

Chapter 1

Introduction & Literature Reviews



1.1 Introduction:

In present decades, energy and water waste management play the prime input of our daily life and industrial process because of the depletion of natural resources rapidly like fossil fuel and pure water.[1] Now alternative of conventional energy resources like petroleum, coal and natural gas, etc., is the need of the time. One of the significant problems with conventional resources is that it increases environmental pollution, leading to increases in global warming and that influences animal and aquatic lives.[2] To overcome these problems and meet the high energy demand, to a large extent, hard work is mandatory to move towards non-conventional energy resources such as wind energy[3], solar cell[4], Fuel cell [5] and redox flow battery (RFB) etc.[6]. These non-conventional energy resources, such as the polymer electrolytes membrane fuel cells (PEMFCs) technology, are alternative, fresh energy, environmental sociable and proficient power sources. The key components of the fuel cell technologies are polymeric electrolytic membrane. [7] Although the polymeric membrane has various applications such as ultrafiltration, microfiltration, nanofiltration, reverse osmosis, adhesive, nanotechnology, sensor, and radioactive waste management's in nuclear power plants.[8][9] Polymeric membrane technology has continuously developed in energy and separation technology last some decades. At that point a lot of advantage of membrane, in particular for the filtrations and PEMFCs progression. This is because of the light weight, easy to design, lower power utilization, cost-effective, during experiments does not change phase and easy handling; as a result, they come across applications in many fields. A well-functionalized polymeric membrane with some specific functional group, predominantly ionic group (sulphates,

nitrates, chlorates, sulphonium, phosphonium, ammonium, etc.), is used for the above listed applications.[10]

1.2 Polymeric membrane:

Polymeric membranes are micro porous films and that act as a semi-permeable barricade to take apart two different phases or selectively allow the specific chemicals. Construction and design of porous membrane have been found in the micron to nanoscale range (**Figure 1.1**). Firstly, a porous polymeric membrane can be the blueprint to illustrate the advantages of well-defined porosity and high surface area. Secondly, the porous polymers have easy process ability. Third, the diversity of synthetic directions for polymers make possible the design and structure of copious porous polymers able of incorporating numerous chemical functionalities keen on porous framework/pore wall surface[11].

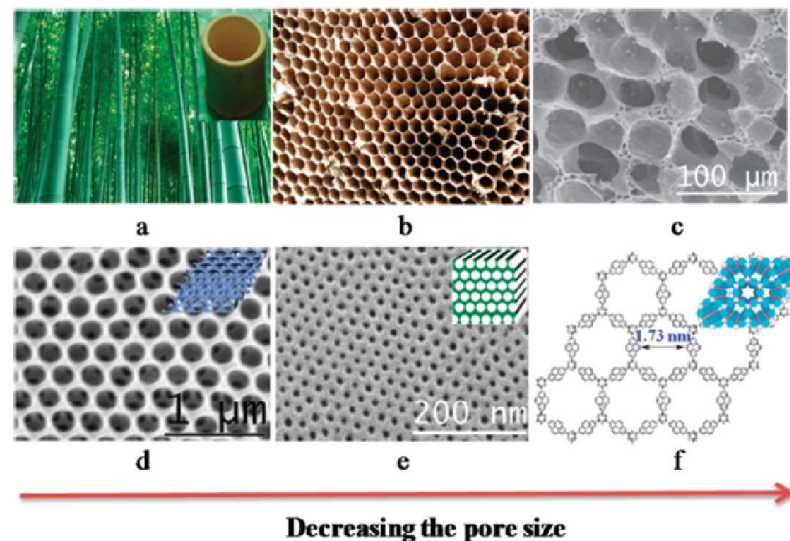


Figure 1.1: Various types of membranes based on the pore size.

The porous membrane can be produced in a moulded monolithic form or in thin films, which generates significant advantages in many practical applications. Various type of separation/ filtrations membranes have been extensively considered and utilized technologically in a variety of fields, including membranes such as microfiltration (0.1 μm to 1.0 μm) [12], ultrafiltration (0.01 μm to 0.1 μm) and nanofiltration (0.001 μm to 0.01 μm) [13], as reverse osmosis, as gas separation and as proton electrolyte membrane (PEM) for fuel cell [14]

1.3 Nanohybrid membrane (NH):

Polymer nanohybrid matrix that consists of organic and inorganic components that link together by the chemical bonding, in polymer nanohybrid one component must be in the range of nano-dimensional fillers like, Quantum Dot (Zero Dimensions), Carbon nanotube (CNT; one-dimensional filler) and two-dimensional layer silicates (30B- Organically modified clay) (**Figure 1.2**) have an enormous impact to get better chemical, physical, mechanical and gas / Methanol barrier properties[15]. The β - or γ - phase formation in nanohybrid (e.g., layered silicate, CNT, mica, Graphene sheet)[16] are generally occurred by the blending with polymers consisting of carbonyl groups followed by the nucleation of the phases and it can also obtain by electro-spinning (directional alignment), poling by high voltage electricity; high pressure melts crystallization. Nanohybrid membrane improves the performance of membrane by improving the many properties of the matrix such as mechanical, barriers, chemical (chemical resistance), physical, corrosion resistance, thermal properties, processability and inferior environmental impact. In the majority of cases, advanced nanohybrid materials are inclined to the different figure of the damage like

radiations, heat energy, acid- bases attack, unexpected load (overload), impact and fatigue etc. while a large number of polymer nanocomposites mainly layered silicates have been described, the layer silicates are organically modified nano dimensional nanoclay that's are compatible with the organic, inorganic matrix leading to the phase transformations and accepts major challenges. Nanohybrid materials have gained much attention in the membrane applications due to the enhancement the thermal, mechanical and electrical as well as electrochemical properties.[17][18]

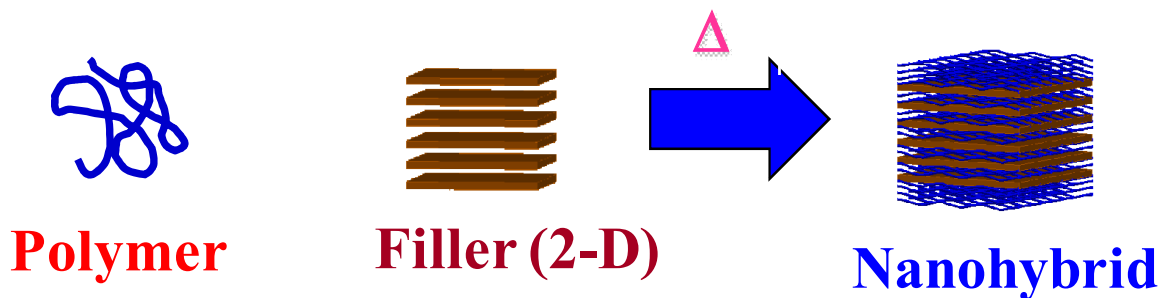


Figure 1.2: Preparation of Nanohybrid membrane.

