Chapter IV

PART I

PREPARATION AND CHARACTERIZATION OF
POLY (ACRYLONITRILE) COMPLEXED WITH LiClO₄

ABSTRACT

Polymer electrolyte films consisting of Poly acrylonitrile (PAN), ethylene carbonate (EC), propylene carbonate and LiClO₄ (Lithium perchlorate) are prepared. These electrolyte films are free standing and dimensionally stable. The solid electrolyte films are characterized by X-ray diffraction, FTIR, Thermal and SEM studies. Conductivity studies of these polymer electrolytes are carried out in the temperature range 301-373K.

4.1.1. INTRODUCTION

There is considerable interest in solid electrolytes (electrically conductive solids with ionic carriers) owing to their potentially wide range of application in such areas as solid-state batteries, fuel cells, and novel chemical sensors [1]. The development of high energy density secondary batteries is of considerable technological and industrial importance today. Polymer composite electrolytes developed at the end of 1970s, have become more widely used in solid state batteries. PEO based lithium salt complex was the compound most studied. It has been playing an important and dominant role as a solid state electrolyte for lithium batteries. The conventional polymer electrolytes composed of complexes of Li salts with long chain polymers have conductivities significantly lower
than the conductivity ($10^{-3}$ S/cm) required for the development of practical batteries capable of discharging at moderate and high rates [2]. The properties of a plasticized solid polymer electrolytes allow for high ionic mobility. Ionic transport is closely coupled to the segmental motions of the polymer chains and high local flexibility. A number of plasticized polymer salt systems exhibits considerable conductivity. Much reach effort has been applied to find the optimized combination of host polymer and dopant salt for fast ionic transport. Recently, it has been suggested that gel type electrolytes [3] in which an organic polymer is impregnated with an electrolyte solution, can suppress the formation of lithium dendrites [4, 5]. Additional advantage of gel type electrolytes are good ionic conductivity that is comparable with that of liquid electrolytes and ease in processing batteries owing to their self-supporting properties. Thus some groups have used gel type electrolytes based chiefly on poly (acrylonitrile) PAN, PMMA and PVdF [6-19]. A large number of studies have been carried out on polymer electrolytes based on PAN containing the alkali metal salts. These materials have a major drawback that the ionic conductivity of $10^{-4}$ S/cm, which is necessary for high power applications, can only be reached at about 100°C. In this respect, most of the research work have been directed to the synthesis and characterisation of new polymer electrolytes based on PAN that exhibit higher ionic conductivity at ambient temperature via various approaches such as using blends [20, 21], copolymers [22], comb branch polymers [23] and crosslinked networks [24, 25]. All these enhancement have been achieved either by reducing the crystallinity of polymers or by lowering the glass transition temperature. The pioneering work of Armand [26] and others [27, 28] led to the development of polymer based electrolyte for battery applications. Reich and Michalei [29] have examined the
conductivity of systems formed by adding LiClO₄ to PAN. Watanabe et al. [8] added PC and EC as plasticizers and solvents to LiClO₄ complexes of PAN and measured the effect on the conductivity by immobilizing a solution of PC and EC containing LiClO₄ in PAN. 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. In the present study polymer films consisting of PAN, LiClO₄, PC and EC have been prepared to overcome the problems inherent to PAN by varying the ratio of plasticizers. This chapter reports the structure and phase behaviour of these complexes investigated by means of x-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Thermal analysis (DTA/TG) and Scanning Electron Microscopy (SEM).

4.1.2. EXPERIMENTAL

PAN, PC, LiClO₄ were used as received from Aldrich and EC received from Merck, Germany was used without further purification for the preparation of films. Appropriate quantities of PC, EC and LiClO₄ were dissolved in dimethylformamide (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 a 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 usually 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 spectrometer. The differential thermal analysis (DTA) was carried out using a Thermal Analysis Systems of thermal analyzer model STA 1500 PL. The films were examined using Scanning Electron microscope (SEM). The bulk electrical conductivities of the polymer complexes were evaluated from the impedance plots in the temperature range 301-373K using Keithley 3330 LCZ meter. The polymer film was sandwiched between stainless steel electrodes for conductivity studies.

