

Membrane in Polymer Fuel Cells

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Abstract

Generally, the membrane is referred to as any thin, permeable or semi-permeable skin or curtain. The membrane has a selective permeability that acts like a dam (barrier). The most important feature of a membrane is its chemical nature. The chemical nature of each membrane contains the presence of molecular groups, its microcrystalline structure, cavity statistics (cavity size, distribute cavity size, density, volume size) and its structural symmetry. The most important properties of each membrane in terms of performance in a separation system are permeability and selectivity. In this paper, we first describe the membrane and its properties, applications, separation mechanism and as well as the membrane in polymer fuel cells. Then, we explain the porous membranes, membrane of polymer nanocomposite, fuel cell of membrane-electrode, layer electrode retaining elements in membrane fuel cells-electrodes, flow collectors, transferring reactants to the membrane electrode fuel cell, the characteristics of the oxidation current/transfer collector plates, characteristics of the collecting plates, the flow/ transfer of the fuel (hydrogen) and the construction of a membrane-electrode fuel cell.

Keywords: Membrane; Transport; Electrode fuel cell; Separation processes; Purification; Condensation; Electrical potential

Introduction

For nearly half a century membrane processes have a very high position in the separation and extraction industries. In fact, the use of membranes in the processes of separation, extraction, condensation, and purification of products is possible continuously and without the addition of another substance. Membrane processes are currently being used in various industries, including the food industry (juicer refinement, milk, and lactose refinement), medicine (hemodialysis with artificial kidneys) and drinking water purification [1]. Membrane processes have the following benefits according to their applications in different industries:

- Energy saving during separation, in most cases, the separation is carried out without changing the phase and the solution temperature
- Simple technology and easy to use
- Environmental compatibility and minimum damage to the environment
- Production of very high-quality products
- High flexibility in system design
- Possibility to combine with other separation processes
- Easy to clean the system

Membrane Separation Processes

A membrane such as a selective physical barrier can be defined; it separates the two phases and limits the transmission of some of the compounds in the solution to the surface of the membrane due to the chemical potential difference. A membrane is permeable to some molecules approximately, and therefore it is called semi-permeable membrane. If the process of separation in a liquid phase is controlled by the difference in pressure, it is called membrane filtration. In this case, it is possible to remove the solvent (In most cases, water) from the solution (or a suspension). A membrane is commonly characterized by two important properties; one outflow from the membrane per unit area or flux and the other is the amount of retention (the molecular percentage that does not pass through the membrane).

Generally, the function of a membrane process is based on two principles:

1. The chemical potential difference of particles in the fluid on both sides of the membrane
2. The ability of the membrane to transport some particles on it

Various motive forces interfere with the transport of materials from a membrane. These forces can be due to differences in pressure, concentration, heat and electrical potential [2].

Separation Mechanisms

In general, there are three types of membrane separation mechanisms:

Molecular sieve

Only compounds whose molecular size is smaller than the diameter of the membrane's pores (typically polymeric materials) can be transmitted through membranes. These types of membranes, called "porous membranes", are used for the filtration process of Liquid-Liquid or Liquid-solid Solutions. According to the definition of IUPAC, porous membranes can be divided into three groups according to the diameter of the pores.

1. A membrane with small pores, the average diameter of the pores in this membrane is less than 2 nm
2. A membrane with medium pores, the average diameter of the pores in this membrane is between 2 and 50 nm

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3. A membrane with large pores, on average, the pores in these membranes are larger than 50 nm [3,4] (Figure 1)

Molecular permeation

In non-porous or dense membranes, the separation mechanism is controlled by the permeation of the molecule into empty spaces within the membrane constructor's macromolecules. Dense membranes, such as homogeneous materials, are considered according to the mechanical performance of a membrane with a thickness between 1 and 300µm. Naturally, as the thickness of the membrane increases, the permeability of the membrane decreases. In such membranes, the ratio of amorphous areas to crystalline areas will have a significant effect on membrane performance. The molecule transfer and selectivity are due to the permeation in which solvent-polymer and solute-polymer interactions play an essential role. These non-porous membranes are often used for gas purification or in the reverse osmosis process [5,6].

The difference in ionic load (Ion charging)

Finally, the third type refers to separation mechanisms are most commonly found in ion exchange membranes. In this mechanism, the separation is controlled and guided by the molecular ion charge in the solution and the density of the ion charge on the membrane surface [7].

Membrane Classification

In all separation processes, in order to transfer material from one phase to another, the motive force is required to overcome the chemical potential difference. Separation processes are divided into different types according to the type of motive force as shown in Table 1.

The concentration gradient is the motive force that results from the chemical potential changes of the two-phase solution divided by the membrane. The two divided solutions have different chemical activity depending on the type and concentration of the various materials present in them (solvent, ions or neutral molecules). These materials are transferred under the mechanism of permeation to the other side of the membrane, to reduce the chemical potential to balance. The electrical potential gradient may be due to the presence of two different ions on

both sides of the membrane. The pressure gradient on the membrane surface may have a physical nature (hydrostatic pressure) or a chemical nature (osmotic pressure). The filtration processes, which are driven by the difference in pressure, are classified into four types of process, depending on the size of the molecule soluble in the solution. The basic methods of filtration are determined by considering the average pores radius, the transfer mechanism and the applied pressure shown in Table 2.

Reverse osmosis

In reverse osmosis type membranes, the diameter of the pores is less than nm and very dense. This type of membrane has a retention of more than 95%. The retention rate in this type of membrane follows to the permeation-solubility mechanism and because of this; the flow rate of the membrane is low. The pressure used in this filtration process is 60 to 80 bar. Industrial reverse osmosis applications that relate to water purification and condensation of solutions include:

- Desalination of salt water and seawater (salt content between 1 and 10 g/l) for the preparation and production of drinking water
- Providing Ultrapure Water for the electronics and pharmaceutical industries
- Concentrate on the juice of antibiotics, amino acids
- Purification and reuse of used water [9,10] (Figure 2)

Nanofiltration

This process depends on the application and type of separation mechanism placed between reverse osmosis and ultrafiltration processes. The size of the particles separated by this type of membrane is in the range of nm (2 to 10 nm) and the applied pressure is between 5 and 30 times.

