CHAPTER VIII

INFLUENCE OF BaTiO$_3$ CONCENTRATION ON PVdC-co-AN BASED COMPOSITE POLYMER ELECTROLYTE

8.1. Introduction

The incorporation of nano fillers in temperate ionic conductors was started in 1973 itself when Liang added Al$_2$O$_3$ particles with LiI and accounted the enhancement of Li$^+$ [1]. An insulating oxide and a reasonable ion conductor coexist in the two phase system where the surface charge effect promotes the ionic conductivity [2]. The heterogeneous composites of lithium ion conducting polymers and oxides have drawn a great consideration as electrolytes in lithium ion secondary batteries in the present scenario. This approach has been proven to be successful in improving the mechanical [3] and interfacial [4-6] properties of poly(ethylene oxide) (PEO) complexed with lithium salt. Besides, the ionic conductivity has been found to increase upon the addition of nano fillers [7-10]. The redefinition of the crystalline kinetics of PEO while incorporating ceramic nano particle has been concentrated in most of the composite polymer electrolyte studies [5, 8, 9, 11].

The blending of copolymer PVdC-co-AN with PEO has also been found to augment the amorphousity which results in microporous membrane into which the conventional electrolyte is immobilized and forms an apparent solid polymer electrolyte [12]. The addition of plasticizer still increases the amorphousity and hence the porosity. Yet, the dispersion of nano fillers can promote the ionic conductivity and thermal stability in addition to the reduction of ion pairing.
In the present work, the composite polymer electrolyte (CPE) films have been prepared and characterized with different concentrations of ferroelectric BaTiO$_3$ fillers and fixed ratio of PEO/PVdC-co-AN/LiClO$_4$/EC.

8.2. Materials and methods

The polymers poly(ethylene oxide) (PEO) $M_w \sim 8000$, poly(vinylidene chloride-co-acrylonitrile) (PVdC-co-AN) $M_w \sim 150,000$, lithium perchlorate (LiClO$_4$), ethylene carbonate (EC) and barium titanate (BaTiO$_3$) filler were purchased from Sigma Aldrich chemicals limited U.S.A. All the materials were used as obtained without any further purification. Fixed ratio of PEO, PVdC-co-AN, LiClO$_4$, EC and various concentrations of BaTiO$_3$ based composite polymer electrolytes were prepared by solution casting technique using THF as solvent. The polymers, salt, plasticizer and filler were separately dissolved in THF. After complete dissolution, they were mixed together. The combination of solvent was stirred for 24h with the help of a magnetic stirrer. In order to obtain a homogeneous solution, the solvent THF was allowed to evaporate slowly. Finally, the gelly solution was cast onto Petri dishes. The Petri dishes containing the solution were dried at 50°C under vacuum for about 12h to remove the residual solvent. The resulting free standing films were smoothly removed, cut into desired dimensions and stored in an evacuated desiccator.

The structural studies of the films at room temperature were carried out by X’pert PRO PANalytical X-ray diffractometer. FTIR analysis in the range 400-4000 cm$^{-1}$ using SPECTRA RXI, Perkin Elmer spectrophotometer was performed to authenticate the complex formation. The ac impedance analysis was done by sandwiching the polymer electrolyte between the Stainless-steel blocking electrodes using a computer controlled micro Autolab type III Potentiostat/Galvanostat in the
frequency range 100Hz–300KHz. PYRIS DIAMOND TG/DTA analyzer was used to characterize the thermal stability of the composite films from room temperature to 750°C at the scan rate of 10°C min⁻¹. Differential scanning calorimetric study using Mettler Toledo DSC (822e) instrument was carried out to identify the glass transition temperature of the films. Cary Eclipse Fluorescence Spectrometer was used to perform the photoluminescence study. JEOL, JSM-840A instrument was used to investigate the surface morphology of the film having a maximum ionic conductivity. AFM (A100SGS) instrument was used to examine the topography image of the film having a maximum ionic conductivity. Computer controlled micro Autolab type III Potentiostat/Galvanostat was employed for cyclic voltammetry and linear sweep voltammetry studies.

