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Investigations on PVdF- HFP - PEMA polymer blend electrolytes doped with different lithium salts

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Abstract. Plasticized polymer blend electrolytes were prepared by incorporating poly (vinylidene fluoride-co-hexafluoropropylene)(PVdF-HFP) and poly(ethylmethacrylate) (PEMA) complexed with plasticizer (PC) and different lithium salts such as LiClO₄, LiBF₄, LiCF₃SO₃ and LiN (CF₃SO₂)₂ using solution-casting technique. X-ray diffraction and Fourier transform infra-red techniques confirms the structural characters and complex formation of the polymer electrolytes respectively. AC impedance analysis was carried out for all the samples in the range 303-373K. The results suggest that among the various lithium salts, LiN (CF₃SO₂)₂ based electrolytes exhibited the highest ionic conductivity ($3.17 \times 10^{-3} \text{ Scm}^{-1}$).

1. Introduction

Studies on polymer electrolyte was initiated by Fenton in 1973 [1], their technological significance was not appreciated until the research undertaken by Armand et al. [2]. To date, several types of polymer hosts have been developed which include poly (ethyleneoxide) (PEO), poly acrylonitrile (PAN), poly (methyl methacrylate) (PMMA), poly (vinyl chloride) (PVC), poly (vinylidene fluoride) (PVdf) etc.,. Recently, copolymer of Vinylidene fluoride with hexafluoropropylene (PVdF-HFP), were used by Gozdz et al. and Tarascon et al.[3-6], which contained amorphous domains capable of trapping large volume of liquid electrolytes, and crystalline regions which provide sufficient mechanical integrity for the process of free - standing films, and thereby, eliminated the need for cross - linking step.

Gel polymer electrolytes based on a copolymer of and a solution of ethylene carbonate (EC), diethyl carbonate (DEC) and LiN(CF₃SO₂)₂ as salt were prepared by Capiglia et al.[7], by changing the content of the polymer. The change in salt concentration was reflected in the conductivity change



in the range of $10^{-2} - 10^{-8} \text{ Scm}^{-1}$. The ionic conductivity and compatibility of PVdF-HFP gel electrolytes with a combination of EC and PC as plasticizers and three different lithium salts (LiClO_4 , LiBF_4 , LiCF_3SO_3) have been reported by Stephan et al.[8]. Among the salts studied, the film which possess LiBF_4 as salt exhibited maximum conductivity and was attributed to the low lattice energy of the salt. On contrary, the films, which possess LiBF_4 exhibited poor compatibility with Lithium metal anode and were identified due to the formation of LiF in the layer. The and cycling profile of LiCoO_2/Li and $\text{LiCoO}_2/\text{MCMB}$ cells comprising gel polymer electrolyte (PVdF-HFP (25%), EC-PC (65%) and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (10%)) have been reported by Kim and Moon [9]. present work has been postulated in finding the appropriate Lithium salt (LiClO_4 , LiBF_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$) with PVdF-HFP-PEMA plasticized with PC, which could be effectively used in Lithium battery applications.

2. Methodology

All polymer electrolyte samples were prepared by solution casting technique. The polymer host PVdF-HFP, PEMA and plasticizer PC was obtained from Aldrich chemical company Inc., USA and the inorganic salt LiClO_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ was obtained from Aldrich, USA and LiBF_4 , LiCF_3SO_3 were obtained from Lancaster, England. The solvent Acetone was bought from E-Merck, Germany were used. The polymers and the Li salts were annealed under vacuum at 100°C , 120°C respectively for 10 hrs and each component was dissolved in pre-distilled Acetone (E-Merck, Germany). The dissolved polymer and salt were stirred continuously for 24 hr at room temperature and at 50°C until homogeneous slurry was obtained. The thus obtained slurry was cast on to Teflon bushes and Teflon covered glass plates. The polymer films were dried under argon atmosphere at room temperature for 24 hrs and at 50°C in order to evaporate the residual solvents present in the polymer electrolyte.