1.4 PVDF and its copolymers:

PVDF is non-reactive, insulating, thermoplastic, semi-crystalline and chemical resistant fluoro-polymer synthesized by polymerization of the vinylidifluoride monomer. The high mechanical and thermal properties as well as good processability make them suitable for the chemical processing equipment, pumps, pipes, tubes and fittings, sensor and actuators etc.[19] PVDF also used in the electronic devices because piezoelectric and pyroelectric properties, the low flame spread and smoke generation of PVDF is a prime asset in these

applications. Fluoropolymer for example poly(vinylidene fluoride) (PVDF) in addition to its copolymers such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE), poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE), are being used to make PEMs.[20] PVDF is an ahead acceptance as a binder in polymer –lithium ions batteries for anodic and cathodic materials [8]. PVDF and its copolymers exist mainly five crystalline phases, they are mostly classify as polar (exist permanent dipole moment) and non-polar phases (does not exist permanent dipole moment). Polar and partial polar phases are β , γ , δ and ε and crystalline nonpolar phase (α) is thermodynamically most stable and most common phase, by addition of the nano fillers the meta-stable polar phases can nucleate for the electrical applications. The chemical structure of the non-polar α -phases and polar β -phase with possible configuration is presented in **Figure 1.3** [21]

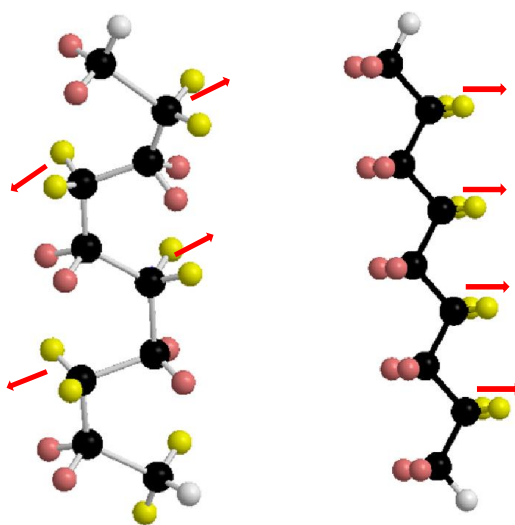


Figure 1.3: Schematic representation of the (a) α -trans gauche conformation; (b) β -all trans conformation of crystalline PVDF, while the black, pink and yellow spheres represent

carbon, hydrogen and fluorine atoms, respectively. The arrows signify $-CF_2$ dipole directions.

1.5 Ions exchange membrane:

There is a huge demand of the stable and high performance polymeric ions exchange membrane (IEMs), because of the their diversified applications in industrials scale process such as electro dialysis (ED), electro deionization, membrane electrolysis, diffusion dialysis and so forth coming for the production of clean water from the salty water, treatments of the industrials effluents .[22] For energy conversion and storage technologies such as fuel cell, redox flow battery, reverse electro dialysis, solar cell or others electrical energy generation process without feeding of the fossil fuels, basically these technologies are electrochemical based.[4][23][24] In additions there are several challenges accept of IEMs for: humidity sensor, carbon dioxide sensor, drug sensor, radioactive materials sensors, carriers for enzymes, solid polymer electrolytes for separators , a carriers for the functional materials, generation of the photo-voltage and photo-current. [5]

In fuel cell technologies, the ionic membrane used as separator cum electrolytes which separate the electron and ions pass through the membrane and radionuclide waste management the ionic group formed complexes or ion exchange mechanism for the removal / sensing of the radionuclide from the aqueous waste which is generated from the nuclear power plants.[25]

There are basically three type ion exchange membranes.

- Cationic membrane
- Anionic membrane
- Bipolar membrane

The most desired properties of the Ionic membrane are:

- High permselectivity- Should be high permeable to counter ions and impermeable co-ions.
- Low electrical resistance –For the counter ions, electrical resistance should be low so that ions easily transfers through the membrane but for co-ions it should be high.
- High mechanical and thermal Properties –The polymeric membrane should be mechanically and thermally stable for desired applications, swelling, leaching and shrinking properties should be low for the various concentration range of solvent.
- High chemical stability- The polymeric membrane should be chemically stable in the 0-14 pH range and also stable in oxidizing as well as reducing agent regents.

1.5.1 Cationic exchange membranes (CEMs):

In cation exchange membrane, the ionic group is of negative charge (SO_3^- , Cl^- , NO_3^- , PO_4^{3-} , COO^- , AsO_3^{2-} etc.) Chemically tag with the pristine polymer chain and which

allows passing of cations (Na^+ , H^+ , K^+ , Ca^{+2} etc.) through the membrane or ions exchange or also formed the complex with the negative charge and electron donating group/atoms present in tag polymer chain.[26] The nature and the extent of the functional group determine of the CEMs membrane using NMR, swelling, water uptake, water content and Ions exchange capacity of the functionalized membrane.

The various ionic groups have significant effect on the selectivity; the sulphonic group is entirely dissociated in complete pH scale while the carboxylic is virtually un-dissociated at lower pH, commercial cation exchange membrane Nafion (DuPont USA), Aciplex™ (Asahi Kasei Corporation, Japan), SELEMION™ (Asahi Glass Japan) have good stability and ionic performance. The std. Nafion provided by the DuPont has high thermal and ionic conductivity. Nafion CEMs contains hydrophobic back bone with fluorinated carbon chain and hydrophilic group attached to be pendent sulphonic acid, to improve the water preservation properties of the Nafion that should blend the nanocomposites.[27][28][29][30] Several types of the CEMs are reported in literature with sulphonic ionic group such as sulphonated poly-(ether ether ketenes) (SPEEKs)[31], poly (arylene ether sulphone) (PAESs)[32], Polyimides (PI)[33], polyphosphazenes[34], polybenzimidazole (PBI)[35], polyphelenes[36] and some other types such as pore-filled[33][37] , organic inorganic nanohybrid materials and ceramic oxo-clusture composites were prepared by the doping of inorganic particles [38][39] , silica nanoparticles[40] , titanium dioxide[41], zeolites[42], carbon nanotube[43], were used for the preparation of the CEMs. It was noticed that from the above discussion the CEMs structure was highly dependent on the type of particle dispersed and extent of the ionic

groups present which enhance the ionic conductivity and water retention ability of membrane and principal of the CEMs illustrated in **Figure 1.4**.

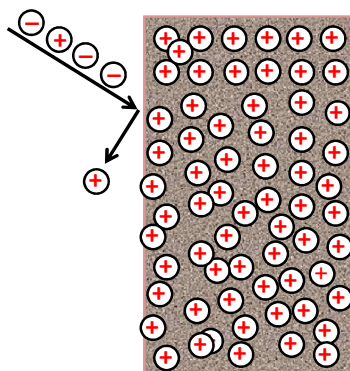


Figure1.4: Cation exchange membrane.

1.5.2 Anion Exchange membranes (AEMs):

Anion exchange membranes (AEMs) bear positive charge on the polymer backbone, means the polymer tag with the cations and they permeable anions only through the membrane. Thus the selectivity of the anions membrane results from exclusions of the co-ions of the membrane phase.[44] The anionic membrane basically contains exchangeable group- NH_3^+ , $-\text{NRH}_2^+$, $-\text{NR}_2\text{H}^+$, $-\text{NR}_3^+$, $-\text{PR}_3^+$, $-\text{SR}_2^+$ etc. and principal of the AEMs illustrated in **Figure 1.5**.

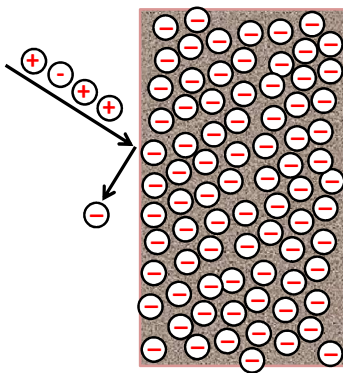


Figure 1.5: Anion Exchange membrane.

According to materials matrix, the anionic membranes are classified into two types: homogenous & heterogeneous. In homogenous the cationic group chemically bonded with membrane matrix, In heterogeneous anionic membrane the ionic group physically mixed with pristine polymer.[45] The most practical AEMs are quaternary ammonium functionalized polymers for example polyethers, polysulphone, polyketones, and poly(phenyl oxide) (PPO) etc.[46][47]

1.5.3 Bipolar membranes (BPMs):

Bipolar membrane is prepared by the stacking of the cation exchange membrane, interfacial layer and anion exchange membrane. Various techniques are used for casting of layer by layer structure of BPMs. Water molecules splits into H^+ and OH^- through interfacial layer (IL) of BPMs with high efficiency and without any harmful gas evaluation under a reverse voltage. These layer work as semiconductor p-n junctions. In these time the BPMs membrane used for the generation of acid and base from their salt solution by electrical potentials. The process of bipolar membrane is a well-known term. The use of bipolar membranes has been advanced in different technical applications. The principle structure of the BPMs and its functions were illustrated in **Figure 1.6**.

