CHAPTER VII
LITHIUM ION CONDUCTION IN PAN-PVdF HYBRID POLYMER ELECTROLYTES

ABSTRACT

The effect of addition of PVdF and plasticizer to PAN based polymer blend are discussed using different analytical techniques such as XRD, FTIR, SEM, DTA/TG and a.c impedance spectroscopy. The ac conductivity studies were performed to evaluate the conductivity of the polymer electrolyte membranes. The addition of PVdF into PAN-LiBF₄-PC-EC complexes enhances the mechanical stability of the thin film electrolyte membrane. Conductivity studies of these polymer electrolytes were carried out in the temperature range 301 – 373K. The results are discussed in detail.

7.1 INTRODUCTION

One of the most striking paradoxes of the existing technology is the mismatch between the progress of the portable consumer electronic devices and that of the batteries which are used to power them. Therefore, there is an urgent need for the development of new design batteries which can combine high energy density with long shelf life [1]. It is almost universally accepted that such combination can only be obtained by using lithium based electrochemical systems to configure the cell or battery [2-6].

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 [7-9]. Reich and Michalei [10] have examined the conductivities of systems formed by adding LiClO$_4$ to PAN. Watanabe et al. [8] added EC and PC as plasticizers and measured the effect on the conductivity. Abraham and Alamgir [7] increased the conductivity to $10^{-3}\text{S/cm}$ by immobilizing a solution of PC and EC containing LiClO$_4$ in PAN. Slane and Salomon [11] have prepared composite polymer electrolyte films consisting of zeolite powders dispersed in PAN based gels with LiAsF$_6$ and reported conductivity greater than $10^{-3}\text{S/cm}$ at room temperature. Even though a high conductance is achieved with PAN electrolyte, 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 Watanabe et al. [12] in 1981. It was found that PVdF can form homogeneous hybrid films with lithium salts, EC and / or PC in the proper proportions. Tsuchida et al. [13, 14] studied the plasticized PVdF system. Jiang et al. [15] studied polymer electrolyte membranes which consist of PVdF, EC, PC and LiX (X=CF$_3$SO$_3$, PF$_6$ or N(CF$_3$SO$_2$)$_2$). They found that the conductivity of the electrolytes was influenced by the viscosity of the medium and the concentration of the charge carriers, which are directly related to the weight ratio of PVdF/(PC+EC) and the type and concentration of the lithium salt. Room temperature conductivities as high as 2.2mScm$^{-1}$ were obtained for some LiN(CF$_3$SO$_2$)$_2$ containing electrolytes. In the present study HSPE's consisting of PAN, PVdF, PC, EC and LiBF$_4$ have been prepared to overcome the problem inherent to PAN by varying the ratio of
PVdF and plasticizer and characterized by XRD, FTIR, thermal, SEM and ac impedance techniques.

7.2 EXPERIMENTAL

Starting materials PAN, PVdF, LiBF₄ and PC were obtained from Aldrich USA and EC was supplied by E-Merck, Germany. All chemicals in this study were of analytical reagent grade. The phase analysis of the polymer films was performed with XRD using Cu-Kα radiation on JDX 8030, JEOL X-ray diffractometer (Japan) at room temperature. The FTIR spectrum in the region 200-4000 cm⁻¹ was recorded on a Perkin-Elmer Paragon spectrophotometer (model 577).

For thermal measurements, a TGA with a heating rate of 10°C/min was used. The complex impedance analysis was attempted in the frequency range 40 Hz - 100 kHz in order to find conductivity of the samples.

The conductivity measurements were carried out with a circular film obtained from the casting technique. The thickness of the polymer film was of the order of ≈ 1 mm. Such a electrolyte film was then placed between two stainless steel electrodes in order to ensure proper electrical contact. A home designed spring loaded stainless steel conductivity cell was used for electrical measurements. For electrical conductivity measurements, a LCZ meter, model 3330, Keithley, was used with a signal amplitude of 10 mV. The temperature range covered was 301-373K. Scanning electron micrographs (SEM) of the polymer film surface were also taken and discussed.
7.3. RESULTS AND DISCUSSION

7.3.1. X-ray diffraction studies

A detailed X-ray diffraction patterns of pure PAN, PVdF and LiBF₄ are presented in fig (7.1.a-c) respectively. The amorphous phase of PAN is revealed from fig (7.1.a). XRD pattern of pure PVdF (fig 7.1(b)) indicates two crystalline peaks at $2\theta = 20$ and $23^\circ$. The crystalline phase of LiBF₄ is clearly seen from the diffraction peaks (fig 7.1.c). The peaks pertaining to PVdF and LiBF₄ appear on the diffractograms of the polymer complexes with changes in intensities of the peaks. The diffractograms corresponding to the complexes show some weak reflections at $2\theta$ values greater than $30^\circ$. The absence of sharp peaks pertaining to LiBF₄ in the polymer complexes indicates that complexation has taken place in the amorphous phase.