8.3. Results and discussion

8.3.1. X-Ray diffraction Analysis

X-ray diffraction analysis is used to determine the structure, complexation and crystallization of the polymer matrix. Fig.8.1 delineates X-ray diffraction peaks of pure PEO, PVdC-co-AN, LiClO₄, BaTiO₃ and the crystallinity changes of the composite polymer electrolytes for different concentrations of BaTiO₃. The sharp, intense peaks at 2θ = 19.1 and 23.3° associated with the lattice planes (1 2 0) and (0 1 0) signify the semi crystalline nature of PEO. The crystalline nature of PVdC-co-AN is affirmed by the diffraction angles at 2θ = 40.25, 46.76 and 67.94° compatible to (1 0 5), (2 0 2) and (2 1 2) lattice planes. The strong crystallinity of LiClO₄ and BaTiO₃ are discerned from the diffraction angles at 2θ = 18.36, 23.2, 27.5, 32.99, 36.58 and 22, 31, 45, 51, 56, 65,70, 75° pertaining to the lattice planes (1 0 1), (1 1 0), (2 0 0), (2 0 1), (2 1 0) and (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), (3 0 1) respectively. Using Debye–Scherrer formula, the particle size of the ferroelectric
filler was calculated for each value of ‘θ’ and the average particle size has been found to be 55 nm.

The crystallinity of the composite polymer electrolyte films goes on decreasing up to 8wt% of BaTiO$_3$ and increases afterwards. The reduction in the crystallinity could be commented on the basis of chain-re-organization of the polymer matrix with the addition of filler particles of small dimension which assists the ionic conductivity [13]. Yet the peaks of BaTiO$_3$ are persistent though the intensities have been reduced considerably. Moreover the disappearance of the peaks corresponding to LiClO$_4$ indicates the complex formation and complete dissolution of the salt in the polymer matrix [14].

8.3.2. FTIR - Studies

Fourier transform infrared spectroscopy has been identified as a powerful tool to investigate the structure, complex formation and interaction between the various constituents of the polymer electrolyte system because of its responsiveness to molecular and structural changes in the polymer matrix.

The FTIR spectra of the pure PEO, PVdC-co-AN, salt and that of the prepared composite polymer films have been plotted as shown in Fig.8.2. The wave numbers and their band assignments are represented in Table 8.1. The broad vibrational peak at 3461 cm$^{-1}$ of –OH group relating to water or moisture absorption, which might have happened during the sample preparation for the spectral analysis has been shifted between 3514 and 3461 cm$^{-1}$ in the composite films [15]. The respective peaks at 2245 and 1642 cm$^{-1}$ correspond to C=≡N and C=N vibrations [15]. The strong absorption peak around 2800 - 2950 cm$^{-1}$ pertains to the symmetric and asymmetric C–H stretching vibrations of CH$_2$ in PEO [16]. The intense ether oxygen group
vibration in PEO at 1799 cm\(^{-1}\) has been displaced from 1797 to 1802 cm\(^{-1}\) in the various samples [17]. The asymmetric wagging of CH\(_2\) in PEO is observed from 1349 to 1351 cm\(^{-1}\) [18]. The peak around 1242 cm\(^{-1}\) exemplifies the symmetric twisting of CH\(_2\) in PEO [17]. The antisymmetric stretching vibration of C - O – C bridge in PEO is represented by the peaks ranging from 1092 to 1114 cm\(^{-1}\) in the different films [19]. The CH\(_2\) bending mode in EC is symbolized by the peak around 1480 cm\(^{-1}\) which has been de-positioned around 1464 cm\(^{-1}\) in the composites [20]. The ClO\(_4^−\) anion vibration is observed at 625 cm\(^{-1}\) [21].

