CHAPTER 4

4. RESULTS AND DISCUSSION

SECTION 4A: A STUDY ON THE COMBINED EFFECT OF VARIOUS SUPPORTING ELECTROLYTES, FLOW CHANNEL DESIGNS AND OPERATING TEMPERATURES IN ORDER TO OPTIMIZED THE DMFC PERFORMANCE

4A.1. Introduction

Establishing a better coordination between operating parameters and flow channel design is one of the most critical factors in achieving an optimum final performance of a fuel cell, since even a marginal change in any of the parameters can sharply affect the cell’s performance. In this section, we report the use of three different acids, viz. sulphuric acid (H$_2$SO$_4$), formic acid (HCOOH) and phosphoric acid (H$_3$PO$_4$) as supporting electrolytes in combination with 2 M methanol fuel, wherein we demonstrated the effects of different combinations of acidic fuels and channel designs on the final cell performance.

4A.2. Acidic fuels

Acidic fuel samples were prepared by mixing variable amounts (molar concentrations) of acids having different pKa values (Table 4A.1) as a supporting electrolyte with 2 M methanol. Three different acids (formic acid, sulfuric acid and phosphoric acid) were introduced into the methanol fuel. Composition of DMFC fuels used in our study is represented in Table 4A.2. 2 M methanol was used as a reference fuel.

Table 4A.1: pKa value of acids

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Acids</th>
<th>1$^{st}$ dissociation (pKa)</th>
<th>2$^{nd}$ dissociation (pKa)</th>
<th>3$^{rd}$ dissociation (pKa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>H$_2$SO$_4$</td>
<td>-3.00</td>
<td>1.99</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>HCOOH</td>
<td>3.77</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>H$_3$PO$_4$</td>
<td>2.12</td>
<td>7.21</td>
<td>12.32</td>
</tr>
</tbody>
</table>
Table 4A.2: Composition of fuel samples.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Fuel samples</th>
<th>M2</th>
<th>M2S0.5</th>
<th>M2S1</th>
<th>M2S2</th>
<th>M2F0.5</th>
<th>M2F1</th>
<th>M2F2</th>
<th>M2P2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Methanol</td>
<td>2 M</td>
<td>2 M</td>
<td>2 M</td>
<td>2 M</td>
<td>2 M</td>
<td>2 M</td>
<td>2 M</td>
<td>2 M</td>
</tr>
<tr>
<td>2.</td>
<td>Sulphuric acid</td>
<td>-</td>
<td>0.5 M</td>
<td>1.0 M</td>
<td>2 M</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>Formic acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5 M</td>
<td>1.0 M</td>
<td>2 M</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>Phosphoric acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2 M</td>
</tr>
</tbody>
</table>

4A.3. Anode flow channel designs

Four types of serpentine channel designs, having different channel lengths and open ratios, were used as anode (Figure 4A.1). These were in turn assembled on the surface of graphite bi-polar plates. The effective area of the MEA for each design was kept constant at 5x5 cm². The depth of the channel was maintained at 1 mm for each channel design. The design A5SF4 was used as a reference (lowest value of open ratio i.e. 48%). The other geometries of the different channel designs utilized in this study are listed in Table 4A.3.

Table 4A.3: Geometry of flow channel designs.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample Designated</th>
<th>No. of flow line</th>
<th>Cross-sectional area (mm²)</th>
<th>Length of flow line (mm)</th>
<th>Width of flow line channel (mm)</th>
<th>Width of rib (mm)</th>
<th>Depth of channel (mm)</th>
<th>Open ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>A5SF1</td>
<td>1</td>
<td>1.00</td>
<td>1250</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>50</td>
</tr>
<tr>
<td>2.</td>
<td>A5SF2</td>
<td>2</td>
<td>2.00</td>
<td>650</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>52</td>
</tr>
<tr>
<td>3.</td>
<td>A5SF4</td>
<td>4</td>
<td>6.00</td>
<td>150</td>
<td>1.50</td>
<td>1.50</td>
<td>1.00</td>
<td>48</td>
</tr>
<tr>
<td>4.</td>
<td>A5SF6</td>
<td>6</td>
<td>9.00</td>
<td>90</td>
<td>1.50</td>
<td>1.50</td>
<td>1.00</td>
<td>56</td>
</tr>
</tbody>
</table>
4A.4. Effect on cell potential (OCV)

Effect on cell potential rendered by the use of various fuel samples were analyzed from the DMFC test for a period of 1 hour. Figure 4A.2, shows the voltage-time curves obtained for the different fuel samples. From the figure, it can be seen that the maximum cell potential obtained for reference fuel (M2) is 0.72 V; however, with the addition of sulfuric acid (M2S2) and phosphoric acid (M2P2), the cell potential drops down marginally to 0.65 V and 0.69 V, respectively. This lowering is due to the fact that the bisulfate and phosphate anions generated at the anode get adsorbed on the active platinum sites (known as poisoning effect) and inhibit the rate of methanol oxidation.
[41]. This decrement in rate of methanol oxidation leads to slight enhancement of methanol crossover. The crossovered methanol gets oxidized at cathode and lowers the cell potential (OCV). Furthermore, it is interesting to note that in the case of fuel containing formic acid (M2F2), the cell potential further drops down significantly to 0.51 V, which is much lower than that obtained for the above two acids. The reasons behind this observation are: (a) co-oxidation of formic acid along with methanol [131], yielding CO₂ as the common byproduct, as shown in the Equations (4.1) and (4.2) below:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad (4.1)
\]

\[
\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (4.2)
\]

(b) lower anodic polarization potential of formic acid (~0.1 V) in comparison to that of methanol on a standard Pt/Ru/C catalyst [3], leading to a slight sluggish electro-oxidation reaction of methanol [131], and (c) methanol crossover is six times greater than formic acid crossover under the same operating conditions[132, 133]. Therefore, in the M2F2 fuel sample, the adsorption of the formic acid on active platinum sites is slightly faster and its crossover rate is Lower than that for methanol. The crossovered methanol in the cathodic side of the cell hampers oxygen reduction by blocking Pt sites on the cathode. This is because methanol after crossover reacts directly with oxygen at these sites and produces H₂O that causes cell flooding and increases the required oxygen stoichiometry.
[131]. In addition, the methanol upon reaching the cathode gets oxidized in presence of Pt catalyst and gives rise to a reverse potential. These two effects lead to the lowering of OCV of the cell significantly.

4A.5. Performance of acidic fuels

The performances of different fuel samples were investigated on a single cell under the same operating conditions. The obtained results, plotted in Figure 4A.3, reveal the voltage versus current density curves. The maximum current densities recorded for fuels M2, M2F0.5, M2S0.5, M2F1, M2S1, M2F2, M2S2 and M2P2 were respectively 50, 50, 60, 52, 85, 55, 120 and 105 mA cm\(^{-2}\) at 0.2 V potential. From the above results, it can be said that an acid acting as a supporting electrolyte, can potentially enhance the performance of DMFC. It is due to the fact that in acidic fuel, the oxidation current increases significantly by virtue of improvement in the solution conductivity [43]. In addition, the kinetics of methanol oxidation at a Pt/Ru electrode is relatively faster, followed by faster deactivation with a maximum current generation [41]. Considering the reaction steps of methanol oxidation, an increase in solution conductivity leads to faster adsorption of methanol (\(k_1\)) (Equation 4.3), which subsequently increases the rate of methanol dehydrogenation (\(k_2\)) (Equation 4.4).

\[
CH_3OH_{\text{sol}} \rightleftharpoons CH_3OH_{\text{ad}} \quad (4.3)
\]

\[
CH_3OH_{\text{ad}} \rightarrow CO_{\text{ad}} + 4H^+ + 4e^- \quad (4.4)
\]

\[
CO_{\text{ad}} + OH_{\text{ad}} \rightarrow CO_2 + H^+ + e^- \quad (4.5)
\]

Furthermore, the current density obtained for fuels containing 0.5 M acid is lower than that corresponding to fuels containing 1 to 2 M acid. It is due to a moderate change of acidity which leads to a lower solution conductivity. On the contrary, fuels containing 1 M acid show significant enhancement in its current density values, which is close to its corresponding fuel sample containing 2 M acid. It is to be noted that the fuel sample M2S2 yielded the best performance among all the employed fuel samples. The maximum current densities obtained for M2P2 (containing 2 M H\(_3\)PO\(_4\)) and M2S2 (containing 2 M
H₂SO₄) were respectively 105 mA cm⁻² and 120 mA cm⁻² at 0.2 V. This result is a definite improvement over that obtained for a simple 2 M methanol feeding. This arises from the lower pKa values of sulfuric acid (-3.00 and 1.99) and phosphoric acid (2.12, 7.21, 12.32) (Table 4A.1), which in turn leads to faster and complete dissociation of H⁺-ions.

![Performance of fuel samples on A5SF4.](image.png)

The dissociation of H⁺-ions from the acids is much quicker than the stripping of H⁺-ions from methanol via its oxidation. The H⁺-ions from the acids form H₃O⁺ ions in the solution, resulting in fast transportation of these ions generated from the electro-oxidation of methanol. Therefore, the conductivity of H⁺-ions gets increased, leading to improved current density of the cell. Hence, it can be safely said that utilization of methanol in acidic solution gets increased at high current density/low voltage region compared to simple methanol feeding. The schematic representation of proton conductivity in acidic fuel, as compared to simple DMFC fuel, is illustrated in Figure 4A.4.
4A.6. Effect of flow channels

From the above results, it appears that the better fuel composition in each category of acid is the fuel containing 2 M acid along with 2 M methanol. Therefore, experiments were henceforth performed considering only these fuel compositions. Our next aim was to investigate the effect of anode flow channel design on DMFC performance. Four anode flow channels with different channel lengths, as well as, different open ratios were employed to analyze their effect on the performance of DMFC for the fuel samples M2, M2S2, M2F2 and M2P2. From the experimental results, plotted in Figures 4A.5-4A.7, it can be seen that the flow field A5SF2 having a channel length of 650 mm and an open ratio of 52%, yielded a better cell performance for each fuel sample compared to the other three flow fields, that is A5SF1, A5SF4 and A5SF6 with open ratios 50%, 48%, 56% and channel lengths of 1250 mm, 150 mm and 90 mm, respectively. Results indicate that the cell performance at each flow channel design with different channel lengths was very close to each other in the lower current density region. However, in the higher current density region, the performance of the cell with a channel length of 650 mm (A5SF2) was much better than the other three flow channel designs.
The current density for fuel samples M2, M2S2, M2F2 and M2P2 at flow channels A5SF4 was recorded as 50, 120, 55 and 105 mA cm\(^{-2}\) (Figure 4A.3) respectively, while at flow channels A5SF6, it was 45, 105, 50 and 90 mA cm\(^{-2}\) at 0.2 V, respectively (Figure 4A.5). The lower current density values obtained in comparison with that obtained for A5SF2 (Figure 4A.6), that is 90, 210, 110, and 180 mA cm\(^{-2}\) are due to the fact that the shorter channel lengths (150 mm and 90 mm) resulted in fast discharging of fuel from the cell, hence causing the fuel to rest in contact with MEA for a very short time. This further diminishes the fuel distribution, leading to direct reduction in mass transfer of methanol from the channel to the MEA. In addition, at the same flow rate (2 ml min\(^{-1}\)) the liquid (fuel) velocity is lower in channel design A5SF4 and A5SF6 than the channel A5SF1 and A5SF2. It is because the cross-sectional areas (Table 4A.3) of these two channels (A5SF4 and A5SF6) are much higher (6 and 9 mm\(^2\), respectively) than those of A5SF1 and A5SF2 (1 and 2 mm\(^2\), respectively). A lower cross-sectional area gives rise to a higher liquid velocity, which in turn enhances the mass transport of methanol from the channel to the MEA [103, 134]. On the other hand, the open ratio for flow design A5SF4 is 48%, while for A5SF6 it is 56%. These are the lowest and the highest value of open ratio among all the flow channel designs employed in this experiment.

Fig.4A.5 Performance of fuel samples on A5SF6.
Fig. 4A.6 Performance of fuel samples on A5SF2.

Fig. 4A.7 Performance of fuel samples on A5SF1.
The lower value of open ratio corresponded to a limited contact area between the PEM and the fuel, while the larger value corresponded to higher contact area. A higher open ratio, in turn, creates two serious problems, namely an increase in both the internal resistance of the cell and the methanol cross-over [103]. Both these cases resulted in a reduction of the overall cell performance. The current densities for A5SF1, obtained in the same voltage region (i.e. 0.2 V), were recorded as 60, 165, 75 and 140 mA cm$^{-2}$ for M2, M2S2, M2F2 and M2P2 respectively, (Figure 4A.7) and these are higher in comparison to both A5SF4 (Figure 4A.3) and A5SF6 (Figure 4A.5). However, these are slightly lower than that obtained for the flow channel design A5SF2 (Figure 4A.6), in spite of the fact that this particular design had the longest channel length among all the flow designs employed. The reason behind this observation is that a higher length of 1250 mm caused much delayed discharge of the oxidized fuel from the channel, thus restricting fresh fuel to come into the cell. The maximum power density obtained for each fuel at each channel design is plotted in Figure 4A.8, which quantifies the cell efficiency. The maximum power densities of 42 and 36 mW cm$^{-2}$ were obtained for the flow channel design A5SF2, corresponding to fuels containing sulfuric acid (M2S2) and phosphoric acid (M2P2), respectively.

