

Effect of complexing salt on conductivity of PVC/PEO polymer blend electrolytes

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Abstract. Solid polymer electrolyte membrane comprising poly(vinyl chloride) (PVC), poly(ethylene oxide) (PEO) and different lithium salts (LiClO₄, LiBF₄ and LiCF₃SO₃) were prepared by the solution casting technique. The effect of complexing salt on the ionic conductivity of the PVC/PEO host polymer is discussed. Solid polymer electrolyte films were characterized by X-ray diffraction, FTIR spectroscopy, TG/DTA and ac impedance spectroscopic studies. The conductivity studies of these solid polymer electrolyte (SPE) films are carried out as a function of frequency at various temperatures ranging from 302 K to 353 K. The maximum room temperature ionic conductivity is found to be $0.079 \times 10^{-4} \text{ S cm}^{-1}$ for the film containing LiBF₄ as the complexing salt. The temperature dependence of the conductivity of polymer electrolyte films seems to obey the Vogel–Tamman–Fulcher (VTF) relation.

Keywords. Solid polymer electrolytes; Li-ion conduction; XRD; FTIR; TG/DTA.

1. Introduction

A driving force in the investigation and development of new polymeric electrolytes is the possibility of their application in various electrochemical devices (MacCallum and Vincent 1987; Vincent 1987; Gray 1991; Scrosati and Neat 1993; Bruce 1995). Much effort has gone into the enhancement of the ionic conductivity at ambient and sub-ambient temperatures of polyether-based electrolytes – the most intensively studied systems. Novel polymeric ionic conductors such as networks (Cheradame and Lee Nest 1987), gels (Abraham 1993), blends (Ingnas 1988) and composites (Croce *et al* 1998) have been synthesized and their structure conductivity characteristics have been discussed. The electrochemical stability of polymeric electrolytes in contact with alkali metal electrodes primarily lithium, and the compatibility of these electrolytes with electrode materials, is crucial in electrochemical devices (Kelley *et al* 1984; Scrosati 1987; Fautex 1988; Croce *et al* 1990; Capuano *et al* 1991; Borkowska *et al* 1993; Appetecchi *et al* 1995). The resistance of passive layer formed between lithium electrode and polymeric electrolyte increases with time, and the uncontrolled passivation phenomena affect the cyclability of lithium electrodes, and therefore the entire lithium battery (Scrosati *et al* 1993). It is presumed that the nature of this layer depends largely on the composition and purity

of the electrolyte. The layer, having properties of solid lithium ionic conductor with a high electrical resistance, acts as a solid phase between the lithium and the electrolyte. Scrosati and others (Croce *et al* 1990; Capuano *et al* 1991; Scrosati 1993) demonstrated that the addition of inorganic fillers, such as LiAlO₂ or zeolites, improves electrode electrolyte compatibility and reduces the passivation phenomena and also Yamamoto and co-workers reported an increase of the electrical conductivity, especially at lower temperature, and a decrease of the interfacial resistance between the lithium anode and the polymer electrolyte (Sun *et al* 2000) by the addition of ferroelectric material, BaTiO₃. Moreover, they investigated the particle size effect of BaTiO₃ on the ionic conduction of composite polymer electrolyte, and large particle size BaTiO₃ would increase the salt dissociation because of ferroelectric domains developed in the ceramics (Capiglia *et al* 2002; Takeuchi *et al* 2002). This has been attributed to the effect of such fillers on polymer impurities (e.g. moisture or low-molecular-weight volatile solvents), which are suspected to react with lithium leading to the formation and growth of these passive layers. In addition to the composite polymer, a blend-based polymer electrolyte, composed of two conductive components and lithium salts, is another example with favourable electrical properties, and, for example, there are (PEO-poly[bis(methoxyethoxyethoxide) phosphazene]–LiN(CF₃SO₂), PEO-poly[bis(triethyleneglycolbenzoate)] capped with an acetyl group – LiN(CF₃SO₂)₂ (Abraham 1991; Wen *et al* 2000; Itoh *et al* 2001) and poly(ethylene oxide) (PEO)–

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LiClO₄ electrolytes with various methacrylic and acrylic polymers used as additives (Borkowska *et al* 1993), which limits the growth of resistance of passive layers. One conductive component in the blend-based polymer electrolytes acts as a plasticizer to reduce the non-conductive crystalline phase of PEO, leading to an increase in the ionic conductivity at low temperatures.

