Chapter 5 – Part A

Physical and electrochemical property of phosphonium ionic liquid based solid and gel polymer electrolyte for lithium secondary batteries

5A. 1 Introduction

The lithium batteries are attractive energy consuming device in the view of their high working voltage, high energy density, long cycle life, better mechanical property and size effective [1-3]. Electrolytes with electro active properties are playing a vital role in these devices in order to gain higher end assets. Electrolytes belonging to polymer electrolytes are in the stage that aim higher conductivity, high thermal and mechanical stability, wide electro chemical window and so on [4-6]. Organic electrolytes as well as solid polymer electrolytes fail in view of their flammability, volatility, lithium dendrites, leakage, hazards to nature and poor contact between electrodes, etc., [7]. On the other hand, ionic liquid incorporated polymer electrolyte matrix provides mechanical support, where as ionic liquid itself gives the anion and cation for ionic conductivity [8]. However, selection of suitable polymer host and an ionic liquid is very important. High chemical stability and strong electron withdrawing functional groups are the most desirable property of a polymer. One of polymer widely investigated is poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-co-HFP)) for its high dielectric constant (ε = 8.4) and facilitation of high number of charge carriers. The crystallinity present in the semi crystalline polymer retains adequate mechanical stability to activate as a separator for the electrodes, while the amorphous phase provides sufficient conducting nature [9-12]. On the other hand, P(VdF-co-HFP) retains more electrolyte solutions due to its low crystallinity associated with excellent chemical resistance, mechanical and thermal properties, etc., [13, 14].
In order to provide modern technology without disturbing the nature of constituency, ionic liquid are considered as one of the best choice of materials for lithium battery fabrication. Molten salts have the appearance of liquid at room temperature are called as ionic liquid. Ionic liquids have received great attention from researchers due to their potential applications with excellent physical and chemical properties. Ionic liquids have very interesting property such as low vapor pressure, non volatility, high thermal stability, high electro chemical window etc., [15, 16]. With the prevailing properties, ionic liquids make them a suitable candidate in lithium battery electrolytes [17, 18]. Poorly coordinating organic or inorganic anions and organic cations forms the ionic liquids. This asymmetric structure makes them hard to crystallize; hence they have liquid nature with wide temperature range [19]. In the first generation of ionic liquids, attention is being paid in imidazolium based cation for its high conductivity and low viscosity. But in the view of its low electrochemical window due to its acidic proton, it has limited applications. Phosphonium ionic liquids have particular strong property of negligible vapor pressure, high thermal capacity, and wide liquid range [20]. Phosphonium architecture based ionic liquids have particular property compared to ammonium, pyridinium and imidazolium cationic counter parts, as it does not have acidic proton [21, 22]. Phosphonium cation has four different substituents and good chance to bonding with large number of anions [23]. Phosphonium based ionic liquids exhibit high thermal stability and high electrochemical stability window. Due to its high viscosity (295.91 mPa-s at 25 °C), it restricts the ionic mobility and offers low ionic conductivity (0.89 mS/cm) compared to other ionic liquids. Coulombic interaction between anion and cation results in high viscosity and highly delocalized cation compose the ionic liquid as liquid at room temperature [24]. Ionic liquids with
Tf$_2$N exhibit low viscosity and wide electrochemical stability due to the delocalized charge in Tf$_2$N, which leads to flexible structure and weak interaction with other charges [25].

Ethylene and propylene carbonate (EC and PC) plasticizer in 1:1 ratio was added to the IL to improve its poor ionic conductivity caused by high viscosity of phosphonium cation. The gel polymer electrolyte formed with organic carbonate provides necessary viscosity to the cationic phosphonium leads to swamped viscosity. Organic carbonates (EC and PC) dissociate the columbic interaction in ionic liquids because of their high dielectric constant such as $\varepsilon = 89.78$ at 40 °C and 64.93 at 25 °C respectively [26].

In this framework, solid and gel polymer electrolytes (SPEs and GPE) were prepared using solution casting method; PVdF-co-HFP polymer has been modified using of trihexyldodecyolphosphoniumbis(trifluoromethylsulfonyl) amide [P$_{14,6,6,6}$][Tf$_2$N] ionic liquid. For energy storage applications, the optimized electrolyte has been elucidated respectively from different ratios of polymer to ionic liquid such as (95-5, 90-10 85-15, 80-20 and 75-25wt %). The GPE has been prepared by adding EC and PC in SPE. The maximum conductivity and the physical as well as electrochemical properties of the polymer matrix have been found out from their optimum ratio for lithium battery application. The effect of ionic liquid and plasticizer in PE has been studied by subjecting them for different characterizations. The physical property has been studied using X-ray diffraction measurements (XRD), Fourier transform infra red spectrometer (FTIR), Thermo gravimetric and differential thermal analysis (TG/DTA), and Scanning electron microscopy (SEM), while the electrochemical properties have been analyzed using AC impedance, linear sweep voltammetry (LSV), cyclic voltammetry (CV) and charge- discharge (C/D) analyses.
5A. 2 Experimental

Poly (vinylidene fluoride -co- hexafluoropropylene) PVdF-co-HFP as polymer matrix, trihexyltetradecylphosphoniumbis(trifluoromethylsulfonyl) amide \([P_{14,6,6,6}][\text{Tf}_2\text{N}]\) ionic liquid, ethylene carbonate (Merck, India) and propylene carbonate are the basic chemicals used in this work. Solution casting method has been employed to prepare the polymer electrolytes in the ratios mentioned in Table 5A.1. The polymer PVdF-co-HFP and ionic liquid \([P_{14,6,6,6}][\text{Tf}_2\text{N}]\) both were received from Sigma Aldrich USA and used without further purification. Tetrahydrofuran (THF) was used as a solvent to dissolve the polymer and to prepare the polymer matrix. Organic solvents were purchased from SRL India and used as received. As mentioned in Table 5A.1, the calculated amount of polymer was dried in vacuum under \(1 \times 10^{-3}\) Torr pressure in a temperature controlled vacuum oven at 100°C for 10 h. The moisture and impurity present in the polymer was removed by the vacuum heating process. An efficient amount of solvent THF was poured in the polymer to make polymer solution by stirring. The calculated amount of ionic liquid or ionic liquid with EC and PC was added to the above polymer solution, which was stirred continuously in order to obtain homogeneity. A flat bottom petri plate has been used to cast the mixture of polymer ionic liquid solution to obtain thin electrolyte film. Finally, freestanding films were dried at 60 °C under vacuum for 5 h.