4.1.3. RESULTS AND DISCUSSION

4.1.3.1. X-ray diffraction studies

X-ray diffraction (XRD) studies can provide a wide range of information on crystal structure, crystal orientation, crystallinity, crystallite size and phase changes of materials [30] including polymers, salts and complexes. Crystalline materials are characterized by sharp diffraction rings or peaks. For amorphous materials, there is no long-range order present, however the non-crystalline samples are characterized by one or two broad "halos", which are not sufficient to give significant information about the position of each atom / molecule. For the present case, the x-ray diffraction method has been used only in a limited perspective to identify or confirm the following,

(i) amorphous, crystalline or semicrystalline nature of the material

(ii) complex formation

(iii) relative amorphicity of the composite film

It is seen that pure PAN exhibits low crystalline phase. The XRD patterns are reproducible for all the compositions.
X-ray diffraction (XRD) patterns of the pure PAN, LiClO₄ and complexed PAN are represented in fig.4.1.1 (a-f) respectively. The patterns of pure PAN and complexed PAN indicate low crystalline and amorphous phases respectively. The degree of crystallinity was calculated for pure PAN and the polymer complexes. The degree of crystallinity of pure PAN is 2.15%. The polymer complex films (F1-F4) do not show any degree of crystallinity. It is found that the degree of crystallinity of the complexes gets reduced after the addition of LiClO₄, PC and EC and indicates that no free salts are available in the complex. The maximum value of conductivity $3.377 \times 10^{-3}$ S/cm is obtained for the film (F4) in accordance with the completely amorphous phase of the film when compared to other films.

4.1.3.2. FTIR spectroscopic studies

FTIR spectroscopy is important for the investigation of polymer structure. FTIR spectra of these materials vary according to their compositions and may be able to show the occurrence of complexation [31-36] and interactions between the various constituents. In the present work, FTIR spectroscopy is used to establish interaction(s) between the polymer (PAN), salt (LiClO₄) and plasticizer (PC and EC). Such interaction(s) can induce changes in the vibrational modes of the atoms or molecules in the material.

FTIR plots of pure PAN, PC, EC and LiClO₄ and polymer electrolyte complexes are shown in fig.4.1.2 (a – h). CH- stretching frequency of PAN appearing at 2940 cm⁻¹ gets shifted to 2939, 2938 cm⁻¹ in the polymer complexes. The band at 2243 cm⁻¹ in PAN is assigned to C≡N stretching vibration. The C≡N stretching vibration of the nitrile group
does not undergo any shift, which implies that this bond length is not altered. Nyquist [37] has observed that C=N frequency shifts in solvents only up to $5 \text{cm}^{-1}$, even if the acceptor number is changed from 0 to 41 like DMSO. Hence the interaction with plasticizer is not exhibited. However, the intensity of the band undergoes modification on complexation. C-N stretching frequency appearing in the pure PAN at $1251 \text{ cm}^{-1}$ is shifted to $1256 \text{ cm}^{-1}$ in the complex. The band at $1790 \text{ cm}^{-1}$ in PC is assigned to C=O stretching frequency. C-C stretching vibration of PAN ($1074 \text{ cm}^{-1}$) is shifted to $1064 \text{ cm}^{-1}$ in the polymer electrolyte complex. The CH$_2$- in-plane vibration for PC occurs at $2927 \text{ cm}^{-1}$ and for EC at $2932 \text{ cm}^{-1}$. In complexes, F1, F2 and F4, it shifts to higher frequencies at $2937 \text{ cm}^{-1}$, whereas no shift is observed in complex F3. Nyquist and Settineri [38] assigned $\nu_{\text{C=O}}$, in the region $1810 \text{ cm}^{-1}$ in ethylene carbonate. In our samples of thin films, it occurs at $1801 \text{ cm}^{-1}$. The Skeletal breathing mode for ethylene carbonate was observed at $897 \text{ cm}^{-1}$ in the liquid phase by Angell [39]. Its location is dependent on the physical state of the sample. One of the significant bands occurring in the $\nu_{\text{C=O}}$ region, is due to the Fermi resonance of the skeletal breathing (i.e) around $1788 \text{ cm}^{-1}$. In our studies, it occurs at $1774 \text{ cm}^{-1}$. On complexation, this skeletal breathing Fermi resonance frequency shows an upward shift, on increasing the reaction field around the sample, whereas, the increase of the reaction field around, results in a downward shift of $\nu_{\text{C=O}}$ fundamental frequency. Hence, the downward shift of $\nu_{\text{C=O}}$ of the carbonate to $1789 \text{ cm}^{-1}$ indicates the interaction of the plasticizer with LiClO$_4$ on complexation. The presence of $1789 \text{ cm}^{-1}$ is an indication of the formation of chloro carbonates [40]. The intensity of this band increases with increase in the strength of the complex. The intensity is largest in F3 and F4.
The band at 1962 cm$^{-1}$ is characteristic of ethylene carbonate and it shifts to higher frequencies in the complexes in the order: F4 > F3 > F2 > F1; which shows approximately, the strength of interaction of the plasticizer in the four complexes studied.