**Fig.4A.8** Power density for fuel samples at each flow channel design.
4A.7. Effect of temperature

To investigate the effect of temperature on the performance of DMFC, the cell was operated at three variable temperatures of 60, 70, and 80 °C. It was observed that with an increase in temperature from 60 °C to 80 °C, the current density of 2 M methanol (M2) increases (Figure 4A.9). The observed increase may be explained by the fact that at higher temperature, the electro-oxidation reaction of methanol in presence of platinum becomes faster [134]. In case of fuel samples M2S2 and M2P2 (Figures 4A.10 and 4A.11), a marginal enhancement of current density is observed within the temperature range from 60 °C to 70 °C. However, at a higher temperature of 80 °C, the current density showed a sharp decrease for sulfuric acid, while a marginal drop was observed for phosphoric acid. This is because platinum or its alloys are invariably used in lower temperature especially in acid electrolytes [135]. Methanol oxidation in presence of Pt or Pt-Ru catalysts is strongly dependent on the pH of the solution and operating temperature [41]. Equation 4.6 shows the relation between pH and pKa value for dissociated acid.

\[
pH = pKa + \log([A^-]/[HA])
\]  

(4.6)

where, \([A^-]\) is the concentration of the conjugate base of the dissociated acid (HA), and \([HA]\) is the concentration of the undissociated acid.

The observed sharp decrease in current density is because of sulfuric acid having lower pKa value (Table 4A.1) than phosphoric acid. A lower pKa value is associated with a higher strength, as well as, faster dissociation rate of an acid (Equation 4.6), and this essentially enhances the concentration of bi-sulfate (for \(H_2SO_4\)) and phosphate anions (for \(H_3PO_4\)) in the fuel at anode. Higher concentration of these anions resulted in inhibiting the kinetics of methanol oxidation either by: (a) blocking the adsorption of methanol on platinum active sites, leading to decrease in \(k_1\) and \(k_2\) values (Equations 4.3 and 4.4, respectively), and/or (b) displacing \(OH_{ad}\) from the surface, which decreases the \(k_3\) (Equation 4.5) [41]. This leads to decrease in electrical efficiency, as evidenced from the sharp drop in current density curve (Figure 4A.10). For fuel sample M2F2 (Figure 4A.12), the obtained result is just contrary to the above observation, i.e. the current density showed an increase upon increasing the cell temperature from 60 °C to 80 °C. The reason behind this observation is that the kinetics of methanol/formic acid oxidation...
increases at higher temperature in presence of standard Pt/Ru/C electrode [25, 136], leading to a better cell performance.

**Fig.4A.9** Effect of temperature on DMFC performance for fuel sample M2.

**Fig.4A.10** Effect of temperature on DMFC performance for fuel sample M2S2.
Part of this section is published in Int. J. Energy Res. 38 (2014) 41–50.

Fig. 4A.11 Effect of temperature on DMFC performance for fuel sample M2P2.

Fig. 4A.12 Effect of temperature on DMFC performance for fuel sample M2F2.
4A.8. CONCLUSIONS

In summary, we observed that an addition of small amount (2 M) of phosphoric and sulfuric acid enhances the performance of DMFC rapidly in terms of current density. The maximum current densities were obtained for the fuels containing 2 M sulfuric acid (M2S2) and 2 M phosphoric acid, represented by values of 210 mA cm\(^{-2}\) and 180 mA cm\(^{-2}\) respectively, when analyzed at 0.2 V potential. On other hand, a double parallel serpentine flow line (A5SF2), having flow channel length of 650 mm at an open ratio of 52\%, yielded the best performance among all the employed flow channel designs. The maximum power densities obtained for fuel samples M2S2 and M2P2 were 42 mW cm\(^{-2}\) and 36 mW cm\(^{-2}\) respectively at flow channel design A5SF2. The effect of temperature was similar for the fuel samples M2S2 and M2P2 and yielded the best performance at 70 °C. While in the case of M2F2, the performance got enhanced upon increasing the temperature from 60 °C to 80 °C, and the effect of temperature was similar to that realized for reference fuel sample M2.
SECTION 4B: INCORPORATION OF CROSSLINKED SULFONATED POLYSTYRENE IN THE BLENDE OF PVDF-CO-HFP/NAFION: A PRELIMINARY EVALUATION FOR APPLICATION IN DMFC

4B.1. Introduction

In this section, Sodium salt of sulfonated styrene (SS) was polymerized in situ within the polymeric blend of PVdF-co-HFP/Nafion. The efficiency of this cross-linked semi-IPN towards application as a polymer electrolyte membrane in direct methanol fuel cell (DMFC) was evaluated. For this purpose, we determined the thermal stability, water uptake, ion exchange capacity (IEC), oxidative stability, methanol crossover, and proton conductivity of the prepared membranes. The electrical efficiency of this cross-linked semi interpenetrating network membranes were evaluated by using DMFC test station.

4B.2. Constituent Details of the semi-IPN Membranes

All the membranes were prepared by following two step methods as illustrated in Fig. 3.4. The constituent details of the different samples prepared are represented in Table 4B.1.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample Designation</th>
<th>PVdF-co-HFP/Nafion (4:1) (%)</th>
<th>SS (%)</th>
<th>AIBN (wt% of SS)</th>
<th>DVB (wt% of SS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S-5</td>
<td>95</td>
<td>5</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>S-10</td>
<td>90</td>
<td>10</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>S-15</td>
<td>85</td>
<td>15</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>4</td>
<td>S-20</td>
<td>80</td>
<td>20</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>5</td>
<td>S-30</td>
<td>70</td>
<td>30</td>
<td>0.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

4B.3. FT-IR analysis

Upon subjecting the membranes to FT-IR analysis, we obtained the spectra depicted in Fig. 4B.1, which confirms the presence of characteristic groups within the semi-IPN membranes. In case of Nafion-117 (used as a reference), two stronger and wider peaks appeared at 1202 cm\(^{-1}\) and 1140 cm\(^{-1}\) due to the Nafion backbone’s C-F stretching.
vibration; while a sharp peak at 1054 cm\(^{-1}\) can be assigned to the S-O stretching vibration of -SO\(_3\)H groups [137]. On the other hand, for the synthesized membranes, peaks appearing at 1068 cm\(^{-1}\) and 1162 cm\(^{-1}\) are due to the symmetric and asymmetric stretching vibrations of -SO\(_3\) groups. It can be clearly seen from the figure that the intensities of both these peaks increased continuously from S-5 to S-30, due to the increasing concentration of -SO\(_3\)H group (SS contains -SO\(_3\)H group in each unit, see Fig.1). The peak obtained at 981 cm\(^{-1}\) for Nafion is due to the stretching vibration of C-O-C bonds. A characteristic peak, appearing at 659 cm\(^{-1}\), can be assigned to the out-of-plane bending vibration of styrene rings. The presence of a sharp peak at 1681 cm\(^{-1}\) is due to the C=C stretching vibration of the aromatic benzene ring of sulfonated polystyrene (SPS), and this peak became more prominent as the concentration of SS increased, reaching the highest value corresponding to S-30 [109]. This characteristic peak is absent in case of pristine Nafion, confirming the successful incorporation of SPS within the blend.

![FT-IR spectra of the samples.](image)

**Fig. 4B.1** FT-IR spectra of the samples.

### 4B.4. XRD analysis

X-ray diffraction was conducted to analyze the presence of crystalline and amorphous zones within the structure of semi-IPN membrane. XRD spectra of samples
S-20 and S-30 are given in Fig. 4B.2, along with PVdF-co-HFP/Nafion blend and pure PVdF-co-HFP membrane as references. From the figure, it can be clearly observed that for the reference blend sample of PVdF-co-HFP/Nafion, the 2θ peak has almost completely disappeared; while for sample S-20, a sharp 2θ peak appeared in the region of 20° to 30°. This is due to the fact that the presence of Nafion (recast) causes the semi-crystalline nature of PVdF-co-HFP to disappear [49], while SS reforms the crystalline structure within the blend of PVdF-co-HFP/Nafion. From the figure, it is also clear that for sample S-30 the intensity of the peak is relatively higher, compared to both S-20 and S-15. This is due to the greater constraints imposed by DVB (Table 4B.1), by the way of forming more linkages within the membrane structure. Hence, the XRD results confirm that the prepared semi-IPN membrane possesses a semi-crystalline structure.

![XRD spectra of the samples.](image)

**Fig. 4B.2** XRD spectra of the samples.

### 4B.5. Analysis of water uptake capacities and swelling ratios of the membranes

The water uptake analysis of the different samples, including the reference (Nafion-117) was done by using equation (3.1), and the results are plotted in Fig. 4B.3. From the figure, it can be seen that at room temperature the water uptake values for samples S-5, S-10, S-15 and S-20 are 8%, 15%, 18% and 24%, respectively. These results reveal an enhancement of water uptake capacity upon an increase in the SPS content within the
membrane. This increased affinity for water is due to the greater polar nature of the SPS polymer. SPS absorbs water on its surface by virtue of strong interactions between its surface \(-\text{SO}_3\) groups and water molecules via formation of strong hydrogen bonds, which essentially promote the liquid retention within the PVdF-co-HFP/Nafion blend membrane. However, the sample S-30, containing the highest percentage of SS (30%), exhibited a slightly reduced water uptake value of 18% at room temperature, compared to that obtained for S-20. This is due to the greater constraints imposed by the cross-linker DVB by forming additional cross-links within the membrane structure, which essentially led to increased rigidness. Nevertheless, samples S-15 and S-20 showed an improvement in water uptake capacity compared to the values of 16% at room temperature obtained for Nafion-117 (Fig. 4B.3). Similarly, the swelling ratio analyses revealed that the sample S-20 exhibited the maximum swelling, followed by the sample S-15 (Fig. 4B.3). Both these samples showed swellings higher than Nafion-117. This result can be explained on a similar basis, and was expected from the results obtained for water uptakes. This enhancement, in turn, shall provide a favorable condition for proton conduction in fuel cells.

![Water uptake and swelling ratio values (%) of the samples.](image)

**Fig. 4B.3** Water uptake and swelling ratio values (%) of the samples.

*Part of this section is published in Applied energy. 123 (2014) 66-74.*
4B.6. IEC analysis

Fig. 4B.4 represents the IEC values as a function of the percentage of SS incorporated within the membrane structure. The IECs obtained were about 0.9 meq g\(^{-1}\) and 0.8 meq g\(^{-1}\) for the samples S-30 (containing 30% SS) and S-20 (containing 20% SS), respectively. The value of 0.8 meq g\(^{-1}\) corresponding to the sample S-20, is equal to that obtained for the reference membrane Nafion-117; while the value of 0.9 meq g\(^{-1}\) obtained for S-30 is slightly higher. Fig. 4B.4 further reveals that the IEC value of the membrane increases with an increase in SS content. This is due to a corresponding increase in the concentration of -SO\(_3\) groups (present within the structure of SS, see Fig. 3.3) with increasing amount of incorporated SS.

![Fig. 4B.4 Ion-exchange capacities of the samples.](image)

4B.7. Analysis of oxidative stability

The oxidative stabilities of the membranes were analyzed by immersing a cut piece of each sample into a 3 wt% aqueous solution of H\(_2\)O\(_2\), and the result has been plotted in Fig. 4B.5. From the figure it can be seen that Nafion-117 shows the highest stability and flexibility, without undergoing any physical changes, among all the membranes studies,
as expected and reported in the literature [138]. In case of the samples S-15, S-20 and S-30, the weight initially exhibited a rapid increase up to 72 h. In addition, a sharp reduction in weight was observed after 72 h, especially in case of the samples S-15 and S-30, since membranes containing SS underwent continuous swelling and decomposition inside the solution [138]. The initial gain in weight can be attributed to the decomposition of crosslinked structure within the membrane [139]. However, after 72 h, the degradation rate of the crosslinked structure was higher than the rate of swelling, resulting in the observed sharp weight loss. From this analysis, it appeared that among all the samples studied, S-20 exhibited the highest swelling rate and the lowest degradation rate.