The PANalyticalX’Pert PRO powder X-ray Diffractometer using Cu-Kα radiation as source and operated at 40 kV had been used to study the variation of crystalline nature as the function of ionic liquid ratio. The FTIR Thermo Nicolet 380 spectrometer was used to study the interactions of different fundamental vibrational groups in the range of 4000 to 400 cm\(^{-1}\). Thermal analysis was performed using STA 409 PL Luxxat a heat rate of 10°C /min within the temperature range from room
temperature to 900 °C under Nitrogen atmosphere. The surface nature has been studied with SEM Model JEOL-JSM-6500F at an accelerating voltage of 5 and 15 kV after sputtering platinum over the samples.

<table>
<thead>
<tr>
<th>PVdF-co-HFP + [P146,6,6][Tf2N] (wt %)</th>
<th>EC + PC (wt %)</th>
<th>Sample code</th>
<th>Ionic Conductivity x 10^6 S/cm at</th>
<th>E_a (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95 + 5</td>
<td>0</td>
<td>K1</td>
<td>0.047 0.058 0.130 0.174 0.194 0.252</td>
<td>0.42</td>
</tr>
<tr>
<td>90 +10</td>
<td>0</td>
<td>K2</td>
<td>0.097 0.242 0.450 0.702 1.154 2.401</td>
<td>0.39</td>
</tr>
<tr>
<td>85 +15</td>
<td>0</td>
<td>K3</td>
<td>1.150 1.514 2.473 4.478 12.14 22.46</td>
<td>0.33</td>
</tr>
<tr>
<td>80 +20</td>
<td>0</td>
<td>K4</td>
<td>1.737 2.217 3.603 6.904 25.50 40.34</td>
<td>0.32</td>
</tr>
<tr>
<td>75 +25</td>
<td>0</td>
<td>K5</td>
<td>3.209 4.187 6.801 19.24 31.48 58.81</td>
<td>0.30</td>
</tr>
<tr>
<td>75 + 25</td>
<td>60</td>
<td>K6</td>
<td>340.2 388.3 484.8 676.3 1205.3 1579.7</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table 5A.1 represents the calculated weight percentage, ionic conductivity and activation energy values of solid and gel polymer electrolytes PVdF-co-HFP, [P1466,6][Tf2N], EC+PC

AC impedance technique has been performed to find out the conductivity of the ionic liquid polymer electrolytes sandwiched between stainless steel blocking electrodes. A computer-controlled micro Autolab III Potentiostat/Galvanostat with frequency range from 1 Hz–500 kHz with a signal amplitude of 10 mV, were used to study the conducting behavior at different temperatures ranging from 303 to 353K. The bulk resistance obtained from the complex impedance plot had been employed for ionic conductivity calculation. For other electrochemical analysis, coin cells have been fabricated for high ionic conducting electrolyte sample. Li had been used as reference and counter electrode. Working electrode has been fabricated with 80:10:10 ratios of LiFePO4: PVdF: Super P carbon. The above combination was prepared as slurry using NMP solvent and coated on Alumina foil and then dried at 80 °C for about 6 h. Then the coin cells (CR 2032) have been fabricated for electrochemical
characterization. The electrochemical studies were carried out using Autolab electrochemical workstation (GPES, PGSTAT 302N).

5A. 3 Result and Discussion

5A. 3.1 X ray diffraction

Fig5A.1 shows X-ray diffraction pattern of pure PVdF-co-HFP and mixed SPEs and GPE in the ratio as mentioned in Table 5A.1. It is clearly visible that the pure polymer PVdF-co-HFP has semi crystalline nature, where the crystalline peaks with 20 angle at 18.44, 20.13 and 39.04 reflect the α phase of crystalline plane [27]. The representation of these peaks makes the atoms to arrange in lattice and remaining amorphous nature is responsible for ionic conductivity [28]. However, in SPEs and GPE, the appeared peaks corresponding to PVdF-co-HFP are wider and reduce the crystalline domains and try to form an amorphous system. Here, intensity of the resultant peaks for PVdF-co-HFP polymer matrix blended with [P14,6,6,6][Tf2N] as well as [P14,6,6,6][Tf2N] + EC+PC decreases drastically, which shows weak peaks with wide nature in all cases. From the patterns, it is noted that intensities of the peak decreases upon increasing IL content. When compared to the SPEs, the diffraction pattern of electrolyte with EC+PC shows nearly a flat pattern. This peak is representing high amorphous nature, which is responsible for high ionic conductivity.
Fig 5A.1XRD diffraction pattern of pure PVdF-co-HFP, different SPE K1- (95:5), K2- (90:10), K3- (85:15), K4- (80:20), K5- (75:25) of PVdF-co-HFP + [P14,6,6,6][Tf2N] and GPE K6-PVdF-co-HFP + [P14,6,6,6][Tf2N] (75:25) + EC+PC (60) wt%.

5A. 3. 2 FTIR analyses

Fig 5A.2 represents the FTIR spectra in the region of 4000 to 400 cm\(^{-1}\) of pure PVdF-HFP and IL imported PEs. The wavenumber between 1000 and 400 cm\(^{-1}\) have been magnified to view the spectrum more clearly. A crystalline phase of PVdF-co-HFP obtained at 490, 512, 531, 614, 761, 796, 976 cm\(^{-1}\) represent the presence of the PVdF-co-HFP in the complex system. The vibrations at 490 and 512 cm\(^{-1}\) represent the bending and wagging modes of CF\(_2\) group, whereas the wavenumber at 531 cm\(^{-1}\) and 976 cm\(^{-1}\) ascribe to nonpolar TGTG trans gauche conformation [29]. The CF\(_2\) bending and CCC skeletal vibration are noted from the wave number at 614 cm\(^{-1}\). The vibrational peak at 796 cm\(^{-1}\) stands for CF\(_3\) stretching for polymer. Here, peaks 839 and 879 cm\(^{-1}\) represent the \(\beta\) amorphous phase of polymer (represented by * in Fig 5A.2 ), where, the mixed mode of CH\(_2\) rocking and CF\(_2\) asymmetric stretching.
appears at 839 cm\(^{-1}\) and 879 cm\(^{-1}\) corresponding to CF\(_2\) and CC symmetric stretching vibrations. The appearance of peaks at 2960 and 3024 cm\(^{-1}\) represent the C-H stretching polymer [11]. The Tf\(_2\)N anion has been confirmed from the obtained peaks at 1348, 1196, 1136 and 1055 cm\(^{-1}\), and the peaks in the complexes are shifted to 1344, 1055 cm\(^{-1}\). The remaining peaks combine together and form may be due to more thickness of the film a single band. A band existing at 1150 cm\(^{-1}\) represent the P=O group in \([P_{14,6,6,6}]\) of IL. The appearance of peaks at 2855 & 2950 cm\(^{-1}\) represent the CH\(_2\) bonds of the aliphatic chains presented in phosphonium cation [30]. The shifting and disappearance of peaks confirms the formation of complexation between the polymer and ionic liquid. While increasing the ionic liquid content, most of the crystalline peaks become weaker and amorphous peak becomes broader. This shows that the high content of ionic liquid tries to form an amorphous phase.
Fig 5A. 2 FTIR of pure PVdF-co-HFP, different SPE K1- (95:5), K2- (90:10), K3- (85:15), K4- (80:20), K5- (75:25) of PVdF-co-HFP + [P$_{14,6,6}$][Tf$_2$N] and GPE K6-PVdF-co-HFP + [P$_{14,6,6,6}$][Tf$_2$N] (75:25) + EC+PC (60) wt% system