Since the conductivity of poly(ethylene oxide) salt complex was reported by Fenton *et al* (1973), researchers were ardent in finding a solution to these PEO-based polymer electrolytes that possessed poor conductivity at low temperatures, later Armand and his collaborators (1979) reported the practical application of PEO for batteries. However, research efforts are still underway to increase the ionic conductivity (Balleard *et al* 1990; Dobrowski *et al* 1991) in conjunction with its thermal stability (Huang *et al* 1996).

Based on the conception (Borkowska *et al* 1993), in the present work an attempt has been made to prepare PVC–PEO polymer-blend electrolytes bereft of plasticizers, which could give higher ionic conductivity and good electrode electrolyte contact (reduced passive layer), with good thermal stability. PVC has been used to blend with PEO because of its commercial availability, inexpensiveness and its widespread use is attributed mainly to the presence of lone pair electrons at the chlorine atom where inorganic salts can be solvated.

The present paper reports on the effect of complexing salt upon the conductivity of PVC–PEO-blended polymer electrolyte. The blend optimization of PVC–PEO has been reported elsewhere (Rajendran *et al* 2007). The polymer electrolytes prepared were subjected to XRD, FTIR for structural elucidation, TG/DTA for thermal stability and a.c. impedance technique for conductivity measurements.

2. Experimental

Poly(vinyl chloride) (PVC) (average molecular weight 1.5×10^5) and poly(ethylene oxide) (PEO) (average molecular weight 1×10^5) purchased from Aldrich, USA, were dried at 100°C and 45°C, respectively, for 5 h; salts LiClO₄, LiBF₄ and LiCF₃SO₃ procured from Aldrich, USA, was dried at 70°C under vacuum for 24 h. The electrolyte thin films were prepared by solution casting technique. Appropriate quantities of PVC, PEO and Li salts were dissolved in predistilled THF and stirred for about 10 h at room temperature and then at 45°C for 2 h before casting the films on glass plates. The films were dried in vacuum oven at 303 K at a pressure of 10^{-3} Torr for 5 h. The phase analysis of the polymer electrolyte was performed with XRD [Bruker (D8 Advance)] diffractometer at room temperature. The FTIR spectrum in the range 4000–400 cm⁻¹ was recorded using Jasco FTIR 460 plus (Japan) spectrophotometer.

Conductivity measurements were carried out on the thin films using Keithley LCZ meter (model 3330) with a signal amplitude of 10 mV in the frequency range 40 Hz–100 kHz. The variation of conductivity with temperature is recorded in the temperature range between 303–353 K. The thermal stability is ascertained from the TG/DTA conducted on the film using PERKIN ELMER (pyres diamond) TG/DTA instrument with a heating rate of 10°C/min.

3. Results and discussion

3.1 XRD analysis

XRD studies provided a wide range of information on crystal structure, orientation, crystallinity and phase changes of materials (Cullity 1978) including polymers, salts and complexes. In the present study, the XRD method has been used only in a limited perspective to identify or confirm the following: (i) amorphous, crystalline or semicrystalline nature of the material and (ii) complex formation.

