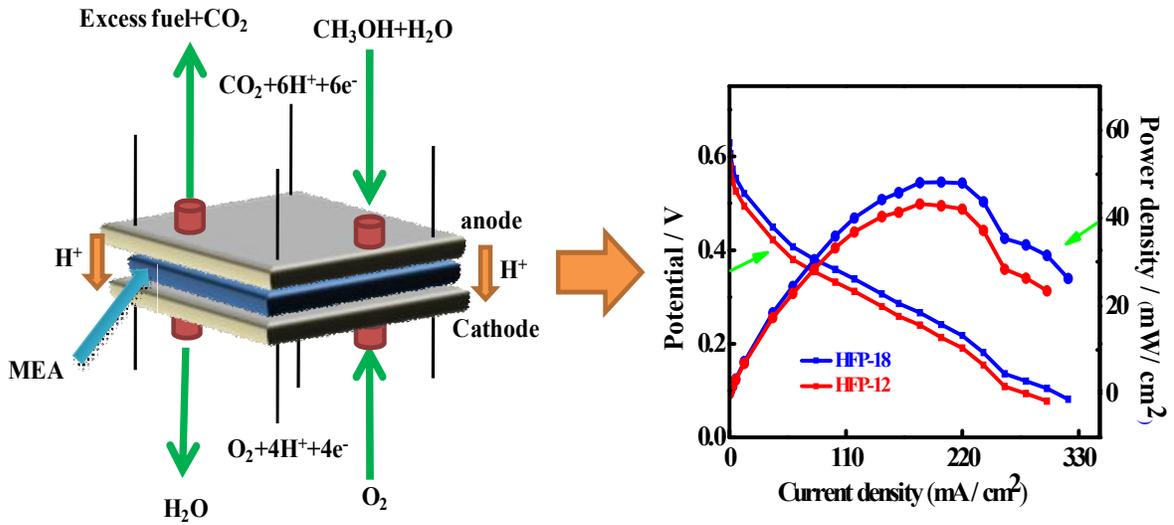


Chapter 3

Functionalized poly (vinylidene fluoride-co-hexafluoro propylene) membrane for fuel cell



3.1 Introduction:

The real problem of the twenty first century are the energy resources as the conventional resources of the energy such as coal, natural gas and petroleum are exhausting very fast. Conventional energy resources also increase the environmental pollution resulting in global warming which affects the animal life including humans.[115]–[118] To solve these energy problems, but huge need, much efforts are required to move towards non-conventional energy sources and stationary portable power sources like solar cell, wind energy, redox flow battery, fuel cell etc.[119]–[121]. In this context, the polymer electrolyte membrane fuel cells (PEMFC's) plays an important role in the future energy demand as it provides the clean energy, environmental friendly, and efficient power source [8][106][122]. Although polymeric membrane has many other applications such as filtrations techniques, ultrafiltration, microfiltration, nanofiltration, reverse osmosis, adhesive, water distillation by electro-dialysis (ED), production of salt from seawater, radionuclide's transporter and proton exchange membrane[123]–[126]. Amongst them, proton exchange membrane is one of the major applications which is useful in fuel cell technology as an electrolyte cum separator and allow proton to pass through the membrane [98][127][128].The membrane for PEMFC should have the desired properties like high ionic conductivity, low fuel permeability, thermally and mechanically stable in operating conditions, low cost, sufficient water uptake for humidity of membrane and better fuel cell performance[129]–[131]. Nafion 117 membrane is widely used for different purpose but has many disadvantages such as fuel crossover, low operating temperature and cost of the membrane [132]. In the present scenario, several scientists have explored the advanced functionalized membranes to replace the Nafion using several technologies such as graft

copolymerization, direct functionalization, high energy swift heavy ions bombardment followed by functionalization, block copolymerization methods etc. [5][133][134]. Now, significant progress has been made to achieve challenges and worldwide use of the target materials in PEMFC, mainly in portable power generation including automobiles industry[135]. The polymer membrane in PEMFC technology use functionalized membranes with different functionalities such as sulphonate group, phosphates group, chloride, nitrite, quaternary ammonium salt, quaternary phosphonium salt etc. to achieve high ionic conductance of membrane[136][137].