5A. 3.3 Ionic conductivity

The ionic conductivity values of the electrolytes have been estimated through AC impedance studies by observing real and imaginary parts for plotting CI plot. Fig5A.3a displays the complex impedance (CI) plot of PVdF-co-HFP polymer electrolyte with different [P$_{14,6,6}$][Tf$_2$N] content and GPE at room temperature. It is noted that the CI plots of SPEs reflects the general of ionic solids with a typical semicircle and a spike behavior, whereas, only spike is appeared in GPE [30, 31]. The intercept of the semicircle or the spike with higher frequency in $Z'$ real axis gives the information about bulk resistance ($R_b$) of the polymer electrolyte [32, 33]. The conductivity values were calculated using the following equation

$$\sigma = \frac{l}{AR_b} \quad --5A.1$$
where, $\sigma$ is the ionic conductivity value, $l$ is thickness of the electrolyte, $A$ is the area of the film and $R_b$ is the bulk resistance. It is observed that from Fig (5A.3a) the size of semicircle portion of Cl plot at room temperature decreases upon the addition of IL; At one stage the semicircle has been disappeared. Also it is noted that the incorporation of the plasticizer causes a complete elimination of the semicircle [34]. The ionic conductivity values are proportional to [P_{14,6,6,6}][\text{TF}_2\text{N}] content (Table 5A. 1). The higher content of [P_{14,6,6,6}][\text{TF}_2\text{N}]suggests more amount of liquid electrolyte with maximum ionic conductivity of $3.209 \times 10^{-6}$ S/cm at 303K with 25 wt% of IL. These can be simply explained as follows: high content of [P_{14,6,6,6}][\text{TF}_2\text{N}] in electrolyte has more number of free ions and these ions have very weak interaction with the polymer compared to the metallic salts [35]. These free ions found in polymer electrolyte have migrated easily through their free volume and results in higher conductivity. The addition of high amount of ionic liquid (beyond 25 wt%) produces higher conductivity among the polymer electrolyte studied. It is comparable with the earlier reports that the 100 % of [P_{14,6,6,6}][\text{TF}_2\text{N}] has ionic conductivity of the order of $8.9 \times 10^{-4}$ S/cm at 303 K [24] and $1.34 \times 10^{-4}$ S/cm at 303 K as reported by Battez et.al [30]. The major disadvantage with ionic liquid limits their use in industrial application due to its high cost. Because of this, the content of ionic liquid is restricted to 25 % in SPEs. The concept of GPE has been introduced to reduce the viscosity of IL in polymer electrolytes. However, the plasticizer selection is made with EC +PC plasticizer with 60 wt%. The inclusion of plasticizer in SPE has found to increase the ionic conductivity up to two orders of magnitude. The prepared gel polymer electrolyte has ionic conductivity of $3.40 \times 10^{-4}$ S/cm at 303 K. Hence, it is concluded that, the inclusion of plasticizer induces the conductivity in ILPE.
Fig 5A. 3a Complex impedance plot for SPE K1- (95:5), K2- (90:10), K3- (85:15), K4- (80:20), K5- (75:25) of PVdF-co-HFP + [P_{14,6,6,6}][Tf_2N] and GPE K6-PVdF-co-HFP + [P_{14,6,6,6}][Tf_2N] (75:25) + EC+PC (60) wt% in the SS/GPE/SS cell at room temperature

In order to understand ionic conducting behavior at different temperatures, the ionic conductivity of K1-K6 has been studied between 303K and 353K and Fig 5A. 3b shows the Cl plot of K5 at various temperatures. In phosphonium based ionic liquids, the higher viscosity with huge number of ions does not form a completely amorphous system leading to poor ionic conductivity, than sulphonium IL based system.

The temperature dependent ionic conductivity plot of all electrolytes in the variation of ionic conductivity values as a function of temperature has been plotted and shown in Fig 5A. 4. The ion conducting behavior of the prepared electrolytes, (K1-K6) obeys the Arrhenius behavior and satisfies the Arrhenius relation given below
\[ \sigma = \sigma_0 \exp\left(\frac{E_a}{kT}\right) \]

where, \( \sigma \) is the conductivity, \( \sigma_0 \) is the pre exponential factor, \( E_a \) activation energy, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. From the slope of the straight line, the activation energy values have been calculated and listed in Table 5A. 1. The activation energies of SPE (K5) and GPE (K6) with and without plasticizer are 0.305 eV and 0.197 eV respectively. The maximum conducting sample in SPE category, it requires minimum activation energy. Still the requirement of energy is reduced upon adding plasticizer 60 wt%.

**Fig 5A.3b Complex impedance plot of K5 PVdF-co-HFP + [P_{14,6,6,6}][Tf_2N] (75:25) at different temperatures**

The conductivity of 5wt% of IL has lower value of conductivity, which is almost non-conducting due to the lesser number of charge carriers and due to the semi crystalline nature of PVdF-co-HFP. With the increase of the temperature, the polymer chains are
more flexible and produce larger number of free volumes, which helps for easy ionic migration leading to higher ionic conductivity. The increase of temperature also lowers the crystalline nature. At high ionic liquid and plasticizer content, the numbers of charge carriers are more and produce simply more pathways for cation and anions.

