Investigation on poly (vinylidene fluoride) based gel polymer electrolytes

S RAJENDRAN*, P SIVAKUMAR[†] and RAVI SHANKER BABU

Department of Physics, Alagappa University, Karaikudi 630 003, India
[†]Department of Physics, H.H. The Rajah's College, Pudukottai 622 001, India

Abstract. An investigation is carried out on gel polymer electrolytes consisting of poly (vinylidene fluoride) (PVdF) as a host polymer, lithium perchlorate (LiClO$_4$), lithium triflate (LiCF$_3$SO$_3$) as salts and mixture of ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers. Polymer thin films were prepared by solvent casting technique and the obtained films were subjected to different characterizations, to confirm their structure, complexation and thermal changes. X-ray diffraction revealed that the salts and plasticizers disrupted the crystalline nature of PVdF based polymer electrolytes and converted them into an amorphous phase. TG/DTA studies showed the thermal stability of the polymer electrolytes. The role of interaction between polymer hosts on conductivity is discussed using the results of a.c. impedance studies. Room temperature (28°C) conductivity of $2 \cdot 786 \times 10^{-3}$ Scm^{-1} was observed in PVdF (24)–EC/PC (68)–LiCF$_3$SO$_3$ (2)/LiClO$_4$ (6) polymer system.

Keywords. Gel polymer electrolyte; XRD; FTIR; impedance studies.

1. Introduction

In consistence with the rapid progress in size, thickness reduction of electronic devices and development of multimedia industries in recent years, demand has been increasing to fabricate small sized portable devices. Today it is almost universally accepted that such combination of size and thickness can only be obtained by using nonconventional electrodes and electrolyte materials and that the most promising choices are those based on lithium operating systems. With this situation, attempts have been made in poly (ethylene oxide) (PEO) based polymer electrolytes to reach an appreciable electrical conductivity at ambient temperature (Wright 1975; Martuscelli *et al* 1984). Generally solid polymer electrolytes have many advantages, viz. high ionic conductivity, high specific energy, wide electrochemical stability windows, light and easy processibility. Apart from this, polymer electrolyte studies have been carried out in poly (vinyl alcohol) (PVA) (Every *et al* 1998), poly (vinyl chloride) (PVC) (Alamgir and Abraham 1993; Sukeshini *et al* 1996; Rajendran and Uma 2000), poly (vinylidene fluoride) (PVdF) (Tsuchida *et al* 1983), poly (acrylonitrile) (PAN) (Watanabe *et al* 1981, 1983; Slane and Salomon 1995) and poly (methyl methacrylate) (PMMA) (Bohnke *et al* 1992; Appetecchi *et al* 1995). Polymer host is doped with inorganic salt and one or more plasticizers in order to enhance the conductivity. The conductivity is related to the glass transition temperature, T_g and is further related to the inter-linking of the polymer chain. Moreover, many experiments have been performed to study the status of the amorphous phase by XRD (Hashmi and Chandra 1995; Yang *et al* 1996; Ramesh and Arof 2001) and such electrolytes exhibit high ionic conductivity. Among these polymers, PVdF is of semi crystalline nature and the electrolytes based on PVdF are expected to have high anodic stabilities due to strong electron withdrawing functional groups and also they have high permittivity, relatively low dissipation factor and high dielectric constant, which assist in higher ionization of lithium salts providing a higher concentration of charge carriers (Choe *et al* 1995).

In the present investigation, structural, thermal and conductivity studies have been performed on poly (vinylidene fluoride) (PVdF) based polymer electrolytes with LiClO$_4$ and LiCF$_3$SO$_3$ as salts and ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers.

