3. MATERIALS AND EXPERIMENTAL TECHNIQUES

3.1. MATERIALS USED

Nafion 117 membrane and Carbon paper (Ballard MGL 370) were bought from M/S Anabond Synergy Fuel Cell Ltd (India). Sulfuric acid, phosphoric acid, chlorosulfonic acid (CSA), formic acid, Dimethyl formamide (DMF), NMP (1-methyl-2-pyrrolidone) and divinyl benzene (DVB) were obtained from Merck Millipore (India). PVdF-co-HFP (Mw: 455,000), PVdF (Mw: 530,000), nano-Al$_2$O$_3$ (≤50 nm), sodium salt of sulfonated styrene, and Nafion resin (5wt.% solution in a mixture of lower aliphatic alcohols and water, density: 0.924 Kgm$^{-3}$) were obtained from Sigma Aldrich Co. (India). All the chemicals were used as received.

3.2. INSTRUMENTS USED

The FT-IR characterization of the membranes was performed using a Bruker Alpha FT-IR spectrophotometer (Model: Alpha E) at 25° C, by employing a wave number window of 550–3000 cm$^{-1}$. The effect of heat on the membranes was analysed by conducting DSC tests following the reported procedure, using a Mettler Star SW 9.01 Differential Scanning Calorimeter. Morphology of the membranes was determined using a Scanning Electron Microscope (EVO 18, Carl Zeiss, Germany). Prior to the analysis, all the samples were sputter coated with gold, using a Hitachi sputter coater (Model-E1010 Ion Sputter), Japan. The mechanical properties of the prepared membranes were determined using Universal Tensile Testing Machine (Nexygen plus, Lloyd Instruments Ltd.), following procedure ASTMD 882-02. The tensile tests were performed using a 5 T tension meter at a crosshead speed of 5 mm min$^{-1}$ at 25° C. Two sets of tensile tests were conducted for each sample, and the average values of the tensile strengths have been reported. An impedance analyser (Potentiostat-600) was used to measure the changes in membrane interface resistance. Since, the sodium salt of styrene is in the form of sodium salt (SO$_3$Na$^+$) and it is necessary to activate the membrane (i.e. protonation; SO$_3$H$^+$) before the test. Therefore, all the membranes were pre-soaked in a 1 M H$_2$SO$_4$ solution for a period of 24 h. The anode was used as the reference electrode, while the cathode
served as the working electrode. Within a frequency range of 100 mHz to 100 kHz, the response towards an applied AC amplitude of 0.05 V was measured. The DMFC performance was analysed with an automated DMFC test station obtained from K-PAS electronic India Ltd. The cell was equilibrated for 2 h prior to analyses. A DC programmable load bank from K-PAS electronic India Ltd., attached with DMFC test station, was used to measure the current and power output of the cell.

3.3. EXPERIMENTAL

3.3.1. Sulfonation of PVdF-HFP polymer

Sulfonation of PVdF-co-HFP was executed in the presence of cholorosulfonic acid using the same method as used in our previous publication [6]. In brief, 3g of vacuum dried PVdF-co-HFP (granules) was allowed to react with 20 mL of cholorosulfonic acid under continuous stirring at 60ºC for 7 hours. After the sulfonation, obtained dark brown pellets were washed with 1, 2 dichloroethane, followed by de-ionized (DI) water and kept into a vacuum oven at 80ºC. A schematic of possible sulfonation reaction is illustrated in Fig. 3.1.

![Fig. 3.1 A schematic of possible sulfonation reaction of PVdf-co-HFP [6].](image)

3.3.2. Sulfonation of PVdF polymer

Similarly, sulfonation of PVdF was conducted in the presence of cholorosulfonic acid. In brief, PVdF (in granular form) was first vacuum dried overnight at 80º C. 3g of polymer was allowed to react with cholorosulfonic acid in a round bottomed flask under
continuous stirring at 60º C for variable period of time. At the end of sulfonation, obtained dark brown pellets were collected and washed with 1, 2 dichloroethane. Again, the pellets were washed with de-ionized water and finally vacuum dried at 80º C. A schematic of possible sulfonation reaction is illustrated in Fig. 3.2.

