Chapter - 4

Polymer Gel Electrolytes: Electrical and Electrochemical Studies
The Present chapter is devoted to the studies on the polymer gel electrolytes based on the liquid electrolytes comprising of ethylene carbonate (EC) and propylene carbonate (PC) with the salts (LiClO₄, NaClO₄ and TEAClO₄), entrapped in two host polymers, namely: poly vinylidene fluoride-co-hexafluoropropylene (PVdF-HFP) and poly methyl methacrylate (PMMA). The preparation technique of the gel electrolytes is broadly described in chapter 3, section 3.2.1.1. The electrical and electrochemical characterisation of the gels and their optimisation have been carried out for their application in electrical double layer capacitors (EDLCs) and redox supercapacitors, described in chapters 5 and 6. The liquid electrolytes and the gel electrolytes have been optimised by studying their composition dependence of electrical conductivity. The temperature dependence of the conductivity of the gel systems has been studied and the results have been qualitatively correlated with the existing models. The transference number and electrochemical stability (working potential range) of the gels have also been estimated, which are useful data from the application point of view as electrolytes in electrochemical devices like supercapacitors, etc.

4.1 Electrical Conductivity

4.1.1 Composition Dependence of Electrical Conductivity: Liquid Electrolytes

In order to synthesize highly conducting polymeric gel electrolytes, which is an excellent alternative for the solvent free polymeric electrolyte systems [123, 314, 315], the primary need is to synthesize non-aqueous liquid electrolytes using different polar solvents. While choosing different solvents, few characteristics have to be taken into considerations, such as high ionic conductivity of the liquid electrolytes (~ 10⁻²) should be achieved at room temperature,
dielectric constant of the solvent should be as high as possible so that it facilitates the salt
dissociation, low viscosity for better ion transport, high boiling point to furnish non-volatility
within the system, low freezing point to prevent sudden decline in the value of conductivity at
low temperatures, good chemical and electrochemical stability, chemical compatibility with
different electrodes, good plasticising properties, good miscibility with the polymer [164] etc
are quite essential. The donor-acceptor concept (acid and base reaction) between the salts and
solvents has to be taken into considerations. Since the salts act as strong Lewis acids [316] such
as LiClO₄, NaClO₄ etc., which furnish their small cations after dissociation, so the best way to
anticipate the solvating power of the solvent is to consider the solvent Lewis basicity (electron
donating ability) [102]. The greater is the electro-donor ability [mostly measured in terms of
the donor number (DN)] of the solvent, the greater is the extent of solvation of the salt by the
solvent. For instance, donor number of EC is 16.4 and that of PC is 15.1, therefore Li⁺ ion is
strongly complexed in EC than in PC [317]. Out of several solvents such as EC, PC, diethyl
carbonate (DEC), dimethylformamide (DMF) etc., particularly EC shows the highest dielectric
constant value of 95.3. Various parameters are given in Table 4.1 [318]. So it can be used for
the synthesis of polymeric gel electrolytes, but as can be seen from the Table 4.1, EC suffers by
two major problems from application point of view.

Table 4.1: Comparisons of various parameters of the solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant (ε) 25°C</th>
<th>Viscosity (η) (cSt) 25°C</th>
<th>Boiling Point (°C)</th>
<th>Melting Point (°C)</th>
<th>Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC (C₃H₄O₃)</td>
<td>95.3</td>
<td>1.406 (40⁰C)</td>
<td>248</td>
<td>36.2</td>
<td>11.63 x 10⁻³</td>
</tr>
<tr>
<td>F. wt = 88.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC (C₄H₆O₃)</td>
<td>65.1</td>
<td>2.093</td>
<td>241-242</td>
<td>-48</td>
<td>7.96 x 10⁻³</td>
</tr>
<tr>
<td>F. wt = 102.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC : PC (1:1 v/v)</td>
<td>80.2</td>
<td>1.696</td>
<td>-</td>
<td>-</td>
<td>9.35 x 10⁻³</td>
</tr>
</tbody>
</table>
Firstly, the melting point of pure EC is relatively high (~36.2°C), which reduces the conductivity of the electrolytes at low temperatures. Secondly, there is an absence of pure liquid phase for the electrolytes at lower concentrations of the salts, say less than 0.6 M concentration [317, 319]. Due to the above limitations, we have to go for some compromise with the pure EC solvent and seek some binary solvent as a substitute. For the purpose PC has been used, which fulfils the requirement and act as a good binary solvent. Hence the mixture of EC and PC shows the good agreement by possessing the intermediate characteristics of the two solvents (Table 4.1). The melting point and boiling point depends on the ratio of EC and PC solvents, but always lie in between the two. Thus the combination of all the above factors made us to choose binary solvent EC-PC (1:1 V/V) for the preparation of liquid electrolytes.

