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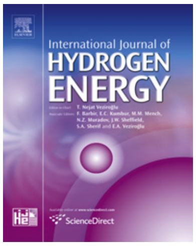

Review of the proton exchange membranes for fuel cell applications

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ABSTRACT

Proton-exchange membrane fuel cells (PEMFCs) are considered to be a promising technology for clean and efficient power generation in the twenty-first century. Proton exchange membranes (PEMs) are the key components in fuel cell system. The researchers have focused to reach the proton exchange membrane with high proton conductivity, low electronic conductivity, low permeability to fuel, low electroosmotic drag coefficient, good chemical/thermal stability, good mechanical properties and low cost. These are classified into the "iron triangle" of performance, durability, and cost. Current PEMFC technology is based on expensive perflourinated proton-exchange membranes (PEMs) that operate effectively only under fully hydrated conditions. There is considerable application-driven interest in lowering the membrane cost and extending the operating window of PEMs. PEMFC system complexity could be reduced by the development of 'water-free' electrolytes that do not require hydration. It also enables the PEMFC to be operated under 'warm' conditions (i.e. above 100 °C) thus further improving its efficiency. Capital cost could also be further reduced because at warmer conditions less Pt could be used. This paper presents an overview of the key requirements for the proton exchange membranes (PEM) used in fuel cell applications, along with a description of the membrane materials currently being used and their ability to meet these requirements. A number of possible alternative candidates are reviewed and presented in this paper. Also discussed are some of the new materials, technologies, and research directions being pursued to try to meet the demanding performance and durability needs of the PEM fuel cell industry. The alternative PEMs are classified into three categories: (1) modified Nafion® composite membranes; (2) functionalized non-fluorinated membranes and composite membranes therein; and (3) acid–base composite membranes. Several commonly used inorganic additives are reviewed in the context of composite membranes. Finally, the general methods of the measuring and evaluating of proton exchange membrane properties have been investigated such as proton conductivity, ion exchange capacity, water uptake, gas permeability, methanol permeability, durability, thermal stability and fuel cell performance test.

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1. Introduction

Fuel cells due to their particular properties are on the verge of creating a vast revolutionary change in the field of electricity. By definition, fuel cell is an electrochemical apparatus that the chemical energy of fuel without fuel combustion turned to electrical energy. Therefore, in a fuel cell system, the chemical energy related to electrochemical reaction of the fuel with oxidant directly change into the water, electricity and heat. Fuels such as H_2, methanol, ethanol, and etc have been usually used in fuel cells. In summary, the reactions have been done in a fuel cell can be explained in following: Hydrogen in Anode electrode change into a hydrogen ion and electrons is released. These electrons move through foreign circuit towards the cathode and produce the electrical current. Anodic and cathodic reactions have been done in the PEM fuel cell with H_2 gas in anode in following:

Anode electrode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode electrode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

the two above reactions will be change the following general reaction after the combination:

General Reaction of cell: $2H_2 + O_2 \rightarrow 2H_2O$

The most important part and in the other words the central core of the fuel cell is the membrane electrode assembly (MEA) which is consist of two part namely electrocatalyst and membrane. In this part, the production of the electrical current process (electrochemical reaction) will be done. The role of membrane between electrodes is the conduction of produced protons from anode to cathode [1]. The existing ions move towards the cathode through the electrolyte membrane and on that place produce water and heat with free electrons. The primary compartments of the PEM fuel cell have been shown in the Fig. 1. Advantages of fuel cells in comparison with other types of equipments which are producing energy are as follows: higher efficiency, no existence of the mobile parts and as a result lack of sonic pollution, no emissions of environmental polluting gases such as SO_x, NO_x, CO_2, CO, and etc. In contrary of benefits, only disadvantage of fuel cells is their higher cost that this problem will be solved by applying the new technologies and also mass production of these fuel cells.

Fuel cells may be classified based on the used criteria to different methods which typically depend on the different parameters related to operating conditions and fuel cell structure. Fuel cell systems have different variables such as type of the electrolyte used in fuel cell, type of the exchanged ion through the electrolyte, type of the reactants (e.g. primary fuels and oxidants), operating temperature and pressure, direct and indirect usage of the primary fuels in fuel cell system, And finally the primary and regenerative systems. Generally, it is common that fuel cells are classified and nominated based on the nature of used electrolyte in the fuel cell. Therefore, based on this classification, fuel cells include the following different types: (1) alkaline fuel cells (AFC) with the alkaline solution electrolyte (such as potassium hydroxide KOH), (2) phosphoric acid fuel cells (PAFC) with acidic solution electrolyte (such as phosphoric acid), (3) solid proton exchange membrane (PEMFC) which are known to polymer electrolyte membrane fuel cells and their electrolyte consist of the proton exchange membrane, (4) molten carbonate fuel cells (MCFC) with molten carbonate salt electrolyte, (5) solid oxide fuel cells (SOFC) with ceramic ion conducting electrolyte in solid oxide form. Table 1 summarizes the operating and applicable properties of five main types of fuel cells [2].