3.Characterizations

Structural characters and complex formation of PVdF-HFP-PEMA composite polymer electrolytes were investigated by XRD studies using BRUKER X-ray diffractometer with $\text{Cu K}\alpha$ radiation in the range $10\text{-}80^\circ$ in steps of $0.02^\circ/\text{sec}$ and FTIR analysis using SHIMADZU IR AFFINITY spectrometer under transmittance mode from 4000 to 400 cm^{-1} respectively. Conductivity of PVdF-HFP-PEMA composite polymer electrolyte membranes (PEMs) were characterized by a.c. impedance spectroscopy using HIOKI 3532-50 LCR Hi TESTER meter in the frequency range of 50 Hz to 5 MHz at different temperature (viz., 303-373K).

4. Results and Discussion.

4.1 Results of XRD.

The X-ray diffraction patterns of pure PVdF-HFP, PEMA, PC, LiX ($\text{X} = \text{ClO}_4^-$, BF_4^- , CF_3SO_3^- , $\text{N}(\text{CF}_3\text{SO}_2)_2^-$) and polymer complexes are shown in Fig [4.1] The Fig [4.1a] shows the characteristic diffraction peaks of the P(VdF-HFP) at angles 18.09 and 20.47° due to the presence of crystalline PVdF in PVdF-HFP [10 - 12]. The semi crystalline nature of the polymer has been considerably reduced upon the addition of the plasticizer and Lithium salts. Most of the peaks pertaining to LiClO_4 , LiBF_4 , LiCF_3SO_3 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in Fig [4.1] are found to be absent in the complexes indicating the complete dissolution of Lithium salts in the polymer matrices. The higher amorphous facilitates better ionic conductivity in the polymer electrolytes. Hence, from the above result, it is confirmed that there exists a definite complexation between the polymers, plasticizer and LiX salts.

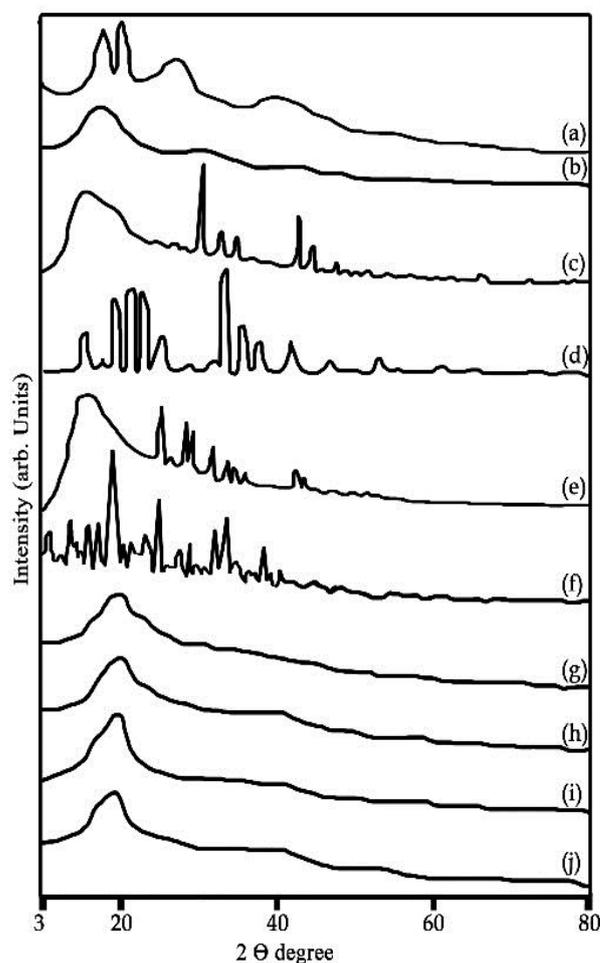


Figure 4.1 XRD Patterns of pure material (a) PVdF-HFP (b) PEMA (c) LiClO₄ (d) LiBF₄ (e) LiCF₃SO₃ (f) LiN(CF₃SO₂)₂ and (g-j) complex polymer electrolytes PVdF-HFP-PEMA-PC-Li (X) [X=ClO₄ (g), BF₄ (h), CF₃SO₃ (i) and N(CF₃SO₂)₂ (j)]