![Image](image_url)

**Fig. 4B.5** Plots representing the oxidative stabilities of the samples.

### 4B.8. Proton conductivity analysis

The proton conductivities of the prepared membranes, along with Nafion-117, were determined by employing the impedance spectroscopic technique, and the obtained results have been presented in Table 4B.2. From the table it can be clearly observed that S-20 exhibited the highest proton conductivity (i.e. $3.16 \times 10^{-2}$ Scm$^{-1}$) among all the samples; while the sample S-30 exhibited a slightly lower value in spite of possessing the highest IEC value (Fig. 4B.4).
Table 4B.2: Membrane thickness, Proton conductivities, methanol permeabilities and membrane selectivities of the samples.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample Designation</th>
<th>Membrane Thickness (µm)</th>
<th>Proton Conductivity (S cm⁻¹)</th>
<th>Methanol Crossover (cm² s⁻¹)</th>
<th>Membrane Selectivity (S cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nafion-117</td>
<td>190</td>
<td>3.02×10²</td>
<td>1.22×10⁶</td>
<td>2.47×10⁴</td>
</tr>
<tr>
<td>2</td>
<td>S-15</td>
<td>201</td>
<td>1.32×10²</td>
<td>1.12×10⁶</td>
<td>1.17×10⁴</td>
</tr>
<tr>
<td>3</td>
<td>S-20</td>
<td>204</td>
<td>3.16×10²</td>
<td>1.76×10⁶</td>
<td>1.80×10⁴</td>
</tr>
<tr>
<td>4</td>
<td>S-30</td>
<td>202</td>
<td>1.82×10³</td>
<td>1.01×10⁷</td>
<td>1.80×10⁴</td>
</tr>
</tbody>
</table>

Since the proton conductivity is directly proportional to the water uptake capacity of the membrane, which in turn depends upon the available free volume, therefore the presence of the highest content of crosslinking agent (DVB) in S-30 led to a decrease in available free volume. This resulted in lowering the mobility of ions, and thus, the proton conductivity.

**4B.9. Analysis of methanol crossover and determination of membrane selectivity**

The methanol permeability of the samples was determined in a glass diffusion cell setup, by using UV-vis spectroscopic technique, and the obtained results have been presented in Table B.2. From the table, it appears that the permeability of each sample is following its respective water uptake (Fig.4B.3) and IEC values (Fig.4B.4), except in case of S-30. Since, the sample S-30 contains a higher concentration of the crosslinker (DVB), therefore, this imparts rigidity and a packed structure to this membrane (as explained in earlier sections). In effect, a reduction in the free volume in the sample S-30 is responsible for causing a decrease in the mobility of liquid through it. However, the maximum value of methanol permeability was recorded for the sample S-20 (1.76×10⁶ cm² s⁻¹), which was comparable to that obtained for Nafion-117 (1.22×10⁶ cm² s⁻¹). The fact that S-20 has exhibited the highest methanol permeability among all the composite membranes is primarily due to it possessing the maximum free volume within the membrane structure, as indicated by its highest swelling ratio among all the samples, this is responsible for allowing high liquid mobility. It should be noted in this respect that with the increase in DVB (the crosslinker) content, the crosslink density increases while the free volume decreases. Along with the increase in DVB content in the compositions,
the content of sodium salt of SS also increases. The increase in crosslink density (due to increase in DVB content) and increase in content of SS have opposing effects in terms of water penetration or swelling (the increase in crosslink density will reduce it, whereas the increase in SS content will increase it). These two opposing effects have been found to be optimum in terms of swelling for the S-20 composition (Fig. 4B.3). Nevertheless, the substantially low methanol permeability of S-30, by about one order of magnitude compared to pristine Nafion, suggests that judicious optimization of the weight ratio of the different constituents of the composite membrane can result in producing a balance between proton conductivity and methanol permeability in order to realize higher membrane selectivity. In fact, it has been reported that by increasing the content of PVdF-co-HFP, as well as, the extent of DVB cross-links, the methanol diffusivity of PEMs can be substantially reduced [139].

Membrane selectivity, which is an important parameter to gauge the efficiency of a PEM, is defined as the ratio between the proton conductivity and the methanol permeability of the PEM. Therefore, we have calculated the selectivity values of the synthesized membranes, and have presented them in Table 4B.2. It can be realized from these tabulated values that the selectivities of the synthesized membranes S-20 and S-30 (i.e. $1.80 \times 10^4$ Scm$^{-3}$ for both the samples) are about 73% of that of pristine Nafion-117 membrane ($2.47 \times 10^4$ Scm$^{-3}$).

4B.10. DMFC performance test

The DMFC performance tests for all the membrane samples were conducted on a single cell, having an MEA area of 5x5 cm$^2$, and at a temperature of 60°C. The obtained results are represented in Fig.4B.6, as a characteristic plot of potential vs. current density. The maximum current density achieved for the samples S-10, S-15, S-20 and S-30 were 55, 70, 120 and 90 mA cm$^{-2}$ respectively, when recorded at a potential of +0.2 V. These values, when compared with the value of 105 mA cm$^{-2}$ obtained for Nafion-117 at the same potential, reveals that the samples which exhibit higher water uptakes and IECs also show better cell performances. Power density values, plotted in Fig. 4B.7, quantify the cell efficiency. From the figure, it is observed that the maximum power density is obtained for the sample S-20. This further confirms that this particular sample
composition have the potential to be further exploited as a partial/complete replacement of traditional Nafion for fabrication of PEMs.

![Graph](image1.png)

**Fig. 4B.6** Plots representing the current density of the samples.

![Graph](image2.png)

**Fig. 4B.7** Maximum power density of the samples obtained at +0.2 V.
4B.11. Conclusion

In summary, we have prepared a semi-IPN membrane and evaluated its potential to be applied as a PEM for application in DMFC. For this purpose, sodium salt of SS along with DVB and initiator were impregnated into the polymeric blend of PVdF-co-HFP/Nafion and subsequently polymerized in situ. We determined the electrical efficiency of this semi-IPN membrane, and characterized it with FT-IR and XRD. The obtained results confirmed the successful incorporation of SS within the polymeric blend of PVdF-co-HFP/Nafion. From the water uptake analysis, we realized that above a threshold value of 20 wt% of incorporated SS, water uptake of the semi-IPN membrane increased up to 24%, with an IEC value equal to Nafion, i.e 0.8 meq g\(^{-1}\). The sample S-20 exhibited the highest swelling rate and the lowest degradation rate amongst all membranes. This sample also exhibited a slightly higher proton conductivity and similar membrane selectivity compared to that of pristine Nafion-117. Moreover, for this membrane, the maximum current density was observed to be 120 mA cm\(^{-2}\) at +0.2 V, with a corresponding power density of 24 mW cm\(^{-2}\) at 60 °C. In effect, the synthesized membrane (S-20) exhibited higher water uptake, swelling ratio, proton conductivity, current density and maximum power density, as well as, comparable IEC, methanol permeability and membrane selectivity to that of Nafion-117 membrane. This, coupled with the use of air in place of oxygen as a cathode reactant, resulted in realizing a cheaper overall DMFC operation. We believe that this novel semi-IPN membrane will set the trend for more such compounds and formulations, and consequently the spectrum of materials used for fabrication of PEM for DMFC will increase.
SECTION 4C: A STUDY ON THE HEAT BEHAVIOUR OF PEM, PREPARED BY INCORPORATION OF CROSSLINKED SULFONATED POLYSTYRENE IN THE BLEND OF PVDF-CO-HFP/NAFION, FOR ITS HIGH TEMPERATURE APPLICATION IN DMFC

4C.1. Introduction

From the earlier analysis (section 4B), sulfonated poly styrene within the blend of PVdF-co-HFP/Naﬁon has shown promising PEM characteristics in terms of improved water uptake/swelling, proton conductivity, and output current/maximum power densities compared to Naﬁon-117. In addition, the semi-IPN membrane exhibited good oxidative stability, comparable ion-exchange capacity and methanol permeability. Nevertheless, prior to extending the applicability of this prospective PEM, it is essential to understand the structure-property relationship and thermal stability of the semi-IPN material. In this section, we have utilized the techniques of FT-IR spectroscopy, scanning electron microscopy, AC impedance, tensile, and differential scanning calorimetry for this purpose. In addition, we have studied the effect of temperature on the cell performance of this prospective PEM.

4C.2. Constituent details of the semi-IPN Membranes

All the membrane samples were prepared by following two step procedures reported in earlier section 3.3.3.1. The constituent details of the membranes utilized for analysis of thermal stability have been tabulated in Table 4C.1.

Table 4C.1: Chemical composition of the prepared membranes.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Samples</th>
<th>PVdF-HFP (Wt. %)</th>
<th>Naﬁon (Wt. %)</th>
<th>SS (Wt. %)</th>
<th>AIBN (Wt. % of g⁻¹ SS)</th>
<th>DVB (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S-0</td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>S-15</td>
<td>68</td>
<td>17</td>
<td>14.4</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>S-20</td>
<td>64</td>
<td>16</td>
<td>19.2</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>4</td>
<td>S-30</td>
<td>56</td>
<td>14</td>
<td>28.8</td>
<td>0.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>
4C.3. Methanol uptake

For analyzing the methanol uptake capacities, the prepared membranes were soaked in variable concentrations of methanol up to 5 M (i.e. 1 M, 2 M and 5 M). 5 M concentration was chosen as the upper limit because in DMFC a maximum of 5 M methanol concentration is usually used. The uptake value was calculated by employing the equation 3.2. The obtained result has been depicted in Fig. 4C.1. From the figure, it can be observed that while the liquid uptake increases marginally with increasing methanol concentration, the maximum uptake value showed sharp increase with increasing content of SS within the membrane, albeit up to 20 wt%. The highly polar nature of the SPS polymer, which essentially promotes the liquid retention within the membrane, is the reason behind this happening. However, a reverse trend can be noticed in case of sample S-30, for each molar concentration of methanol, probably due to the presence of rigid packed structure, resulting from the high crosslink density. This is caused by a higher dose of DVB, which essentially laid constraints on the mobility of the polymer chains, leading to lower liquid uptake [140, 141].

![Fig. 4C.1 Methanol uptake of the membrane samples in 1 M, 2 M and 5 M aqueous methanol solutions.](image)
4C.4. DSC

Heat stability of a PEM material is critical in realizing its potential use in high temperature DMFC application. For this purpose, we have analyzed the heat behavior of all the prepared membranes, along with the reference sample S-0, by DSC. The obtained result, plotted in Fig. 4C.2, reveals that the position of the \( T_m \) peaks for all the prepared samples are much closer to that of the reference sample S-0. In addition, increased SS-content of the membrane resulted in marginal broadening of the melting peak and simultaneous reduction in the peak temperature compared to that of the reference sample. It is obvious that the non-fluorinated polymer SPS, having slightly lower \( T_m \) than PVdF-co-HFP, caused this phenomenon. However, here too, the sample S-30 showed a contrasting behavior in having a slightly higher melting temperature compared to the reference. The most probable reason behind this observation is the presence of higher crosslink density in S-30, that resulted in imposing higher constraints on the polymer chain mobility [140, 142]. Therefore, from this thermal analysis, we can safely say that although the incorporation of SS within the blend membranes does not critically affect the heat stability of the membranes, and is therefore, acceptable for application in DMFC. The quantity of crosslinker DVB used plays an important role in affecting their heat behavior.

![Fig. 4C.2 DSC plots of the prepared membrane samples.](image-url)
4C.5. Tensile strength and surface morphology

Mechanical integrity of a PEM is one of its important aspects, considering its durability in a fuel cell. We have, accordingly, tried to gauge the mechanical behaviour of the semi-IPN/blend membranes by measuring their tensile strengths, and have compared them with both Nafion and the reference S-0. The tensile strengths of Nafion and S-0 were recorded to be 12.79 MPa and 14.49 MPa, respectively (Fig. 4C.3a). The effect of incorporating SS within the blend membranes can be clearly seen in the figure. The presence of SS as well as its amount resulted in a marked decrease in the tensile strengths and tensile elongation (Fig. 4C.3b) of the membranes. Similarly, the presence of extensive DVB crosslinks within the PEM structure is also responsible to a certain extent in reducing its tensile strength, as can be evidenced from the sharply reduced strength of S-30 (5.83 MPa). It is well-known that polymer chains (SPS) in a polyelectrolyte complex that can form electrostatic interactions with other polymer chains (PVdF-co-HFP/Nafion) suffer from restricted chain mobility [140-142]. This hindrance towards chain mobility essentially results in increased rigidity, and thereby, can affect the tensile strength. In summary, among the three proposed membranes, the mechanical integrity of S-15 and S-20, exhibiting tensile strengths of 10.84 MPa and 10.10 MPa respectively, are comparable to that of Nafion (12.79 MPa).

(a)
Fig. 4C.3 (a) Tensile strengths of the samples and (b) Effect of SS content on tensile elongation of the samples.
Fig. 4C.4 Scanning electron micrographs of the membrane samples. Scale: (a) 20µm and (b) 1µm.

Fig. 4C.4 shows the effect of incorporation of SS on the morphology of the semi-IPN/blend membranes. For example, upon incorporation and simultaneous increase in the SS-content of the membranes, the smooth surface morphology of S-0 progressively changed to a very rough one (Fig. 4C.4a). In addition, pores got generated within the membrane structure with increasing SS-content; the largest numbers of pores are observed in case of sample S-30. As can be expected, this particular sample also revealed the smallest pores in terms of diameter, due to the presence of higher number of crosslinks (Fig. 4C.4b). This progressive increase in porosity with increasing SS-content can be well-related to the progressive decrease in their tensile properties (Fig. 4C.3).