In order to optimise the molar concentration of the salts in liquid electrolytes, the conductivity measurements were performed at room temperature, by varying the concentration of salts from 0.1 M to 2.0 M in the solvent mixture of EC:PC (1:1 V/V). Fig. 4.1 shows a general trend of conductivity variation with respect to molar concentration of salts. It has been observed for all the liquid electrolytes that initially the ionic conductivity increases with the increase in salt concentration upto 1.0 M concentration of each salt, thereafter the conductivity either remains constant or starts decreasing at about 2.0 M concentration of each salts. Further increase in the salt concentration leads to the decrease in conductivity of the liquid electrolyte. The above behaviour of the liquid electrolyte can be explained in the following manner. Initially, as the salt concentration increases, the number of free mobile ions also increases, which leads to the increase in conductivity. At higher concentrations of the salt, ion-aggregation is likely to play a major role in limiting the ionic conductivity of the electrolyte [315, 316]. Finally we have chosen EC:PC (1:1 V/V) – 1.0 M salts (LiClO₄, NaClO₄ and TEAClO₄) as liquid electrolytes for the synthesis of polymeric gel electrolytes.
Fig 4.1: Variation of Electrical conductivity as a function of varying salt concentration in the solvent mixture EC:PC (1:1 V/V).
4.1.2 Composition Dependence of Electrical Conductivity: Polymer Gel Electrolytes

As it is well established that in the polymeric gel electrolytes, liquid electrolytes are immobilized in a polymer matrix in which the polymer acts as a container and gelling agent for liquid electrolytes and imparts high viscosity to the liquid electrolyte without affecting its ionic conductivity significantly [123, 320]. It is also important that upon incorporation of any polymer in non-aqueous liquid electrolyte, the resulting homogeneous gel should possess a mechanical stability comparable to that of solid electrolyte and simultaneously should retain a room temperature ionic conductivity of the order of $10^{-3}$ S cm$^{-1}$, which is comparable to that of liquid electrolytes [164, 321-323]. Further it is well known that the ion conduction in polymer electrolytes is confined to the amorphous regions of the polymeric material and that any tendency to crystallization leads to the decrease in ionic conductivity [147, 324]. In view of the above facts, in present investigations two polymers, namely, poly(vinylidene fluoride–hexa fluoro propylene) (PVdF-HFP) and poly (methyl methacrylate) (PMMA) have been selected as they possess larger content of amorphicity and have many of the desired above mentioned properties. The chemical structure of these polymers along with their other properties, are shown in Table 4.2.

Table 4.2: Polymers used in the present studies and their different characteristics:

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular Weight</th>
<th>Tg, Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>1,20,000</td>
<td>114°C</td>
</tr>
<tr>
<td>PVdF-HFP</td>
<td>4,00,000</td>
<td>140-145°C</td>
</tr>
</tbody>
</table>
Chapter 4: Polymer Gel Electrolytes: Electrical and Electrochemical Studies

PVdF alone has high degree of crystallinity due to the presence of single monomer throughout the polymer chain, which provides less free volume to the mobile ions, resulting in lower conductivity. In order to create disorder or amorphicity in PVdF polymer, another monomer HFP is introduced. Introduction of HFP in PVdF leads to the higher amorphicity in the copolymer due to the steric hindrance provided by CF₃ pendant group in HFP monomer units which is randomly mixed with the VDF (-CH₂CF₂-) monomers in the polymer chain. Higher amorphicity provides mobile ion greater free volume giving rise to higher conductivity. Apart from providing good mechanical stability to the electrolytes, the polymer plays a passive role in conduction and acts as a stiffener for the solvent which solvates the salt and also provides a continuous conduction path through the solvent for ion migration [320].

