CHAPTER IV

Optimization of PVdF/PVC, salt and plasticizers

Section A

4.1 Effect of polymer composition

Introduction

Poly (vinylidene fluoride) (PVdF) is a technologically important semicrystalline polymer and polymer electrolytes based on PVdF are expected to have high anodic stability due to strong electron withdrawing functional group [1]. PVdF has high permittivity, relatively low dissipation factor and high dielectric constant, which assist in greater ionization of lithium salt, providing a high concentration of charge carriers. Poly (vinyl chloride) (PVC) is commercially available polymer, which acts as good mechanical stiffener and highly compatible with many polymers [2, 3].

Jacob et al. [4] studied the effects of PEO on PVdF-LiClO₄ complex and reported the conductivity value as 2.62x10⁻⁵ Scm⁻¹ at room temperature. Periyasamy et al. [5] have made an electrochemical investigation on PVdF based gel polymer electrolytes with the addition of EC and PC as plasticizers and reported the ionic conductivity of the order of 10⁻⁴ – 10⁻³ Scm⁻¹ and also mentioned that certain films were found to be fragile.

With a view to improve both mechanical strength and conductivity, an attempt is made on PVdF/PVC based blend electrolytes with the incorporation of LiBF₄ as salt with various compositions of PVdF and PVC are prepared and reported here. The best composition of PVdF and PVC has been optimized so as to enable for use in lithium battery applications.
Experimental

PVdF and PVC were dried under vacuum oven at 100° C for 10 hrs. LiBF₄ was used after drying it in vacuum at 160° C for 10 hrs. The polymer compositions are prepared as (100-x) PVdF- x PVC - LiBF₄ (8), where x = (a) 0, (b) 10, (c) 20,...100 ratios. Throughout this investigation, the quantity of salt was fixed as 8 wt %. The required amounts of polymers and salt were dissolved in tetrahydrofuran (THF). After complete dissolution, these solutions were mixed together and a homogeneous solution was obtained by stirring for 24 hours at room temperature. The polymer electrolyte was prepared by casting the solution on to a glass plate. The obtained films were characterized and discussed.

4.1.1 XRD studies

X-ray diffraction studies were conducted to examine the crystallinity of the polymer electrolytes. XRD pattern of pure PVdF, PVC, LiClO₄ and LiBF₄ are shown in Fig 4.1. XRD pattern of PVdF-PVC-LiBF₄ complexes are depicted in Fig 4.2. Sharp peaks at 18.1° and 19.7° in pure PVdF are shifted as a broad peak at 20.4° in all complexes, which is due to the incorporation of lithium salt. Small broad peak at 26.4° in pure PVdF is completely absent in polymer complexes. It is also observed that the intensities of the shifted peaks are greatly reduced in complexes, which implies that the addition of salt has disturbed the crystalline region of the polymer electrolytes and increases the amorphous phase [6]. The peak observed in fig 4.2fk is broader than the peak observed in fig 4.2ace. It reveals that the amorphicity of the films 4.2fk is higher than films 4.2ace. In fact, the amorphicity of the films (fig 4.2fk) is higher, the ionic conductivity of the films becomes very less because the PVC rich phase exhibits mechanically rigid phase, hence it blocks the mobility of ion in the polymer matrix [7]. Further, the film 4.2a & b showed mechanically fragile and
exhibited considerably higher conductivity than other films. In connection with mechanical stability and conductivity, the 80:20 ratio of PVdF/PVC polymer complex (film 4.2c) has exhibited considerably better performance than other complexes. It is concluded that the XRD pattern of fig 4.2c shows broad diffraction band, which reveals that the sample is more amorphous and leads to better ionic conductivity with good mechanical strength among the PVdF rich phase electrolytes. No peaks corresponding to pure LiBF4 are observed in the polymer complexes. It reveals that there is no excess salt in the polymer complexes.

4.1.2 FTIR studies

IR spectra of pure PVdF, PVC, LiCF3SO3, LiClO4 and LiBF4 are shown in Fig 4.3. FTIR spectra of the polymer complexes based on PVdF-PVC-LiBF4 are shown in Fig 4.4. FTIR spectra of PVdF - PVC - LiBF4 complexes in the range 2000 - 400 cm\(^{-1}\) are depicted in Fig 4.4(i). The vibrational peaks around 3010, 2980 and 1716 cm\(^{-1}\) in pure PVdF are assigned to CH\(_2\) asymmetric, symmetric stretching and C=C stretching vibration, which are shifted to 3020, 2978 and 1723 cm\(^{-1}\). The absorption peaks at 1274 and 1073 cm\(^{-1}\) are due to in-plane CH deformation and ring breathing mode and are shifted to 1280 and 1076 cm\(^{-1}\) in the Fig 4.4a. The absorption peaks for pure PVC at 2970, 1256, 1096 and 690 cm\(^{-1}\) are shifted to 2973, 1234, 1086 and 676 cm\(^{-1}\) in PVdF-PVC-LiBF4 complexes (Fig 4.4b,j). The medium intensity sharp peak appeared at 890 cm\(^{-1}\) is assigned to CH rocking vibration of PVC and it shifted to 898 cm\(^{-1}\) in the complexes. At higher percentage of PVC, the peak intensity becomes diminished, which may be due to the greater interaction of polymer with PVdF and salt.