Fluoropolymers like poly(vinylidene fluoride) (PVDF) and its copolymers are nonreactive, insulating, mechanically tough, thermally and electrochemically stable. Fluoropolymers are the most encouraging polymer as compared to Nafion117 for fuel cell membrane application [138][139]. Fluoropolymer (PVDF) and its copolymers exist in a semi-crystalline form with crystallinity varying from 35 to >70 %, depending upon the preparation method. These crystalline forms of the polymer involve lamellar and spherulitic morphology [140]. Unique molecular configurations in comparison to other known synthetic polymers, they exhibit a complex crystalline polymorphism. Due to this polymorphism properties, they show five crystalline phases such as α , β , γ , δ and ϵ phases possessing different molecular conformations[141][142]. Out of the five phases mentioned above, the α -phase is the most common non-polar phase and the β - and γ -phases are the polar piezoelectric phases. The α -phase exists in $TGT\bar{G}$ (Trans-gauche-trans-gauche) conformation and it is thermodynamically stable while the β -phase exists in TTTT (all trans) conformation and is thermodynamically meta-stable phase[139][143]–[145].

Amongst them, the electro active β/γ -phase are responsible for the different application of polymers such as sensors, actuators and electrochemical systems[80][146].

In this work, main aim is to prepare fuel cell membrane with low cost, high ionic conductivity with lower fuel crossover membrane through direct sulphonation of poly (vinylidene fluoride-co-hexafluoro propylene) (PVDF-co-HFP) polymer. Non-conducting polymer like PVDF is functionalized with chlorosulphonic acid to prepare ionomer in the main chain for fuel cell applications. The evidence of sulphonation and its extent are understood from various spectroscopic techniques. Thermal and mechanical stability have been measured to obtain the suitability of the membrane. Electrical and water uptake have been measured to get the appropriateness of the membrane for fuel cell. Molecular level phenomena along with structural details have been revealed. Efficiency of the membrane has been worked out by making stacks of membrane electrode assembly and found to be a good option for fuel cell application.

3.2 Experimental

3.2.1 Materials: Granules of poly (vinylidene fluoride-co-hexafluoro propylene) (PVDF-co-HFP) abbreviated as HFP. Membrane preparation through the compression molding by melt extruder method as discussed in **Chapter 2**.

3.2.2 Functionalization of the membrane: HFP membrane was functionalized using 98% chlorosulphonic acid at different temperature and predetermined time. Finally, an optimized condition of functionalization was chosen so that mechanically stable polymer membrane was produced after the functionalization. The membranes change colorless to light brown to deep brown during the functionalization of the membrane followed by

immersion in deionized water, until the residual water pH becomes 7 and adsorbed water on the membrane was shocked using tissue paper. Then functionalized membrane was dried under the reduced pressure at 70 °C for 20 hours. The sulphonation of membrane was done using two different temperatures of 65 and 75 °C for a fixed time period of 45 min. Hence forth, functionalized species will be termed as HFP-12, and HFP-18. The numbers after HFP indicate the degree of sulfonation. Small pieces of membrane were mixed and make uniform thickness of ~80µm of 4×4 cm² size using compression molding machine (S.D. Instruments, Kolkata, India) at 180°C under the 2.5 ton of pressure for fuel cell efficiency measurements. Details of the experimental technique used of the functionalized membrane were discussed in the **Chapter 2**.

3.3 Results and discussion

3.3.1 Ionomer preparation:

HFP copolymer has been sulphonated with varying degree of functionalization using chlorosulphonic acid. The evidence and degree of sulphonation has been confirmed through ¹H-NMR shown in **Figure 3.1a**. Pure HFP shows two characteristic peaks at $\delta = 2.08$ ppm due to tail to tail (T-T) and $\delta = 2.88$ ppm, head to tail (H-T), conformation attached with polymer backbone and are designated as ‘a’ and ‘b’, respectively [147]. Two new peaks (characteristics peak) designated as ‘c’ and ‘d’ have appeared at the peak position $\delta = 8.2$ and 6.4 ppm, respectively[98]. The intensity of two new peaks has increased with increasing temperature of sulphonation, for a fixed time, suggesting greater sulphonation at higher temperature. The degree of sulphonation (DS) is calculated using the ratio of peak area (c + d) (X) and the sum of peak areas of a, b, c and d (Y) using **Eqⁿ**.

(1) which are found to be the values of 12 and 18% and are designated as HFP-12 and HFP-18 for low and high temperature of sulphonation, respectively. NMR measurements clearly indicate that greater sulphonation occurs at higher temperature. This is to mention that functionalization (sulphonation) occurs in both C-H and C-F linkages of the polymer chain and the ratio of the integral peak area of d/b are 0.15 and 0.25, while the ratio of the integral peak area of c/b are 0.030 and 0.034 for HFP-12 and HFP-18, respectively. It appears that most of the sulphonation occur in C-F linkages as compared to C-H linkages and the peak ratio continuously increases with increasing the sulphonation temperature [98]. To understand the functionalization and structural change in the polymer chain, FTIR studies have been performed which show new and characteristic peaks at 1021 cm^{-1} presumably due to S=O stretching vibration arising from the attachment of sulphonate groups in the main chain after functionalization (**Figure 3.1b**). Further, a broad peak has been observed at 3345 cm^{-1} after sulphonation which is due to -OH stretching vibration [37]. The intensities of the above peaks increase with the extent of sulphonation. PVDF and its copolymers such as P(VDF-co-HFP) (HFP), P(VDF-co-CTFE) and P(VDF-co-TrFE) mostly crystallize in α form as evident from the FTIR peaks at 759 and 794 cm^{-1} stretching frequency [149][150][151]. On the other hand, a new peak at 840 cm^{-1} in functionalized HFP indicates the presence of electroactive β/γ phase after the sulphonation. Further, a band at 1234 cm^{-1} clearly suggests the formation of γ -polymorph exclusively after functionalization. [152]–[154].