### 8.3.3. Complex impedance analysis

The ionic conductivity of the prepared composite films with the variation of BaTiO\(_3\) was studied using ac impedance spectroscopy. Fig.8.3 shows the effect of nano fillers on the ionic conductivity of composite polymer electrolytes at ambient temperature. It is evident from the low frequency spikes that the ionic conductivity is purely due to ions [22]. The X- intercept on the complex impedance plot gives the bulk resistance of the electrolyte. With the knowledge of film thickness ‘l’ and area ‘A’ of the film, the ionic conductivity is calculated for all the films individually using the formula \(\sigma = l/(R_oA)\). It could be seen that the conductivity value increases from zero wt% of BaTiO\(_3\), reaches maximum at 8wt% and then decreases slowly. The maximum ionic conductivity value 2.57×10\(^{-3}\) S cm\(^{-1}\) at 303K has been found for the sample SE3.

In the present study, the increase in ionic conductivity at lower filler concentration has been attributed to the following factors.

(i) The Lewis acid–base interactions enhance ionic conductivity. The strong acidic surface group of BaTiO\(_3\) filler competes with the cations to interact with
the basic ether oxygen of the polymer [23]. This interaction reduces the ionic coupling of the oxygen and the cation and hence promotes the dissociation of the salt. Sun et al. [24] reported a similar observation in the case of PEO/LiClO₄/BaTiO₃.

(ii) Lewis acid-base type interaction is not only the factor which contributes to the enhancement of ionic conductivity. The enhancement in the ionic conductivity has also been attributed to the formation of highly conductive layer in the neighbourhood of the filler particles, which provides easier pathways for the ion migration [25, 26].

(iii) In the case of the CPE, the interaction of dipoles of the ferroelectric filler with dipole moments of the polymer acts as the driving force to facilitate the conduction process, in addition to the hopping of the ions in the crystalline-rich phase of the polymer, the segmental motion-assisted transport mechanism in the elastomeric-rich phase of the polymer.

The decrease in the ionic conductivity after 8wt% of BaTiO₃ is ascribed to the increase of filler concentration which acts as a mere insulator and obstructs the ion mobility. The phase discontinuity result in blocking effect of which scrouges the segmental motion of the polymer and the ion mobility and thus leads to the decrease of ionic conductivity. Fig.8.5 depicts the variation of ionic conductivity as a function of filler concentration. The log of conductivity values was plotted against the inverse of temperature as shown in Fig.8.4. Table 8.2 displays the ionic conductivity in response to the variation of temperature in the range 303–353K. It is observed that the increase of temperature increases the free volume of the composite polymer electrolyte which facilitates the segmental motion of the polymer chains and hence promotes ionic conductivity of the system. The non-linearity observed in the plots
embraces that the polymer electrolyte films with ferroelectric fillers obey VTF (Volgel-Tamman-Fulcher) relation [27–29].

### 8.3.4. Thermogravimetry/differential thermal analysis (TG/DTA)

The thermal stability of the composite polymer electrolytes also becomes a paramount factor for their reliable performance at elevated temperature in view of safety concerns. Fig.8.6(a-f) shows the TG/DTA curves of all the films prepared with nano fillers.

TG/DTA curves disclose the first weight loss of the films which is about 2-3% in the temperature range 86-88°C due to the removal of residual solvent and moisture if any. The next weight loss of the films is perceived at 270-276°C. This heavy weight loss is ascribed to the structural changes in the polymer which is about 22-33%. Thereafter there is no weight loss up to 395°C and the samples exhibit weight loss around 74-82% in the temperature range from 395-408°C which might be due to the complete decomposition of the composites. Maximum thermal stability 222°C is observed for the sample SE0. Table 8.3 evinces the weight losses relating to the temperature variation. The endothermic peaks between 68-73°C and the exothermic peaks between 233- 234°C & 264-274°C of DTA plots of various samples are also compatible with TGA results.