The vibrational peaks pertaining to pure LiBF4 at 1633 and 1083 cm\(^{-1}\) are shifted to 1640 and 1080 cm\(^{-1}\) in the polymer complexes. Some absorption peaks of
PVdF (796 and 532 cm⁻¹), PVC (1333, 690 and 494 cm⁻¹) and LiBF₄ (1320 and 520 cm⁻¹) are found to be absent in the complexes. In addition to this some new peaks are observed at 2297, 1541, 1516 and 1122 cm⁻¹ in the complexes.

The vibrational peaks at 1382 and 1224 cm⁻¹ [8] are assigned to C-F stretching vibration and CF₂ stretching vibration of PVdF. A weak band at 976 cm⁻¹ is assigned to vinylidene group shown in Fig 4.4. The frequency at 878 cm⁻¹ is assigned to C-H out of plane bending. The peak at 638 cm⁻¹ is due to C-Cl stretching vibration of PVC in the complexes. All the above analysis and shifting of peaks established the complex formation in PVdF-PVC-LiBF₄ system.

4.1.3. Electrical Conductivity

Fig 4.5 shows the complex impedance plot of PVdF-LiBF₄, PVC-LiBF₄ and PVdF(80)-PVC(20)-LiBF₄ complexes at room temperature. The impedance response behaviour in Fig 4.5a & b shows the disappearance of the high frequency semicircular portion, which leads to conclude that the total conductivity is purely based on ion conduction. The small arc in high frequency region (film c) can be attributed to the electrolyte resistance [9]. The electrical conductivity of the polymer electrolyte has been calculated from the bulk resistance (Rₐ) from impedance plot, known area (A) and thickness (t) and these values are shown in Table 4.1. The room temperature conductivity is found in the order of 10⁻⁵ – 10⁻⁷ S cm⁻¹ for various weight percentage of PVdF and PVC with LiBF₄ as salt. The electrolyte containing PVdF - LiBF₄ shows higher conductivity than other complexes, but its mechanical strength is poor. In order to improve its mechanical strength, PVC is added with PVdF - LiBF₄ system in the ratio of (100-x) PVdF- x PVC, where x = 0, 10, 20,... etc. Among the above compositions, PVdF(80)-PVC(20)-LiBF₄ showed better mechanical strength and higher conductivity 1.026 x 10⁻⁵ S cm⁻¹ in the absence of plastiziers. Even though
PVC-LiBF$_4$ electrolyte shows more amorphous phase, its conductivity is less due to higher percentage of PVC, which behaves as a solid like medium, and the mobility of ion is restricted to penetrate this phase. Due to such a blocking of the PVC rich phase, the transport of ion must occur through indirect motion along a convoluted path restricted, which would be responsible for the low conductivity.

The complex impedance diagram of PVdF (80)-PVC (20)-LiBF$_4$ is depicted in Fig. 4.6 in the temperature range of 303-363 K. The plot indicates that the conductivity increases with increasing of temperature. As temperature increases, the polymer can expand easily and produces free volume. Thus, ions solvated molecules or polymer segments can have a free mobility through this free volume and hence the conductivity increases [10]. Fig 4.7 represents the Arrhenius plot for ionic conductivity of PVdF (80)-PVC (20)-LiBF$_4$ polymer complex. The overall feature of the Arrhenius plot is quite similar for the polymer films. The curvature shown in this plot indicates that the ionic conduction obeys the VTF relation that describes the transport properties in a viscous matrix.

4.1.4 Thermal Studies

TG and DTA thermographs of PVdF-LiBF$_4$, PVdF (80) - PVC (20) - LiBF$_4$ and PVC - LiBF$_4$ results are depicted in Fig 4.8. It is observed from the TG curve (fig 4.8a) that there is no weight loss upto 260° C, which indicates that the sample is free from moisture. Fig 4.8b shows a gradual weight loss of about 3-5% upto 263° C, which may be due to the evaporation of moisture from the electrolyte. It is well known that the thermal stability of PVdF-LiBF$_4$ and PVC-LiBF$_4$ samples uniformly extended up to ~270° C. The endothermic peak observed at 263°C in PVdF (80)-PVC (20)- LiBF$_4$ film shows its maximum thermal stability, which lies between the melting temperature of pure PVdF and PVC. This implies that the addition of PVC to

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PVdF-LiBF₄ system increases its thermal stability and lowering of Tₘ indicates the miscibility of polymer and salt. From DTA curve, the endothermic peaks observed at around 160°C and 310°C in Fig. 4.8a & b reveal the decomposition of PVdF and polymer electrolyte respectively. The peak at 95°C in Fig. 4.8c is due to the loss of moisture in the electrolyte. Hence it is obvious that PVdF(80)-PVC(20)-LiBF₄ polymer electrolyte can be used effectively upto 263°C.