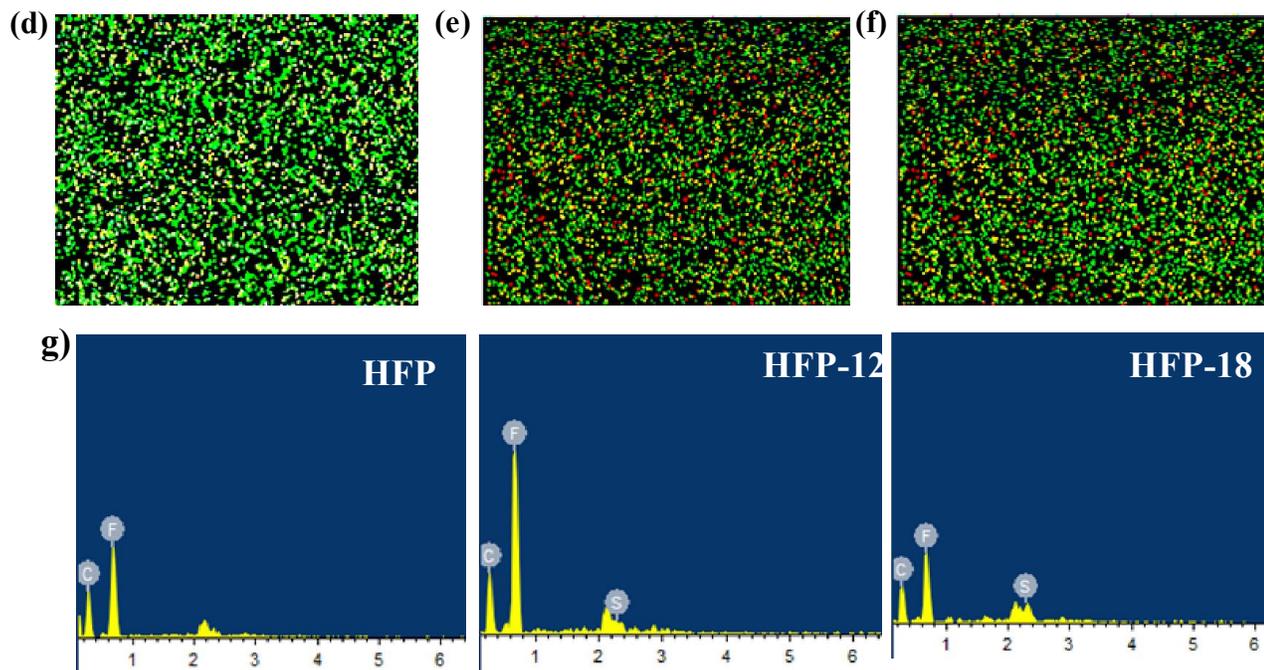
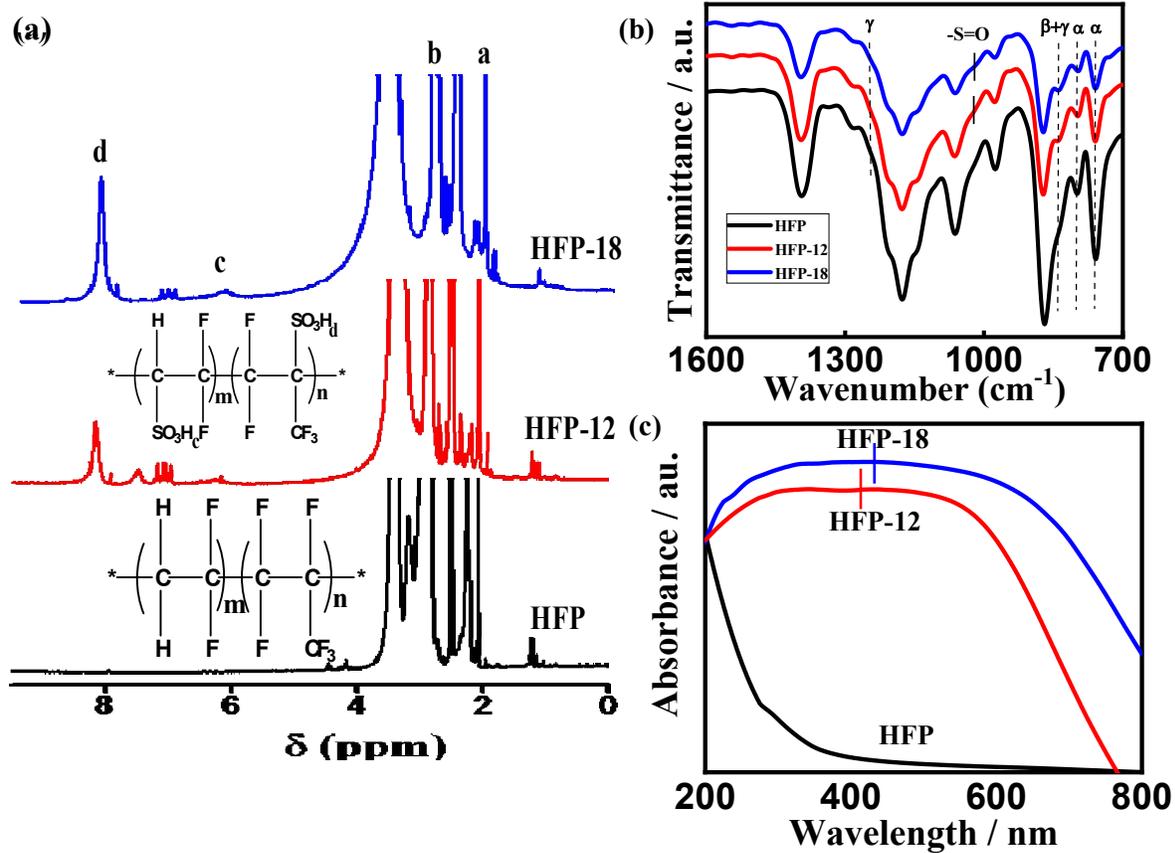