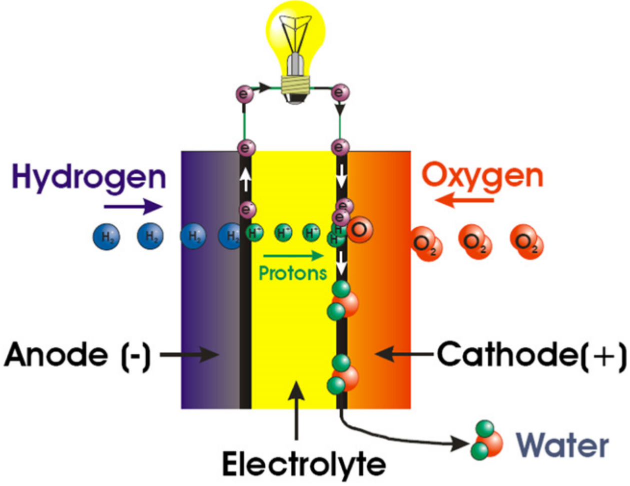


Fig. 1 – Schematic design of the PEM fuel cell.

Ion-exchange membranes have been used in various industrial processes, e.g., in the electrodialytic concentration of seawater to produce edible salt, as a separator for electrolysis, in the desalination of saline water by electrodialysis, in the separation of ionic materials from non-ionic materials by electrodialysis, in the recovery of acid and alkali from waste acid and alkali solution by diffusion dialysis, in the dehydration of water-miscible organic solvent by pervaporation, etc [3]. As mentioned at above section, in PEM fuel cells will be used from solid polymeric electrolytes which have the ability of proton transferring. These ionic polymer electrolytes are including the gel-like polymeric structures that were severely swollen and carrying fixed positive and negative charges. These polymers don't have the ability of proton transferring in dry conditions and only have this property in the moist state and will be increase the ionic conductivity with increasing the water inside them. In 1970s, a chemically stable cation-exchange membrane based on sulfonated polytetrafluoro-ethylene was first developed by Dupont as Nafion®, leading to a large scale use of this membrane in the chlor-alkali production industry and energy storage or conversion system (fuel cell) [4]. This fluorinated sulfonic acid Nafion membrane developed by DuPont Co. was selected as a standard membrane for polymeric electrolyte fuel cells. Fig. 2 shows the types of ion exchange membranes and time of their development from the beginning of appearance.

Traditionally, ion exchange membranes are classified into anion exchange membranes and cation-exchange membranes depending on the type of ionic groups attached to the

Table 1 – Operating and applicable properties of five main types of fuel cells.

Type of Fuel Cell	Operating Temp. (°C)	Power Density (mW/cm^2)	Fuel Efficiency (Chem. to Elec.)	Lifetime (hr)	Capital Cost ($/kW)	Area of Application
AFC [2]	60–90	100–200	40–60	>10,000	>200	Space, Mobile
PAFC	160–220	200	55	>40,000	3000	Distributed Power
PEMFC	50–80	350	45–60	>40,000	>200	Portable, Mobile, Stationary
MCFC	600–700	100	60–65	>40,000	1000	Distributed Power Generation
SOFC	800–1000	240	55–65	>40,000	1500	Baseload Power Generation

membrane matrix. Cation exchange membranes contain negatively charged groups, such as $-SO3^-$, $-COO^-$, $-PO_3^{2-}$, $-PO_3H^-$, $-C_6H_4O^-$, etc., fixed to the membrane backbone and allow the passage of cations but reject anions. While anion exchange membranes contains positively charged groups, such as $-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, $-PR_3^+$, $-SR_2^+$, etc., fixed to the membrane backbone and allow the passage of anions but reject cations [5,6].

According to the connection way of charge groups to the matrix or their chemical structure, ion exchange membranes can be further classified into homogenous and heterogeneous membranes, in which the charged groups are chemically bonded to or physically mixed with the membrane matrix, respectively. Homogenous ion exchange membranes have good electrochemical properties but don't have any required mechanical strength, while, the heterogeneous ion exchange membranes have a good mechanical strength but the electrochemical Performance of these membranes are weak [7]. The other difference between homogenous and heterogeneous ion exchange membranes is related to their dimensional stability that the heterogeneous ion exchange membranes have a good dimensional stability compared with homogenous ion exchange membranes [8].

During the past few years, many advances have been made but there are still technical and economic obstacles in the commercialization of fuel cell. In this regard, many efforts have been made to develop membranes for PEMFC's with improved performance and durability. Also, other studies have been done on reducing the cost of fuel cell membranes. Much of the research on new materials for PEMFC membranes, while promising, may be too far away from commercialization to meet this timeframe, and could be the next generation technology. Today's research is based on materials that can accelerate commercialization of fuel cell. This paper is a review of past and present research in the field of development of proton exchange membranes for fuel cell to achieve better performance, higher durability and lower cost.

