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Structural and morphological studies on nanocomposite polymer blend electrolytes for Li-ion battery applications

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Abstract : Poly (Methylmethacrylate) (PMMA), Poly (Vinylidene Fluoride –co- Hexa Fluoro Propylene) and Barium titanate ($BaTiO_3$) based composite polymer electrolytes were prepared by solvent casting technique. The ionic conductivity of the polymer composite electrolytes was investigated by varying the filler concentration. The maximum ionic conductivity was found to be 3.58 x 10^{-5} S/cm at room temperature for PMMA (6.25 wt %) - PVdF-co-HFP (18.75 wt%)-$LiClO_4$ (08 wt %) - $BaTiO_3$ (08 wt %). The structural studies were carried out by X-ray diffraction analysis. The complex formation between the polymer and salt was confirmed by FT-IR study. Surface morphology of the sample having maximum ionic conductivity was scrutinized by SEM.

Key Words : Polymer electrolyte, PVdF-co-HFP, $BaTiO_3$, SEM

1. Introduction

Polymer electrolytes in Lithium ion batteries have drawn considerable attention of the researchers due to its high energy density, light weight, safety, good cyclability and ease fabrication [1]. The dissolution of low lattice energy salts into a solvating polymer leads to the formation of polymer electrolytes [2]. A numerous methods have been reported for improving the ionic conductivity, thermal stability and mechanical stability of polymer electrolytes including cross linking, grafting, copolymerization, blending, plasticization and composite[3]. Some of the polymer electrolytes have been utilized on Poly (Acrylonitrile) [4], Poly (Vinylidene fluoride) [5], Poly (Vinyl chloride)[6], Poly (Ethylene oxide) [7], Poly (Pyrollidone) [8]. The ionic conductivity in polymer electrolytes is mainly influenced by the ionic mobility. As ionic transport occurs mainly through a coupling between the ions and the polymer segmental motion, pioneering work has been carried out to experimentally investigate the properties of polymer- metal salt complexes. Poly (Methylmethacrylate) is one of the host polymer used in the plasticized polymer electrolyte. PMMA is an amorphous polymer and light weight material. It is preferred because of its easy handling, processing and low cost [9]. Poly (Vinylidene fluoride-co-hexa fluoro propylene) has found much attention recently as a promising material because of its desirable properties such as hydrophobicity, ionic conductivity, and excellent chemical stability [10]. The salt lithium per chlorate ($LiClO_4$) was chosen because of its lowest dissociation energy among the various inorganic salts, which in turn lead to high ionic conductivity [11]. In the present study, an investigation on the ionic conductivity of PMMA/PVdF-HFPpolymer blend electrolytes with 5 different $BaTiO_3$ concentrations is carried out by the AC impedance technique in the temperature range of 303- 353K. XRD and FTIR techniques are adopted to confirm the complexation and the phase structure of the prepared samples. The surface morphology is ascertained from the SEM analysis.

2 Experimental techniques

Polymer blend electrolytes of various$BaTiO_3$concentrations were prepared by solution casting technique. PMMA, PVdF-HFPand $LiClO_4$ were purchased from Aldrich (USA) and were dried under vacuum at 100, 80 and 110°C respectively, using Logitech DTC 5050 vacuum oven. The polymer electrolytes were prepared by dissolving appropriate amount of the corresponding constituents in anhydrous THF (SRL, Mumbai). The solution was stirred continuously in a magnetic stirrer for 24 h to obtain a homogeneous mixture. The solvent THF in the polymer solution is allowed to evaporate slowly at room temperature for 48 h. To get solvent free films, the films were further dried in vacuum at 60°C for 10 h to remove the residual traces of THF. The obtained films were visually examined for its dryness and free standing nature.