The main applications of nanofiltration can be found in the following:

- Water treatment involves desalination groundwater and surface water

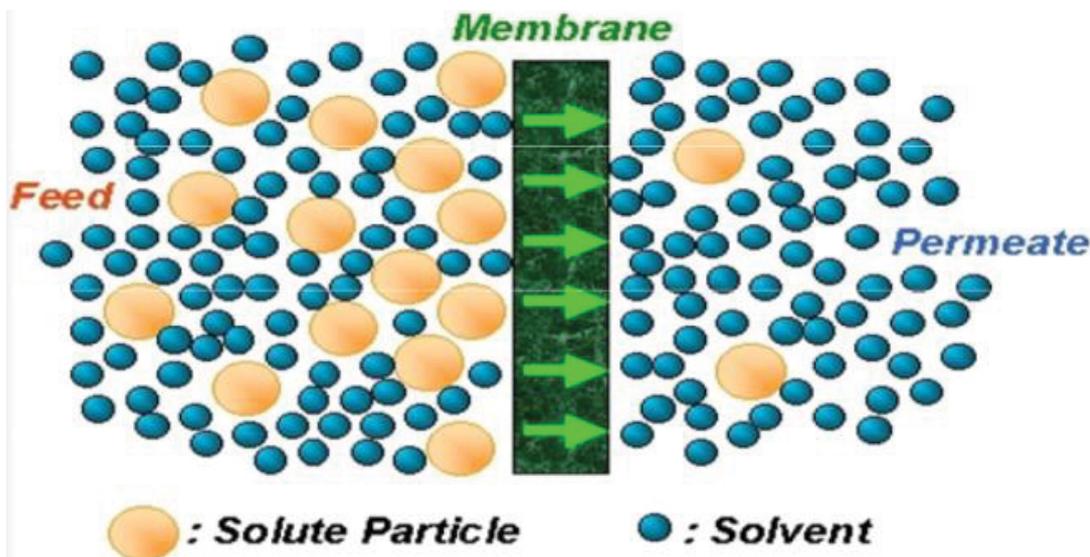


Figure 1: A schematic of how the membrane functions [3].

Process	Nature of concentrated solution	Nature of the purified solution	Motive force	Membrane structure
Microfiltration	Liquid	Liquid	Pressure	Membrane with large pores
Ultrafiltration	Liquid	Liquid	Pressure	Membrane with medium pores
Nanofiltration	Liquid	Liquid	Pressure	Membrane with small pores
Reverse Osmosis	Liquid	Liquid	Pressure	Dense membranes
Dialysis	Liquid	Liquid	Concentration	Membrane with medium pores
Evaporation	Liquid	Steam	Chemical activity	Dense membranes
Electrodialysis	Liquid	Liquid	Electric potential	Ion-exchange membranes

Table 1: Categorization of membrane processes for purification of solution.

Processes	Reverse osmosis	Nanofiltration	Ultrafiltration	Microfiltration
Pores radius (nm)	Less than 0.5	0.2-5	2-50	More than 50
Pressure (MPa)	2-8	0.2-5	0.1-5	0.0-1.5
Transmission mechanism	Permeation- solubility	Permeation- solubility	Displacement	Displacement
		Displacement	Molecular sieve	Molecular sieve
		Ionic repulsion		

Table 2: Features of various filtration processes.

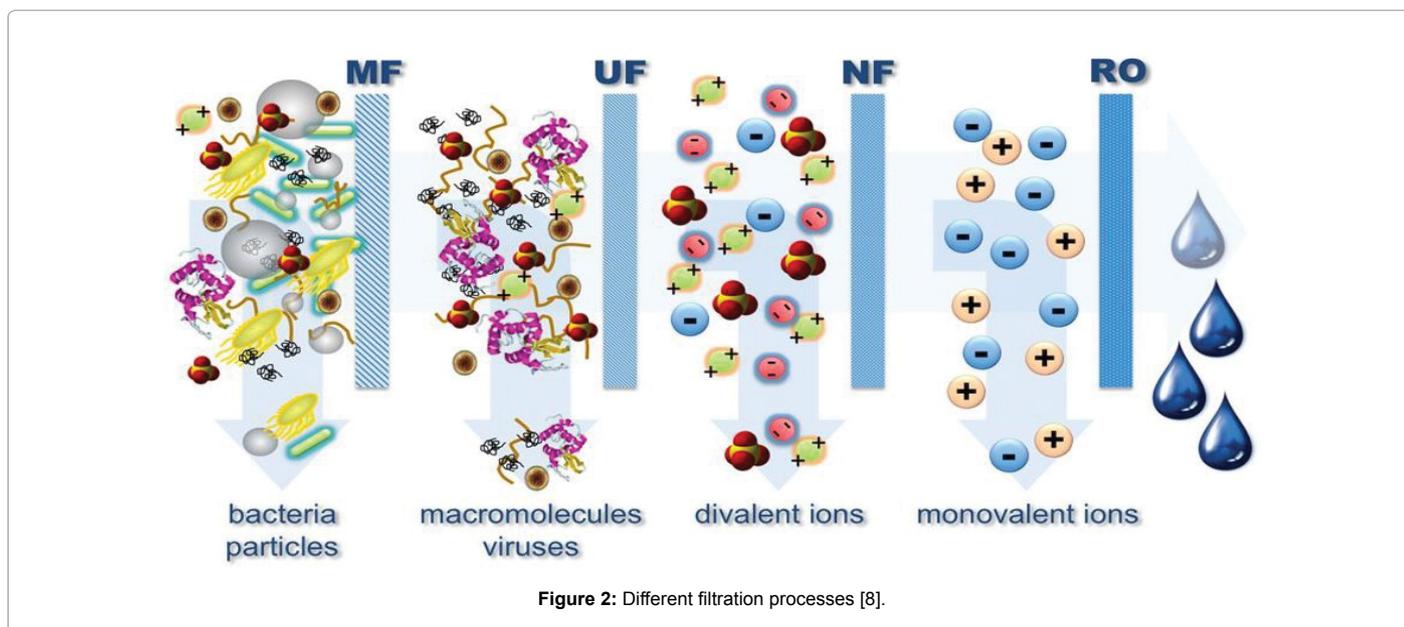


Figure 2: Different filtration processes [8].

- Food and milk industries, including the isolation of minerals such as lactose, amino acid separation, and peptides
- Wastewater in the paper, wood and dyeing industries [11-14]

Ultrafiltration

Ultrafiltration is used to condense macromolecules or emulsions and low molecular weight solute can easily pass through this type of membrane. The applied pressure in this process is between 0.5 and 10 times.

The main applications of this process are:

- Purify and disinfect drinking water
- The concentration of lactose and milk proteins
- Isolation of water-oil emulsions
- Purification of dye bath by electrophoresis [15-17]

Microfiltration

This process is used to separate solid particles and suspensions. The size of the particles separated by this membrane is about 0.2-10 micrometers. Due to the type of membranes with large pores, the outflow is very high. The pressure range used in this type of process is between 0.1 and 5 bar. In fact, microfiltration is used in the food and biological industry to separate suspended particles and bacteria [18].