2. Experimental

PVdF with an average molecular weight of $5 \cdot 34 \times 10^5$ (Aldrich), ethylene carbonate (EC) (E Merck), propylene carbonate (PC) (Aldrich), lithium perchlorate (LiClO$_4$) (Aldrich) and lithium triflate (LiCF$_3$SO$_3$) (Aldrich) were used for the preparation of polymer electrolytes. LiClO$_4$ and LiCF$_3$SO$_3$ were used after drying at 70°C under vacuum for 24 h. EC, PC and PVdF were used without un-

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*Author for correspondence (sraj54@yahoo.com)

dergoing any further purification. Distilled tetrahydrofuran (THF) (E Merck) was used as solvent and an appropriate quantity of PVdF, EC, PC and [xLiCF$_3$SO$_3$ + (8 − x) LiClO$_4$] (where x = 0, 2, 4, 6, 8%) salts were dissolved in THF separately. The dissolved polymer solution, plasticizers and salts were mixed together and the solution was stirred continuously to obtain a homogeneous mixture. The polymer solution was allowed to evaporate slowly at 28°C until gelly state was achieved. Then it was poured on a clean glass plate and Teflon bushes.

The polymer films were prepared in different concentrations of LiClO$_4$ and LiCF$_3$SO$_3$, while keeping EC, PC and PVdF in constant weight ratios. As reported by Periasamy *et al* (1999), 10 wt% of PVdF was fragile, 20–25 wt% of PVdF was good in mechanical strength and 30 wt% of PVdF had highest strength, further it was also suggested that the higher percentage of lithium salt lowers the conductivity of the gel polymer electrolyte. In order to focus the above discussion, especially PVdF was kept as 24 wt%, salt was fixed as 8 wt% and plasticizers were kept as 68 wt% in this investigation. Thin films thus obtained were subjected to FTIR and XRD studies to investigate the complexation behaviour and the nature of crystallinity of the polymer electrolytes using Perkin–Elmer – (Paragon 500 grating) IR spectrophotometer and Bruker (D8 Advance) diffractometer. Thermal stability of the films was also characterized by TG/DTA analyser using Perkin Elmer (pyres Diamond TG/DTA) at a heating rate of 10°C per min from room temperature to 400°C. The electrical conductivity of polymer complexes were measured from impedance plots at different temperatures using Keithley 3330 LCZ meter. The impedance measurements were recorded in the frequency range 40–100 kHz with a signal amplitude of 10 mV. The polymer complexes were sandwiched between stainless steel electrodes for the conductivity measurements.

3. Results and discussion

3.1 *XRD measurements*

Figure 1 shows the X-ray diffraction patterns of pure PVdF, LiClO$_4$ and LiCF$_3$SO$_3$. The patterns for [(x)LiCF$_3$SO$_3$ + (8 − x) LiClO$_4$]–PVdF–EC/PC complexes with x = 0, 2, 4, 6, 8 wt%, are depicted in figure 2. The following points are observed while comparing pure XRD spectra with complexed PVdF system: (i) the diffraction peaks observed between 2θ = 18° and 19·6° in pure PVdF are shifted as one broad peak at 20·1° with less intensity in plasticized PVdF based electrolytes, (ii) no peaks corresponding to LiClO$_4$ and LiCF$_3$SO$_3$ are observed in complexed systems. It reveals the absence of excess salt (uncomplexed) in the polymer films. A less intense peak at 26·4° in pure PVdF completely disappeared in the complexed polymer systems, which is evident from figures 2a–e and (iii) com-