PMMA is a thermoplastic polymer, which act as a framework for gel electrolytes. It is an atactic polymer having an amorphous morphology that imparts a mechanical strength and dimensional stability to the gel electrolytes. Incorporation of PMMA polymer in liquid electrolytes enhances its macroscopic viscosity by several orders of magnitude thereby imparting mechanical stability to the system. Since the decrease in conductivity occurs only by a factor and not by an order, it is assumed that polymer addition does not alter the conduction mechanism that prevails in liquid electrolyte significantly. In view of the above mentioned properties of both the polymer viz. PVdF-HFP and PMMA, they are chosen as a host polymer matrix for the preparation of polymeric gel electrolytes.

Hence in the present studies the compositions of (PVdF-HFP / PMMA)-EC-PC-salts (LiClO₄, NaClO₄ and TEAClO₄) based gel electrolytes are first optimized to get high ionically conducting and mechanically stable materials. Fig 4.2 shows the typical variation of electrical conductivity (σ) of the gel systems as function of polymer content in liquid electrolytes (EC-PC-salts). The similar pattern of variation has been observed for the other polymeric gel
Fig 4.2: Effect of polymer addition on the ionic conductivity of gel electrolytes.
electrolytes under present investigation. The values of $\sigma$ decrease substantially due to the addition of the host polymer PVdF-HFP or PMMA. The variation in conductivity can be divided in two regions $S_I$ and $S_{II}$ as indicated in Fig. 4.2. The decrease in conductivity in the lower polymer concentration region i.e. region $S_I$ is steep as compared to higher polymer region $S_{II}$. This indicates that only a partial amount of liquid electrolyte could be utilized in gel formation while the excess of it remains phase separated in the region $S_I$ (i.e. below 25 wt% PVdF-HFP content and below 20 wt% PMMA content). On addition of the host polymer beyond $\sim$25 wt% for PVdF-HFP system and $\sim$20 wt% for PMMA system, liquid electrolytes are fully utilised in the gel formation. On further addition of the host polymer, stiffening of the gel electrolytes occur which results in the continuous decrease in conductivity.

Further, an important point may be noted that the electrical conductivity of the gel electrolytes containing even upto 10 wt % of the host polymer is slightly higher than that of the liquid electrolytes, EC-PC-salts systems (Fig.4.2). Similar observations have recently been obtained and systematically studied by Chandra and co-workers [325, 326] in a different system of PMMA based gel electrolytes. Such observations have been found to be in full agreement with the “Breathing Chain model” proposed by Chandra et al [325, 326]. According to this model, polymeric gel is considered to consist of dissociated ions (free ions), ion pairs, undissociated ions, solvents and polymeric chains (folded or partially/fully unfolded chain). At low polymer concentration, the system behaves as a liquid electrolyte as a result of dissociation of salts. With an increase in polymer concentration, viscosity comes into picture and it tends to decrease conductivity by effectively decreasing the mobility of free ions. However, a competitive phenomenon is assumed to occur at microscopic level. The polymer chain ‘breathes’ while it opens or folds occupying different volumes in the process at different time span. Therefore folding and unfolding of polymeric chains lead to localized pressure
fluctuations in the surrounding volumes and this localised turbulent pressure leads to the
dissociation of ion pairs and enhance mobility [325, 326].

The final compositions of the gel electrolytes, PVdF-HFP or PMMA (20 wt%)-EC:PC
(1:1 V/V) - 1.0 M LiClO₄/NaClO₄/TEAClO₄ salts, were chosen for the construction of different
supercapacitors (described in chapters 5 and 6). All these electrolytes possess the conductivity
of the order of 10⁻³ S cm⁻¹ at room temperature with good mechanical strength in the form of
freestanding films for PVdF-HFP based gel electrolytes and flexible as well as semitransparent
lump materials for PMMA based gel systems. This order of conductivity is acceptable for use
in supercapacitors fabrication, as they offer low resistance, when used in the form of thin films
of thickness about 100-200 micron.