The XRD pattern of pure PVC, PEO, LiX (X = ClO₄⁻, BF₄⁻ and CF₃SO₃⁻) is shown in figure 1. The amorphous phase of PVC is evident from figure 1a. The XRD pattern of PEO manifests two distinct crystalline peaks (Such *et al* 1989) at 19.7° and 23.9° (figure 1b). The peaks pertaining to PEO are found with reduced intensities in the complexes, which could be due to the complexation of PEO with polymer PVC and salt LiX. The crystalline peaks pertaining to pure LiClO₄, LiBF₄ and LiCF₃SO₃ (figures 1c–e) are found to be absent in the complex figures 1f–h, indicating the complete dissolution of the salt in the polymer matrix, which is in accordance with the statement that complexation between the salts and polymer takes place in the amorphous region (Carre *et al* 1988), hence the confirmation of complexation.

3.2 FTIR spectroscopic studies

FTIR spectroscopy is important for the investigation of polymer structure. FTIR spectra of these materials vary according to their compositions and may be able to show the occurrence of complexation (Alamgir and Abhram 1994) and interactions between the various constituents. In the present work, FTIR spectroscopy is used to establish interactions between the polymers (PVC and PEO) and salts (LiClO₄, LiBF₄ and LiCF₃SO₃), which can make changes in the vibrational modes of the atoms or molecules in the materials.

FTIR spectra of pure PVC, PEO, LiClO₄, LiBF₄, LiCF₃SO₃ and complexes are shown in figure 2. The bands at 1333, 1254 and 950 cm⁻¹ in pure PVC are assigned to CH₂ deformation, CH rocking and CH wagging respectively. The bands at 2900, 1950 and 1430 cm⁻¹ in

pure PEO are assigned to CH symmetrical stretching, asymmetric stretching and asymmetric bending vibration, respectively. The absorption peaks appearing at 1450 cm^{-1} in pure PEO is shifted to a higher frequency region in the complexes. The absorption peak at 1333 cm^{-1} in pure PVC is shifted to 1342 cm^{-1} in all the complexes irrespective of the type of lithium salt added. The characteristic frequency of PVC at 1254 cm^{-1} is found to be shifted around 1244 cm^{-1} in all the complexes. The trans CH wagging of PVC is shifted from 956 cm^{-1} to 946 cm^{-1} .

The vibrational peaks appearing at 2741 , 2559 , 1435 , 1199 and 890 cm^{-1} of PVC and the peaks 2900 , 1600 , 1325 , 1255 cm^{-1} of PEO, are found to be absent in the polymer complexes. The frequencies of pure LiCF_3SO_3 (3477 , 1639 and 1084 cm^{-1}), LiClO_4 (1070 and 626 cm^{-1}) and LiBF_4 (1450 cm^{-1}) are shifted to (3465 , 1638 , 1079 cm^{-1}), (1080 and 614 cm^{-1}) and (1466 cm^{-1}) in polymer complexes respectively. This may be due to the change in environment for the CF_3SO_3^- , BF_4^- and ClO_4^- ions in the complexes.

