ChemTech



International Journal of ChemTech Research

CODEN (USA): IJCRGG ISSN: 0974-4290 Vol.8, No.2, pp 605-611, 2015

# Characterization of Polymer Electrolytes Based on Poly(vinylidene fluoride-*co*-hexafluoropropylene) and Lithium Triflate

# Merhawi Abreha<sup>1</sup>\*, A. R. Subrahmanyam<sup>2</sup>, J. Siva Kumar<sup>1</sup>

<sup>1</sup>Department of Physics, Osmania University, Hyderabad – 500007, India <sup>2</sup>Department of Physics, MVSR Engineering College, Hyderabad -5, India

**Abstract:** Solid polymer electrolytes composed of poly (vinylidene fluoride-*co*-hexafluoro propylene) (PVdF-HFP) and various concentrations of lithium trifluoromethanesulfonate (lithium triflate) were prepared by the solution casting technique in order to determine the optimal composition of the lithium salt for maximum ionic conductivity. Structural changes and complex formations of the polymer-salt systems were ascertained from x-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy studies. Scanning electron microscope (SEM) investigation results confirm morphological changes upon the addition of the salt to the polymer. Measurements of the temperature-dependent ionic conductivity of the electrolytes were performed in the temperature range 303 - 393 K using a DC conductivity setup. The results reveal that the ionic conductivity of the polymer electrolytes containing various salt concentrations increases with temperature and obeys the Arrhenius rule. Also, it was found that the electrolyte containing 25 wt.% of lithium triflate exhibits the highest room temperature (303 K) ionic conductivity of 1.44 × 10<sup>-5</sup> S cm<sup>-1</sup>. The conductivity results are consistent with the structural and morphological properties of the electrolyte samples. Keywords: Solid Polymer electrolyte, PVdF-HFP, Lithium triflate, Ionic conductivity.

## 1. Introduction

Solid polymer electrolytes (SPEs) attract a great deal of attention from many materials researchers because of their potential applications in a variety of electrochemical devices such as lithium ion batteries, fuel cells, supercapacitors, electrochromic displays and sensors [1-7]. Owing to the ever-growing need for safe, reliable and more efficient electrical energy storage systems in portable devices and automotive industries, much research has been taking place in the area of polymer lithium ion battery technologies. The major advantages of polymer electrolytes over the conventional liquid electrolytes are their intrinsic properties such as ease of processing, good mechanical properties, high energy density, no risk of leakage and their ability to form good electrode-electrolyte interfacial contact. Furthermore, with the use of polymer electrolytes in lithium ion batteries, low cost of fabrication can be expected.

SPEs are prepared by complexing polymer matrices with alkali metal salts and usually contain both crystalline and amorphous phases. It has been widely accepted that the electrical conductivity of the electrolyte takes place through the amorphous phase of the polymer [8,9] and depends largely on the proportion of amorphous component and the mobilities of the ions within the amorphous regions [10]. Since the early works of P. V. Wright on ionic conductivity of alkali metal salt complexes of poly(ethylene oxide) (PEO) in 1973 [11] and the proposal by M. Armand of using polymer electrolytes for electrochemical cells in 1978 [12], an enormous amount of research has been conducted in the field of polymer electrolytes to find the optimal combination of host polymer matrix and dopant salt for adequate ionic conductivity [13-18].

Polymer electrolytes which are composed of poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP),  $[-CH_2CF_2-]_x[-CF_2CF(CF_3)-]_y$ , are expected to have good electrochemical stability and non-combustibility owing to the strong electron-withdrawing functional groups, -C-F-, in the VdF units ]19] and plasticity due to steric hindrance provided by -CF\_3- pendant group in the HFP monomors [20]. Also, PVdF-HFP possesses advantageous characteristic properties such as high dielectric constant ( $\varepsilon = 8.4$ ), high degree of amorphocity and low glass transition temperature. These inherent properties should assist in providing mobile lithium ions more free volume giving rise to higher ionic conductivity. Therefore, PVdF-HFP is a highly promising material for polymer electrolyte of lithium ion batteries [21-23].

