CHAPTER VII

ROLE OF DIFFERENT PLASTICIZERS ON PAN/PMMA BASED POLYMER BLEND ELECTROLYTES

7.1. Introduction

Active research in the field of polymer electrolytes is due to its applicability in various fields [1] due to its diverse properties it possesses. The use of polymer for battery application dates back 1975 by Wright [2] and followed by others.

Gel electrolytes have attained precedence over conventional polymer electrolytes due to its unique hybrid network structure. It possesses simultaneously both the diffusive transport properties of liquid electrolyte and cohesive properties of solid electrolyte. In recent years, few reported gel electrolytes are polymer network of polymethyl methacrylate (PMMA), polyacrylonitrile (PAN), polyvinylidene fluoride (PVdF) and polyethylene oxide (PEO) [3]. The properties of the polymer electrolytes can also be improved by blending these polymers. Blending of two polymers is easy preparation and easy control of their physical properties within the compositional regime. Many blend electrolytes have been reported based on PEO-PAN [4], P(VdF-HFP)-PVAc [5], PVC-PMMA [6] and so on. Among them, PAN-PMMA not only has excellent miscibility with organic liquid to form gel polymer electrolyte (GPE) but is also a very stable binder for both anode and cathode of Li-ion batteries [7-9].
Implementation of polymer electrolytes in commercial batteries requires an increase in ionic transportation at ambient temperature. The increase in ionic conductivity of polymer electrolytes is connected with the changes of the phase structure of the polymeric materials. Berthier et.al [10] established that the ionic conductivity in polymer electrolytes is associated with the amorphous phase of the studied samples. Attempts have been made to attain the amorphous phase of polymer electrolytes and it has been achieved either by reducing the crystallinity or by lowering the glass transition temperature. So in each approach, which is used for enhancement of conductivity at ambient temperature, the initial step is to increase the amorphous content in polymer electrolytes. Adding plasticizers is a common approach among the several strategies to enhance the amorphous phase and thus the ionic conductivity value [11]. The plasticizers used for these are low-molecular-weight aprotic solvents having high dielectric constant ($\varepsilon$) such as propylene carbonate ($\varepsilon=64.4$) and ethylene carbonate ($\varepsilon=89.6$) [12-15]. In plasticized polymer electrolytes, the role of host polymer is secondary in the conducting matrix. The salt-solvating power and sufficient mobility of ion necessary for ionic conduction are provided by the imparted plasticizer [16].

The solvents used should have low freezing point and high boiling point, so that it can be used over wide temperature regions. The low viscosity of plasticizer helps to increase the mobility of carriers and the low melting temperature of plasticizer results in an increase in the amorphous content of plasticized polymer electrolytes, while the higher dielectric constant of
plasticizer as compared to polymer helps in the dissociation of ion aggregates. On the other hand if the dielectric constant of the plasticizer is less than that of the polymer, then it may not help in ion dissociation and as a result the conductivity may not show an increase. The decrease in $T_g$ results in an increase in local chain flexibility and hence conductivity value.

The present work aims to investigate the effect of different plasticizers, viz EC, DMC, DEC, GBL and PC on the conductivity of the polymer blend PAN/PMMA(18 wt. %/6 wt. %)– LiClO$_4$ (8 wt. %).

7.2. Experimental

The polymers poly (acrylonitrile) (PAN) (average molecular weight 94,000), poly (methyl methacrylate) (PMMA) (average molecular weight 120,000) and Lithium perchlorate (LiClO$_4$) were purchased from Aldrich chemicals, USA. The polymers PAN and PMMA were dried at 373 K under vacuum for 10 hours; LiClO$_4$ was annealed at 343 K under vacuum for 24 hours. PC, EC, DMC, DEC, GBL were used as received. All the samples were prepared by solution casting technique. Appropriate quantities of PAN, PMMA and LiClO$_4$ were dissolved in distilled Di-Methyl Formamide (DMF) (E-Merck, Germany) separately. The mixed polymer-salt solution was stirred with the addition of plasticizer for 48 hours at room temperature and at 60 °C until homogeneous slurry was obtained. Thus, the obtained slurry was cast onto a polished Teflon bushes and Teflon covered glass plates. The films were dried in a vacuum oven at 333 K. The resulting films were visually examined for
their dryness and free standing nature. Finally the prepared films were stored in a highly evacuated desicator.

