Optical And Ionic Conductivity Studies Of Gel Polymer Electrolytes Based On PVDF:CH₃COOLi

G. Sunita Sundari, K. Sravanthi and Harikrishna Erothu

Abstract: Gel polymer electrolytes (GPEs) received much attention because of both characteristics like solid and liquid electrolytes and much more applicable towards lithium ion batteries (LIBs). A series of PEs at room temperature has been prepared and discussed. Polymer electrolyte (PE) films are prepared using solution casting technique based on poly(vinylidene fluoride) (PVDF) and lithium acetate (CH₃COOLi) with different weight ratios (PVDF:CH₃COOLi wt %) (60:40, 70:30, 80:20 wt %). FTIR analysis used to know the various functional groups in PE samples. From optical absorbance studies, the band gap values are studied and least value is 3.0 eV. From AC impedance studies, PVDF:CH₃COOLi (60:40 wt %) shown the highest value of conductivity is 6.785 x 10⁻² S/cm at 303 K.

Index Terms: Gel polymer electrolytes, Lithium salt, PVDF, Conductivity studies, UV-Visible spectroscopy.

1. INTRODUCTION

Polymer electrolyte (PE) has been a very crucial material in many electronic devices like dye-sensitized solar cell (DSSC’s), fuel cells sensors and super capacitors, lithium ion batteries as it acquires ion transport [1-2]. The intension of solvating inorganic salts in polymer develop ion conduction in electrolyte is known as solid polymer electrolyte (SPE). Choosing a suitable polymer host is necessary where the functional groups in the polymer will be called as solvating groups, which can dissolve most of metal cations by initiating a coordination bond between them [3]. The key factors that influence the resulting interactions between polymer-metal ions are like molecular weight, structure, inter-space between atoms, behavior of the atoms joined to the polymer backbone, amount of branching. When subjected to electric field the cations moves from one coordinated site to another because of weak coordination between the sites along polymer chain and to the cations [4]. Recently, gel-type polymer electrolyte (GPE) has become more priority in the polymer electrolyte field. In GPE, the liquid constituents are trapped in polymer host matrix which can be treated as both liquid-type and solid-type electrolytes due to many advantages in both, such as flexible, high safety and high ionic conductivity [5]. PVDF is selected as host polymer due to its attractive properties high transparency, structure itself due to the existence of fluorine, carbon functional groups cause affect on detachment of lithium salts which favours to increase in charge carrier concentration and also increases electrochemical stability. The existence of fluorine, hydrogen and carbon atoms develops polymers with chemical and thermal stability which holds their thermoplastic nature, also allows ease of fabrication. Crystalline nature of PVDF has given attention for high dielectric constant which is inversely proportional to attractive force between cation and anion of lithium salt, which makes ease of ionization of lithium salt, which enhances ionic conductivity [6-8]. From experimental aspect, lithium ion batteries (LIBs) made up of GPEs should cope up with certain requirements such as excellent chemical stability, high ionic conductivity, electrochemical stability and favorable Li-ion transference number [9].

2.0 MATERIALS

Poly(vinylidene difluoride) (PVDF) with average molecular weight of ~ 320,000 g/mol and lithium acetate (CH₃COOLi) from Sigma-Aldrich and DMF solvent used directly without any further purification.

2.1 Preparation method

Polymer electrolytes are prepared using solution casting technique with different ratios of (PVDF:CH₃COOLi) (60:40, 70:30, 80:20 wt %). PVDF as host polymer and CH₃COOLi as dopant salt, DMF as solvent for complexation. The blended solution stirred until to get homogeneous solution and dried in polypropylene dishes to get films.

2.2 Characterization

Polymer electrolytes (PVDF:CH₃COOLi) with wt% (PVDF: 80:20, 70:30, 60:40) were subjected to different characterizations. FTIR spectroscopy revealed the presence of functional groups in material using Perkin Elmer Alpha-E spectrophotometer. Using JASCO V-670 spectrophotometer energy band gap of material is studied. Using HIOKI LCR HITESTER conductivity and dielectric studies are carried out with frequency range in between 42 Hz to 5000000 Hz.