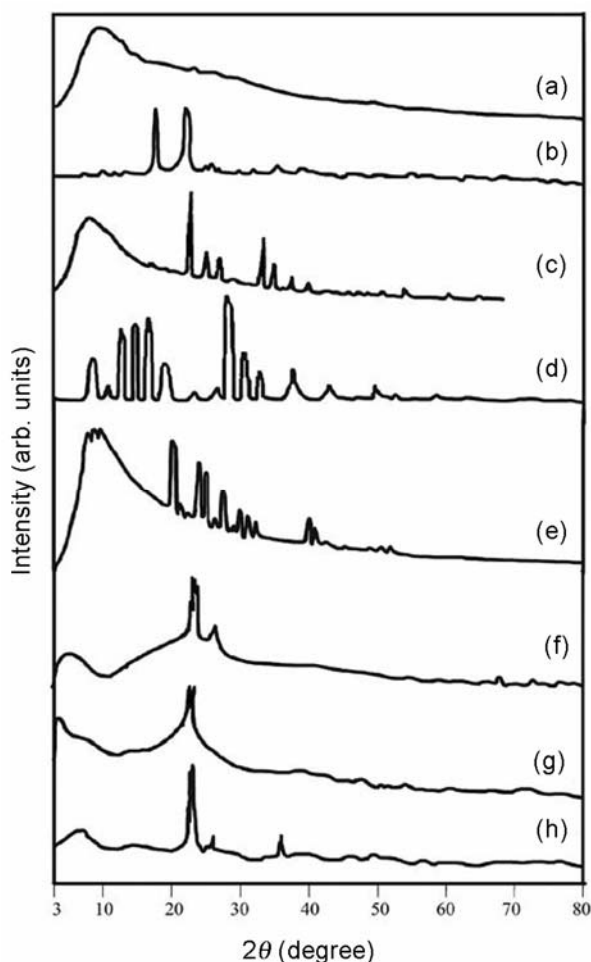


Figure 1. XRD patterns of pure (a) PVC, (b) PEO, (c) LiClO_4 , (d) LiBF_4 , (e) LiCF_3SO_3 , (f) PVC-PEO- LiClO_4 , (g) PVC-PEO- LiBF_4 and (h) PVC-PEO- LiCF_3SO_3 .

In addition to the above, there are some new peaks obtained at around 3458 , 2878 , 1078 and 841 cm^{-1} in the complexes. The above analysis as a whole establishes the formation of polymer-salt complexes (Vien *et al* 1991).

3.3 Conductivity measurements

The ionic conductivity of a polymer electrolyte depends on (i) the actual concentration of the conducting species and (ii) their mobility. The low ionic conductivity in a polymer complex results from the crystalline phase that affects the mobility of ions. In the present work, blended polymer electrolytes were prepared using polymers PVC, PEO and different inorganic lithium salts such as LiClO_4 , LiBF_4 and LiCF_3SO_3 , employing solvent casting technique.

Polymer electrolytes with fixed ratios of polymers and salt [PVC(23)-PEO(69)- $\text{LiX}(8)$; ($\text{X} = \text{ClO}_4^-$, BF_4^- , CF_3SO_3^-)] were prepared in order to find the appropriate salt suitable to be competent in lithium battery applications. The polymer electrolyte films prepared were found to be translucent and free-standing. The ionic conductivity measurements have been carried out on these polymer

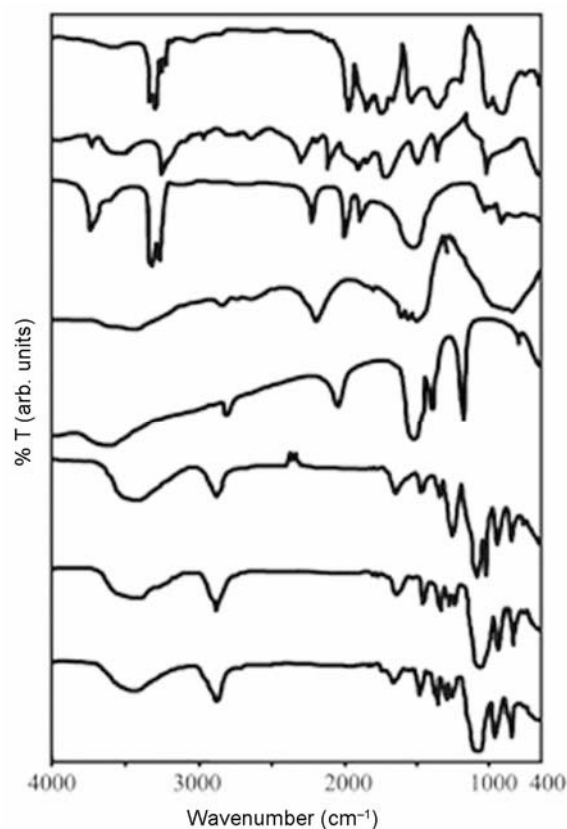
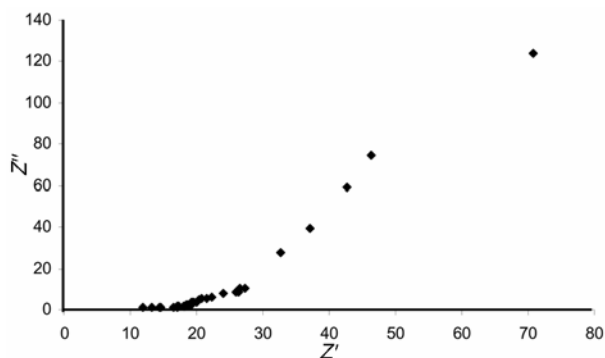
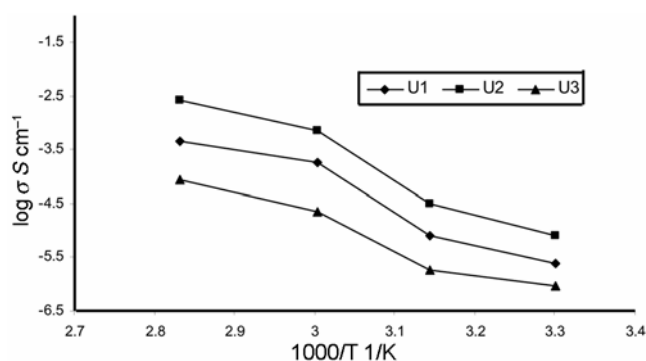