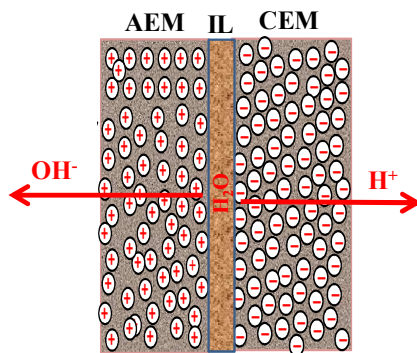


Figure 1.6: Schematic Presentation of BPM.

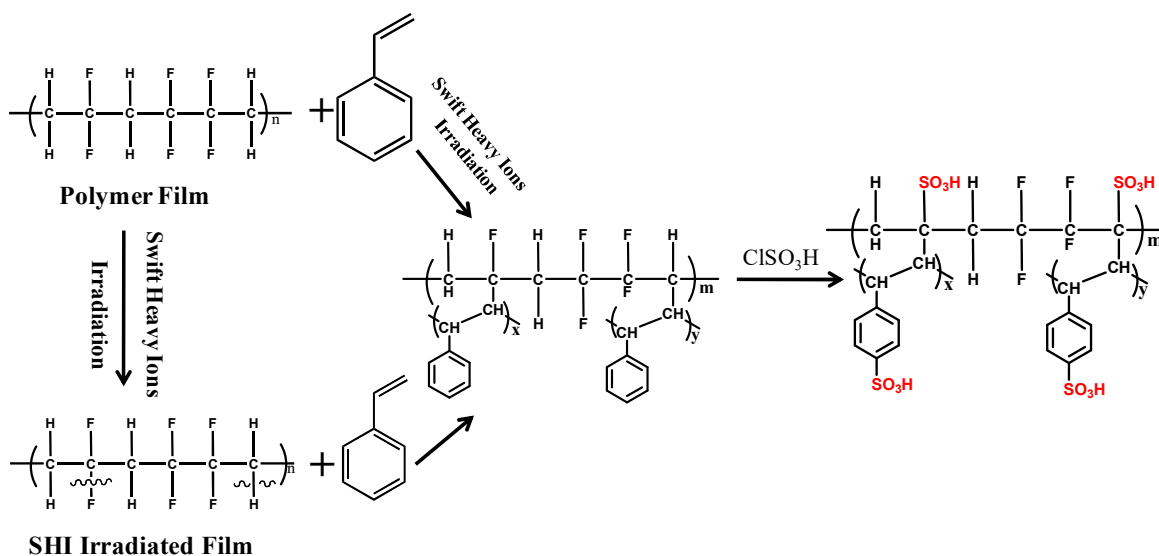
1.6 Various Techniques used for the Fabrications of the Ionic membrane:

To achieve the desired properties of the membrane, the grafting and functionalization is of prime importance for tuning of the characteristic properties of the membrane for further application as PEMFCs. Based on the nature of materials and functionalization route, the polymer electrolytes membranes are classified as follows:

1.6.1 Functionalized membrane preparation via radiation induced grafting:

Radiation induced graft copolymerization followed by the functionalization is an easy way for alteration of the existing polymer with enhanced and imprinting the novel properties without changing the inherent properties of the polymer. There are particular interests to introduce the variety of functional group on the backbone of the polymer. In radiation induced grafting method, the reactive sites created in the backbone of base polymer via high energy radiation such as, γ -radiation, electrons beam radiation and swift heavy ions (SHI)[48] particle radiations etc. The irradiated polymer is passed through the monomer solution, which propagate the side chain polymerization followed by its termination [49]. Two standard methods are followed for the radiation induced polymerization; first method is pre-irradiation in an inert atmosphere and trapped the radicals followed by copolymerization. In this technique, the irradiated polymer is deep in the monomer solution under the optimized polymerization condition. If the irradiation experiment is performed in air the free radicals formed by the irradiation react with air to produce peroxide and hydro peroxide species which can be decomposed at elevated temperature and subsequently they can be used for copolymerization [50]. Second method is the simultaneous irradiation and copolymerization, also known as direct method. In this method, the polymer and the

monomer solution kept together before irradiation. Each of above radiation induced grafting has its own advantages/ disadvantages depending upon the polymer-monomer recombination condition [51]. The direct method leads to the larger degree of tagging of monomer by reason of efficient consumption of the free radicals formed after the irradiation. While the pre-irradiation manner is more effective, mainly when the monomer is more reactive, to obtain the desired level of tagging of monomer and optimization of the factors are required. The chemical processes of these two methods are shown in reaction scheme 1.1.



Scheme 1.1: Chemical representation of synthesis of functionalized membrane (PVDF) through direct and pre-irradiation tagging of styrene monomer followed by sulfonation.

The radiation-induced graft copolymerization has several advantages against the other methods for various reasons including simplicity, flexibility of the chemical reaction, the extent of graft moieties which can be controlled by the variation of the doses of radiation.

This provides an analytical method to develop special design (tuning of properties of the membrane) of membrane for the various applications [52]. The development of the functionalized membrane materials via the radiation induced grafting for the relevant applications has been developed many researchers and industrial people. The membrane fabrications by the radiation-induced grafting supply the cost effective and suitable for industrial process.[23] Amongst these radiation techniques, the swift heavy ions is one of the capable technique for the generation of active sites for example free radicals[53]the details of SHI were given in below sections.

1.6.2 Functionalized to prepare chemical modified membrane:

The direct functionalization of polymer matrix using the catalyst and monomer solution followed by different ionic group insertion leads to enhance the ionic properties (ionic conductivity) of the membrane. Fabrication of the membrane is done through compression moulding for further applications. There are several literature reports available for direct functionalization followed by the fabrication of fuel cell step-up. Prakash et al. accounted the direct sulphonation of PVDF-co-HFP and enhanced the pristine properties of the polymer [23]. Direct sulphonation of PVDF with variation of temperature and reaction time generate differentially stable polymer membrane suitable for PEMFCs.[49]The variations of the proton conductivity noticed in synthesized polybenzimidazole (PBI) based proton exchange membrane, by variations of the different dicarboxylic acids, in cyclohexyl (aliphatic) based dicarboxylic acid lower proton 114 mS cm^{-1} found as compare to terephthalic (aromatic dicarboxylic acid)(220 mS cm^{-1}).[54] Coupling of poly (aryene ether) dicarboxylic acid functional group with diamine functional group shows the proton

conductivity of 47 mS cm^{-1} and has been valuable for practical use as proton exchange membrane. The direct chemical approaches of several research groups have utilized for fabrication sulphonted aromatic copolymers by introducing the sulphonate ionic groups on the backbone of the polymer chain. The direct sulphonation is an alternative and easy handling approach for the fabrication of polymer electrolyte membrane. This method gives the controlled design of molecules and degree of sulphonation. Major drawback of this method is the location of functionalization and overall mechanical stability of the membrane. To avoid these problems, fluoropolymer without aromatic ring is being considered for membrane design. The chemical modification is one of the important routes to tailor the proton conductivity of functionalized membrane by altering the grafting as well as doping extents for better polymer electrolytes membrane for fuel cell technology.