monly it is observed that the diffraction peaks are broader and less prominent in all polymer electrolytes. Especially the intensity of the peak in figure 2b is expected to be half when compared with pure PVdF. It reveals that the sample with x = 2 wt% of salt composition is more amorphous and leads to higher conductivity. These observations apparently reveal that the polymer undergoes significant structural reorganization while adding plasticizers and salts.
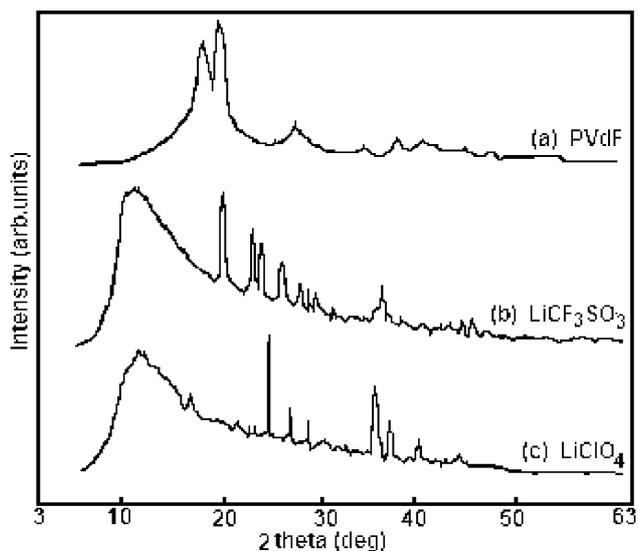
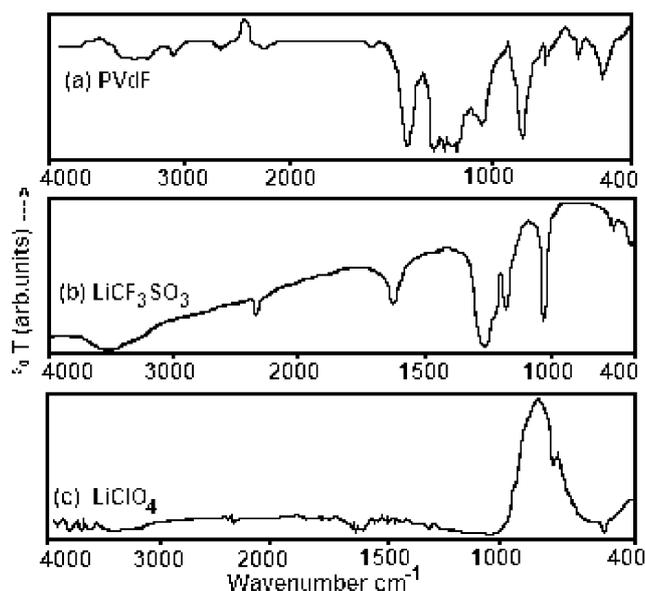**Figure 1.** XRD spectra of pure (a) PVdF, (b) LiCF$_3$SO$_3$ and (c) LiClO$_4$.
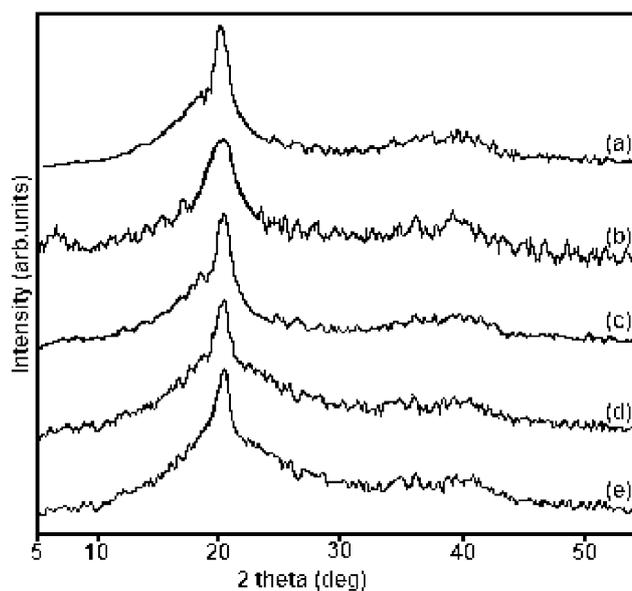
Figure 2. XRD spectra of PVdF (24)–EC/PC (68)–[(x) LiCF$_3$SO$_3$ + (8 − x) LiClO$_4$] where (a) x = 0, (b) x = 2, (c) x = 4, (d) x = 6 and (e) x = 8.

3.2 *FTIR spectroscopic studies*

FTIR spectra of pure PVdF, LiClO$_4$, LiCF$_3$SO$_3$ and its complexes are shown in figures 3 and 4. The complexation of pure PVdF with salts and plasticizers are extensively studied using IR spectroscopy. The vibrational peaks at 1426, 1269, 852 cm^{-1} of pure PVdF, 2996, 1774, 1474, 1165, 973 cm^{-1} of EC, 1789, 1484, 1077, 951, 543 cm^{-1} of PC, 2954, 1463, 1087 cm^{-1} of pure LiClO$_4$ and 1270, 1184, 1015, 767 cm^{-1} of pure LiCF$_3$SO$_3$ are shifted to 1403, 1262, 872 cm^{-1}, 2978, 1778, 1479, 1187, 977 cm^{-1}, 1785, 1480, 1071, 944, 510 cm^{-1}, 2971, 1479, 1082 cm^{-1} and 1262, 1187, 1030, 778 cm^{-1}, respectively.

