CHAPTER VI

DEVELOPMENT OF SPVDF-co-HFP/PWA COMPOSITE PEM LAMINATED BY POLYPYRROLE FOR DIRECT METHANOL FUEL CELLS

6.1 Introduction

Addition of inorganic material with organic polymer extended great attention in the fabrication of novel PEM for DMFCs (Kim et al. 2008). The inorganic additives like heteropoly acids (HPA) are widely employed to improve the proton conductivity and mechanical stability of Nafion and other PEMs (Cui et al. 2007). Among the various heteropolyacids, herein, phosphotungstic acid (H$_3$PW$_{12}$O$_{40}$) (PWA) was chosen as inorganic additive material because of its high proton conductivity and its discrete ionic structure (Xu et al. 2010). But the solubility of PWA in polar solvents leads to the leaching of PWA from the composite membrane which reduces the cell performance of PEM. This problem can be minimized by surface coating of PEM which alter the surface properties of the PEM. Recently surface coating of polypyrrole (PPY) on the hybrid membranes such as SPEES/TPA and SPEEK/TPA diminishes the leaching process and also decreases the methanol crossover significantly (Xu et al. 2006). Modification of SPEEK by PPY layer shows good membrane selectivity than pristine SPEEK and Nafion 117 (Li et al. 2013). Based on these concepts, herein, novel PEM was developed by (i) sulfonation of PVdF-co-HFP, (ii) incorporation of SPVdF-co-HFP with phosphotungstic acid (PWA) which improves the proton conductivity, and (iii)
lamination of polypyrrole on the composite SPVdF-co-HFP/PWA PEM that prevents the leaching and controls the methanol crossover.

6.2 Results and discussion

6.2.1 Water uptake

Water uptake of sulfonated polymers plays an essential role in transport nature and mechanical behavior of the proton exchange membrane. Fully hydrated form of sulfonated polymers dissociates into mobile protons and immobile sulfonic acid groups in an aqueous solution (Yuan et al. 2008). The developed SPVdF-co-HFP/PWA blend membrane exhibited higher water uptake of 31.8% than SPVdF-co-HFP, because the hydrophilic and hygroscopic nature of phosphotungstic acid which assists the blend membrane to attract huge amount of water molecules (Jung et al. 2004). This hydrophilic nature of PWA can afford additional sites for hydrogen bonding and new acid sites for water absorption. When the developed PEM absorbs the large amount of water, the number of accessible exchange sites per cluster increases, consequently increases the proton conductivity value of PEM. The Figure 6.1 clearly shows that the water uptakes of SPVdF-co-HFP/PWA/PPY-n laminated membranes are decreasing steadily by increasing the number of polypyrrole layer. SPVdF-co-HFP/PWA/PPY-n (where n = 0, 1, 3, 5 denotes the number of times coating process was repeated.) PEMs have the water uptake values in the range of 29.1% to 22.8%. This decreasing nature of water uptake of PPY laminated PEMs are due to the formation of hydrogen bond between amine group of PPY and sulfonic acid group of SPVdF-co-HFP. Thus the results of water uptake specify that
lamination of PPY layer on the SPVdF-co-HFP makes the surface into less hydrophilic.

Figure 6.1 Water uptake and swelling ratio of pure SPVdF-co-HFP, SPVdF-co-HFP/PWA, SPVdF-co-HFP/PWA/PPY-n and Nafion PEMs
6.2.2 Swelling ratio

Swelling ratio is one of elementary property to understand the mechanical stability of PEM. The swelling ratio of pure SPVdF-co-HFP, SPVdF-co-HFP/PWA and SPVdF-co-HFP/PWA/PPY blend PEMs are shown in Figure 6.1. The swelling ratio value was increased from 18.2% to 20.3% by blending with hydrophilic PWA, whereas the swelling ratio values were decreased regularly by increasing the layer of PPY on SPVdF-co-HFP/PWA membrane. Due to the interaction of SPVdF-co-HFP and PPY the swelling ratio of fabricated PEM was lowered (Honma et al. 2001). This may be the reason for the suppression of swelling ratio. But, the coating of PPY on SPVdF-co-HFP/PWA composite PEM can improve the mechanical stability of fabricated membranes, which is promising feature for the PEM to be used in DMFCs (Prifti et al. 2012).