2. Proton exchange membranes for fuel cell applications

As mentioned above, in general Membrane is the core component of the PEM fuel cell. Triple roles of the polymeric membrane in the PEM fuel cells are as follows: charge carrier for protons, to separate of the reactant gases, and electronic insulator for not passing of electrons through the membrane (due to have a negative charge from SO_3^- and electron repelling). In 1970s, DuPont developed a perfluorosulfonic acid called "Nafion®" that not only showed a two-fold increase in the specific conductivity of the membrane but also extended the lifetime by four orders of magnitude (104–105 h). This soon became a standard for PEMFC and remains so till today. The Dow Chemical Company and Asahi Chemical Company synthesized advanced perfluorosulfonic acid membranes

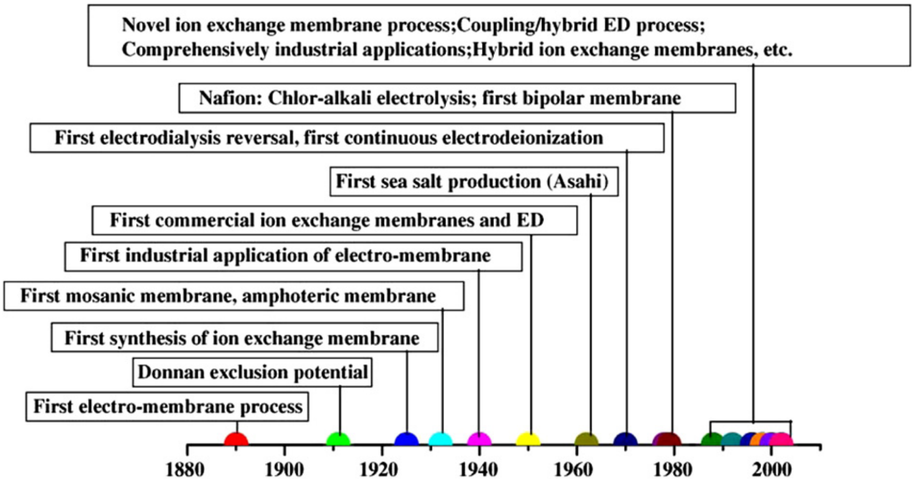


Fig. 2 – Types of the ion exchange membranes based on their development time (reprinted with permission from [8]).

with shorter side chains and a higher ratio of SO_3H to CF_2 groups [9]. Table 2 provides a comparison of some commercial cation-exchange membranes [10].

This Nafion membrane, has a structure of copolymer from flouoro 3,6-dioxo 4,6-octane sulfonic acid with polytetra-fluorethylene (PTFE) that Teflon backbone of this structure gives the hydrophobic nature for membrane and hydrophilic sulfonic acid groups (HSO_3^-) have been grafted chemically into backbone. These ionic groups have caused the absorption of the large amount of water by polymer and therefore, lead to hydration of polymer. Thus, the factors affecting the performance of the suitable proton exchange membrane are the level of hydration and thickness of the membrane which is playing an important role in deciding their suitability for application in fuel cell [11]. The proton exchange membrane performance related to the extent of its proton conductivity and the proton conductivity also related to the extent of the humidity of the membrane. Higher proton conductivity achieve by the higher extent of the humidity. One of the ways to avoid water drag or water crossover is to reduce the membrane thickness thereby enabling an improvement in the fuel cell performance. Other advantages of reduced thickness include lower membrane resistance (and therefore an enhancement in membrane conductivity), lower cost and rapid hydration. However, there is a limit to the extent to which membrane thickness can be reduced because of difficulties with durability and fuel by-pass. To achieve high efficiency in fuel cell applications, the polymer electrolyte as membrane must possess the following desirable properties: high proton conductivity to support high currents with minimal resistive losses, zero electronic conductivity, adequate mechanical strength and stability, chemical and electrochemical stability under operating conditions, moisture control in stack, extremely low fuel or oxygen by-pass to maximize columbic efficiency and production costs compatible with intended application [10]. Fig. 3 shows the chemical structures of Nafion® and other famous perfluorinated electrolyte membranes [12].

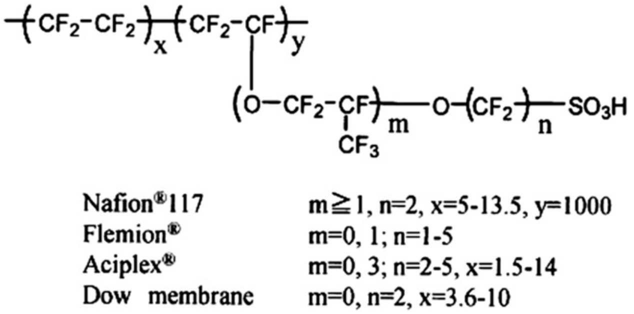


Fig. 3 – Chemical structures of perflourinated polymer electrolyte membranes (reprinted with permission from [12]).

3. Proton conduction mechanisms in proton exchange membranes

Proton conduction is fundamental for proton exchange membrane fuel cells and is usually the first characteristic considered when evaluating membranes for potential fuel cell use. Resistive loss is proportional to the ionic resistance of the membrane and high conductivity is essential for the required performance especially at high current density. At a molecular level, the proton transport in hydrated polymeric matrices is in general described on the basis of either of the two principal mechanisms: (1) "proton hopping" or "Grotthus mechanism" and "diffusion mechanism" which water is as vehicle or "vehicular mechanism" [13–15].

In proton hopping mechanism protons hop from one hydrolyzed ionic site (SO_3^- H_3O^+) to another across the

Table 2 – Properties of commercial cation-exchange membranes.