![Graph](image)

**Fig 5A. 4 Arrhenius plot of samples SPE K1-(95:5), K2- (90:10), K3- (85:15), K4- (80:20), K5- (75:25) of PVdF-co-HFP + [P14,6,6,6,6][Tf₂N] and GPE K6-PVdF-co-HFP + [P14,6,6,6,6][Tf₂N] (75:25) + EC+PC (60) wt% between the temperature 303 to 353K**

5A. 3.4 Scanning Electron Microscope (SEM) Studies

The surface morphology of the prepared PVdF-co-HFP + [P14,6,6,6,6][Tf₂N] electrolytes was studied using SEM. Fig 5A.5 represents the surface structure of pure PVdF-co-HFP as well as PVdF-co-HFP + [P14,6,6,6,6][Tf₂N] or PVdF-co-HFP + [P14,6,6,6,6][Tf₂N] + EC+PC electrolytes with the magnification of 1K. The pure PVdF-co-HFP electrolyte shows many spherical spot and they are uniformly distributed though out the matrix. These spots are responsible for the crystalline nature of the polymer matrix [27]. The addition of [P14,6,6,6,6][Tf₂N] reduces the size of the spherical spot and produces flat surface with lesser number of pores. Adding 25 wt% of [P14,6,6,6,6][Tf₂N]produces maximum pores in prepared SPEs, while GPE has more
number of pores than that. These pores were responsible for ionic conduction and reduced spherical spot forms more amorphous network which results in high ionic conductivity, as discussed in XRD and ionic conductivity studies.

![SEM images of pure PVdF-co-HFP, SPE K1-(95:5), K2-(90:10), K3-(85:15), K4-(80:20), K5-(75:25) of PVdF-co-HFP + [P14,6,6,6][Tf2N] and GPE K6-PVdF-co-HFP + [P14,6,6,6][Tf2N] (75:25) + EC+PC (60) wt% magnification of 1K](image)

**Fig 5A.** 5 SEM image of pure PVdF-co-HFP, SPE K1-(95:5), K2-(90:10), K3-(85:15), K4-(80:20), K5-(75:25) of PVdF-co-HFP + [P14,6,6,6][Tf2N] and GPE K6-PVdF-co-HFP + [P14,6,6,6][Tf2N] (75:25) + EC+PC (60) wt% magnification of 1K

**5A. 3.5 Thermal Studies**

The thermo gravimetric and differential thermal analysis (TGDTA) was used to study the thermal stability of the prepared electrolyte samples. Generally, the pure [P14,6,6,6][Tf2N] ionic liquid has the thermal stability of 350 °C as reported by Battez et
al. [29], whereas the ionic liquid incorporated polymer electrolyte has maintained the maximum thermal stability of 300 °C with 22% weight loss. The thermal stability of prepared electrolytes was measured from 32 to 900 °C having two weight loss regions. The first degradation temperature has been found nearly at 320 °C corresponding to the decomposition of the ionic liquid medium with the weight loss of 20wt%. The complete decomposition temperature of polymer electrolyte has appeared around 500 °C showing the melting of the polymer electrolyte in nitrogen controlled atmosphere. The deep weight loss of about 60 % is also noted indicating the decomposition temperature of polymer electrolyte. Among the samples studied, the electrolyte with higher ionic conductivity has maximum thermal stability of 260°C. Compared to SPEs, the GPE has less stability around 260 °C, due to the evaporation of molecular solvents. The maximized region in Fig 5A.6 clearly shows the weight loss region of the individual polymer electrolytes. The remaining weight percentage may be due to the presence of residual carbon in the polymer electrolytes. A typical DTA curve for the polymer electrolytes (SPE) has also been displayed. Corresponding exothermic curves also noted around 300, 470 and 720°C shows the inline behavior of the TG and DTA. The higher ionic conducting sample has been found as a suitable electrolyte for further electrochemical studies.
Fig 5A. 6 TGDTA graph of SPE K1- (95:5), K2- (90:10), K3- (85:15), K4- (80:20), K5- (75:25) of PVdF-co-HFP + [P_{14,6,6,6}][Tf_2N] and GPE K6-PVdF-co-HFP + [P_{14,6,6,6}][Tf_2N] (75:25) + EC+PC (60) wt% and typical DTA plot of SPE

5A. 3.6 Linear sweep voltammetry

The linear sweep voltammetry technique (LSV) was used to find the electrochemical stability of polymer electrolyte and presented in Fig 5A.7. A significant electrochemical stability upto 4.8 V (K5) and 5V (K6) were noted with a scanning rate of 5mV/s. This stability is higher than the commercially available electrolytes for lithium batteries with the working voltage of 4.2V. Also the electrolytes with plasticizer (GPE) have electrochemical stability slightly higher than the SPE. The anodic current is stable upto 4.8V and after that, a sharp increase in anodic current is noted. This represents the electrochemical reaction of the electrode with the polymer electrolyte [34].
Fig 5A. 7 LSV of SPE K5PVdF-co-HFP + [P_{14,6,6,6}][Tf_2N] (75:25) and GPE K6-
PVdF-co-HFP + [P_{14,6,6,6}][Tf_2N] (75:25) + EC+PC (60) wt% at a scan rate of
5mV/s

5A. 3.7 Cyclic Voltammetry

Cyclic voltammetry of coin cell with PVdF-co-HFP (75wt%) +
[P_{14,6,6,6}][Tf_2N] (25 wt%) and (75:25) of PVdF-co-HFP (75 wt%)+ [P_{14,6,6,6}][Tf_2N]
(40wt%)+EC+PC (60 wt%) as electrolytes with LiFePO_4 cathode taken at room
temperature for the first three consecutive cycles at a scan rate of 5 mVs^{-1} is shown in
Fig 5A.8 (a,b). The first scan starts with an oxidation peak (3.2V) followed by a
reduction peak (3.42 for K5 and 3.57 for K6). The appearance of oxidation and
reduction peaks suggests the strong reversible behaviour of electrolyte material. It is
also noted that the oxidation happens within clear and high current conduction for the
phosphonium based sample. However, a feeble current conduction was observed for
sulfonium based electrolytes which is due to the lesser corrosive nature of phosphonium IL with the electrode in the cell.