The degree of crystallinity of pure PAN, PVdF and LiBF₄ is found as 2.15, 18.37 and 42.55% respectively. The degree of crystallinity of the polymer complexes is estimated as 4.77, 6.93, 12.58 and 13.45% (F17-F20). The conductivity value ($9.706 \times 10^{-4} \text{S/cm}$) for the film F17 at room temperature is found to be the maximum conductivity among the four compositions studied. This highest conductivity value of the film (F17) is in accordance with the lowest degree of crystallinity (4.77%) among the four films.

7.3.2. FTIR spectroscopic studies

FTIR spectroscopy is important for the investigation of polymer structure. In the present work, IR spectroscopy is used to establish interaction(s) between the polymer, salt and plasticizers. Such interactions can induce changes in the vibrational modes of the
atoms or molecules in the material. The FTIR plots of pure PAN, PVdF, LiBF₄, EC, PC and polymer electrolyte complexes are shown in fig (7.2). In this system also, C=\text{N} band at 2240 cm⁻¹ is fairly stable. The 1962 cm⁻¹ band of EC shifts to higher frequencies in all the four complexes. The v_{\text{C=O}} at 1801 cm⁻¹ of EC shifts to 1785 cm⁻¹ in complex F19 and 1778 cm⁻¹ in complex F20. In complex F18, there seems to be no frequency shift (v_{\text{C=O}} 1802 cm⁻¹). C=\text{C} stretching frequency of PAN (1251 cm⁻¹), C=\text{F} stretching vibration of PVdF (763 cm⁻¹), C=\text{O} stretching frequency of PC (1789 cm⁻¹) and C=\text{O} stretching frequency of PC (1119 cm⁻¹) are found absent in the polymer complexes. In addition to this, the following vibrational bands of PAN (3541 cm⁻¹), of PVdF (1546, 1528, 976, 613, 488, 411 cm⁻¹), of LiBF₄ (2351, 771 cm⁻¹), of PC (3563, 2988, 2924, 1586, 1485, 1454, 1389, 1353, 956, 849, 776, 536 cm⁻¹), of EC (2775, 2702, 2659, 2488, 2329, 1550, 893, 526 cm⁻¹) are found absent in the polymer complexes. Further the following peaks 2245, 1970 cm⁻¹ pertaining to EC are also shifted in the polymer electrolyte systems. A new peak at 2508 cm⁻¹ is observed in the polymer complexes. The crystalline state bands at 777 cm⁻¹ and 712 cm⁻¹ of EC are also and PC, are also seen in complexes F18, F19 and F20 which show that the conduction must be less in these complexes. From the above analysis, the complexation of PAN, PVdF with LiBF₄ has been confirmed.

7.3.3. SEM studies

SEM photographs of PAN-PVdF-LiBF₄-PC-EC complexes for two different magnification (x500, x2000) are shown in fig (7.3.a, b) respectively. Conducting grain boundaries are shown as white patches. Fig. (7.3. a) resembles with that of mushroom coral appearance. On further decreasing the magnification to 500, it leads to total absence
of mushroom coral appearance on the surface. It is very similar to the appearance of Islets of langerhans.

### 7.3.4. Thermal studies

DTA and TGA curves of PAN-PVdF-LiBF₄-PC-EC system are shown in fig (7.4). The DTA curve shows no noticeable peaks up to 253.1°C indicating that the film is relatively thermally stable up to this temperature. A small endothermic peak observed at 253.1°C may be attributed to the eutectic transition and a large exothermic peak at 271.95°C (Table 7.1) indicates that the polymer film is decomposing as evidenced by the rapid weight loss observed from the TG curve. The first, second and third decomposition of the film take place in between 80-100, 250-270 and 300-350°C (fig 7.4(a)) respectively and the corresponding weight losses were 3, 6 and 9.8% at various temperatures of 100, 200 and 300°C respectively.

The DTA curve (fig 7.4(b)) shows no peak up to 266.06°C indicating the film F18 is relatively thermally stable up to this temperature. A large endothermic peak at 278.57°C indicates that the polymer film is decomposing as evidenced by a rapid weight loss observed from the TG curve. The first, second and third decomposition of the film take place in between 140-180, 270-300 and 320-350°C respectively and the corresponding weight losses were 4, 7.4 and 10.8% at various temperatures of 100, 200 and 300°C respectively.