Characteristics of Filtration Membranes

Permeability coefficient

The membrane permeability coefficient is the flux output of the membrane per unit pressure, which is obtained using the following formula [19].

$$L_p = J/P_e$$

L_p = Permeability coefficient of the membrane in liters per hour per square meter per bar

P_e = Effective pressure on the membrane in bar

J = The flux of the outlet flow from the membrane is typically in liters per hour per square meter or in m^3/s

Nanomembrane structure

The membranes used in the nanofiltration process are made of organic or inorganic nature, made of polymers or metal oxides and have an asymmetric structure. A nanomembrane consists of three layers, each of which has a special role:

- An initial layer has pores with diameters greater than 50 nm in order to provide good mechanical strength to the membrane and the possibility of obtaining a high flow rate
- One or more intermediate layers with a pore diameter of between 2 and 50 nm, which provides a connection between the protective layer and the active layer
- An active layer through which the separation is performed by the Nano-filtration process. The thickness of this layer is relatively low and is often less than the micron and the diameter of the pores is on a nanometer scale. The size distribution of these pores is too narrow. This layer, while having high flow rates, has a special feature in selecting the process of separating ionic and nonionic particles with molecular masses of less than 2,000 grams per mole

Beyond this general structure, nanomembranes possess special physical and chemical properties related to their organic or mineral nature [20-23].

Characteristics of Organic Polymeric Membranes

Nanomembranes made of organic polymer material, similar to the reverse osmosis membranes, have a composite structure that is made in a two-stage process as follows:

1. First, a polymeric porous layer with a pore diameter larger than 50 nm in the thickness between 40 and 100 μm is placed in the middle layer on a woven or non-textured surface
2. Then, an active layer with a low thickness (1-2 μm), is produced by processes such as polymerization on the previous layer

The intermediate layer is an anisotropic element that is often based on polysulfone. This layer has a very high permeability. Some

membranes may have several mid-layers. The active layer should have good mechanical and chemical resistance, in addition to having special retention in the separation process. For example, some of the active layer through interlayer polymerization is created by three-component aromatic compounds on the middle layer. In the first view, the ability to isolate the active layer is considered to be under the influence of a physical barrier created by the membrane that passage of this membrane depends on the molecular size of the particles. In other words, particles that have a diameter less than the diameter of the pores of the active layer can pass through this layer and thus the larger particles remain. The ability of nanomembrane separation is related to the effect of ionic load due to the chemical nature of the polymers used in the manufacture of this active layer.

In fact, there are active groups, such as amide, carboxyl, and even sulfone, among the active ingredients that make up the active layer of nanomembranes. These groups may either become permanently or pH-dependent solutions that come in contact with this membrane to be ionized. The effects of ion load on the transfer properties of nanomembranes in the next chapters will be discussed theoretically (Figure 3) [24,25].

Theory Based on the Thermodynamics of Irreversible Processes

Based on this theory, the equations describing the solvent flux (J_v) passing through the membrane are respectively.

$$J_v = L_p (\Delta p - \Delta \Pi)$$

$$(C_m - C_p) + (1 - \delta) J_v \bar{c} (J_s = \omega)$$

Δp : Pressure gradient imposed on the membrane

$\Delta \Pi$: Osmotic pressure difference on both sides of the membrane

\bar{c} : Medium concentration in the membrane

$C_m - C_p$: Radium concentrations on both sides of the membrane

L_p : Solvent permeability coefficient (m/sec/pa)

ω : Resolved permeability coefficient (m/sec)

δ : Reflux coefficient (That is numeric without dimension and between 0 and 1 varies by type of solved).

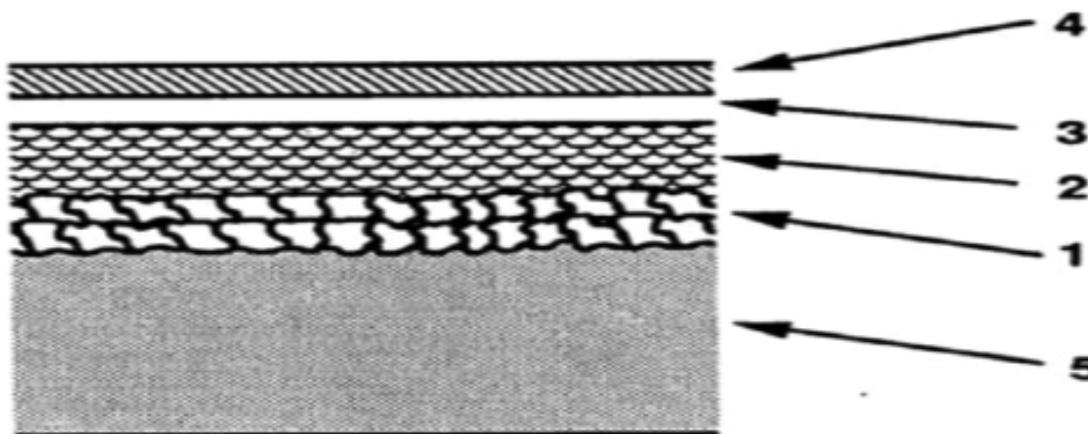


Figure 3: Introducing the schematic structure of a multilayer nanomembrane structure [24].

For $0=\delta$, Transition phenomenon Similar to the ultrafiltration process was generally of the type of displacement and for $1=\delta$ Transition Phenomenon Similar reverse osmosis, all are intrusive.

Intrinsic retention (R_{int}) of a Solved is based on its concentration on the membrane surface on the retention side (C_m) and its concentration permeated on the side (C_p) as follows is defined.

$$R_{int} = \frac{(C_m - C_p)}{C_m}$$

Therefore, the intrinsic retention can be described in terms of the Flow of solvent in Equation.

$$J \left[\frac{(1-\delta)\Delta X}{P} \right] = \ln \left[\frac{C_{p,\delta}}{C_p - C_m(1-\delta)} \right]$$