1.6.3 Blend /composites membrane:

Several research groups proposed the incorporation of fillers such as acids-base /ionic group in commercial/conventional polymer electrolyte membranes, such as Nafion / anion exchange resin by enhancing the water maintenance factor and thereby, providing the additional path for ion transport. These factors give important parameter of proton conductivity improvements at high temperature and relatively lower humidity as operating condition required for the functioning of fuel cell. In these aspects, organic/inorganic composite membranes such as Nafion, PFSA, PBI, SPSF, SPEEK and PVDF etc. are used.[55] Polymer membrane with inorganic nano-fillers, so called composite membrane, can be produced using different advanced techniques. The water absorbing inorganic oxide (fine powder) impregnation in porous polymeric membrane is one of the conventional

routes. Other method is the addition of precursor such as acidic metal alkoxides/ ion conducting oxides solution into the pores of the membrane followed by the transfer of precursor for selective ion transportation. Most of the cases, the addition of varieties of metal oxides with desire amount in solid commercial membrane Nafion117 leads to enrichment of proton conductivity of functionalized membrane at elevated temperature. Hydrophilic inorganic filler, for example SiO_2 , TiO_2 , ZrO_2 , zeolites etc.[56] Composite Nafion membranes enhance the water retain capacity by increasing the binding energy of water and strength of acids with the water molecules and thereby, alter the ion conduction path of the membrane. These nano-filler narrow down the hydrophilic channels of Nafion matrix (7.9 to 6.5 nm) [57] which leads to inhibit the fuel permeability of the membrane. Some others proton conductor fillers such as zirconium phosphate ($\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$), a layered titanium phosphate ($\text{Ti}(\text{H}_2\text{PO}_4)\text{PO}_4 \cdot 2\text{H}_2\text{O}$), cesium phosphates (Cs_3PO_4) and heteropolyacids (it's combinations of the metal , hydrogen and oxygen framework) have to be looked at to make the possible proton transportation at reduced /zero humidity levels in the matrix.[58][59] Prakash et. al. incorporated the organically modified nanofiller (30B) in PVDF and its copolymer matrix to alter the proton conductivity and other properties for example barriers, mechanical, thermal and electrical property of the functionalized membrane. The functionalization has been done through the accelerator and subsequent chemical modification.[60] Some limitations of the polymeric membrane for PEMFCs still exist which require extra attention. Successful membrane for PEMFCs should have sufficient mechanical strength / free standing form membrane, long durability, cyclability, easy processing and design issues including catalyst compatibility and scale-up.

1.7 Swift Heavy ions (SHI):

Particles radiation high swift heavy ions display significant efforts to alter the properties of the materials in controlled manner to provide possibility of make them functional for specific applications en route for futuristic technologies. Now, the variety of the materials irradiated with the help of the SHI and effect of SHI studies using the sophisticated instruments like, spectroscopic (IR, NMR, UV), for structural alternations XRD, RBS, thermal measurements TGA, DSC and for morphological AFM, SEM , high resolution SEM are used . The modification in the membrane materials are being connected with the various parameter of the ions beam and achieve desire properties of materials. Polymer are very much radiation resistant but swift heavy ions can modify the molecular and structural properties leading to alter in their chemical, electronic, electrical, tribological and optical properties. Ion beams track produced by SHI cause the bond cleavage and produced free radical reactive sites. SHI is accountable for the most chemical transformations in polymer matrix: bond formations, cross linking, and chain scission and theses changes lead to the formation of the alkenes and alkynes, allenes. The structural alteration of polymer membrane depended electronic loss (S_e) over the nuclear loss (S_n) and fluence of the ions beam.[61] Beyond the S_e (electronic energy) the swift heavy ions produced amorphous zone along the ion track trajectory (ions track).[62][63][64] The S_e loss along the ion tracks are discretely, not continuous because energy are quantize in nature and such energy loss range of the 30-40 eV which is higher than the bond energy of the various bond present in polymer backbone result in formation of the reactive sites in matrix.[65] In many soft solid materials like polymer SHI releases sufficient energy to produce cylindrical ion track (mostly amorphous) followed by the chemical etching produced nanometer size

nanochannel and membrane known as etched membrane and now lots of application of these etched membrane in industrials processes.[48][66] However from the above discussion it's clear that the SHI bombardment on the polymers membrane offers many useful applications depending on ion beams its energy and fluence. Bombardment of polymer membranes allows developing nonporous membranes for various applications. Bombardment of SHI on polymer film can create many phenomena including physical and chemical changes in polymer matrix.

1.7.1 Physical changes after the SHI:

The one of the most important effect of the SHI after the bombardment implantation in soft solid materials and introduced the macro-stretched latent track. Ion track firstly seen by silk in 1959 on mica through the electron microscope [67] latter on price and walker treatment of the chemical etchant and detect the nuclear tracks by fission fragment produced in mica sheet which is seen by optical microscopy.[68] Afterwards latent track morphology was examined using various techniques which bare spherical discontinuous/continuous; cylindrical / spherical regions.[69] Therefore, during the bombardment of the SHI ion tracks are produced next to the path of ion beam and due to the electronic loss and LET (linear energy transformations) in polymer matrix the path are amorphous after that the membrane subjected to the selective chemical etchant and produced hallow pores / nanochannels . [70] The channel dimension can be altered by the variation of the chemical etching procedure and conditions, the shape and size of the etched nanochannel was examined. Their pore size may be cylindrical, funnel like, double funnel like, canonical, cone like, cigar-like so that the membrane should have produced transportations and

retention properties for the further applications in relevant field of the applications. [71] A numerous efforts also have been made to characterize the ions beam bombardment porous membrane by gas permeation experiments.

1.7.2 Chemical changes after the SHI:

The swift heavy ions is the most promising techniques for the chemical transformations and as it passes through soft polymer materials that encourages magnificent changes like formations amorphization zone, bond scission, free radicals generations, cross linking, multiple bond formation, ions tracks etc[72] in the matrix molecules. Fabrication of the reactive sites like free radical, ionic species cations and anions etc. through SHI is most common changes but free radical reactive sites in one important reactive species for the radiation induced grafting that have sufficient potentials to begin the grafting progression on the macromolecules formations while surface free radicals are labile to produced peroxy(POO[•]) radical by reaction of the atmospheric oxygen that further react to oxygen and moisture, furthermore other chemical species like epoxies, hydroperoxides (POOH), acids formation by the developed radicals.[73] The reactive radical inside the wall / nanochannel are very stable at long time before that chemical processing but after the chemical etching the radical are active for the chemical transformations and other various chemical processing. [74] Chemical changes illustrated by the **Figure 1.7** after the SHI bombardments.

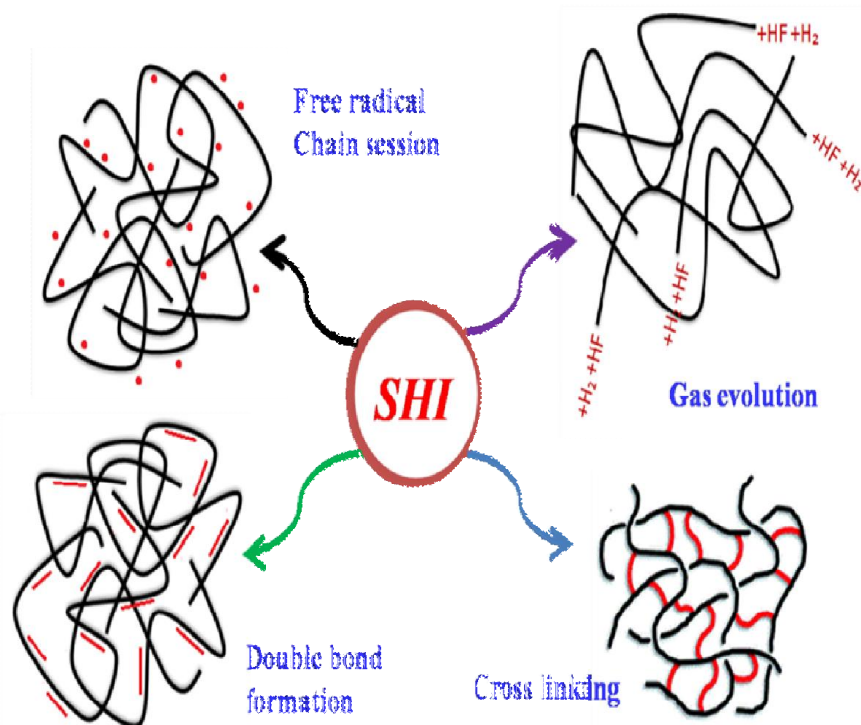


Figure 1.7: Schematic of the chemical changes after the Swift Heavy Ions bombardments[8].