The 1556 cm$^{-1}$ band which is characteristic of the COO$^-$, is fairly stable in all the four complexes, with varying intensities. The rocking mode of the CH$_2$ group in ethylene carbonate is split into 777 cm$^{-1}$ and 712 cm$^{-1}$, which shows that EC is in a crystalline state in thin films. However, introduction of LiClO$_4$ makes it non-crystalline as, only one frequency is found in complexes F1, F2, F3. A feeble presence of splitting is noticed in complex F4. It is all well known that the conductivity is larger in non-crystalline systems. Significantly, a new band at 902 cm$^{-1}$ appears in complex F4, which is absent in other complexes, showing the complexity of this system. The band at 849 cm$^{-1}$, characteristic of EC, shifts on complexation to higher frequencies.

In addition to this, the following bands 3834, 1732, 1714, 1514 cm$^{-1}$ of PAN, 3564, 3561, 2992, 1556, 1484, 1455, 1360, 1046, 851, 778, 719 cm$^{-1}$ of PC, 2492, 2327, 2320, 2324, 1970, 1969, 1966, 1769, 1551, 1486, 1393, 975, 894, 719 cm$^{-1}$ of EC are slightly shifted in the polymer complexes. Vibrational bands 2878 cm$^{-1}$ of PAN, 1610, 920, 750 cm$^{-1}$ of LiClO$_4$, 2306, 1188, 956, 536 cm$^{-1}$ of PC, 4161, 2775, 2702, 2659, 2550, 2046, 1801, 1163, 1073 cm$^{-1}$ of EC are found to be absent in the complexes. Further some new peaks 4399, 4098, 4034, 3897, 3756, 3654, 3626, 3584, 2816, 2518, 2517, 2358, 1972, 1694, 1682, 1644, 1634, 1567, 1564, 1462, 1416, 933, 865, 624 cm$^{-1}$ are observed in the polymer complexes. From the above analysis the complexation of PAN with LiClO$_4$, PC and EC has been confirmed.
4.1.3.3. SEM studies

SEM micrographs of PAN-LiClO$_4$-PC-EC system in fig.4.1.3 (a, b) reveal the amorphous phase showing no spherulite structure due to crystalline phase. The white portion shows conducting channels. When the magnification is 2000, the appearance of the polymer electrolyte film resembles with that of Tumor. When the magnification is reduced to 500, the surface morphology leads to tumor cells.

4.1.3.4. Thermal Studies

TG and DTA curves of PAN-LiClO$_4$-PC-EC polymer complexes of different compositions are shown in fig.4.1.4. (a - d). The DTA curve shows no clear melting of the polymer till 230°C and an endothermic peak appears at 230.4°C which may be due to the eutectic transition taking place. The accompanied weight loss indicates the decomposition of the polymer and thermal stability of the polymer film (F1) up to 280°C. The first, second and third decomposition ranges may lie in between 50-80, 140-170 and 200-250°C respectively. The corresponding percent weight losses at 100, 200 and 300°C were noticed to be 0.6, 3.1 and 7% respectively.

DTA and TG analysis of polymer complex (F2) is shown in fig.4.1.4. (b). In the DTA curve a sharp endothermic peak at 56.39°C indicating the melting of the polymer film is observed. The small exothermic peaks at 262.14°C and 281.39°C without appreciable weight loss indicate the pre-decomposition of the polymer and a clear larger exothermic peak at 363.62°C indicates the final decomposition confirmed by the simultaneous weight loss. From this, it is found that the film is thermally stable up to 260°C. The initial weight loss as in the TG curve up to 60°C may be due to the result of
adsorbed moisture and impurities in the polymer electrolyte thin film. From TG curve it can also be seen that the first decomposition occurs in between 60-80°C, second and third decompositions of the polymer film take place in between 300-330 and above 330°C respectively. The weight losses were 9.6, 10 and 11.1% at various temperatures of 100, 200 and 300°C respectively.

The TG and DTA curves of the film F3 are shown in fig.4.1.4. (a). From the DTA curve the melting of the polymer takes place at 50.33°C as indicated by an endothermic peak. The larger exothermic peak at 277.89°C confirms the decomposition of the polymer film along with the loss of weight of the material. Till 240°C, the polymer behaves thermally stable. The weight loss upto 55°C shown by the TG curve may be due to the melting of the polymer. The first, second and third decomposition of the polymer were noticed to be in between 60-100, 240-280 and 300-350°C respectively and the corresponding weight losses were 6.2, 6.8 and 9% at various temperatures of 100, 200 and 300°C respectively.