It is also found that some of the peaks disappeared in the complexes such as 3198, 2854, 2782, and 2854 cm^{-1}. In addition to this, few new peaks were observed at 3021, 2485, 2282, and 2086 cm^{-1} in polymer complexes. The absorption peak at 1775 cm^{-1} represented the carbonyl group (C=O) vibration of EC, which shifted to 1781 cm^{-1}. The vibrational peak at 3089 cm^{-1} is assigned to C–H stretching vibration in vinylidene group. Peaks at 3010 cm^{-1} and 2989 cm^{-1} are assigned as asymmetric and symmetric stretching vibrations of CH$_2$ molecules.

The predominant peaks at 1385 cm^{-1} (medium) and 976 cm^{-1} (strong) are assigned to CH$_2$ bending vibration and C–F stretching vibrations of vinylidene group, which are shifted to 1396 and 984 cm^{-1} in the complexed films. The peak at 1225 cm^{-1} is assigned to in-plane C–H deformation. Vibrational peaks at 914 cm^{-1}, and 779 cm^{-1} are assigned to C–O stretching vibration of PC and ring breathing mode of EC and PC. An occurrence of peak at 715 cm^{-1} is due to ClO$_4^-$ stretching vibration and shifted to 720 cm^{-1} (Subramania *et al* 2004).

It is observed that few vibrational peaks of pure PVdF, EC, PC, LiClO$_4$ and LiCF$_3$SO$_3$ shifted to higher as well as lower frequency regions in the polymer complexes. It indicates significant degree of interaction between polymer and EC, PC molecules. The decrease in width of the band upon the addition of lithium salt is attributed to the formation of local structure or at least narrow distribution of inter-molecular interactions.

3.3 *Thermal studies*

The TG/DTA curves for gel polymer electrolytes are shown in figure 5. A clear endothermic peak at about 154°, 158° and 162°C are attributed to the melting temperature of PVdF in figures 5a, b and c, respectively. This temperature is in good agreement with the value reported by Jiang *et al* (1997) in PVdF–EC/PC–imide salt systems. Beyond this endothermic peak, no other peaks are observed up to 384°C indicating that PVdF based electrolytes are suitable for this temperature as evident from figure 5a and this value is in good agreement with the value reported by Subramania *et al* (2004) in PVdF–EC/PC–LiClO$_4$–ZrO$_2$ systems. In fact, the TG curve shows an abrupt weight loss in all polymer electrolytes, which may be attributed to the evaporation of moisture and plasticizers or the volatilization of monomers and oligomers adsorbed in the matrix can also be responsible for this initial loss (Mano *et al* 1996). Peaks exhibited in DTA curve at about 60° and 106°C in figure 5b are attributed to the eutectic transition or evaporation of residual solvent in the electrolytes and the evaporation of moisture and impurities, mainly due to hydrogen fluoride (Manuel Stephan *et al* 2005). The peak observed after 320°C revealed the first decomposition of

Figure 3. FTIR spectra of pure (a) PVdF, (b) LiCF$_3$SO$_3$ and (c) LiClO$_4$.
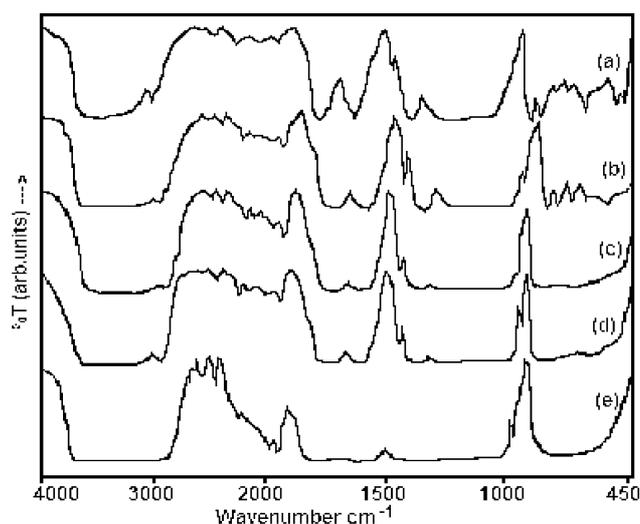
Figure 4. FTIR spectra of PVdF (24)–EC/PC (68)–[(x) LiCF$_3$SO$_3$ + (8 – x) LiClO$_4$] where (a) x = 0, (b) x = 2, (c) x = 4, (d) x = 6 and (e) x = 8.