**Conclusion**

Solid polymer blend electrolytes comprising of PVdF-PVC-LiBF₄ for different compositions of (1-x) PVdF- x PVC - LiBF₄ (where x = 0, 10, 20, ... etc) are prepared. The structural, complexation and thermal behaviours have been confirmed by XRD and FTIR studies. It is observed that PVdF(80)-PVC(20)-LiBF₄ complex gives appreciable conductivity above room temperature with good mechanical strength.
Fig 4.1 X-ray diffraction patterns of pure PVC, PVdF, LiClO₄, LiBF₄ and LiCF₃SO₃

Fig 4.2 XRD patterns of (100-x) PVdF- x PVC-LiBF₄ (where x = (a) 0, (b) 10, (c) 20, ..., 100)
Fig 4.3 FTIR spectra of pure PVdF, PVC, LiCF$_3$SO$_3$, LiClO$_4$ and LiBF$_4$
Fig 4.4 FTIR spectra of (100-x) PVdF- x PVC-LiBF$_4$

(Where x = (a) 0, (b) 10, (c) 20..., 100)
Fig 4.4(i) FTIR spectra of (100-x) PVdF-x PVC-LiBF$_4$ complexes (the range from 2000 – 400 cm$^{-1}$) (where x = (a) 0, (b) 10 , (c) 20... , 100)
Fig 4.5 Complex impedance plot of (a) PVdF (100)- LiBF$_4$, (b) PVdF (80)-PVC (20)- LiBF$_4$ and (c) PVC (100)-LiBF$_4$

Fig 4.6 Complex impedance plot of PVdF(80)-PVC(20)-LiBF$_4$ system in the temperature range of 302-363 K.
Fig 4.7 Arrhenius plots of (100-x) PVdF-x PVC-LiBF₄ complexes. (where x = (a) 0, (b) 10, (c) 20,...100)
Fig 4.8 TG/DTA curves of (a) PVdF(100)-LiBF₄, (b) PVdF(80)-PVC(20)-LiBF₄ and (c) PVC(100)-LiBF₄
Table 4.1

Conductivity values of (1-x) PVdF - (x) PVC - LiBF₄ (where x = (a) 0, (b) 10, (c) 20,... 100)

<table>
<thead>
<tr>
<th>Film</th>
<th>Conductivity $\sigma = (x10^{-5})$ S/cm</th>
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<tbody>
<tr>
<td></td>
<td>303K</td>
</tr>
<tr>
<td>b</td>
<td>2.271</td>
</tr>
<tr>
<td>c</td>
<td>1.026</td>
</tr>
<tr>
<td>d</td>
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</tr>
<tr>
<td>e</td>
<td>0.206</td>
</tr>
<tr>
<td>f</td>
<td>0.245</td>
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<tr>
<td>g</td>
<td>0.234</td>
</tr>
<tr>
<td>h</td>
<td>0.204</td>
</tr>
<tr>
<td>i</td>
<td>0.127</td>
</tr>
<tr>
<td>j</td>
<td>0.065</td>
</tr>
<tr>
<td>k</td>
<td>0.087</td>
</tr>
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</table>
Section B

4.2 Effect of lithium salt concentration in PVdF/PVC based polymer electrolyte

Introduction

The addition of salt with polymer has a highly disturbing effect on the arrangement of polymer chain and the ensuing conductivity. In order to realize high lithium ion conduction (i) polymer should have compatibility with inorganic salts and their disassociated ions, (ii) polymer should provide a connected polar domain as conduction path and (iii) polymer should not interact with carrier ions too strongly in order to avoid complete trapping of carrier ions.

Experimental

In order to focus the above parameters, an appropriate amount of salt ratio is highly necessary to achieve a favorable conductivity in lithium ion batteries. In the present study, polymer films consisting of PVdF (80) - PVC (20) – with the different weight ratios of salt such as LiBF$_4$ and LiClO$_4$ were prepared. Throughout this investigation, PVdF and PVC were kept constant as 80:20 weight % as following from the previous work.