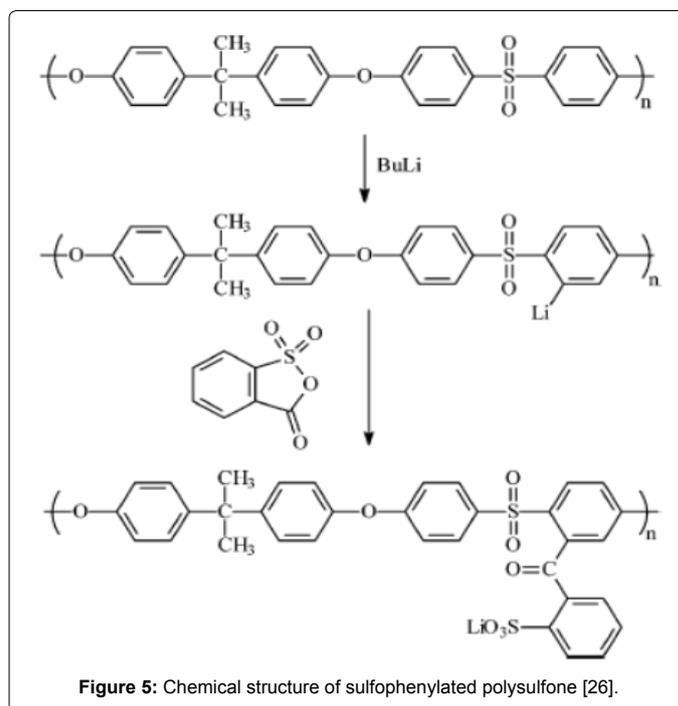
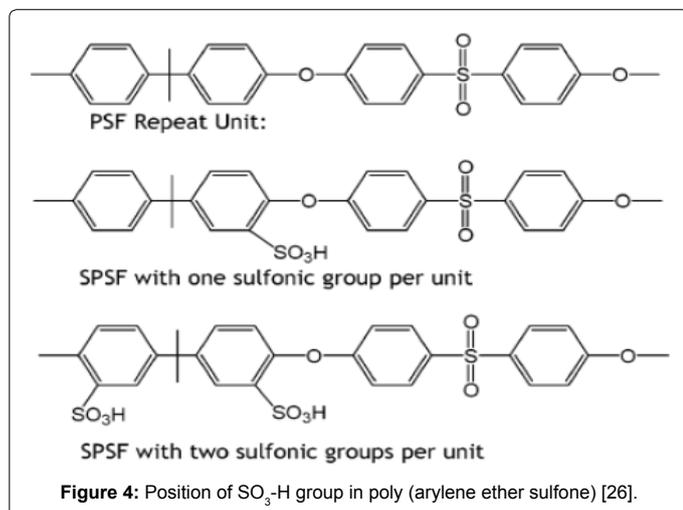
Therefore, the amount of intrinsic retention can be described in terms of solvent flux in the form of the following equation [26,27]:

$$R_{int} = \frac{\delta(1-\beta)}{1-\delta\beta}$$

$$\beta = \exp \left[-\frac{(1-\delta)J_v\Delta X}{P} \right] = \exp[-P_c]$$

Material and Methods of Making Nanomembranes

Asymmetric membranes consist of a multi-layered structure in a way that Porosity, pore size, and even combination and the kind of membrane change from the different side. Usually, these membranes have a delicate and selective layer that is supported by a thick layer with more permeability. Due to the low thickness of the selective layer, the Debi of the passing current of the membrane is high. The secondary layer provides the required mechanic resistance of the membrane for the application in the membrane process until Loeb and S Sourirajan produced the first membrane with high permeability, which is Suitable for reverse osmosis process. The importance of asymmetric membranes was not known. Today, the method of making this type of membrane is known as this S Loeb and S Sourirajan method. The discovery of them revolutionizes the membranous processes and the asymmetric reverse osmosis membranes produced by them have higher permeability compared to the previously produced symmetric membranes and the same polymeric materials. For a while, the aforementioned technique was the only method used to make asymmetric membranes until other methods were applied from the 1960s onwards (Figures 4 and 5) [26-28].



Manufacturing Methods

Loeb and Sourirajan used a primary polymer in the manufacturing of membranes and only the porosity and size of the pores were different in diverse layers of the membrane. Today, with the development of new methods, asymmetric membranes are produced and manufactured with different polymer materials. One of the most important of these methods is the interlayer polymerization process that was used for the first time by John Cadott. The most important methods for making asymmetric membranes are mentioned below [29].

Phase separation

The application of this method in producing the membrane, which is the S Loeb and S Sourirajan technique, requires the coagulation and deposition of a 10-fold polymeric film when immersed in a non-solvent (typically water) polymer. For coagulation, various other methods, such as coagulation by solvent evaporation, coagulation through the absorption of water from the vapor phase and coagulation by reducing the polymer film temperature, can also be used [30].

Intermediate polymerization

In this method of polymerization of a suitable monomer, a polymer film is used as a very thin layer at the surface of another polymer layer which is previously prepared for asymmetric membranes [31].

Soluble coating

In order to provide these membranes, one or more layers of thin and dense are coated on another polymeric surface.

Corrective methods

There are other corrective methods for the preparation of asymmetric membranes, which are fully referred to in the previous section.

Polymeric Materials Consumed in Nanomembrane

Among the polymeric materials that are mostly used in the manufacturing of nanomembranes as protective coatings, the following materials can be mentioned: Polysulfone, Polyethersulfone, Cellulose acetate, polyacrylonitrile [32].

Polysulfone membranes

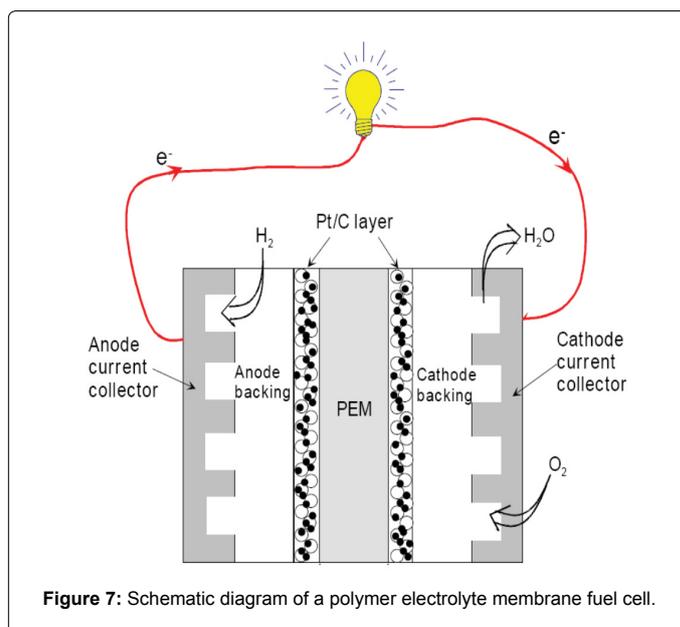
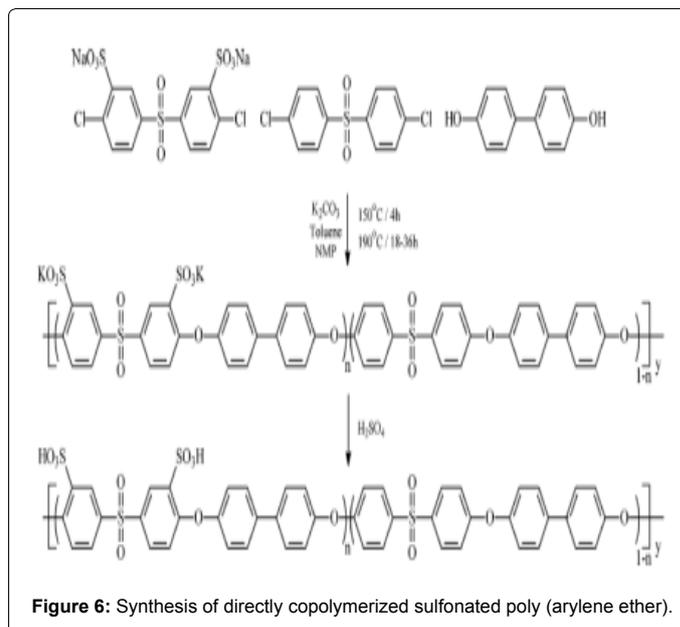
Polysulfone and polyethersulfone polymer materials for mechanical, thermal, and chemical resistance and also because of their homogeneous properties, they are so much used to produce ultrafiltration membranes or microfiltration as raw material.