the polymer electrolytes. It is also observed that the concentration of LiCF$_3$SO$_3$ increases, the position of the first decomposition peak at 384°C in figure 5a is shifted towards lower temperature and with further increase in LiCF$_3$SO$_3$, the corresponding peak split into a doublet, which are evident from figures 5b and c. Also increase in temperature of the first weight loss is a consequence of increase in T_g value (Ramesh and Arof 2001).
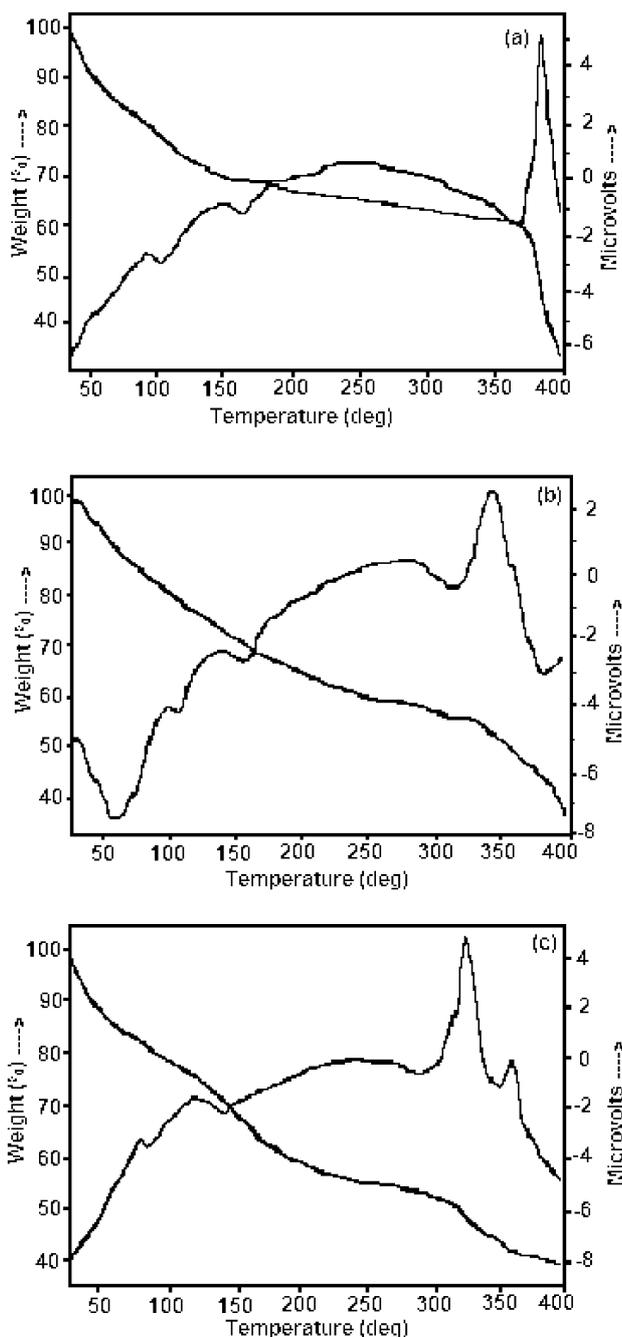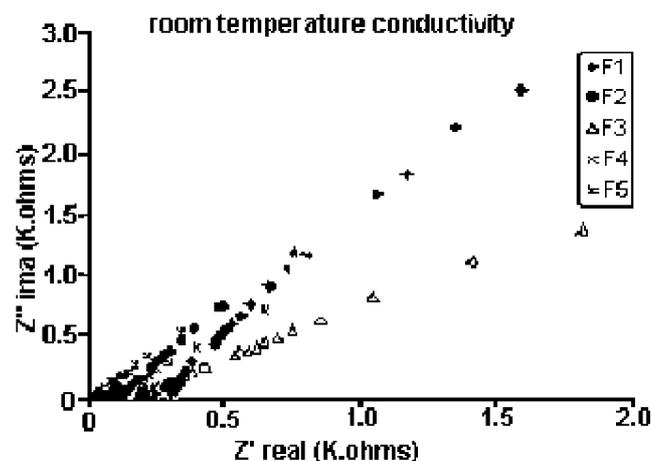
Similar observations are also noticed in figure 5c. The above discussions reveal the stability of the polymer electrolyte at about 300°C and is preferred in the polymer batteries as its operating temperature is normally in the range 30–70°C.