4.2.1 X-ray Diffraction studies

XRD patterns of (i) PVdF(80) – PVC(20) - LiBF$_4$ and (ii) PVdF(80) - PVC(20) - LiClO$_4$ complexes are shown in Fig 4.9 and these patterns reveal more amorphous phase, which may be due to the addition of salt such as LiBF$_4$ and LiClO$_4$ with PVdF - PVC polymer blend. The addition of salt at various weight % induces significant disorder in polymer structure, hence the crystallinity of polymers were abruptly reduced, as evident from the broad peak obtained at $2\theta = 20.5^\circ$ in Fig 4.9a-e. Similar changes are also observed in the Fig 4.9f-j with the addition of LiClO$_4$ as salt in the polymer blend. A less intense and broad peak has been observed at $2\theta = 20.32^\circ$ in all
complexes irrespective of salts. The broad XRD peak reveals that the polymer blend containing 8-weight % of salt is found to be more amorphous. This leads to higher ionic conductivity.

4.2.2 FTIR Studies

FTIR spectra of (i) PVdF(80) – PVC(20) - LiBF$_4$ and (ii) PVdF(80)-PVC(20)-LiClO$_4$ complexes are shown in Fig 4.10. FTIR spectra of PVdF - PVC - LiBF$_4$ / LiClO$_4$ complexes in the range 2000 - 400 cm$^{-1}$ are depicted in Fig 4.10(i). It is observed from the FTIR spectra that no peaks have occurred from 4000 – 3100 cm$^{-1}$, which reveals that the samples are free from moisture content. The absorption peaks of pure PVdF (2980, 1716, 1407, 1224 and 857 cm$^{-1}$), PVC (2913, 1426, 690 and 603 cm$^{-1}$), LiBF$_4$ (1633 and 1320 cm$^{-1}$) are shifted to (2975, 1723, 1405, 1234 and 838 cm$^{-1}$), (2910, 1404, 682 and 611 cm$^{-1}$) and (1644 and 1321 cm$^{-1}$) in complexes. The absorption peak at 2957 cm$^{-1}$ is shifted to 2973 cm$^{-1}$ and the vibrational peaks at 1097 and 1463 cm$^{-1}$ pertaining to LiClO$_4$ disappeared in the complexes. The vibrational peaks in PVdF (796 and 532 cm$^{-1}$), PVC (1426, 1256 and 1096 cm$^{-1}$) and LiBF$_4$ (2346 cm$^{-1}$) are absent in the polymer complexes. The vibrational peaks 1328, 1234, 686 and 610 cm$^{-1}$ are assigned to CH$_2$ deformation, in-plane CH deformation, C-Cl stretching and cis CH wagging in PVC. The absorption peaks at 1655, 1404 and 1235 cm$^{-1}$ are due to C=C stretching, C-F stretching and very strong mode of –CF$_2$- ring breathing vibrational modes in PVdF. The absorption band appearing at 838 cm$^{-1}$ may be assigned to the characteristic frequency of vinylidene compounds. The absorption band at 940 cm$^{-1}$ is assigned to the formation of perchlorate anion [11] and it is shifted to 975 cm$^{-1}$ in the polymer complexes. Further, this peak has again shifted to 985 cm$^{-1}$, which is evident from Fig 4.10. This implies the aggregation of multiple ions when salt concentration is increased (>8 wt %). Moreover the vibrational peak
observed at 712 cm$^{-1}$ is attributed to Li ions and it is shifted to 740 cm$^{-1}$ in polymer complexes with weak intensity and the characteristics frequencies related to the BF$_4^-$ and ClO$_4^-$ ions had no obvious changes, hence it was assumed that the interaction inside the system mainly occurred between the Li ions and the polymer chain molecules. As the salt content in the complex increases, the peak intensities of the bands first decrease up to 8 wt %, this corresponds to maximum conductivity. Upon further increasing the salt concentration (i.e. >8 %), the peak intensity of the electrolytes is also found to increase. Consequent to this, a decrease in conductivity is observed. This is an indication that the complex becomes more ordered when salt content increases beyond a particular concentration (i.e. 8 wt %) of LiBF$_4$ or LiClO$_4$.