TG/DTA curves of the polymer film F4 are shown in fig.4.1.4. (b). The DTA curve of the polymer clearly indicates that the polymer film is thermally stable upto 240°C as there are no peaks in the range. The exothermic peak observed at 268.31°C is attributed to the eutectic transition of the polymer and an exothermic peak observed at 308.88°C accompanied by an appreciable weight loss of the material confirms the decomposition of the polymer film. The first, second and third decomposition of the polymer electrolyte take place in between 200-250, 270-300 and 300-350°C respectively, and the corresponding weight losses were 2.2, 2.6 and 3.4% at various temperatures of 100, 200 and 300°C respectively.
The conductivity of the film F4 is found to be $3.377 \times 10^{-3} \text{S/cm}$ at room temperature which is higher than the values obtained for other films (F1-F3). Film F4 is thermally stable up to a temperature of 240°C. The weight losses for the film F4 (Table 4.1.1) are estimated as 2.6 and 3.4% at 200 and 300°C respectively which are found to be minimum among the weight losses calculated for other films. Hence it is concluded that film F4 is superior among the four films.

4.1.3.5. Conductivity studies

Fig (4.1.5) shows the complex impedance diagram of the polymer electrolyte PAN-LiClO$_4$-PC-EC at 301K. In the impedance response behaviour, the disappearance of the high frequency semicircular portion in the complex impedance plot led to a conclusion that current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction. At low frequency the complex impedance plot must show a straight line parallel to the imaginary axis but the double layer at the blocking electrodes causes the curvature [41]. Electrical conductivity measurements have been carried out by employing complex ac impedance technique. The polymer electrolyte films are sandwiched between two stainless steel (SS) electrodes attached to the conductivity jig specially designed and fabricated for the present study whose fabrication details are described elsewhere in chapter III.

The ionic conductivities of PAN-LiClO$_4$-PC-EC electrolyte thin films containing various compositions of PC and EC are found in the temperature range 301 – 373K and are tabulated in Table (4.1.2). As can be seen from Table (4.1.2) that the increasing EC and decreasing PC as plasticizer in PAN-LiClO$_4$ system favours the enhancement in ionic
conductivity. Accordingly the composition of 26% of PC and 45% of EC in PAN-LiClO₄ gives the conductivity of 6.523x10⁻³ S/cm at 373K which is indeed a high conductivity value achieved hitherto for PAN-LiClO₄ polymer electrolyte. In order to examine the temperature dependence of conductivity of the PAN-LiClO₄-PC-EC polymer electrolyte system, the temperature dependent ionic conductivity measurements have been carried out. Fig. 4.1.6 depicts the Arrhenius plots of conductivity of PAN-LiClO₄-PC-EC polymer electrolyte in the form of thin films and it seems to obey the VTF relation. The completely amorphous nature of the present polymer electrolytes facilitate the fast Li-ion motion in the polymer network and it further provides a higher free volume upon increasing the temperature. The overall conductivity effect upon adding the plasticizer in PAN-LiClO₄ may be explained as follows. It seems likely that intramolecular co-ordinations are more effective in PAN-LiClO₄ electrolyte leading to a greater dissociation.

The ionic mobility in the plasticized networks is determined mainly by the plasticizer. However, it has been taken into account that a contribution for the ionic conduction is possible assuming a certain degree of segmental motion.

The effect of the plasticizers on the polymer mobility and conductivity depends on the specific nature of the plasticizer including viscosity, dielectric constant, polymer-plasticizer interaction, and ion-plasticizer coordination. The effect of the plasticizers on the conformation and mobility of the host polymer depends on the plasticizer structure and the molecular weight, which influence the degree of mixing and the polymer-polymer or polymer-plasticizer interactions. EC is a solid material at room temperature
with a molecular weight of 88.05. The molecular weight of PC is 102.09 and at room temperature it is a viscous liquid.

In practice, anion solvation usually occurs via hydrogen bonds, but polymers in which a fraction of the hydrogen atoms bears a net positive charge, e.g. when attached directly to an electronegative element, show extensive chain to chain interactions. These interactions result in high cohesive energy, and therefore such polymers are quite unfavourable media for diffusion in the absence of a protic, high dielectric constant plasticizer. In comparison with the other plasticizers, the dielectric constants of EC and PC are rather high, with values 95.3 and 64.4 respectively at 25°C.

The conductivity values of PAN(20)-LiClO₄(9)-PC(26)-EC(45) electrolyte system presented in this work is estimated as 3.377x10⁻³ S/cm at 301K. This value is found to be higher than the value 2.0x10⁻³ S/cm reported by Croce et al. [42] for PAN(16)-PC(23)-EC(56.5)-LiN(CF₃SO₂)₂(4.5) at ambient temperature. It is noticed that as the temperature increases the conductivity values also increase. This behaviour can be rationalized by recognizing the free volume model [43]. As the temperature increases, the polymer can expand easily and produce free volume. Thus ions, solvated molecules, or polymer segments can more into free volume [44]. 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 inverse in ion mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds.
Table 4.1.1.