3.4 *Conductivity studies*

The room temperature conductivity of gel polymer electrolytes are measured by knowing the bulk resistance, area and thickness of the films. The typical impedance plot of PVdF (24)–EC/PC (68)–[(x)LiCF$_3$SO$_3$ + (8 – x) LiClO$_4$] (where x = 0, 2, 4, 6, 8%) at ambient temperature is shown in figure 6. The conductivity value of PVdF (24)–EC/PC (68)–[(2) LiCF$_3$SO$_3$ + (6) LiClO$_4$] electrolyte system is estimated as $2\cdot786 \times 10^{-3}$ S/cm at 28°C. This value is in close agreement with the value reported by Subramania *et al* (2004) in PVdF–EC/PC–LiClO$_4$–ZrO$_2$ system and this value is higher as compared with PVdF gel based polymer electrolytes and PVdF/PMMA based polymer systems (Magistris *et al* 2001; Rajendran *et al* 2001b).

The change in ionic conductivity with different quantities of salt content for fixed PVdF, EC and PC systems at room temperature is depicted in figure 7. It is found that the PVdF–EC/PC–LiClO$_4$ system shows higher conductivity than the corresponding PVdF–EC/PC–LiCF$_3$SO$_3$ system. Such an effect shows that one order of magnitude is associated with the amorphizing properties of the large LiClO$_4$ anion that strongly reduces the crystallinity of the complexes even at room temperature (Appetecchi *et al* 2001). The polymers with LiCF$_3$SO$_3$ complex show a negative trend of conductivity (Appetecchi *et al* 2001; Rajendran *et al* 2001a) with salt concentration as a result of the strong tendency of the salt to form ionic aggregates

Figure 5. TG/DTA plots for PVdF (24)–EC/PC (68)–[(x) LiCF$_3$SO$_3$ + (8 – x) LiClO$_4$] where (a) x = 0, (b) x = 2 and (c) x = 8%.

Figure 6. Impedance diagram of PVdF (24)–EC/PC (68)–[(x) LiCF$_3$SO$_3$ + (8 – x) LiClO$_4$] where (F1) x = 0, (F2) x = 2, (F3) x = 4, (F4) x = 6 and (F5) x = 8 at room temperature.

Table 1. Conductivity values of PVdF (24)–EC/PC (68)–[xLiCF$_3$SO$_3$ + (8 − x) LiClO$_4$] where (F1) $x = 0$, (F2) $x = 2$, (F3) $x = 4$, (F4) $x = 6$ and (F5) $x = 8$.