Fig 5A. 8 a, b Cyclic voltammetry of a) SPE K5PVdF-co-HFP + [P14,6,6,6][Tf2N] (75:25) and b) GPE K6-PVdF-co-HFP + [P14,6,6,6][Tf2N] (75:25) + EC+PC (60) wt% at a scan rate of 5mV/s

5A. 3.8 Charge discharge studies

Coin cells have been assembled with Li metal/LiFePO4 electrodes containing PVdF-co-HFP (75wt%) +[P14,6,6,6][Tf2N] (25wt%) and (75:25) ratio of PVdF-co-HFP +[P14,6,6,6][Tf2N] (40wt%) - EC+PC (60wt%) electrolyte in order to investigate the charge discharge performance. Fig. 5A.9 (a, b) shows the cyclic voltage profile of first, fifth and tenth cycles. A flat voltage plateau has been obtained with voltage range of 3.4V. A columbic efficiency of above 85% has been obtained in the first cycle for both samples. The coin cell fabricated with K5 sample delivers a discharge value of about 137mAh/g, whereas, the plasticizer embedded system delivers 146 mAh/g [36]. Finally, in the tenth cycle, the capacity values of charge / discharge reached to 142mAh/g / 131mAh/g (K5) and 157mAh/g / 136mAh/g (K6) respectively.
From the above studies, it is concluded that the plasticizer embedded system has more discharge capacity and is suitable as electrolyte for lithium secondary batteries.

![Graphs showing charge discharge profile](image)

**Fig. 5A. 9 a, b** Charge discharge profile of a) SPE K5PVdF-co-HFP + [P_{14,6,6,6}][Tf_2N] (75:25), b) GPE K6-PVdF-co-HFP + [P_{14,6,6,6}][Tf_2N] (75:25) + EC+PC (60 wt%) for first ten cycles

**5A. 4. Conclusion**

This study reports the physical and electrochemical properties of polymer electrolytes composed of phosphonium ionic liquid incorporated with PVdF-co-HFP solid and gel polymer electrolytes. All the electrolytes were characterized using XRD, FT-IR, TG-DTA and SEM. It is concluded that the 75:25 wt% of PVdF-co-HFP: Phosphonium IL electrolytes exhibit maximum conductivity and this drives the properties too. Also using this ratio of polymer and IL, the effect of addition plasticizer has been tested and concluded with the appreciable properties in all aspects. The addition of plasticizer would result in higher ionic conductivity and wide working voltage, however affects the thermal stability. From the experimental studies,
it is observed that all the electrolytes follow Arrhenius behavior, where the best ionic conductivity of $3.40 \times 10^{-4}$ S/cm at 303 K has been achieved for the GPE with minimal activation energy value of 0.197 eV. Samples containing maximum ionic conductivity have necessary porosity with network structure, which is revealed by SEM images. The sample K6 is found to have thermal stability up to 260 °C, wide electrochemical window of 5V and discharge capacity of 146 mAh/g in lithium battery.

References


Chapter 5 – Part B

Role of inorganic fillers in the polymer electrolyte incorporated with phosphonium ionic liquid for lithium ion battery fabrication

5B. 1 Introduction

Polymer electrolytes play vital role in energy storage applications specifically electrochemical devices, etc., [1]. The successive application and operation of EC devices like batteries, super capacitors, fuel cell as well as solar cell are strongly dependent on the characteristic properties of polymer electrolyte [2-6]. In ionically conducting polymer electrolytes, the ion transport occurs through the amorphous region associated with polymer segmental mobility [7, 8]. The poly (vinylidenefluoride-co-hexafluoropropylene) (P(VdF-HFP)) has been used successively because of its high dielectric constant (ε = 8.4) and migration of high number of charge carriers. The PVdF-co-HFP copolymer is semicrystalline in nature, whereas the presence of HFP and VdF lead to amorphous property, which entraps large liquid electrolyte and provides mechanical support for polymer matrix [9-11].

Addition of ionic liquid in polymer matrix enhances the flexibility as well as the ionic conductivity when compared to conventional metallic salt. Poorly coordinating anions and cations make themselves as a liquid below 100°C known as ionic liquid [12]. Attractive properties of ionic liquid such as thermal stability, non-volatility, wide electrochemical potential window, and high ionic conductivity make them suitable electrolyte for different applications [13-15]. Bulky asymmetric cation and inorganic anion make the ionic liquids with excellent property. Addition of ionic liquid and common plasticizer in polymer electrolyte affects the mechanical property
of polymer electrolyte because of the liquid nature and plasticization effect but, enhances the electrochemical properties [16,17].

Ionic liquid based composite electrolytes are attractive friendly electrolytes, which have high ionic conductivity, strong mechanical property and thermal stability like a solid polymer electrolyte [18-20]. The polymer electrolyte quality has been enhanced by sufficient additive fillers, producing high aspect ratio and large surface area [21]. Further, the addition of fillers in polymer electrolyte reduces the ion pairs with their Lewis acid surface center resulting in high ionic conductivity [22].

In this work, trihexyltetradecylphosphonium cation based ionic liquid (IL) had been chosen for the preparation of polymer electrolyte. Such IL has high thermal as well as electrochemical stability window. However, its slight high viscosity (295.91 mPa s at 25°C) offers low conductivity at room temperature and limiting its application [23]. In particular combination with NTf₂⁻ ion, for example, [P16,4,4,4] NTf₂ (trihexyltetradecylphosphoniumbis(trifluoromethylsulfonyl)amide) shows comparatively a higher ionic conductivity of 1.34 X 10⁻⁴ S/cm at 303 K, than their other counterparts as a result of delocalized charge of the anion [24, 25].

However, very limited number of studies has been focused on this IL, incorporated with polymer as well as inorganic filler and the present study provides an effective role of these components in improving the performance of composite gel polymer electrolyte. In this work, thermal, surface and electrochemical properties of IL containing polymer electrolytes and TiO₂ fillers have been studied and discussed in detail.
5B. 2 Experimental section

5B. 2.1 Preparation of polymer electrolytes

The solution casting method has been employed for the preparation of composite IL based gel polymer electrolyte. Poly (vinylidene fluoride -co - hexafluoropropylene) PVdF-co-HFP (30 wt%) / trihexyltetradecylphosphoniumbis(trifluoromethylsulfonyl) amide [P14,6,6,6][Tf2N] (10 wt%) / ethylene carbonate (Merck Germany) + propylene carbonate (SRL India) (60 wt%) with different amount of titanium dioxide (TiO2 = 3, 6, 9 wt%) were used to prepare polymer electrolyte. PVdF-co-HFP, P14,6,6,6][Tf2N] and filler are purchased from Aldrich USA. Tetrahydrofuran (THF, SRL) was used as a solvent. The PVdF-co-HFP and TiO2 were dried in a vacuum controlled oven (1x10^{-3}Torr pressure) at 100 °C for 12h, in order to remove the moisture and impurities. The appropriate amount of PVdF-co-HFP was dissolved in common (THF) solvent and stirred continuously for 24 hrs. At the same time, the liquid electrolyte had been prepared by adding a known quantity of IL ([P14,6,6,6][Tf2N]) to EC+PC mixture. After complete dissolution of the polymer, liquid electrolyte was added and stirred further to obtain homogeneous nature. Then calculated ratio of TiO2 was added and the resulting composites were named as S1 (3wt%), S2 (6wt%) and S3 (9wt%). The TiO2 particles were dispersed uniformly with simultaneous heating at 40 °C until the solution becomes gelly nature. The gelly solution was poured on to flat bottom glass petri plate and kept at room temperature to evaporate the solvent for 24h. The deposited film on a petri plate was placed in the vacuum oven and 60°C is maintained to remove excess solvent present in the polymer electrolytes. The thickness of the prepared film was ~100μm.
5B. 2.2 Characterization techniques