Membrane	Membrane Type	IEC (mequiv./gr)	Thickness (mm)	Gel water (%)	Conductivity (S/cm) at 30 °C and 100% R.H.
Asahi Chemical Industry Company Ltd., Chiyoda-ku, Tokyo, Japan [10]					
K 101	Sulfonated polyarylene	1.4	0.24	24	0.0114
Asahi Glass Company Ltd., Chiyoda-ku, Tokyo, Japan					
CMV	Sulfonated polyarylene	2.4	0.15	25	0.0051
DMV	Sulfonated polyarylene	–	0.15	–	0.0071
Flemion	Perflourinated	–	0.15	–	–
Ionac Chemical Company, Sybron Corporation, USA					
MC 3470	–	1.5	0.6	35	0.0075
MC 3142	–	1.1	0.8	–	0.0114
Ionics Inc., Watertown, MA 02172, USA					
61AZL386	–	2.3	0.5	46	0.0081
61AZL389	–	2.6	1.2	48	–
61CZL386	–	2.7	0.6	40	0.0067
DuPont Company, Wilmington, DE 19898, USA					
N 117	Perflourinated	0.9	0.2	16	0.0133
N 901	Perflourinated	1.1	0.4	5	0.01053
Pall RAI Inc., Hauppauge, NY 11788, USA					
R-1010	Perflourinated	1.2	0.1	20	0.0333

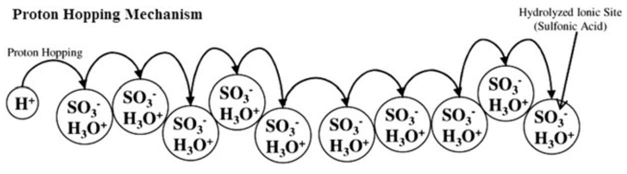


Fig. 4 – The simple scheme of the hopping mechanism (reprinted with permission from [16]).

membrane. The produced proton by oxidation of hydrogen in anode adheres to water molecule than the provisional hydronium ion is formed and one different proton from same hydronium ion hops on the other water molecule. In this mechanism, ionic clusters were swelled in presence of water and formed the percolation mechanism for proton transferring. The simple scheme of the hopping mechanism has been shown in Fig. 4 [16]. The hopping mechanism has little contribution to conductivity of perflourinated sulfonic acid membranes such as Nafion.

The second mechanism is a vehicular mechanism. In this mechanism hydrated proton (H_3O^+) diffuses through the aqueous medium in response to the electrochemical difference. In vehicular mechanism, the water connected protons ($H^+(H_2O)_x$) in the result of the electroosmotic drag carry the one or more molecules of water through the membrane and itself are transferred with them. The major function of the formation of the vehicular mechanism is the existence of the free volumes within polymeric chains in proton exchange membrane which allow the transferring of the hydrated protons through the membrane. The schematic design of the vehicular mechanism in proton conduction in pristine and nanocomposite membranes has been shown in the Fig. 5(a,b). Water also has two suggested transport mechanisms: electroosmotic drag and concentration gradient driven diffusion (this probably occurs as self-associated clusters: $(H_2O)_y$). The hydrophobic nature of Teflon backbone facilitates the water transfer through the membrane because the surfaces of the hydrophobic holes tend to repel the water molecules [16].

The prevalence of one or the other mechanism depends on the hydration level of the membrane. On the other hand, the mechanism of proton transport within nanocomposite and hybrid systems based on the aforementioned membranes is a much more complex process as it involves both the surface and chemical properties of the inorganic and organic phases. Although the exact role of inorganic components in stabilizing the proton transport properties of nanocomposites based on Nafion and other polymers is still under discussion, it may be presumed that the primary function of the nanoparticles is to stabilize the polymer morphology with increasing temperature. If the inorganic additive happens to be an alternative proton transporter like heteropolyacids, their contribution to the transport processes has also to be analyzed. Proton conductivity improvements would, however, depend upon whether the fraction of bulk water and the bulk proton concentrations are increased as a result of the inorganic additives or not.

