CHAPTER V
EXPERIMENTAL INVESTIGATIONS ON PAN-PEO HYBRID POLYMER ELECTROLYTES

ABSTRACT

Hybrid solid polymer electrolytes (HSPEs) of high ionic conductivity were prepared using Poly acrylonitrile (PAN), Poly ethylene oxide (PEO), Propylene carbonate (PC), Ethylene carbonate (EC) and LiCF$_3$SO$_3$. These electrolyte films were free standing and dimensionally stable. The HSPE films were characterized by X-ray diffraction, FTIR, SEM, thermal and a.c impedance spectroscopic techniques. Conductivity studies of these polymer electrolytes were carried out in the temperature range 301-373K.

5.1 INTRODUCTION

In recent years, there has been increasing interest in research and development of rechargeable lithium batteries employing solid polymer films as electrolytes. Polymer gel electrolytes formed by immobilization of liquid electrolyte in poly (acrylonitrile) have ionic conductivities greater than solvent free poly (ethylene oxide) based electrolytes [1-3]. Reich and Michalei [4] have examined the conductivity of systems formed by adding LiClO$_4$ to PAN. Watanabe et al. [2] added EC and PC as plasticizers and solvents to LiClO$_4$ complexes of PAN and measured the effect on the conductivity. Abraham and Alamgir [1] increased the conductivity to 10$^{-3}$ S/cm by immobilizing a solution of PC and EC containing LiClO$_4$ in PAN. Slane and Salomon [5] have prepared composite polymer electrolyte films consisting of zeolite powders dispersed in PAN based gels with LiAsF$_6$.
and reported conductivity greater than $10^{-3}$ S/cm at room temperature. Even though a high conductance is achieved with PAN electrolytes, dimensional stability of these films is poor. They are gels rather than solid polymer films. Poor dimensional stability is due to the existence of a liquid solution entrapped in the PAN matrix.

On the other hand, Poly ethylene oxide has been studied extensively as a solid polymer electrolyte (SPE) medium following the direction proposed by Wright [6] and Armand et al. [7]. Specific conductivity ($\sigma$) is of the order of $10^{-8}$ S/cm at ambient temperature, when a SPE film is prepared by complexing PEO with a lithium salt [8]. Several procedures for preparation of highly conducting ($\sigma \geq 10^{-3}$ S/cm) SPE films are reported in the literature [8-16]. These studies include modifications of PEO based SPE as well as investigations of different polymer media. Munichandriah et al. [17] have reported the ionic conductivity ($3.7 \times 10^{-4}$ S/cm) at ambient temperature for HSPE consisting of PEO, PAN, PC, EC and LiClO$_4$. In the present study HSPE consisting of PAN, PEO, PC, EC and LiCF$_3$SO$_3$ have been prepared to overcome the problems inherent to PAN by varying the ratio of PEO and plasticizers.

5.2. EXPERIMENTAL

PAN, PEO, PC and LiCF$_3$SO$_3$ were used as received from Aldrich, USA and EC received from Merck, Germany was used without further purification for the preparation of HSPE films. Appropriate quantities of PEO, PC, EC and LiCF$_3$SO$_3$ were first dissolved in Dimethyl formamide (DMF). After adding the required quantity of PAN, the solution was stirred continuously for several hours until a homogeneous suspension was obtained. A film was cast by spreading the suspension on teflon-covered glass plate and allowing
DMF to evaporate slowly. Finally, the film was dried at 70°C under vacuum for about 4 hours. The resulting film was visually examined for its dry and free standing nature.

Chemical storage, film casting and cell assemblies were performed in a vacuum atmosphere. The XRD equipment used in this study was JEOL, JDX 8030 X-ray diffractometer. FTIR measurements were made in the range 200–4000 cm\(^{-1}\) using a Perkin Elmer 577 IR Spectrophotometer. The bulk electrical conductivities of the polymer complex were evaluated from the impedance plots in the temperature range (301 to 373K) using a Keithley 3330 LCZ meter. The plots were recorded in the frequency range 40 Hz to 100 kHz with a signal amplitude of 10mV. The polymer film was sandwiched between stainless steel electrodes for conductivity studies.