The prepared thin films were subjected to X-ray diffraction (XRD) and Fourier transform infrared (FTIR) studies to identify the crystalline nature and the complexation behavior of the polymer electrolytes using X'pert PRO PANalytical X-ray diffractometer and SPECTRA RXI, Perkin Elmer spectro–photometer in the range of 400 – 4000 cm^{-1} respectively. The ionic conductivity measurements of the polymer complexes in the temperature range of 303-353K were recorded with the help of computer controlled microautolab Type III Potentiostat/Galvanostat in the frequency range of 40 Hz – 300 KHz. Scanning electron microscopes (JEOL, IXA-840 Japan) was used for micro structural studies.

3 Results and Discussion

3.1X-ray diffraction

X-ray diffraction is propitious in determining the nature of the sample, phase identification, quantitative analysis of a mixture of phases, and physical imperfections, etc. Amorphous nature of the polymer ordains ionic conductivity in a polymer electrolyte; hence it is necessary to determine the crystalline and amorphous phases of the polymer electrolyte. The X-ray diffraction patterns of pure PVdF-HFP, PMMA, LiClO4, $BaTiO_3$and PC the complexes are shownFig.1. Based complexes are shown in fig shows that the two peaks at angles $2\theta=15.07^o$ and 22.7^o PVdF-HFP. Fig Shows diffraction peaks at $2\theta=17.20^o$and 30.82^owhich are ascribed to PMMA. The diffraction pattern of $LiClO_4$.Show intense peak at angles at $2\theta=18.36^o 23.2^o 27.5^o 32.99^o$ and 63.58^o It reveals the crystalline nature of ionic salt. .In the blended system reveals that the amorphous nature is predominant in complex. It is due to the addition of plasticizers such as PC respectively. The presence of sharp diffraction peaks in Fig. 1(c) betokens the crystalline nature of $LiClO_4$. Addition of Acetone and $LiClO_4$ considerably reduces the crystallinity of the polymer which is evident from the absence of the above said crystalline peaks in Fig.1 (a-b). Moreover peaks pertaining to $LiClO_4$ are not observed indicating that the salt is complexes in the polymer matrix and does not remain as separate phase in the electrolytes. With the addition of filler, it is a well-known fact that the intensity of the crystalline peaks decreases and noticeably broadened and additional decreases of crystallinity is obtained[12].

3.2 FTIR –Analysis

Infra red spectroscopy analysis is a powerful tool for identifying the nature of banding and different functional groups present in sample by monitoring the Vibrational energy levels of the molecules [13].Polymer structure and the chemical species could be investigated using FTIR spectroscopy. The infra red spectra of these materials vary according to their composition and may be able to show the occurrence of complexation [14] and interaction between the various constituents. The mutual interaction between them generates change in their vibrational modes of the atoms or molecules in material which introduces change in physical and chemical properties of the constituents of the complex. Vibrational bands at 1072, 976, 763, 614cm^{-1} and bands at 879 and 841 cm^{-1} are characteristic of the crystalline phase and amorphous phase of PVDF-HFP [15] respectively. These group frequencies are found to be shifted to the lower side indicating some alteration in their physical property of PVDF-HFP. The vibrational frequency at 1072and 841 cm^{-1} is missing in the complexes indicating the reduction in crystallinity and increase in amorphicity of the complexes. The vibrational frequencies at 1688, 839 cm^{-1} are assigned to –CH=CF- skeletal breathing, CH_2rocking of PVDF-HFP is found to be shifted to lower side hierarchically on subsequent films indicating the increase in polymer – plasticizer interaction with increase of plasticizer content. The frequency 1483cm^{-1} CH_3 asymmetric bending presented in the complex formation. It confirms the PMMA present in the system. The vibrational peaks around 3022 and 2980 cm^{-1} appears on the addition of $LiClO_4$ to polymer. These bands are associated with non symmetric and symmetric stretching vibration of CH_2 groups. This appearance is due to the interaction between Li+ ions and F atoms leading to weakening the interaction between H atoms of CH_2 and F atoms of CF_2, repercussion of this is evident with the shift of vibration peak at 1403 cm^{-1} shifting towards a higher side [16]. Some additional new peaks (3644cm^{-1} 1972 cm^{-1} 1483cm^{-1} 081cm^{-1} 1059cm^{-1} 1099cm^{-1} 976cm^{-1} 847cm^{-1} and 778cm^{-1}) were found to be appearing in the complex formation in the developed electrolytes.