![Sulfonation Reaction Diagram](image)

**Fig. 3.2** A schematic of possible sulfonation reaction of PVdF.

### 3.3.3. Membrane Fabrication

#### 3.3.3.1. Formation of Semi-IPN Membrane

PVdF-co-HFP copolymer was fully dissolved in DMF. Nafion resin was then added drop wise with continuous stirring at 80ºC for 2 h. The mixture was stirred vigorously until the solution turned homogeneous, transparent and viscous. The resulting viscous solution of the polymeric blend was casted on a flat glass plate and kept in an oven overnight at 80ºC. The obtained blend film was then redissolved in DMF and the resulting blend solution was transferred into a three-necked round bottom flask containing sodium salt of styrene. This was followed by the addition of initiator AIBN and cross-linker DVB. The resultant mixture was left under stirring condition at 110ºC to allow the SS to polymerize in situ. Finally, a viscous solution was obtained, that was again casted on the flat glass plate and kept in the oven at 80ºC for 24 h. The chemical structures of the polymers utilized and a schematic of the process involved in the preparation of the semi-IPN membranes is illustrated in Fig.3.3 and Fig. 3.4 respectively.
Fig. 3.3 The chemical structures of the polymers.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. PVdF-co-HFP</td>
<td>[ CH_2\text{-CF}_2 ]_x [ \text{CF}_2\text{-CF}_3 ]_y</td>
</tr>
<tr>
<td>2. Sodium salt of styrene</td>
<td>CH\text{=CH} \quad \text{SO}_3\text{Na}</td>
</tr>
<tr>
<td>3. Nafion</td>
<td>[ \text{CF}_2\text{-CF}_2 ]_x [ \text{CF}_2\text{-CF}_2 \text{-O} ] \text{CF}_3 \text{SO}_3\text{H}</td>
</tr>
<tr>
<td>4. DVB</td>
<td>CH\text{=CH} \quad \text{CH=CH}_2</td>
</tr>
</tbody>
</table>

Fig. 3.4 A schematic illustrating the process involved in the preparation of the membranes.
3.3.3.2. Preparation of coated membrane

For coating, S-PVdF and pure PVdF was separately dissolved in NMP in a beaker at 80°C with continuous stirring to get the desired viscous solution. The pretreated [10] Nafion-117 membranes were dipped in to the the respective viscous solution of PVdF/S-PVdF for a period of 15 minutes, followed by air drying. This process was repeated 4-5 times and finally the dip coated membranes were vacuum dried overnight in an oven at 80°C.

3.3.3.3. Preparation of laminate membrane

For lamination, two sets of membrane for each polymer i.e. S-PVdF and pure PVdF were prepared by simple casting technique. The concentration of polymer solution was kept constant at 10% w/v solution. A suitable amount of the solution was then cast onto a clean glass substrate and kept in an oven at 80°C for 12 h to obtain ~50 µm thick membrane. Furthermore, the pretreated Nafion-117 (thickness ~191 µm) membrane was hot pressed in a compression mould at 130°C for a period of 3 minutes under 20 MPa pressure. It was hot-pressed to reduce the thickness of the membrane such that on subsequent lamination, the final thickness should be comparable to the thickness of corresponding Nafion 117 membrane. Finally, the pre-compressed Nafion-117 membrane (thickness ~130 µm) was allowed to sandwich within each sets of the respective casted membrane at 135°C temperature and under 30 MPa of compression pressure. Pure PVdF was used as a reference.

3.3.3.4. Synthesis of nanocomposite membrane

Sulfonated PVdF-co-HFP (S-PVdF-co-HFP) was allowed to completely dissolve into NMP, afterward Nafion resin is added drop wise. The whole blend mixture was allowed to stir continuously until it turned into homogeneous solution. Furthermore, appropriate amount of nano-Al₂O₃ (≤50nm) filler was added into the blend solution under continuous stirring at 60°C. After getting optimum viscosity, the composite mixture was simply casted on a flat glass plate and kept into the oven overnight at 80°C. A schematic of the process involved in membrane preparation is illustrated in Fig. 3.5.
3.3.4. Membrane Pre-Treatment and protonation

The membranes were pre-treated by first immersing into a 5 M H$_2$O$_2$ solution, followed by treatment with a mixture of water and H$_2$SO$_4$ (7:3) for 2 h under continuous stirring condition. The membranes were then neutralized by washing with DI water, and were finally kept in an oven under a constant temperature of 80°C.

3.3.5. Membrane characterization

3.3.5.1. Water Uptake

A cut piece from each membrane was vacuum-dried, weighed and subsequently immersed into beakers containing DI water for proper dousing. After leaving undisturbed for 48 h, respective cut pieces of each sample were taken out, followed by wiping off the unabsorbed liquid, and then subjected to weighing analysis. Water uptakes of the prepared membranes were calculated from the following equation (3.1):

\[
\text{Water uptake} (%) = \frac{(W_{\text{wet}} - W_{\text{dry}}) \times 100}{W_{\text{dry}}}
\]  

\( \ldots 3.1 \)
where, $W_{\text{wet}}$ represents the weights of wet membranes obtained after soaking in the water for 48 h, and $W_{\text{dry}}$ is the weight of the respective dry membranes.