Film	Salt concentration	Conductivity values ($\times 10^{-3}$ S cm^{-1})							
		303 K	315 K	325 K	325 K	345 K	355 K	365 K	375 K
F1	$x = 0$	1·241	1·547	1·753	2·625	2·916	3·134	3·521	7·452
F2	$x = 2$	2·786	2·980	3·471	5·721	6·474	7·315	7·850	9·137
F3	$x = 4$	2·045	2·362	2·401	4·712	5·714	5·975	6·471	6·834
F4	$x = 6$	1·475	1·510	1·782	2·045	2·362	2·402	4·521	5·714
F5	$x = 8$	0·390	0·571	0·615	0·792	0·827	0·888	0·920	0·941
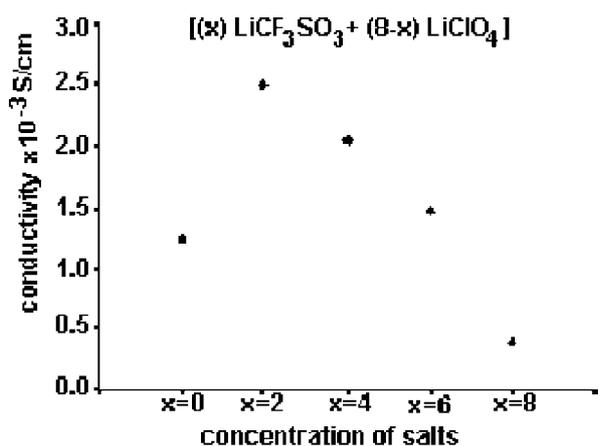
Figure 7. Concentration of salts vs conductivity plot of (24)–EC/PC (68)–[(x)LiCF$_3$SO$_3$ + (8 − x) LiClO$_4$] where $x = 0, 2, 4, 6, 8$% at room temperature.
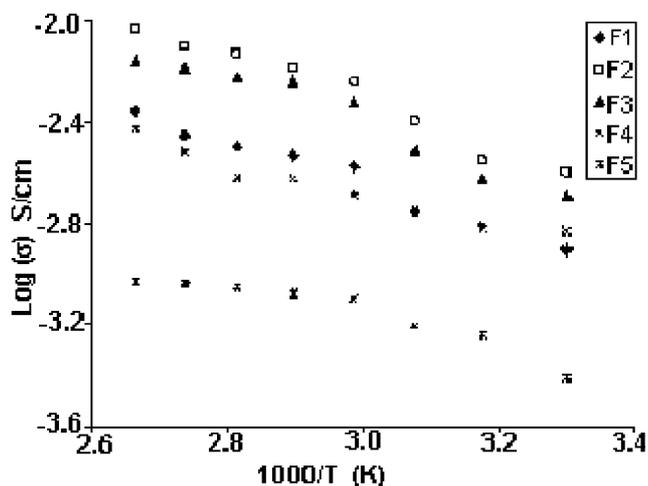
Figure 8. Arrhenius plots of log (σ) against reciprocal temperature (1000/T) for PVdF (24)–EC/PC (68)–[(x)LiCF$_3$SO$_3$ + (8 − x) LiClO$_4$] where (F1) $x = 0$, (F2) $x = 2$, (F3) $x = 4$, (F4) $x = 6$ and (F5) $x = 8$.

(Robitaille and Fauteux 1986; Sekhon *et al* 2002). Increasing ionic conductivity is purely due to the amorphization of the polymer structure even at room temperature and a relatively moderate tendency to form ionic aggre-gates. Especially, the concentration of lithium salts plays an important role for conductivity rather than the nature of salts. In other words, the ionic conductivity is also affected by the diffusion rate of ions, which depends on the size of the ion. Larger size of anion of LiClO$_4$ and the appropriate quantity of salt dictate the choice of higher conductivity. In that sense, lower concentration of Li salt in the polymer electrolyte shifts to maximum conductivity. The amorphization of the polymer electrolyte is more for $x = 2$ wt% in the above composition than single salt system, which is evident from figure 2b. It reveals that the LiClO$_4$ salt has higher lattice energy than any of the other lithium salts and the interaction between the polymer and the lithium salt is relatively small. This effect influences the electro-chemical stability window. When the temperature approaches the maximum towards the melting point of polymer host, the effects of ionic aggregation begin to play a role.

The temperature-dependent conductivities of PVdF–EC/PC–[xLiCF$_3$SO$_3$ + (8 − x) LiClO$_4$] (where $x = 0, 2, 4, 6, 8$%) systems are displayed in figure 8 for different temperature ranges. The figure explains that (i) the conductivity increases with increase in temperature for all polymer electrolytes and (ii) the conductivity–temperature plots follow non-linearity at low temperature. Such features are generally observed for high viscous electrolytes or much amorphous polymeric systems. They cannot be described by Arrhenius relationship but possible by the Vogel–Tamman–Fulcher (VTF) expression based on the free volume concept (Kim *et al* 1996). The increase of conductivity with temperature is interpreted as being due to a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymers. As the amorphous region progressively increases, however, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This in turn, favours the hopping of inter-chain and intra-chain ion movements and the conductivity of the polymer electrolyte becomes high (Rao *et al* 1995).