3. Results and Discussion

3.1 FTIR

FTIR studies give the interaction of polymer electrolyte complexes and also defines the presence of various functional groups [10]. From Fig.1, FTIR spectra for various bending and stretching vibrations of molecules are recorded for PVDF:CH₃COOLi (80:20, 70:30, 60:40 wt %). Different wave number regions are observed, the peak at 1066 (cm⁻¹) is arising due to C-C symmetric stretching and sharp absorption peak at 1184 (cm⁻¹) is observed due to CH₂ twisting. Towards the higher wave number absorption peak observed at 1400 (cm⁻¹) is of CF stretching vibration. A new peak is arising at 1580 (cm⁻¹) due to addition of salt because of stretching vibration of C=O. The stretching of C-H and N-H bonds at
2355 (cm\(^{-1}\)) gives the absorption peak and is gradually decreased with increasing of salt concentration. At 3019 (cm\(^{-1}\)), an absorption peak is arising due to symmetric stretching \[11\-12\]. Because of OH functional group wide peak has appeared near 3064-3698 (cm\(^{-1}\)). The shifting of absorption peak at 672 (cm\(^{-1}\)) towards the lower wave number is due to \(-\text{CH}-\text{H}\) bending vibration \[13\-14\].

Table 1. FTIR Spectra of different functional groups from absorption data

<table>
<thead>
<tr>
<th>Frequency range (cm(^{-1}))</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>652</td>
<td>(-\text{CH}-\text{H}) bending</td>
</tr>
<tr>
<td>1066</td>
<td>C-C symmetric stretching</td>
</tr>
<tr>
<td>1184</td>
<td>(\text{CH}_2) twisting</td>
</tr>
<tr>
<td>1400</td>
<td>CF stretching</td>
</tr>
<tr>
<td>1580</td>
<td>C=C stretching</td>
</tr>
<tr>
<td>2355</td>
<td>N-H stretching</td>
</tr>
<tr>
<td>3019</td>
<td>symmetric stretching</td>
</tr>
<tr>
<td>3064-3698</td>
<td>OH stretching</td>
</tr>
</tbody>
</table>

3.2 Optical analysis

Optical analysis for different ratios of polymer electrolytes are shown in Fig. 2 (b), 2 (c) & 2 (d) with the wavelength region in between 200-8000 nm \[15\]. It is a direct method to calculate bandgap of the materials. From UV-Visible analysis optical band gap values are derived from Tauc’s plot \[16\]. The absorption coefficient value is,

\[
a(\nu) = T (k_\nu - E_g)^n
\]

Where, ‘\(E_g\)’ energy band gap, ‘\(T\)’ is constant structure of specimen, ‘\(k\)’ is Planck’s constant, ‘\(\nu\)’ represents frequency of incident light.

’a’ is absorption coefficient and photon energy is obtained as

\[
(2.303\times A)/d
\]

Where ‘A’ is absorbance, ‘d’ represents thickness of the sample.

From Fig. 2 (a), around 260-400 nm it clearly shows that by increasing salt ratio the absorption peak is decayed due to \(\pi - \pi^*\) transition \[17\]. The energy of photon excites from lower level to higher energy level. The number of possible transitions can be described as absorption edge \[18\-19\]. By increasing salt concentration for the ratio (PVDF: \(\text{CH}_3\text{COOLi}\) (60:40) has obtained least energy band gap and it is reduced from 4.3 (eV) to 3.0 (eV).
FIG. 2 (c) PVDF:CH\(_3\)COOLi (Pure PVDF, 80:20, 70:30, 60:40 wt %) polymer electrolytes for Indirect energy band gap.

FIG. 2 (d) PVDF:CH\(_3\)COOLi (Pure PVDF, 80:20, 70:30, 60:40 wt %) polymer electrolytes for Absorption edge.