3.3 **A.C Impedance Spectroscopy**

Fig.3 shows the complex impedance spectra of PMMA/PVDF-HFP/PC/$BaTiO_3$ electrolyte at different temperatures. The linear spike observed in the lower region confirms that the conduction process in the polymer electrolyte is mainly by ions and not due to the electrons [17]. The bulk resistance R_b of the membranes at different temperatures could be obtained from the intercept on the x-axis of the complex impedance plot of the samples. Temperature dependent ionic conductivity values are calculated and are listed in table 4.1AC impedance method is employed to study the conductivity mechanism. The ionic conductivities of the gel polymer electrolytes are calculated from the relation $\sigma=L/R_bA$; where L and A represent thickness and area of the electrolyte sample respectively. R_b is the bulk resistance of the gel electrolyte obtained from complex impedance measurements. It is widely accepted. That R_b could be obtained from the intercept on the real axis at high frequency end of the Nyquist plot of the complex impedance.

Table.1 Ionic conductivity values for PMMA (6.25) – PVDF-HFP (18.75) - $LiClO_4$ (8 wt %) – PC (67) – $BaTiO_3$ (X wt %) (Where X= 0, 2, 4, 6, 8) Polymer electrolyte systems

Sample code	**Ionic conductivity values at different temperatures (Scm^{-1})**				
	303K	**313K**	**323K**	**333K**	**343K**
A	$9.15X10^{-8}$	$8.14X10^{-8}$	$7.61X10^{-8}$	$5.31X10^{-7}$	$2.71X10^{-7}$
B	$4.02X10^{-8}$	$5.31X10^{-8}$	$6.11\ X10^{-7}$	$7.31X10^{-7}$	$1.09X10^{-6}$
C	$2.23X10^{-6}$	$2.83X10^{-6}$	$3.51X10^{-6}$	$6.74X10^{-6}$	$8.42X10^{-6}$
D	$5.35X10^{-6}$	$6.11X10^{-6}$	$6.31X10^{-6}$	$6.92X10^{-6}$	$3.11X10^{-5}$
E	$3.58X10^{-5}$	$3.61X10^{-5}$	$4.31X10^{-5}$	$5.31X10^{-5}$	$6.71X10^{-5}$

From the table it is observed that the ionic conductivity of the composed polymer electrolyte is increased with the increase of temperature. The incorporation of plasticizer alone would yield polymer electrolyte with enhanced conductivity but results in a loss of mechanical stability. This problem can be overcome by the addition of barium titanate filler which increases the ionic conductivity of polymer salt complex with a maximum conductivity of 6.71×10^{-5} S/cm at 8 wt% of $BaTiO_3$ and good mechanical stability. The increase in conductivity may be attributed to a increase occurring in the flexibility of the composite by introducing $BaTiO_3$ into PMMA/PVDF-HFP matrix, due to the high interface area between the matrix and the dispersed nano $BaTiO_3$ particle.

