CHAPTER V

EFFECT OF LiClO₄ CONCENTRATION ON PAN/PMMA BASED POLYMER BLEND ELECTROLYTES

5.1 Introduction

Polymer electrolytes have been the emerging field of research for scores of years since the first report by Armand and co-workers in 1979[1]. Polymer electrolytes envisage the advantage of solid electrolyte as well as the property of liquid electrolyte. The interest in this study is continually growing due to their potential applications in lithium batteries, electrochromic devices etc [2-4]. The development of polymer system with high ionic conductivity and stability is the congenital objectives in polymer research. Hence polymer should possess fundamental properties like low glass transition temperature (Tₕ) so that the conformations of polymer chains and segmental motion can significantly assist transport of ions at the operating temperature ensuing conductivity. Hence, the polymer electrolyte should possess low degree of crystallinity as the conduction in polymer electrolytes is through the amorphous domain of the polymer salt system.

Various approaches viz. copolymerization[5], grafting[6], physical cross linking[7], blending[8], plasticization[9] and addition of inert ceramic oxides into the matrix[10] are applied to modify structure and properties of polymeric electrolytes in insinuation of preparation of polymer electrolytes with high ionic conductivity and appreciable thermal stability at ambient temperature. In
comparison, blending has been found to be more useful because of ease of preparation and control of the properties of polymer electrolytes by changing the composition of blended polymer matrix. In connection with this, copolymerization or blending technique for matrix polymers of polymer electrolytes has been considered for enhancing the properties of polymer electrolytes [11, 12]. The blending of polymers may lead to the increase in stability due to one polymer portraying itself as a mechanical stiffener and the other as a gelled matrix supported by the other.

The salt LiClO$_4$ is chosen since it has higher anionic radius. When the anions are large, substantial delocalization of the negative charge occurs with reduction in the lattice energy of the salt. This infers that the large anions reduce the ion-ion interaction. It is found that the LiClO$_4$ based complex exhibits significantly higher conductivity among the other salt-based complexes. This is due to the smaller dissociation energy of perchlorate salt. Hence, LiClO$_4$ is added to increase the amorphicity and the introduction of conducting moieties into the matrix. The scope of PAN as a host polymer was first reported by Reich and Micheali [13]. The applications of PAN based electrolytes were further extended by many researchers [14-21]. Slane and Salomon [22] studied composite polymer electrolyte that consisted of zeolite powders dispersed in PAN based gel electrolytes with LiAsF$_6$ as complexing salt. PMMA having high tensile strength can act as a mechanical stiffener in the electrolyte. Optimization of PAN/PMMA blend ratio has been explained elsewhere (chapter IV). On the basis of ionic conductivity and the thermal
stability, we have optimized the PAN/PMMA ratio in the electrolyte for constant LiClO₄ salt ratio [23]. In order to improve the ionic conductivity of the PAN/PMMA blend matrix, the effect of salt concentration is studied because the conducting species in the matrix mainly depends on the salt concentration. In the present work, solid polymer electrolyte films consisting of PAN, PMMA and LiClO₄ are examined for various concentrations of lithium salt by keeping PAN/PMMA blend ratio as a constant with a view to optimize the dominant salt concentration which could give the maximum conductivity at ambient temperature. The prepared polymer electrolyte films are characterized by XRD, FTIR, ac impedance, SEM, TG/DTA and DSC for the structural, complexation, conductivity, surface morphology and thermal stability, respectively.

5.2. Experimental

All the films were prepared by solution casting technique [24-26]. The electrolytes were prepared from poly (acrylonitrile) (PAN) (Aldrich, average molecular weight 94,000) and poly (methyl methacrylate) (PMMA) (Aldrich, average molecular weight 120,000) which were dried at 100 °C under vacuum for 10 hours. LiClO₄ was annealed at 70 °C under vacuum for 24 hours. Appropriate quantities of each component were dissolved in distilled DMF (E-Merck Germany) and then stirred continuously for 48 hours at room temperature and at 60 °C until homogeneous slurry was obtained. The obtained mixture was cast onto teflon bushes and glass plates. DMF was allowed to evaporate slowly at room temperature and then at 50 °C for the removal of the
residual DMF content if any. The obtained film was visually examined for its dryness and free standing nature.