TG/DTA results in PAN-LiClO₄-PC-EC polymer complexes

<table>
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<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>
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<td>First</td>
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<td>F1</td>
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<td>(20-9-35-36)</td>
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<td>F2</td>
<td>60-80</td>
<td>300-330</td>
<td>above 330</td>
<td>9.6</td>
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<td>60-100</td>
<td>240-280</td>
<td>300-350</td>
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<td>F4</td>
<td>200-250</td>
<td>270-300</td>
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<td>(20-9-26-45)</td>
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<td>Sample</td>
<td>Composition</td>
<td>Conductivity values of PAN-LiClO$_4$-PC-EC $\times 10^{-3}$ S/cm</td>
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<td>301K</td>
<td>328K</td>
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Fig 4.1.1. XRD patterns for PAN, LiClO$_4$ and the polymer complexes
(a) pure PAN, (b) LiClO$_4$, (c) PAN-LiClO$_4$-PC-EC (20-9-35-36),
(d) PAN-LiClO$_4$-PC-EC (20-9-32-39), (e) PAN-LiClO$_4$-PC-EC (20-9-29-42).
(f) PAN-LiClO$_4$-PC-EC (20-9-26-45)
Fig 4.12 FTIR plots for PAN, LiClO₄, PC, EC and the complexes
(a) pure PAN, (b) pure LiClO₄, (c) pure PC, (d) pure EC,
(e) PAN-LiClO₄-PC-EC (20-9-35-36), (f) PAN-LiClO₄-PC-EC (20-9-32-39),
(g) PAN-LiClO₄-PC-EC (20-9-29-42), (h) PAN-LiClO₄-PC-EC (20-9-26-45)
Fig. 4.1.3. SEM micrographs for PAN-LiClO₄-PC-EC polymer complex with two different magnifications (a) x2000, (b) x500
Fig 4.1.4. DTA and TGA scans of polymer complexes
(a) PAN-LiClO₄-PC-EC (20-9-35-36), (b) PAN-LiClO₄-PC-EC (20-9-32-39),
(c) PAN-LiClO₄-PC-EC (20-9-29-42), (d) PAN-LiClO₄-PC-EC (20-9-26-45)
Fig. 4.1.5. Typical complex impedance plots of PAN-LiClO₄-PC-EC system.
Fig. (4.1.6). Arrhenius plot of conductivity against reciprocal temperature for
(a) PAN(20)-LiClO₄(9)-PC(35)-EC(36)
(b) PAN(20)-LiClO₄(9)-PC(32)-EC(39)
(c) PAN(20)-LiClO₄(9)-PC(29)-EC(42)
(d) PAN(20)-LiClO₄(9)-PC(26)-EC(45)
4.1.4. REFERENCES


PART II
STRUCTURAL, THERMAL AND CONDUCTIVITY STUDIES OF
POLY (ACRYLONITRILE) COMPLEXED WITH LiCF_3SO_3

ABSTRACT

Solid polymer electrolytes of high ionic conductivity are prepared using polyacrylonitrile (PAN), propylene carbonate (PC), ethylene carbonate (EC) and LiCF_3SO_3. The polymer films are characterized by x-ray diffraction, FTIR, SEM, thermal and ac impedance spectroscopic techniques. The conductivity studies of PAN-LiCF_3SO_3-PC-EC polymer electrolyte systems are carried out in the temperature range 301-373K. The temperature dependence conductivity of the polymer films seems to obey the VTF relation. The conductivity values are presented and the results are discussed.

4.2.1. INTRODUCTION

The mechanisms governing ionic transport through a macromolecular polar solvent are considerably different as compared to the case in liquid organic or aqueous electrolytes where solvent molecules are macroscopically mobile and typically form solvation sheaths that surround solvated ion [1]. Investigations of ionically conducting polymer-salt complexes are primarily motivated by a great potential for a range of electrochemical applications including all-solid state thin-film batteries [2,3].

Solvent-free solid polymeric electrolytes are under active investigations because of their potential application in high energy storage devices [4-11]. A large number of studies have been carried out on the solid state batteries utilizing the gel polymer
electrolytes in which the liquid electrolyte solution has been immobilized by incorporating into a polymer matrix such as poly acrylonitrile [12-14].

The attractive mechanical and electrical properties ($\sigma \approx 10^{-4}-10^{-3}\text{ S/cm}$) at 100°C of poly ether complexes resulted in further investigation on ionically conducting polymers [15-22]. However their application to solid state batteries has not been fully documented. There are only a few instances on the use of these polymer electrolytes in practical demonstration cells [23-26].

In an attempt to look for good lithium ion conducting polymer electrolyte, new plasticized polymer electrolyte composed of PAN as the host polymer PC, EC as plasticizer and LiCF$_3$SO$_3$ as a salt has been studied. Ionic conductivity of these electrolytes at ambient temperature is of the order of $10^{-3}\text{ S/cm}$ and is comparable with the values reported for similar systems [27-29].