4.1.3 Temperature Dependence of Electrical Conductivity: Polymer Gel Electrolytes

From the application point of view, one of the most important properties of solid
electrolyte is the temperature dependence of the d.c. conductivity σ (T). The main objective of
the present studies is to check the suitability of the polymeric gel electrolytes in different
electrochemical devices such as supercapacitors over a substantial temperature range as these
devices are normally required to be operated over a temperature range, from below freezing
point to about 90°C or so [327]. Generally the polymeric materials show some peculiar type of
characteristics. The σ (T) curves for most of the polymer electrolytes show one of the five
patterns of behaviour [72]:

- Vogel-Tamman-Fulcher (VTF) behaviour throughout the available temperature range,
in which σ vs. 1/T plot shows a curved nature.

- Arrhenius behaviour for low temperatures showing linear σ vs. 1/T plot and VTF
  behaviour at higher temperatures.
Arrhenius behaviour throughout, but with two different activation energies, high $E_a$ closer to glass transition temperature, $T_g$, and a smaller $E_a$ at higher temperatures.

- VTF behaviour for temperatures slightly greater than $T_g$, but Arrhenius behaviour at higher temperatures.

- Behaviour, which is very unlike either Arrhenius or VTF at all temperatures.

The temperature dependence of electrical conductivity i.e., $\sigma$ vs. $1/T$ for all the polymeric gel electrolytes under present studies are shown in Fig. 4.3. As can be seen from the figures, the temperature dependence of conductivity indicates an activated process. Conductivity increases with increasing temperature and the Arrhenius behaviour often provides a good representation of the data [72, 73, 328]. On having minute inspection, it can be observed in the figure that there is a change in slope and curvature of the $\sigma$ vs. $1000/T$ plots for all the polymeric gel electrolytes in present studies. This particular behaviour i.e. non-linearity of conductivity plots is typical of highly viscous and amorphous polymeric electrolytes [126, 147, 329]. When conductivity is plotted in Arrhenius coordinates, we may observe the pattern either straight or curved lines, which can be fitted in Arrhenius or Vogel-Tamman-Fulcher (VTF) forms [72, 147, 319, 328].

\[
\text{Arrhenius Equation} \quad \sigma = \sigma_0 \exp \left(-\frac{E_a}{kT}\right) \quad \ldots (4.1)
\]

\[
\text{VTF Equation} \quad \sigma T^{1/2} = \sigma_0 \exp \left[-\frac{B}{K} \left(T-T_0\right)\right] \quad \ldots (4.2)
\]

where, $E_a$ is the activation energy of conduction in Arrhenius form, $T_0$ is the “ideal or equilibrium” glass transition temperature i.e. the temperature at which the free volume extrapolates to zero, $\sigma_0$ is pre-exponential factor, related to the number of charge carriers and $k$ is the Boltzmann constant. $B$ is a constant, whose dimensions are in fact that of energy which is not simply interpreted as an activation term. VTF equation is basically an empirical
Fig 4.3: Temperature Dependence of electrical conductivity of the polymer gel electrolytes.
generalization, which is based on the free volume model and describes the temperature
dependence of ionic conductivity adequately [72, 75, 328]. Free Volume model was given by
Cohen and Turnbull [330], according to which the ionic motion is supposed to be a non-
thermally activated process and occurs as a result of redistribution of free volume within the
material. By increasing the temperature, the segmental motion of the polymeric materials gives
rise to enhancement in the ion motion by making and breaking the coordination sphere of the
solvated ion and by providing the local voids i.e. free volume which are generally created by
the expansion of the polymeric materials into which the ion may diffuse under the influence of
an electric field [96].

This phenomenological model is based on the considerations involving the critical role
of the glass transition temperature (T_g) and of the so-called equilibrium glass transition
temperature (T_0). Above T_g, the polymeric material becomes microscopically rubbery rather
than glassy [328]. This can be well understood by considering that the local environment of any
given polymer chain becomes liquid like at the glass transition temperature. Hence it is only the
thermal energy, which in excess of the glass transition temperature provides the actual mobility
of the local polymer chain segments. Thus the Arrhenius behaviour involving the inverse of the
temperature is replaced by the VTF equation, which involves the inverse of \( T - T_0 \), where T_0 is
the temperature at which all the free volume of the materials vanishes or at which all polymer
segmental motion disappears. Generally T_0 lies 40-50 K below the actual glass transition
temperature T_g [315, 316].