The complexation and phase structure of the polymer complexes are studied by Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analyses. Thermal behaviour of the films has been analysed with the help of differential scanning calorimeter (DSC) and thermogravimetric/differential thermal analysis (TG/DTA). The ionic conductivities of PAN: PMMA ((75/25) wt %): LiClO$_4$ (X wt %) (where X=2, 5, 8, & 11) complexes are studied by means of ac impedance technique. The surface morphology of the film having maximum ionic conductivity is analysed with the help of SEM.

5.3 Results and discussion

5.3.1 XRD analysis

X-ray diffraction studies are performed for the structural elucidation of the polymer electrolytes. Ionic conductivity in polymer electrolyte is determined chiefly by the amorphous nature of the polymer where the rocking chair model of the ionic motion is assisted. Hence, it is necessary to determine the crystalline and amorphous phases of the polymer electrolyte. The XRD patterns of pristine PAN, PMMA, LiClO$_4$ and the complexes are shown in Fig. 1. The diffraction peaks of pure PAN is observed at 2$\theta$=16.43 and 29.24°. Fig.1 elucidates the amorphous nature of PMMA with a broad halo peak, whereas a sharp crystalline peak obtained in Fig.1 indicates the complete crystalline nature of LiClO$_4$. It has been observed (Fig.1.B1-B3) that the incorporation of salt disturbed the crystalline region and increased the amorphous phase of PAN.
and hence intensity of the peak is reduced. It can be interpreted in terms of the criterion of Hodge et al. [27] that have established a correlation between the height of the peak and the degree of crystallinity. The diffraction peak corresponding to 8 wt% of the salt is broader and less prominent revealing the amorphous nature of the complex which is responsible for higher ionic conductivity. The sharp crystalline peaks pertaining to LiClO₄ (Fig. 1) were found to be absent in the complexes, indicating the complete dissolution of lithium salts in the polymer complexes. These observations suggest that the polymer undergoes significant structural reorganization. Salt content at 11 wt. % reduces the ionic conductivity of the electrolyte film. This may be due to the formation of separate crystallization phase of excess salt in the complex, which confirms the presence of small hump in the complex of XRD pattern shown in (Fig.1.B4).

5.3.2 FTIR analysis

FTIR is an efficient tool to study the local structural changes in polymers. The infrared spectra of these materials vary according to their composition and assist in confirming the complex formation among polymer matrices [28-33] and the interaction between the various constituents. The FTIR spectra of PAN, PMMA, LiClO₄ and the complexes are shown in Fig. 2.

The C≡N stretching band in the IR spectrum is by far the most characteristic feature of nitrile group which appears at 2249 cm⁻¹ in pure PAN. The band corresponding to nitrile group is displaced towards lower frequency region in all the complexes due to the inductive effect created by the interaction
of N atoms in –C≡N with Li+ ions [34]. The peak at 1246 cm\(^{-1}\) which is assigned to the C-N stretching of pure PAN is shifted to higher frequency (1251, 1249, 1253, 1251 cm\(^{-1}\)) in the complexes B1, B2, B3 and B4, irrespective of salt concentration. The vibrational peaks at 2939, 1632 cm\(^{-1}\) are assigned to CH\(_2\) asymmetric stretching and CH asymmetric stretching of PAN. They are found to be shifted to (2941, 2941, 2942 and 2941 cm\(^{-1}\)) & (1666, 1665, 1679 and 1664 cm\(^{-1}\)) in the complexes B1, B2, B3 and B4 respectively. The band at 1735 cm\(^{-1}\) assigned to C═O stretching of PMMA is shifted to lower frequency side around 1727 cm\(^{-1}\) in all the complexes. The vibrational peak at 1382 cm\(^{-1}\) corresponding to CH\(_3\) symmetric bending vibration is shifted to lower frequency side and then increases with increase of salt concentration and the shift is maximum for the film having higher percentage of salt (11%). The characteristic CH\(_2\) wagging at 980 is found to be shifted around 982 cm\(^{-1}\) and the CH\(_2\) rocking observed at 754 cm\(^{-1}\) is shifted around 758 cm\(^{-1}\) in all the complexes.