- Heat resistance: In most cases, temperatures up to 75°C are used. (Some polysulfonated membranes can also be used up to 125°C)
- Usable in a wide range of PH: Poly-sulfone can be used continuously within the PH range from 1-13, therefore resistant to acid or alkaline washings
- Sufficient resistance to chlorine: most manufacturers recommend using chlorine up to 50 ppm continuously and even 200 ppm to clean and maintain membranes described
- Easy to produce membranes in different geometric shapes
- Provision of different geometric aperture sizes for ultrafiltration applications ranging from 1 to 20 nanometers in proportion to MWCO between 1 and 500 kilo Daltons (kDa or kD)

On the other hand, the polysulfone polymer is naturally photoactive and produces radicals due to ultraviolet radiation. This study was examined by Belfort and his colleagues in 1995. In their studies, they used different modeling compounds, each of which introduced a part of the polysulfone polymer. They are solutions of Phenolic sulfone, phenolic ether, one mixture of phenolic ether or base (phenyl 4 hydro) sulfone as optical light for polymerization 2-hydroxyethyl methacrylate (vinyl monomer) used under the influence of ultraviolet radiation with a wavelength of 253.7 nm and measured the amount of polymer formed as a function of time. They observed that the Base (Phenyl 4 Hydro) Sulfone is the most optical light. And this part of the polymer molecule is the main chromophore that makes the polysulfone the more photoactive. Therefore, they suggested the following observations and the mechanism for optical modification of polysulfone membranes. According to the proposed mechanism, in the first step the combination of base (phenyl 4-hydroxy) sulfone in the polysulfone polymer chains and absorbing light and production of two free radicals. This two free radical has been active and polymerization reaction in the presence of Monomer Vinyl occurs in these places (Figures 6 and 7) [33-35].

Cellulose acetate membranes

Loeb and S Sourirajan used materials of Polymeric of cellulose acetate to make their first commercial reverse osmosis membranes. These membranes are asymmetrical and has a retention rate of 99.5 per cent of the solution of 52.5 grams per liter of sodium chloride with the outflow rate of 5 to 10 gallons per square foot per day (equivalent 9 to 19 liters per square meter per hour) within a range of pressures of 1500 to 2000 psig was. Acetate cellulose membranes are prepared from Stainless cellulose. Cellulose is a natural polymer found in plants such as cotton. Cellulose is a linear and relatively inflexible polymer. Due to this feature, the membranes made from it have good mechanical resistance. Acetylation of cellulose occurs by acetic anhydride in the presence of a sulfuric acid catalyst. The degree of acetylation, which represents the number of substituted groups instead of the hydroxyl



groups on cellulose, varies between zero to 3 where zero represents unreacted cellulose and 3 represents full cellulose acetylation, which is called cellulose tri-acetate. The degree of acetylation affects the properties of the resulting membranes so that with increasing that, the amount of retention by the membrane increases, but its permeability decreases and vice versa. Commercial acetate cellulose membranes used for the reverse osmosis process have an acetylation degree equal to 2.7 that in this case, there is an optimum state between the amount of salt retention and the permeability. Also, in the production of some membranes, a mixture of two polymers of cellulose acetate and cellulose tri-acetate is used. Mixing the two polymers increases mechanical resistance and resistance to hydrolysis, but reduces permeability. Cellulose acetate membranes have advantages that refer to them below:

- Easy preparation of these types of membranes

- It has excellent mechanical properties
- Resistance to chlorine (Free chlorine 5 ppm)
- Has a relatively high permeability

But they also have the following disadvantages:

- Sensitivity to hydrolysis, which reduces retention
- Sensitivity to PH changes (Only in the range of 4 to 6 are stable)
- Reduced the percentage of salt retention with increasing temperature (Therefore, the solution temperature should not rise from 35°C) [32-36]

Polyacrylonitrile

Polyacrylonitrile is a polymer produced by the polymerization reaction of acrylonitrile monomer by a radical chain mechanism. Acrylonitrile monomer is a Monomer vinyl which produces a reaction between propylene with ammonia and oxygen in the presence of a suitable catalyst which produces a reaction between propylene with ammonia and oxygen in the presence of a suitable catalyst. Polyacrylonitrile has high crystallinity and has a melting point and glass transition temperature of 319 and 87 degrees Celsius respectively. Polyacrylonitrile is used as a homopolymer in various industries, such as gas filtration systems, tents, shipping industries; construction as fibers for reinforcing concrete and for the production of ultrafiltration membranes, as well as for the preparation of nanomembranes as a protective layer. Polymers described in combination with other monomers are used as fibers in the textile industry as well as thermoplastic polymer materials in various industries. The copolymer produced by the polymerization of acrylonitrile and styrene monomers in the presence of polybutadiene is used in the manufacture of car bodies. The copolymer is very sturdy and lightweight which this is due to the presence of Nitrel groups in the polymer chain. Nitrile groups are very polar in acrylonitrile units. So they are strongly attracted to each other and causes the polymer chain to approach each other. Chains approaching increases the strength of the resulting polymer. Among the features that caused to be taken into consideration polyacrylonitrile widely available in the production of membranes, especially nanomembranes, are:

- Their high resistance to solvents
- Having high hydrophobicity into other Polymers to being used in the manufacture of membranes such as polysulfone, Polyethersulfone, Polyethylene, Polypropylene. (This makes the membrane less susceptible to the process of filtration of aqueous solutions than the pores obstruction phenomenon.)
- Resistant to chlorine solution and cleaning agents such as sodium hypochlorite and sodium hydroxide
- Providing membranes as easily as possible which is often done by a fuzzy separation method. In this method, using this polymer, the porosity and pore size of the membrane can be controlled by changing the concentration of the polymer and increasing the number of additional materials such as ionic salts and organic acids in the casting solution
- Easy modification of polyacrylonitrile membranes made from ultra to nanomembrane by processes such as changing the nature of nitrile groups, photopolymerization, plasma, etc. in the presence of vinyl monomers such as acrylic acid