Figure 3.1: (a) ^1H NMR spectra of HFP and sulfonated membranes with the assignment of their characteristic peaks position; (b) FTIR spectra of pure HFP and its functionalized membranes and indicate the extra peak arises after the sulphonation using vertical lines; (c) UV-visible absorption spectra of the HFP, HFP-12 and HFP-18 indicating the peak position; and (d-f) are overlay EDS mapping of the HFP, HFP-12, and HFP-18, respectively (from left to right), the red spot indicate the position of sulphur atom; (g) EDX spectra of the HFP, HFP-12 and HFP-18 are respectively.

Figure 3.1c shows the UV-visible spectra of pure HFP and its ionomer in their thin film. Pure HFP does not exhibit any peak while a strong and broad absorption band is observed at 414 and 434 nm in HFP-12 and HFP-18, respectively, after the sulphonation mainly due to $n \rightarrow \pi^*$ transition of the sulphonate group present in functionalized membrane [98][155] [156]. A considerable red shift along with broader band in HFP-18 as compared to HFP-12 is due to greater number of sulphonate groups present in the polymer chain. Energy dispersive X-ray spectroscopy (EDS) has been used for elemental mapping before and after the functionalization to understand the presence of new element after sulphonation and are presented in **Figure 3.1d-f**. Overlay image of the polymer before sulphonation (pristine HFP) indicates the presence of two elements namely carbon and fluorine as yellow and green colour dots, respectively, while red colour dots appear in the specimens after sulphonation clearly signifies the presence of sulphur atom. EDX spectra are shown in **Figure 3.1g**. All the above discussions confirm the presence of sulphonate group present in the polymer chain. However, NMR, FTIR, UV-vis and EDS studies indicate the sulphonation in the main chain and the extent of sulphonation increases considerably at higher temperature.