4.2. Results of FTIR characterization

FTIR spectrum is an indispensable record which gives sufficient information about the structure of the polymer. FTIR spectra of these materials vary according to their composition and may be able to show the occurrence of complexation [13, 14] and interactions between the various constituents. Here, it is used to establish interactions between the polymers PVdF-HFP, PEMA, Plasticizer PC, LiX (X = ClO₄⁻, BF₄⁻, CF₃SO₃⁻, N(CF₃SO₂)₂) salts and monitoring the co-ordination of Li⁺ ions. Such interactions impart some changes in the vibrational modes of the atoms or molecules in the material. FTIR spectra of pure P(VdF-HFP), PEMA, PC, LiX salts and polymer complexes are shown in [Fig 4.2]. The vibrational bands at 1072, 976, 763 and 614 cm⁻¹ are characteristics of the crystal phase, and bands at 879 and 841 cm⁻¹ correspond to the amorphous phase for PVdF-HFP.

The carbonyl group C = O (1730 cm⁻¹), CH₂ scissoring (1485 cm⁻¹), CH₂ wagging (947 cm⁻¹) and CH₂ rocking (756 cm⁻¹) vibrations of PEMA are found to be shifted in all the complexes due to the effect of polymers and LiX salts. The peak at 881 cm⁻¹ is assigned to vinylidene group of polymer [Fig 4.2]. Frequencies at 1483 and 1400 cm⁻¹ are assigned to CH₃ asymmetric bending and C - O stretching

vibrations of PC which are found to be shifted to a higher side in all the complex. This could be due to the interaction of polymers, plasticizer and LiX salts.

The frequency appearing at 510 cm^{-1} of the complex with LiBF_4 can be attributed to the bending mode of BF_4^- . The band which appears at 765 cm^{-1} is assigned to $\nu(\text{CF}_3)$ mode of the CF_3SO_3^- . Lithium imide salt also shows a band at 1355 cm^{-1} corresponding to the $\nu(\text{SO}_2)$ stretching frequency. The band at about 950 cm^{-1} is assigned to the totally symmetric vibration of perchlorate anion.

In addition to the above, there are some new peaks obtained at around 3900 , 3000 , and 2900 cm^{-1} in the complexes. The above analysis as a whole establishes the formation of polymer-salt complexes [15].