4. Conclusions

PVdF based gel polymer electrolytes were prepared by solution casting technique. All electrolytes show apprecia-

ble conductivities even at room temperature. PVdF (24)–EC/PC (68)–[(2) LiCF$_3$SO$_3$/(6) LiClO$_4$] system was found to be good in conductivity and thermal stability. Spectroscopic studies were used to confirm their complexation behaviour and structural status of the gel polymer electrolytes.

References

Alamgir M and Abraham K M 1993 *J. Electrochem. Soc.* **140** L96

Appetecchi G B, Croce F and Scrosati B 1995 *Electrochim. Acta* **40** 991

Appetecchi G B, Alessandrini F, Carewska M, Caruso T, Prosini P P, Scaccia S and Passerini S 2001 *J. Power Sources* **97** 790

Bohnke O, Rousseiot C, Gillet P A and Truche C 1992 *J. Electrochem. Soc.* **139** 1862

Choe H S, Giaccai J, Alamgir M and Abraham K M 1995 *Electrochim. Acta* **40** 2289

Every H A, Zhou F, Forsyth M and Macfarlane D R 1998 *Electrochim. Acta* **43** 1465

Hashmi S A and Chandra S 1995 *Mater. Sci. & Eng.* **B34** 18

Jiang Z, Corroll B and Abraham K M 1997 *Electrochim. Acta* **42** 2667

Kim D W, Park J K, Bae J S and Pyun S I 1996 *J. Polym. Sci. B Polym. Phys.* **34** 2127

Magistris A, Mustarelli P, Parazzoli F, Quartarone E, Piaggio P and Bottino A 2001 *J. Power Sources* **97–98** 657

Manuel Stephan A, Gopukumar S, Renganathan N G and Anbu Kulandainathan M 2005 *Eur. Polym. J.* **41** 15

Martuscelli E, Pracella M and Yue W P 1984 *Polymer* **25** 1097

Mano A, Felishersti M I, Matencio T and De Paoli M A 1996 *Polymer* **37** 5165

Periasamy P *et al* 1999 *Solid State Ionics* **126** 285

Rajendran S and Uma T 2000 *Mater. Letts* **44** 208

Rajendran S, Kannan R and Mahendran O 2001a *J. Power Sources* **96** 406

Rajendran S, Kannan R and Mahendran O 2001b *Mater. Letts* **49** 172

Ramesh S and Arof A K 2001 *J. Power Sources* **99** 41

Rao S S, Reddy M J, Narsaiah E L and Rao U V S 1995 *Mater. Sci. Eng.* **B33** 173

Robitaille C D and Fauteux D 1986 *J. Electrochem. Soc.* **133** 315

Sekhon S S and Singh Harinder Pal 2002 *Solid State Ionics* **152–153** 169

Slane S and Salomon M 1995 *J. Power Sources* **55** 7

Subramania A, Kalyanasundaram N T, Lakshmi Devi S, Gangatharan R and Vasudevan T 2004 *J. Electrochem.* **20** 247

Sukeshini M, Nishimoto A and Watanabe M 1996 *Solid State Ionics* **86** 385

Tsuchida E, Ohno H and Tsunemi E 1983 *Electrochim. Acta* **28** 591, 833

Watanabe M, Kanaba M, Matsuda H, Mizoguchi K, Shinohara I, Tsuchida E and Tsunemi K 1981 *Macromol. Chem. Rapid Commun.* **2** 741

Watanabe M, Kanaba M, Nagaoka K and Shinohara I 1983 *J. Polym. Sci. Polym. Phys. Ed.* **21** 939

Wright P V 1975 *Br. Polym. J.* **7** 319

Yang C R, Perng J T, Wang Y Y and Wan C C 1996 *J. Power Sources* **62** 89