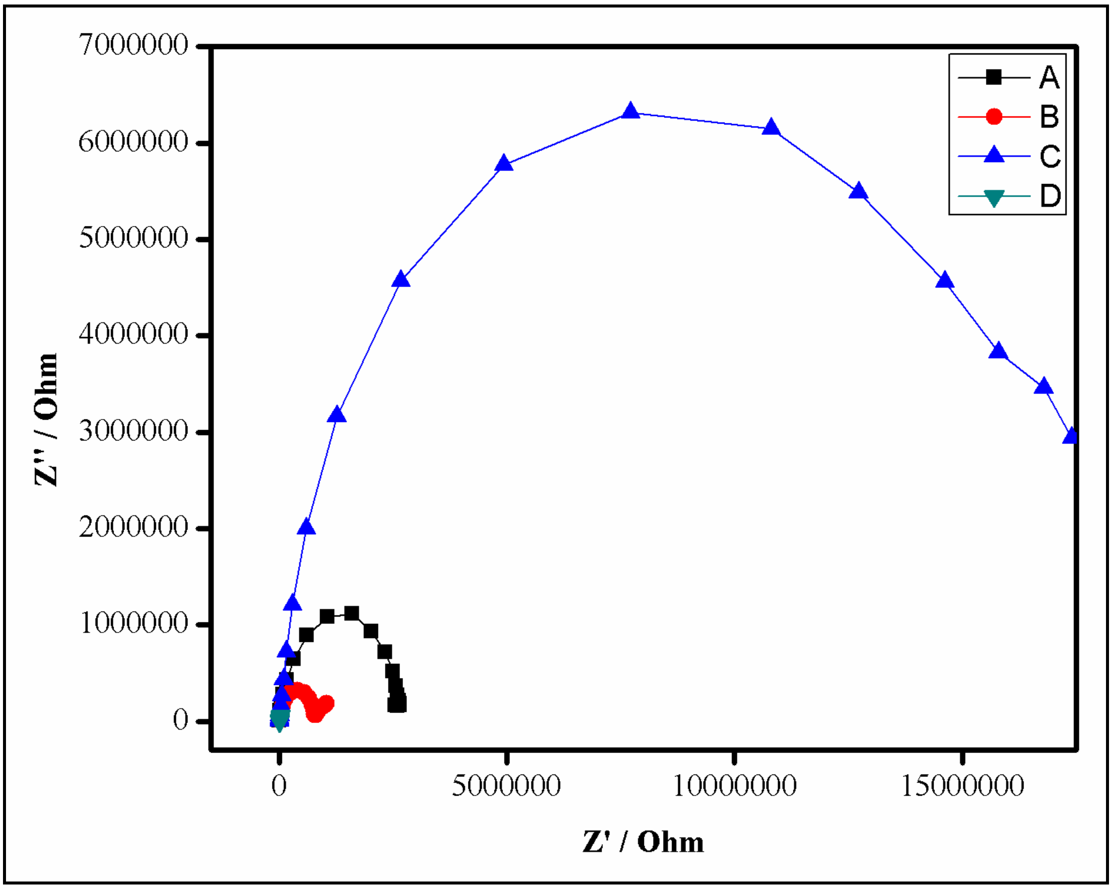

Fig. 3. Room temperature complex impedance plot of the prepared samples

Moreover, the increase in amorphous phase within the PMMA/PVDF-HFP matrix is due to the addition of nano $BaTiO_3$ causes on enhancement in the segmental motion of polymer chains and hence increases the conductivity. The small particle of $BaTiO_3$ in our samples (50 nm) was more efficient. This shows that the small particle size of filler plays an important role in enhancing the conductivity of the system [18]. Fig. 4. Shows a non linear increase in ionic conductivity of the composite with increasing the concentration of nano $BaTiO_3$ filler. This increase is possibility due to the dissociation of salt ion aggregates into the free ions with the addition of nano-sized $BaTiO_3$ particles [19]. The curvature of the plot indicates that the ionic conduction seems to obey VTF behavior, which describes that the ionic transport occurs in the viscous matrix. It supports the idea that the ions move through the plasticizer rich phase which also includes the solvating ions. The ionic conductivity of the CPEs appears to have increased considerably because of the addition of inorganic filler up to a certain limit. The polymer electrolyte system at low filler compositions may be imagined as a conducting medium, where filler grains are randomly and uniformly distributed through the volume. The presence of the filler grains could give rise of additional favorable conducting pathways in the vicinity of the surface of the grains. At lower filler composition where the grains are still well separated, these surface interactions could account for the observed conductivity increase with increasing filler concentration. As the filler concentration is further increased, the filler grains get close enough to each other such that the high conducting region within the vicinity of the grain surfaces become interconnected. The migrating ionic species can now travel along and between these interconnected high conducting pathways, giving rise to the increase in conductivity. At higher filler concentrations however, the grains get too close to each other such that the blocking effect or the geometrical constrictions imposed by the more abundant alumina grains become large. This enables the long polymer chains to become more “immobilized” leading to a lower conductivity. Consequently, the conductivity reaches a maximum followed by a subsequent drop .