The films thus obtained are subjected to XRD and FTIR spectroscopic studies to investigate the status of degree of crystallinity and the complexation behaviour of the polymer electrolytes. Thermal stability of polymer electrolyte samples is studied using thermogravimetry/differential thermal analysis (TG/DTA). Conductivity measurement is performed by impedance spectroscopy in the temperature range of 303-373K. Scanning Electron Microscope is used for micro structural studies.

7.3. Results and discussion

7.3.1 XRD studies

X-ray powder diffraction patterns of pure PAN, PMMA, LiClO₄ and the complexes PAN-PMMA-LiClO₄ with different plasticizers are shown in Fig. 1. The pure PAN has its characteristic peaks at angles 2θ = 16.43° and 29.24°. Out of which the peak at 16.43° is moderately sharp (diffused) and the other peak is less intense and appears as a broad hump in the higher angle side. This reveals that PAN is predominantly amorphous in nature. Since pure PMMA is in amorphous phase, no diffraction peak appears. All the complexes exhibited only the broader peak, which is the typical characteristic of amorphous materials. This may be due to the addition of plasticizers. The increase in the amorphous nature causes a reduction in the energy barrier to the segmental motion of the polymer electrolyte which in turn improves ionic conductivity.
The absence of strong crystalline peaks of LiClO$_4$ salt in the polymer complexes confirms the complete dissolution of LiClO$_4$ salt which reveals the complexation of the constituents.

7.3.2 FTIR analysis

FTIR spectra of pure PAN, PMMA, LiClO$_4$ and the complexes are presented in Fig.2. The vibrational bands at 2939, 1632, 1246 cm$^{-1}$ are assigned to CH$_2$ asymmetrical stretching, CH asymmetrical stretching, inplane symmetrical C-N stretching frequencies of pure PAN and the nitrile band, C≡N, assigned to stretching band in the FTIR spectrum appeared at 2249 cm$^{-1}$ is displaced towards the lower frequency around 2245 cm$^{-1}$ due to inductive effect created by the interaction between the nitrogen atoms in C≡N with Li$^+$ ion from the salt [17]. The vibrational frequencies at 2956, 1735, 1450, 1382, 1151, 981, 842, 754 cm$^{-1}$ are assigned to CH$_3$ stretching, C=O stretching, OCH$_3$ stretching, CH$_3$ symmetrical bending, CH$_2$ twisting, CH$_2$ wagging, C-O-C stretching, CH$_2$ rocking modes of PMMA respectively. The vibrational peaks at 1488, 1173, 1155, 774 cm$^{-1}$ of EC, 1450, 1280, 1100, 920 cm$^{-1}$ of DMC, 2049, 1649, 625 cm$^{-1}$ of DEC, 2035, 1462, 676 cm$^{-1}$ of GBL, 1486, 1340 cm$^{-1}$ of PC are shifted to (1485, 1192, 1133, 776), (1486, 1275, 1123, 910), (2032, 1665, 627), (2031, 1487, 669) and (1488, 1392) cm$^{-1}$ in the complexes respectively.

One of the significant bands in the $\nu_{c=0}$ region is due to Fermi resonance of skeletal breathing around 1788 cm$^{-1}$. This band shifts to 1776, 1774, 1775,
1782, 1786 cm\(^{-1}\) in the complexes D1, D2, D3, D4 and D5 respectively. These shifts indicate the interaction of the plasticizer with LiClO\(_4\) on complexation. The absorption band at 940 cm\(^{-1}\) is assigned to the perchlorate anion [18] and is shifted to around 932 cm\(^{-1}\) in all the polymer complexes. It is also found that some of the peaks appearing in the pure polymers, salt and plasticizers disappear in the complexes (ie) 1362, 1078, 541 cm\(^{-1}\) of PAN 2956, 2627, 1258, 485 cm\(^{-1}\) of PMMA and 2854, 1092 cm\(^{-1}\) of LiClO\(_4\) are absent in all the complexes. The peaks at 1866, 1554, 1071, 894 cm\(^{-1}\) in EC based complex, 1098, 580 in DMC based complex, 2700, 1210, 860, 795 cm\(^{-1}\) in DEC based complex, 535,495 cm\(^{-1}\) in GBL based complex and 2849, 1098, 1100, 580 cm\(^{-1}\) in PC based complex are absent. In addition to this, new peaks are observed at (2532, 670), (2517, 1800, 627), (2031, 1670), (2022, 1116), (2514, 628, 577) cm\(^{-1}\) in the complexes D1, D2, D3, D4 and D5 respectively. Thus the above analysis confirms the complex formation in the developed electrolytes.