The DTA curve (fig 7.4(c)) shows no noticeable peaks up to 265.9°C indicating that the film is relatively thermally stable up to this temperature. The endothermic peak observed at 161.34°C may be due to solvent adsorbed on to the surface of the polymer.
film and other impurities. Larger exothermic peak at 281.02°C indicates that the polymer is decomposing as evidenced by the rapid weight loss in the TG curve. The first, second and third decomposition of the film take place in between 110-140, 200-250 and 300-320°C respectively and the corresponding weight losses were 5.2, 7.6 and 12.2% at various temperatures of 100, 200 and 300°C respectively.

DTA and TG curves of the polymer film F20 are shown in fig (7.4(d)). The polymer film exhibits a distinctive endothermic peak at 68.3°C indicating the melting of the polymer film and then the polymer film exhibits thermal stability upto 161°C. Though not clear, the trend in the curve along with appreciable loss of weight of polymer indicates the decomposition of the film above 201.1°C. The TG curve also reflects a linear weight loss of materials. This indicates that the material has lesser degree of thermal stability. The first, second and third decomposition of the film take place in between 60-80, 130-160 and 190-250°C respectively and the corresponding weight losses were 16, 53 and 59% at various temperatures of 100, 200 and 300°C respectively.

Conductivity for the film F20 is found to be $9.706 \times 10^{-4}$ S/cm at room temperature. This value is found to be higher compared to the values of other films. However, the thermal stability of the film F20 extends upto 161°C. Weight losses are found to be 3, 6 and 9.8 % for the film F17 at 100, 200 and 300°C respectively. This weight losses are found to be minimum among the four compositions studied. The conductivity of the film F18 is found to be $1.749 \times 10^{-4}$S/cm. But the film F18 possess good thermal stability upto a temperature of 266°C. Hence it is concluded that the film F18 is superior among the four films on the basis of thermal stability.
7.3.5. Conductivity studies

Impedance data are presented in the form of imaginary, \( Z'' \) (capacitive) against real \( Z' \) (resistive) impedances. The typical impedance plots (\( Z' \) Vs \( Z'' \)) for the different compositions of PAN-PVdF-LiBF₄-PC-EC are shown in fig (7.5). The impedance response on the thin films was analyzed by means of a spring load conductivity cell whose details are described elsewhere (chapter III). The electrodes of the cell were made up of stainless steel as blocking electrodes. The bulk impedance values were calculated from the complex impedance plots in the usual manner and used to calculate the bulk conductivity values.

Table (7.2) summarizes the ionic conductivity values of PAN-PVdF-LiBF₄-PC-EC in the temperature range 301K- 373K. The conductivity values for PAN-PVdF-LiBF₄-PC-EC system are found in the range from \( 0.2 \times 10^{-4} \) S/cm to \( 9 \times 10^{-4} \) S/cm at 301K. The effect of adding PVdF shows a pronounced effect on the conductivity values. The conductivity values are found to decrease upon increasing the concentration of PVdF. This may be due to reduction in the concentration of EC. Considering the conductivity and mechanical integrity, only PAN-LiBF₄-PVdF-PC-EC (21:8:10:27.7:33.3) composition renders the maximum conductivity of \( 9.706 \times 10^{-4} \) S/cm at 301K.

It indicates that when the weight ratio of PVdF concentration increases, the conductivity of the gel polymer electrolyte decreases. A decrease in the plasticizer (EC) concentration in the gel polymer electrolyte will decrease the concentration of charge carrier ions, which should have a negative effect on the conductivity. Ionic conductivity in polymer electrolytes is strongly coupled to the flow behaviour of the polymer. Lower \( T_g \) produces higher polymer flow and greater ionic diffusivity, i.e high ionic conductivity.
is obtained in polymers having slightly flexible backbones and low glass transition temperatures.

