6.1 INTRODUCTION

Since 1970, lots of efforts were done on the preparation of polymer gel electrolytes which have a major role in batteries, super capacitors, fuel cells, sensors and Electrochromic displays [1]. Due to their remarkable advantages, lithium based electrolyte membranes were widely used in electronic instruments. Currently, lots of polymer host materials such as Poly(ethylene oxide) PEO, Poly(acrylo nitrile) PAN, Poly(methyl methacrylate) PMMA [2, 3], Poly(vinylidene fluoride) PVdF [4, 5], etc. have been studied to produce polymer electrolyte membranes with enhanced electrochemical properties. These polymers are usually based on the oxygen atoms or nitrogen atoms. Gel polymer electrolytes (GPE) were generally synthesized by incorporating inorganic solvent and lithium salts into polymer hosts [6]. The solvents can be ethylene carbonate, propylene carbonate, gamma butyrolactone, diethylene carbonate, etc. and having appreciable properties such as high boiling point, high dielectric constant and low viscosity. The solubility of salt in a particular solvent is determined by the energy and entropy changes associated with the transfer of its constituent ions in the solution. The complex formation between polymer and salt can occur when the free energy change is negative, which mainly depends on the ion size and polarizability. The conductivity studies on polymer electrolytes based on polyethylene oxide (PEO)/MCF$_3$SO$_3$ (M= Li, Na, K, Rb, and Cs) indicate that the cation size can be effectively complexed with the polymer [7]. In case of small and highly electropositive cations like Li$^+$, larger and more polarisable anions will have
lesser tendencies to form ion-pairs and hence lead to higher conductivities [8]. It has been reported that the anions with a large delocalisation of charges like ClO$_4^-$ and CF$_3$SO$_3^-$ show higher conductivity [9-11]. In addition, the vast difference in the activation energy values of different anions makes its role in polymer electrolyte as significant.

Based on the above studies, an attempt has been made to find the possibility of using gel polymer electrolyte based on PVdC-AN/PMMA blend in practical applications with different lithium salts since both the polymer motion and cation motion are responsible for ionic transport in polymer electrolytes. The commonly used inorganic salts in lithium battery electrolytes are LiPF$_6$, LiAsF$_6$, LiBF$_4$, LiClO$_4$, and LiTFSI that can readily be dissolved in high molecular weight polymers and but have poor thermal stability, hygroscopic, corrosive towards aluminium, and may have toxic byproducts. Among the salts commonly used, an attempt has been made to choose the best salt for PVdC-AN/PMMA blend at ambient temperature at the electrochemical point of view.

6.2. MATERIALS AND METHODS

PVdC-AN (Avg $M_w$ 150,000, Aldrich, USA), PMMA (Avg $M_w$ 120,000, Aldrich, USA), plasticizer EC (Alfa Aesar, India), and inorganic salts LiClO$_4$ (Aldrich, USA), LiBF$_4$ (Aldrich, USA), and LiCF$_3$SO$_3$ (Aldrich, USA) and LiAsF$_6$ (Aldrich, USA) were used as received. All electrolyte membranes were prepared using solution casting technique. Appropriate weights of PVdC-AN, PMMA, and different lithium salts were dissolved separately in the organic solvent Tetrahydrofuran (THF; Merck, India) at room temperature. The polymer and salt solutions were mixed together and stirred continuously for 12 h to obtain a homogeneous solution. Then suitable amount of EC was added to the polymer
solution. The obtained homogeneous, highly viscous solution was degassed to remove air bubbles and cast onto the well-cleaned petri-dishes to get desired thin film membranes. Then the solvent was allowed to evaporate slowly at 60 °C for about 6 h using vacuum oven. Finally, the harvested electrolyte membranes were analysed using various techniques.