1.7.3 Chemical etching and formations of the Latent track:

After the bombardment of the of the particle radiation SHI on the polymeric film, the chemical as well as physical changes observed and SHI energy chosen such way, the ions pass through the membrane, the path of the swift heavy ions are preferentially amorphous in nature, by removing the amorphous zone of the bombardment membrane using the chemical reagent term as chemical etchant [75] construct the through latent track in the polymeric membrane, whose dimensions depends upon the linear energy transfer (LET) of ions and LET basically dependent the mass , energy of ions per nuclei and fluence of the ion. The dimension of the through latent track were around 10-120nm, dimension is much

show dependency of the chemical reagent and etching condition like temperature. [76] The shape of the track dimension formed after the chemical etchant may be conical, spherical, and cylindrical and funnel like. The pore size and mechanical stability of the functionalized membrane controlled by the above discussed parameters, consequently a membrane with specific functionalities, transportations and separations of impurities can be hold with the proper pore dimension.

1.7.4 Fabrications of the conducting nanochannels:

The nanochannel / latent track were fabricated after the SHIs bombardment followed by the selective chemical etching with help of chemical reagent (alkaline solution of potassium permanganate) , because of the particle radiation SHI on polymer, the chain of the polymer breaking and formation of new reactive species generated like double bond, free radical, cationic and anionic species. Afterwards, the reactive side free radical utilized for the radiation induced grafting and copolymerization of the block polymers. In the mechanistic way the radiation induced grafting technique initiator is not required but it should be well known whether the polymer stable in radiation range. After then the functionalization of the graft species inside the channel were carried out with help of the sulphonating agent like chlorosulphonic acid and others. The tagging of the monomer subsequent sulphonation of the conducting channel makes the nanochannel to conducting nanochannel for the ions transportation. Moreover, the grafted specie coiled or straight chain inside the nanochannel influence the ions transport behavior through channel, in the monomer styrene grafting the copolymerization inside the channel were coiled were in case of 3-hexyl thiophene straight structure.

1.8 Applications of the ionic membrane:

Ionic membrane has several applications such as filtration, electro dialysis, radio nuclide sensor and proton exchange membrane (PEM) in Fuel cell technology. In PEMFCs technology, membrane is used as electrolytes cum electron separator. The main focus of the thesis is fabrications of fuel cell stack using ionic membrane.

1.8.1 Fundamentals of Fuel cell Technology and working Principle:

Electrochemical device fuel cell is an energy generating device where chemical energy converted into the electrical energy and heat takes place with high efficiencies by the oxidation of different class of fuel in presence of air with the help of redox couple reaction. Electrochemical based devices are able technologies for the renewable energy, stationary power management, energy storage, pollution control and green house gas reduction. These devices optimize the cost and size of the electronic devices. Fuel cell is one of the promising electrochemical devices and produce power from few mW to MW and is being utilized in various applications.[77] Fuel cell produces energy only if there is a supply of fuel and hence, continuous fuel supply is the most important requirements for the cell operation.

The electrochemical process in the fuel cell is not governed by the thermodynamics law like Carnot's cycle; hence, their function is trouble-free as against the internal combustion (IC) process. Elevated efficiency make them an alternative choice of the future power source for the large area of applications like transportation, stationary and portable electronic power bank such as computer, laptop, mobile, watches and video camera etc.[78] Fuel cells consist of electrode, fuel and electrolytes. When fuel get towards the anode side

of the electrode to the cathode side it converts its ions and electrons after reacting with catalyst and the ions pass through the electrolytes which highly resist the flow of electrons through the electrolytic membrane alkaline solution.[8] Further, electrons flow in the outer circuit to balance the chemical reaction. In fuel cells, the net chemical reaction is similar to the combustion of the fuels but the fuel is separated with an electrolyte, while in combustion there is a direct contact. The fundamental driving force of the migration of the ions through the membrane is its ionic group present in the backbone of the polymer electrolyte membrane or the concentration gradient electrode-electrolytes interface. [8] The typical open circuit voltage of the polymer electrolytes membrane was reported ~ 0.7 V. In 1900s, the development of fuel cell started as power sources but was used limited and used in defense and space research organizations.[79] [80] New efforts are made to build up fuel cell at the end of 1900's or beginning of twenty first century. [81] In recent years, the fuel cell technologies have been more efficient and environment friendly and act as sustainable energy resources. Presently, the fuel cell technologies are in the verge of commercialization almost in every sector of market, but the overall efficiency is still low and need improvements. The schematic of the fuel cell set-up is shown in **Figure 1.8**.

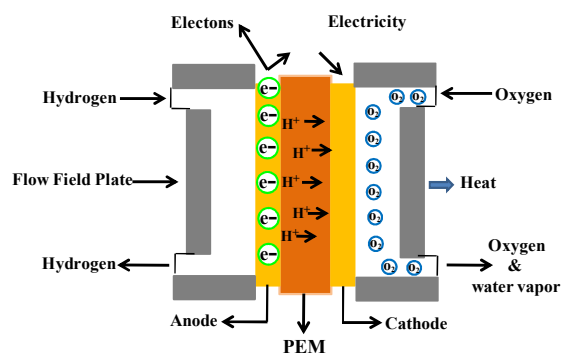


Figure 1.8: Schematic presentation of a fuel cell set-up.

Based on the fuel, electrolytes and operating condition the fuel cell is classified in different types. The working principle, used electrolytes, chemical reaction, advantages and disadvantages are presented in the **Table 1.1**.

Table 1.1: Classification of the fuel cell devices based on fuel, electrolytes and operating temperature.

Fuel cell	Electrolytes	Electrode reactions	Advantages	Disadvantages	Application	Ref.
PEMFC	Polymer membrane (Nafion117)	Anode $H_2 = 2H^+ + 2e^-$ Cathode $1/2O_2 + 2H^+ + 2e^- = H_2O$	LT, quick start up , reduced corrosion due to Solid Film	Expensive catalyst, Highly pure fuel used	Transportation , Stationary, Portable electronic devices	[8]
DMFC	Polymer membrane		LT, quick start up , reduced corrosion due to Solid Film	Expensive catalyst,	Transportation Stationary, Portable ,electronic devices	[49]
AFC	Aqueous solution of KOH/NaOH or anion exchange membrane	Anode $H_2 + 2OH^- = H_2O + 2e^-$ Cathode $H_2O + 2e^- = 2OH^-$	Low cast and fast electrode reactions in alkaline medium.	Sensitive to air and CO ₂ , electrolyte management and design of cell.	Transportation , Stationary, Portable electronic devices	[82]
PAFC	Phosphoric acid	Anode $H_2 = 2H^+ + 2e^-$ Cathode $1/2O_2 + 2H^+ + 2e^- = H_2O$	Enables CHP due high temp. ,increases the torulence of fuel	Long start up time, Pt catalyst, design of the cell.	Military, stationary power generation output in range 100 kW-400 kW.	[83]
MCFC	Molten K ₂ CO ₃ and Li ₂ CO ₃	Anode $H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^-$ Cathode $CO_2 + 2e^- + 1/2O_2 = CO_3^{2-}$	High efficiency, Fuel flexibility, enables CHP, variety of the catalyst.	Long start up time, High temperature corrosion of the fuel cell components.	Transportation , Distributed power energy ,	[84]

SOFC	Ytria stabilized zirconia (YSZ), Lanthanum gallate, doped Bi ₂ O ₃ , doped ceramic etc.	Anode $H_2 + O^{2-} = H_2O + 2e^-$ Cathode $1/2O_2 + 2e^- = O^{2-}$	High efficiency, Fuel flexibility, High temperature, non noble catalyst	Long start up time, size and design High temperature corrosion of the fuel cell components.	Distributed power energy, Auxiliary Power units in vehicles and stationary power generation.	[85]
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The electrical efficiencies of the fuel cell devices depend upon the operating temperature. Based on the functioning temperature, the fuel cell technology is classified into three classes: low temperature (LT); in this category polymer electrolytes membrane fuel cell lies whose operating temperature is below 100 °C, solid oxide fuel cells (SOFCs), also known as high temperature (HT) which operated ≥ 800 °C and moderate temperature (MT) fuel is molten carbonate fuel cell where the operating temperature is between 100 - 800 °C.[86]

The low temperature operating condition of PEMFCS makes it lower efficiency fuel cell while the SOFCs make them highest electrical efficiencies.