3.2.2 Structure and morphological changes due to functionalization:

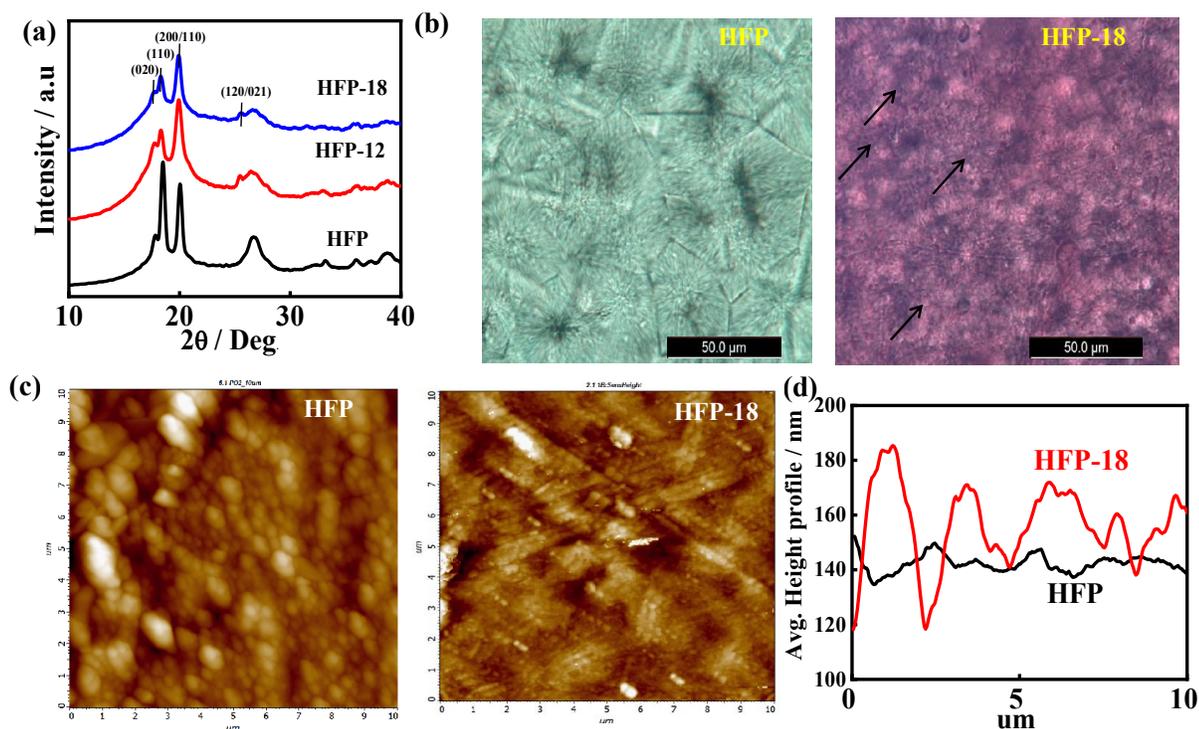


Figure 3.2: (a) XRD spectra of HFP, HFP-12 and HFP-18 indicating the crystalline planes; (b) polarizing optical images of spherulitic morphology of HFP and HFP-18 membrane indicating the position γ -spherulite by arrows; (c) AFM images for surface morphology of HFP and HFP-18; (d) average height profile of HFP and HFP-18 membranes.

The structural investigation of the HFP membrane before and after sulphonation is carried out using XRD and is presented in **Figure 3.2a**. The XRD pattern of pristine HFP is very similar to PVDF and shows the characteristic peaks corresponding to the α -phase at 17.6° (020), 18.3° (110) and 19.9° (111). In contrast, another peak at $2\theta = 25.5^\circ$ (120/021) is evident in sulphonated species indicating the presence of γ -phase in addition to the α -phase peak as mentioned in pure HFP. The nucleation of piezoelectric γ -phase in the presence of hydrophilic sulphonate group is presumably due to suitable interaction with the polymer

chain and sulphonate group [157][158][159]. The polarizing microscope image (POM) of pristine HFP shows crystalline α -phase with fibrillar and spherulitic morphology while disordered α - and γ -phase morphology is evident in sulphonated specimens (**Figure 3.2b**). **Figure 3.2c** shows the surface morphology (AFM images) indicating rough surface in sulphonated sample than that of pristine HFP. Average height profile compares the relative surface roughness and exhibit 120-250 nm in HFP-18 against 90-130 nm roughness observed in pristine HFP (**Figure 3.2d**).

3.3.3 Thermal, mechanical and electrical properties:

Thermogravimetric analysis (TGA) is used for to measure the thermal stability of the membrane from the weight loss vs. temperature curve as shown in **Figure 3.3a**. Pure HFP degrades at 430°C (temperature corresponds to 5 wt.% weight loss) and show sharp degradation while the degradation temperature decrease ~ 210 °C after sulphonation and gradually decrease with increasing the sulphonation temperature as well as reaction time. Sulphonated membranes show two steps degradation pattern; first step at 195 °C which indicate the degradation of $-\text{SO}_3\text{H}$ group and the second step at 290 °C specifying the degradation of polymer main chain [151]. The melting behaviour and heat of fusion of sulphonated polymer are investigated using differential scanning calorimetry (DSC) and is shown in **Figure 3.3b**. The melting point of sulphonated membrane gradually decreases to 160 °C as compared to pristine HFP melting at 178.1 °C presumably due to disordered crystalline structure and greater interaction in ionomer systems as discussed earlier [49].