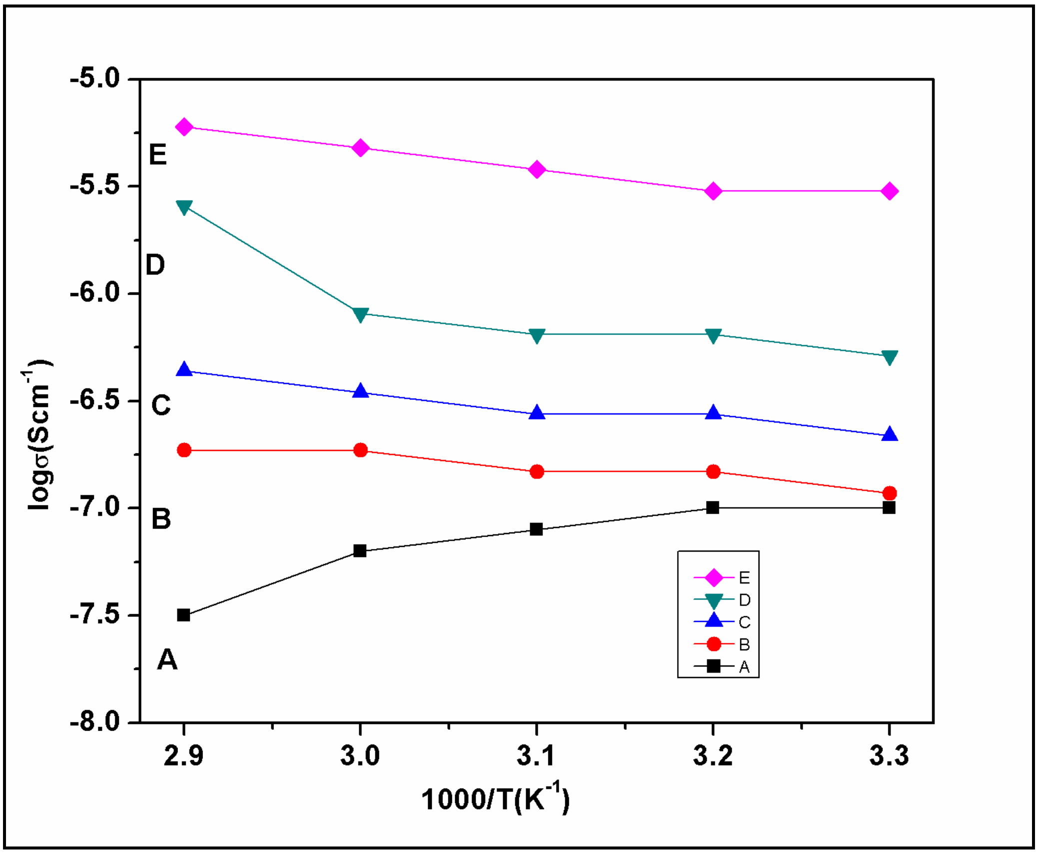

Fig.4. Temperature dependent ionic conductivity plots of the prepared samples

4 SEM Analyses

Scanning electron micrographs of PC based samples are show in **Fig. 5.** .All the developed electrolytes are found to be salt and plasticizers are completely dissolved and also sample are having the porous structure is a complex process that depends on the interaction of the solvent with polymers and its controlled by relative rates of evaporation of compounds the sample containing PC as Plasticizer shows maximum ionic conductivity which is due to interconnected micro pores and maximum dispersion medium for the sample. It is observed that the surface of the electrolyte has more number of inter connected micro pores the pores in the complex are responsible for entrapping the large volume of solution (plasticizer + salt) in the cavities. The ion transport may be due to the hopping motion with the help of pores, accounting for enhanced ionic conductivity. **Fig. 5** shows SEM photograph of the PMMA (6.25)-PVDF-HFP(18.75)-$LiClO_4$(8)-PC (67)-$BaTiO_3$(8) polymer electrolyte prepared by solution casting method for 24 hours. The morphology of polymer electrolyte depends on the kind of host polymer, salt, solvent and preparative technique, as well as evaporation rate of solvent, which have an influence on the electrochemical and physical properties. The SEM image shows porous structure with approximate diameter 40 nm.