4.2.3 Electrical conductivity studies

The room temperature conductivity of the polymer electrolytes with different salt ratios has been measured by complex impedance spectroscopy. Fig 4.11 illustrates the impedance pattern of (i) PVdF(80)-PVC(20)-LiBF$_4$ and (ii) PVdF(80)-PVC(20)-LiClO$_4$ systems containing 8 weight percentage of salt in polymer blend at room temperature. This figure shows an arc followed by a slanted spike. The high frequency semi circular region is attributed to the electrolyte resistance. The electrical conductivity of the electrolyte was measured from the observed bulk resistance, the known thickness and surface area of the film. It is observed that the conductivity values of PVdF - PVC - Li salt complexes are $10^3$ times higher than the host polymer. The highest room temperature conductivities observed at the salt concentration of 8 wt % for PVdF (80) - PVC (20) - LiBF$_4$/LiClO$_4$ (8 wt %) complexes are $7.026 \times 10^{-5}$ S/cm and $5.781 \times 10^{-5}$ S/cm respectively. The improved ionic conductivity is due to the enhancement of the ionic mobility and the larger number of carrier ions as already reported [12]. The conductivity of the polymer electrolyte initially increases due to
the increment of the number of charge carriers being introduced into the complex, which is evident from Table 4.2. As salt concentration increases in higher percentage, the number of carrier ions and $T_g$ of the complex increase and this leads to stronger ion – ion interaction and, there by, possibly impedes the polymer backbone’s segmental motion and ultimately causes a lowering of the conductivity [13], in other words, the higher concentration in the amorphous region may increase both the number of carrier ions and $T_g$. The decrease in ionic mobility due to the increasing of $T_g$ seems to nullify the increase in the number of carrier ions at higher salt concentrations. Thus, ionic conductivity decreases as the salt concentration increases, which is represented in the Fig 4.12. A similar phenomenon occurs in PAN, PEO or PPO based electrolytes with the addition of LiClO$_4$ [14, 15].

The temperature dependence of the electrical conductivity of PVdF – PVC containing various concentrations of lithium salts such as LiBF$_4$ and LiClO$_4$ is shown in Fig 4.13. The conductivity of the electrolyte increases with increase of temperature. This implies that the increase in conductivity does not originate from the SPE’s residual organic solvent, but is purely due to the segmental motion of polymer backbone. As the temperature approaches the $T_g$ of SPE, the polymer backbone’s segmental motion is severe [14]. Thus, the present finding corroborates previous ones [16,17]. The temperature dependent conductivity plots follow Arrhenius behaviour for the electrolytes.

4.2.4 Thermal analysis

The Thermogravimetric and differential thermal analyses of (i) PVdF(80)-PVC(20)-LiBF$_4$ (8 wt%) and (ii) PVdF(80)-PVC(20)-LiClO$_4$ (8 wt%) are depicted in Fig 4.14. The TG curve shows a gradual weight loss of about 10-12 % from room temperature to 95°C, which may be due the evaporation of moisture or fluorine
content in the polymer electrolytes [18,19]. Volatilization of monomers and oligomers adsorbed in the matrix can also be responsible for this initial weight loss [20]. The second weight loss of about 20% occurs at around 296°C as shown in Fig. 4.14 a & b, which may be due to the decomposition of the polymer electrolyte. From DTA curve, it is observed that the endothermic peak occurring at 162°C reveals the melting temperature of PVdF, which is in good agreement with the value reported by Muniyandi et.al and Jiang et.al [3, 21] in DSC discussion of PVdF based gel electrolytes. The gradual weight loss of about 3-5% at 100-200°C is attributed to the decomposition of low molecular weight compounds in the complex. The second weight loss with increased temperature is a consequence of the increase in T_g value [22]. The endothermic peak occurring at about 300°C reveals the complete decomposition of polymer electrolytes with the weight loss of about 30% in the complexes. This result indicates the electrolytes is stable over 200°C and are preferred in lithium polymer batteries.

**Conclusion**

Polymer electrolytes based on PVdF- PVC with LiBF_4 / LiClO_4 as salt at different concentrations were prepared. The highest room temperature ionic conductivity is observed at a salt concentration of 8-wt% for both LiBF_4 and LiClO_4 based polymer complexes. The conductivity results for all polymer electrolytes show very similar Arrhenius behaviour, irrespective of the salt concentrations. The XRD studies explained the occurrence of complexation in amorphous phase and TG/DTA revealed the thermal stability of the electrolytes. FTIR studies confirmed the strong coordination between the molecules of PVdF-PVC and lithium salt.
Fig 4.9 XRD spectra of pure (i) PVdF (80)-PVC (20) - (x) LiBF$_4$
[where x= (a) 4, (b) 6, (c) 8, (d) 10, (e) 12]
(ii) PVdF (80)-PVC (20) - (x) LiClO$_4$
[where x= (f) 4, (g) 6, (h) 8, (i) 10, (j) 12]
Fig 4.10 FTIR spectra of pure (i) PVdF(80)-PVC(20)-LiBF$_4$(x) 
[where x= (a) 4, (b) 6, (c) 8, (d) 10 (e) 12] 
(ii) PVdF(80)-PVC(20)-LiClO$_4$(x) 
[where x= (f) 4, (g) 6, (h) 8, (i) 10 (j) 12]
Fig 4.10(i) FTIR spectra of pure (i) PVdF(80)-PVC(20)- LiBF$_4$ (x) in the range of 2000-500 cm$^{-1}$ [where x= (a) 4, (b) 6, (c) 8, (d) 10 (e) 12]

(ii) PVdF(80)-PVC(20)- LiClO$_4$(x) in the range of 2000-500 cm$^{-1}$
[where x= (f) 4, (g) 6, (h) 8, (i) 10 (j) 12]
Fig 4.11 Impedance diagram of (i) PVdF(80)-PVC(20)-8 % of LiBF₄
(ii) PVdF(80)- PVC(20)- 8 % of LiClO₄ at 304 K.