Figure 2. FTIR spectra of pure (a) PVC, (b) PEO, (c) LiClO_4 , (d) LiBF_4 , (e) LiCF_3SO_3 , (f) PVC-PEO- LiClO_4 , (g) PVC-PEO- LiBF_4 and (h) PVC-PEO- LiCF_3SO_3 .

Table 1. Conductivity values of PVC-PEO-LiX (X = ClO₄, BF₄, CF₃SO₃) at different temperatures.

Films	Composition PVC-PEO-LiX (23-69-8)	Conductivity values of PVC-PEO-LiX in 10 ⁻⁴ S cm ⁻¹			
		302 K	318 K	333 K	353 K
U ₁	LiClO ₄	0.024	0.079	1.782	4.459
U ₂	LiBF ₄	0.079	0.316	7.249	26.300
U ₃	LiCF ₃ SO ₃	0.009	0.018	0.226	0.891

**Figure 3.** Z real vs Z imaginary plot for PVC:PEO:LiBF₄ at room temperature.**Figure 4.** Arrhenius plot of $\log \sigma$ against reciprocal temperature of PVC:PEO:LiX (X = ClO₄, BF₄ and CF₃SO₃).

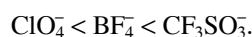
electrolytes by employing variable frequency complex a.c. impedance technique. The thin films of polymer complex were sandwiched between the two stainless steel electrodes attached to the conductivity jig specially designed for the ionic conductivity measurements. The two SS electrodes act as blocking electrodes for Li⁺ ions under an applied electric field.

The conductivity of the polymer electrolyte was calculated from the measured resistance (obtained from Cole-Cole plot) for the known area 'A' and thickness of the polymer film 'l', using the relation $\sigma = l/R_b A$, where R_b is the bulk resistance. Table 1 shows the conductivity values of the complex in the temperature range 303 K to 333 K. The impedance isotherm for the PVC-PEO-LiBF₄ (film U₂) at room temperature is shown in figure 3. The disappearance of high-frequency semicircular portion in

the impedance curve leads to a conclusion that the current carriers are ions, and this leads one to further conclude that the total conductivity is mainly the result of ion conduction (Izuchi *et al* 1987). At low frequency, the complex impedance plot must show a straight line parallel to the imaginary axis, but the double layer at the blocking electrodes causes the curvature (Kim *et al* 1999).