7.3.3.1 Conductivity studies

Impedance spectroscopy is used to establish the conduction mechanism, observing the participation of the polymeric chain, mobility and carrier generation processes [19]. Typical Nyquist plot of the polymer–salt complexes with different plasticizers is shown in Fig.3. It is noted that the semicircle at high frequencies completely disappears in all the complexes indicating that only the resistive component of the polymer electrolyte prevails and the total conductivity is mainly the result of ion conduction [20]. The bulk resistance of
the electrolyte has been measured by extrapolating intercept of the plot on the real axis, which gives $R_b$ value. The ionic conductivity is calculated using the equation $\sigma = l/R_b A$, where $l$ is the thickness of the polymer electrolyte film and $A$ the surface area of the film.

The increase in conductivity is observed for all the complexes compared with unplasticized samples which were reported in earlier studies. The increase in conductivity value with the addition of same amount of different plasticizers (EC, PC, GBL, DEC, DMC) is in the following order: GBL<DEC<DMC< PC <EC. The conductivities of these electrolytes critically depend on the physical properties of the plasticizer such as its viscosity and dielectric constant. Plasticizers with high dielectric constant dissociate more salt by increasing the relative permittivity of the system while plasticizers with high viscosities impede the mobility of ions [21]. The plasticizers are also known to lower the $T_g$ of the polymer host thereby increasing the polymer chain mobility and to lower the crystallinity of some polymers. The maximum conductivity is obtained for the film containing EC, as EC is less viscous (1.90 cP) and also, the dielectric constant ($\varepsilon=85.1$) is greater than the dielectric constants of other plasticizers used. The combined effects of the possession of viscosity as well as dielectric constant are responsible for the increase in conductivity.

### 7.3.3.2 Temperature dependent ionic conductivity

Temperature-dependent ionic conductivity plots are shown in Fig. 4. It is observed that, as temperature increases, the conductivity increases for all the
compositions (Table 7.2). The behaviour of conductivity enhancement can be understood in terms of the free-volume model [22]. 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. The resulting conductivity, represented by the overall mobility of ions and the polymer, is determined by the free volume around the polymer chains. Therefore, as temperature increases, the free volume increases. This leads to an increase in ionic mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds. The temperature dependent ionic conductivity plots indicate that the ionic conduction in the polymer electrolyte system obeys the VTF (Vogel–Tamman–Fulcher) relation, which describes the transport properties in a viscous matrix [23-26]. It supports the idea that the ions move through the solvent rich phase, which is the conducting medium and inturn involves the plasticizer, salt and polymers.

7.3.4 TG/DTA analysis

TG/DTA is an effective tool to identify the thermal stability and the transition behaviour of the electrolyte material. TG/DTA analyses of polymer electrolytes containing EC, DMC, DEC, GBL, PC are given in Fig.5. All the films show a weight loss of 8 to 22% around 100 °C. This is mainly the result of the volatilization of monomers and oligomers adsorbed in the matrix which may be responsible for the initial weight loss [27-29].
From the TG data, it is observed that all the complexes under investigation degrade thermally through similar two step route. The first degradation step is due to the degradation of polymer host and the evaporation of plasticizers. And another step may be due to the degradation of salt. Beyond this a small residue obtained may be due to the formation of impure crystalline metal oxide.

The TG/DTA curve of the electrolyte film D1 is shown in Fig.5a. From the thermogram, it is observed that the sample D1 is thermally stable upto 200 °C with a weight loss of 22%, beyond which there is a gradual weight loss of 33% in the temperature range 200-270 °C. The large exothermic peak appearing around 289 °C indicates the decomposition of the film which is evidenced from the TG curve. TG curve of the sample D3 (Fig.5c) shows that the decomposition starts at 210 °C with the corresponding weight loss of 20%. There follows a rapid weight loss of 31% upto 275 °C. The complete decomposition of the film takes place beyond 275 °C. DTA curve of the sample shows an exothermic peak at 295 °C, which is well correlated with the weight loss of the sample observed in the TG curve. The first degradation of the film D5 (Fig.5e) takes place at 203 °C, with the corresponding weight loss of 29%. After that temperature, there is an appreciable weight loss of about 39% upto 277 °C. Complete decomposition of the film takes place beyond the temperature. The large exothermic peak appearing around 296 °C indicates the decomposition of the film which is evidenced from the TG curve.
The conductivity of the film D1 is found to be $0.661 \times 10^{-4}$ Scm$^{-1}$ at room temperature which is higher than the values obtained for other films. Film D1 is thermally stable up to a temperature of 200 °C. Hence, it is concluded that EC-based polymer film D1 is found to be superior on the basis of appreciable conductivity and good thermal stability.