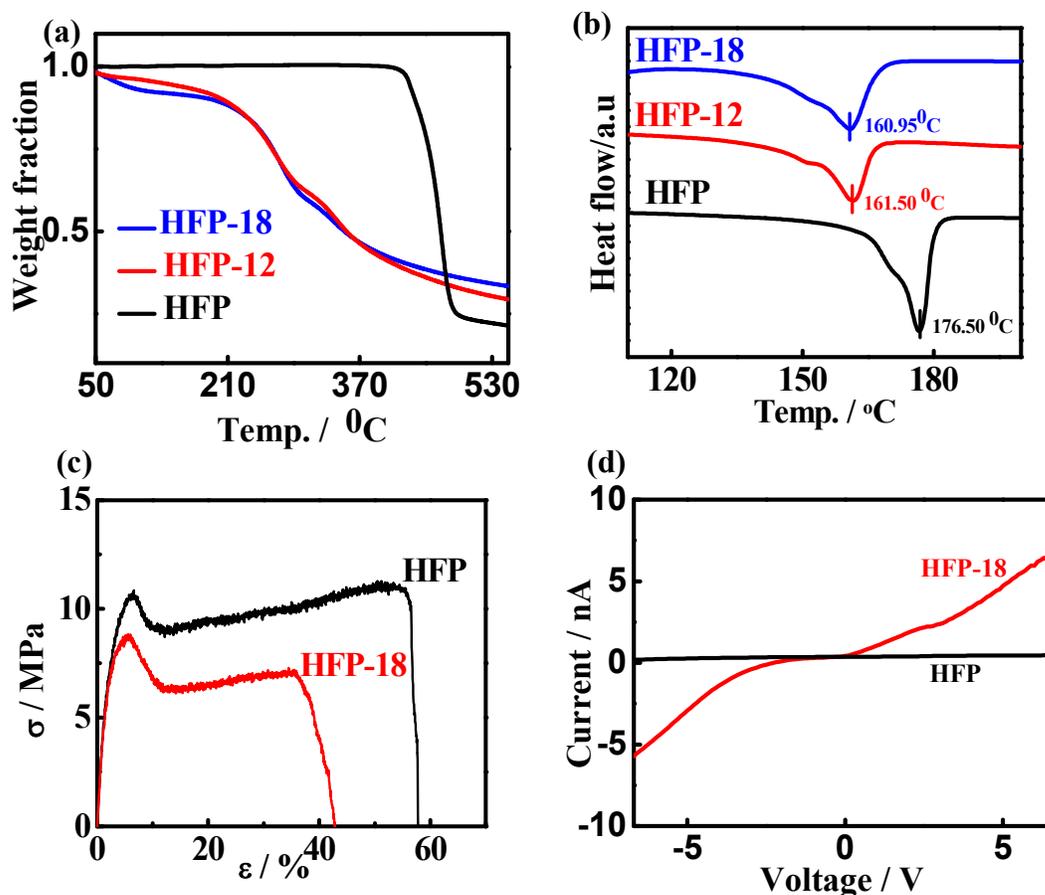


Figure 3.3: (a) Thermo-gravimetric analysis (TGA) of pristine HFP and functionalized HFP-12, and HFP-18 membranes; (b) differential scanning calorimetric (DSC) thermogrammes of HFP, HFP-12, and HFP-18 for the determination of melting point; (c) stress-strain curves of pristine HFP and functionalized HFP-18 membrane showing their relative ductility and mechanical strength; and (d) I-V characteristics of HFP and HFP-18 membrane.

An ideal proton exchange membrane for fuel cell application should be sufficiently mechanically stable and free standing film. The toughness and stiffness of the functionalized membrane are done using universal testing machine at a constant stretching

rate. The stress-strain curve is shown in **Figure 3.3c** exhibiting considerably high elongation at break both in pristine HFP as well as sulphonated specimens. Toughness value is measured from the area under the strain-stress curve of the membrane are 5.35 and 2.67 MJ/m³ for pure HFP and HFP-18, respectively. Slight less toughness in sulphonated specimen arises from its rough surface but the value is sufficient for membrane application and has good flexibility. Elastic moduli, calculated from the initial linear region, are 425 and 414 MPa for pure HFP and HFP-18 membrane, respectively. Electrical conductivity of sulphonated membrane is measured from surface contact method using AFM. Sulphonated polymer shows the I-V characteristics in a range of semi-conducting range against the insulating behaviour of the pristine polymer (**Figure 3.3d**). The higher conductivity in sulphonated membrane is due to the presence of sulphonate ion in the main chain.