In this study, ion conducting SPE films consisting of PVdF-HFP as host polymer and lithium triflate as the source of charge carriers (Li-ions) were examined in order to determine the optimal composition for maximum ionic conductivity. DC conductivity measurements have been carried out for complexes of various polymer-salt compositions. XRD, FTIR spectroscopy and SEM analyses were conducted to investigate the structural and morphological changes in the electrolyte films.

### 2. Experimental

#### 2.1 Preparation of Samples

All polymer electrolyte films were prepared by the solution casting technique. PVdF-HFP (Aldrich, USA) as polymer matrix, lithium triflate (Aldrich, USA) as dopant salt and anhydrous tetrahydrofuran (THF) (SRL, India) as common solvent were used to prepare the electrolyte films. For each sample, a fixed amount of PVdF-HFP was first fully dissolved in THF to form the polymer matrix of the electrolyte system. Then lithium triflate (LiTf), LiCF<sub>3</sub>SO<sub>3</sub>, was added to the polymer solution and the resulting mixture was vigorously stirred for several hours for polymer-salt complex to occur. The polymer-salt solution was then cast as film onto a clean petri dish to allow THF to evaporate slowly at room temperature. Then mechanically stable and free-standing polymer-salt films of thickness ranging from  $120 - 250 \mu m$  were formed. The films with various compositions of LiTf obtained after the evaporation of THF were further dried in a temperature-controlled hotair oven at 333 K for 4 hours to remove any traces of THF. The various compositions of PVdF-HFP and LiTf used in preparing the polymer electrolytes are depicted in Table 1.

#### 2.2 Characterization of Samples

X-ray diffraction (XRD) studies of the electrolyte films were carried out using PHILIPS X'Pert diffractometer, operating at 40 kV, in the glancing angles ranging from  $2\theta = 10^{\circ}$  to  $80^{\circ}$ . Fourier transform infrared (FTIR) spectra were recorded with IRPrestige-21 spectrometer over the wavenumber range of 4000 – 250 cm<sup>-1</sup>. The films were also examined under scanning electron microscope (SEM) (ZEISS EVO18) for their morphological properties. The electrical conductivity analysis of the various electrolyte samples was carried out by sandwiching each sample between two stainless steel blocking electrodes using a locally designed DC conductivity setup. The DC ionic conductivity ( $\sigma$ ) of each sample, at various temperatures between 303 and 393 K, was obtained from bulk resistance measurements performed using the Keithley Model 196 System DMM. The calculations of the conductivity were done using the equation  $\sigma = t/\pi r^2 R_b$ , where t is the thickness, r is the radius, and  $R_b$  is the bulk resistance of the polymer electrolyte disc sandwiched between the blocking electrodes.

Sample designation	PVdF-HFP (wt.%)	LiTf (wt.%)
LiTf00	100	0
LiTf10	90	10
LiTf15	85	15
LiTf20	80	20
LiTf25	75	25
LiTf30	70	30
LiTf35	65	35

Table 1 Composition (wt.%) of PVdF-HFP and LiTf

## 3. Results and Discussion

### 3.1 XRD Analysis

In order to investigate the structural nature of the polymer electrolyte films, XRD was performed. The XRD patterns of pure LiTf powder, pure PVdF-HFP pellets and films of PVdF-HFP/LiTf complexes containing various weight percentages of LiTf are presented in Fig. 1. Fig. 1 (a) shows that well distinguished sharp peaks with high intensity of pure LiTf are observed at  $2\Theta = 13.41^{\circ}$ ,  $16.13^{\circ}$ ,  $19.37^{\circ}$ ,  $20.01^{\circ}$ ,  $22.07^{\circ}$ ,  $24.17^{\circ}$ ,  $25.03^{\circ}$ ,  $27.47^{\circ}$ ,  $32.59^{\circ}$ ,  $33.11^{\circ}$ ,  $39.83^{\circ}$ ,  $41.17^{\circ}$  and  $42.43^{\circ}$ . It can be noted from Fig. 1 (b) that the sharp crystalline peaks corresponding to LiTf are absent in all the polymer-salt complexes confirming that a complete complexation occurred between the polymer and the lithium salt in all the samples studied.