### 3.3.5.2. Methanol uptake

In a similar way, cut pieces of each membrane was weighed and subsequently immersed into a beaker containing 2M and 5 M of methanol. After leaving undisturbed for 48 h, the cut pieces of each sample were taken out, wiped out the unabsorbed liquid, and subjected to weighing. Respective methanol uptakes of the prepared membranes were calculated from the following equation (3.2):

$$\text{Methanol uptake (\%)} = \frac{(M_{\text{wet}} - M_{\text{dry}}) \times 100}{M_{\text{dry}}} \quad \cdots 3.2$$

Where, $M_{\text{wet}}$ and $M_{\text{dry}}$ is the weight of wet and dry membranes, respectively.

### 3.3.5.3. Swelling ratio (SR)

A cut piece from each membrane, having dimensions of $2 \times 2 \text{ cm}^2$, was first dried at $80^\circ \text{C}$ under vacuum. Their thicknesses were then measured by a thickness gauge, and they were subsequently immersed into beakers containing DI water for proper dousing. After leaving undisturbed for 24 h, respective cut pieces of each sample were taken out, and their thicknesses were once again measured in order to determine their swelling extent. Respective swelling ratios of the prepared membranes were calculated from the following equation (3.3):

$$\text{Swelling ratio (\%)} = \frac{(T_{\text{wet}} - T_{\text{dry}}) \times 100}{T_{\text{dry}}} \quad \cdots 3.3$$

where $T_{\text{wet}}$ represents the respective thicknesses of wet membranes soaked in DI water for 24 h, and $T_{\text{dry}}$ is the respective thicknesses of dry membranes.

### 3.3.6. Degree of crosslinking

A conventional solvent extraction method was utilized for the determination of degree of crosslinking. A cut piece of each membrane sample was properly wrapped by a filter paper and immersed into the beaker containing DMF (solvent) at $60^\circ\text{C}$ for 12 hours. The gel (crosslinked part of membrane), which remained undissolved during the whole process, was dried and weighed. The gel fraction of the membranes (used to determine the degree of cross-linking) was calculated from equation (3.4):

$$W_{\text{gel}} (\%) = \left( \frac{W_1}{W_0} \right) \times 100 \quad \cdots 3.4$$
where, \( W_0 \) is the original weight of the dried membrane, and \( W_1 \) is the weight of the membrane after solvent extraction.

### 3.3.6.1. Oxidative Stability

The oxidative stabilities of the prepared membranes were determined by measuring the changes those occurred in their respective weights upon exposure to \( \text{H}_2\text{O}_2 \) and temperature for a given time [43]. In brief, a cut piece of size 3×3cm\(^2\) of each membrane was immersed in a 3wt% aqueous solution of \( \text{H}_2\text{O}_2 \) at a temperature of 25ºC. After every 24 h, the samples were taken out, quickly wiped with a tissue paper to remove the excessive surface liquid, and were weighed immediately using an electronic balance. The reduction that occurred in the weight of each sample was used as a measure to evaluate its oxidative stability.

### 3.3.6.2. Ion-Exchange Capacity

A cut piece of each membrane was soaked for 24 hours in a large volume of 1M \( \text{H}_2\text{SO}_4 \) solution. Furthermore, the respective membranes were washed repeatedly with DI water and finally transferred in 50mL of 1M NaCl solution, heated to 40ºC, and equilibrated for at least 24 hours. The remaining solution was then titrated with 0.01N NaOH solution, using phenolphthalein as the indicator. The IEC value (in milliequivalents/gram abbreviated as meqg-1) was calculated using the following equation (3.5):

\[
\text{IEC} = \frac{(V_{\text{NaOH}})(S_{\text{NaOH}})}{W_{\text{dry}}} \quad \ldots 3.5
\]

Where, \( V_{\text{NaOH}} \) is the volume (in mL) of NaOH used in the titration, \( W_{\text{dry}} \) is the dry weight of the membrane (in g), and \( S_{\text{NaOH}} \) is the strength (in N = meqM\(^{-1}\)) of NaOH used for the determination of IEC.

