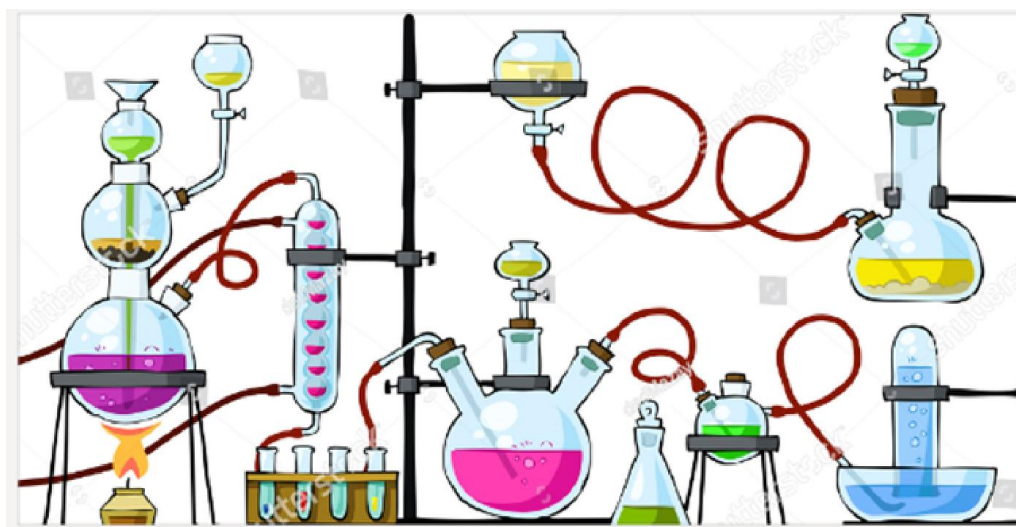


## Chapter 2

# Materials, Experiments and Characterization





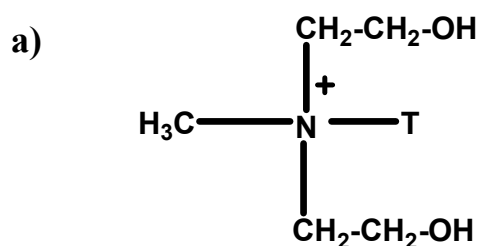
## 2.1 Materials

### 2.1.1 Polymers:

A commercial poly (vinylidene fluoride) (*PVDF*) (SOLEF 6008; Ausimont, Italy) with PDI ~2.1 commercial product without any additive with molecular weight  $1.45 \times 10^5 \text{ gmole}^{-1}$ , with a melt flow index of 24 g/10 min at  $230^\circ\text{C}$  under a 5 kg load, and that's copolymer SOLEF 11008 (supplied by Ausimont, Italy; the copolymer will be termed as (*HFP*) were used study.

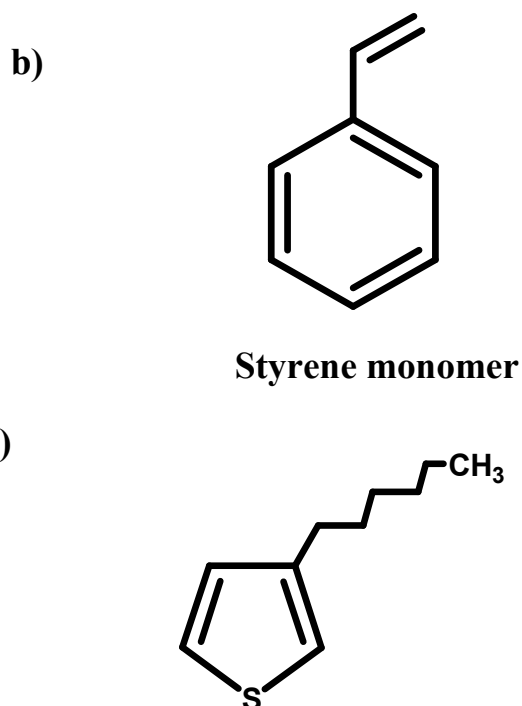
### 2.1.2 Organically modified Nanoclay and monomer solutions:

An organically modified clay, Cloisite 30B [bis (hydroxyethyl) methyl tallow ammonium ion exchanged montmorillonite], Southern clay, U.S., CEC 110 meq/100g, was used as the nanofiller (**Figure 2.1a**). Tallow is a mixture of  $C_{16}$  and  $C_{18}$  long chain alkenes. The monomer styrene (Sigma-Aldrich, 99+ %) (**Figure 2.b**) and 3-hexylthiophene (3HT, Sigma-Aldrich, 99+ %) (**Figure 2.1c**) were used for grafting purpose.