The diffractogram of pure PVdF-HFP (LiTf00) as indicated in Fig. 1 (b) reveals two peaks at  $2\theta = 18.71^{\circ}$  and  $20.23^{\circ}$ . These peaks indicate the semicrystalline nature of pure PVdF-HFP [20]. However, it is observed that the two peaks of the crystalline part of pure PVdF-HFP disappear and a new broadened peak with slightly reduced intensity is observed for the polymer-salt complexes. This suggests an increase by a small fraction of the amorphous region as a result of disruption of the crystalline phase of the PVdF-HFP by addition of LiTf and the occurrence of complexation between PVdF-HFP and LiTf. As the salt concentration increases above 25 wt.%, it is observed that the amorphocity of the polymer complexes slightly decreases, which could be the reason for the observed decrease in electrical conductivity of LiTf30 and LiTf35.



Fig. 1 XRD patterns of (a) LiTf and (b) PVdF-HFP/LiTf complexes containing 0, 10, 15, 20, 25 and 30 wt.% of LiTf

#### 3.2 FTIR Analysis

FTIR spectroscopy studies were carried out in order to investigate the interaction between PVdF-HFP and LiTf. FTIR spectra of the salt-free PVdF-HFP film, pure LiTf powder and a sample of PVdF-HFP/LiTf complex with the wavenumber ranging from 4000 to 470 cm<sup>-1</sup> are shown in Fig. 2. The characteristic vibrational peaks of pure PVdF-HFP at 976, 760, 613 and 531 cm<sup>-1</sup> can be assigned to the crystalline phase of

the polymer [15, 24, 25], and the peak at 872 cm<sup>-1</sup> corresponds to the amorphous phase of PVdF-HFP [16]. The frequency peaks found around 613 and 490 cm<sup>-1</sup> are assigned to the wagging vibrations of -C-F- and  $-CF_2$ -, respectively [25,26]. Upon addition of LiTf to PVdF-HFP, the frequencies 976 and 760 cm<sup>-1</sup> were observed to disappear. Whereas, the frequencies 490, 531, 613, and 872 cm<sup>-1</sup> shifted to 482, 548, 590 and 868 cm<sup>-1</sup>, respectively. In addition to this, some new peaks when compared to those of PVdF-HFP spectrum were observed. These results confirm complex formation in the prepared polymer electrolytes.



Fig. 2 FTIR spectra of LiTf100, LiTf00 and LiTf25



Fig. 3 Scanning electron micrographs of (a) LiTf00 at 2,500X, (b) LiTf00 at 10,000X, (c) LiTf25 at 2,500X and (d) LiTf25 at 10,000X

#### 3.3 SEM Analysis

Fig. 3 shows the scanning electron micrographs of the salt-free PVdF-HFP film and the polymer electrolyte exhibiting maximum ionic conductivity (LiTf25) at magnifications 2,500X and 10,000X. From the SEM results, it can be seen that the surface morphology of PVdF-HFP was altered due to the addition of lithium triflate. It is observed from the SEM images in Fig. 3 (c) and (d) that the surface of the salted polymer electrolyte has a numerous network of interconnecting microstructures as compared to the smoother structures of the salt-free electrolyte in Fig. 3 (a) and (b). These interconnecting structures, formed as a result of phase separation between the polymer and the solvent during evaporation, are another evidence that the addition of salt to the polymer has resulted in a completely different morphological structure. These microstructures can

help for ion hopping in the polymer-salt complex and hence they are responsible for enhancing ionic conductivity of the polymer electrolyte.

#### 3.4 Ionic Conductivity Studies

Generally, ionic conductivity depends on the concentration and mobility of the carrier ions according to the definition  $\sigma = ne\mu$ , where *n*, *e* and  $\mu$  represent the concentration of ions, the electric charge, and the mobility of the ions, respectively. In the present study, the electrical conductivity of PVdF-HFP-based lithium ion conducting solid polymer electrolyte was investigated using DC conductivity apparatus in order to determine the optimal salt concentration for maximum conductivity. The room temperature conductivity data of the polymer electrolyte as a function of salt concentration are presented in Table 2. It was observed that the ionic conductivity increases significantly with salt content up to 25 wt.%, and then decreases on further increase of concentration of the salt. The polymer electrolyte comprising 25 wt.% of lithium triflate exhibited maximum ionic conductivity of 1.44 X 10<sup>-5</sup> S cm<sup>-1</sup> at room temperature (303 K). The enhancement in ionic conductivity with the addition of LiTf is attributable to an increase in mobility and concentration of salt after a certain content can be due to ion-ion association at higher salt concentrations. These results are in good support of the observations in the structural and morphological studies.