The X-ray diffraction patterns were recorded using X’pert PRO PANalytical diffractometer in the scanning range 2θ = 10 to 80° with Cu-Kα (wavelength, λ=1.541 Å) radiation as a source. The Fourier Transform Infrared (FT-IR) spectra of the samples were recorded with Thermo Fisher Nicolet iS10 FT-IR Spectrometer in the range of 4000-400 cm⁻¹ in the transmittance mode. The polymer membranes were cut into circular disc, sandwiched between two SS (stainless steel) blocking electrodes and subjected to the µ-Autolab Type-III Potentiostat/Galvanostat in the frequency range 1 Hz – 1 MHz. The measurements were taken between 303 K and 353 K. The value of bulk resistance $R_b$ was found to be the intercept on the x-axis of the impedance plot. The conductivity ($\sigma$) was calculated using the formula $\sigma=\frac{l}{R_bA}$, where $l$ is the thickness of the polymer electrolyte film, $R_b$ is the bulk resistance, and $A$ is the surface area of the polymer electrolyte film. The dielectric parameters are derived from the impedance data.

All the polymer complexes were subjected to thermal analysis, which was carried out using Netzsch STA 449 F3 Jupiter thermal analyser. The thermogravimetric curves were recorded in nitrogen atmosphere from room temperature to 600 °C. The heating rate was 10 °C/min. From TG plots, temperature of maximum process rate, temperature at the end of decomposition, and weight loss were determined.
6.3. RESULTS AND DISCUSSIONS

6.3.1 Structural Analysis

In view of the fact that, the amorphous nature of electrolyte membranes results in greater ionic diffusivity and high ionic conductivity, the structural analysis was carried out using X-ray Diffraction for all the complexes. Figure 6.1 and Figure 6.2 show that the diffraction patterns of the pure samples and polymer complexes respectively. Three diffraction peaks were observed at 40.25, 46.76 and 67.94° for PVdC-AN, which validate the crystalline state of the polymer, and the diffractogram of PMMA furnish characteristic nature of pure PMMA as amorphous. The characteristic peaks related to the crystalline phase of polymer PVdC-AN were vanished in the complexes which indicate the complete dispersion of polymer and salt at the molecular level. Moreover, the crystalline peaks corresponding to lithium salts shown in the figure also faded away in the diffraction pattern of polymer complexes, which indicate the complete dissolution of the salt. The addition of plasticizer ethylene carbonate also helps to attain amorphous nature. Similar results of the significant structural reorganization of polymer while adding plasticizers were also observed by Abraham et al. [12]. This confirms that there is a good interaction between functional groups of polymer and salt in the presence of ethylene carbonate that results new systems with improved properties.

6.3.2 Electrochemical Impedance Analysis

The ionic conductivity values of the electrolyte membranes were evaluated by the electrochemical impedance spectroscopic (EIS) technique. Different electrolyte membranes with different lithium salts were prepared and kept in a cell of known diameter. The data were handled typically as Nyquist plots which gave the resistive response of the sample. A small semicircle at high frequencies and a spike at low
Frequencies were the general characteristic nature of Nyquist plots [13]. The bulk resistance ($R_b$) was obtained from the extrapolation of the semicircle which meets the slope of the spike at the real axis of the complex impedance plot. Figure 6.3 represents the impedance response of the prepared polymer electrolyte membrane containing different lithium salts, LiBF$_4$, LiClO$_4$, LiCF$_3$SO$_3$ and LiAsF$_6$ respectively for fixed salt content (8 wt.%). The ionic conductivity values of the electrolyte membranes calculated for various temperatures were listed in Table 6.1. It is seen from Figure 6.3 that the system containing LiAsF$_6$ as salt possesses the least bulk resistance compared to other membranes and hence the highest ionic conductivity value i.e. $1.29 \times 10^{-5}$ S cm$^{-1}$ at room temperature. A similar result was reported by Moumouzias et al. [14]. The high ionic conductivity should be the outcome of a compromise between a high level of salt dissociation and mobility [15, 16]. The ionic conductivity results of other electrolyte membranes calculated are $0.12 \times 10^{-5}$ S cm$^{-1}$, $0.095 \times 10^{-5}$ S cm$^{-1}$, $0.032 \times 10^{-5}$ S cm$^{-1}$ respectively for LiBF$_4$, LiClO$_4$, and LiCF$_3$SO$_3$ at room temperature. Jung et al. [17] reported that the coordinating nature of anions is in the order of CF$_3$SO$_3^-$ > PF$_6^-$ > ClO$_4^-$ > BF$_4^-$ > AsF$_6^-$ . The strong electron-withdrawing nature of fluorine atom causes least coordinating ability of AsF$_6^-$ and BF$_4^-$ . Consequently, the conductivity values of LiAsF$_6$ and LiBF$_4$ containing membranes possess comparatively higher value. The orders of ion mobility for some commonly available salts are as follows:

\[
\text{LiBF}_4 > \text{LiClO}_4 > \text{LiPF}_6 > \text{LiAsF}_6 > \text{LiCF}_3\text{SO}_3.
\]