### Methyl tallow bis-2 hydroxyethyl ammonium salt

Where T is tallow (~65%  $C_{18}$ ; ~30%  $C_{16}$ ; ~5%  $C_{14}$ )



**Figure 2.1:** Structure of (a) organic modifier used in 30B; (b) styrene monomer; (c) 3-hexyl thiophene monomer.

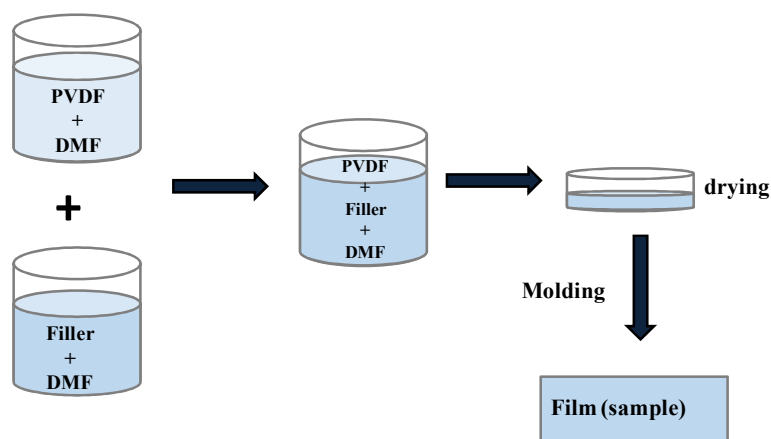
### 2.1.3 Regents and Solvents:

KMnO<sub>4</sub> (Potassium Permanganate) and NaOH (Sodium Hydroxide) LOBA Chemie were used as chemical etchant and potassium metabisulphite (K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) (Sigma-Aldrich, 99+%) was used for removing MnO<sub>2</sub> green color solution on the membrane surface. chlorosulphonic acid (HSO<sub>3</sub>Cl, LOBA Chemie) with 97% purity used for the Sulphonation. Toluene sigma Aldrich with 97 % purity, HNO<sub>3</sub> (LOBA Chemie) with 69% purity, HCl (Merck) with 37% purity, Oxalic acid Merck and Sulphuric acid used for the electrochemical analysis. EDTA (ethylene diamine tetra acetic acid) purchase from Merck.