In the case of liquid electrolytes, cations and anions move with their solvent sheath
intact and charge transport is related to the macroscopic viscosity of the electrolyte. Whereas in
the case of gel electrolytes, which encompass high molecular weight polymers, the ion-
transport is decoupled from the macroscopic viscosity of the electrolyte. The polymer chains
become increasingly entangled and cannot therefore move to a long distance with the ions [75]. In this case one point should be noted that the VTF model describes the motion of the polymer chains whereas the conductivity refers to the migration of charged species i.e. the ions introduced by the presence of salt. The ionic diffusion is closely related to the polymeric motions but they are not exactly the same, as the pure polymer does not conduct, so that the VTF behaviour for the ions does not immediately follow from the VTF behaviour for the polymer [72].

In this regard, conductivity studies have been performed by Bohnke and co-workers [147, 320] by varying the different weight ratios of the polymeric materials. They showed that as the polymer is added, the effective area/length of the high conductivity path decreases. Consequently, $T_\theta$, $\sigma_0$ and $B$ (activation energy of conduction) increase and $T_0$ decreases. Decrease in ionic conductivity was observed to be very small for gels containing less than 30 wt% of polymer. Whereas for gels with higher polymer content (greater than 30 wt% of the polymer), the ionic conductivity decreases very rapidly. Gel electrolytes with lower polymer content (less than 30 wt%) can be conveniently regarded as the liquid electrolytes encaged in a polymer matrix. Ions can easily migrate through the solvent domain surrounding the polymer matrix. As the activation energy increases very slightly upon addition of polymer, it was concluded that the ion-migration is not severely influenced by the addition of polymer content. These assumptions lead to a very small decline in conductivity upon polymer addition upto 30 wt%. All the polymeric gel electrolytes under present investigations as shown in the Fig. 4.3 exhibit distinct curved profiles thereby rendering them to be non-Arrhenius in nature and therefore conductivity behaviour can be best expressed using the VTF equation. The interconnection between Arrhenius and VTF conductivity versus temperature behaviour are widely reported and discussed in literature [72]. The ionic conductivity for all polymer gel
electrolytes investigated in present studies increases as a function of temperature over the entire temperature under present studies. Conductivity increment occurs utmost by an order of magnitude. No colossal enhancement in conductivity was observed over the entire temperature range (280-370 K). This is an important and most advantageous property of polymeric gel electrolytes to be used in supercapacitors like devices. Lesser the magnitude of the change associated with the ion conducting properties of polymer electrolytes with temperature, greater is the feasibility for their useful practical applications.

4.2 **Electrochemical Stability of Polymer Gel Electrolytes**

The electrochemical stability of the electrolytes, which limits the working voltage range (i.e. electrochemical potential window) of the devices, including supercapacitors, is an important aspect to be evaluated. The potential windows of different gel electrolytes, in the present studies, were estimated by linear sweep voltammetry using symmetrical stainless steel like almost inert electrodes with two electrodes configuration. Fig. 4.4 illustrates the linear sweep voltammograms of different gel electrolytes at a voltage scan rate 2 mV sec\(^{-1}\).

**Fig 4.4:** Linear sweep voltammograms of different gel electrolytes with two-electrode configuration of stainless steel at scan rate 2 mV sec\(^{-1}\).
observed I-V characteristics are the combined effect of anodic and cathodic responses for the two electrodes configuration (Fig 4.4). For all the gel electrolytes under present studies, the values of current goes on increasing gradually with the increase in the applied voltage across the cells upto a certain voltage, which is termed as “Electrochemical Potential Window or Working Voltage”, after that point current increases abruptly as shown in the Fig. 4.4. The abrupt increase in current takes place due to the decomposition of the electrolytes. It provides the information regarding the voltage level upto, which the electrolyte can function properly and safely. Almost all the gels under present studies show the same working voltage range (~ 4 V). The potential range of the electrochemical stability of liquid electrolytes is larger (> 4 V) as compared to that of the solid electrolytes. The wider range of working voltage is indicative of the liquid like characteristics of the gel electrolytes under present investigations.