4C.6. AC impedance

The impedance test was conducted (at 20 °C and 70% RH) in a single cell in order to analyze the interfacial resistance of the prepared membranes. The obtained results have
been plotted in a characteristic graph, known as Nyquest impedance plot, in Fig. 4C.5. From the figure, it can be observed that the interfacial resistance value of Nafion was the lowest among all the membranes. Fig. 4C.5 further reveals that with an increase in the SS-content from S-15 to S-20, the interfacial resistance becomes lower; however, S-30, having the highest SS and DVB contents, showed a higher resistance than S-20. These observations can be related to the water uptake capacities of the three prepared membranes, since lower water uptake often leads to reduced proton conductivity (section 4B, Table 4B.2). Again, the IEC of the membrane S-20 was found to be equal to that of Nafion (section 4B, fig. 4B.3), although its water uptake capacity was higher than Nafion (section 4B, fig. 4B.4). Considering the water uptake analysis alone, it can be expected that S-20 should exhibit higher proton conductivity, as well as, lower interfacial resistance.

![Graph showing impedance plots of membrane samples](image)

**Fig. 4C.5** Ac impedance plots of the membrane samples.

However, the impedance test result showed a higher interfacial resistance value for sample S-20. This contradicting nature is probably due to the fact that higher water uptake capacity led to higher rate of methanol crossover. The crossovered methanol at the cathodic side reacted directly with oxygen present in the supplied air at the cathode and produced H$_2$O that caused cell flooding, and thereby, increased the required oxygen
stoichiometry [143]. In addition, the crossovered methanol upon reaching the cathode got oxidized in the presence of Pt catalyst, giving rise to a reverse potential. These two effects are responsible for the production of a higher interfacial resistance in S-20. Nevertheless, it is inspiring to notice that among the three prepared membranes, S-20 possessed the lowest interfacial resistance.

4C.7. Effect of temperature on DMFC performance

High temperature operation is one of the desirable aspects of DMFC research. In order to investigate the effect of temperature on the cell performance, the cell was operated at three variable temperatures viz. 80, 90, and 100 °C. At 80 °C, the maximum current densities for the samples S-0, S-15, S-20 and S-30 were recorded as 122, 125, 165 and 155 mA cm\(^{-2}\), respectively, at +0.2 V (Fig. 4C.6a); these were much higher than the corresponding current densities recorded at 60 °C for the respective membranes in our previous study (i.e. 55, 70, 120 and 90 mA cm\(^{-2}\), respectively) (section 4B). This observed enhancement is a consequence of the faster electro-oxidation reaction of methanol in the presence of platinum catalyst at higher temperature [144, 145]. Following a similar trend, the cell performance at 90 °C showed increased current densities for all the samples, except S-0 (Fig. 4C.6b). Membrane dehydration at higher temperatures, leading to lower liquid mobility, should have resulted in reduction of proton conductivity, and hence, current density for S-0. Nevertheless, this dehydrating effect was not evident in case of membranes S-20 and S-30 at 90 °C, since they exhibited higher current densities at this temperature compared to those at 60 °C and 80 °C. However, upon increasing the temperature to 100 °C, the dehydrating effect got more pronounced, resulting in reduction of the current density values for all the samples (Fig. 4C.6c). It should be noted that compared to lower cell operating temperatures of 60 °C and 80 °C, at higher temperatures of 90 °C and 100 °C, the membrane S-30 showed better performance than S-20, and this became more pronounced at 100 °C. It is well known that sulfonic acid groups, which are attached to aromatic benzene rings, are more acidic than the ones attached to aliphatic chains. Therefore, since S-30 possessed the maximum SS-content, it enjoyed the ability to attract more water molecules at higher temperatures due to the presence of more acidic and more polar sulfonated polystyrene within its structure [109]. Therefore, in summary, it is observed that impregnation of SS within the
blend membranes can effectively reduce the anhydrous condition of the membrane, while operating at higher temperatures.

(a)

(b)
4C.6. Conclusions

In summary, we have analyzed the thermal stability of semi-IPN/blend mixture having composition SPS/PVdF-co-HFP/Nafion, and evaluated its potential to be applied as a PEM material for high temperature DMFC application. Successful incorporation of SS within the polymeric blend of PVdF-co-HFP/Nafion was confirmed from the obtained FT-IR spectra. This promising PEM exhibited comparable tensile strength to that of Nafion, as well as, good thermal stability and low interfacial resistance. Moreover, the potential membranes S-20 and S-30 produced an improved power densities i.e 33-39 mW cm$^{-2}$ at higher temperatures (i.e. 80-90 °C), indicating that impregnation of SS within the blend membranes can effectively reduce the anhydrous condition of the membrane while operating at higher temperatures.

(c)

Fig. 4C.6 DMFC performance using the prepared membranes at operating temperatures (a) 80 °C, (b) 90 °C, and (c) 100 °C.
SECTION 4D: FORMATION OF SEMI-IPN MEMBRANE COMPOSED OF CROSSLINKED SPS-[PVDF-CO-HFP/NAFION] FOR APPLICATION IN DMFC: A FINE TUNING BETWEEN CROSSLINKER AND INITIATOR

4D.1. Introduction

As shown in earlier sections (4B and 4C), the semi-interpenetrating (semi-IPN) membrane composed of crosslinked sulfonated polystyrene (SPS) within the host blend of PVdF-co-HFP (Polyvinylidene fluoride-co-hexafluoropropylene) and Nafion has already been tested as a promising polymer electrolyte membrane (PEM) in terms of improved water uptake, proton conductivity and electrical efficiency for application in the direct methanol fuel cell (DMFC). These desired results have generated further curiosity about a fine tuning between the contents of divinylbenzene (DVB) as a crosslinker and azobis-isobutyronitrile (AIBN) as an initiator for the optimization of PEM characteristics. Since, the crosslink density directly affects the physiochemical properties of the semi-IPN membrane; an increase in cross-linker (DVB) content within the membrane can raise the crosslink density, while increment in initiator (AIBN) content results in the opposite. These two opposing effects are investigated in this section for optimization of PEM performance in terms of lower methanol crossover and higher proton conductivity, leading to higher membrane selectivity. A number of tests have been executed such as water uptake, swelling ratio, XRD, crystallinity, proton conductivity and methanol crossover.

4D.2. Constituent Details of the semi-IPN Membranes

Table 4D.1: Variation in the ratio of AIBN/DVB in semi-IPN membrane*

<table>
<thead>
<tr>
<th>SL. No.</th>
<th>Samples</th>
<th>AIBN (wt.% of SS)</th>
<th>DVB (wt.% of SS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>A-20</td>
<td>0.2</td>
<td>1.4</td>
</tr>
<tr>
<td>2.</td>
<td>B-20</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>3.</td>
<td>C-20</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>4.</td>
<td>D-20</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>5.</td>
<td>E-20</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>6.</td>
<td>F-20</td>
<td>1.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

[*membrane composed of 64 wt. % of PVdF-HFP, 16 wt. % of Nafion and 20 wt. % of SPS.]
All the membranes were prepared by following two step methods as illustrated in Fig. 3.4 and the proposed semi-IPN structure is depicted in Fig. 4D.1. The variation in the ratio of AIBN/DVB in Semi-IPN membrane is tabulated in Table 4D.1.

![Figure 4D.1](image1.png)

**Fig. 4D.1** A schematic of proposed structure for crosslinked semi-IPN membrane.

4D.3. X-ray Diffraction (XRD) analysis

XRD test was conducted to analyze the effect of variation of the contents of crosslinker and initiator on the crystallinity of the PEM. The obtained XRD-spectra are depicted in Fig. 4D.2.

![Figure 4D.2](image2.png)

**Fig. 4D.2** XRD of the different samples.
From the figure, it can be observed that the intensity of peak at 2 theta of 21.9° becomes more intense and sharper with an increase in the dose of DVB (crosslinker) (F-20 to A-20). It is well known that a polymer with higher degree of crystallinity exhibits a sharper and more intense XRD peak, whereas a relatively weaker and/or less intense peak signifies the amorphous region [6]. This observation signifies a transition from the crystalline to amorphous region, occurring due to the increase in AIBN content. The XRD results indicate that the increasing concentration of crosslinker leads to an increase in crystallinity, whereas the increasing concentration of initiator causes reduction in the crystallinity. Furthermore, the (%) crystallinity and the inter-chain separation, R (nm) value was calculated from the equation (4.7) and (4.8), respectively and presented in Table 4D.2.

\[
\% \text{ Crystallinity} = \frac{A_{\text{Crystalline}} \times 100}{A_{\text{Total}}} \tag{4.7}
\]

Where, \( A_{\text{Crystalline}} \) represents the area of the crystalline regions, and \( A_{\text{Total}} \) represents the total area under the peak.

\[
R = \frac{5\lambda}{8 \sin\theta} \tag{4.8}
\]

Where, \( \lambda \) is the wavelength, and \( \theta \) is the Bragg angle.

From the Table, it is observed that with an increase in the DVB content, the % crystallinity enhances, while the inter chain separation decreases. The reason behind this observation is that the presence of more rigid and packed structure causes the lowering in inter-chain separation, hence causes higher crystallinity.

Table 4D.2: Characteristic properties of the prepared membranes.

<table>
<thead>
<tr>
<th>SL. No.</th>
<th>Samples</th>
<th>Thickness (µm)</th>
<th>Inter-Chain separation, ( R ) (nm)</th>
<th>Crystallinity (%)</th>
<th>Degree of crosslinking (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>A-20</td>
<td>206</td>
<td>0.176</td>
<td>44.3</td>
<td>30.8</td>
</tr>
<tr>
<td>2.</td>
<td>B-20</td>
<td>204</td>
<td>0.192</td>
<td>41.1</td>
<td>29.7</td>
</tr>
<tr>
<td>3.</td>
<td>C-20</td>
<td>203</td>
<td>0.201</td>
<td>40.8</td>
<td>26.3</td>
</tr>
<tr>
<td>4.</td>
<td>D-20</td>
<td>202</td>
<td>0.208</td>
<td>39.9</td>
<td>21.5</td>
</tr>
<tr>
<td>5.</td>
<td>E-20</td>
<td>201</td>
<td>0.214</td>
<td>37.6</td>
<td>17.2</td>
</tr>
<tr>
<td>6.</td>
<td>F-20</td>
<td>203</td>
<td>0.217</td>
<td>36.3</td>
<td>14.7</td>
</tr>
</tbody>
</table>
4D.4. Analysis of thermal behavior of membrane

Effect of various ratios of AIBN and DVB on the thermal behavior was analyzed from the DSC results. The test was conducted only for the sample A-20 (AIBN/DVB, 0.2/1.4), D-20 (AIBN/DVB, 0.8/0.8) and F-20 (AIBN/DVB, 1.2/0.4) containing the highest concentration of crosslinker (DVB), equal amounts of AIBN: DVB and the highest content of initiator (AIBN), respectively (See Table 4D.1). The obtained result as plotted in Fig. 4D.3 reveals that the position of the melting temperature ($T_m$) peaks for sample A-20 (AIBN/DVB, 0.2/1.4) is slightly sharper and more intense than D-20 and F-20 (AIBN/DVB, 1.2/0.4). The most probable reason behind this observation is the presence of higher crosslink density (Table 4D.2) in A-20 (AIBN/DVB, 0.2/1.4) (as explained earlier), that imposes higher constraints on the polymer chain mobility [140].