The high boiling points and low vapour pressure 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 is necessary to optimize the specific solvent mixture compositions with respect to conductivity and dimensional stability of the Hybrid Solid Polymer Electrolyte (HSPE) blend. The highest conductivity has been obtained for polymer electrolyte containing 27.7 m/o PC and 33.3 m/o EC (Table 7.2). The conductivity value of PAN(21)-PVdF(10)-LiBF₄(8)-PC(27.7)-EC(33.3) electrolyte system presented in this work is estimated as 9.706 x10⁻⁴ S/cm at 301 K. This value is found to be higher than the value of 2.1 x10⁻⁴ S/cm reported by Periyasamy et al. [17] for PVdF(20)-(PC+EC)(75)-LiBF₄(5) at room temperature. It is noticed from Table (7.2) that as the m/o of PVdF increases from 10 to 25, the σ values decrease gradually. This may be due to an increase in crystallinity which is measured from x-ray diffraction techniques. Moreover the number of diffraction peaks observed in fig(7.1(d)) is less compared to the diffraction peaks in fig (7.1(g)). The complex film F17 (fig (7.1 d) almost exhibits an amorphous nature and hence the increase in conductivity. Thus in the present study the benefit from the conductivity point of view, the composition of PAN(21)-PVdF(10)-LiBF₄(8)-PC(27.7)-EC(33.3) favours the conductivity enhancement. The temperature dependence of electrical conductivities for the polymer blends is shown in fig (7.6) and it
seems to obey VTF relation. Hence, the properties of PAN-PVdF-LiBF₄-PC-EC polymer electrolyte look very desirable and promising for battery application.
Table 7.1
TG/DTA results in PAN-PVdF-LiBF₄-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>Endo-Thermic (°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>F17 (21:10:8:27.7:33.3)</td>
<td>80-100</td>
<td>250-270</td>
<td>300-350</td>
<td>3</td>
</tr>
<tr>
<td>F18 (21:15:8:27.7:28.3)</td>
<td>140-180</td>
<td>270-300</td>
<td>320-350</td>
<td>4</td>
</tr>
<tr>
<td>F19 (21:20:8:27.7:23.3)</td>
<td>110-140</td>
<td>200-250</td>
<td>300-320</td>
<td>5.2</td>
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<tr>
<td>F20 (21:25:8:27.7:18.3)</td>
<td>60-80</td>
<td>130-160</td>
<td>190-250</td>
<td>16</td>
</tr>
</tbody>
</table>
Table 7.2.
Conductivity values of PAN-PVdF-LiBF₄-PC-EC polymer electrolytes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Conductivity values of PAN-PVdF-LiBF₄-PC-EC x10⁻² S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>301K</td>
</tr>
<tr>
<td>F17</td>
<td>(21-10-8-27.7-33.3)</td>
<td>9.706</td>
</tr>
<tr>
<td>F19</td>
<td>(21-20-8-27.7-23.3)</td>
<td>1.747</td>
</tr>
<tr>
<td>F20</td>
<td>(21-25-8-27.7-18.3)</td>
<td>0.229</td>
</tr>
</tbody>
</table>
Fig 7.1. XRD patterns for PAN, PVdF, LiBF₄ and the polymer complexes
(a) pure PAN, (b) pure PVdF, (c) pure LiBF₄.
(d) PAN-PVdF-LiBF₄-PC-EC (21-10-8-27.7-33.3)
(e) PAN- PVdF-LiBF₄-PC-EC (21-15-8-27.7-28.3)
(f) PAN-PVdF-LiBF₄-PC-EC (21-20-8-27.7-23.3)
(g) PAN-PVdF-LiBF₄-PC-EC (21-25-8-27.7-18.3)
Fig. 7.2. FTIR plots for PAN, PVdF, LiBF₄, PC, EC and the complexes (a) pure PAN, (b) pure PVdF, (c) pure LiBF₄, (d) pure PC, (e) pure EC.
(f) PAN-PVdF-LiBF₄-PC-EC (21-10-8-27.7-33.3)
(g) PAN- PVdF-LiBF₄-PC-EC (21-15-8-27.7-28.3)
(h) PAN-PVdF-LiBF₄-PC-EC (21-20-8-27.7-23.3)
(i) PAN-PVdF-LiBF₄-PC-EC (21-25-8-27.7-18.3)
Fig. 7.3. SEM micrographs for PAN-PVdF-LiBF₄-PC-EC polymer complex with two different magnifications (a) x2000, (b) x500
Fig. 7.4. DTA and TGA scans of polymer complexes
(a) PAN-PVdF-LiBF$_4$-PC-EC (21-10-8-27.7-33.3)
(b) PAN- PVdF-LiBF$_4$-PC-EC (21-15-8-27.7-28.3)
(c) PAN-PVdF-LiBF$_4$-PC-EC (21-20-8-27.7-23.3)
(d) PAN-PVdF-LiBF$_4$-PC-EC (21-25-8-27.7-18.3)
Fig. 7.5. Typical complex impedance plots of PAN-PVdF-LiBF$_4$-PC-EC system.
Fig. (7.6). Arrhenius plot of conductivity against reciprocal temperature for
(a) PAN(21)-PVdF(10)-LiBF₄(8)-PC(27.7)-EC(33.3)
(b) PAN(21)-PVdF(15)-LiBF₄(8)-PC(27.7)-EC(28.3)
(c) PAN(21)-PVdF(20)-LiBF₄(8)-PC(27.7)-EC(23.3)
(d) PAN(21)-PVdF(25)-LiBF₄(8)-PC(27.7)-EC(18.3)
REFERENCES