Apart from the shift in frequencies, some new peaks appear and few peaks are found absent in the complexes. The vibrational peaks (1454, 1362, 1078 and 779 cm\(^{-1}\)) of PAN, (2956, 1630, 1258, 485 cm\(^{-1}\)) of PMMA and (2854, 1097, 950, 712 and 515 cm\(^{-1}\)) of LiClO\(_4\) are found to be absent in the complexes. And the new peaks at 2353, 1790, 1666, 845, 670 cm\(^{-1}\) are present in all the complexes. Thus the above analysis confirmed the complex formation in the developed electrolytes.
5.3.3 Conductivity studies

The electrochemical impedance spectroscopy is an excellent tool to characterize many of the electrical properties of the material. It may be used to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material. In the present study the ionic conductivities of PAN-PMMA solid polymer electrolyte film with different concentration of LiClO$_4$ have been analyzed with an intention of finding out the part played by LiClO$_4$ in the blend. The conductivity values of the polymer complexes are calculated from the bulk resistance ($R_b$) obtained from the intercept of the Cole-Cole plot, known area of the film (A) and measured thickness of the film (l), using the formula $\sigma = l / R_b A$. The complex impedance plot of PAN (75 wt.%)-PMMA (25 wt.%)-LiClO$_4$ (8 wt.%) at various temperatures is given in Fig 3. The disappearance of high frequency semicircular portion in the complex impedance plot indicates that the conductivity is mainly due to the ion conduction [35].

The ionic conductivity as a function of different wt% of LiClO$_4$ over the temperature range 303-373K is given in Table 5.2. As the temperature increases, the conductivity increases for all the complexes irrespective of salt concentration, and this behavior is in agreement with Armand et al. [36]. The rising temperature increases the vibrational energy of the polymer segment, enabling it to push against the hydrostatic pressure imposed by its neighboring atoms and creating a small amount of space surrounding its own volume through which the ionic motion can occur [2]. Furthermore due to the increase
in volume, it reduces the retarding effect of ion clouds which could be the reason for higher conductivity at elevated temperatures.

The Arrhenius plot of the ionic conductivity of PAN/PMMA blend with different salt concentrations is given in Fig.4. The temperature dependence of the ionic conductivity is not linear which indicates that the ionic conduction fits well with the WLF (William Landel Ferrey) mechanism.

Salt concentration dependent ionic conductivity plot of the prepared electrolyte samples is shown in Fig. 5. The ionic conductivity of the polymer electrolyte depends on the effective number of carrier ions and the ions mobility. The effective number of carrier ions is related to the concentration of the dissolved ions. The ion mobility in a polymer electrolyte, formed by the dissolution of ions in the polymer, is facilitated by the segmental mobility of the polymer chains. The variation of ionic conductivity has been analyzed by varying the salt content and keeping the PAN/PMMA blend ratio constant. It is found that ionic conductivity increases with increase of salt concentration until an optimum concentration is reached and found to retard with further addition. This could be due to the increase of charge carrier up to the optimum concentration (8 wt.% of LiClO₄) which gives the highest ionic conductivity among the various polymer films characterized. As the concentration is increased above the optimum concentration, the conductivity is found to decrease that could be ascertained due to formation of ion pairs or ion clusters [37].
5.3.4 Thermo gravimetric analysis

TG (thermo gravimetric) technique has been widely used to study the physical changes encountered by the polymer electrolyte during thermal excitation which gives a rough idea of the kind of changes the polymer electrolyte may undergo in the working atmosphere. The process involves change in weight attributed to moisture uptake and thermal stability of the polymer electrolyte.