PANalytical X’Pert PRO powder X-ray Diffractometer with Cu-Kα radiation was used for XRD analysis instrument operated at 40 kV. FTIR Thermo Nicolet 380 spectrometer was used to study the complexation behavior within the range of 4000 to 400 cm\(^{-1}\). STA 409 PL Luxxat a heat rate of 10 °C /min was used to study the thermal behaviour of the prepared electrolytes from room temperature to 900 °C under nitrogen atmosphere. Surface characterizations has been studied with SEM Model JEOL-JSM-6500F at an accelerating voltage of 5 and 15 kV after sputtering platinum over the samples. The prepared electrolytes were sandwiched between stainless steel electrodes and AC impedance technique has been adopted to obtain complex impedance plot, a computer-controlled micro Autolab III Potentiostat/Galvanostat with frequency range from 1 Hz–500 kHz with signal amplitude of 10mV, were used. A CR2032 type coin cells have been used to fabricate the cells to study the electrochemical properties. Using Li/ CPE/ LiFePO\(_4\) cell couple. The working electrode LiFePO\(_4\) had been fabricated with 80:10:10 ratios of LiFePO\(_4\):Super P carbon: PVdF. Using the NMP solvent (Merck Germany), the above composition was made as slurry and coated on an Alumina foil and dried at 80 °C for about 6h. Autolab electrochemical workstation (GPES, PGSTAT 302N) and the charge/discharge life cycle was used to study the electrochemical characterization. The total mass of the active substance was nearly 1 mg. Quasi-equilibrated coin cell had been used for all electrochemical studies.
5B. 3 Results and Discussion

5B. 3.1 XRD analysis

Fig 5B. 1 shows XRD spectra of pure PVdF-co-HFP, TiO₂, the prepared electrolyte samples with the composition PVdF-HFP(30) : [P₁₄,₆,₆,₆][Ti₂N] (10) : EC+PC (60) with different TiO₂ compositions such as 3, 6 & 9% represented as S1, S2 and S3. The XRD pattern with low TiO₂ content (3wt %) follows the polymer pattern and high content (9wt %) follows the TiO₂ (filler) pattern. The PVdF-co-HFP at 2θ = 20.1° shows its semi crystalline nature and slightly shifted in ILGPE TiO₂ crystalline peaks at 2θ = 25.27, 36.9, 37.7, 38.5, 48, 53.8, 55, 62.6, 68.7, 70.2 and 75° with the corresponding hkl values of (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), (215) respectively match with JCPDS - 894203. The intensity of peaks pertaining to both polymer and filler are found to decrease upto 6wt% of TiO₂ addition in the ILGPE. Further addition of TiO₂ causes more ion aggregation into the matrix and degree of crystallinity. The addition of inorganic fillers induces the amorphous nature of the polymer matrix and the crystalline peaks obtained by the addition of TiO₂ act as an inert medium [26]. There is no chemical reaction between the TiO₂ and the electrolyte medium, as confirmed by TiO₂ resultant peaks. The filler particle induces some positive effect in terms of electrochemical studies, which would be discussed in the electrochemical characterization part. This effect has been reduced upon further addition beyond 6wt% of TiO₂.
Fig 5B. 1 XRD patterns of pure PVdF-co-HFP, TiO$_2$, ILCGPE 3(S1), 6(S2) and 9(S3) wt% of TiO$_2$ based PVdF-co-HFP (30) + [P14,6,6,6][Tf$_2$N] (10) +EC+PC (60) wt% system

5B. 3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is a tool to investigate the fundamental vibration of pure and complex materials and it is performed for pure polymer, composite electrolytes in the range 4000 – 400 cm$^{-1}$ and shown in Fig5B.2. The appeared peaks represent the PVdF-co-HFP, EC, PC, [P$_{14,6,6,6}$][Tf$_2$N], EC, PC, TiO$_2$ where the values tabulated in Table 5B.1, which give the actual value, shifted value and the corresponding peak assignments. From the table, it is noted that peak shift occurs due to the formation of complex molecules.
<table>
<thead>
<tr>
<th></th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Shifted wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVdF-co-HFP</td>
<td>2980</td>
<td>2958</td>
<td>symmetrical stretching mode of CH$_2$ group</td>
</tr>
<tr>
<td></td>
<td>3022</td>
<td>3020</td>
<td>asymmetrical stretching mode of CH$_2$ group</td>
</tr>
<tr>
<td>PVdF-co-HFP $\alpha$ phase</td>
<td>489</td>
<td>481</td>
<td>bending and wagging vibration of CF$_2$</td>
</tr>
<tr>
<td></td>
<td>614</td>
<td>618</td>
<td>CF$_2$ bending mode</td>
</tr>
<tr>
<td></td>
<td>796</td>
<td>776</td>
<td>CF$_3$ stretching vibration</td>
</tr>
<tr>
<td></td>
<td>976</td>
<td>974</td>
<td>CF stretching mode</td>
</tr>
<tr>
<td>PVdF-co-HFP $\beta$ phase</td>
<td>838</td>
<td>838</td>
<td>CH$_2$ rocking</td>
</tr>
<tr>
<td></td>
<td>881</td>
<td>881</td>
<td>CF$_2$ symmetric stretching vibration [27, 20]</td>
</tr>
<tr>
<td>[P$_{14,6,6,6}$]</td>
<td>2855</td>
<td>2855</td>
<td>CH$_2$ bonds of the aliphatic chains</td>
</tr>
<tr>
<td></td>
<td>2950</td>
<td>2958</td>
<td>CH$_2$ bonds of the aliphatic chains</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>1132</td>
<td>P=O group [23]</td>
</tr>
<tr>
<td>[Te$_2$N]</td>
<td>1062</td>
<td>1062</td>
<td>$\nu_6$ S–N–S peak</td>
</tr>
<tr>
<td></td>
<td>1341</td>
<td>1341</td>
<td>C-SO$_2$–N bonding mode</td>
</tr>
<tr>
<td></td>
<td>570</td>
<td>570</td>
<td>CF$_3$ asymmetric bending mode</td>
</tr>
<tr>
<td></td>
<td>602</td>
<td>602</td>
<td>SO$_2$ deformation [28]</td>
</tr>
<tr>
<td>PC</td>
<td>1791</td>
<td>1747</td>
<td>C=O stretching</td>
</tr>
<tr>
<td></td>
<td>712</td>
<td>716</td>
<td>symmetric ring deformation</td>
</tr>
<tr>
<td></td>
<td>777</td>
<td>767</td>
<td>ring deformation [29]</td>
</tr>
<tr>
<td>EC</td>
<td>1774</td>
<td>1747</td>
<td>C=O bending</td>
</tr>
<tr>
<td></td>
<td>1803</td>
<td>1807</td>
<td>C=O bending [30, 31]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>667</td>
<td>655</td>
<td>Ti-O bond</td>
</tr>
<tr>
<td></td>
<td>505</td>
<td>512</td>
<td>Ti-O bond</td>
</tr>
<tr>
<td></td>
<td>447</td>
<td>443</td>
<td>Ti-O bond</td>
</tr>
<tr>
<td></td>
<td>655</td>
<td>655</td>
<td>symmetric O-Ti-O stretch</td>
</tr>
<tr>
<td></td>
<td>443</td>
<td>443</td>
<td>vibration of Ti-O bond</td>
</tr>
<tr>
<td></td>
<td>512</td>
<td>512</td>
<td>vibration of Ti-O bond [32]</td>
</tr>
</tbody>
</table>