![DSC of the different samples.](image)

4D.5. Analysis of mechanical strength

Tensile strength of the membrane defines the mechanical integrity of a PEM and is very important and crucial for considering its durability in a fuel cell. All the membranes in their dry-state were subjected to tension under a UTM for measuring their tensile strengths, and their tensile properties were compared with those for Nafion-117 membrane. The tensile strength along with corresponding elongation (%) of various
membranes is depicted in Fig. 4D.4a and 4D.4b respectively. From the figure, it can be observed that with an increase in the DVB content, the tensile strength initially increases, reaches a maxima and then decreases; while for the increase in AIBN content, there is an initial increase in tensile strength, followed by its continuous fall. It is well known that the increase in the content of crosslinker always leads to an increase in tensile strength, whereas the increase in the content of initiator leads to the lowering in tensile strength [146-148]. The possible reasons behind this observation are (a) SPS polymer chains get crosslinked through the crosslinker and form semi-IPNs (Fig. 4D.1) with other polymer chains (PVdF-co-HFP/Nafion), leading to the restricted chain mobility [146, 147] and (b) Higher content of DVB causes a lowering in the inter-chain separation (Table 4D.2) and it is responsible for the restricted chain mobility. This hindrance towards chain mobility results in increased rigidity, and thereby lowers the elongation of membrane as observed in Fig. 4D.4b. Nevertheless, among all of the prepared membranes, B-20 (AIBN/DVB, 0.4/1.2) shows highest tensile strength (11.92 MPa) and is acceptable for application in DMFC.
4D.6. Analysis of membrane morphology

Figure 4D.5 reveals the rough and porous morphology of the semi-IPN membrane. The formation of pores within the semi-IPN structure is probably due to phase separation during casting of the membrane. Since, water vapour (a non-solvent of the semi-IPN) from humidified air is fully miscible with DMF (a solvent of the semi-IPN), the mixed solvent can penetrate the membrane film by diffusion, leading to porous morphology [148-150]. Furthermore, it is observed that with an increase in the DVB content, the rough surface morphology of F-20 (AIBN/DVB, 1.2/0.4) (Fig. 4D.5c) is progressively changed to slightly smooth surface in A-20 (AIBN/DVB, 0.2/1.4) (Fig. 4D.5a), resulting in relatively smoothened membrane surface. This progressive decrease in porosity and rough surface can be rationalized with high degree of crosslinking and less Inter-chain separation (R-value) as depicted in Table 4D.2.
Fig. 5D.5 Scanning electron micrographs of membrane sample containing variable ratio (wt. %) of AIBN/DVB: (a) A-20 (0.2/1.4), (b) D-20 (0.8/0.8) and (c) F-20 (1.2/0.4) [Scale: 2µm; Magnification: 5,000x].
4D.7. Analysis of Water uptake and swelling ratio

The water uptake test was conducted at various temperatures and the calculated value is depicted in Fig. 4D.6 (a). From the figure, it is observed that at 20 °C, the water uptake increases with the increasing content of the initiator (AIBN); on the other hand, with an increase in the content of crosslinker (DVB), the water uptake decreases. The reason behind this observation is that the higher content of AIBN will lead to the formation of short and crosslinked chains of sulfonated polystyrene (SPS) embedded in the blends of PVdF-co-HFP and Nafion, thus provide more free volume in the membrane structure. This essentially promotes more water retention within the membrane. On the other hand, the high crosslink density of SPS caused by a higher dose of DVB in the semi-IPN membrane forms rigid packed structures, which essentially restrict the mobility of the polymer chains leading to the lower water uptake [140]. Moreover with an increase in the temperature from 20 °C to 80 °C, the water uptake of respective membrane slightly enhances. It is due to the higher interaction between acidic sulfonated group (-SO$_3$H) present in the membrane structure and the surrounding water.

![Image](image_url)

**Fig. 4D.6 (a)** Water uptake values of the samples at variable temperature.

The extent of polymer swelling is directly proportional to the water uptake capacity. Therefore, the swelling (in thickness) for each membrane is analyzed and calculated values are depicted in Fig. 4D.6 (b). It is observed from the figure that the
swelling ratio of a sample follows the similar trend as for its water uptake. It is interesting to note that the sample E-20 (AIBN/DVB, 1.0/0.6) and F-20 (AIBN/DVB, 1.2/0.4), having higher doses of initiator than crosslinker, reveals slightly higher swelling than its respective water uptake while sample A-20 (AIBN/DVB, 0.2/1.4) containing lower dose of initiator than crosslinker, shows lower swelling than its water uptake. This result is in good agreement with the porous morphology (Fig. 4D.5). The higher content of AIBN provides additional available free volume (in terms of pore distribution) in the membrane and is responsible for allowing high mobility of water, while the higher content of DVB increases the crosslink density thus restricts the availability of any additional free volume. Moreover as expected, the degree of swelling ratio increases upon increasing the temperature from 20 °C to 80 °C. This is due to the same reason as that for water uptake.

![Swelling ratio of the samples at variable temperature.](image)

**Fig. 4D.6 (b)** Swelling ratio of the samples at variable temperature.

### 4D.8. Analysis of Proton conductivity

The proton conductivity of membrane was conducted by using an ac- impedance spectroscopic technique and was calculated by the equation-(6). The obtained results are plotted in Fig. 4D.7. From the figure, it is observed that with an increase in the dose of DVB (crosslinker) in the semi-IPN, the value of proton conductivity sharply decreases.
Fig. 4D.7 further reveals that with an increase in the AIBN (initiator) content and a decrease in the content of DVB (crosslinker), the proton conductivity of the membrane increases. These observations can be related to the water uptake and swelling ratio capacities of the prepared membranes. The proton conductivity is always a function of (a) concentration of –SO₃H groups available within the membrane and (b) available free volume or water uptake capacity of the membrane. In this study, the case (a) i.e. the concentration of –SO₃H group is fixed as the basic composition of the polymeric membrane is fixed (Table 4D.1) and it is expected that the polymeric membranes should have a fixed value of proton conductivity. Contrary to the expectation, the proton conductivity is found to be varying with the variation in the concentration of crosslinker and initiator. When DVB is used as a crosslinker, a highly crosslinked surface layer is formed because of the faster reaction rate of DVB as compared to styrene or sulfonated styrene; the high crosslink density creates barrier against water penetration in the membrane. On the other hand, protons can be conducted through the exchange of the hydronium ion (H₃O⁺) with the pendent sulfonic acid groups of the polymeric membrane [6, 109]. The rate of exchange is also dependent on the penetration of water inside the membrane. Since, proton usually gets conducted across the PEM via association with water molecules, the ability of the water molecules to be associated with proton and its ultimate exchange with the pendent sulfonic acid groups present on the surface of membrane leads to successful proton conduction. Any kind of interruption to the flow either by blocking of pores or reduction of pore distribution in membrane will essentially lead to low proton conductivity. In addition, lower water uptake (Fig. 4D.5) often leads to higher interfacial resistance and thereby slightly reduced proton conductivity is observed for more crosslinked membrane. Nevertheless, the sample F-20 (AIBN/DVB, 1.2/0.4) exhibits the maximum proton conductivity (3.55 × 10⁻² S cm⁻¹) which is higher than that for the Nafion-117 membrane (3.02 × 10⁻² S cm⁻¹). However, among all of the prepared membranes, only A-20 (AIBN/DVB, 0.2/1.4) shows lower conductivity than that for the Nafion-117. The increase in the concentration of crosslinker and initiator has opposing effects on the crosslink density as evidenced in Table 4D.2. The increase in the content of crosslinker will increase the degree of crosslinking, whereas the increase in the concentration of initiator will lead to side reaction as chain scission and thus less degree
of crosslinking [151, 152]. For the sample of A-20 (AIBN/DVB, 0.2/1.4), the maximum content of crosslinker nullifies the effect of minimum content of initiator and thereby a highly crosslinked membrane is formed. This causes minimum water penetration and thus sample A20 is showing minimum proton conductivity amongst all of the membranes including Nafion 117 membrane.

![Fig. 4D.7 Proton conductivity of the samples.](image)

**4D.9. Analysis of Methanol crossover and selectivity ratio**

The methanol permeability of the IPN membrane was determined by using a UV-vis spectroscopic technique, and was calculated by the equation (7). The obtained results are presented in Fig. 4D.8 and compared with Nafion-117. From the figure, it appears that the permeability of each sample is following the same trend as that for water uptake (Figure 4D.6). In the similar way as proton conduction principle, methanol molecules get permeated across the PEM via tortuous pores of the membrane along with association of water molecules; therefore, blocking of pores or reduction of pore distribution in membrane will essentially lead to low permeability. Since, the presence of DVB within the membrane essentially leads to packed structure (see the SEM images in Fig 4D.5) with lesser pore distribution, this leads to the lowering of methanol permeability. Moreover, Table 4D.2 shows that the crystallinity of semi-IPN membranes increases on
increasing the DVB content. Since, highly crystalline membrane exhibits packed structure (as evidenced by a decrease in R-value) and thereby, exhibits low liquid mobility, this leads to lower methanol crossover. Agreeably, the substantially low methanol permeability of A-20 (AIBN/DVB, 0.2/1.4) and B-20 (AIBN/DVB, 0.4/1.2) is due to the presence of higher content of DVB (crosslinker) within the membrane.

![Fig. 4D.8 Methanol crossover of the samples.](image)

Membrane selectivity can be defined as “the ratio between proton conductivity and methanol permeability of the PEM”. The membrane selectivity of all membranes are calculated and depicted in Fig. 4D.9. As observed from the Fig. 4D.9, the sample A-20 (AIBN/DVB, 0.2/1.4) and B-20 (AIBN/DVB, 0.4/1.2) exhibit superior selectivity ratio as compared to Nafion-117. The reason for higher membrane selectivity is that the membrane A-20 (AIBN/DVB, 0.2/1.4) and B-20 (AIBN/DVB, 0.4/1.2) exhibit 19.6% and 34% lower methanol crossover in comparison to Nafion 117 membrane, whereas the comparative lowering in their proton conductivity is only 3.3% and 13.53%, respectively. These results are inspiring and encourage us to further examine the electrical efficiencies of these membranes in a DMFC cell.

Part of this section is published in Mat. Chem. and physics. 164 (2015) 188-197.
4D.10. Effect on cell potential (OCV)

Effect of variation of the ratios of AIBN and DVB in the membranes on the cell potential was measured in a single cell, fed by 5M methanol and tested on a fuel cell station at 80 °C for 300 minutes. From the Fig. 4D.10, it is observed that the maximum cell potential as recorded in first 0-60 minutes duration of the test for the membrane A-20 (AIBN/DVB, 0.2/1.4), followed by B-20 (AIBN/DVB, 0.4/1.2) is 0.9 V and 0.89 V, respectively. However, between 60-120 minutes, a sharp drop in OCV i.e. 0.87 V and 0.81 V can be observed and become stable at 0.85 V and 0.81 V, respectively. This decrement in OCV value can only be due to the slightly higher methanol crossover rate which is almost zero at the initial stage. It is well known that the crossovered methanol gets oxidized at cathode, causes cross potential and hence, lowers the cell potential (OCV) [109]. Nevertheless, these results indicate an enhancement in the OCV for A-20 and B-20 over to corresponding Nafion-117 membrane.
4D.11. DMFC performance

The DMFC performance tests were conducted only for the membranes which exhibited higher membrane selectivity i.e. A-20 (AIBN/DVB, 0.2/1.4) and B-20 (AIBN/DVB, 0.4/1.2). The entire test was carried out on a single cell, having an MEA area of 5x5 cm², fed by 2 M, 5 M and 8 M methanol as fuel and operated at variable cell operating temperature. Before the test, the cell was allowed to run for 24 hour. The obtained results are represented in Fig. 4D.11 (a), (b) and (c), as a characteristic plot of potential vs. current/power density. The maximum current density recorded for the samples, A-20 (AIBN/DVB, 0.2/1.4) and B-20 (AIBN/DVB, 0.4/1.2) was 155 and 245 mA cm⁻² respectively, at +0.2 V, while for the pristine Nafion 117 membrane, it was 195 mA cm⁻² at the same potential; these results are obtained upon feeding the DMFC cell with 2 M methanol (Fig. 4D.11.a). These results indicate that the membranes with higher water uptake and proton conductivity exhibit higher current density. On the other hand, upon feeding the cell with 5 M of methanol, the maximum current density increases rapidly up to 260 mA cm⁻² for B-20 (AIBN/DVB, 0.4/1.2) membranes, at +0.2 V; whereas for feeding with 8 M of methanol, the current density drops down significantly to 140 mA.
Thus, unlike the case of 2 M of methanol feed, the efficiency in current production depends only on the methanol crossover and the membrane selectivity for higher molar concentration of fuel (i.e. 5M and 8M methanol) feed. However, the obtained results were compared with the previously reported value for this particular semi-IPN membrane and presented in Table 4D.3. From the Table 4D.3, it is clearly observed that in the preliminary study as reported earlier, the maximum power density was recorded to be only 24 mW cm\(^{-2}\) (operated at 60°C and with 2M methanol feed). Furthermore, improving the thermal behaviour, this particular semi-IPN membrane exhibited enhanced power density i.e. 39 mW cm\(^{-2}\) (operated at 90°C and 2M methanol feed). However, in this study, the maximum power density was recorded to be 56 mW cm\(^{-2}\) (operated at 90°C and with 5 M methanol feed) (Fig. 4D.11.c); this value is higher than that observed for Nafion-117. The high DMFC performance achieved in this study can be explained by the reduction of methanol crossover with an increase in the content of DVB (crosslinker) and thereby membrane selectivity increases for these modified membranes, leading to higher electrical efficiency (in terms of power density) at higher concentration of methanol.

Fig. 4D.11 (a) DMFC single cell performance of the samples with 2 M methanol feed at anode.
Fig. 4D.11 (b) DMFC single cell performance of the samples B-20 at 5M and 8M of methanol feed.

Fig. 4D.11 (C) DMFC single cell performance of the samples B-20 at 90 °C and 100 °C operating temperature with 5 M methanol feed at anode.
Table 4D.3: A comparison of the DMFC performance obtained in this study using same semi-IPN membrane with previously reported values.