From the Table 6.1, it can be observed that at higher temperature the ionic conductivity of membranes with LiBF$_4$ is greater than that with LiAsF$_6$. This is because, at higher temperature the polymer chains become more flexible and hence the higher ionic mobility as well as smaller ionic radius (0.229 nm) of BF$_4^-$ anion
helps greater conduction. The reported anion radii of other salts were 0.237 nm (ClO$_4^-$), 0.260 nm (AsF$_6^-$), and 0.270 nm (CF$_3$SO$_3^-$) [18].

6.3.3 Temperature dependent Ionic conductivity

Figure 6.4 shows the dependence of log conductivity (log $\sigma$) on inverse temperature in Kelvin (1/T) for the membrane systems. The plot shows that conductivity increases with respect to temperature non-linearly. The observed non-linearity in the plot can be explained by invoking the concept of free volume. The non-linear behaviour of the temperature dependence on the ionic conductivity can be expressed by $\sigma = AT^{-1/2} \exp(-B/K(T - T_0))$ the VTF (Vogel- Tamman- Fulcher) expression where $A$ is a constant proportional to the number of charge carriers, $B$ is a constant, and $T_0$ is the temperature at which configurational entropy becomes zero [19]. This shows the close-correlation between ionic conductivity and visco-elastic properties of polymer membranes. The addition of plasticizer ethylene carbonate (EC) to PVD-C-AN/PMMA blend reduces the viscosity of complex. Since both macroscopic flow of polymer and segmental motion are permitted for viscous solutions, it is suggested that the segmental motion plays an important role in the ionic migration in the polymer electrolytes. The semi-random motion of polymer segments will create new coordination sites for the cations, while the old sites disappear. The hopping of ions from site to site either along the same chain or between chains occur and increase of chain flexibility assists ion transport, which leads to rise in the ionic conductivity of the polymer–salt complex.

6.3.4 Frequency dependent conductivity (Conductance spectra)

The variation of $\sigma_{ac}$ with frequency for all the prepared electrolyte membranes at room temperature has been given in Figure 6.5. The electrode polarization at low frequency, a direct current plateau at intermediate frequency and the dielectric
relaxation phenomena at high frequency could be distinguished in the conductance spectra. This behaviour follows Jonscher’s power law \( \sigma_{ac}(\omega) = \sigma_{dc} + A\omega^n \), where \( \sigma_{dc} \) is the DC conductivity (frequency independent plateau in the low frequency region), \( A \) is the pre exponential factor, \( \omega \) is the angular frequency \( (\omega = 2\pi f) \) and \( n \) is the fractional exponent [20]. DC conductivity values were obtained by taking the \( y \)-intercept of \( \log \sigma \) at zero frequency. The values were found to be in the order of \( 10^{-5} \) S cm\(^{-1} \) which is in good agreement with the values calculated from Nyquist plots. The values of \( \sigma_{dc}, A, \) and \( n \) were determined by fitting the \( \sigma_{ac}(\omega) = \sigma_{dc} + A\omega^n \) and are listed in Table 6.2. The observed values of the power law exponent lie in between 0.7 and 0.8. In general, power law exponents \( (n) \) can be between 1 and 0 signifying the ideal long-range pathways and diffusion limited hopping (tortuous pathway) of ion movement for ionic conductors. The overall behaviour of \( \sigma_{ac} \) observed for the polymer membranes follows the universal dynamic response [21], which has widely been reported for disordered materials like ionically conducting glasses, conducting polymers, and also doped crystalline solids and is generally believed to be reflected in the mechanism of charge transport behaviour of charge carriers [22, 23].