TABLE 2 Band gap values for PVDF:CH\(_3\)COOLi based polymer electrolytes

<table>
<thead>
<tr>
<th>Polymer electrolytes of PVDF:CH(_3)COOLi</th>
<th>Band gap energy</th>
<th>Indirect band gap (eV)</th>
<th>Direct band gap (eV)</th>
<th>(E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVDF</td>
<td>4.9</td>
<td>3.9</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>PVDF:CH(_3)COOLi (80:20)</td>
<td>4.2</td>
<td>3.4</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>PVDF:CH(_3)COOLi (70:30)</td>
<td>3.8</td>
<td>3.0</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>PVDF:CH(_3)COOLi (60:40)</td>
<td>3.50</td>
<td>2.8</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

4.0 CONDUCTIVITY STUDIES

AC conductivity studies provide the conductivity of the material [22]. Here in this case we have plotted impedance spectra for different ratios of PVDF:CH\(_3\)COOLi (80:20, 70:30, 60:40) polymer electrolyte films with the help of HIoki LCR Hi-TESTER [23]. The cole-cole plots are drawn for both real and imaginary parts of impedance analysis by using the formula

\[
\sigma = \frac{T}{R_b} \times S
\]

Where ‘S’ is polymer electrolyte area, ‘R\(_b\)’ is bulk resistance and ‘T’ as width of the sample.

In the case of impedance analysis with the addition of salt concentration for different ratios of polymer electrolyte films, a semi-circular arc appears towards higher frequency and as frequency decreases the structure deforms to spikes [24]. From Fig. 3 (a), (b) and (c), reveals that as salt concentration increases spikes are obtained due to the effect of blocking electrodes effect. As salt concentration increases the crystallinity of the polymer decreased and amorphous phase approaches and hence it results in highest ionic conductivity [25]. As per the result the highest conductivity obtained for the ratio PVDF:CH\(_3\)COOLi (60:40) is 6.785\(\times\)10\(^{-7}\) S/cm.

FIG. 3(a) Impedance Spectrum of PVDF:CH\(_3\)COOLi (80:20 wt %) polymer electrolyte.

FIG. 3(b) Impedance Spectrum of PVDF:CH\(_3\)COOLi (70:30 wt %) polymer electrolyte.

FIG. 3(c) Impedance Spectrum of PVDF:CH\(_3\)COOLi (60:40 wt %) polymer electrolyte.

TABLE 3 Conductivity values for PVDF:CH\(_3\)COOLi based polymer electrolytes

<table>
<thead>
<tr>
<th>Combination of polymer electrolyte</th>
<th>Obtained Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80:20</td>
<td>3.854 (\times)10(^{-7})</td>
</tr>
<tr>
<td>70:30</td>
<td>2.678 (\times)10(^{-8})</td>
</tr>
</tbody>
</table>
5. CONCLUSION
Different weight percentages of polymer electrolyte films PVDF:CH₃COOLi (Pure PVDF, 80:20, 70:30, 60:40 wt %) are prepared by solution casting method. From FTIR analysis, various functional groups are figured out due to interaction of polymer and salt complexes. UV-visible spectroscopic studies define that the rapid electronic transitions are taken place when the salt ratio is increased which results in decreasing the energy band gap and is reduced from 4.3 to 3.0 (eV) for the ratio PVDF:CH₃COOLi (60:40 wt%). Impedance spectra revealed the effect of salt ratio results in enhancing the conductivity for the ratio PVDF:CH₃COOLi (60:40 wt%) obtained is 6.785×10⁻⁷ S/cm. From all these results, the material could be a good ionic mediator for battery applications.

ACKNOWLEDGMENTS
The authors thankful to Koneru Lakshmaia Education Foundation (KLEF) & Dr K. Swapna for supporting this work. Also thankful to UGC-DAE Kalpakam CSR-KN/CRS-120/2018-19/1058 and SR/FST/PS-1/2018/35 - Department of Science & Technology, Government of India.

REFERENCES