### 8.3.5. DSC analysis

Differential scanning calorimetry (DSC) allows us to know the quantitative changes in endothermic or exothermic enthalpy. It is also used to analyse the melting process in partially crystalline plastics, glass transition and chemical reactions such as curing of thermosetting resins [30].
In this work, the variation of glass transition in different filler concentration has been focused. Fig. 8.7 shows the DSC curves of all the composite polymer films prepared with different filler proportions. It is visualized that the first endothermic phase transition occurs between 24.8-27°C which is attributed to the glass transition temperature $T_g$ because the $T_g$ value of PEO is from -53 to -45°C and that of PVdC-co-AN is nearly 50°C. Among the different compositions, the film SE3 exhibits minimum $T_g$ value and its ionic conductivity value has also been found to be maximum.

8.3.6. Photoluminescence studies

Fig. 8.8 shows the photoluminescence plots of the composite polymer electrolytes at an excitation wavelength of 280nm. The local viscosity of the medium is inversely proportional to the local free volume, which is directly correlated with the carrier mobility of the polymer electrolyte system. But the local viscosity is inversely related to excitation intensity [31, 32]. It is seen that the polymer electrolyte film containing EC and BaTiO$_3$ (8wt%) displays minimum intensity which concerns to the maximum ionic conductivity of the sample. It is also clear that the incorporation of the ferroelectric fillers into the polymer matrix decreases the local viscosity up to an optimum value and the further addition of the filler leads to the aggregation which results in an increase of crystallinity and viscosity. This outcome agrees with the ionic conductivity and XRD results.

8.3.7. Scanning electron microscopic studies

The scanning electron microscope was employed to study the surface morphology of the sample SE3 having a maximum ionic conductivity. Fig. 8.9 (a and b) shows the micrographs taken at two different magnifications 1000X and 5000X.
The uniformly distributed spherical micro grains in the electrolyte system could be observed from these micrographs. The membrane exhibits highly porous structure. This increase in porosity is capable of entangling large volume of liquid which constitutes the increase in ionic conductivity [33]. The hopping of the ions is enabled and enhanced in the interconnected micropores of the membrane. Increase of amorphousity and solvent retention ability are also responsible for the increase of ionic conductivity.

8.3.8. Atomic force microscopic analysis

The two and three dimensional topographical images of the composite polymer sample possessing maximum ionic conductivity were observed using atomic force microscope and are represented in Fig.8.10. It is discerned from the images that the nanofillers have been dispersed haphazardly within the scanned area of 10×10 μm. The small pores enmesh the liquid solution [34] and contribute for higher ionic conductivity.

8.3.9. Cyclic voltammetric test

The cyclic voltammograms of the sample SE3, exhibiting maximum ionic conductivity has been plotted as shown in Fig.8.11 for different scan rates. Almost all the plots resemble to be rectangular in shape and there is no trace of any redox currents on both anodic and cathodic regions which indicates the high capacitive behaviour of the film. It has also been observed that the electrolyte film possesses good cyclability and reversibility. The area of the rectangles increases with the increase of scan rates [35].
8.3.10. Linear sweep voltammetric test

Linear sweep voltammetry is generally used to determine the electrochemical stability window of the polymer electrolytes [36]. From Fig.8.12, it is observed that the electrolyte decomposition occurs from the onset of rapid rise in current in the anodic high voltage range and cathodic low voltage range. The electrochemical stability window for this sample is found to be -2.6 to +2.8V. This increase may be due to the incorporation of Barium titanate nano fillers with the plasticized gel polymer electrolyte.