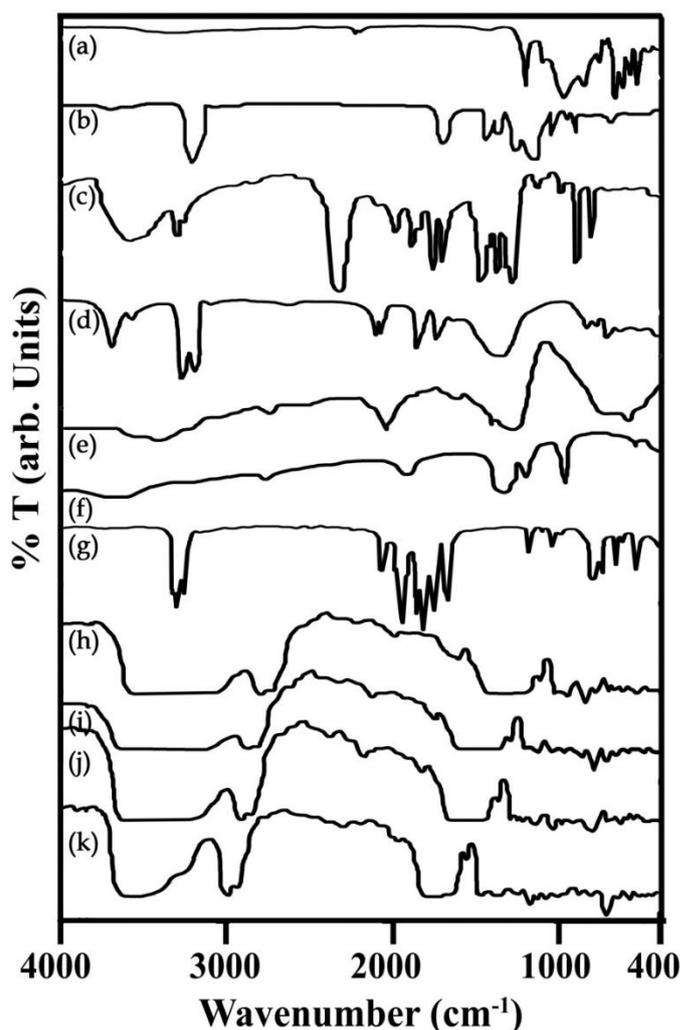


Figure 4.2 FTIR Spectra of pure (a) PVdF-HFP (b) PEMA (c) PC (d) LiClO_4 (e) LiBF_4 (f) LiCF_3SO_3 (g) $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and (h-k) complex polymer electrolytes PVdF-HFP-PEMA-PC-Li (X) [X= ClO_4 (h), BF_4 (i), CF_3SO_3 (j) and $\text{N}(\text{CF}_3\text{SO}_2)_2$ (k)]

4.3 Results of conductivity studies

The ionic conductivity has been identified as a potential tool to characterize the electrical properties of many materials. In general, the ionic conductivity of the polymer electrolyte depends on the actual concentration of the conducting species and their mobility. In this present work, blended polymer electrolytes were prepared using polymers PVdF-HFP, PEMA, PC and different lithium salts such as LiClO_4 , LiBF_4 , LiCF_3SO_3 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. Polymer electrolytes in the ratio PVdF-HFP(20) - PEMA(5) - PC (67) - LiX (8); ($\text{X}=\text{ClO}_4^-$, BF_4^- , CF_3SO_3^- , $\text{N}(\text{CF}_3\text{SO}_2)_2^-$) were prepared in order to find the salt suitable to be used in lithium battery applications. The ionic conductivity measurements are carried out on these polymer electrolytes by employing variable frequency complex ac 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 conductivity values of the polymer complexes were calculated from the resistance values obtained from the intercepts of the isotherm in the Cole-Cole plot and are tabulated in Table (4.1). The graphical plotting of the variation of Z' with Z'' for the film B₄ is shown in Fig (4.3).

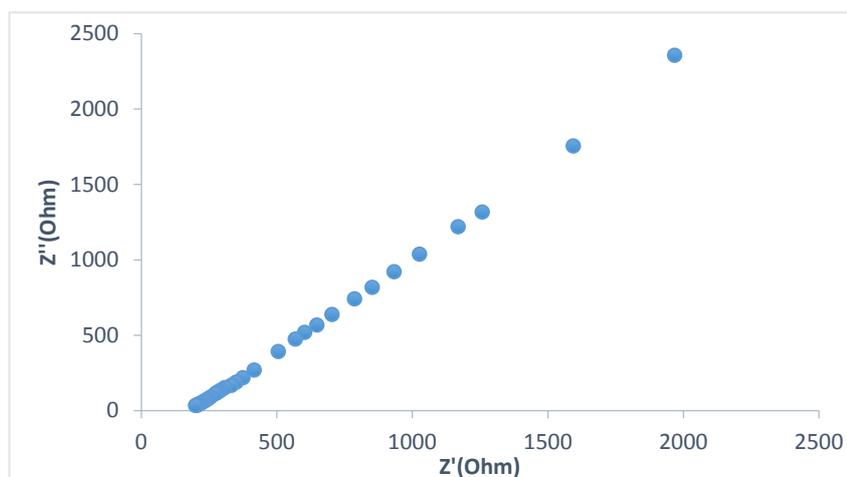


Figure 4.3 Z real Vs Z imaginary plot for PVdF-HFP -PEMA-PC- $\text{LiN}(\text{CF}_3\text{SO}_2)$