4.2.2. EXPERIMENTAL

PAN, LiCF$_3$SO$_3$, PC were purchased from Aldrich, USA and EC received from E-Merck, Germany was used without further purification for the preparation of polymer films. Appropriate quantities of PC and 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 a teflon covered glass plate and allowing DMF to evaporate slowly. Finally the film was dried at 70°C under vacuum for about 4 hrs. 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
4.2.3. RESULTS AND DISCUSSION

4.2.3.1. X-ray diffraction studies

XRD patterns of pure PAN, LiCF₃SO₃ and polymer electrolyte complexes are shown in fig (4.2.1). The diffraction peaks indicate the crystalline phase of LiCF₃SO₃ (fig 4.2.1.b). It is found that the polymer electrolyte systems PAN- LiCF₃SO₃-PC-EC remain in the amorphous phase even after LiCF₃SO₃ is added. The peaks corresponding to LiCF₃SO₃ are found absent in the polymer complexes. This indicates that the complexation has taken place in the amorphous phase and no free salt is present in the complex phase.

The degree of crystallinity for pure PAN and LiCF₃SO₃ is estimated as 2.15 and 7.19% respectively. The polymer complex films (F5-F8) do not show any degree of crystallinity. After the addition of LiCF₃SO₃, PC and EC, the degree of crystallinity gets reduced. The maximum value of conductivity (3.073x10⁻³ S/cm) is obtained for the film F8 at room temperature which is indeed a high value component compared to other compositions. Our value is found to be higher than the values 1.5x10⁻³ S/cm reported by Ferry et al. [27] for PAN-LiCF₃SO₃ system at 368K. This may be due to the addition of plasticizers (PC, EC).
4.2.3.2. FTIR spectroscopic studies

The FTIR spectrum of a thin film of polymer electrolyte is shown in fig (4.2.2). The peaks were assigned by comparing this spectrum with the spectra of individual components of the polymer electrolyte, which are reported in the literature [30-32]. In this system also, the C=N stretching frequency at 2244 cm\(^{-1}\) is fairly stable on complexation, but a slight shift in complex F5 is noticed. The intensity change is also large in F5. C-C stretching frequency of PAN (1251 cm\(^{-1}\)), C-O stretching frequency of PC (1119 cm\(^{-1}\)) are found absent in the polymer complex. The characteristic 1962 cm\(^{-1}\) band of EC, shifts to higher frequencies in all the four complexes and from the intensities of the bands, it appears that all the four complexes are of equal strength. In addition to this, the following vibrational bands (3878, 3830, 3813, 3776, 3718, 3742, 3699, 3686, 3626, 3542, 2941, 1766, 1727, 1710, 1659, 1652, 1632, 1548, 1560, 1531, 1514, 1494, 1358, 1074, 540, 411 cm\(^{-1}\)) of PAN, (3564, 2360, 1269, 1184, 1038, 767, 646, 580, 520 cm\(^{-1}\)) of LiCF\(_3\)SO\(_3\), (4161, 3566, 2997, 2932, 2775, 2702, 2659, 2550, 2488, 2329, 2049, 1942, 1801, 1774, 1551, 1482, 1393, 1163, 1072, 973, 894, 774, 717, 527 cm\(^{-1}\)) of EC and (3663, 2989, 2925, 2306, 1790, 1556, 1485, 1454, 1389, 1354, 1188, 1052, 956, 849, 777, 712, 537 cm\(^{-1}\)) of PC are absent in the polymer complexes. 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 [33]. The following bands appearing at 3854, 3651, 3645, 3642, 2240 and 1682 cm\(^{-1}\) in PAN are slightly shifted in the polymer complexes. Further some new peaks at 4402, 4400, 4279, 4036, 4028, 3651, 3645, 3016, 2519, 2319, 1970, 1968 cm\(^{-1}\) are observed in the polymer complex. From the above analysis, the complexation of PAN with LiCF\(_3\)SO\(_3\) has been confirmed.
4.2.3.3. **SEM studies**

The electron micrographs of PAN-LiCF₃SO₃-PC-EC complex for two different magnifications (x500, x2000) are shown in fig (4.2.3). It is found that the film is compact. However, it shows heterogeneous distribution. The SEM photographs reveal the amorphous phase and the surface morphology resembles with the skin of shark showing placoidscales. As the magnification is decreased to 500 (fig.4.2.3.a), it exhibits the same morphology.