<table>
<thead>
<tr>
<th>SL. No.</th>
<th>Methanol Concentration</th>
<th>Oxidant (O₂/Air)</th>
<th>Humidification</th>
<th>Operating Temp. (°C)</th>
<th>Power density (mW cm⁻²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2 M</td>
<td>Air</td>
<td>No</td>
<td>60</td>
<td>24</td>
<td>[19]</td>
</tr>
<tr>
<td>2.</td>
<td>2 M</td>
<td>Air</td>
<td>No</td>
<td>80</td>
<td>33</td>
<td>[20]</td>
</tr>
<tr>
<td>3.</td>
<td>2 M</td>
<td>Air</td>
<td>No</td>
<td>90</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>2 M</td>
<td>Air</td>
<td>No</td>
<td>100</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>2 M</td>
<td>Air</td>
<td>Yes</td>
<td>80</td>
<td>49</td>
<td>This study</td>
</tr>
<tr>
<td>6.</td>
<td>5 M</td>
<td>Air</td>
<td>Yes</td>
<td>80</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>8 M</td>
<td>Air</td>
<td>Yes</td>
<td>80</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>5 M</td>
<td>Air</td>
<td>Yes</td>
<td>90</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>5 M</td>
<td>Air</td>
<td>Yes</td>
<td>100</td>
<td>26</td>
<td></td>
</tr>
</tbody>
</table>

4D.12. Conclusions
In concise, the effects of variation of the content of DVB (crosslinker) and AIBN (initiator) on characteristic properties of semi-IPN membrane composed of crosslinked sulfonated styrene 20 wt% within the blend of PVdF-co-HFP 64 wt% and Nafion 16 wt% are investigated for their potential application as PEM material. With an increase in AIBN (initiator) concentration, the water uptake, swelling ratio and proton conductivity of the membrane increases significantly. On the other hand with an increase in the DVB (cross-linker) content, methanol crossover gets reduced and leads to higher membrane selectivity. These two opposing effects were found to be optimum in terms of proton conductivity, tensile strength and membrane selectivity for the semi-IPN membrane consisting of 0.4 wt% of AIBN and 1.2 wt% of DVB. In addition, the maximum power density recorded for this particular PEM is 56 mW cm⁻² upon the feeding of 5 M methanol at the anode.
SECTION 4E: COATING AND LAMINATION OF NAFION117 WITH PARTIALLY SULFONATED PVDF FOR LOW METHANOL CROSSOVER IN DMFC APPLICATIONS

4E.1. Introduction
In this section, sulfonated PVdF resin was utilized as a laminate and/or coating material for the modification of Nafion-117. Sulfonation of PVdF was carried out in the presence of chlorosulfonic acid at 60 °C and characterized with FT-IR, XRD and DS. Furthermore, the coated and laminated Nafion-117 membrane was characterized with number of test in terms of water uptake, proton conductivity and methanol crossover. In addition, single cell performance of DMFC was also analyzed.

4E.2. Analysis of the sulfonation of PVdF
Sulfonation of PVdF is conducted by treating PVdF granules with chlorosulfonic acid at 60°C with varying the reaction time (Table 4E.1). A schematic of Sulfonation reaction is presented in Figure 3.2.

![Figure 4E.1 FTIR spectra of pure and sulfonated PVdF polymer.](image)

The success of the process of sulfonation of PVdF is confirmed by the analysis of FT-IR spectra as depicted in Figure 4E.1. From the FTIR spectra, a sharp peak at 1027 cm⁻¹ and
1392 cm$^{-1}$ is assigned for the symmetric and asymmetric stretching of the characteristic S=O bond of sulfonic acid (–SO3H) group. Furthermore, another broader peak at 3342 cm$^{-1}$ is assigned for the stretching –OH bond of sulfonated group. As observed in FTIR spectra, the intensity of a new peak (1170 cm$^{-1}$) increases with an increase in reaction time. On the other hand, the peak at 1408 cm$^{-1}$ remains unchanged for both of pure PVdF and sulfonated PVdF. The degree of substitution (DS) is calculated by the rationalization of these particular peaks [6, 153, 154]. The calculated value of DS is depicted in Figure 4E.2. Figure 4E.2 further reveals that initially, with an increase in the duration of sulfonation from 0 to 2 hrs., the value of DS increases rapidly up to 33%. However, beyond 2 hrs of reaction duration, a sharp decrease in DS value is observed. It is due to the formation of sulfone cross-links at higher temperature [6]. The crosslinking is more pronounced for the duration of sulfonation of 4 hours (SP-4) as the sulfonated PVdF turns into a viscid material. This observation is a good agreement with the reduction in size of PVdF with an increase in reaction time. Since, PVdF have a very straight chain structure having lower density of fluorine in comparison to PVdF-co-HFP, it allows comparatively faster interaction with acids at the same reaction temperature [154]. The variation in size and nature of the polymer granules upon sulfonation is reported in Table 4E.1.

Table 4E.1: Constituent detail of sulfonation reaction (time, temperature) and variation of granules Size.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample Designation</th>
<th>Sulfonation period (Hrs.)</th>
<th>Reaction Temperature (°C)</th>
<th>Mean height of granules (h) (in mm)</th>
<th>Mean width of granules (D) (in mm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SP-0</td>
<td>0</td>
<td>60</td>
<td>2.26</td>
<td>4.78</td>
<td>Good</td>
</tr>
<tr>
<td>2</td>
<td>SP-1</td>
<td>1</td>
<td>60</td>
<td>2.23</td>
<td>4.76</td>
<td>Good</td>
</tr>
<tr>
<td>3</td>
<td>SP-2</td>
<td>2</td>
<td>60</td>
<td>2.14</td>
<td>4.61</td>
<td>Good</td>
</tr>
<tr>
<td>4</td>
<td>SP-3</td>
<td>3</td>
<td>60</td>
<td>1.88</td>
<td>4.12</td>
<td>Sticky</td>
</tr>
<tr>
<td>5</td>
<td>SP-4</td>
<td>4</td>
<td>60</td>
<td>NA</td>
<td>NA</td>
<td>Viscid</td>
</tr>
</tbody>
</table>

Moreover, it is interesting to note that the S-PVdF exhibits 33% of DS upon sulfonation for the period of 2 hrs, whereas the DS value is reported to be 32% for S-PVdF-co-HFP.
at 7 hrs of period of sulfonation. From the above analysis, one can judge that the rate of sulfonation of PVdF is higher than that for PVdF-co-HFP at the same temperature. Nevertheless, amongst the sulfonated samples, the maximum DS is exhibited by the sample SP-2, which is expected to be for more suitable as a PEM in DMFC. Therefore SP-2 is utilized for further studies.

![Figure 4E.2](image)

**Figure 4E.2** Degree of sulfonation (DS) and crystallinity of pure and sulfonated PVdF.

**4E.2. Analysis of XRD**

XRD test is conducted for the analysis of the effect of sulfonation on the crystalline domain of PVdF. The obtained XRD pattern is depicted in Figure 4E.3. As observed in figure, pure PVdF exhibits a highly intense and sharp peak at 2 theta of 20.07°. At the same angle, the intensity of the peak for the sulfonated polymers continuously decreases with an increase in the period of sulfonation. In addition, it is also observed that with an increase in the duration of sulfonation reaction, the peak gets shifted towards the higher value of 2 theta. A similar trend was also observed for sulfonated PVdF-co-HFP. Since, higher degree of crystallinity exhibits a sharper and more intense XRD peak, whereas a relatively weaker and less intense peak signifies the amorphous regions [153, 155]. The percentage of crystallinity of different samples is calculated by the following equation (4.7) and the calculated value of crystallinity for different samples is plotted as a bar diagram in Figure 4E.2. From the figure, it is observed that the crystallinity (%) of the
PEM decreases with an increase in the duration of sulfonation. This is expected as increasing sulfonation disrupts regular structure and thereby diminishes the crystalline regions [6].

![XRD patterns](image)

**Figure 4E. 3** XRD patterns of pure and sulfonated PVdF.

### 4E.3. Analysis of laminate structure

Laminate structure was visually examined carefully to avoid any physical defect like entrapped air voids/fracture. Since, any fracture or weak adhesion between two polymer surfaces will definitely cause the high interfacial resistance and thereby lead to poor DMFC performance. For more justification, we have conducted the “Peel off” test by using UTM (Universal testing machine, H5K5; piniusolsen, USA). The ultimate adhesion force between Nafion-117 and S-PVdF was recorded 0.783 N.

### 4E.4. Analysis of water uptake capacities and Methanol Uptake of the membranes

The water uptake capacity (WU %) of the sulfonated and non sulfonated samples, along with the reference sample (Nafion-117) is calculated from the equation (3.1) and the obtained values are plotted in Figure 4E.4. As observed from the figure, the water uptake values for pure PVdF at 20 °C and 60 °C is only 0.5% and 1%, respectively; while after sulfonation, the corresponding uptake value increases rapidly up to 11% and 13%,
respectively. This increased affinity for water is due to the polar nature of the \(-\text{SO}_3\) group present in the sulfonated PVdF. Sulfonated PVdF absorbs the water molecule on its surface by virtue of strong interactions between \(-\text{SO}_3\) groups and water molecules via formation of strong hydrogen bonds. A similar trend is observed for the samples modified with sulfonated PVdF (Nafion-SPL and Nafion-SPC) and non sulfonated PVdF (Nafion-PPL and Nafion-PPC). Moreover, Nafion-SPL and Nafion-SPC exhibits higher WU compared to Nafion-PPL and Nafion-PPC, respectively. However, the water uptake capacities of the Nafion membranes modified with sulfonated PVdF are higher than the Nafion membranes modified with non-sulfonated PVdF membranes but are slightly lower than the pristine Nafion-117. This decreased affinity for water is due to the blocking of straight channels in Nafion by S-PVdF polymer layer.

![Figure 4E.4 Water uptake capacity of membrane samples at 20 °C and 60 °C.](image)

**Figure 4E.4** Water uptake capacity of membrane samples at 20 °C and 60 °C.

Methanol uptake is one of the important parameters that indicate the affinity of PEM towards methanol before being exposed to the aqueous solution of methanol within the DMFC cell. In DMFC test, usually 2-5 M methanol is used. Therefore, all the membranes are subjected to test for methanol uptake against the recommended range of concentration of methanol (2 -5 M) to have an idea about the effect of concentration of methanol on the methanol uptake of the membranes. The methanol uptake value for the membranes is
calculated by using the equation (3.2) and obtained value is depicted in Figure 4E.5 as bar diagram.

From the figure 4E.5, it can be observed that the methanol uptake value for each membrane is higher for 5M methanol in comparison to that obtained for 2M methanol and the trend is very similar to the respective water uptake. However, it is interesting to note that pristine Nafion-117 exhibits much higher value of methanol uptake i.e. 26% and 31% for 2 M and 5 M methanol respectively, compared to its corresponding water uptake value (16.5%). The only reason behind this observation is the strong affinity of Nafion-117 towards methanol in comparison to the water molecules [153].

![Figure 4E.5 Methanol uptake capacity of membranes at 2M and 5M.](image)

**4E.5. Proton conductivity analysis**

The proton conductivities of the coated and laminated membranes, along with Nafion-117, are determined by employing the impedance spectroscopic technique (Fig. 3.6) at room temperature, and the obtained results have been presented in Table 4E.2. From the table, it is observed that the Nafion-117 membrane exhibits the maximum proton conductivity ($3.16 \times 10^{-2} \text{ S cm}^{-1}$) among all of the samples; sulfonated polymer modified Nafion 117 i.e. Nafion-SPL and Nafion-SPC show a slightly lower value i.e.
5.11×10⁻³ S cm⁻¹ and 5.91×10⁻³ S cm⁻¹ respectively. Since, the proton conductivity is directly proportional to the water uptake capacity of the membrane that in turn depends upon the available free volume. Therefore, the coated and laminated membranes provide a barrier to the pores of Nafion-117, leading to a decrease in water uptake and hence exhibiting slightly lower proton conductivity.

**Table 4E.2:** Characteristic properties of polymer membrane.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample Designation</th>
<th>Sample description</th>
<th>Membrane Thickness (μm)</th>
<th>Proton Conductivity (S cm⁻¹)</th>
<th>Methanol Crossover (cm² s⁻¹)</th>
<th>Membrane selectivity (S cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nafion-117</td>
<td>Nafion-117</td>
<td>193</td>
<td>3.02×10⁻²</td>
<td>1.22×10⁻⁶</td>
<td>2.47×10⁴</td>
</tr>
<tr>
<td>2</td>
<td>S-PVDF</td>
<td>Sulfonated-PVdF</td>
<td>173</td>
<td>1.01×10⁻⁴</td>
<td>4.12×10⁻⁹</td>
<td>2.45×10⁴</td>
</tr>
<tr>
<td>3</td>
<td>Nafion-PPL</td>
<td>Nafion-Pure PVdF laminated</td>
<td>213</td>
<td>1.37×10⁻³</td>
<td>3.23×10⁻⁸</td>
<td>4.24×10⁴</td>
</tr>
<tr>
<td>4</td>
<td>Nafion-SPL</td>
<td>Nafion-Sulfonated PVdF laminated</td>
<td>214</td>
<td>5.11×10⁻³</td>
<td>3.32×10⁻⁸</td>
<td>1.53×10⁵</td>
</tr>
<tr>
<td>5</td>
<td>Nafion-PPC</td>
<td>Nafion-Pure PVdF coated</td>
<td>201</td>
<td>1.69×10⁻³</td>
<td>2.69×10⁻⁸</td>
<td>6.28×10⁴</td>
</tr>
<tr>
<td>6</td>
<td>Nafion-SPC</td>
<td>Nafion-Sulfonated PVdF coated</td>
<td>199</td>
<td>5.91×10⁻³</td>
<td>4.18×10⁻⁸</td>
<td>1.41×10⁵</td>
</tr>
</tbody>
</table>

**4E.6. Analysis of methanol crossover, Air permeability and determination of membrane selectivity**

The methanol permeabilities of the samples are determined by using UV-vis spectroscopic technique (Fig. 3.7), and the obtained results have been presented in Table 4E.2. From the table, it is observed that the permeability of each sample is following its respective trends for water and methanol uptakes (Fig. 4E.4 and 4E.5). However, amongst all of the membranes, the methanol permeability for Nafion-117 is observed to be maximum i.e. 1.22×10⁻⁶ cm² s⁻¹. This is possibly due to the possessing of maximum free volume within the membrane structure, as indicated by its highest value of water uptake amongst all of the samples. Nevertheless, the substantially low methanol permeability of coated and laminated membrane by about two orders of magnitude compared to the pristine Nafion-117 is due to the blocking of the pore channels of Nafion...
as evidenced from the air permeability (test conducted on capillary flow porometer; SCFP-1100AL) of S-PVdF in Figure 4E.6. From the figure, it can be observed that with an increase in pressure, the specific flow rate of air is low for S-PVdF coated/laminated membrane in comparison to the pristine Nafion-117 membrane; this provides an idea about the low porosity of S-PVdF coated/laminated membranes, compared to the Nafion 117 membrane.