Fig 4.12 Concentration of salt Vs room temperature conductivity
Fig 4.13 Arrhenius plots of Log (σ) against reciprocal temperature for (i) PVdF(20)-PVC(20)-X % of LiBF₄ and (ii) PVdF(20)-PVC(20)-X % of LiClO₄, where X = 4, 6, 8, 10 and 12 weight %.
Fig 4.14 TG/DTA plots of (i) PVdF(80)-PVC(20)-8 % of LiBF₄

(ii) PVdF(80)-PVC(20)-8 % of LiClO₄
Table 4.2
Conductivity values of PVdF (80)-PVC (20) - X% of salt

<table>
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<th>X %</th>
<th>Conductivity (σ) = x 10⁻⁵ S/cm</th>
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<tr>
<td></td>
<td>303K</td>
</tr>
<tr>
<td>-----</td>
<td>--------</td>
</tr>
<tr>
<td>(i) PVdF (80)-PVC (20)-LiBF₄ (X %)</td>
<td></td>
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<tr>
<td>X= 4</td>
<td>0.317</td>
</tr>
<tr>
<td>X= 6</td>
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<tr>
<td>(ii) PVdF (80)-PVC (20)-LiClO₄ (X %)</td>
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<tr>
<td>X= 4</td>
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<td>X= 6</td>
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<td>X=10</td>
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<tr>
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</table>
Section C

4.3 Effect of plasticizers in PVdF/PVC polymer electrolyte

Introduction

Even though the PVdF/PVC (80:20) ratio of polymer complex exhibits favorable mechanical properties, their electrical conductivities are not appreciably high at room temperature. Various attempts have been made to modify the structure of polymer electrolytes in order to improve their electrical, electrochemical and mechanical properties. Generally plasticizers are used to change the mechanical and electrical properties of polymer electrolytes by reducing the degree of crystallinity and lowering the glass transition temperature $T_g$. Moreover the plasticized polymer electrolytes using propylene carbonate, ethylene carbonate, dimethyl formamide etc, have greatly improved the electrical conductivity of the electrolytes.

Experimental

Based on the optimization of PVdF/PVC and salt, solid polymer electrolytes (SPE) consisting of PVdF (20) – PVC (5) – LiClO$_4$ (8) – X (67) (where X = (a) DMF, (b) EC, (c) YBL, (d) PC, (e) DMSO, (f) DMP, (g) DBP and (h) BEP) systems were prepared using solvent casting technique. Followed by our previous investigations [23], polymers (PVdF/PVC) were fixed as 4:1 ratio and LiClO$_4$ is fixed as 8 wt % in this work. The effects of different plasticizers are discussed in terms of their ionic conductivity values measured from ac impedance studies. Complex formation and the thermal stability of the electrolytes were analyzed using XRD, FTIR and TG/DTA spectroscopic techniques.
4.3.1 XRD Studies

The structural analysis of the polymer samples was examined by XRD measurements to confirm their amorphicity. XRD spectra of PVdF (20) – PVC (5) – LiClO₄ (8) – X (67) (where X = DMF, EC, YBL, PC, DMSO, DMP, DBP and BEP) systems are depicted in Fig 4.15. From these patterns, it is possible to conclude that the incorporation of plasticizer in the polymer electrolyte has completely disturbed the characteristic peaks of PVdF appearing at 18.1° and 19.7° (Fig 4.1) and they are shifted as one broad peak at 2θ = 20.4° in the polymer complexes. No other peaks are observed corresponding to PVC and LiClO₄ in the polymer complexes, which indicate the complete dissolution of lithium salts in the polymer matrices. The diffraction peak is broader and of less intensity in all the complexes. The addition of plasticizer with polymer complex induces the amorphicity and produces greater ionic diffusivity resulting in high ionic conductivity.