5.3. RESULTS AND DISCUSSION

5.3.1. X-ray diffraction studies

Fig (5.1) shows the XRD patterns of PAN-PEO-LiCF\(_3\)SO\(_3\)-PC-EC complexes compared to those of pure LiCF\(_3\)SO\(_3\), PEO and PAN. It is seen that the PAN based lithium salt complex exhibits an amorphous phase. The XRD pattern of pure PEO (fig.5.1.b) indicates two crystalline peaks at 19.7 and 23.9° [18]. These peaks are found to be absent in the polymer complexes. The absence of sharp peaks pertaining to LiCF\(_3\)SO\(_3\) in the polymer complex indicates that complexation has taken place in the amorphous phase and no free salt is present in the polymer complexes.

The degree of crystallinity for pure PAN, PEO and LiCF\(_3\)SO\(_3\) is found as 2.15, 36.36 and 7.19% respectively. The polymer complexes (F9-F12) do not show any degree
of crystallinity. It is observed that the degree of crystallinity of polymer complexes is reduced after the addition of LiCF$_3$SO$_3$, PC and EC.

5.3.2. FTIR spectroscopic studies

The FTIR plots of pure PAN, PEO, LiCF$_3$SO$_3$, EC, PC and polymer electrolyte complexes are shown in fig (5.2). C-H stretching frequency of PEO appearing at 2900 cm$^{-1}$ gets shifted to 2935 cm$^{-1}$ in the complex. Asymmetric stretching vibration at 1950 cm$^{-1}$ and asymmetric bending vibration at 1450 cm$^{-1}$ of pure PEO are shifted to 1966 and 1455 cm$^{-1}$ in the polymer complex respectively. The band at 1455 cm$^{-1}$ is attributed to CH$_2$ bending vibration in the complex. The C≡N frequency at 2244 cm$^{-1}$ is fairly stable. CN stretching vibration appearing in the pure PAN at 1251 cm$^{-1}$ is shifted to 1260 cm$^{-1}$ in the polymer complexes. The $\nu_{C=O}$ at 1801 cm$^{-1}$ of EC shifts to 1785 and 1778 cm$^{-1}$ in complexes F11 and F12 respectively. The doblet due to the crystallinity of EC at 777 cm$^{-1}$ and 712 cm$^{-1}$, merges into 760 cm$^{-1}$ in complexes, F10, F11, F12, showing the non-crystalline nature of the complexes. Upon addition of the lithium salt, there appeared a higher frequency shoulder in the spectrum. If the N atoms of the –C≡N groups are coordinated to Li$^+$ ions, the –C≡N stretching peak will be shifted to higher energy side due to an inductive effect [19]. The IR bands at 1291, 1210, 1180, 1031, 639 and 579 cm$^{-1}$ have been reported for silver triflate and are assigned to the triflate anion [20]. In addition to this, the following bands at 2941, 2244, 1660, 1548, 1074 and 540 cm$^{-1}$ are slightly shifted in the polymer complex. Vibrational bands (3851, 3813, 3776, 3718, 3686, 3542, 2360, 1727, 1652, 1358, 1184 and 1038 cm$^{-1}$) pertaining to pure PAN, PEO and LiCF$_3$SO$_3$ are found to be absent in the polymer electrolyte system. Further, some new
peaks (3478, 2321, 674 cm\(^{-1}\)) are observed in the polymer complex. From the above analysis, the complexation of PAN-PEO with LiCF\(_3\)SO\(_3\) has been confirmed.

5.3.3. SEM studies

Typical SEM photographs of PAN-PEO-LiCF\(_3\)SO\(_3\)-PC-EC polymer complex with different magnifications (x500, x2000) are shown in fig (5.3). Conducting grain boundaries are shown as white patches. When magnification is 2000, the surface morphology resembles with that of brain corals. When magnification is reduced to 500, it leads to emulsification of fats appearance on the surface.