4.2.3.4. **Thermal studies**

DTA and TG curves of PAN-LiCF₃SO₃-PC-EC system are shown in fig (4.2.4). The DTA curve shows two exothermic peaks at 226.85°C and 257.62°C(fig 4.2.4.a). The peak at 226.85°C may be attributed to the initial decomposition of the polymer electrolyte and the peak at 257.62°C may be attributed to the final decomposition of the polymer film without much appreciable weight loss. This indicates that the PAN-LiCF₃SO₃-PC-EC system is thermally stable upto 250°C. The initial weight loss upto 100°C may be due to the adsorbed moisture and any other volatile impurities present in the polymer complex. The first, second and third decomposition of the film take place in between 50-100, 220-250 and above 300°C respectively and the corresponding weight losses were 9, 9.8 and 12.2% (Table.4.2.1.) at various temperatures of 100, 200 and 300°C respectively.

TG and DTA curves of PAN-LiCF₃SO₃-PC-EC (14:8:39:39) polymer complex are shown in fig (4.2.4.b). The peak at 236.49°C may be attributed to the initial
decomposition of the polymer and the peak at 257.28°C is attributed to the final decomposition of the polymer without much appreciable weight loss. The first, second and third decomposition of the polymer film take place in between 100-150, 200-250 and above 300°C respectively and the corresponding weight losses were 5.2, 6.5 and 8.6% at various temperatures of 100, 200 and 300°C respectively.

TG and DTA curves of PAN-LiCF₃SO₃-PC-EC (13.5:11.5:37.5:37.5) polymer complex are shown in fig (4.2.4 c). DTA curve shows a larger exothermic peak at 264.35°C which may be due to the initial decomposition of the polymer. From the TG curve, it is observed that the thermal stability of the polymer film extends up to 270°C. The initial weight loss up to 100°C may be due to moisture and other impurities present in the polymer film. The first, second and third decomposition of the film take place in between 70-110, 270-300 and above 300°C respectively and the relative weight losses were 15, 17.8 and 20% at various temperatures of 100, 200 and 300°C respectively.

From the DTA curve (fig. 4.2.4 d), it can be seen a large exothermic peak at 257.1°C which may be attributed to the initial decomposition of the polymer. The thermal stability of the polymer film may extend (F8) up to 240°C. As in the previous case, the same trend of the TG curve was noticed. The initial weight loss up to 100°C may be due to moisture and other impurities present in the film. The first, second and third decomposition of the film take place in between 60-100, 170-220 and above 300°C respectively and the corresponding weight losses were 9.4, 11.2 and 13.2% at various temperatures of 100, 200 and 300°C respectively.

Thermal stability is found to be maximum (~270°C) for the film F7 (Table 4.2.1). However, conductivity value at room temperature is estimated as 2.774×10⁻³ S/cm for the
film F7. Conductivity is found to be maximum $3.073 \times 10^{-3} \text{S/cm}$ for the film F8 and the film is thermally stable up to a temperature of 240°C. From TGA graph, the weight losses are found to be minimum for the film F6. Film F8 is found to be superior compared to other films on the basis of conductivity.

4.2.3.5. Conductivity studies

Fig (4.2.5) shows the complex impedance diagram of PAN- LiCF$_3$SO$_3$-PC-EC system at 301 K. In the impedance response behaviour, the disappearance of the high frequency semicircular portion in the complex impedance plot led to a conclusion that current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction [34]. At low frequency the complex impedance plot must show a straight line parallel to the imaginary axis but the double layer at the blocking electrode causes the curvature [35]. The intercept on the real axis gives the electrolyte bulk resistance. The conductivity of the polymer electrolyte was calculated from the measured resistance for the known area and thickness of the polymer film. The ionic conductivities of polymer electrolyte films containing various compositions of plasticizers are obtained in the temperature range 301-373 K and are given in Table 4.2.2. It can be seen that the conductivities at 301 K for all the electrolytes are greater than $1 \times 10^{-3} \text{S/cm}$. It is found that the conductivity value of PAN- LiCF$_3$SO$_3$-PC-EC (F8) at 301 K is $3.073 \times 10^{-3} \text{S/cm}$ (Table 4.2.2) which is indeed a high value component compared to other compositions. Our value is found to be higher than the values $1.5 \times 10^{-4} \text{S/cm}$ reported by Ferry et al. [27] for PAN-LiCF$_3$SO$_3$ system at 368 K. This may be due to the addition of plasticizers (PC, EC).
Fig (4.2.6.) represents the Arrhenius plot of the ionic conductivity for polymer electrolytes with various compositions of PAN, LiCF₃SO₃, PC and EC. The overall features of the Arrhenius plot were quite similar for the polymer films. The curvatures shown in this plot indicate that the ionic conduction obeys the VTF relation, which describes the transport properties in a viscous matrix. It supports the idea that the ion moves through the plasticizer-rich phase. Because the conducting medium, i.e., plasticizer-rich phase, involves the plasticizer, the salt and PAN, the characteristics of the viscous matrix are brought out. It is noted that as the temperature increases the conductivity values also increase and this behaviour is in agreement with theory [30]. Thus in the present study the benefit from the conductivity point of view the composition of PAN-LiCF₃SO₃-PC-EC (F8) favours the conductivity enhancement. It is noticed that the highest room temperature conductivity is found for the polymer membrane rich in EC (F8). This may be due to higher value of dielectric constant (89.6) of EC compared to the dielectric constant (64.4) of PC. The lower viscosity of EC may also be partially responsible for the enhancement in conductivity. This is in agreement with the findings of Appetecchi et al. [36] for PEO based electrolyte systems. The plasticizing effect of EC on PAN is greater than that of PC. The higher the plasticizing effect, the lower the microscopic viscosity for carrier migration.
Table 4.2.1.