4.3.2 FTIR Studies

FTIR spectra of PVdF (20) – PVC (5) – LiClO₄ (8) – X (67) (where X = DMF, EC, YBL, PC, DMSO, DMP, DBP and BEP) systems are shown in Fig 4.16. The vibrational peaks of pure PVdF (3010, 2980, 1735, 976 and 879 cm⁻¹), PVC (2913, 2849, 1734, 1717, 1650, 1541 and 603 cm⁻¹) and LiClO₄ (2954, 2853, 1632, 1097, 720 and 626 cm⁻¹) are shifted to (3014, 2995, 1739, 966, and 886 cm⁻¹), (2930, 2864, 1739, 1720, 1659, 1554 and 626 cm⁻¹) and (2978, 2864, 1659, 1094, 727 and 636 cm⁻¹) in the polymer complexes. The absorption peaks of pure PVdF (1716, 1407, 1224 and 532 cm⁻¹), PVC (2816, 1426, 1333 and 1256 cm⁻¹) and LiClO₄ (3527, 1463 and 556 cm⁻¹) are found to be absent in the complexes. Some new peaks have been observed at 1518, 1489 and 1388 cm⁻¹ in the complexes. The absorption peaks at 1650, 1257, and 976 cm⁻¹ are assigned to C=C skeletal stretching vibration, -CF₂- and
C-F stretching vibrations of vinylidene group. A sharp peak at 875 cm$^{-1}$ is assigned to the vinylidene group frequency of PVdF. Peaks at around 618, 762, 796 and 840 cm$^{-1}$ for CH$_2$ rocking mode regions appear with considerable shift in complexes. The predominant peaks at 2980 and 2850 cm$^{-1}$ are commonly represented the CH$_2$ asymmetrical and symmetrical vibration. Further the peaks at 954 and 630 cm$^{-1}$ are assigned to trans CH rocking and cis CH wagging of PVC. The peak at 1389 cm$^{-1}$ indicates the CH$_3$-C- vibration of propylene carbonate. The peak at 1777 cm$^{-1}$ represents the C=O stretching vibration of γBL and it is shifted to 1771 cm$^{-1}$ in the lower region (Fig 4.16f). The vibrational frequency of C=O at 1781 cm$^{-1}$ indicates the interaction of the plasticizer with LiClO$_4$. As reported by Colthup [15,24], the peak occurring at 1789 cm$^{-1}$ in the complex is an indication of chloro carbonate. The above results indicate the complex formation of polymer, salt and plasticizer.

4.3.3 Conductivity studies

The ionic conductivities of PVdF- PVC- LiClO$_4$ with plasticized complexes are derived from the complex impedance measurements. The variation of conductivity as a function of different plasticizers is displayed in Fig 4.17 at ambient temperature. The plot indicates that the conductivities of polymer electrolytes are varied in the order of $10^{-4}$-$10^{-3}$ S/cm for the different plasticized complexes. The addition of plasticizer in the polymer electrolyte increases the overall conductivity. It appears that the addition of the plasticizer with polymer electrolyte causes a decoupling of the ionic motion from that of the polymer chain and increases ionic conductivity by decreasing the potential barrier to ionic transport.

Fig 4.18 shows the impedance diagram of PVdF (20) - PVC (5) - LiClO$_4$ (8) with 67 wt% of plasticizer at room temperature. The absence of the high frequency semicircular portion leads to the conclusion that the current carriers are ions and
therefore the total conductivity is mainly due to ion conduction [4]. It is observed that the conductivity values of PVdF (20)- PVC (5)-LiClO₄ (8)- with plasticizer are considerably higher in the order of EC, PC, γBL etc., as evident from Table 4.3. It reveals that the ionic mobility and conductivity depends on the specific nature of the plasticizer such as viscosity, dielectric constant, polymer- plasticizer interaction and ion – plasticizer interaction. In this investigation, higher conductivity value is obtained for the EC based polymer complex due to its high dielectric constant. The high dielectric constant of the plasticizer leads to an increase in the salt dissociation, whereas their low viscosity leads to high mobility and hence higher conductivity. In general, it is believed that the conductivity increases as the degree of crystallinity decreases or, in other words, the flexibility of the polymeric backbone increases. The increasing free volume would facilitate the motion of ion charge [10], i.e. the migration of ions through the amorphous regions.

The variations of conductivity as a function of temperature for polymer complexes are displayed in Fig 4.19. It is found that the conductivity increases with increasing temperature. As reported by Druger et.al [25, 26], the increase in conductivity with temperature is due to polymer segmental motion. At higher temperature, the segmental motion either permits the ions to hop from one site to another or it provides necessary voids for ions to move in the polymer matrix. Polymer chains acquire faster internal modes in which the bond rotations produce faster segmental motion [27]. This, in turn, favours the hoping inter and intra – chain ion movements and the conductivity of the polymer electrolyte increases accordingly. Temperature - dependent ionic conductivity plots seem to obey the VTF relation [28-30], which describes the transport properties in a viscous matrix.
4.3.4 Thermal analysis