## 2.2 Experiments

### 2.2.1 Preparation of pristine membrane and Nanohybrid:

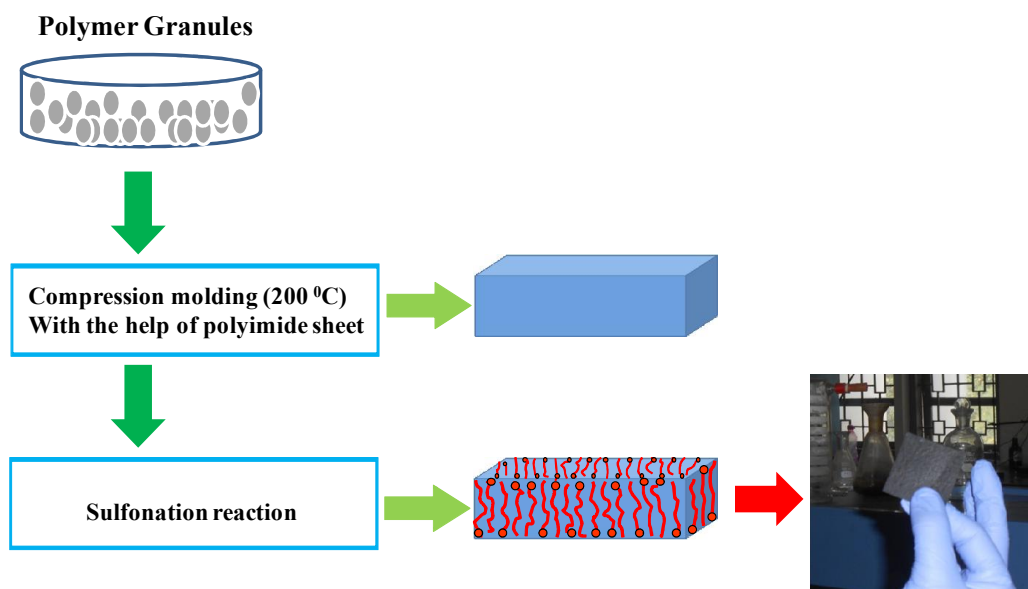
The nanocomposites referred as nanohybrid was prepared by way of solution medium by dissolving known amount of the pristine PVDF (spherical granules) in DMF solvent in a 100 mL beaker followed by high rpm magnetic stirring at 65<sup>0</sup>C and predetermined (4 wt. % with respect to polymer weight) of nanofiller 30B organically modified nanoclay was proper dispersed in another beaker with the help of the probe sonicator. Now these two solutions was mixed followed by stirring at high speed magnetic stirrer to avoid the nanoclay settling for 2 hour at 65<sup>0</sup>C, subsequently solvents were dehydrated immediately using magnetic hot plate followed by drying in vacuum oven. From now on, the *PVDF* nanohybrid will be labeled as “*NH*” having 4 wt. % of nanoclay in the Pristine PVDF. Now prepared the size 4×4 cm<sup>2</sup>, thin polymeric membrane with various thickness of both pristine PVDF and its nanohybrid (NH) for irradiation experiments and other uses through melt pressed compression molding machine (S.D. Instruments, Kolkata, India), the thickness of the membrane controlled by the aluminum spacer. The schematic of the nanohybrid preparation followed by their membrane fabrication has been shown in **Figure 2.2**.



**Figure 2.2.** Nanohybrid preparation by solution route.

### 2.2.2 Direct Functionalization of the Pristine Polymer:

Polymeric membrane was functionalized using 98 % pure chlorosulphonic acid at different temperature and optimized time for mechanically stable membrane was produced after the functionalization. The colorless pristine membrane change brown color, with increases the extent of the sulphonation the brown to deep brown / black color membrane achieved in the schematic of the chemical reaction shown in **Figure 2.3**.



**Figure 2.3:** Schematic of the direct Functionalization.

The functionalized membrane were cleaned using the double distilled water until the residual water had a pH  $\sim 7$  and absorbed remaining water using the filter paper. After that the proper washing of the membrane, dried it at  $70^{\circ}\text{C}$  under the vacuum oven (reduced pressure). From the surface to bulk properties the membrane cut into small pieces and mold with the help of the compression molding (S.D instruments Kolkata) and make  $4 \times 4 \text{ cm}^2$  membrane for the proton exchange membrane.

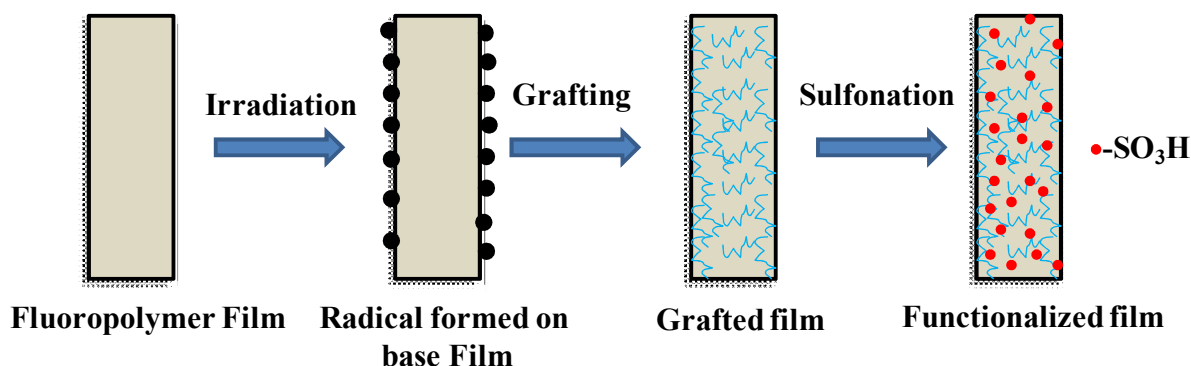
### 2.2.3 Fabrication of the Nanochannel via the Particle radiation swift Heavy ions:

The neat polymer and its nanohybrid (NH) films of varying thickness (20-100  $\mu\text{m}$ ) were irradiated by various ions and fluences, like  $\text{Ag}^+$  and  $\text{Si}^+$  ion with fluences (ions per unit area) were used  $1 \times 10^6, 1 \times 10^7, 5 \times 10^7$ , ions/ $\text{cm}^2$  to ensure the effect of fluence and ions on membrane properties. The irradiation experiment was carried out in General Purpose Scattering Chamber (GPSC) in inter university accelerator center (IUAC) New Delhi, India. The scattering experiment performs under the low pressure  $\sim 10^{-6}$  mbar and ions scattered through the thin gold foil  $\sim 250 \mu\text{g}/\text{cm}^2$  thickness and similar experiment also carried out for the  $\text{Li}^+$  with variation of the Fluences. To ensure the formation of the through channel were chosen thickness of the polymer films and energy such a way where kinetic energy of the ions is greater than the thickness of the films so refusal of ions implant in the films. The energy and projectile length calculation perform with the help of the SRIM 2013 software. The irradiated neat polymer and its nanohybrid films were etched with the help of the selective chemically etchant such as alkaline aqueous solution ( $9 \text{ mol L}^{-1}$  NaOH) and  $0.25 \text{ mol L}^{-1}$   $\text{KMnO}_4$  for 4 h at  $60^\circ\text{C}$ . After the etching process, all the samples developed a brownish precipitate of  $\text{MnO}_2$ . The precipitated etched films were quickly immersed in a  $\text{K}_2\text{S}_2\text{O}_5$  saturated solution for 20 min followed by washing in distilled water. The remaining water at the surface was absorbed with a filter paper and dried at  $60^\circ\text{C}$  for 12 h in an oven under reduced pressure and membrane term as porous membrane for further applications.

### 2.2.4 Functionalization of the nanochannel formed by Swift Heavy ions:

Because of the high energy particle radiation swift heavy ions (SHI) the porous etched membrane having reactive sites free radical on the peripheral and inside of the

nanochannels. Now etched membrane were dipped in non-ionized monomer solution followed by the solvent addition to initiate the grafting process with stirring at optimized time and temperature after that homopolymer other than graft washed in solvent for 3-4 times. Finally, the films were washed with non-solvent and dried at 60 °C overnight under reduced pressure. Ionomer (Sulphonation Electrophilic substitution reaction) has been performed on the grafted pristine and its *NH* membrane were done using chlorosulphonic (HSO<sub>3</sub>Cl) acid at 65 °C for optimized time. For the mechanically stable / free standing functionalized polymer membrane the optimizations of the sulphonation were carried out by changing the temperature and time. Ionomer tag membrane washed with double distilled water in several times and was dried at 60 °C for 24 h under reduced pressure using the vacuum oven. Hereafter, we will term the etched, etched + grafted, and etched+grafted+sulfonated specimens as *-e*, *-g*, and *-g-s* respectively **Figure 2.4**.



**Figure 2.4** Schematic of the Radiation induced grafting.

### 2.3 Characterizations Techniques

Various techniques are used for the characterization of the pristine and functionalized membrane followed by the measurements.



**2.3.1 Field emission scanning electron microscopy (FE-SEM):**

The high resolution images obtained using FE-SEM is used for the morphological investigation of the functionalized and non-functionalized membrane and high resolution images obtained using FE-SEM. In SEM measurements, the accelerated electrons after the interactions with the sample produced a variety of signals, these different kinds of signals provide the different topology, morphology of the specimens and elemental analysis. Secondary electrons (SE) generally carry surface information due to its lower energy ( $\leq 50$  eV) which limits to electron emission from the matrix at only certain depth. The electron beam is generated either thermionic emission or electric field gradient emission. In FE-SEM the electric field gradient is used for accelerating the electrons beam. Generally lanthanum hexaboride ( $\text{LaB}_6$ ) filament is used to generate the electron source. These dispersed electron beams focused to narrow beam with the help of the different magnetic lens in high vacuum. The surface architecture of etched, graft and functionalized thin membrane was examined by using Field emission Scanning Electron Microscopy (FE-SEM), FEI Company of USA (S.E.A.) PTE, LTD after Pd-Au (20:80) alloy coating for 90 Sec. In the present study the EDS attached to FE-SEM was used to ensure the chemical composition of the matrix followed by their elemental mapping.