TG/DTA results in PAN-LiCF$_3$SO$_3$-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>
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<tbody>
<tr>
<td></td>
<td>First</td>
<td>Second</td>
<td>Third</td>
<td>100</td>
</tr>
<tr>
<td>F5</td>
<td>50-100</td>
<td>220-250</td>
<td>above 300</td>
<td>9</td>
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<tr>
<td>(14.2-7.2-39.3-39.3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F6</td>
<td>100-150</td>
<td>200-250</td>
<td>above 300</td>
<td>5.2</td>
</tr>
<tr>
<td>(14-8-39-39)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F7</td>
<td>70-110</td>
<td>270-300</td>
<td>above 300</td>
<td>15</td>
</tr>
<tr>
<td>(13.5-11.5-37.5-37.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F8</td>
<td>60-100</td>
<td>170-220</td>
<td>above 300</td>
<td>9.4</td>
</tr>
<tr>
<td>(13-13-14.8-59.2)</td>
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</table>
Table 4.2.2.
Conductivity values of PAN-LiCF₃SO₃-PC-EC polymer electrolytes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Conductivity values of PAN-LiCF₃SO₃-PC-EC x10⁻³ S/cm</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>301K</td>
</tr>
<tr>
<td>F7</td>
<td>(13.5-11.5-37.5-37.5)</td>
<td>2.774</td>
</tr>
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</table>
Fig 4.2.1. XRD patterns for PAN, LiCF$_3$SO$_3$, and the polymer complexes  
(a) pure PAN, (b) LiCF$_3$SO$_3$, (c) PAN-LiCF$_3$SO$_3$-PC-EC (14:2.7:2:39:3:9.3).  
(d) PAN- LiCF$_3$SO$_3$-PC-EC (14-8:39-3), (e) PAN- LiCF$_3$SO$_3$-PC-EC (13.5- 
11.5:37.5:37.5), (f) PAN- LiCF$_3$SO$_3$-PC-EC (13-13:14.8:59.2)
Fig. 4.2.2. FTIR plots for PAN, LiCF$_3$SO$_3$, PC, EC and the complexes
(a) pure PAN, (b) pure LiCF$_3$SO$_3$, (c) pure PC, (d) pure EC,
(e) PAN-LiCF$_3$SO$_3$-PC-EC (14.2-7.2-39.3-39.3),
(f) PAN-LiCF$_3$SO$_3$-PC-EC (14.8-39.3-39.3), (g) PAN-LiCF$_3$SO$_3$-PC-EC (13.5-
11.5-37.5-37.5), (h) PAN-LiCF$_3$SO$_3$-PC-EC (13.13-14.8-59.2)
Fig. 4.2.3. SEM micrographs for PAN-LiCF₃SO₃-PC-EC polymer complex with two different magnifications (a) x2000, (b) x500
Fig 4.2.4. DTA and TGA scans of polymer complexes
(a) PAN-LiCF$_3$SO$_3$-PC-EC (14.2-7.2-39.3-39.3)
(b) PAN- LiCF$_3$SO$_3$-PC-EC (14-8-39-39)
(c) PAN- LiCF$_3$SO$_3$-PC-EC (13.5-11.5-37.5-37.5)
(d) PAN- LiCF$_3$SO$_3$-PC-EC (13-13-14.8-59.2)
Fig. 4.2.5. Typical complex impedance plots of PAN-LiCF$_3$SO$_3$-PC-EC system.
Fig.(4.2.6). Arrhenius plot of conductivity against reciprocal temperature for
(a) PAN(14.2)-LiCF$_3$SO$_3$(7.2)-PC(39.3)-EC(39.3)
(b) PAN(14)-LiCF$_3$SO$_3$(8)-PC(39)-EC(39)
(c) PAN(13.5)-LiCF$_3$SO$_3$(11.5)-PC(37.5)-EC(37.5)
(d) PAN(13)-LiCF$_3$SO$_3$(13)-PC(14.8)-EC(59.2)
4.2.4. REFERENCES


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