6.2.3 Ion exchange capacity and Lambda value

The ion exchange capacity is an extent of the capacity of ion exchanging and ion transferring of membranes. The number of ion exchangeable species per unit mass (IEC) value plays a vital role in the determination of proton conductivity of membranes used in DMFCs. From Figure 6.2, it is inferred that the addition of phosphotungstic acid (PWA) exclusively increases the IEC value of SPVdF-co-HFP membrane (Li et al. 2006 b). An incorporation of PWA with SPVdF-co-HFP improves the acidic property of the SPVdF-co-HFP/PWA composite membrane, supplying new strong acidic sites and is estimated to be favorable for enhancing the proton conductivity of the membrane and water absorbing capacities. Figure 6.2
also indicates that SPVdF-co-HFP/PWA composite membranes exhibited an IEC value of 0.484 meq. g\(^{-1}\) whereas for PPY laminated SPVdF-co-HFP/PWA composite membranes, it was declined to 0.437 meq. g\(^{-1}\). This declining trend was attributed due to the reduction of ionic sites in PPY and the hydrophobic nature of PPY.

Figure 6.2  IEC and Lambda value of pure SPVdF-co-HFP, SPVdF-co-HFP/PWA and SPVdF-co-HFP/PWA/PPY composite PEMs

Lambda value for all the PEMs was determined and displayed in Figure 6.2. The electrochemical properties such as water uptake, swelling ratio, ion exchange capacity and lambda value for all the PEMs follows the same pattern. The
presence of hydrophilic PWA increases the lambda value and hydrophobic PPY decrease the lambda value, since it is calculated from water uptake and IEC.

6.2.4 FT-IR

Figure 6.3 represents the FT-IR spectrum of (a) SPVdF-co-HFP, (b) SPVdF-co-HFP/PWA and (c) SPVdF-co-HFP/PWA/PPY-5 proton exchange membranes (PEMs). The FT-IR spectrum of all PEMs showed bands around 3900 cm\(^{-1}\), 1400 cm\(^{-1}\), and 1076 cm\(^{-1}\), representing –OH stretching present in the sulfonic acid group and symmetric and asymmetric stretching vibrations of S=O bond of the sulfonic acid group in SPVdF-co-HFP. Three characteristic peaks are already assigned for Keggin structure of pristine PWA powders. In the FT-IR spectra of SPVdF-co-HFP/PWA (b) composite PEM and SPVdF-co-HFP/PWA/PPY-5 (c) PEM, characteristic peaks assigned for Keggin structure of PWA are observed. In the blend PEM and PPY coated blend PEM, the terminal oxygen band of PWA is red shifted from 968 cm\(^{-1}\) to 950 cm\(^{-1}\) and the bridging oxygen bands are also red shifted from 887 cm\(^{-1}\) and 797 cm\(^{-1}\) to 880 cm\(^{-1}\) and 770 cm\(^{-1}\) respectively (Li & Wang et al. 2006). This shifting of frequency was probably due to the columbic interaction between the terminal oxygen and the bridging oxygen of the PWA and sulfonic acid group of the polymer matrix in connection with water molecules (Kim et al. 2003 b).
Figure 6.3  FT-IR spectra of (a) pure SPVdF-co-HFP, (b) SPVdF-co-HFP/PWA and (c) SPVdF-co-HFP/PWA/PPY-5 PEMs

In the SPVdF-co-HFP/PWA/PPY-5 (c) spectra, the band at 1486 cm$^{-1}$, and 1600 cm$^{-1}$ is attributed to C=C stretching, the band at 1320 cm$^{-1}$ is assigned to C-N stretching, the band at 1690 cm$^{-1}$ is assigned to C=N stretching and new band formed at 3550 cm$^{-1}$ is assigned for N-H stretching respectively. The bands observed
in the present study match well with literature value of polypyrrole (Arora et al. 2005, MA et al. 2011) confirming the coating of PPY in SPVdF-co-HFP/PWA/PPY-5 PEM.

### 6.2.5 Contact angle measurement

The relative nature of hydrophilicity/hydrophobicity of the fabricated PEMs can be evaluated by contact angle measurements. Generally, the sample with more hydrophilic nature shows the smaller the contact angle (Zhong et al. 2007). Table 6.1 lists out the contact angle values of the pure SPVdF-co-HFP, SPVdF-co-HFP/PWA and SPVdF-co-HFP/PWA/PPY composite membranes. From Table 6.1, the contact angle of SPVdF-co-HFP PEM is lower due to the presence of hydrophilic –SO$_3$H acid group and it is further reduced by increasing PWA content, whereas the contact angle steadily increased by increasing the coating of hydrophobic PPY as expected.