8.4. Conclusion

The X-ray diffraction patterns of the pure and prepared composites exemplify the correlation of amorphousity with ionic conductivity. The complete dissolution of the salt LiClO$_4$ is confirmed by the absence of peaks pertaining to it. The complex formation between the polymers, salt, plasticizer and filler particles is ascertained from the shifts, appearance of few new peaks and the disappearance of certain existing peaks in the FTIR spectra of the virgin samples and that of the prepared CPEs. The ionic conductivity value calculated using a.c impedance spectroscopy has been found to be maximum ($2.57 \times 10^{-3}$ S cm$^{-1}$ at 303K) for the sample SE3. This result is substantiated by the low $T_g$ value obtained from DSC analysis and the minimum photoluminescence intensity observed for this sample. SEM and AFM images of the film having a maximum ionic conductivity exhibit porous nature which entraps large volumes of the liquid plasticizer and enhances ionic conductivity. The CV plots of SE3 reveal excellent cyclability and reversibility for the film. The electrochemical stability window determined using LSV for this sample is -2.6 to +2.8V.
Fig. 8.1. XRD patterns of the pure and prepared samples.
Fig. 8.2. FTIR spectra of the pure and the prepared samples.
Fig. 8.3. Room temperature complex impedance plots of the prepared samples.
Fig. 8.4. Temperature dependent ionic conductivity plots of the prepared samples.
Fig. 8.5. Effect of filler concentrations on the ionic conductivity of the composites at different temperatures.
Fig. 8.6 (a-f). TG/DTA plots of the prepared composite polymer electrolytes.
Fig. 8.7. DSC curves of the prepared composite polymer electrolytes.
Fig. 8.8. Photoluminescence spectra of the prepared complexes.
**Fig. 8.9.** SEM analysis of the sample (SE3) having a maximum ionic conductivity at different magnifications, (a) 1000X; (b) 5000X.
Fig. 8.10. The topographic image of the sample (SE3) having a maximum ionic conductivity, (a) 2D image; (b) 3D image.
Fig. 8.11. Cyclic Voltammetric plots of the sample (SE3) having a maximum ionic conductivity for different scan rates.
Fig. 8.12. Linear Sweep voltammogram of the sample (SE3) having a maximum ionic conductivity.
Table 8.1. Assignments of FTIR absorption bands for the prepared membranes.

<table>
<thead>
<tr>
<th>Band assignment</th>
<th>Wavenumber (cm(^{-1}))</th>
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<tbody>
<tr>
<td></td>
<td>PEO</td>
</tr>
<tr>
<td>-OH group vibration</td>
<td>-</td>
</tr>
<tr>
<td>-CH(_2) Sym Stretching</td>
<td>2884</td>
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<tr>
<td>C=N Stretching</td>
<td>-</td>
</tr>
<tr>
<td>Ether oxygen group</td>
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<tr>
<td>C=N Stretching</td>
<td>-</td>
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<tr>
<td>-CH(_2) Wagging</td>
<td>1360</td>
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<tr>
<td>-CH(_2) Twisting</td>
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<tr>
<td>C–O–C Asym. stretching</td>
<td>1100</td>
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<tr>
<td>CH(_2) sym.rocking</td>
<td>962</td>
</tr>
<tr>
<td>-CH(_2) rocking</td>
<td>845</td>
</tr>
<tr>
<td>ClO(_4^-) anion</td>
<td>-</td>
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Table 8.2. Ionic conductivity values of the prepared samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Composition of the prepared samples in wt%</th>
<th>Conductivity values for different temperatures (σ) × 10^3 S·cm⁻¹</th>
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<tbody>
<tr>
<td></td>
<td>PEO(64)/PVdC-co-AN(16)/LiClO₄(8)/EC(12)/BaTiO₃(X)</td>
<td>303K</td>
</tr>
<tr>
<td>SE0</td>
<td>X = 0</td>
<td>0.300</td>
</tr>
<tr>
<td>SE1</td>
<td>X = 4</td>
<td>0.993</td>
</tr>
<tr>
<td>SE2</td>
<td>X = 6</td>
<td>1.440</td>
</tr>
<tr>
<td>SE3</td>
<td>X = 8</td>
<td>2.572</td>
</tr>
<tr>
<td>SE4</td>
<td>X = 10</td>
<td>1.103</td>
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<tr>
<td>SE5</td>
<td>X = 12</td>
<td>0.934</td>
</tr>
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Table 8.3. TG/DTA results of the prepared samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Decomposition temperature (°C)</th>
<th>Weight loss of the samples in %</th>
<th>Exothermic peaks (°C)</th>
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<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>SE0</td>
<td>88</td>
<td>272</td>
<td>395</td>
</tr>
<tr>
<td>SE1</td>
<td>87</td>
<td>276</td>
<td>402</td>
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<tr>
<td>SE2</td>
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