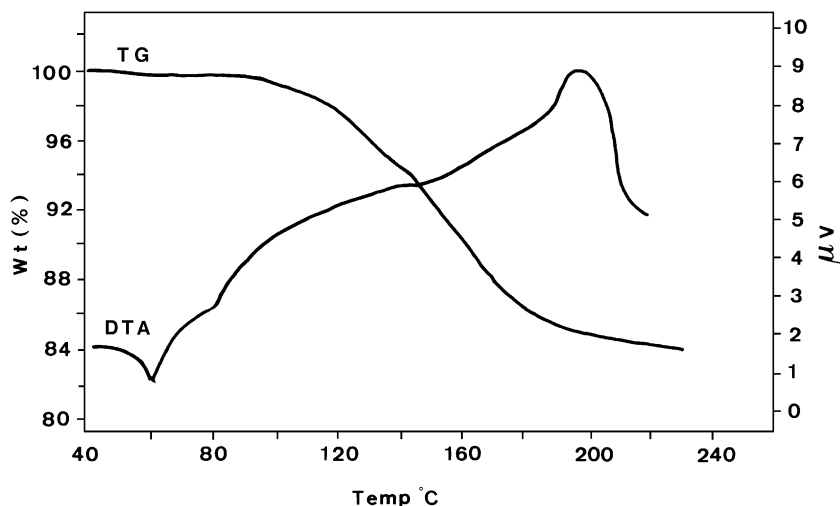


Fig. 5. TG-DTA traces of PVC-PMMA-EC-PC-LiN(CF₃SO₂)₂ electrolyte.

and EC in the electrolyte plays an important role on the growth of “Ri” on the surface of lithium. It is also clear from these studies that the lithium passivation in the composite electrolytes is a controlled phenomenon and these may have better compatibility with lithium electrode to allow safe-operation in rechargeable Li batteries than those prepared with liquid plasticizers.

3.3. TG-DTA analysis

In order to ascertain the thermal stability of the polymer electrolytes, the prepared films were subjected to TG-DTA analysis. The TG and DTA analyses are shown in Fig. 5. It is interesting to note that from the TG-DTA analysis for the polymer film, PMMA-PVC-EC-PC-LiN(CF₃SO₂)₂, an endothermic peak is seen at about 55 °C with less than 2% weight loss, which is attributed to the presence of moisture and impurities mainly due to fluorine [17]. Above 100 °C, i.e. after complete dehydration, no further weight loss is observed until irreversible decomposition commenced at approximately 90 °C following an endothermic peak. The polymer electrolyte decomposes at about 90 °C [17,18]. Obviously, one can claim from these observations that these films can be operated up to 90 °C and are preferred in the lithium polymer batteries as its operating temperature is normally in the range of 40–70 °C [10].

4. Conclusion

We conclude that (i) LiN(CF₃SO₂)₂-based blend polymer films show appreciable conductivities above 30 °C. The ratio of 75:25 PMMA/PVC polymer blend films is found to be suitable from the conductivity and thermal stability points of view; (ii) PMMA in the polymer blend considerably reduces the interfacial resistance; (iii) the polymer composite electrolytes containing TiO₂ are more compatible with lithium metal anode than the films with liquid plasticizers such as EC and PC. Further, FTIR investigations of the lithium polymer blend interface as well as charge–discharge studies on lithium cells with these blend polymer electrolytes are in progress.

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