Table 5B. 1 represent the FTIR spectrum actual value, shifted value and the corresponding peak assignments
Fig 5B. 2 FTIR images of pure PVdF-co-HFP, ILCGPE 3(S1), 6(S2) and 9(S3) wt% of TiO₂-based PVdF-co-HFP (30)+[P14,6,6,6][TF₂N] (10)+EC+PC (60) wt% system
**5B. 3.3 Conductivity**

The ionic conductivity has been measured by recording complex impedance plots for prepared electrolyte by sandwiching in between the stainless steel electrodes. The complex impedance plots obtained at room temperature represented in Fig 5B.3 Generally, the CI plot has traditional trend with two regions, a semi circle and a spike [33]. However, in this case, only spike is noted, as a result of suppression of semicircle by added plasticizer leading to low resistance. The bulk resistance values are gained from the intercept of CI plot in high frequency region. The ionic conducting values are strongly depending on the bulk resistance values are calculated using equation given below.

\[
\sigma = \frac{l}{AR_0} \quad 5B. 1
\]

where \(\sigma\) is the ionic conductivity, \(l\) is the thickness of the prepared electrolytes, \(A\) is the area of the film and \(R_0\) is the bulk resistance. Using the bulk resistance value, the ionic conductivity of the prepared electrolytes were calculated and displayed in Table 5B. 2. From the table, it is visible that the ionic conductivity of the prepared electrolytes is increased upon TiO\(_2\) addition upto 6wt%. At 6 wt%, it exhibits the higher ionic conductivity of \(1.15 \times 10^{-3}\) S/cm at 303K. This is higher than that of the neat [P\(_{14,6,6,6}\)][\(\text{TF}_{2}\text{N}\)](1.34X \(10^{-4}\) S/cm at 303 K) [23]. Literature studies also reveal that the inclusion of the polymer in bare IL leads to mechanically stable electrolyte [34]. Further addition of TiO\(_2\) reduces the ionic conductivity. Similar trend was observed in the sulfonium based ILCGPE. This value is lower than the sulfonium based electrolytes.
Fig 5B. 3 Complex impedance spectra of 3, 6, 9 wt% TiO$_2$ based PVDF – Co – HFP(30) IL(10) – EC+PC(60)wt% system at room temperature (Inset: High frequency region)

The temperature dependent ionic conductivity plot for the prepared composite polymer electrolytes is shown in Fig 5B. 4. The increase of temperature causes an increase in ionic conductivity due to the reduced viscosity of the ionic liquid. The reports based on composite polymer electrolyte with metallic salt shows that 2 to 9 wt% are the optimized ratio for the addition of fillers and also the ionic conductivity first increases and then decreases in high filler content [35]. As expected, the same trend follows in the present study. The conductivity values initially increases with TiO$_2$ content until 6 wt% and then increasing to 9 wt%, the conductivity value falls down. The incorporation of TiO$_2$ creates enhanced volume to store large amount of liquid electrolyte leading to high amorphous nature and appreciable conductivity. But the excess amount of fillers form barrier for ionic migration. All the plots in the figure follow the Arrhenius relation.
\[ \sigma = \sigma_0 \exp(-E_a/kT) \] 5B. 2

where \( \sigma_0 \) is the pre-exponential factor, \( E_a \) the activation energy, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. From the slope of plots, the activation energies have been calculated and listed in Table 5B. 2. The activation energy defined as the energy required igniting the chemical reaction and it is the reciprocal to the ionic conductivity value. A minimum activation energy of 0.162 eV has been obtained for the sample CPE S2, having maximum ionic conductivity. The free volume model explains this behavior, where the increase of temperature leads to an increase in the ionic mobility due to lattice vibration.

<table>
<thead>
<tr>
<th>Sample PVdF-co-HFP (30) + [P14,6,6,6][Ti2N] (10) + EC+PC (60) + TiO2 (X)wt%</th>
<th>Ionic conductivity ( \times 10^{-2} ) S/cm at</th>
<th>( E_a ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
<td>313K</td>
</tr>
<tr>
<td>S1=3</td>
<td>5.49</td>
<td>7.09</td>
</tr>
<tr>
<td>S2=6</td>
<td>11.5</td>
<td>12.3</td>
</tr>
<tr>
<td>S3=9</td>
<td>2.15</td>
<td>5.13</td>
</tr>
</tbody>
</table>

Table 5B. 2 represents the calculated weight percentage, ionic conductivity and activation energy values

Fig 5B. 4 Arrhenius plot of 3, 6, 9 wt% TiO2 based PVDF – co – HFP(30) IL(10) – EC+PC(60) wt% system
5B. 3.4 Scanning Electron Microscopic (SEM) analysis

Fig 5B. 5 represents the IL GPEs with different contents of TiO$_2$ namely 3, 6, 9 wt% (S1, S2 and S3) at 5K magnification. Pure PVdF-co-HFP polymer electrolyte is also displayed with same magnification for comparison. The dispersed filler particles are visible in the magnified surface and spread uniformly throughout the matrix. In the bare PVdF-co-HFP polymer, there are many sponge like structure. However, in the prepared composite polymer electrolyte, the surface becomes smooth without the well defined PVDF-co-HFP crystallites and have very well interconnected networks.