**6.3.5 Dielectric permittivity and loss analysis**

The complex permittivity \( (\varepsilon^*) \) or dielectric constant of a system is defined by \( \varepsilon^* = \varepsilon' - i\varepsilon'' \), where real \( \varepsilon' \) and imaginary \( \varepsilon'' \) components represent storage and loss of energy in each cycle of applied electric field. The main contribution to dielectric spectra arises from re-orientational motions which results in dipolar relaxation phenomena, and from translational motions, which results ionic charge transport. Figure 6.6 shows the variation of dielectric constant \( (\varepsilon') \) and dielectric loss \( (\varepsilon'') \) as a function of frequency for different gel polymer electrolytes having ionic salt LiBF\(_4\), LiClO\(_4\), LiCF\(_3\)SO\(_3\), and LiAsF\(_6\). A strong dispersion at low frequency region and a
frequency independence of the high frequency region are found from for both graphs. It is due to electrical relaxation at low frequency, and decrease in the ionic and orientational source of polarizability at high frequency electric field. A similar result was obtained for PVA based nano composite electrolyte by Agrawal et al. [24]. This is possibly associated with the large dipole moment of the carboxyl (C=O) group as well as nitrile (C≡N) group in the blend and their strong dipole interactions which might be responsible for the high values of $\varepsilon''$ observed at low frequencies [25]. A dielectric constant value between 0.36 and 0.78 at 1 MHz has been obtained for this polymer electrolyte system. From the figure, the dielectric constant, $\varepsilon'$ of LiAsF$_6$ containing gel polymer complex (PVdC-AN/PMMA) is the highest, reminding one that the electrolyte contains more mobile ions. This dielectric constant result is in good agreement with the impedance analysis result.

6.3.6 Functional group Analysis

PVdC-AN/PMMA gel membranes were analysed by Fourier-transform Infrared spectroscopic analysis. The chemical interactions or conformational changes are expected to cause spectral differences in compatible blends. The change in inter- and intra-molecular interaction of the components of the polymers in the gel polymer system changes the vibrational spectra from the pure samples. Figure 6.7 represents the FTIR spectra of polymer complexes with different lithium salts. In methacrylate-based electrolytes, the lithium ions associate with oxygen atoms, whereas in acrylonitrile-based electrolytes the Li$^+$ ions associate with the nitrogen atoms since the nitrile is a strong electron dopant [26, 27]. The nitrile band, C≡N can be assigned to strong stretching vibration in the infrared spectrum and appears at 2247 cm$^{-1}$ for the acrylonitrile based polymers. In the spectra, the nitrile band has been displaced towards the lower wavenumber around 2245 cm$^{-1}$ due to the inductive effect created
by the lithium cation interaction with the nitrogen atom in C=N. In the spectra, the symmetrical stretching vibration of the carbonyl group, \( \nu(C=O) \) at 1725 cm\(^{-1}\) and ether group (C–O–C) at 1100–1200 cm\(^{-1}\) in methacrylate group and ethylene carbonate are broadened with the addition of salt and PVdC-AN. The shift in wavenumber observed in salt-doped gel electrolyte system compared to pure polymer clearly emphasizes the specific interaction between Li ion from salt with polar group of polymer. The hydrogen bonding between cations and anions can destroy the charge symmetry and hence it is not possible to isolate the bands originating only due to anions in the spectra of electrolyte membranes [28]. This signifies that the salt solvates very well in a polymer matrix, resulting in the absence of pure salt phase in the complexes. This leads to the formation of polymer-salt complexes.

### 6.3.7 Thermogravimetric Analysis

To ascertain the thermal stability and decomposition temperature of the gel polymer electrolytes, the samples were subjected to thermogravimetric analysis (the residual weight percentage versus temperature). The TGA results are plotted in Figure 6.8. It can be observed from the Figure 6.8 that the polymer complexes have undergone two-step degradation upon increasing the temperature. The reported decomposition temperature of PMMA was 230 °C while for PVdC-AN it was 200°C [29]. The observed reduction in thermal stability of the polymer blend membranes compared to pure polymers can be attributed to the addition of plasticizer. The weight loss occurred from 165 to 280 °C is mainly due to the evolution of vinylidene chloride in PVDC, which is considered to account for a major proportion of the weight loss in this low temperature range. Also at the same temperature region, there is a possibility to occur scissions at the chain-end initiation and random internal scission of the polymer-chain in the methacrylate part of the polymer complex. The production of
free radicals at low-temperature induces further depolymerization at high temperatures through chain transfer processes. Though vinylidene chloride polymers are highly resistant to oxidation, permeation of small molecules, and biodegradation, they are extremely durable under most use conditions. These types of materials are thermally unstable and, when heated at moderate temperature (< 200 °C), undergo degradative dehydrochlorination.