Fig. 4E.6. Air permeability of Nafion-117 and S-PVdF membrane.

Membrane selectivity is one of the most important and crucial parameter to evaluate the applicability of a PEM in DMFC and can be defined as “a ratio between the proton conductivity and the methanol permeability of the PEM”. The membrane selectivity of all of the membranes are calculated and reported in Table 4E.2. As observed from the table, the coated and laminated membrane exhibit 5-6 times higher membrane selectivity in comparison to the pristine Nafion-117 membrane. The reason for this higher membrane selectivity is that the laminated and coated Nafion-117 membrane exhibit lower methanol crossover by two orders of magnitude (as explained earlier), while at same time, they have to compromise with marginal loss in their proton conductivity.

4E.7. Effect on cell potential (OCV)

Effect on cell potential by the lamination/coating of S-PVDF on Nafion 117 membrane was analyzed on the DMFC test station (with feeding 2M methanol at anode
as standard fuel in DMFC) at 60 °C for a period of 1 h. Figure 4E.7 shows the voltage-time curves recorded for different PEM samples. It can be observed that the maximum cell potential obtained for coated (Nafion-SPC) and laminated (Nafion-SPL) membrane is 0.81 V and 0.84 V respectively. These values are much higher than the corresponding OCV value recorded for the pristine Nafion117 membrane i.e. 0.71 V. Since, it is well known that the OCV of the cell is primarily a function of methanol crossover; therefore, higher methanol crossover leads to the lowering of cell potential. This is because methanol after crossover reacts directly with oxygen at these sites and produces H₂O that causes cell flooding and increases the required oxygen stoichiometry. In addition, the methanol upon reaching the cathode gets oxidized in presence of Pt catalyst and gives rise to a reverse potential. These two effects lead to the lowering of the OCV of the cell significantly.

![Fig. 4E.7 OCV recorded for the PEM samples.](image)

**4E.8. DMFC performance test**

The DMFC performance tests for all of the membranes are conducted on a single cell, having an MEA area of 5x5 cm². The cell is operated at 60 °C by using two variable molar concentrations of fuel i.e. 2 M and 5 M. The obtained results are represented in Figure 4E.8 (a) and (b), as a characteristic plot of potential vs. current density. The maximum current density recorded for the samples, Nafion-SPL and Nafion-SPC are 145 mA cm⁻² and 155 mA cm⁻² respectively at a potential of +0.2 V, while for pristine Nafion
117, it is 195 mA cm$^2$ at the same potential. These results indicate that the membrane with higher water uptake and proton conductivity exhibits higher current density, operated with feeding 2 M of methanol as a fuel.

Fig. 4E.8(a) DMFC performance of samples at 2M methanol feed at anode.

Fig. 4E.8(b) DMFC performance of samples with 5 M methanol feed at anode.
On feeding the cell with higher concentration of fuel i.e. 5 M of methanol, the maximum current density rapidly raises up to 220 mA cm$^{-2}$ and 215 mA cm$^{-2}$ recorded for the respective Nafion-SPL and Nafion-SPC membranes at the same potential of 0.2 V; whereas for the pristine Nafion 117 membrane, the current density measured under the similar conditions is observed to be 180 mA cm$^{-2}$. These results can be explained by the reduction of methanol crossover on lamination and coating and thereby membrane selectivity increases for these modified membranes, leading to the higher electrical efficiency at the higher concentration of methanol.

4E.9. Conclusions

In brief, the partial sulfonated PVdF is utilized as a laminate and coating material on the surface of Nafion-117. In the first part of our experiment, we have conducted the sulfonation of PVdF in the presence of a strong sulfonating agent, i.e chlorosulfonic acid at 60 °C. The sulfonation of PVdF is confirmed by the FTIR and XRD spectra. The degree of sulfonation is optimized by modulating the duration of sulfonation reaction. The maximum degree of substitution is attained up to 33% on sulfonation for 2 hours. Furthermore, modified Nafion membrane (by using sulfonated PVdF as laminating and coating materials) exhibits lower methanol crossover by magnitude of two orders, leading to higher membrane selectivity. The OCV of the coated and laminated membranes is also observed to be higher than the pristine Nafion-117. The maximum power density recorded for the laminated membrane (Nafion-SPL) and coated membrane (Nafion-SPC) is 44 and 43 mW cm$^{-2}$ respectively; these values are higher than the recorded power density value of 36 mW cm$^{-2}$ for the pristine Nafion-117. This result indicates that on the lamination and coating of S-PVdF on Nafion117 membrane, the methanol crossover significantly reduces and thereby allowing feed of higher concentration (5 M of methanol) and increasing the electrical efficiency in direct methanol fuel cell.
SECTION 4F: INCORPORATION OF NANO-AL$_2$O$_3$ WITHIN THE BLEND OF SULFONATED-PVDF-CO-HFP AND NAFLON FOR HIGHTEMPERATURE APPLICATION IN DMFCs

4F.1. Introduction

In this section, Nano-Al$_2$O$_3$ was incorporated into the blend of sulfonated-PVdF-co-HFP/Nafion using NMP (1-methyl-2-pyrrolidone) as a common solvent with the aim to develop an alternate membrane to be used in a single cell direct methanol fuel cell (DMFC). Furthermore, the synthesized nano-composite membranes were subjected to different tests such as FTIR, XRD, water uptake, swelling, IEC (ion exchange capacity), proton conductivity and methanol crossover. In addition, we have studied the effect of temperature on the cell performance of this prospective PEM.

4F.2. Constituent Details of the composite Membranes

Nano-composite membrane was prepared by incorporation of Nano-Al$_2$O$_3$ into the blend of Sulfonated-PVdF-co-HFP/Nafion using NMP (1-methyl-2-pyrrolidone) as a common solvent (as illustrated in fig. 3.5). The chemical composition of the membrane is tabulated in Table 4F.1.

Table 4F.1: A chemical composition of the composite membrane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S-PVdF-co-HFP</th>
<th>Nafion</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt.% (g.)</td>
<td>wt.% (mL.)</td>
<td>wt.% (g.)</td>
</tr>
<tr>
<td>S-0</td>
<td>80 (2.40)</td>
<td>20 (12)</td>
<td>0 (0.00)</td>
</tr>
<tr>
<td>S-2</td>
<td>78 (2.34)</td>
<td>20 (12)</td>
<td>2 (0.06)</td>
</tr>
<tr>
<td>S-5</td>
<td>75 (2.25)</td>
<td>20 (12)</td>
<td>5 (0.15)</td>
</tr>
<tr>
<td>S-7</td>
<td>73 (2.19)</td>
<td>20 (12)</td>
<td>7 (0.21)</td>
</tr>
<tr>
<td>S-10</td>
<td>70 (2.10)</td>
<td>20 (12)</td>
<td>10 (0.30)</td>
</tr>
</tbody>
</table>

4F.3. Analysis of FTIR spectra

The presence of characteristics/functional group within the composite membrane is confirmed by the analysis of FT-IR spectra, depicted in Fig. 4F.1. In the FTIR spectra,
peaks appeared at 1230 cm\(^{-1}\) and 1164 cm\(^{-1}\) are due to the Nafion backbone’s C-F stretching vibration; while a sharp peak at 1067 cm\(^{-1}\) can be assigned to the S-O stretching vibration of \(-\text{SO}_3\text{H}\) groups present in host polymer blend [6] A characteristic peak appeared at 830 cm\(^{-1}\) and 874 cm\(^{-1}\) is assigned for the crystalline and amorphous phase of S-PVDF-co-HFP, respectively. The intensity of these peaks diminishes continuously with an increase in the content of alumina Nano-filler (as evidenced in sample S-10). It is due to interaction of inorganic filler (alumina) with polymer chain. Al\(_2\)O\(_3\) reveals strong band at 400-800 cm\(^{-1}\) assigned for inorganic segment of Al-O-Al. However, a new peak appeared at 1639 cm\(^{-1}\) is close to literature [128] value of 1623 cm\(^{-1}\) and it is assigned to the Al–O stretching modes which is not present in the blend of S-PVdF-co-HFP/Nafion. This hindrance towards the intensity of characteristic peaks confirms that the nano particles of alumina interact at polymer-filler interface.

![FTIR spectra of samples.](image)

**Fig. 4F.1** FTIR spectra of samples.

**4F.4. Analysis of XRD spectra**

XRD test is conducted for the analysis of the crystalline-amorphous domain of the composite membrane. The obtained XRD pattern is depicted in Fig. 4F.2. As observed in Fig. 4F.2, S-PVdF-co-HFP/Nafion exhibited high intense and sharp peak at 2 theta of
around 20.8°. Furthermore, upon incorporation of Al₂O₃ (up to 5wt.%), two diffraction peaks tend to resemble as a single peak around 22.5°, whereas the third peak appearing at 39.5° is diminished probably due to the incorporation of inorganic filler. The presence of inorganic filler interferes in the close and ordered packing of S-PVdF-co-HFP/Nafion host polymer chain, leading to its reduced crystallinity. The presence of higher degree of crystallinity in polymer causes to exhibit a sharper and more intense XRD peak, whereas a relatively weaker and/or less intense peak signifies the amorphous regions [107]. However, further incorporation of Al₂O₃ (>5wt.%) causes to appear three diffraction peaks at 38.3, 39.7 and 43.5° due to the accumulation of Al₂O₃-nanoparticles [127,129,130].

Fig. 4F.2 XRD patterns of membrane samples.

Moreover, the percentage of crystallinity and chain separation value (R Value) is calculated by equation (4.7) and (4.8) respectively and the calculated value of crystallinity along with R-value for the different samples is tabulated in Table 4E.2. From the table, it is observed that the crystallinity (%) of the composite membrane decreases continuously with an increase in the filler content (up to 5wt%), while, on the other
hand, the crystallinity goes up with higher doses (more than 5wt.% alumina) of nano filler. The most probable reason behind this observation is that the interaction of inorganic filler with polymer chain varies from material to material. A schematic of possible interaction of Al₂O₃ with blend polymer chains is illustrated in Fig. 4F.3.

![Interaction of nano filler with host polymer chains](image)

**Fig. 4F.3** Interaction of nano filler with host polymers chain.

The incorporation of alumina nano-particle (up to 5wt.%) diminishes the electrostatic interaction between the Nafion and S-PVdF-co-HFP chain that causes the chain reorganization and facilitates free volume within the membrane as evidenced from reduction in chain separation (R) value (Table 4F.2). This observation is quite anticipated [156-158]. Since, nano-alumina interacts not only with the polymer surface, but also with the polymer group (as observed in FTIR-spectra and explained in sec. 4F.2), thus the high filler loading causes formation of ordered structure of polymer nano-composite and thereby exhibits high crystallinity.

**Table 4F.2**: The crystallinity (%) and R-value obtained for different samples.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample</th>
<th>Crystallinity (%)</th>
<th>Inter chain separation, R (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>S-PVdF-co-HFP*</td>
<td>34.4</td>
<td>0.214</td>
</tr>
<tr>
<td>2.</td>
<td>S-0</td>
<td>31.2</td>
<td>0.205</td>
</tr>
<tr>
<td>3.</td>
<td>S-2</td>
<td>29.1</td>
<td>0.213</td>
</tr>
<tr>
<td>4.</td>
<td>S-5</td>
<td>27.7</td>
<td>0.221</td>
</tr>
<tr>
<td>5.</td>
<td>S-7</td>
<td>35.5</td>
<td>0.192</td>
</tr>
<tr>
<td>6.</td>
<td>S-10</td>
<td>37.2</td>
<td>0.188</td>
</tr>
</tbody>
</table>

*Data compared with Ref (13)
4F.5. Analysis of water uptake/swelling capacities

The water uptake capacity (WU %) of the composite membranes were calculated by following equation (3.1) and compared the results with corresponding Nafion-117 membrane. As observed in the Fig. 4F.4, the water uptake values for Nafion-117 and S-PVdF-co-HFP is 16.2% and 21.7% respectively; while upon charging the nano-alumina, the corresponding water uptake values increase rapidly up to 34.8%. This increase in water affinity is due to the (a) hygroscopic nature of Al₂O₃ present in the composite membranes and (b) increase in the free volume due to the presence of very high concentration of polymer–filler interfaces.