5.3.4. Thermal Studies

TG and DTA analysis for PAN-PEO-LiCF\(_3\)SO\(_3\)-PC-EC (21:2:8:27.7:41.3) system is shown in fig (5.4). From this, it can be seen that the polymer film is thermally stable upto 290°C and at 326.28°C there appears an exothermic peak (fig.5.4.a) accompanied by a weight loss. The peak is attributed to melting of the polymer. An endothermic peak at 41.65°C may be attributed to the moisture and impurities in the polymer complexes. Weight loss occurs more or less uniformly above 100°C. From TG curve it can be seen that the first decomposition occurs in between 50 and 100°C and second, third decompositions of the polymer film take place in between 170-200°C and 300-350°C respectively. The concurrent weight losses were 10.1, 12.8 and 16.6% (Table 5.1) at various temperatures of 100, 200 and 300°C respectively.

The analysis of TG and DTA curves for PAN-PEO-LiCF\(_3\)SO\(_3\)-PC-EC (21:5:8:24.7:41.3) is shown in fig (5.4.b). From the DTA curve it can be seen an
endothermic peak at 52.43°C which may be attributed to the melting of the polymer complex. A broad exothermic peak appears at 320.5°C with weight loss. This peak is attributed to the decomposition of polymer electrolyte. Between these two endothermic and exothermic peaks the polymer behaves thermally stable. The first, second and third decomposition range of the polymer are noticed in between 70-110°C, 200-220°C and 300-340°C respectively. Similarly the percentage of weight losses at 100°C, 200°C and 300°C were 4.5, 5.4 and 6.9% respectively. This polymer complex is thermally stable upto 320°C.

TGA/DTA of polymer complexes of PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21:10:8:27.7:33.3) is shown in fig (5.4.c). From the DTA curve, an endothermic peak at 63.83°C occurs due to the melting of polymer electrolyte and a small unnoticeable exothermic peak at 102.77°C has also taken place, which may be due to the eutectic transition of the polymer film. From then the polymer film seems to be thermally stable upto 300°C. There appears a large exothermic peak at 335.4°C indicating the decomposition of the polymer film F11 along with a sharp weight loss as seen from the TG curve. The first, second and third decomposition ranges lie in between 70-100°C, 250-280°C and above 300°C respectively and the corresponding percent weight losses at 100, 200 and 300°C were noticed to be 10.2, 11.2 and 12.6% respectively.

From the DTA curve (fig 5.4.d), the film F12 has two smaller endothermic peaks at 63.3 and 159.76°C. The first endothermic peak may be due to the melting of the polymer as in the previous cases. The second endothermic may be due to the eutectic transition taking place in the complex. A large exothermic peak as in the preceding fig (5.4.(d)) is observed at 338.28°C. This exothermic peak is due to the final decomposition
of the polymer complex accompanied by a distinctive weight loss. The initial melting of the polymer film as indicated by the endothermic peak is also reflected in the TG curve with a loss of material till 70°C. From the DTA curve, it is seen that the polymer film is thermally stable up to 306°C. The first, second and third decomposition ranges lie in between 70-100, 300-350 and above 350°C respectively and the corresponding percent weight losses were 7, 11.4, 12.1% at 100, 200 and 300°C respectively.

5.3.5. Conductivity studies

Complex impedance diagrams of the electrolyte films (PAN-PEO-LiCF$_3$SO$_3$-PC- EC system) at 301K are shown in fig (5.5). The ionic conductivities for PAN-PEO-PC- EC-LiCF$_3$SO$_3$ complex films containing various compositions of PEO and plasticizer obtained in the temperature range 301-373K and are tabulated in Table (5.2). The plasticizers used here have the following structures and some of their physical properties are given in Table (5.3).