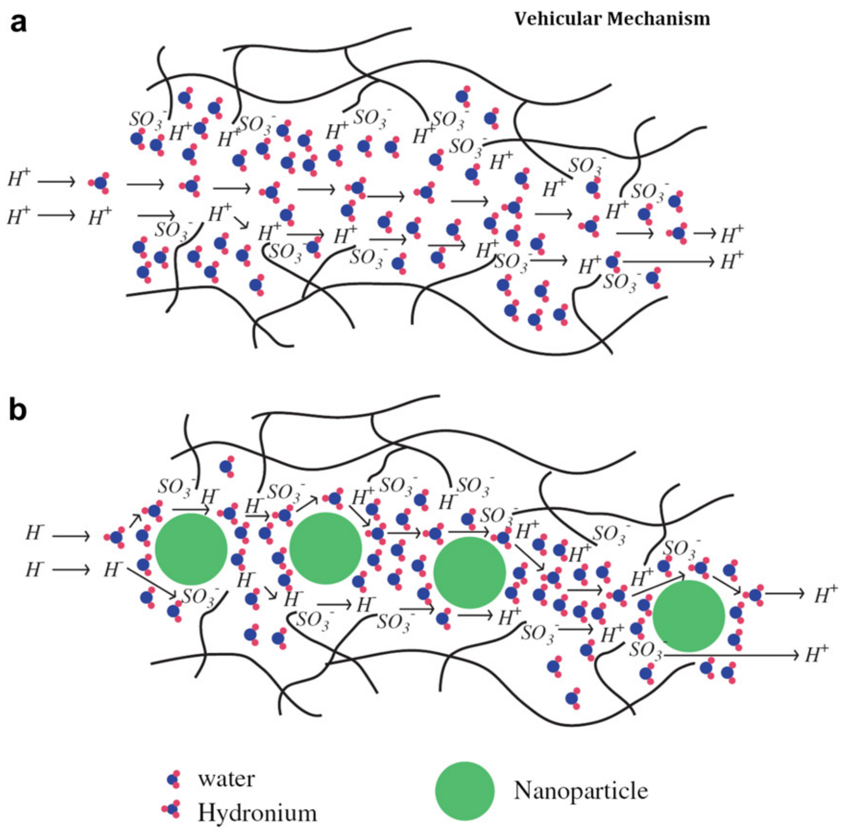


Fig. 5 – The Schematic design of the Vehicular Mechanism as proton conduction in (a) pristine membranes and (b) polymer/nano-particle composite membranes (reprinted with permission from [13,17]).

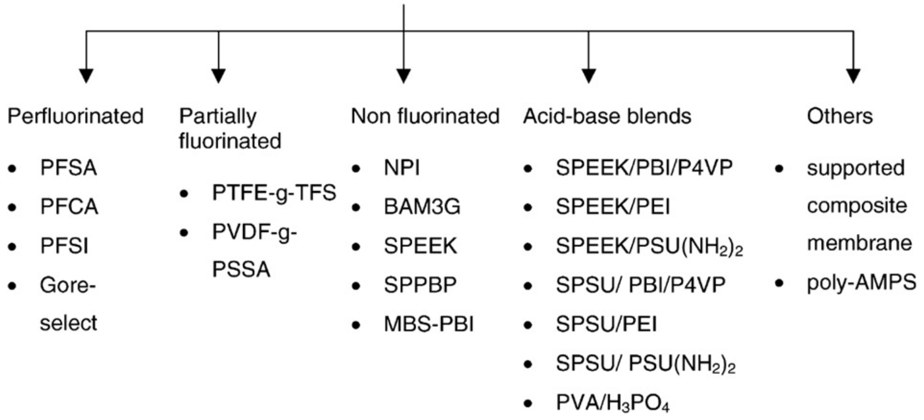


Fig. 6 – Classification of membranes based on materials (perfluorinated, partially fluorinated and non-fluorinated) and preparation method (acid-base blends and others) (modified with permission from [10]).

4. Classification of the materials used in proton exchange membranes synthesis

In general, the materials used in synthesis of the polymer electrolyte membranes can be classified into three vast groups: perflourinated ionomers (or partially perflourinated), non-flourinated hydrocarbons (including aliphatic or aromatic structures), and acid–base complexes. In Fig. 6, the classification of membranes based on materials (perfluorinated, partially fluorinated and non-fluorinated) and preparation method (acid–base blends and others) has been shown [10].

4.1. *Perflourinated ionomeric membranes*

The Perflourinated polymers due to the small size and the high electronegativity of the fluorine atom have a strong C–F bond and a low polarizability. These polymers due to their thermostability, chemical inertness and the enhanced acidity of sulfonic acid group in $-CF_2SO_3H$, have been utilized in chlor-alkali process and as proton exchange membranes for fuel cell applications [19]. These membranes are prepared by the polymerization of monomers, which contain a moiety that can be made either cationic or anionic by further treatment. These membranes are the fluorocarbon-based ion-exchange membranes (Nafion) with good chemical and thermal stability have been developed by DuPont. The four-step synthesis procedure of these membranes such as Nafion which introduced by DuPont in 1966 has been shown in Fig. 7. These are high equivalent weight (EW) perflourinated membranes and have limited their use in fuel cells because they consume high power density [3]. Similar polymers are Flemion® produced by Asahi Glass and Aciplex-S® produced by Asahi Chemical. Among the three major types, the DuPont product is considered to be superior because of its high proton conductivity, good chemical stability and mechanical strength [20].

4.2. *Non-fluorinated hydrocarbon membranes*

The other type of materials used in proton exchange membrane synthesis, are non-fluorinated hydrocarbon polymers which can be aliphatic or aromatic polymers having benzene ring structures in the polymeric backbone of membrane or in the bulky pendant groups from this membrane polymeric backbone. Presently, one of the most promising routes to high-performance proton conducting polymer electrolyte membranes is the use of hydrocarbon polymers for polymer backbones [12]. Hydrocarbon membranes provide some definite advantages over perflourinated membranes. They are less expensive, commercially available and their structure permits the introduction of polar sites as pendant groups [10]. Hydrocarbon polymers containing polar groups have high water uptakes over a wide temperature range, and the absorbed water is restricted to the polar groups of polymer chains. Decomposition of hydrocarbon polymers can be depressed to some extent by proper molecular design. Hydrocarbon polymers are easily recycled by conventional methods. These chemical structures of the hydrocarbon membranes are illustrated in Fig. 8 [12].