![Water uptake and swelling ratio of different membrane samples.](image)

Fig. 4F.4 Water uptake and swelling ratio of different membrane samples.

However, increased water retention is a prerequisite for enhanced proton conduction, where the mechanical stability and durability of membrane become the next question. In order to rationalize it, the samples are subjected to swelling analysis (equation 3.3). The maximum swelling ratio recorded for Nafion-117 and S-PVdF-co-HFP/Nafion blend membrane are 12.3 and 11.1 % respectively (Fig. 4F.4). On the other hand, relatively reduced swelling ratio value is observed upon incorporation of alumina nano-fillers.
Nevertheless, the maximum swelling ratio for sample S-5 is recorded to be 9.8%. The possible reason behind this observation may be (a) partial substitution of S-PVdF-co-HFP by the inorganic filler (Al₂O₃), which in turns reduced sulfonic acid sites within the composite structure and (b) high interface between inorganic filler with polymer chain [129].

4F.6. Analysis of Morphology and mechanical integrity

Fig. 4F.5 shows the effect of incorporation of nano-Al₂O₃ on the morphology of the casted membranes. From the figure, it is observed that with an increase in the Al₂O₃-content within the host polymer blend, the smooth surface morphology of S-0 turned in to a very rough one. In addition, some free space (like bee-bodies) gets generated on the membrane surface (in S-5), which is well dominated by the increasing content of Al₂O₃. Initial increase in free space with increasing Al₂O₃-content can be well-related to their chain separation (R) value (Table 4F.2).

![Fig. 4F.5 FESEM image of different membrane samples; [Scale: 10µm; Magnification: 5,000x and in inset 100nm; Magnification: 30,0000x].](image)

Mechanical integrity of a PEM is one of its important aspects, considering its durability in a fuel cell. The tensile strength of S-0 is recorded to be 11.06 MPa (Fig. 4F.6a). The
effect of tensile strength upon incorporation of nano-Al2O3 within the blend membranes is noticed in Fig. 4F.6a. Initially, the increase in Al2O3-content (up to 5 wt.%) causes marked increase in the tensile strength.

![Graph of Tensile Strength](image)

![Graph of Elongation](image)

Fig. 4F.6 (a) Tensile strength and (b) Elongation (%) of different membrane samples.
On the other hand, the presence of higher Al2O3 content within the PEM structure (>5 wt.%) is responsible to a certain extent in reducing its tensile strength, as evidenced from a sharp reduction of tensile strength in S-7 and S-10. It is well-known that polymer membrane loaded with higher content of nano-fillers suffers with restricted chain mobility [140, 141]. This hindrance towards chain mobility essentially results in increased rigidity, and thereby, can affect the tensile strength as well as corresponding elastic properties as depicted in Fig.4F.6b in terms of elongation (%). In summary, among all the proposed membranes, the mechanical integrity of S-5, exhibiting acceptable tensile strength of 14.88 MPa, is comparable to that of corresponding blend sample S-0 (11.06 MPa).

4F.7. IEC of membranes

Using equation (3.5), the ion exchange capacities (IEC) of the prospective membranes were calculated (Table 4F.3).

Table 4F.3: Characteristic properties of composite membrane samples.

<table>
<thead>
<tr>
<th>Sl. NO.</th>
<th>Sample Designation</th>
<th>Thickness (µm)</th>
<th>IEC (meq g⁻¹)</th>
<th>Proton Conductivity (S cm⁻¹)</th>
<th>Methanol Crossover (cm² s⁻¹)</th>
<th>Membrane Selectivity (S cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Nafion-117</td>
<td>190</td>
<td>0.81</td>
<td>3.02×10⁻²</td>
<td>1.22×10⁻⁶</td>
<td>2.47×10⁴</td>
</tr>
<tr>
<td>2.</td>
<td>S-PVdF-co-HFP</td>
<td>204</td>
<td>0.42</td>
<td>3.75×10⁻³</td>
<td>2.44×10⁻⁷</td>
<td>1.53×10⁸</td>
</tr>
<tr>
<td>3.</td>
<td>S-0</td>
<td>202</td>
<td>0.73</td>
<td>2.32×10⁻²</td>
<td>6.21×10⁻⁷</td>
<td>3.79×10⁸</td>
</tr>
<tr>
<td>4.</td>
<td>S-2</td>
<td>201</td>
<td>0.70</td>
<td>2.76×10⁻²</td>
<td>6.22×10⁻⁷</td>
<td>4.43×10⁸</td>
</tr>
<tr>
<td>5.</td>
<td>S-5</td>
<td>202</td>
<td>0.68</td>
<td>3.57×10⁻²</td>
<td>6.41×10⁻⁷</td>
<td>5.56×10⁸</td>
</tr>
<tr>
<td>6.</td>
<td>S-7</td>
<td>200</td>
<td>0.57</td>
<td>1.77×10⁻²</td>
<td>4.92×10⁻⁷</td>
<td>3.59×10⁸</td>
</tr>
<tr>
<td>7.</td>
<td>S-10</td>
<td>203</td>
<td>0.53</td>
<td>1.21×10⁻²</td>
<td>3.78×10⁻⁷</td>
<td>3.20×10⁸</td>
</tr>
</tbody>
</table>

*Data compared with Ref (13)

From table, it is observed that the blend membrane (S-0) shows about 9% lower IEC (0.72 meq g⁻¹) value in comparison to Nafion-117 (0.81 meq g⁻¹). On the other hand, upon charging of 2-10% of nano filler within the blend membrane, the respective IEC value of composite membrane decreases about 4-27% in comparison to IEC value obtained for S-
0. This result is quite expected due to the reduction of the concentration in \(-\text{SO}_3\text{H}\) groups in the blend and composite membrane. Nevertheless, the composite membrane S-5 composed of 5 wt.% of nano filler reveals only about 16% and 7% lower IEC value than the corresponding Nafion-117 and blend membrane (S-0), respectively. The IEC value of 0.68 meqg\(^{-1}\) exhibited by composite membrane S-5 can be considered as PEM in DMFC.

4F.8. Proton conductivity analysis

The proton conductivities of the casted membranes along with Nafion-117 were determined by employing the impedance spectroscopic technique at 20 °C (Table 4F.3). The proton conductivities of the membranes follow the same trend as those for water uptake results. It is observed that the proton conductivities can be directly correlated with the water uptake capacities of the membranes. Initially, with an increase in nano-alumina content up to ~ 5 wt.%, proton conductivity increases about 18-54% for S-2 and S-5 composite membranes in comparison to the blend membrane (S-0), while further loadings of alumina (7-10 wt.%) leads to around 42-60% reduction in proton conductivity (in S-7 and S-10). Proton conduction across a membrane is a function of (a) concentration of \(-\text{SO}_3\text{H}\) groups available within the membrane, (b) available free volume or water uptake capacity and (c) alignment of the tortuous pores across the membranes. Since, the membrane composed of less than 5 wt.% Al\(_2\)O\(_3\), the active sulfonated group at surface does not vary too much (as evidenced from the IEC results in Table 4F.3). On the other hand, with the incorporation of nano-alumina, a reduction in the electrostatic interactions between S-PVdF-co-HFP and Nafion is observed (as evidenced from the chain separation (R) value depicted in Table 4F.2). This increases the free volume space within the membrane structure, leading to the increase in the water retention and proton conductivity in the composite membranes. However, increased concentrations of nano fillers (>5 wt.%) blocks the open channels of the tortuous pores, resulting in lower inter-space volume and considerably fewer \(-\text{SO}_3\text{H}\) groups are exposed for proton conduction. Due to this hindered water flow across the membrane, relatively reduced proton conductivity occurs with the excess incorporation (>5 wt.%) of nano-fillers. Nevertheless, Sample S-5 (5 wt.% Al\(_2\)O\(_3\)) exhibits about 54% enhanced proton conductivity value (3.57×10\(^{-2}\) S cm\(^{-1}\)) than the corresponding blend membrane S-0 (2.32×10\(^{-2}\) S cm\(^{-1}\)), which is comparable to Nafion-117 membrane (i.e. 3.02×10\(^{-2}\) S cm\(^{-1}\)).
4F.9. Analysis of methanol crossover and membrane selectivity

The methanol permeability of the composite membrane is determined by using UV-vis spectroscopic technique (Table 4F.3). The permeability of the samples follows the same trend as that of % crystallinity and chain separation (R-value), except in the case of S-0 membrane. In comparison to pristine Nafion-117 (1.22×10^{-6} cm^2 s^{-1}), about 49% lower methanol crossover value (6.21×10^{-7} cm^2 s^{-1}) is observed for corresponding blend membrane S-0 (partial sulfonated PVdF-co-HFP/Nafion). The plausible reason may be (a) comparatively lower concentration of sulfonic acid group present in the partially sulfonated PVdF-co-HFP [6] polymer than Nafion-117 and (b) higher electrostatic interaction between both chains, which are responsible for the higher crystallinity of the membrane as S-PVdF-co-HFP is highly compatible with Nafion [48-50, 159]. Thus, owing to its lower chain separation and proton conductivity, reduced methanol permeability is observed in S-0 membrane. Furthermore, upon incorporation of aluminum oxide up to 2-5 wt.%, the corresponding value of methanol crossover is increased about 0.1-2% than that for sample S-0. It is due to the available free volume space (caused by the incorporation of Al_2O_3) within the composite membrane structure, as mentioned earlier in section 4F.7. However, the methanol crossover value exhibited by sample S-5 is 6.41×10^{-7} cm^2 s^{-1}, which is about 47% less than the corresponding methanol crossover value of Nafion-117 (1.22×10^{-6} cm^2 s^{-1}). It is probably due to the less affinity of composite membrane material towards methanol, leading to preferential uptake of water molecules. Membrane selectivity is one of the most important parameter to evaluate the applicability of a PEM in DMFC. The selectivity of all membranes is calculated by rationalizing the value of corresponding proton conductivity and methanol crossover of the membranes. As observed from Table 4E.3, the composite membrane (S-5) exhibits about 18% higher proton conductivity and 47% less methanol crossover compared to Nafion-117 and thereby leads to two fold increase in its membrane selectivity (i.e. 5.56×10^4 S scm^{-3}).

4F.10. DMFC performance

DMFC performance tests were conducted for all the membranes on a single cell having MEA area of 5x5 cm^2. The maximum current density recorded for the blend membrane (S-0) and Nafion-117 at 60 °C is 245 and 195 mA cm^{-2} respectively, at +0.2 V
(Fig. 4F.7), whereas for composite membranes S-2, S-5, S-7 and S-10, it is only 155, 175, 140 and 120 mA cm$^{-2}$. These observations indicate that the membrane with higher IEC and lower methanol crossover value exhibits higher current density at lower temperature. Furthermore, operating at high temperature (90–110 °C), a sharp drop in current densities for all the membrane is observed except for the composite membranes (Fig. 4F.8). The maximum current density recorded for corresponding Nafion-117 and blend membrane (S-0) is 140 and 160 mA cm$^{-2}$ at 90 °C (Fig. 4F.8); whereas operating at 110 °C (Fig. 4F.9), it is only 55 and 75 mA cm$^{-2}$ respectively. The decreased current density at high temperature is due to the dehydration of membranes, resulting in lower liquid mobility and thus hinders the transverse proton conduction. Nevertheless, among all of the composite membranes, the maximum current density produced by sample S-5 is 285 mA cm$^{-2}$ at 90 °C (Fig. 4F.8) and 270 mA cm$^{-2}$ at 110 °C (Fig. 4F.9). The reason could be attributed to the hygroscopic nature of nano filler (i.e. Al$_2$O$_3$) present within the composite membranes that results in higher water uptake in comparison to Nafion-117 and corresponding blended membranes (Fig. 4F.4).

![Fig.4F.7 DMFC performance of samples at 60 °C.](image)
Fig. 4F.8 DMFC performance of samples at 90 °C.

Fig. 4F.9 DMFC performance of samples at 110 °C.
4F.11. Conclusions

In summary, nano-composite membranes composed of nano- \( \text{Al}_2\text{O}_3 \) within the blend of partially sulfonated PVdF-co-HFP and Nafion were evaluated as PEM for high temperature application in DMFC. A higher water uptake with increased proton conductivity and lower methanol crossover in the nano-alumina filled composite membrane exhibited its potency as an efficient membrane over the commercially used membrane, Nafion-117. In addition, the composite membrane showed good mechanical stability and higher power density in a single cell of DMFC, indicating its applicability at higher operating temperatures.