![SEM images of pure PVdF-co-HFP, prepared ILCGPE 3, 6, 9 wt% TiO$_2$ based PVDF – co – HFP(30) IL(10) – EC+PC(60)wt% system](image)

5B.3.5Thermo Gravimetric and Differential Thermal Analysis (TG/DTA)

Thermal stability of the prepared electrolytes was studied using TG/DTA analyses in order to study their suitability for the application in lithium battery. Fig5B.
6 (a-c) shows the trace of TG / DTA curves of polymer electrolyte containing different weight percentage of TiO₂ filler such as 3,6 and 9 wt %. The TG curves of IL CGPEs shows two stages of transmission as similar as the TG of bare IL. From the figure, it is observed that the first weight loss region appears around 273, 280, 267 °C respectively followed by the endothermic peak around 300 °C, confirming the thermal stability of [P₁₄,₆,₆,₆][Tf₂N] ionic liquid [23]. About (25-30%) of weight of the electrolyte. After that, next sharp transition occurs with the weight loss around 60% at 440, 475, 435°C respectively, with corresponding endothermic peak at 400 °C. The presence of residual carbon has the mass of nearly 24 wt%, upto 900°C. However, the high ionic conducting electrolyte has maximum thermal stability, compared to all other samples. Based on these studies, it is concluded that the sample with 6wt% of TiO₂ shows extended range of thermal stability of 280°C and hence, this composition have been chosen for the following electrochemical experiments such as linear sweep voltammetry, cyclic voltammetry and charge/ discharge analyses.

Fig 5B. 6 a TGDTA graph of prepared ILCGPE  S1 = S1= PVdF-co-HFP (30) + [P₁₄,₆,₆,₆][Tf₂N] (10) +EC+PC (60) + TiO₂ (3)wt%
Fig 5B. 6b TGDTA graph of prepared ILCGPE S2= PVdF-co-HFP (30) + [P14,6,6,6][Tf₂N] (10) + EC+PC (60) + TiO₂ (6) wt%
5B. 3.6 Linear sweep voltammetry (LSV)

The linear sweep voltammogram (LSV) of PVDHFP(30) : [P_{14,6,6,6}][Tf_2N] (10) : EC+PC (60) + TiO_2 (6wt%) sample at a scan rate of 5mV/s is displayed in Fig 5B. 7. As noted from figure, the negligible oxidation current has been observed up to 5.2V vs Li. After that, the current rises from 5.3V rapidly, which reveals the decomposition of polymer electrolyte. One can conclude that this electrolyte is stable up to this 5.2 voltage, and safe for lithium battery applications [36]. The sharp increase of anodic current represents

![Graph showing LSV](image)

Fig 5B. 7 LSV of PVD-HFP (30) + [P_{14,6,6,6}][Tf_2N] (10) + EC+PC (60) + TiO_2(6)wt% at a scan rate of 5mV/s

5B. 3.7 Cyclic voltammetry (CV)

Fig 5B. 8 represents the cyclic voltammetric curves of the PVDHFP(30) : [P_{14,6,6,6}][Tf_2N] (10) : EC+PC (60) + TiO_2 (6wt%) sample at a scan rate of 5 mV/s at first three cycles. The appearance of anodic and cathodic peak shows strong reversible
reaction of polymer electrolyte with Li electrode. The reduction peak representing the plating of lithium is about 3.28 V Vs Li/Li$^+$ and the oxidation peak corresponding to the stripping of lithium is around at 3.46 V vs Li/Li$^+$. The decrease of the current in the second cycle represents the formation of solid electrolyte interface (SEI) layer on the electrode surface, which will further reduce the reaction of electrode and electrolyte [37].

![Graph](image)

**Fig 5B. 8CV of PVdF-co-HFP (30) + [P$_{14,6,6,4}$][Tf$_2$N] (10) + EC+PC (60) + TiO$_2$ (6wt% at a scan rate of 5mV/s)**

**5B. 3.8 Charge-discharge performance**

The charge discharge study has been performed with Li anode and LiFePO$_4$ cathode for the electrolyte PVdF-HFP (30) : [P$_{14,6,6,6,5}$][Tf$_2$N] (10) : EC+PC (60) + TiO$_2$ (6wt%) for first ten cycles (Fig 5B.9). The flat and 3.4 V profile shows the active role LiFePO$_4$ cathode. The discharge capacity of 149 mAh/g is observed for first cycle. The discharge capacity slowly decreases in the consecutive cycles and at 10$^{th}$ cycle, the discharge value falls to 139 mAh/g A columbic efficiency of more than
90% is reached with this polymer electrolyte, which can be efficiently used in the operation of lithium batteries.

![Graph showing voltage vs capacity](image)

**Fig 5B.** 9 Charge discharge of PVdF-co-HFP (30) + [P_{14,6,6,6},][Te_2N] (10) + EC+PC (60) + TiO_2 (6)wt% at a scan rate of 5mV/s

**5B. 4 Conclusion**

The composite ionic liquid polymer electrolyte containing PVdF-co-HFP as copolymer and [P_{14,6,6,6},][Te_2N]/ EC+PC as IL with the incorporation of different compositions (3,6 and 9 wt%) of TiO_2 filler had been prepared and characterized. The maximum ionic conductivity of 1.15 \times 10^{-3} \text{ S/cm} was obtained for the polymer IL electrolyte with 6wt% of filler. XRD and FT-IR analyses elucidate the complexation occurred in the complexes upon addition of TiO_2. The prepared electrolyte with 6wt% of filler based system thermally stable upto 280 °C, which is confirmed by thermal analysis. Surface morphologic characteristics obtained from SEM images show that polymer electrolyte has well interconnected network after adding TiO_2. The
well crystalline region of pure PVdF-HFP has been completely smoothened upon the addition of IL and plasticizer and TiO₂ as well. LSV and CV studies confirm that the electrochemical stability is up to 5.2V and the CPE with 6wt% of TiO₂ delivers an excellent discharge capacity of 149 mAh/g. This study provides a platform that the sulphonium IL based electrolytes have also provided the better ionic conductivity, the discharge capacity. But, the phosphonium IL based electrolytes have delivered discharge capacity than sulphonium electrolytes with rather lower ionic conductivity. From these analysis, phosphonium based ILCGPE can be served as a potential candidate in Li- secondary battery fabrication.

References


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