In order to enhance stability at elevated temperatures, aromatic hydrocarbons can be (a) incorporated directly into the backbone of a hydrocarbon polymer or (b) polymers modified with bulky groups in the backbone to render them suitable for conduction of protons [10,21]. Polyaromatic membranes are high temperature rigid polymers with $T_g > 200\ ^\circ C$ owing to the presence of inflexible and bulky aromatic groups [22]. The aromatic rings offer the possibility of electrophilic as well as nucleophilic substitution. Polyether sulfones (PESF) [23–25], polyether ketones (PEK) with varying number of ether and ketone functionalities (such as PEEK, PEKK, PEKEKK, etc.), poly(arylene ethers), polyesters and polyimides (PI) are some of the relevant examples of main chain polyaromatics [26]. Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) can meet most of the requirements for application in PEMFCs because it is a hydrophobic polymer with high glass transition temperature ($T_g = 210\ ^\circ C$), high mechanical strength, and excellent hydrolytic stability. Although the structure of PPO is simple as compared to other aromatic polymers, it allows many modifications in both aryl and benzyl positions: (1) electrophilic substitution on the benzene ring, (2) radical substitution of the hydrogen from the methyl groups, (3) nucleophilic substitution of the bromomethylated PPO, (4) capping and coupling of the terminal hydroxyl groups in PPO chains, and (5) metalation of PPO with organometallic

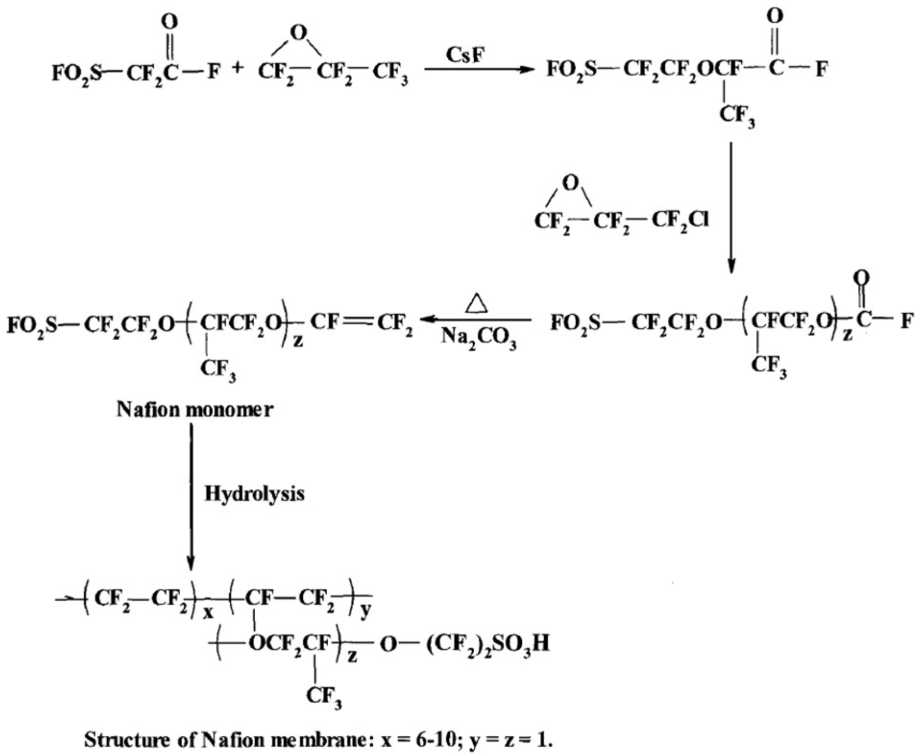


Fig. 7 – Nafion membrane and its preparation scheme (reprinted with permission from [3]).

compounds [27]. Polyaromatics are often preferred for fuel cell application due to their thermal stability. Also, the polyaromatics from oxidant point of view are stable in the acidic medium.

4.3. *Acid–base complexes*

Acid–base complexes have been considered as a viable alternative for membranes that can maintain high conductivity at elevated temperatures without suffering from dehydration effects. In general, the acid–base complexes considered for fuel cell membranes involve incorporation of an acid component into an alkaline polymer base to promote proton conduction [10].

The structures of prominent acidic and basic polymers and their complexes are given in Fig. 9.