#### Table 6.1 Oxidative stability, contact angle, tensile strength, elongation at yield and Young’s modulus of fabricated SPVdF-co-HFP based PEMs

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Oxidative stability (%)</th>
<th>Contact angle (°)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at yield (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPVdF-co-HFP</td>
<td>26.53</td>
<td>66.7±0.20</td>
<td>20.01</td>
<td>28.20</td>
<td>381.67</td>
</tr>
<tr>
<td>SPVdF-co-HFP/PWA</td>
<td>26.31</td>
<td>74.0±1.86</td>
<td>17.21</td>
<td>25.70</td>
<td>371.42</td>
</tr>
<tr>
<td>SPVdF-co-HFP/PWA/PPY -1</td>
<td>26.51</td>
<td>42.0±1.42</td>
<td>19.11</td>
<td>28.00</td>
<td>380.95</td>
</tr>
<tr>
<td>SPVdF-co-HFP/PWA/PPY -3</td>
<td>26.74</td>
<td>60.4±1.39</td>
<td>20.81</td>
<td>30.20</td>
<td>390.20</td>
</tr>
<tr>
<td>SPVdF-co-HFP/PWA/PPY -5</td>
<td>26.99</td>
<td>65.8±1.12</td>
<td>22.41</td>
<td>32.20</td>
<td>399.21</td>
</tr>
</tbody>
</table>
6.2.6 Thermal stability

Thermal gravimetric analysis was performed to probe the effect of coating of PPY on the SPVdF-co-HFP/PWA PEM on thermal stability of fabricated PEMs.

Figure 6.4 TGA curves of (a) SPVdF-co-HFP, (b) SPVdF-co-HFP/PWA and (c) SPVdF-co-HFP/PWA/PPY-5 PEMs

Figure 6.4 displays TGA curves of SPVdF-co-HFP, SPVdF-co-HFP/PWA, and SPVdF-co-HFP/PWA/PPY-5 membranes. All these TGA curves can be divided into three regions corresponding to different weight loss ranges. First weight loss range was around 100 °C to 120 °C due to the loss of residual water present in the fabricated PEM. The de-sulfonation process was related with the second weight loss in the temperature range of 200 °C to 250 °C (Huang et al. 2011). In SPVdF-co-HFP
PEM the decomposition of polymer backbone was occurred at 500 °C, for SPVdF-co-HFP/PWA and SPVdF-co-HFP/PWA/PPY – 5 PEM, it was occurred at 466 °C and 315 °C respectively. This was the third weight loss of PEMs.

This suggests that SPVdF-co-HFP and SPVdF-co-HFP/PWA blend membranes were highly stable compared to SPVdF-co-HFP/PWA/PPY-5. Lamination of PPY on SPVdF-co-HFP/PWA PEM can reduce the thermal decomposition of polymer chain which is mainly due to the ionic interaction between the secondary ammonium groups of PPY and sulfonic acid group of SPVdF-co-HFP in the SPVdF-co-HFP/PWA/PPY-5 hybrid membrane (Park et al. 2006). The thermal behavior of the PPY layered PEMs are satisfactory for the working temperature of the PEM used for DMFCs.

### 6.2.7 Mechanical stability

Mechanical behavior of a PEM is one of its significant aspects, considering its stability in DMFCs. The tensile strength at break of the developed PEMs was studied at room temperature in dry condition and was displayed in Figure 6.5. The tensile strength at break, elongation at yield and Young’s modulus of PEMs were given in Table 6.1. The tensile strength of the SPVdF-co-HFP/PWA composite membrane was lesser than those of SPVdF-co-HFP membrane. This fall in tensile strength had been shown the lack of physicochemical contact between the PWA and SPVdF-co-HFP matrix (Smitha et al. 2005 a).