3.3.4 Proton conductivity and methanol permeability of functionalized membrane:

Besides the above properties like thermal, electrical and mechanical stability, proton conductivity and methanol permeability are the other important properties in order to be using it as fuel cell membrane. Higher the proton exchange capacity and lower the fuel permeability of membrane, greater will be fuel cell performance. The open circuit voltage drops considerably when fuel passes through the membrane continuously resulting reduced power as well as current density. Proton conductivity as a function of temperature and methanol permeability of the functionalized membranes (HFP-12 and HFP-18) is shown in **Figure 3.4a** and **Table 3.1**, respectively.

Table 3.1: Comparison of proton conductivity (K^m), methanol permeability (P), Activation Energy (E_a) and selectivity parameter (SP) of HFP-12 and HFP-18 with the standard Nafion117 membrane at 25°C and 50% water-methanol mixture.

Membrane	$K^m(\times 10^{-2} \text{ S.cm}^{-1})$	$P(\times 10^{-7} \text{ cm}^2.\text{s}^{-1})$	$E_a \text{ (kJ mol}^{-1}\text{)}$	$SP(\times 10^5) \text{ S.cm}^{-3}.\text{s}$
HFP-12	3.46	4.43	7.13	0.78
HFP-18	3.70	4.61	6.56	0.81
Nafion117	9.56	13.10	6.52	0.72

Amongst the functionalized membranes, higher sulphonated membrane (HFP-18) shows better proton conductivity values in the whole range of temperature studied. Higher value of $3.70 \times 10^{-2} \text{ S.cm}^{-1}$ conductivity is reported for HFP-18 against the value of $3.46 \times 10^{-2} \text{ S.cm}^{-1}$ for HFP-12 mainly due greater sulphonation or ions present in HFP-18 vis-a-vis HFP-12. This is to mention that these conductivities values are slightly less than the commercial membrane like Nafion ($9.5 \times 10^{-2} \text{ S.cm}^{-1}$) [97]. However, the water uptake of sulphonating membrane shows the greater hydrophilicity of the functionalized membrane as compared to pristine HFP. HFP-18 exhibit higher water uptake of 12% against meager value of pristine HFP mainly due to ionomer present in the main chain (**Figure 3.4b**). The value of the percentage water uptake and proton conductivity increases with increasing the extent of sulphonation indicating better membrane having higher degree of sulphonation. Hence, higher sulphonate groups are more favorable both for water uptake and proton conductivities. However, the slope of the conductivity vs. temperature ($1000/T$) curve indicates the activation energy to understand the stability of membrane at high temperature.

Activation energy is the minimum energy required for proton transport phenomena across the membrane, which decrease in HFP-18 (6.56 kJ mol^{-1}) as compared to HFP-12 (7.13 kJ mol^{-1}). The activation energy value is slightly higher than Nafion 117 (6.52 kJ mol^{-1}), [97]. Further, the activation energy values also explain the thermal stability of sulphonated membrane at higher temperature predicting greater performance at higher temperature. Ionomer (sulphonate; $-\text{SO}_3\text{H}$ group) is responsible for the proton transport across the membrane.