Typical thermogram obtained for the films containing constant PAN/PMMA ratio (75:25) with different concentration of LiClO$_4$ are shown in Fig. 6(a-d). TG curve shows that there is a gradual weight loss until the sample reaches 120 °C irrespective of the salt concentration which could be due to the evaporation of moisture absorbed while loading the sample. The films having 2, 5, 8 wt.% of LiClO$_4$ are found to be stable up to 230, 230 and 240 °C with gradual weight loss of about 10, 8, 16% respectively. The sample with 11 wt.% of salt is found to have a weight loss of 8% with thermal stability up to 250 °C. Beyond the second transition temperature, the polymer electrolytes suffer a rapid weight loss associated to the degradation and could be ascertained from DSC results. DTA curve of the samples show an exothermic peak at around 303 °C for the samples B1, B2, B3 respectively and at 323 °C for the sample B4, which is well correlated with the weight loss of the sample observed in TG curve. Even though the polymer electrolyte with 8 wt.% of salt is found to have a thermal stability of 240 °C, this film is considered to be the best film on the basis of conductivity.
5.3.5 DSC analysis

Fig.7 shows DSC thermogram of the synthesized polymer electrolyte samples. The actual \( T_g \) values of pure PAN and PMMA are 85 and 105 °C respectively. The complexes show a single \( T_g \) indicating the compatibility of the polymers. The incorporation of LiClO\(_4\) to the polymer blend matrix decreases the \( T_g \) value, and is minimum for 8wt.% salt content. On further increase of salt concentration, \( T_g \) value is increased. This observation suggests the increase of crystallinity of the complexes because of the presence of excess salt. It is also evident from conductivity studies that the conductivity of the complexes increases with increase of salt concentration and decreases for higher concentration of salt due to formation of ion cluster. It is observed that all the samples start to melt around 250 °C. This is in good agreement with TGA results.

5.3.6 SEM analysis

Fig.8a and b reveal the surface morphology of the polymer complex PAN/PMMA/LiClO\(_4\) having maximum ionic conductivity at two different magnifications X1000 and X2000. The polymer complex has maximum number of highly interconnected pores and the pore size is in the order of few \( \mu \)m. The difference in the pore size is related with the difference in the driving force for phase separation. The presence of pores is mainly due to the solvent removal [32, 33] and increased amorphicity. A fully amorphous morphology has increased ionic conductivity, since the ionic conductivity of the electrolyte depends on the segmental motion of the blended polymers and solvated carrier
ions. The segmental motion either permits the ions to hop from one site to another or provides the pathway for ions to move. Hence, the conductivity gets increased.