Tensile strength of PPY layered SPVdF-co-HFP/PWA composite membranes were steadily increased. Thus the coating of PPY on the SPVdF-co-HFP/PWA composite membrane enhanced the rigidity of the membrane due to the electrostatic interaction between the PPY with PWA and SPVdF-co-HFP. Moreover,
all the developed PEMs possessed high tensile strength compared to Nafion 117 (12.79 MPa) (Kumar et al. 2014). These results specified that the SPVdF-co-HFP/PWA/PPY membranes are good enough for the PEM in DMFCs.

Figure 6.5   Tensile strengths of pure SPVdF-co-HFP, SPVdF-co-HFP/PWA and SPVdF-co-HFP/PWA/PPY composite PEMs
6.2.8 Oxidative stability

Oxidative stability of all the fabricated PEMs was calculated using Fenton’s reagent and it was improved by increasing the layer of PPY. All of the composite membranes retained more than 95% of their original weight after the immersion period in Fenton’s reagent. If the number of PPY coating increases, PEM becomes little harder for free radicals to attack the polymer matrix (Neelakandan et al. 2015 b). Thus, compared to SPVdF-co-HFP PEM, PPY laminated hybrid membranes show good oxidative stability.

6.2.9 AFM analysis

The surface morphology study in terms of surface roughness of the developed PEMs was estimated using the tapping mode AFM technique.
Figure 6.6  AFM images of (a) SPVdF-co-HFP, (b) SPVdF-co-HFP/PWA, and (c) SPVdF-co-HFP/PWA/PPY-5 PEMs.

Figure 6.6 shows the both two dimensional and three dimensional AFM images of membrane surface for SPVdF-co-HFP, SPVdF-co-HFP/PWA, SPVdF-co-
HFP/PWA/PPY-5 at a scan size of 5 × 5 mm² and the surface roughness values of the PEMs are given in Table 6.2. The roughness of the surface is raised by blending PWA to SPVdF-co-HFP. The surface roughness values for SPVdF-co-HFP/PWA/PPY-n PEMs decreases regularly when PPY coating is increased. SPVdF-co-HFP/PWA/PPY-5 AFM image (Figure 6.6-2D C, 3D C) clearly shows that the coating of PPY causes considerable change in surface morphology of the laminated PEM. The PPY laminated membranes had smooth surfaces compared to other PEMs. The change in surface morphology may lead to the change in the properties such as, water uptake, swelling ratio and proton conductivity (Zhao et al. 2010). The trend observed in the surface roughness parameters are analogous to those found in water uptake and proton conductivity. Thus the surface roughness parameter increases by the addition of PWA and decreases with increasing the PPY coating on the PEM surface.

Table 6.2 Roughness parameter of SPVdF-co-HFP, SPVdF-co-HFP/PWA and SPVdF-co-HFP/PWA/PPY composite membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Roughness parameter</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sa</td>
<td>Sq</td>
<td>Sz</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(nm)</td>
<td>(nm)</td>
<td>(nm)</td>
<td></td>
</tr>
<tr>
<td>SPVdF co HFP</td>
<td>42.00</td>
<td>53.70</td>
<td>235.80</td>
<td></td>
</tr>
<tr>
<td>SPVdF co HFP/PWA</td>
<td>48.74</td>
<td>64.52</td>
<td>283.13</td>
<td></td>
</tr>
<tr>
<td>SPVdF-co-HFP/PWA/PPY-1</td>
<td>22.90</td>
<td>29.37</td>
<td>120.69</td>
<td></td>
</tr>
<tr>
<td>SPVdF-co-HFP/PWA/PPY-3</td>
<td>18.81</td>
<td>25.69</td>
<td>130.01</td>
<td></td>
</tr>
<tr>
<td>SPVdF-co-HFP/PWA/PPY-5</td>
<td>15.51</td>
<td>20.03</td>
<td>89.93</td>
<td></td>
</tr>
</tbody>
</table>
6.2.10 Proton conductivity