- Having high thermal resistance (up to 130°C)

M Bryjak, et al. investigated the modification of polyacrylonitrile ultrafiltration membranes with sodium hydroxide. They noticed that the nitrile groups in the polyacrylonitrile polymer chain were hydrolyzed in the cadmium hydroxide solution and reduced the diameter of the membrane pores. Due to hydrolysis, the average diameter of the membrane apertures decreased from 2.6 to 0.6 nm. It was also observed that modified membranes were used in the nanofiltration process range. As the amount of calcium carbonate solution retention increases from zero to 50% [37-39]

Structure of Porous Membrane

Many methods are available to measure porosity. The most common methods is the method of Atomic microscopy or electron microscopy. Thermometry is also used to measure pore size and distribute them to the membrane surface. Different microscopic methods are used to observe the morphology of nanomembranes. Scanning Electric Microscope (SEM) is a method for obtaining an image of a sample by its radiation with an electron beam. Image separation power depends on the voltage used. In the case of polymer membranes, materials are ruined when using high voltages and usually, the isolation power is not greater than 5 nm, this method can only provide information about the membrane's macromolecular structure. Transmission Electron Microscope (TEM) for the analysis of morphology, thin surfaces of ultrafiltration membranes are used because its separation strength is greater than that of SEM [40,41]. Field scanning electron microscopy is used to overcome tool constraints, low separation power in SEM, and uncertainty in TEM. Field Scanning Electron Microscopy (FESE) is used to overcome tool constraints, low separation power in SEM, and uncertainty in TEM. With the electron microscope, the macromolecular structure of the membrane is well Visible, but it is difficult to verify and quantitatively the presence of pores smaller than one nanometer and There is also no information about the non-porous active layer. The thickness of the layer can also be determined using these methods for nanofiltration membranes. The Atomic Force Microscope (AFM) is one of the newest techniques for viewing the topography of the surface of the material. This technique has advantages in comparison with scanning electron microscopes and transmission electron microscopy such advantages as higher separation power, non-degradation of the polymer and the minimum need for special equipment for sample preparation. In this method, you can get a 3D image of the surface. This method is useful for obtaining information about the surface roughness of a nanoscale membrane and the interpretation of the membrane obstruction phenomenon. There is a direct correlation between surface roughness and membrane obstruction. The obstruction is higher in membranes with higher surface roughness, which causes the flow rate of the membrane to drop dramatically. Also, the Atomic Force Microscope (AFM) has been used to determine the pore size distribution in nanomembranes and from the dark sections in the profile of the stored digital lines, the size of the apertures is calculated.

Compounds used in Polymer Membranes

The membrane with per fluorosulfonic acid in its composition. The sulfonic acid groups are strong acid factors and are used as the catalyst in many reactions. In addition to sulfonic acid, carboxylic acid or a mixture of carboxylic acid and sulfonic acid could be used [42].

Keeping Polymer Membrane Moisture

In order to achieve a desirable function of the polymer fuel battery,

its polymer membrane should be kept moist. To do so, a fuel, which enters anode, is moisture by steam in order to send the necessary water to the electrolyte. (The water entering the anode are carried across polymer by protons and are added to the water produced in cathode) (The water accumulated in cathode should leave it). This water is transferred in two methods: one is its flow in electric osmotic and the other is reverse penetration of water. In other words, the water returns from the cathode. Thus, the water balance in the polymer electrode depends on the degree of electrical smoke and water reverse penetration. Usually, in order to achieve such an equilibrium, it is necessary to wet the gas in the anode so that it can reach the amount of water needed by the electrolyte. If air is used to oxidize water, its volume in stoichiometric term should be 2.5 times than hydrogen in anode; in this respect, 2.5 times of the produced water is discharged from cathode together with air. Hence, the amount of flow gas in the cathode is more than anode part that leads to water deficiency in the cathode. In order to transfer water on electrolyte polymer membrane, a mathematical model is suggested in which, the quantity of water transfer in the polymer is the difference between the electric osmotic flows, reverse penetration of water, as shown in following equation [43].

$$J_m = si / F$$

In which, F is the Faraday constant, J_m is the amount of water transferred from the polymer membrane, s is the net flow of water per electron mole and/or the current intensity.

J_m is the amount of water produced in the cathode section as defined below:

$$J_w = i / 2F$$

Electrodes are made of fine particles of catalyzed carbon. The proton conductor membrane is located between the electrodes and anode; too, has hygrophilous characteristics and more water-escaping property than cathode electrode.

The PH of the carbon particles solution in the anode is around 6-7 and in the cathode, it is 8-10; therefore, the carbon particles solution used in anode has more acidity characteristics proportion to the solution used in the cathode. The carbon particles of electrode have two types of pores:

1. The internal pores that appear in carbon particles as pits
2. The slit-shaped pores that exist between particles [44]

The carbon particles in anode have pores in 90 to 110-angstrom size. In cathode, their radius is 60-80 angstrom. In order to have a suitable and homogenous distribution of pores size, ball equipment is used.

1. Accumulator of the cathode current
2. Cathode-Anode current
3. Ionic exchange membrane
4. Anode
5. Collector

The catalyzed graphite layers are compressed to the membrane surface to connect each other. Before the connection of the electrode to the electrolyte, the organic and inorganic impurities of the electrode should be removed and the places of proton exchanges that do not exchange hydrogen ions convert into hydrogen ion exchange places. Therefore, prior to warming the electrodes for the purpose of

compression to the membrane, the electrodes are warmed up to the necessary temperature for the evaporation of volatile fluids. In the warm press place, the pressure enforce is around 1000-2000 pounds per square inch and the temperature degree of 120-150 for 1-5 minutes. The amount of pressure imposed might change per time; that is, less pressure for a longer time; vice versa.

Producing Membrane-Electrode Fuel Battery

In this fuel battery, the membrane of proton exchange is connected to anode and cathode. In any battery with high output, the degree of contact between porous electrodes and a proton exchange membrane is one of the important factors. If the electrode thickness is not homogenous and is not sufficient between electrode and membrane, a part of electrode stops operating and subsequently, output reduces. In this connection, it has been tried to have a full connection of electrodes to both membrane sides in polymer fuel batteries. This type of batteries is called membrane-electrode fuel battery. In this battery, two electrodes are connected to both sides of membranes; respectively and each one of the electrodes is inserted in the membrane in a given depth.