4.3 Transport Number of Polymer Gel Electrolytes

As described earlier, the transport number is defined as the net number of moles of an ion that cross a reference plane fixed with respect to the solvent when one Faraday of current is passed between the electrodes. In pure polymeric systems, the transport number helps in distinguishing the ionic contribution from the electronic contribution towards total current. Total ionic transport number “$t_{\text{ion}}$” for all the gel electrolytes under present studies are determined using “Polarization method” as described in chapter 3, section 3.2.1.2 (b). The polarisation current versus time plots for all the polymeric gel electrolytes in present studies are shown in Figs. 4.5 and 4.6. The voltage applied across the cells was kept well within the electrochemical stability range of all the polymeric gel electrolytes. In the present case it has been chosen to 0.5 V. The values of ionic transport number have been evaluated using mathematical expressions 3.41 (chapter 3) and are listed in Table 4.3.
Fig 4.5: Polarisation Current as a function of time for different polymer gel electrolytes (Applied Voltage ~0.5 V).
Fig 4.6: Polarisation Current as a function of time for different polymer gel electrolytes (Applied Voltage ~ 0.5 V).
From the Figures 4.5 and 4.6, it can be calculated that the values of transport number for all the polymeric gel electrolytes are in the range of 0.96-0.98, which shows that the charge transport is mainly due to the contribution of ions.

Table 4.3: Ionic transport number of different polymeric gel electrolytes.

<table>
<thead>
<tr>
<th>Polymeric Gel Electrolyte Systems</th>
<th>Ionic Transport Number ($t_{\text{ion}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVdF-HFP (20 wt%)-EC:PC (1:1 V/V)-1.0 M LiClO$_4$</td>
<td>0.97</td>
</tr>
<tr>
<td>PVdF-HFP (20 wt%)-EC:PC (1:1 V/V)-1.0 M NaClO$_4$</td>
<td>0.96</td>
</tr>
<tr>
<td>PVdF-HFP (20 wt%)-EC:PC (1:1 V/V)-1.0 M TEAClO$_4$</td>
<td>0.96</td>
</tr>
<tr>
<td>PMMA (20 wt%)-EC:PC (1:1 V/V)-1.0 M LiClO$_4$</td>
<td>0.96</td>
</tr>
<tr>
<td>PMMA (20 wt%)-EC:PC (1:1 V/V)-1.0 M NaClO$_4$</td>
<td>0.97</td>
</tr>
<tr>
<td>PMMA (20 wt%)-EC:PC (1:1 V/V)-1.0 M TEAClO$_4$</td>
<td>0.98</td>
</tr>
</tbody>
</table>

4.4 Conclusions

Combining all the above results, we may conclude that:

- 1M concentration of each salts i.e. LiClO$_4$, NaClO$_4$ and TEAClO$_4$ in binary solvent EC:PC (1:1 V/V) is sufficient for the preparation of polymeric gel electrolytes in order to achieve maximum conductivity of the order of $10^{-3}$ S cm$^{-1}$ at room temperature.
- 20 wt% of the polymer content i.e. PVdF-HFP as well as PMMA is sufficient in order to achieve the acceptable value of conductivity of the gel electrolytes with good mechanical properties.
- All the polymer gel electrolytes show a wide electrochemical stability of $\sim$ 4 Volt, indicative of liquid like behaviour.
• The ionic transport number $t_{\text{ion}}$ has been found to be in the range of 0.96-0.98, which shows that the charge transport in the gel electrolytes is predominantly ionic in nature.

• The temperature dependence of electrical conductivity (i.e. $\sigma$ vs $1/T$) plots show the VTF behaviour over a temperature range of 280-370 K indicating that the polymeric gel electrolytes are thermally stable.

• All the polymeric gel electrolytes investigated are flexible enough to mould in the desirable area and thickness. The order of conductivity ($10^{-3}$ S cm$^{-1}$) is also acceptable for use in supercapacitors application as they offer low resistance. Being the flexible materials, they are able to form proper interfacial contacts for the maximum accessibility of the active electrode materials.