The TG/DTA measurements are carried out under nitrogen atmosphere to investigate the thermal stability of PVdF(20)-PVC(5)-LiClO$_4$(8)-X(67) (where X- (a) DMF, (b) EC, (c) YBL, (d) PC and (e) DMSO) plasticized systems are depicted in Fig 4.20. From the thermographs, it is clearly seen that there is a small weight loss of 2-3% at around 55° and 98° C in all the complexes, which is due to the evaporation of residual solvent or moisture or any other volatile impurities present in the polymer electrolytes. Above 100° C, no further weight loss is observed upto 150°- 165° C in all the complexes, which is due to the melting temperature of PVdF in the polymer complexes. Beyond this temperature, a heavy weight loss of about 20-30 % is observed. It reveals an initial decomposition of the polymer electrolytes, which is also evident from DTA curves. Moreover peaks at 208°, 235°, 287°, 286°, and 227° C reveal the evaporation or decomposition of plasticizers such as DMF, EC, YBL, PC and DMSO respectively. The broad endothermic peak at about 160° C in DTA curve is attributed to the melting of PVdF and exothermic peaks at 290° C and 385° C in the polymer complexes are attributed to the melting of PVC or the second decomposition of polymer systems. From the above observation, it is concluded that the thermal stability of the polymer electrolytes are stable up to 160° C.

4.3.5 Surface Morphological Studies

SEM photographs of unplasticized and plasticized polymer electrolytes under x2000 magnification are shown in Fig 4.21. In contrast to the micrographs, it is observed that the grain sizes are uniform and no trace of spherulites structure is noticed. The dark region in the SEM photograph is attributed to the amorphous part of the films. The surfaces of the electrolytes show fine holes in the polymer matrix, which aid ion mobility. It is well known that the formation of porous structure is a
complex process that depends on the interaction of the solvent with the polymers and is kinetically controlled by relative rates of evaporation of compounds. Further, it is confirmed that the amorphous nature of the electrolytes is increased due to the addition of salt and plasticizer.

Conclusion

This study explained the salient features of the PVdF-PVC blend based polymer electrolytes towards lithium battery applications. Solid polymer electrolytes comprising of PVdF-PVC-LiClO₄ with the addition of different plasticizers are prepared. DMF, EC, YBL and PC based polymer electrolytes exhibit higher conductivity than other plasticized polymer films. It is also proved that the amorphous phase aids the conductivity as is evident from the XRD studies. The complex formation and thermal behaviour of the samples were confirmed by FTIR and TG/DTA studies.
Fig 4.15 XRD spectra of PVdF(20)-PVC(5)-LiClO₄(8)-X(67) where (a) X=DMF (b) X=EC (c) X=YBL (d) X=PC (e) X=DMSO (f) X=DMP (g) X=DBP and (h) X=BEP
Fig 4.16 FTIR spectra of PVdF(20)-PVC(5)-LiClO$_4$(8)-X(67) where (a) X=DMF (b) X=EC (c) X=YBL (d) X=PC (e) X=DMSO (f) X=DMP (g) X=DBP and (h) X=BEP
Fig 4.17 The plot of conductivity as a function of different plasticizers

Fig 4.18 Impedance diagram of PVdF (20)-PVC(5)-LiClO$_4$(8)-X (67) where (a) X=DMF (b) X=EC (c) X=YBL (d) X=PC (e) X=DMSO (f) X=DMP (g) X=DBP and (h) X=BEP at ambient temperature.
Fig 4.19. Arrhenius plots of Log (σ) against reciprocal temperature for PVdF (20)-PVC(5)-LiClO₄ (8)-X (67) where (a) X=DMF  (b) X=EC  (c) X=YBL  
(d) X=PC  (e) X=DMSO  (f) X=DMP  (g) X=DBP and  (h) X=BEP
Fig 4.20. TG/DTA plots for PVdF (20)-PVC(5)- LiClO₄(8)-X (67) where (a) X=DMF (b) X=EC (c) X=YBL (d) X=PC (e) X=DMSO
Fig 4.21 SEM photos of (a) PVdF(80)-PVC(20)-LiBF₄(8)
(b) PVdF(80)-PVC(20)-LiClO₄(8) (c) PVdF(20)-PVC(5)-LiClO₄(8)-DMF(67)
(d) PVdF(20)-PVC(5)-LiClO₄(8)-EC (67) (e) PVdF(20)-PVC(5)-LiClO₄(8)-YBL (67) (f) PVdF(20)-PVC(5)-LiClO₄(8)-PC(67)
Table 4.3
Conductivity data for polymer electrolytes PVdF (20)-PVC (5)-LiClO4 (8)-X (67)
where X = DMF, EC, γBL, PC, DMSO, DMP, DBP and BEP

<table>
<thead>
<tr>
<th>Systems</th>
<th>Conductivity values (x10⁻³ S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
</tr>
<tr>
<td>DMF</td>
<td>0.863</td>
</tr>
<tr>
<td>DMSO</td>
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<tr>
<td>DMP</td>
<td>0.183</td>
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<tr>
<td>DBP</td>
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</tr>
<tr>
<td>BEP</td>
<td>0.024</td>
</tr>
</tbody>
</table>
References