Sample designation	PVdF-HFP (wt.%)	LiTf (wt.%)	σ (S cm <sup>-1</sup> )
LiTf00	100	0	2.22 X 10 <sup>-10</sup>
LiTf10	90	10	1.64 X 10 <sup>-7</sup>
LiTf15	85	15	6.64 X 10 <sup>-7</sup>
LiTf20	80	20	2.01 X 10 <sup>-6</sup>
LiTf25	75	25	1.44 X 10 <sup>-5</sup>
LiTf30	70	30	8.02 X 10 <sup>-6</sup>
LiTf35	65	35	6.99 X 10 <sup>-6</sup>

Table 2 Ionic conductivity of PVdF-HFP based electrolytes with various LiTf concentrations at room temperature (303 K)



Fig. 4 Arrhenius plots of PVdF-HFP based polymer electrolytes containing various weight percentages of LiTf

The variation of ionic conductivity with temperature for the polymer electrolytes was also investigated. The polymer electrolyte containing 25 wt.% of LiTf (LiTf25) offers the maximum ionic conductivity of 6.44 X  $10^{-5}$  S cm<sup>-1</sup> at 393 K. Arrhenius plots of the ionic conductivity on a logarithmic scale (log  $\sigma$ ) versus temperature inverse of the polymer electrolyte for various salt concentrations is shown in Fig. 4. As it may be noted from the figure, the conductivity values do not show any abrupt jump at any stage indicating the fact that the polymer electrolytes exhibit a completely amorphous structure [29]. In fact, the logarithm of conductivity versus reciprocal temperature plots of the samples studied show nearly linear variation, with the calculated linear regression values close to unity. This behaviour suggests that the temperature-dependent ionic conductivity of

the polymer electrolytes obeys the Arrhenius relation,  $\sigma = \sigma_0 \exp(-E_a/k_BT)$ , where  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy for conduction and  $k_B$  is the Boltzmann constant. From the figure, it can be observed that the ionic conductivity increases with temperature for all concentrations of salt. This result shows consistency with the theory established by M. Armand in 1978 [12] and other earlier reports on conductivity property of various polymer electrolytes [16, 18, 28, 30-32]. The observed increase in conductivity could be due to increased segmental motion of the polymer chains and mobility of ions, which may be explained with the help of the free volume theory in polymers [33,34]. When the temperature - and hence the thermal energy - increases, the polymer electrolyte gains higher free volume. This free volume promotes segmental motion of the polymer temperature in conductivity in the polymer network.

#### 4. Conclusions

Lithium ion conducting solid polymer electrolytes based on PVdF-HFP copolymer and various concentrations of LiTf were prepared using the solution casting method. XRD and FTIR analyses reveal increase in amorphous nature of the polymer-salt electrolyte films and confirm interaction and complexation between the polymer and the salt. Moreover, morphological examination of the electrolyte films using the SEM indicates increase in amorphocity and porosity of the films upon the addition of salt to the polymer, which could be the reason for enhanced ionic conductivity. An increase in conductivity is observed with the increase in lithium ion concentration up to a certain salt content. The ionic conductivity is found to be maximum at the salt concentration of 25 wt.%. For all salt concentrations, the ionic conductivity of the polymer electrolyte increases with the increase in temperature, which can be attributed to the expansion of the polymer to produce free volume for enhanced movement of polymer chains and mobile lithium ions.

#### Acknowledgements

The authors are grateful to the Department of Physics, Osmania University, India for providing experimental research facilities. They would also like to thank the Department of Chemistry, Osmania University, India for their FTIR Spectrometer. One of the authors, Merhawi, acknowledges the Ministry of Education of the Federal Democratic Republic of Ethiopia for the financial support provided under the Ethiopian Government Scholarship scheme.