### 7.3.5 SEM analysis

Scanning electron micrographs of PAN-PMMA–LiClO$_4$ with different plasticizers are shown in Fig. 6. From the figure it is observed that electrolyte film is a two phase system having polymer and the liquid electrolyte. Here all the films are interspersed with pores filled with liquid electrolyte, which form a connected path through the polymer matrix [30]. Among the three films, D1 has large number of pores. The increased porosity leads to the entrapment of large volume of the liquid in the cavities accounting for the increased ionic conductivity. The presence of pores in the microstructure is mainly due to the solvent removal [31, 32], increased amorphicity and solvent retention ability in the electrolyte system.

### 7.4. Conclusion

In the present study, PAN–PMMA-LiClO$_4$ polymer blend electrolytes with different plasticizers are prepared and their physical and thermal properties have been studied. XRD and FTIR analyses have confirmed the existence of strong interaction between the polymers, plasticizers and the salt.
The surface morphology has been observed in the micrographs and appears to be consistent with the changes in the electrical properties. The highest ionic conductivity achieved is $0.661 \times 10^{-4}$ Scm$^{-1}$ at room temperature when EC is added. The mobility of Li$^+$ ion and the number of charge carriers are responsible for the increase in ionic conductivity. The results of conductivity and thermal stability taken together confirmed that the polymer electrolyte PAN (18 wt.%)-PMMA (6 wt.%)-LiClO$_4$ (8 wt.%)- EC (68 wt.%) is found to be suitable for lithium battery applications even at high temperature.
Fig. 1 X-ray diffraction patterns of pure and the prepared complexes
Fig. 2 FTIR spectra of pure and the prepared complexes
Fig. 3 Complex impedance plot of PAN (18)-PMMA (6) LiClO$_4$ (8) EC (68) at various temperatures.
Fig. 4 Temperature dependent ionic conductivity plot of the prepared samples
(a)

(b)
Sample code D3

Sample code D4
Fig. 5 TG/DTA analysis of (a) D1; (b) D2; (c) D3; (d) D4; (e) D5.
Fig. 6 SEM photographs of (a) D1; (b) D3; (c) D5.
Table 7.1 FTIR assignments of the prepared samples

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<th>Band Assignments</th>
<th>Wavenumber (cm(^{-1}))</th>
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<td>PAN</td>
</tr>
<tr>
<td>CH(_2) (asym.stret)</td>
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<td>C≡N (stretching)</td>
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<td>C═O (stretching)</td>
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### Table 7.2 Temperature dependent ionic conductivity values

<table>
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<tr>
<th>Sample Code</th>
<th>PAN (18) - PMMA (6)</th>
<th>LiClO₄ (8)/ X(68) (wt.%)</th>
<th>Temperature dependent conductivity values x 10⁻⁴ S cm⁻¹</th>
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<td>303K</td>
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<tr>
<td>D1</td>
<td>X=EC</td>
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<tr>
<td>D2</td>
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<tr>
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<td>X=GBL</td>
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<tr>
<td>D5</td>
<td>X=PC</td>
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<td>0.219</td>
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Table 7.3. TG/DTA results of the prepared samples

<table>
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<tr>
<th>Sample code</th>
<th>Complex compositions</th>
<th>Decomposition Temperature (°C) (± 3°C)</th>
<th>% Wt. loss of the samples (±2 Wt%)</th>
<th>Exothermic Peaks (°C) (± 3°C)</th>
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<tbody>
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<td>73 200 270 18 22 33 87 - 289</td>
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<tr>
<td>D2 X=DMC</td>
<td>83 203 270 17 19 31 104 - 295</td>
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<td></td>
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<tr>
<td>D3 X=DEC</td>
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<td>D4 X=GBL</td>
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</tr>
<tr>
<td>D5 X=PC</td>
<td>74 203 277 24 29 39 81 - 296</td>
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References