**2.3.2 Atomic Force Microscopy (AFM):**

The scanning Probe Microscopy (SPM) is imaging technique which does small dimension probe scans of the specimens. The surface topography and surface physical properties are estimated using the probe motion. The technique SPM generally used for the surface properties are examined through probe motion. The SPM includes atomic force microscopes (AFMs) and scanning tunneling microscopes (STMs). In current work, AFMs

were used for the morphology study of the functionalized and pristine membrane. The entire AFM samples were scanned in the semi - contact mode over the sample surface using the NT-MDT, Russia. The silicon nitride tip mounted with the 100  $\mu\text{m}$  long single beam cantilever with 240-255 kHz resonant frequency corresponding to the spring constant 11.5 N/m.

### **2.3.3 Polarizing Optical microscope (POM):**

The bulk surface morphology of the entire specimen were examined using the Polarizing Optical Microscope (POM), Leica and the specimens were crystallized using Mettler hot stage with variation of the time and temperature. The distribution of functionality on the membrane surface was studied using alpha track radiography. The developed alpha tracks were observed under a transmission optical microscope (Olympus fully motorized microscope BX63, attached with a QIMAGING QICAM CCD camera and cell Sens dimension package for image analysis obtained from Olympus, Tokyo, Japan).

### **2.3.4 Ultra-violet visible (UV-vis) spectroscopy:**

Light absorption is used as the tool for the qualitative as well as quantitative estimation of the specimens. In this technique, the specimen exposed the electromagnetic radiation UV-Vis and measures the electronic transitions. UV-visible absorption measurement of pristine and functionalized membrane was recorded using Jasco V-650 spectrometer in the range of the 200-800 nm wavelengths with constant scan rate 200 nm/min.

### **2.3.5 Fourier-transform infrared (FTIR) spectroscopy:**

Fourier-transform infrared (FTIR) spectroscopy is based on the existent of change of dipole moment when electromagnetic infra-radiation exposed on specimens. FTIR spectra were

recorded in ATR mode on the diamond crystal in 600-4000  $\text{cm}^{-1}$ , 100 scan with resolution 4  $\text{cm}^{-1}$  using the Thermo Scientific Nicolet summit FTIR spectrometer.

### 2.3.6 Nuclear Magnetic resonance (NMR):

The Proton ( $^1\text{H}$ )-NMR measurement was performed of the functionalized membrane and pristine polymer in  $d_6$ -DMSO solvent using the Bruker 500 MHz spectrometer at chemical shift range 0-10 ppm. The degree of the sulphonation of the functionalized membrane against the PVDF membrane were calculated from ratio of the integrals peak area using the *Eq. (1)* [98]

$$\text{DS (\%)} = \frac{X}{X+Y} \times 100 \quad (1)$$

Where, X and Y are the integration peak area of the NMR spectra. The X refers the sum of the peak area of the sulphonated proton and Y peak area of the characteristics of polymer chain. Hence, using these integral peak area and degree of the sulphonation is calculated.

### 2.3.7 XRD for structural modifications:

X-ray diffraction spectra were examined using *Cu K $\alpha$*  source with monochromatic wavelength ( $\lambda = 0.154 \text{ nm}$ ) (Rigaku Miniflex) with constant current (15mA) and voltage of the generator. Functionalized as well as pristine thin films were positioned on the grooves of quartz holder at RT and were scanned at diffraction angle ( $2\theta$ ) from  $2^\circ$  to  $40^\circ$  at a scanning rate of  $3^\circ/\text{min}$  to examine the crystalline structure and quantification of the conversion of phase fraction after the dispersion of nano filler and SHI irradiation.

### **2.3.8 Thermogravimetric analysis (TGA):**

Thermogravimetric analysis (TGA) were carried out of the pristine PVDF and functionalized membranes using Mettler–Toledo in the temperature range 40 -600 °C at the heating rate of 20 °/ min under inert environment to find out the thermal stability of functionalized membranes.

### **2.3.9 Differential scanning calorimetry (DSC):**

Differential scanning calorimetry (DSC) measurements were conducted on functionalized samples using a Mettler-Toledo 832 with the automated Star-e evaluation software. The DSC device was calibrated with In/Zn before experiment and the melting temperature ( $T_m$ ) and heat of fusion ( $\Delta H$ ) were measured using Star-e evaluation software. The samples were heated with constant heating rate of 10 °/min under inert environment.