In order to examine the temperature dependence of ionic conductivity, PVC-PEO-LiX films were subjected to conductivity measurements at four different temperatures viz. 30, 45, 60 and 80°C. It is evident that as the temperature increases (table 1 and figure 4) the conductivity is also found to increase. This behaviour could be explained on the basis of free volume model. At higher temperatures, thermal movement of polymer chain segments and the dissociation of the salts are improved, thereby increasing ionic conductivity. However, at low temperature the presence of lithium salt leads to salt-polymer or cation-dipole interactions, which increases the cohesive energy of polymer networks. As the free volume decreases, polymer segmental motion and ionic mobility are restricted, hence ionic conductivity decreases. This is in agreement with the theory.

The conductivity value of the film U₂ [PVC(23)-PEO(69)-LiBF₄(8)] is found to be 0.079×10^{-4} S cm⁻¹, which is indeed a higher value when compared to the other films that consist of LiClO₄ and LiCF₃SO₃. This may be due to the reason that a smaller conductivity enhancement factor that for the LiCF₃SO₃ salt can be attributed to the larger anionic radius of the ion, similar results was reported (Shodai *et al* 1994). The degree of dissociation of the various lithium salts has been previously compared, and it was reported that the association tendency of the anions with Li⁺ ions in non-aqueous aprotic solvents increases in the following order



This result suggest that ion pairing takes place to a lesser extent in the electrolytes containing LiClO₄ or LiBF₄ compared with the electrolyte that contains LiCF₃SO₃.

3.4 TG/DTA analysis

In order to ascertain the thermal stability of the polymer electrolyte with maximum conductivity, the film was sub-

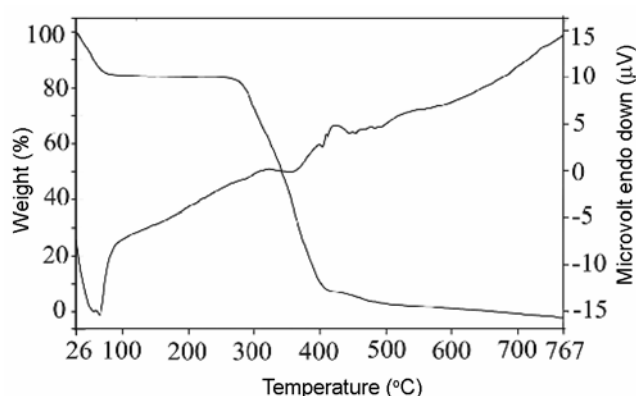


Figure 5. TG/DTA analysis of PVC-PEO-LiBF₄.

jected to TG/DTA analysis in the range 25°C to 800°C at a heating rate of 10°C/min. The TG/DTA spectrum of the polymer electrolyte PVC-PEO-LiBF₄ is shown in figure 5. The TG curve shows a first degradation at 70°C accompanied by a weight loss of 14%, which may be due to the evaporation of moisture absorbed by the sample during loading or the volatile impurities present (Scott and Macosko 1995; Stephen *et al* 2002). This first degradation is substantially asserted by the DTA curve giving an endothermic peak around 65–75°C. The film is found stable from 70 to 276°C, with a meager weight loss of 1%, beyond 276°C the film loses its weight drastically up to 400°C. This could be attributed to the decomposition of the polymer electrolyte. This result is found consistent with the DTA result. These results indicate that the samples are stable up to 276°C. Since the polymer electrolyte maintains its stability in the range 70°C to 276°C with very meager weight loss, this indicates the evaporation/deterioration of polymers in the polymer electrolyte is absent. Hence, it is concluded that the polymer electrolyte is stable up to 276°C.

4. Conclusions

Three different electrolyte systems consisting of PVC-PEO-LiX (X = ClO₄⁻, BF₄⁻, CF₃SO₃⁻) have been studied. Among the three films, (film U₂) the film with LiBF₄ is found to be the best on the basis of conductivity. The conductivity of the polymer electrolyte PVC-PEO-LiBF₄ is found to be 0.079×10^{-4} S cm⁻¹, and the film has a thermal stability up to 276°C. Hence, the properties of PVC-PEO-LiBF₄ polymer electrolyte look very desirable and promising for lithium battery applications.

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