5.4. Conclusion

Polymer electrolyte systems consisting of PAN (75 wt. %) – PMMA (25 wt. %) – LiClO₄ for various salt concentrations have been prepared using solvent casting technique. The complex formation of the electrolytes has been confirmed from FTIR and XRD studies. Melting temperature and thermal stability of the electrolytes have also been ascertained with the help of differential scanning calorimetry and TG/DTA respectively. The maximum ionic conductivity of the polymer electrolyte PAN (75 wt. %) – PMMA (25 wt. %) – LiClO₄ (8 wt. %) is found to be 0.56 x 10⁻⁵ S cm⁻¹ at 303 K. The surface morphology of the polymer electrolytes has been studied and the presences of the pores are identified using scanning electron microscope. From the above analysis, it is concluded that the properties of PAN (75 wt. %) – PMMA (25 wt. %) – LiClO₄ (8 wt. %) polymer electrolyte look very desirable and promising for lithium battery applications.
Fig. 1. XRD patterns of pure and the prepared complexes.
Fig. 2. FTIR spectra of pure and the prepared complexes
Fig.3. Complex impedance plot of PAN (75) PMMA (25) LiClO₄ (8) at various temperatures.
Fig. 4. Temperature dependent ionic conductivity plot of the prepared samples
Fig. 5. Conductivity of PAN: PMMA (75:25) blend as a function of LiClO$_4$ concentration at different temperatures.
Fig. 6. TG/DTA traces of the prepared complexes
Fig. 7. DSC curves of the prepared polymer electrolytes
Fig. 8. SEM image of the sample PAN (75 wt.%) PMMA (25 wt.%) LiClO$_4$ (8 wt.%) at a) X1000 and b) X2000
<table>
<thead>
<tr>
<th>Band Assignments</th>
<th>Wave number (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAN</td>
</tr>
<tr>
<td>CH$_2$ (asym.stret)</td>
<td>3522</td>
</tr>
<tr>
<td>CH$_2$ (asym.stret)</td>
<td>2939</td>
</tr>
<tr>
<td>C≡N (stretching)</td>
<td>2249</td>
</tr>
<tr>
<td>CH (asym.stret)</td>
<td>1632</td>
</tr>
<tr>
<td>CH(bend.vib)</td>
<td>1454</td>
</tr>
<tr>
<td>C-N (stretching)</td>
<td>1246</td>
</tr>
<tr>
<td>C-C(sym.stret)</td>
<td>1078</td>
</tr>
<tr>
<td>CH$_3$ (stretching)</td>
<td>2956</td>
</tr>
<tr>
<td>C═O (stretching)</td>
<td>1735</td>
</tr>
<tr>
<td>OCH$_3$ (stretching)</td>
<td>1450</td>
</tr>
<tr>
<td>CH$_3$ (sym. bending)</td>
<td>1382</td>
</tr>
<tr>
<td>CH$_2$ twisting</td>
<td>1151</td>
</tr>
<tr>
<td>CH$_2$ Wagging</td>
<td>981</td>
</tr>
<tr>
<td>C–O–C bending</td>
<td>842</td>
</tr>
<tr>
<td>CH$_2$ rocking</td>
<td>754</td>
</tr>
</tbody>
</table>

Table 5.1 FTIR assignments of the prepared samples
Table 5.2. Ionic conductivity values at different temperatures

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Complex compositions</th>
<th>Ionic conductivity values × 10^{-5} S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt%</td>
<td>303K</td>
</tr>
<tr>
<td>B1</td>
<td>75/25/2</td>
<td>0.01</td>
</tr>
<tr>
<td>B2</td>
<td>75/25/5</td>
<td>0.02</td>
</tr>
<tr>
<td>B3</td>
<td>75/25/8</td>
<td>0.56</td>
</tr>
<tr>
<td>B4</td>
<td>75/25/11</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Table 5.3. TG/DTA results of the prepared samples

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Complex compositions PAN/PMMA/LiClO₄ 75/25/X (Wt %)</th>
<th>Decomposition Temperature (°C) (± 3 °C)</th>
<th>% Wt loss of the samples (± 2Wt %)</th>
<th>Exothermic Peaks (°C) (± 3 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>X=2</td>
<td>100 230 331 6 10 24</td>
<td>-</td>
<td>303 342</td>
</tr>
<tr>
<td>B2</td>
<td>X=5</td>
<td>- 230 320 - 8 22</td>
<td>-</td>
<td>303 350</td>
</tr>
<tr>
<td>B3</td>
<td>X=8</td>
<td>64 240 324 11 16 30 67</td>
<td>304 355</td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>X=11</td>
<td>120 250 316 5 8 18 -</td>
<td>323 -</td>
<td></td>
</tr>
</tbody>
</table>
References