### **2.3.10 Ion exchange capacity of the membranes using radionuclide tracer:**

For the computation of ion exchange capacity (IEC) of the functionalized membrane initially, 100 ml 0.1m CsCl aqueous solution was prepared using double distilled water later than the known activity of the radiotracer of  $^{137}\text{Cs}^+$  spiked for the computation of ion exchange capacity. Two standards were ready by spreading known quantity of prepared solution on  $2 \times 2 \text{ cm}^2$  filter paper. The quantity of  $\text{Cs}^+$  (mmole) per unit weight of the prepared membrane was determined by comparing the activity of  $^{137}\text{Cs}^+$  in the membrane sample with the reference standards having similar shape and size as that of the membrane samples. The activity of  $^{137}\text{Cs}^+$  in the membranes and the reference standards was analyzed using a NaI (TI) based Gamma-ray spectrometer detector.

### 2.3.11 Water uptake (WU):

To determine the percentage water uptake (% WU) of the functionalized membrane against the pristine membrane at room temperature, the functionalized membranes were first dehydrated in vacuum oven at 65 °C for 48 h and took their weight ( $W_{\text{dry}}$ ) immediately followed by deep in double distilled water for 48 h and calculated the weight of wet membrane ( $W_{\text{wet}}$ ) after removing of the extra water on the membrane. Percentage Water uptake (%WU) was determined using the following *Eq. (2)*[19]

$$\text{WU}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (2)$$

### 2.3.12 Mechanical Testing:

The mechanical properties of the functionalized membrane compared against the pristine membrane with the help of Universal Testing Machine (UTM) Instron 3369 at strain rate of 5 mm/min and calculated the toughness (area under the strain –stress curve), modulus (using the slop fitting of stress –strain curve ) and % elongation of the prepared membrane.

## 2.4 Quantification of Radionuclide Waste

### 2.4.1 Sorption studies:

The sorption kinetics of the modified polymeric membranes was analyzed using the known kinetics of a radioactive tracer ( $^{241}\text{Am}^{+3}$ ), spiked in 5ml of nitric acid ( $\text{HNO}_3$ ) solution of pH~2. The % sorption of  $\text{Am}^{+3}$  were calculated as a function of time after placing the functionalized membrane in to the radioactive solution. The total uptake was calculated by placing the functionalized membranes in 10 mL of  $\text{Am}^{+3}$  solutions for 2 hrs. The amount of  $^{241}\text{Am}^{+3}$  in the membrane was quantified using the aqueous samples taken from the

solution before and after equilibration of the membrane. The total uptake of  $\text{Am}^{3+}$  in polymer substrate was obtained from the following equations (3).[25]

$$\% \text{ Uptake efficiency} = \frac{A_i - A_f}{A_i} \times 100 \quad (3)$$

Where,  $A_i$  and  $A_f$  are the initial and final activity of  $^{241}\text{Am}^{3+}$  ions present in the aqueous nitric acid solution.

#### 2.4.2 Alpha spectrometry study:

Alpha spectrometry was carried out using a silicon surface barrier detector. The detector signal, after amplification and digitization, was fed to a computer based Multichannel Analyzer (MCA). For the measurement, the target (alpha source loaded membranes) and detector were placed in a vacuum chamber with desired vacuum pressure. The  $^{241}\text{Am}$  containing membrane was exposed to the detector through a 5 mm collimator at a distance of about 10 cm from the detector to minimize the variation of the path length of alpha particles inside the membrane before reaching the detector. Alpha spectrometry was carried out by exposing both surfaces of the membranes one after the other.

#### 2.4.3 Alpha track radiography:

The distribution of functionality on the membrane surface was studied using alpha track radiography. Radiography of alpha track was carried out using the solid state CR-39 detector; the  $2\pi$  geometry of detector was kept on the  $^{241}\text{Am}^{3+}$ -loaded functionalized membrane. The track of alpha particle on C-39 detector make amorphous, by removing of the amorphous zone using high alkaline sodium hydroxide solution (~6 M) at 60 °C for ~5 h. The growing alpha tracks were examined using transmission optical microscope.