### 3.3.6.3. Proton Conductivity

Proton conductivity was measured by ac impedance spectroscopic technique, employing a potentiostat (Gamry potentiostat-600). Frequency range employed was 0.01 Hz to 10,000 Hz. A schematic illustration of the setup used for analyzing the proton conductivities of the membranes has been illustrated in Fig. 3.6.
Fig. 3.6. A schematic illustration of the setup employed for the proton conductivity test.

Before the test, the membranes were activated in 1 M H$_2$SO$_4$ solution for 24 h. The conductivities of all the prepared samples ($\sigma$) were measured in the transverse direction at 20° C and under 70% relative humidity, and were calculated from the following equation (3.6):

$$\sigma = \frac{T}{R.A}$$  \[3.6\]

Where, $T$ is the thickness of the sample, $A$ is the surface area of the sample, $R$ is the resistance (derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Real (Z) axis).

3.3.6.4. Methanol Permeability

Methanol crossover tests were conducted in a glass diffusion cell at 20°C. The cell was divided in two equal sized glass cylinders. Part-A was filled with the fuel (2 M methanol), while Part-B was filled with DI water, both having equal volume. The membrane, having an area of 15.2 cm$^2$, was placed vertically between the two cylinders. A schematic illustration of the employed setup has been illustrated in Fig. 3.7. After an equal time duration (i.e. every 30 min), the crossover methanol (from Part-A to Part-B)
was collected from Part-B and mixed with an equal volume of a chromogenic reagent, known as “SNP” (prepared by mixing 5g of sodium nitroprusside in 50 mL water, 5 g of potassium ferrocyanide in 50 mL water, and 2.5 g of NaOH in 50 mL water at a temperature of 4° C), and was examined by UV-vis spectroscopic technique, employing an Optizen UV-vis spectrophotometer [24,44]. The methanol permeability was calculated by using the equation (3.7), as mentioned below:

\[ j_A = \frac{V_B \cdot dC_B}{dt} = A \cdot D \cdot K \cdot (C_A - C_B)/l \] …3.7

where, \( j_A \) is the flux of methanol from Part-A to Part-B; \( V_B \) is the volume of the reservoir B; \( C_B \) and \( C_A \) are the methanol concentration in the reservoirs B and A, respectively; \( dC_B \) is the change in methanol concentration occurring at reservoir B; \( dt \) is the time interval between two successive readings; \( A \) is the membrane area; \( D \) is the methanol diffusivity (which was assumed to be constant inside the membrane); \( K \) is the partition coefficient (constant); \( D \cdot K \) is the membrane permeability; and \( l \) is the thickness of the membrane.

3.3.6.5. Membrane Selectivity Ratios

Applicability of a membrane as a PEM in DMFCs could be better gauged by its membrane selectivity and relative selectivity ratios, which were determined by the following equations (3.8):

Membrane selectivity = Proton conductivity/Methanol permeability … 3.8
3.3.7. Fabrication of Membrane Electrode Assembly and DMFC test

3.3.7.1. Fabrication of Membrane Electrode Assembly

60 wt% of Pt/Ru and 40 wt% of C (30:30:40) mixture was used as the anode and 60 wt% of Pt and 40 wt% of C (60:40) mixture was used as the cathode. The catalyst mixtures were magnetically stirred with isopropanol and ion exchange resin (5 wt% Nafion solutions), followed by sonication for a period of 30 min separately until a fine ink of catalyst mixture was obtained. The obtained ink was then carefully deposited onto the surface of carbon paper by employing a simple painting technique. A total of 4 mg cm\(^{-2}\) of the respective metal catalysts was then loaded onto the respective electrodes and baked at 80\(^{\circ}\)C for 12 h. The entire set up was finally hot pressed for 6 min at 135\(^{\circ}\)C, applying a pressure of ~5.9 M Pa (~1.5 T), to get the final MEA [40,80]. A schematic illustration of the different constituents comprising the MEA has been presented in Figure 3.8.

![Figure 3.8. Constituent parts of an MEA: gasket seal (1 and 7), gas diffusion layers (2 and 6), catalyst layers (3 and 5), and polymer electrolyte membrane (4).](image)

3.3.7.2. DMFC Test

For analyzing the DMFC performance, the stack was loaded and well connected with an automated DMFC test station (K-PAS electronic India Ltd). The cell was allowed to operate for 2 hours to achieve performance equilibration. Fuel samples were pumped at the anode side, while at cathode, air/oxygen was supplied. A DC programmable load bank (K-PAS electronic India Ltd) attached with DMFC test Station was used to measure the current and power output of the cell. The cell efficiency was calculated from the power density output data.