Thermal decomposition in gel membrane with LiBF₄, LiClO₄, LiCF₃SO₃ and LiAsF₆ starts at about 204, 202, 202 and 170 °C respectively. All the polymer membranes show weight losses of about 13.4, 16.9, 10.6 and 13.4% respectively at 190 °C. Acrylonitrile based polymers release a small amount of hydrogen cyanide (HCN) and ammonia as well as hydrogen chloride (HCl) [30] since degradation apparently begins in vinylidene chloride units adjacent to monomer units. The gaseous products may arise from the splitting off of the side or end groups of polymers. It is observed that there is no significant weight loss of all the polymer electrolytes beyond 420 °C. The residual mass about 22 % at 600 °C can be assigned to the carbonaceous residue formed in both previous stages.

6.4. CONCLUSION

A novel polymer membrane composed of PVdC-AN/PMMA/EC with different inorganic lithium salts was prepared using solution casting technique. Sensitive techniques such as TGA to find the thermal decomposition of the membranes, electrochemical analysis, and FT-IR spectroscopy for detecting the structural changes were employed in combination. A substantial change in the ionic conductivity for different samples can be observed due to the combined effect of ionic mobility, cation radii and dissociation constant. Further analysis, such as conductance spectra, and complex dielectric analysis shows that the sample containing LiAsF₆ salt
shows better performance. The conductance spectra are found to obey Jonscher’s power law. There is stronger interaction between oxygen atoms in the ether and carbonyl groups and lithium ions, than that with nitrogen atoms, which can be found from infrared spectroscopic analysis. The thermogravimetric analysis shows that the thermal decomposition starts at about 190°C for all the membranes.
Figure 6.1: XRD patterns of pure samples used.
Figure 6.2: X-ray diffraction pattern of electrolyte membranes with different Lithium salts.
Figure 6.3: Impedance response of polymer electrolyte membranes at 303 K.
Figure 6.4: Temperature dependence of log conductivity.
Figure 6.5: Variation of AC conductivity with respect to frequency.
Figure 6.6: Frequency dependence of real part $\varepsilon'(\omega)$ and (inset) imaginary part $\varepsilon''(\omega)$ at room temperature.
Figure 6.7: FT-IR transmission spectra of gel polymer membranes.
Figure 6.8: Thermogravimetric (TG) curves of gel polymer membranes.
Table 6.1: Ionic conductivity values of polymer electrolyte membranes.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>PVdC-AN/PMMA/EC/LiX</th>
<th>Conductivity $\sigma$ (10^{-5}) S cm^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>X=LiBF$_4$</td>
<td>0.114 0.227 1.288 9.290 79.55 181.8</td>
</tr>
<tr>
<td>S2</td>
<td>X=LiClO$_4$</td>
<td>0.095 0.197 0.892 4.389 28.93 97.90</td>
</tr>
<tr>
<td>S3</td>
<td>X=LiCF$_3$SO$_3$</td>
<td>0.032 0.066 0.237 1.429 7.298 35.85</td>
</tr>
<tr>
<td>S4</td>
<td>X=LiAsF$_6$</td>
<td>1.292 1.968 6.119 18.45 90.91 142.8</td>
</tr>
</tbody>
</table>
Table 6.2: Comparison of parameters obtained from fitting the experimental data to power law.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>PVdC-AN / PMMA / EC/LiX</th>
<th>( \sigma_{dc} ) (10^-3)</th>
<th>A</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>X=LiBF_4</td>
<td>0.145</td>
<td>2.31×10^-10</td>
<td>0.79</td>
</tr>
<tr>
<td>S2</td>
<td>X=LiClO_4</td>
<td>0.124</td>
<td>5.08×10^-10</td>
<td>0.76</td>
</tr>
<tr>
<td>S3</td>
<td>X=LiCF_3SO_3</td>
<td>0.039</td>
<td>1.94×10^-10</td>
<td>0.77</td>
</tr>
<tr>
<td>S4</td>
<td>X=LiAsF_6</td>
<td>1.581</td>
<td>3.71×10^-10</td>
<td>0.84</td>
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</tbody>
</table>
REFERENCES


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