Prior to measurements of proton conductivity, all the PEMs were immersed in deionized water for hydration. Partial sulfonation of PVdF-co-HFP increases the proton conductivity of PEM. Blending of high strength heteropoly acid, such as phosphotungstic acid (PWA) again increases the proton conductivity of PEMs as shown in Figure 6.7. The ionic cluster size, water uptake tendency, acid site density, heteropoly acid strength, hydrophilicity are the crucial properties that affect the proton conductivity of the composite membrane. Heteropolyacid like PWA has enormously high proton mobility and Keggin anions of PWA are also quite movable. SPVdF-co-HFP/PWA blend membrane possesses high proton conductivity of $7.9 \times 10^{-3}$ S/cm due to the hydrophilic nature of PWA and sulfonic acid group present in the SPVdF-co-HFP polymer matrix. The proton conductivities of PPY layered SPVdF-co-HFP/PWA composite PEMs were decreased gradually with increase in the number hydrophobic polypyrrole layer on the surface of the membrane. The interaction between PPY with SPVdF-co-HFP and PWA will lead to more compact structure. Due to the compact structure, the ionic cluster mobility will be limited in PPY surface coated membrane, which will shrink the proton conductivity (Muthumeenal et al. 2016 b).
Figure 6.7  Proton conductivity values of Nafion-117, SPVdF-co-HFP, SPVdF-co-HFP/PWA, SPVdF-co-HFP/PWA/PPY-n composite membranes

6.2.11  Methanol crossover

As well-known, methanol crossover through the membranes is a very important detrimental barrier that reduces the DMFCs performance. In general, proton exchange membrane with high proton conductivity yields ionic cluster
regions containing protons, alcohols and sulfonic acid groups used for the permeation of methanol from anode that oxidized at cathode and consequently decreases the performance of the DMFCs (Gumus et al. 2011). The methanol crossover of the SPVdF-co-HFP, SPVdF-co-HFP/PWA and SPVdF-co-HFP/PWA/PPY-n composite membranes were determined at room temperature and the results of methanol crossover experiments were given in Figure 6.8. For the SPVdF-co-HFP/PWA/PPY-n hybrid PEMs, the methanol crossover values decreases regularly by increasing the number of polypyrrole layer in SPVdF-co-HFP/PWA. The pristine SPVdF-co-HFP shows the methanol crossover value of $2.34 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}$, while, SPVdF-co-HFP/PWA/PPY-n hybrid PEMs shows the methanol crossover values in the range of $2.28 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}$ to $1.73 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}$. The reduction in methanol crossover values in SPVdF-co-HFP/PWA/PPY-n hybrid PEMs are due to the hydrophobic nature of PPY which forms dense structure on the membrane surface. Thus lamination of polypyrrole layer on SPVdF-co-HFP/PWA composite membranes reduces the methanol crossover by reducing the number of sulfonic groups, which are important for development of transport channel (Li et al. 2013). Nafion have a high proton conducting capacity; though it possess high methanol crossover. Hence, it is a great task for the researchers to develop membranes with low methanol crossover, although maintaining comparable proton conductivity value to that exhibited by Nafion. Herein, all the prepared PEMs have much lower methanol crossover values compared to Nafion -117 whose value is $63 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}$. 
6.2.12 Selectivity ratio

All the fabricated PEMs had greater selectivity ratio compared to Nafion-117 (0.994 × 10^4 Scm^3s) From Figure 6.8, the selectivity ratio of SPVdF-co-HFP/PWA/PPY-5 composite PEM possess highest value of 2.937 × 10^4 Scm^3s,
since this selectivity ratio purely depends on both proton conductivity and methanol crossover parameter.

6.3 Conclusions

SPVdF-co-HFP/PWA/PPY-n composite PEM was successfully developed, in which polypyrrole was laminated on the SPVdF-co-HFP/PWA membrane surface using in-situ polymerization technique. The loading of inorganic additive phosphotungstic acid (PWA) to SPVdF-co-HFP PEM afforded admirable increase in the proton conductivity in the PEM. In addition, coating of PPY on the both sides of SPVdF-co-HFP/PWA PEM helped to reduce leaching of PWA. Addition of inorganic heteropoly acid such as PWA and the surface coating of polypyrrole to the SPVdF-co-HFP organic polymer were confirmed by FTIR spectral analysis. The surface morphological study using AFM technique proved that surface coating of PPY layer on the SPVdF-co-HFP/PWA PEM decreased the surface roughness of the membrane. The water uptake, ion exchange capacity, proton conductivity values were found to be improved with the addition of PWA while the tensile strength, oxidative stability and thermal stability were enhanced by surface coating of PPY on the hybrid PEM. Lamination of PPY on SPVdF-co-HFP/PWA led to the reduction of methanol crossover and the enhancement of selectivity ratio values showed that the fabricated SPVdF-co-HFP/PWA/PPY composite PEM was a promising material as PEM used for DMFCs.