1.8.2 Polymer Electrolytes fuel cell membrane:

The polymer membranes are used as electrolytes cum separator of electrons in fuel cell electrochemical devices. In fuel cell stack the three major components is the prime need for the operational cell followed by the energy generation such as Fuel, electrode materials and electrolytes. The electrolytes are the key component of the fuel cell technology as previously discussed in **section 1.8.1** and based on the electrolytes, the fuel cell technology classified into various types but electrolytes polymer, is the important for various reasons like polymer based electrolytes, light weight, during chemical reaction does not change the phase, easy handling and product etc. For Polymer electrolytes membrane (PEM) the

polymer (Functionalized ionic membrane) should meet following properties, like high ionic conductivity, for hydrophilicity sufficient water uptake and on exchange capacity, for proper functioning of the cell, functionalized membrane should have low fuel permeability.[87] Ionic membrane free standing form means mechanically and thermally stable at operating conditions such as excellent electrochemical stability in acid/base solution, moderate swelling during the electrochemical reactions and one most important factor of comparatively low cost and long durability. [88] To fulfill the above criteria, the membrane materials selection and processing for the functionalization is more important for the efficient membrane.

1.8.3 Direct Methanol fuel cell (DMFCs)

Direct methanol fuel cell (DMFCs) is a kind of polymer electrolytes membrane fuel cell, which utilizes the methanol–water ($\text{CH}_3\text{OH} - \text{H}_2\text{O}$) mixture anodic fuel (Oxidation reaction) to generate electricity. The methanol fuel is used directly in fuel cell setup without any reforming unit, when methanol fuel is in contact with anodic catalyst with the help of peristaltic pump the methanol get oxidized as proton, electron and carbon monoxide. The protons pass through the membrane electrode assembly and combine with the oxygen to form water as a waste product and heat energy. The membrane separates the electrons and passes through the external circuits and electronic load for storage or instant applications. At anode side Pt-Ru / carbon catalyst is used while cathode side the Pt/ carbon catalyst is used. The basic reason occurs with ruthenium catalyst at anode side as it forms better complex with carbon monoxide, hazardous gases which need to be removed during the electrochemical redox reactions. Direct methanol fuel cells are eco-friendly and greener

technology. The schematic of DMFCs were given in **Figure 1.9**. Alternative energy / renewable energy are the need of time, for further development of the DMFCs with high stability and greater electrical efficiency still challenging and desirable.

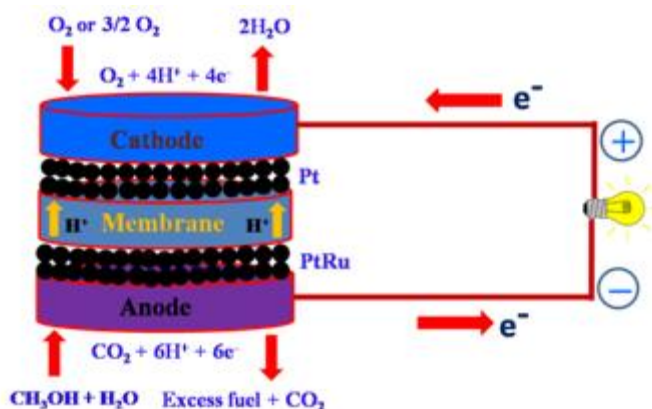


Figure 1.9: Working principle and cell reaction based Schematic of the DMFCs. [19]

1.9 Nafion membrane (Commercial)

Nafion membrane is the first synthetic thermoplastic ionic membrane (Sulphonated tetrafluoroethylene) developed by Walter Grot of DuPont around 1960s. [89] Fluoropolymer Nafion contains sulphonate ionomer (SO_3^-) in the backbone of the polymer chains and having sufficient ionic properties and makes the membrane ionic. Nafion is the commercial proton exchange membranes with proton conductivity range $\sim 10^{-2} \text{ S cm}^{-1}$ at moderate temperature. The water retention capacity of Nafion increases by increasing the number of the sulphonate group on the main chains. The greater hydrophilic nature of the Nafion and other properties like high mechanical, good thermal, electro-osmosis drag and oxidative properties etc. of the Nafion membrane controlled by the structure of the Nafion. There are number of models proposed for the explaining of unique properties of Nafion.

Cluster channel model is one of the models which explain the hydrophilic / water management followed by the good proton conductivity of the Nafion. The Nafion membrane is wide applications in field of membrane technology and high proton conductivity indicates the Nafion used in field of the fuel cell technology as an electrolytes cum electron separator and allow different chemical reactions for the energy generations.

[90] Chemical structure of Nafion shown in **Figure 1.10**.

The Nafion membrane in the field of PEM has several disadvantages such as high cost, fuel cross over-phenomena and high temperature stability now the replacement of the commercial membrane and development of the new membrane is need of the hour.



Figure 1.10: Chemical structure of the Nafion.

1.9.1 Advantages:

For the application as fuel cell membrane the membrane should have the excellent proton conductivity for the utilization of electrolytes in fuel cell technology: fluoropolymer Nafion membrane fulfill all the criteria as a proton exchange membrane in PEMFCs. Nafion has several advantages as electrolytes, such as good proton conductivity, excellent thermal stability; free standing membrane form means great thermal stability. [91]

1.9.2 Disadvantages:

On the other hand, the commercial Nafion membrane still has several drawbacks, mainly when they are used as electrolytes in direct methanol fuel cells (DMFCs). The first dilemma is methanol permeability, when methanol pass through the membrane materials the drop of cell potential is observed after that cell dead may also happen and Second dilemma is the cost of Nafion which is very high and processing of membrane also difficult and another drawback of the Nafion membrane is at high temperature (above 90 °C) the proton conductivity decreases this is due to the loss of water content at high temperature. [92]

1.9.3 Developments:

Last few decades the researchers has been significant efforts and designed little new membrane which is alternative of the commercial membrane with resolved short coming of the standard membrane like cost, permeability, high temperature operating conditions and others.

1.10 Ionic membrane in field of the nuclear waste management's:

The quantitative estimation of the radionuclide elements and its fission product in their aqueous solution which is generated from the radio-pharmaceutical waste experiments, fuel processing in radionuclide's plants and nuclear forensic aqueous sample, the detection of the radionuclide sample needs highly sensitive instruments for measurements and hyphenated with appropriates sample purification and source preparation methods to avoid possible interfaces. [25] But, in many such applications, the sample has to subject to a pre-

concentration step for bringing the concentration of analyte in measurements range of radio analytical method. For example, the dangerous level accumulated Pu in human body is 10^{-12} g/g. [10] This highlights the compilation to monitor the much lower levels in the surroundings environments in order to evaluate of the bio-accumulations of radio toxic elements. For nuclear forensic and decontaminations application also, a very low concentration of Pu at sub-ppb level has to measure. The measurement of trace level radio nuclide concentration is also very important for monitoring the release of the radioactivity from the various operations in nuclear industries. Moreover, functionalized polymer membrane based α -spectrometry could combine the sample purifications, pre-concentration and source preparation. In recent times, it has been exposed that the thin polymeric membrane fabricated nanochannel followed grafted membrane can be used for the capturing of the radionuclide from aqueous sample and subsequent quantifications. [93]