### References

- 1. Croce F., Sacchetti S., Scrosati B. (2006) J Power Sources 162: 685–689
- 2. Harsányi G. (2000) Sensor Rev 20, 98–105
- 3. Rajendran S., Sivakumar P., Babu R. S. (2007) J Power Sources 164: 815–821
- 4. Stephan A. M. (2006) *Eur Polym J* 42: 21–42
- 5. Wright P. V. (1998) Electrochim Acta 43: 1137–1143
- 6. Xie H., Tang Z., Li Z., He Y., Liu Y., Wang H. (2008) J Solid State Electr 12: 1497–1502
- 7. Sequeira C., Santos D. (Eds.). (2010), Woodhead Publishing, Cambridge.
- 8. Berthier C., Gorecki W., Minier M., Armand M. B., Chabagno J. M., Rigaud P. (1983) Solid State Ionics 11: 91–95
- 9. Ward I. M., Boden N., Cruickshank J., Leng S. A. (1995) Electrochim Acta 40: 2071–2076
- 10. Wright P. V. (1975) Brit Polym J 7: 319-327
- 11. Fenton D. E., Parker J. M., Wright P. V. (1973) Polymer 14: 589
- 12. Armand M. B., Chabagno J. M., Duclot M. (1978) In: Second International Meeting on Solid Electrolytes: Extended Abstracts, St. Andrews, UK
- Ataollahi N., Ahmad A., Hamzah H., Rahman M. Y. A., Mohamed N. S. (2012) Int J Electrochem Sc 7: 6693–6703
- 14. Aziz S. B. (2013) Iran Polym J 22: 877-883
- 15. Ibrahim S., Yassin M. M., Ahmad R., Johan M. R. (2011) *Ionics* 17: 399–405
- Kuo C.-W., Li W.-B., Chen P.-R., Liao J.-W., Tseng C.-G., Wu T.-Y. et al. (2013) Int J Electrochem Sc 8: 5007–5021
- 17. Noor M. M., Careem M. A., Majid S. R., Arof A. K. (2011) Mater Res Innov 15: S157-S160
- 18. Singh T. J., Bhat S. V. (2003) B Mater Sci 26: 707–714
- 19. Choe H. S., Giaccai J., Alamgir M., Abraham K. M. (1995) Electrochim Acta 40: 2289–2293

- 20. Saikia D., Kumar A. (2004) Electrochim Acta 49: 2581–2589
- 21. Kim K. M., Park N.-G., Ryu K. S., Chang S. H. (2002) Polymer 43: 3951–3957
- 22. Meyer W. H. (1998) Adv Mater 10: 439-448
- 23. Scrosati B., Garche J. (2010) J Power Sources 195: 2419–2430
- 24. Aravindan V., Vickraman P. (2008) J Appl Polym Sci 108: 1314–1322
- 25. Li Z., Su G., Wang X., Gao D. (2005) Solid State Ionics 176: 1903-1908
- 26. Angulakshmi N., Thomas S., Nahm K. S., Stephan A. M., Elizabeth R. N. (2011) Ionics 17: 407-414
- 27. Isa K. M., Osman Z., Arof A., Othman L., Zainol N., Samin S., Chong W., Kamarulzaman N. (2014) Solid State Ionics 268: 288–293
- 28. Kumar R., Sharma J. P., Sekhon S. S. (2005) Eur Polym J 41: 2718–2725
- Michael M. S., Jacob M. M. E., Prabaharan S. R. S., Radhakrishna S. (1997) Solid State Ionics 98: 167– 174
- 30. Stephan A. M., Kumar S. G., Renganathan N. G., Kulandainathan M. A. (2005) Eur Polym J 41: 15-21
- 31. Stephan A. M., Kumar T. P., Renganathan N. G., Pitchumani S., Thirunakaran R., Muniyandi N. (2000) *J Power Sources* 89: 80–87
- 32. Subramania A., Sundaram N. T. K., Kumar G. V., Vasudevan T. (2006) Ionics 12: 175–178
- 33. Miyamoto T., Shibayama K. (1973) J Appl Phys 44: 5372–5376
- 34. Ramesh N., Duda J. L. (2001) J Membrane Sci 191: 13-30

#### \*\*\*\*