## 2.5 Electrochemical Analysis

### 2.5.1 Electrochemical impedance spectroscopy (EIS):

The proton conductivity ( $\kappa^m$ ) of functionalized membranes was studied by AC impedance spectroscopy connected with a 32M FRA frequency response analyzer potentiostat/galvanostat (Auto Lab M204). The samples (Functionalized membrane) were sandwiched between two domestic Titanium circular electrodes (~20mm dia.). A Sinusoidal AC frequency (0.1 -10<sup>5</sup> Hz) with constant scanning rate along with the circular electrodes. Before resistance measurement of the functionalized membrane, blank short – circuit cell resistance was also measured and which subtracted from the functionalized membrane resistance. The resistance of the functionalized membrane fixed from the Nyquist plot measurement and examine the proton conductivity ( $\kappa^m$ ) of the membrane using the Eqn. (4) [97]

$$\kappa^m(S/cm) = \frac{L(cm)}{[R(\Omega) \times A(cm^2)]} \quad (4)$$

where, L equivalent to gap between to homemade circular electrode, R is equivalent resistance of the each membranes and A is the effective cross-sectional surface area of the membrane. Bode phase and moduli were measured at the same time during the EIS.

### 2.5.2 Activation energy:

Activation energy is the key properties for the proton transportation, lower value of activation energy indicates the better proton transportation through the membrane and higher activation energy value indicates grater thermal stability for higher temperature applications. Value of the activation energy calculated of the functionalized membrane using the Arrhenius plot by eq. *eq. (5)*;

$$\ln \kappa^m = -\frac{E_a}{RT} + \ln A \quad (5)$$

Where, R equivalent to the universal gas constant and T indicates the absolute temperature and A is pre-exponent coefficient.[114]

### 2.5.3 Linear Polarization Studies:

For the corrosion rate, corrosion potential and inhibition efficiency of the functionalized materials examine by liner polarization measurement using the AutoLab204 instruments in potential range +1V to -1V w.r.t. open circuit potential at 10 mV/s scan rate and the corrosion inhibition efficiency of functionalized materials was calculated using the following equation (6):

$$\%IE = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100 \quad (6)$$

where, the initial current density is  $I_{corr}^0$  without materials, and final current density  $I_{corr}$ , respectively.[1]

### 2.5.4 Methanol Permeability:

A diaphragm diffusion cell, consisting of two compartments with a capacity of approximately (100 mL), separated by a vertical membrane with 20 cm<sup>2</sup> effective area are used for examining the methanol permeability (P) of the functionalized membrane. The functionalized membrane was intact in between the two compartments. The membranes were equilibrated before the experiment in the water-methanol mixture for 12 h. Initially, one compartment (A) contained 50% methanol-water mixtures while other (B) contained double distilled water. Methanol flux across the membrane aroused due to a concentration gradient. Methanol concentration in compartment B with respect to time was observed by



measuring the refractive index with a digital refractometer (Mettler Toledo RE40D). The methanol permeability (P) was obtained from the equation given below:

$$P = \frac{1}{A} \frac{C_{B(t)}}{C_A(t - t_0)} V_B L \quad (7)$$

where,  $A$  is the effective membrane area,  $L$  the thickness of the membrane,  $C_{B(t)}$  the methanol concentration in compartment B at time  $t$ ,  $C_A(t - t_0)$  is the change in the methanol concentration in compartment A between time 0 and  $t$ , and  $V_B$  the volume of compartment B. All experiments were carried out at 30 °C. Uncertainty for each measurement was less than 5%.

#### 2.5.4 Membrane Electrode Assembly (MEA):

Fabrication of the MEA is prime importance for the measurement of the fuel cell efficiency, for the fabrication of the MEA consisting three layer system (anode, membrane and cathode layer). The Pt/Ru/C are used as anodic reactions and Pt/C are used for cathodic reactions was coated on the carbon paper with 4 mg/cm<sup>2</sup> loading on carbon paper for both the electrodes. The stack made with the help of the compression moulding at pre-melting (125 °C FOR PVDF). After that the fabricated MEA is used for the polarizing curve measurement at activated temperature (~70 °C) with single cell assembly of Fuel cell. The fuel used is Methanol –water (30%) mixture as anodic fuel and for oxidation purpose pure Oxygen is used.