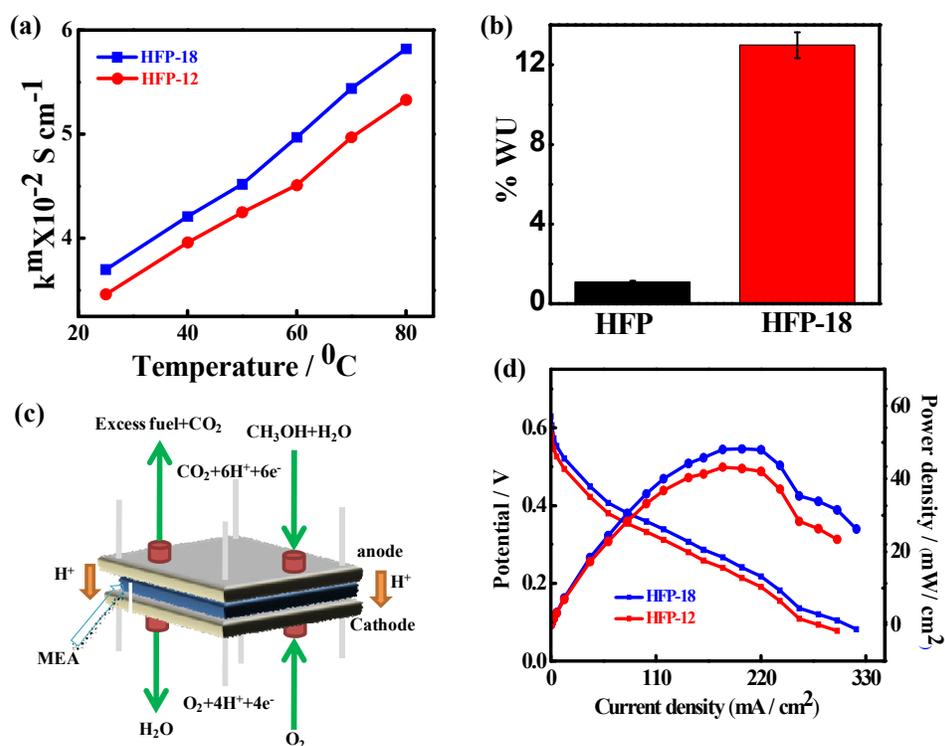


Figure 3.4:(a) Proton conductivity of HFP-12 and HFP-18 membranes as a function of temperature; (b) water uptake of sulphonated membrane (HFP-18) comparing the value of pristine HFP; (c) stacking pattern of fuel cell assembly; and (d) direct methanol fuel cell performance of HFP-18 and HFP-12 showing potential and power density as a function of current density

Methanol permeability studies are performed in a quartz cell, separated by the functionalized membrane. One side of the membrane is filled with 50% methanol-water mixture and another side of membrane is filled with deionized distilled water. Methanol permeability generally occurs through the membrane and the methanol fuel transport to the other side of the membrane whose concentration is measured using reflective index of that solution and ultimately calculates the permeability value using the equation (7). [98] The methanol permeability of functionalized membrane is measured and compared with the commercially available membrane Nafion117 in the similar condition which is presented in **Table 3.1**. The permeability value of HFP-18 and HFP-12 are 4.61×10^{-7} and $4.43 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively, and are lower than Nafion 117 ($13.10 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) [2], [156]. The lower methanol permeability of HFP sulfonated polymer is due to the compact microstructure and crystallinity of the copolymer. The combination of methanol permeability and proton conductivity describe the efficiency of the membrane in terms of the selective parameter (SP) which is the ratio of proton conductivity and methanol permeability (k^m/P). The selectivity parameter values are 0.81×10^5 and $0.78 \times 10^5 \text{ S.cm}^{-3} \cdot \text{s}$ for HFP-18 and HFP-12 functionalized membrane, respectively, (**Table 3.1**) and indicate that the functionalized membranes are better for fuel cell as electrolyte membrane.

3.3.5 Fuel cell efficiency using functionalized membrane:

Water uptake, degree of sulphonation and the selective parameter of the functionalized membrane implies that they are appropriate for its use in fuel cell especially in direct methanol fuel cell (DMFC). The direct methanol fuel cell performance is measured in a single cell membrane electrode assembly as shown in **Figure 3.4c**. Polarization curve (voltage vs. current density) along with power density has been shown

in **Figure 3.4d**. The open circuit voltage are found to be 0.63 and 0.60 V for HFP-18 and HFP-12 functionalized membrane, respectively, while the commercially available Nafion 117 membrane exhibit 0.73 V under similar condition. Further, the power density as a function of current density display the maximum power density values of 48.34 and 42.98 mWcm^{-2} for HFP-18 and HFP-12, respectively, at a current density of 190.22 mA cm^{-2} which is slightly lower than Nafion 117 membrane (51.2 mW cm^{-2}). [98][8][97] The higher performance of the HFP-18 membrane along with high OCV indicate higher conduction of ions through the membrane (anode to cathode side) and is due to the greater extent of sulphonation which leads to better performance of the cell assembly.

3.4 Conclusion:

Poly(vinylidene fluoride-co-hexafluoro propylene) has been functionalized for its use as membrane in fuel cell. The sulphonation of HFP membrane is carried out in an optimum condition (after optimizing temperature and time of functionalization) to maintain the stiffness and toughness of the membrane for fuel cell application. The evidence and extent of sulphonation is confirmed from NMR studies followed by endorsement through FTIR and UV-vis measurement. EDS mapping of samples before and after functionalization also corroborate the incorporation of sulphur element after functionalization. However, XRD studies indicate the nucleation of piezoelectric γ -phase after functionalization which is also supported from the optical images and FTIR measurement. Electrical conductivity of the functionalized membrane has increased up to semiconducting range against the insulating nature of pristine polymer. The proton conductivity of the functionalized membrane has increased significantly due to functionalization while the methanol permeability reduced considerably than that of

standard Nafion117 which lead to almost similar value of the selective parameter (0.81×10^5 S.cm⁻³.s for HFP-18) as compared to standard Nafion 117 membrane (0.72×10^5 S.cm⁻³.s). Higher water uptake of the functionalized membrane also supports the higher proton conductivity of the functionalized membrane vis-à-vis pristine HFP. The membrane electrode assembly (MEA) is prepared using optimally functionalized membrane and cell performance at high temperature exhibit open circuit voltage of 0.63 V leading to power density of 48.34 mW/cm².