The phosphoric acid-doped polybenzimidazole (PBI/H_3PO_4) membrane seems so far the most successful system for high temperature PEMFC preferably under ambient pressure. It has in recent years motivated extensive research activities covering polymer synthesis, membrane casting, physicochemical characterizations and fuel cell technologies. Acid-doped PBI

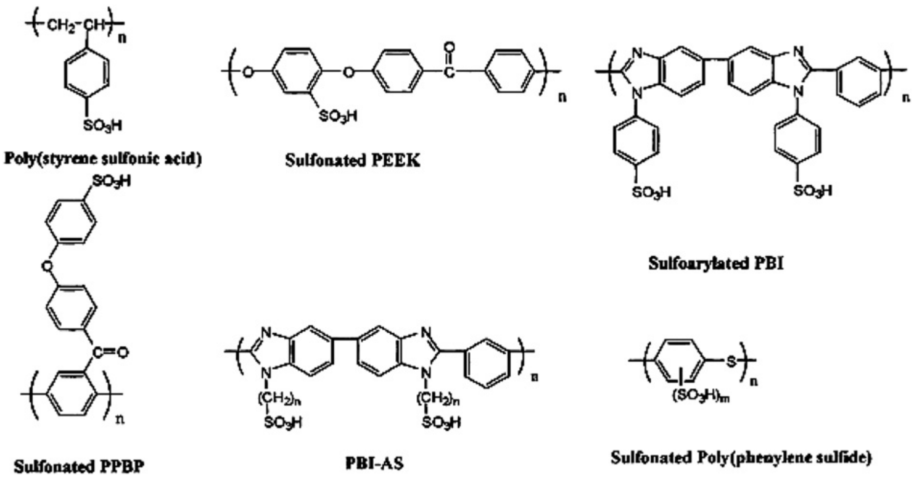


Fig. 8 – Chemical structure of polymer electrolyte membranes based on hydrocarbon polymers (reprinted with permission from [16]).

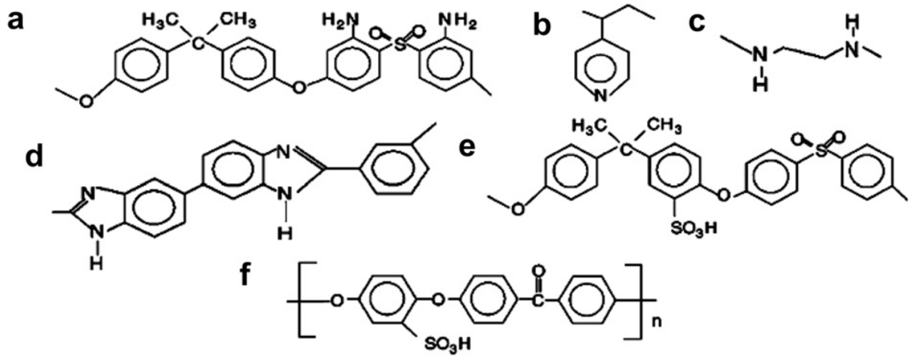


Fig. 9 – Structure of basic polymers (a–d) and acidic polymers (e, f) (reprinted with permission from [10]).

membranes have been extensively characterized. Related fuel cell technologies have been developed and high temperature PEMFC has been successfully demonstrated at temperatures of up to 200 °C under ambient pressure. No gas humidification is mandatory, which enables the elimination of the complicated humidification system, compared with Nafion cells. Other operating features of the PBI cell include easy control of air flow rate and cell temperature (in a wider range) [28].

To date, many studies have been carried out to develop alternative membranes with good fuel cell performance and low cost. Among those alternatives, acid–base polymer blends are promising materials. The interactions between acid and base polymers, such as ionic crosslinking (electrostatic forces) and hydrogen bonding bridges, contribute markedly to the control of membrane swelling without a decrease in flexibility. Therefore, these membranes have low water uptake, reduced crossover, high proton conductivity, good thermal stability, and high mechanical flexibility and strength [29].

For application in fuel cells, a series of hybrid acid–base polymer membranes were prepared by blending sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (sPPO) with 3-aminopropyl) triethoxysilane (A1100) through a sol–gel process. Experiments have shown that, the acid–base interaction improves not only the membrane homogeneity and thermal stability but also the mechanical strength and flexibility [29].

The novel acid–base membranes composed of acidic sulfonated polymers (sPPENK, sPPESK and sPBEK) and basic polyetherimide (PEI), prepared and showed excellent resistance to swelling, thermostability, hydrolysis resistance and oxidative resistance with highly proton conductivity. Accordingly, they are expected promising fuel cell proton exchange membrane materials in the future [30].

The conductivity of acid–base complex membrane does not depend on humidity in contrast to Nafion® but it is strongly sensitive to the doping level of complex. In general, the conductivity of the acid–base complexes is sensitive to the doping level and temperature. The extent of doping of the alkaline polymer is defined as a phosphoric acid mole percent per any repeating unit of polymer. As the doping increases, the distance between the clusters of acid sites decreases and the anion moieties support the proton hopping between imidazole sites. Data reported by Bouchet et al. also supports a Grotthus mechanism for PBI membrane doped with phosphoric acid as acid–base complex (PBI/H_3PO_4) [31].

For example, at 450% doping and a temperature of 165 °C, the conductivity of PBI membrane was about 4.6×10^{-2} S/cm. It was also observed that at very high levels of doping (around 1600%), the conductivity could reach 0.13 S/cm. A fuel cell was operated with a doped PBI/H_3PO_4 membrane at 190 °C and atmospheric pressure yielding a power density of 0.55 W/cm^2 and a current density of 1.2 A/cm^2 [32].

Kerres et al. made sPEEK/PBI membranes were composed of sulfonated poly(etheretherketone) sPEEK as the acidic compound and poly (benzimidazole) PBI as the basic compound. The membranes showed good proton conductivities at ion-exchange capacities IEC of 1, and they showed excellent thermal stabilities (decomposition temperatures >270 °C). Also, the membranes were tested in a H_2 membrane fuel cell and showed good performance [146].