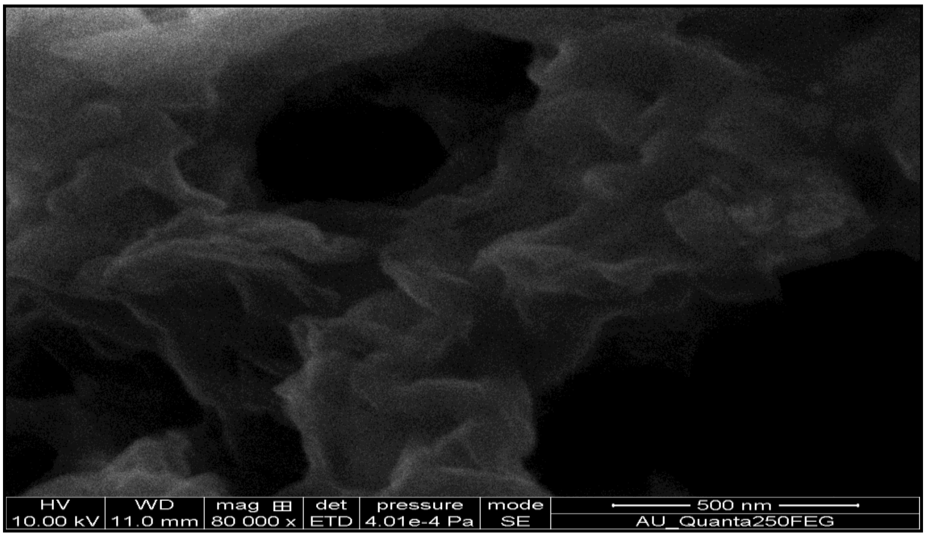

Fig. 5. SEM Micrograph of PMMA (6.25)-PVDF-HFP (18.75)-$LiClO_4$(8)PC (67)-$BaTiO_3$(8)

Conclusion

The present work is concerned with the studies on Nano composite polymer electrolytes based on the PMMA/PVDF-HFP with constant salt ratio of $LiClO_4$and the plasticizer Acetone were prepared for various concentrations of $BaTiO_{3.}$ All polymer electrolyte films were prepared by solvent casting technique and the electrolyte films were subjected to various characterization techniques namely XRD, FTIR, SEM, AC impedance analysis. X-ray diffraction analysis revealed the amorphous nature of all the polymer blend electrolytes which helps for ionic conduction. The interaction of the cation (Li) and anion (ClO_4) with the polymer host and the plasticizers have been confirmed by FTIR spectroscopy analysis. The maximum conductivity obtained at 343 K 6.71×10^{-5} S/cm temperature depended ionic conductivity plots of the electrolytes seem to obey VTF relation. The surface morphology of the prepared polymer electrolytes has been analyzed by SEM images. This can be used as an electrolyte in Li batteries and other electrochemical device.

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