1.11 Literature survey on uniform latent track fabrication:

There are several reports available in literature for the SHI irradiation on the polymer film for generation of porosity has been characterized in various ways after the treatments of the chemical reagents. It is well known that when high energy swift heavy ion beam pass through the thin soft polymer film approximate few nanometer area of the of the soft polymer film melted due to polymer – ion beam interaction and sudden quenching leads to semi-crystalline zone converted into amorphous zone followed by the generation of the free radical inside the amorphous zone. The amorphous zone such as path of ion beam/ latent track was oxidized using the optimized condition of the selective chemical etchant, potassium permanganate and alkaline sodium hydroxide solution at 65 °C for 4 h. The

nanochannel dimension can be tailored by the influence of the Fluence of the heavy ions (ions/cm²), nature of heavy ions; bombardment condition like direct beam or scattered beam and polymer matrix, the etching condition such as temperature, time and etchant condition also influence the channel dimensions. How to tune the channel dimension by the variation of the above parameter. Nanochannel Dimensions are significantly varies in nanohybrid membrane against to the Pristine PVDF membrane, this variation in the channel dimension due the dispersion of the 2-D layer silicate in pristine PVDF which intercalates the polymer chain and gives the mechanical strength and Toughness of the membrane.[94] Because of this intercalation after the irradiation the uniform nanochannel is formed in case of the Nanohybrid membrane. The role of the nanoclay to control the channel dimension and uniformity of the channel [21]. Channel size of the membrane can be controlled either by using different size swift heavy ion or Fluence (ions / cm²).

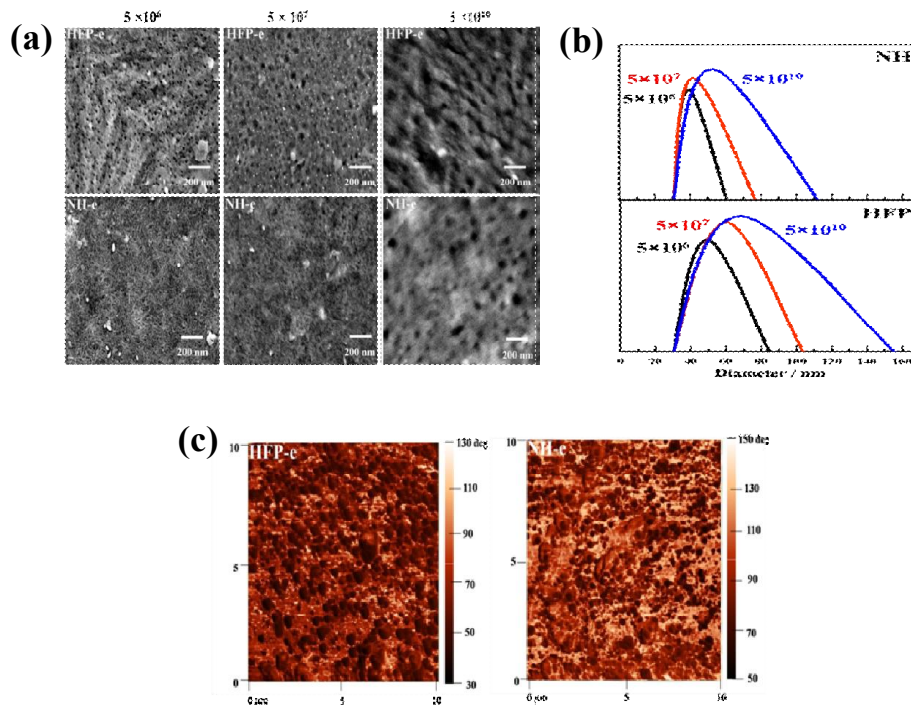


Figure 1.11: Morphological studies (a) SEM mages of the HFP and its nanohybrid membrane with various fluence: (b) channel distribution analysis using the Image-J software after the chemical etching; (c) AFM morphology of HFP-e and NH-e at a fluence of 5×10^{10} ion/cm².

In Jana et. al, they varied the fluence to manage the pore size [49] keeping the similar ion (Si), The average channel dimension varies ~ 45 nm and ~ 35 nm in HFP and nanohybrid membrane at fluence 1×10^7 ions/cm², but after the fluence variations (1×10^{10} ions/cm²) the lager channel dimension for example ~ 60 and ~ 44 nm in case of HFP and nanohybrid membrane respectively, and the morphological studies SEM and AFM images with channel distribution were shown in **Figure 1.11**. The basic reason large channel dimension is the greater number of the ions irradiated same locations means overlapping of ions beam leads to the larger channel dimension after the chemical treatment of the amorphous zone and another previous paper of Jana et .al. varied the size of the swift heavy ions (Li^+ and Ag^+) keeping the constant fluence 5×10^7 ions/cm² [19] in nanohybrid membrane, formed controlled channel size & their distribution, from the size variation of the ions we are notify that the variation of size of the bombardment particle also effect the channel size, in the case of the Li^+ ion bombardment the avg. size of the channel has been found as 30 ± 5 nm and in case of the Ag^+ ions bombardment the avg. size were found as 60 ± 5 nm.

The channel dimension and its number density also influences due to the variation of the temperature. From the literature survey Rohani et al. explained the variation of the nanochannel dimension after the variation of the etching temperature.[95] The SEM images

shown in **Figure 1.12**, and conclusion of the SEM images with increases the temperature increase the channel dimensions

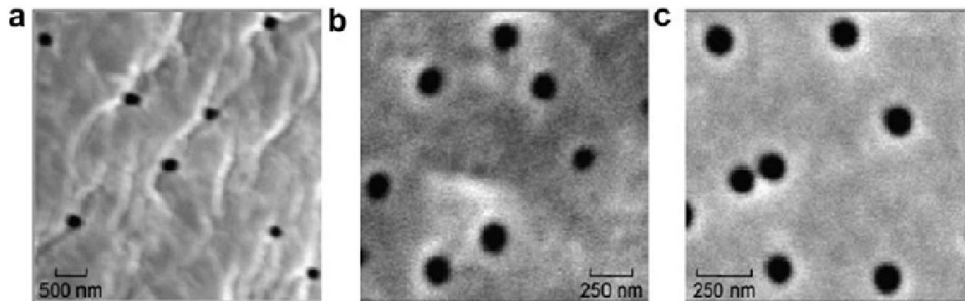


Figure 1.12: Surface latent track after the variation of the temperature keeping the ions (^{129}Xe) and fluence is constant and chemical etchant used alkaline KMnO_4 (a) $120\text{ }^\circ\text{C}$ channel dimensions $\sim 180\text{ nm}$ (b) $25\text{ }^\circ\text{C}$ channel dimension $\sim 120\text{ nm}$ (c) $-84\text{ }^\circ\text{C}$ channel dimension $\sim 100\text{ nm}$.[95]

Grasselli et al. have prepared etched track membrane by the bombardment of the Heavy ions (Sn) beam on the piezoelectric β -phase PVDF foil and reported the variation of the channel dimension by the variation of the etching time and etchant conc. at constant temperature and fluence. The details of the channel dimension shown in **Table 1.2:**

Table 1.2: Channel diameter after etching process of Sn exposed on the piezoelectric β -phase PVDF thin foils at oxidizing agent 0.25 mol L^{-1} aqueous KMnO_4 solutions with various alkaline conc.[96]

S.No.	Alkaline Conditions	Temperature ($^{\circ}\text{C}$)	Time (h)	Pore diameter
1	KOH 9 mol Lit^{-1}	55	1	82 ± 8
2	KOH 9 mol Lit^{-1}	55	5	114 ± 18
3	KOH 0.9 mol Lit^{-1}	55	5	No tracks
4	KOH 0.9 mol Lit^{-1}	55	18	$< 20 \text{ nm}$
5	KOH 0.1 mol Lit^{-1}	55	5	No tracks
6	KOH 0.1 mol Lit^{-1}	55	18	No tracks

Furthermore, the variation of the channel dimension after the irradiation of the various ions with energy is reported in **Table 1.3**.