The maximum volumetric flow rate of water supplied to the membrane in the anode section is shown in the equation below.

$$J_A(\text{Max}) = PW(T) / (P_A - PW(T)) i / 2aF$$

a=amount of hydrogen used

P_A =Hydrogen consumption pressure

$PW(T)$ =saturated vapor pressure at temperature T (°C)

The maximum amount of water output from the cathode section, $J_C(\text{Max})$ is expressed as follows.

$$J_C(\text{Max}) = (PW(T) / (P_C - PW(T))) 5 i / 4cF$$

c=amount of air used

P_C =Consumable air pressure

In the process of oxidation-reduction reaction, one should pay attention to the point that the sum of water transferred from anode to cathode and the water produced in cathode should be balanced with the amount of water discharge and air from the cathode. In addition, it is an important point that the amount of water transferred via polymer electrolyte must be balanced with the amount of water consumed in the anode. If an amount of the water discharged from the cathode is more than an amount of water transfer (J_m) and produced water (J_m), it becomes possible to have the water remained in cathode part and subsequently, the cathode becomes dried. On the other hand, if the water consumed in the anode is less than water transferred, anode becomes dried and in both cases, the battery function becomes disordered. The maximum amount of J_m and the maximum amount of J_m depends on heat; that is, they increase as the temperature increases. Similarly, the values of J_c and J_a increase as temperature goes higher and ultimately, when the consumed air temperature is high, cathode dries out. For this reason, in order to prevent cathode, it is suitable to have the fuel battery operate in low temperature to save air and electrolyte from reduction. When the temperature of the consumed gas is low, the amount of water consumption and transferred water balance in the anode. When temperature lowers to a specific level, the amount of water consumption becomes less than transferred water and the problem of cathode dryness appears again. By lowering the thickness of polymer electrolyte membrane, the reverse penetration flow increases and in turn, amount of water transfer in general decreases, caused by

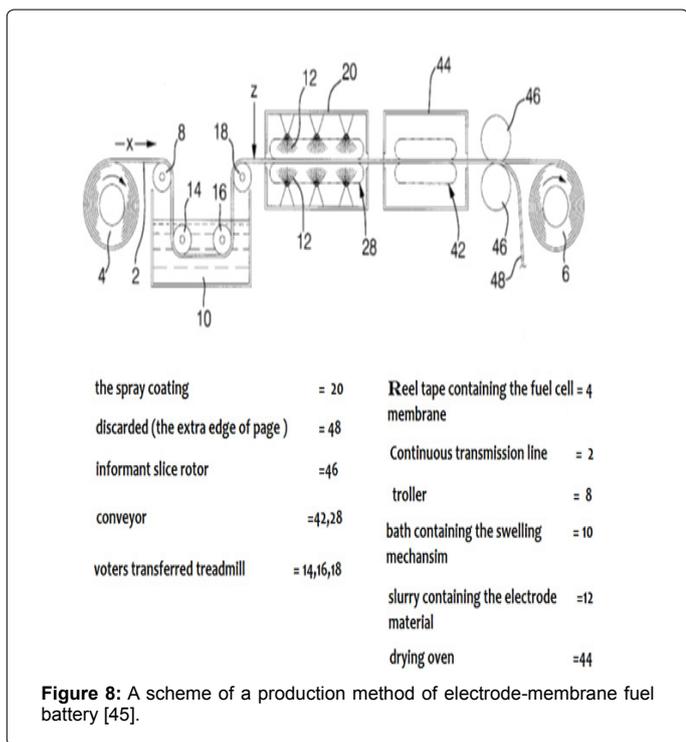
the gradient of water density in the membrane between cathode and anode and based on this case, it is suitable to reduce the thickness of membrane to save anode from drying [43,45].

Polymer Membrane Properties

Among the properties required for the membrane is its thinness (at high current density, the electrical resistance of the cell is proportional to the thickness of the membrane). By increasing the thickness of the membrane, the electrical capacity of the cell significantly decreases (Thickness less than 1.0 mm is desirable). The low membrane resistance increases its proton exchange capacity. There are a lot of Transverse Connections in Membrane (No transverse membranes have a limited capacity for proton exchange) Therefore, it's thickening, especially when working at high temperatures, loses its mechanical properties. In this way, the polymer material used in the membrane, whose crosslinking materials can lose volume. In this way, the polymer material used in the membrane, whose crosslinking materials can lose volume. However, other polymers, including polystyrene sulfone, can be used for membranes. But, they do not have the desired chemical stability for a long time. Among the optimal properties of the proton exchange membrane, it lacks the sensitivity during flow disconnection and bonding, and resistivity to layering (Figure 8) [45].

Polymer Membrane Preparation Method at Laboratory Scale

To prepare a proton exchange membrane, 25 g of polyether, which is up to 90% sulfone, is dissolved in 100 ml of dimethyl formaldehyde. The homogeneous solution is poured on a glass plate and then the surface is flattened. Once the membrane dried at room temperature for 24 hours, it can be detached from the plate (To separate the glass plate in a water bath). The polymer plate is heated to precipitate the catalyst (platinum) and under the pressure of about 5 mgcm⁻² platinum is covered on the membrane surface [43,45].



F=Faraday constant

J_m=The amount of water transferred from the polymer membrane

S=Net flow of water per mole of electrons

i=Flow

J=The amount of water produced in the cathode is expressed as follows.

$$J_w = i / 2F$$

Providing the amount of water required for the fuel cell of the membrane-electrode allows the membrane fuel cell to remain moist. The layers also transfer water generated in the cathode to prevent the phenomenon of immersion of the cathode, the maintenance layers are often coated with Teflon, so that the holes in the carbon fiber or the carbon plate are not closed with water and the reaction of the reactants to the catalyst layer is carried out at a suitable speed.

Flow-collector sheet and reactants transported to the membrane-electrode fuel cell

There is another plate outside of each layer of electrode-membrane fuel cell holder that has a dual role in the fuel cell performance:

1. Current collector
2. Reactants transporter

The sheets are made of light, solid, electron conductive materials and impervious to gas. Usually, these sheets are made of graphite and metals, but recently composite sheets have also been used. The first application of each page is to transfer the reactants to a membrane-electrode fuel cell. A part of the sheet that is in contact with the retaining layers has channels that remove gas from the reactant. The method of design of the channels, width, and depth of them has a great impact on the distribution of reactant gases, transport and delivery of water to the membrane. Because 0.021 of the air is oxygen in order to deliver enough oxygen to the cell, the amount of entering air should be 2 to 3 times the stoichiometric amount. As a result, the size of the oxidation passage canals should be wider than the size of the fuel passage channels. The best way to create a canal on the sheets is to use photolithography and chemical engraving, which makes the depth of channels more than 0.1 to 1 mm with an optimal depth of about 0.4 mm. The second function of these sheets is to collect the flow. The electrons which are obtained from the hydrogen oxidation should reach from the anode to the retaining layers. The sponge must be latticed. With such a design for the catalyst during the fuel cell operation, the pressure drop is not created. Also, the context from ceramic or carbon fiber or glass wool or zirconia fibers can be selected [45].