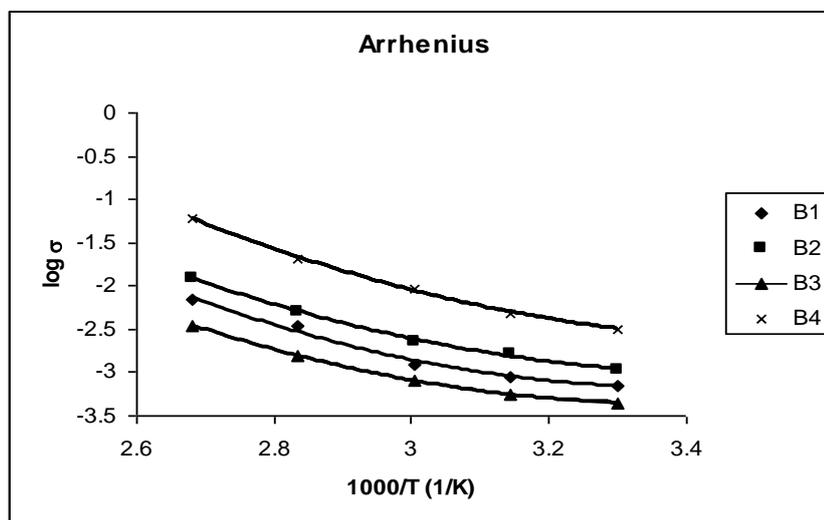


Figure 4.4 Arrhenius plot of $\log \sigma$ against reciprocal temperature of PVdF - HFP- PEMA - PC - LiX [X = ClO_4^- , BF_4^- , CF_3SO_3^- , $\text{N}(\text{CF}_3\text{SO}_2)_2^-$]

At room temperature conductivity, PVdF-HFP(20) - PEMA(5) - PC (67) - LiX (8) films were subjected to conductivity measurements at five different temperatures viz. 30°, 45°, 60°, 80° and 100°C. It is evident that as the temperature increases (Table (4.1) and Fig (4.4)) the conductivity is also found to increase. This behavior could be explained on the basis of free volume model theory.

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 B₄ [PVdF-HFP(20)-PEMA(5) - PC(67) -LiN(CF₃SO₂)₂ (8)] is found to be $3.17 \times 10^{-3} \text{ Scm}^{-1}$ which is higher when compared to the other films consisting of LiClO₄, LiBF₄ or LiCF₃SO₃ and is attributed to the fact that there is a higher dissociation of bulky anion in the polymer host. Also, the large flexible anion of LiN(CF₃SO₂)₂ acts as plasticizer; which reduces the glass transition temperature of PEO/LiXsystems [16, 17].

The degree of dissociation of the various lithium salts has been previously compared and it was reported in the following order. This result suggests that ion-pairing takes place to a lesser extent in the electrolytes containing LiN(CF₃SO₂)₂, LiClO₄ or LiBF₄ compared with the electrolyte which contains LiCF₃SO₃. The conductivity order based on the anion type is not fully understood for both liquid and polymer electrolytes for lithium batteries. The conductivity can be affected by the ionic mobility, ion-ion interactions, anion size, lattice energies and salt dissociation and also anion polarization, all of which depend on salt concentration. $\text{LiCF}_3\text{SO}_3 < \text{LiBF}_4 < \text{LiClO}_4 < \text{LiIm}$

Films	PVdF-HFP(20)- PEMA(5)-PC(67)- LiX(8)	Conductivity values of PVdF-HFP-PEMA-PC- LiX in 10^{-3}Scm^{-1}				
		303 K	318 K	333 K	353 K	373 K
B ₁	LiClO ₄	0.71	0.89	1.22	2.69	6.85
B ₂	LiBF ₄	1.07	1.65	2.28	5.10	12.30
B ₃	LiCF ₃ SO ₃	0.43	0.54	0.72	1.32	3.63
B ₄	LiN(CF ₃ SO ₂) ₂	3.17	4.90	9.55	26.91	35.40

Table 4.1 Conductivity values of PVdF-HFP -PEMA-PC- LiX[X = ClO₄⁻, BF₄⁻, CF₃SO₃⁻, N(CF₃SO₂)₂⁻] at different temperatures.

5. Conclusion

The Polymer electrolytes PVdF-HFP - PEMA - PC - LiX [X = ClO₄⁻, BF₄⁻, CF₃SO₃⁻, N(CF₃SO₂)₂⁻] have been prepared. Among the four films, the film with LiN(CF₃SO₂)₂ is found to be the best on the basis of conductivity. The conductivity of the polymer electrolyte PVdF-HFP -PEMA - PC - LiN(CF₃SO₂)₂ is found as $3.17 \times 10^{-3} \text{ Scm}^{-1}$. Hence, it is concluded that PVdF-HFP - PEMA - PC - LiN(CF₃SO₂)₂ polymer electrolyte could be a promising one for lithium battery applications.

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