![Structures of EC and PC](image)

The high boiling points and low vapour pressures of these solvents make them desirable as plasticizers for the preparation of electrolytes with EC and PC providing minimal changes in the composition from solvent evaporation during storage. They also
have high dielectric constants which should allow the preparation of high conductivity electrolytes. Both solvents have been used previously in liquid electrolyte-based primary and secondary Li batteries. However, it was necessary to optimize the specific solvent mixture compositions with respect to conductivity and dimensional stability of the HSPE blend. The highest conductivity has been obtained for 27.7\% PC and 33.3\% EC (Table 5.1). The conductivity value of PAN(21)-PEO(10)-LiCF$_3$SO$_3$(8)-PC(27.7)-EC(33.3) electrolyte system presented in this work is estimated as 2.1x10$^{-2}$S/cm at 301K. This value is found to be higher than the values of 2.16x10$^{-3}$S/cm reported by Huang et al. [21] for PAN(20)-EC(35)-BL(40)-LiClO$_4$(5) at 295K and 9x10$^{-4}$S/cm reported by Bandara et al. [22] for PEO-LiCF$_3$SO$_3$-EC system at 332K. It is noticed from Table(5.2) that as the m/o of PEO increases from 2 to 10, the $\sigma$ values increase gradually. It is found that there is a drop in $\sigma$ value when m/o of PEO is enhanced to 15. This may be due to the decrease in the concentration of plasticizer (EC, PC). It is observed from table(5.2) that as the temperature increases, the conductivity values also increase for all the compositions [23]. This behaviour is in agreement with the theory [24]. This behaviour can be relationalized by recognizing the free volume model [25]. As the temperature increases, the polymer can expand easily and produce free volume. Thus ions, solvated molecules, or polymer segments can move into the free volume [26]. The resulting conductivity represented by the overall mobility of ion and polymer is determined by the free volume around the polymer chains. Therefore, as the temperature increases, the free volume increases. This leads to an increase in ion mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds. The variation of the logarithm of electrical conductivity (log$\sigma$) with inverse absolute
temperature for various polymer electrolytes is presented in fig (5.6). The overall features of the Arrhenius plots are similar for the electrolyte systems that no linear dependence could be obtained seems to suggest that ion conduction follows the Williams-Landel-Ferry (WLF) mechanism [27]. In other words, the non-linearity indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion [28]. Thus, the result may be more effectively represented by the empirical Vogel-Tamman-Fulcher (VTF) equation [29-31]

\[ \sigma = AT^{-1/2} \exp \left(-\frac{B}{T-T_g}\right) \] 5.1

where A and B are constants and \( T_g \) is the reference temperature taken as the glass transition temperature here. Constant A in the VTF equation is related to the number of change carriers in the electrolyte system and constant B is related to the activation energy of ion transport associated with the configurational entropy of the polymer chains. The temperature dependence of ionic conductivity suggests that the ion moves through the plasticizer rich-phase. Because the conducting medium i.e plasticizer-rich phase, involves the plasticizer, the salt and polymers, the characteristics of the viscous matrix are brought out.

It is concluded that the polymer electrolyte film having 27.7m/o PC, 33.3m/o EC and 10m/o PEO gives the maximum conductivity value (2.10x10^{2} S/cm) at 301K. It can be used as an electrolyte in Li batteries.
Table 5.1.