Electrodes retaining layers in membrane-electrode fuel cell

In the fuel cell of the membrane-electrode, the design of the retaining layers and bipolar sheets is such that the maximum flow is obtained from it. The supporting layers are attached to the anode and cathode and are made of a porous carbon sheet (carbon fiber or carbon paper). The thickness of the sheet is 100 to 300 microns (thickness 4 to 12 sheets of paper). These layers are made of electron conductive materials to transmit electrons to the cathode. Because these layers are porous, reactants can penetrate the catalyst bed of the fuel cell of the membrane-electrode. When the reactants enter the retaining layers, they penetrate the electrode membrane fuel cell through the pores of

the layers. The protective layers during the work of the fuel cell help to regulate the water inside the cell. If these layers are well designed from the point of view of the amount of ingredients and granulation.

Membrane-electrode fuel cell (MEA)

By connecting the anode and the membrane and the cathode to each other, a set is formed, which is called a membrane-electrode fuel cell. The first membrane-electrode fuel cell was built in the 1960s for the Gemini space program. In the building of each cell, 2 cm and 4 mg platinum was used. At present, the amount of platinum used in the membrane-electrode fuel cell is 0.25 mg cm^{-2} . In the laboratory scale, the amount of platinum used has reached 0.15 mg cm^{-2} . In the membrane-electrode fuel cell, an electrolyte is located between the anodes. The thickness of the catalyst layer depends on the amount of platinum applied to each electrode. If the catalyst layer has about 0.15 mg cm^{-2} of platinum, the thickness of the layer will be about 10 microns, which is approximately half the thickness of one sheet of paper. The interesting point is that for square centimeters of the membrane-electrode fuel cell with a thickness of 200 microns or 0.2 mm is generated about a half ampere of current and the voltage between the anode and the cathode is about 0.7 volts. The heating under pressure also causes a uniform distribution of catalyst particles. The proportion of materials used in the membrane-electrode fuel cell is preferable to this. If we divide this piece into 100 parts, then 30 to 50 parts of that proton conductor material are 15 parts of the platinum catalyst and the other carbon. In optimizing the membrane-electrode fuel cell, many attempts have been made to directly deposit the metal catalyst on the membrane. But because the metal salt of a catalyst placed on free areas from the membrane, during the reduction, it increases the membrane pore size. It is impossible to deposit a large amount of catalyst metal on the membrane. However, in order to have a thin, permeable monotonic metal layer, on the electrolyte surface, depositing the catalyst on the membrane is not a suitable method. A better way is to spread the catalyst ink on the surface of the membrane.

The Method of the Membrane-Electrode Fuel Cell on a Laboratory Scale

First, a solution containing catalyzed carbon and Nafion, and Teflon (Polytetrafluoroethylene) are prepared (the catalyzed carbon contains 10% platinum dispersed on the Vulcan XC-72R). The amount of Nafion is different and forms 20 to 50% by weight of the solution. Teflon is also in the range of 0 to 30% by weight. Then the resulting solution is coated on two surfaces of the Nafion 117 membrane (coating is done by the brush). The coating is then heated at $90\text{-}95^\circ\text{C}$ for 30 minutes to remove alcohol (dispersing agent). Then, the membrane is coated at 150°C for 1 minute under pressure of 1000 to 2000 pounds per square inch. In this way, a thin film of electrodes is created on both sides of the membrane, and the electrodes are partially inserted into the electrolyte. Then, the membrane-electrode thin film layer is boiled in 0.5 M molar hydrogen peroxide (H_2O_2) for 30 minutes to get better quality and finally rinsed a few times. The thickness of the membrane-electrode layer is 200 to 225 microns. The easiest way is to spread the ink contains a catalyst on a dry membrane. Then the membrane catalyst wet layers are heated to dry the catalyst layer. The above process is repeated on the other side of the membrane. In this way, the catalyst layers are placed on both sides of the membrane. The dried membrane-electrode fuel cell is dipped in a dilute acid solution with a boiling point to ensure that the membrane has H^+ to act on the fuel cell. After the membrane-electrode fuel cell was washed in distilled water, it is ready to use [45].

Characteristics of collector screens and oxidant transfer

These pages should create the following conditions:

1. A uniformly effective flow of air at very low pressure and with a very low-pressure drop to the electrode surface
2. Establish an effective electrical contact with the electrode and have a very low resistance to the current in the cell
3. The possibility of air circulation in the sheets channels makes no significant drop in pressure
4. Prevent the accumulation of water generated in the sheet's canals

Characteristics of the collector plates and the transfer of fuel (hydrogen)

These pages should create the following conditions:

1. A uniform and effective flow of hydrogen at low pressure and very low drop to the electrode surface
2. Make an effective electrical contact with the electrode and have a low resistance to the flow inside the cell
3. Provides the possibility of fuel rotation in the plate's channels
4. Exit water and impurities that may be collected in the plate's channels by the hydrogen flow that did not react

Build fuel membrane-electrode fuel cell

Membrane-electrode fuel cells are made in different ways. The following process is one of several methods used in the Los Alamos National Laboratory. That way: The platinum powder distributed on carbon and a solution of the membrane-forming material dissolved in the alcohol is thoroughly mixed to produce a uniform mixture of ink. The resulting solution is added to the solid membrane. There are several methods for placing a solution containing a catalyst on the membrane.

Conclusion

Membrane processes are very interesting for cleaning textile wastewater. Microfiltration is suitable for bleaching colored wastewater from colloid dyes and ultrafiltration is effective for the retention and removal of polymer materials (macromolecules) such as polyvinyl alcohol. For the treatment of colored wastewater, ultrafiltration and reverse osmosis are recommended as a pre-treatment step. The process of nanofiltration makes it possible to isolate low molecular weight organic molecules such as water-soluble dyes and bivalent salts from wastewater. Finally, reverse osmosis is appropriate for the complete removal of monovalent salts and the potential residues of dyes in the wastewater to produce ultrapure water. Unlike the reverse osmosis process, the nanofiltration process is of particular importance when removing ionic contaminants from the solution due to the use of charged nanomembranes. In this process, the separation mechanism also uses an electrostatic repulsion mechanism in addition to the electrostatic mechanism. This feature creates this location so that in the case of solutions containing dyestuff and electrolyte, and with the proper selection of the nanomembrane, the separation, and removal of the dye, without causing the problem of high osmotic pressure, results in the retention of a high proportion of electrolyte.

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