Table 1.3: Results of the etching of the PVDF films which were irradiated with various ions and fluence.[95]

Ions Beam	Energy (MeV/n)	Fluence (Ions /cm ²)	Pore diameter (nm)
^{208}Pb	11.1	3×10^6 to 3×10^{11}	305 ± 31
^{29}Xe	3.5	3×10^6 to 3×10^{11}	118 ± 11
^{84}Kr	6.2	3×10^6 to 3×10^{11}	109 ± 14
^{58}Ni	6.7	3×10^6 to 3×10^{11}	93 ± 8

1.12 Literature survey on Ionic Membrane characteristics:

Moreover, the evidence of the functionalization carried out using the NMR, FTIR, UV-Vis. and EDX are reported in literature, structural modifications by XRD, XRD deconvolution used for phase fraction, thermal and mechanical characterization using TGA and UTM respectively. After the evidence of the functionalization the membrane characteristics for

example water uptake for hydrophilicity, ion exchange capacity (IEC) and using these two value calculate the water content and others parameters like proton conductivity, activation energy and degree of the functionalization / degree of sulphonation examine of the functionalized membrane. The parameters of membrane characteristics against various membrane materials and their processing technique were given in **Table 1.4**.

Table 1.4: Ionic membrane characteristics of the various functionalized membrane materials.

Membrane/ properties	Processing/ Technique	Thickness(μm)	(% WU)	IECm mole /gram	(%DS)	($\text{k}^{\text{m}}/\text{S}\cdot\text{cm}^{-1}\times 10^{-2}$)	Ref.
Nafion@117	Chemical	175	38	0.9	27	9.56	[97]
PVDF-s	Chemical	130	22	0.36	27	0.06	[98]
PVDF -NH-s	Chemical	130	27	0.50	32	0.50	[49]
HFP-18	Chemical	80	12	0.78	18	3.72	[23]
PVDF-sty-s	Radiation	30	10	0.22	14	0.05	[1]
NH-sty-s	Radiation	30	14	0.33	16	0.13	[1]
PVDF-3HT-s	Radiation	50	15	-	25	4.59	[60]
NH-3HT-s	Radiation	50	20	-	30	4.21	[60]
QAPPESK	Chemical	50-100		-		0.052	[100]
QAPVA	Chemical	~300		-		0.073	[101]
FEP-g PVBMAOH	Chemical	~50		1.0		0.011	[102]
FEP-g PVBMAOH	Chemical	~60		0.7		0.021	[103]

QPESN-2	Chemical	~200		2.12		0.067	[104]
FPAES-Im-52	Chemical	-		1.92		0.036	[105]

1.13 Literature survey for Polymer electrolytes membrane and fuel cell efficiency:

The functionalized membranes used for fabrication of the fuel cell stack followed by measurement of electrical efficiency. Different membrane material such as including poly(phenylene oxide), Polybenzimidazole, poly(ether sulfone), and poly(ether imide) and fluoropolymer such as poly(vinylidene fluoride) (PVDF) and its copolymers such as (PVDF-HFP), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-CTFE), (PVDF-TrFE), poly(vinylidene fluoride-co-chlorotrifluoroethylene), poly(vinylidene fluoride-co-trifluoroethylene) and one most important membrane Nafion are being used to make PEMs. In all above listed polymer the PVDF is suitable polymer for fuel cell membrane because of the cost, flexibility, thermal stability and long term durability.[106] The electrical efficiency / Fuel cell of various membrane electrode assemblies were are given in **Table 1.5**.

Table 1.5: Comparative Fuel cell efficiency of the various membrane electrodes stack.

Membrane	E_a (KJ mol ⁻¹)	$P(\times 10^{-7}$ cm ² s ⁻¹)	$SP(\times 10^5$ S s cm ⁻³)	OCP (V)	P_{max} (mW/c m ²)	I_{max} (mA/cm ²)	Ref.
Nafion 117	6.52	13.10	0.72	0.73	51.2	140	(97)
HFP-g-s (styrene)	6.36	2.91	3.7	0.60	28	140	[8]
HFP-NH-g-s (styrene)	5.79	1.84	1.8	0.63	31	140	[8]
CTFE-g- s(styrene)	8.2	4.54	0.56	0.60	30	200	[99]

CTFE-NH-g- s(styrene)	8.3	4.43	0.78	0.53	44	200	[99]
HFP-3HT-s	6.09	5.86	1.3	0.66	39	140	[21]
HFP-NH- 3HT-s	4.74	6.76	1.3	0.68	45	140	[21]
PVDFNF- Nafion	3.0	-	-	0.89	240	470	[107]
Poly(arylene ethers)	-	-	-	0.71	161	446	[108]
Cross-linked poly(vinyl alcohol)	2.69	1.14	3.00	-	-	-	[109]

1.14 Literature survey on the Radionuclide managements and tracing:

Ion exchange is the process of the exchange of the ions between a solution and a solid subtract, leading to the purifications, separation, and decontaminations of the many ions containing aqueous solution using the solid inorganic or organic ions exchangers. The ion exchanger has fixed charge sites allow to exchange the opposites charged mobile ions. Ion exchange membranes mainly cation exchange membrane has played important role in the field of the radionuclide waste management technology and cation exchange groups like strongly acidic sulphonate group or less acidic phosphate groups and covalently bonded carboxilates on the back of the polymer are generally are used for the f-block element separations. The ion exchange capacity depends upon the particular fixed ions potentials. All Pu species example Pu^{+4} , Pu^{+3} , PuO_2^{2+} , hexavalent UO_2^{2+} , and Am^{3+} are retained well in low acidic solution and the wash out as high acid concentration.[110][25] Several polymer based ion exchanger are reported in literature or developed used as sorbent for radionuclide tracing. Two bi-functional polymers HEMP-co-AMPS and HEMP-co-APTAC synthesis by free radical polymerizations using phosphoric monomer for the trace amount

of Pu (IV) extraction in large excess U (VI). [110] PES membrane for different morphology and surface grafting membrane are carried out sorption experiments towards U (VI), Pu (IV), and Am(III) ions in acidic medium. For Pu determinations thin film of quaternary amine bearing polymer [111] and polymer films formed on glass or silicon substrate using the deep coating or spin coating method.[112] Recently, many amide and fluoropolymer based sulphate and phosphate bearing porous polymer thin film are used for the radionuclide waste management the reasons behind it is these thin film are radiations resistances.[113]

1.15 Motivation of the works and objective of the present work:

Through literature survey, I have found that Nafion membrane have been widely used in fuel cell technology as electrolytic membrane. But due to some drawback of the commercial Nafion membrane like high cost, high methanol cross-over and reduce the proton conductivity at higher temperature. Many research group have reported and developed various functionalized membrane with various techniques used which is leads to easy production and replace the commercial membrane by removing shortcoming of the Nafion membrane and motivated me to do my research work in this area. On the other hand, in the view of above crucial points, the following objectives are considered for my present work.

- ✓ To study the controlled nano-channel formation PVDF and its copolymer (HFP, CTFE, TrFe) and also see the effect of the nanoclay dispersion.
- ✓ To study the electro active phase conversion such as β - and γ -phase of PVDF and its copolymer after the nanoclay dispersion.

- ✓ To analyze the chemical etching conditions after the formation of the latent track in both pristine polymer as well as its nanohybrid membrane.
- ✓ To study the extent of the grafting within the nanochannel and grafting / tagging of the monomer inside the channel confirm through the spectroscopic techniques.
- ✓ To study the ionomer formation after the grafting of the nanochannel for fuel cell membrane.
- ✓ And further investigate the membrane characteristics such as Water uptake (WU), Ion exchange capacity (IEC), Proton conductivity (k^m), Activation energy (E_a) and fabricate the fuel cell stack of the functionalized membrane and measure the fuel cell electrical efficiency.
- ✓ Furthermore, the functionalized membrane used for radio waste management in nuclear power plant.