TG/DTA results in PAN-PEO-LiCF3SO3-PC-EC polymer complexes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Decomposition Range (°C)</th>
<th>%Wt. loss (±2%) at various temperatures (°C)</th>
<th>Endothermic (°C)</th>
<th>Exothermic (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First</td>
<td>Second</td>
<td>Third</td>
<td>100</td>
</tr>
<tr>
<td>F9</td>
<td>50-100</td>
<td>170-200</td>
<td>300-350</td>
<td>10.1</td>
</tr>
<tr>
<td>(21:2:8:27.7:41.3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F10</td>
<td>70-110</td>
<td>200-220</td>
<td>300-340</td>
<td>4.5</td>
</tr>
<tr>
<td>(21:5:8:24.7:41.3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F11</td>
<td>70-100</td>
<td>250-280</td>
<td>above 330</td>
<td>10.2</td>
</tr>
<tr>
<td>(21:10:8:27.7:33.3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F12</td>
<td>70-100</td>
<td>300-350</td>
<td>above 350</td>
<td>7</td>
</tr>
<tr>
<td>(21:15:8:24.7:31.3)</td>
<td></td>
<td></td>
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### Table 5.2.
Conductivity values of PAN-PEO-LiCF$_3$SO$_3$-PC-EC polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Conductivity values of PAN-PEO-LiCF$_3$SO$_3$-PC-EC x10$^{-3}$S/cm</th>
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<tr>
<td></td>
<td></td>
<td>301K</td>
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<tr>
<td>F13</td>
<td>(21-2-8-27.7-41.3)</td>
<td>0.314</td>
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<tr>
<td>F14</td>
<td>(21-5-8-24.7-41.3)</td>
<td>2.794</td>
</tr>
<tr>
<td>F15</td>
<td>(21-10-8-27.7-33.3)</td>
<td>20.969</td>
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Table 5.3.
Physical properties of plasticizers

<table>
<thead>
<tr>
<th>Component</th>
<th>Dielectric constant</th>
<th>Viscosity(cP)</th>
<th>Boiling point (°C)</th>
<th>Melting point (°C)</th>
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<tbody>
<tr>
<td>Ethylene carbonate(EC)</td>
<td>89.6</td>
<td>1.85</td>
<td>238</td>
<td>36.5</td>
</tr>
<tr>
<td>Propylene carbonate(PC)</td>
<td>63.8</td>
<td>2.53</td>
<td>240</td>
<td>-55</td>
</tr>
</tbody>
</table>
Fig 5.1. XRD patterns for PAN, PEO, LiCF$_3$SO$_3$, and the polymer complexes
(a) pure PAN, (b) pure PEO, (c) pure LiCF$_3$SO$_3$,
(d) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-2-27.7-41.3)
(e) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-5-8-24.7-41.3)
(f) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-10-8-27.7-33.3)
(g) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-15-8-24.7-31.3)
Fig. 5.2. FTIR plots for PAN, PEO, LiCF$_3$SO$_3$, PC, EC and the complexes
(a) pure PAN, (b) pure PEO, (c) pure LiCF$_3$SO$_3$, (d) pure PC, (e) pure EC,
(f) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-2-27.7-41.3)
(i) PAN- PEO-LiCF$_3$SO$_3$-PC-EC (21-5-8-24.7-41.3)
(j) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-10-8-27.7-33.3)
(i) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-15-8-24.7-31.3)
Fig. 5.3. SEM micrographs for PAN-PEO-LiCF$_3$SO$_3$-PC-EC polymer complex with two different magnifications (a) x2000, (b) x500
Fig. 5.4. DTA and TGA scans of polymer complexes

(a) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-2-27.7-41.3)
(b) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-5-8-24.7-41.3)
(c) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-10-8-27.7-33.3)
(d) PAN-PEO-LiCF$_3$SO$_3$-PC-EC (21-15-8-24.7-31.3)
Fig. 5.5. Typical complex impedance plots of PAN-PEO-LiCF$_3$SO$_3$-PC-EC system.
Fig.(5.6). Arrhenius plot of conductivity against reciprocal temperature for
(a) PAN(21)-PEO(2)-LiCF$_3$SO$_3$(8)-PC(27.7)-EC(41.3)
(b) PAN(21)-PEO(5)-LiCF$_3$SO$_3$(8)-PC(24.7)-EC(41.3)
(c) PAN(21)-PEO(10)-LiCF$_3$SO$_3$(8)-PC(27.7)-EC(33.3)
(d) PAN(21)-PEO(15)-LiCF$_3$SO$_3$(8)-PC(24.7)-EC(31.3)
5.4. REFERENCES


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