Vargas MA et al. have synthesized a new protonic conductor gel (PVAL/H_3PO_2/H_2O) using PVAL (polyvinyl alcohol) and H_3PO_2 (hypophosphorous acid) as prime chemicals; the common solvent was water. The gels are transparent and have good mechanical properties. With this system they have reached the highest electrical conductivity at ambient and subambient temperatures in this type of material reported up to now in the literature (in the order of 10^{-1} S cm^{-1}). The variation of the electrical conductivity with temperature and acid concentration was studied. The highest open fuel cell voltage, measured at 23 °C was 435 mV. The performance of the fuel cell improved when it was fed with humidified hydrogen [94].

The most important blends in the preparation of acid–base complex are presented in Table 3. The main advantage of using high temperature specialty polymers is related not only to the thermal stability, but more to the expected stability in oxidative, reducing and acidic environments.

5. Fabrication and preparation methods of proton exchange membranes

The development of cost-effective and functional materials and components for the polymer electrolyte fuel cell (PEFC) is an important stepping stone towards the commercialization and market introduction of this technology. In addition to the noble metal catalyst, the proton exchange membrane (PEM) material is a major contributor to the cost of the membrane

Table 3 – The most important blends in the preparation of acid–base complex.

S. No.	Membrane Materials	Blend Ration	Physical Properties	Observations	In situ Performance
1	sPEEK/PBI [10]	90/10	High temperature tolerance at 350 °C; thermally stable; good miscibility	Short-term tests (300hr) yield comparable performance to Nafion 112	Higher voltages of 650 mV obtainable at High current densities of 1000 mA/cm^2 for Hydrogen fuel cell
2	PVA/H_3PO_4	Highly doped	Good mechanical Strength	With decreasing acid concentration, grotthus transport mechanism decreases Mechanism likely at low temperatures	Low open cell voltage (a max. of 436 mV With very low current Density of 1 mA/cm^2) Maximum conductivity of 10^{-1} S/cm at 100 MV
3	PBI/H_3PO_4	500% doping	Good mechanical Strength; thermally stable	Doped PBI shows greater potential for fuel cell operating at moderate temperatures	Conductivity of 6×10^{-2} S/cm achievable

electrode assembly (MEA). The state-of-the-art technology is mostly based on perfluorinated membrane materials, such as Nafion® (DuPont, USA), Flemion® (Asahi Glass, Japan) and Aciplex® (Asahi Kasei, Japan), and composites. These materials are expensive due to the complex fluorine chemistry involved in the fabrication [33]. Therefore, the development of the membranes with low cost and higher performance is necessary. Today, the new membranes as a substitute for the Nafion membranes that are including the membranes with hydrocarbon polymer matrixes, inorganic – organic hybrid membranes, acid–base complexes and grafting membranes by irradiation. The radiation grafting method is of interest and suitable method for the preparation of proton exchange membranes for fuel cell and other electrochemical applications. Generally, there are four methods for fabrication and preparation of the proton exchange membranes are as follows: (1) grafting polymerization method with using of the γ-ray irradiation, (2) grafting polymerization method with using of the plasma, (3) the Crosslinking method, (4) sol–gel method and (5) direct polymerization of monomers. In follow, the above methods are explained in detail [34–35].

5.1. *Irradiation grafting polymerization method*

Graft polymerization, by means of electron-beam, γ-ray, and ultraviolet (UV) light irradiation or by plasma, is a convenient method for the preparation of ion exchange membranes because a rapid formation of active sites on an appropriate polymer matrix can be achieved [36]. The radiation-grafted membranes have been reviewed by Nasef and Jegzey [37]. The advantages of radiation-grafted membranes include the lack of need for chemical initiators or catalysts, the easy preparation from the already prefabricated base film, and the easy control of the degree of grafting and ion exchange capacity of the membranes. The grafting can be initiated by high-energy irradiation such as γ-ray, electron-beam and swift heavy ions. The base film in the polymer electrolyte membrane is a function as hydrophobic host that constrains the membrane swelling in water and provides the mechanical strength and dimensional stability. In addition, the price of commercial radiation-grafted membranes is said to be in the range of 50–100 US $\$m^{-2}$ [38]. The process for the preparation of the new polymer electrolyte membrane by irradiation grafting as shown in Fig. 10, in which three steps are as follows: In first step the polyethylene tetrafluoro ethylene (ETFE) films were pre-irradiated in argon gas at room temperature. In this step, the ETFE films were activated in a pre-irradiation step and then grafted with monomers in a subsequent step (second step) which is named substitution stage. Finally, the grafted ETFE films were sulfonated in a chlorosulfonic acid solution to introduce the sulfonic acid groups into the membranes which is followed by hydrolysis in distilled water. Characterization of the new polymer electrolyte membranes was carried out by means of the Fourier transform infra-red (FT-IR) and thermogravimetric analysis (TG-DTA) [38]. The dimensional unit of the irradiation in the preparation of the polymer electrolyte membranes by grafting method is kGy that is defined as an extent of absorbed energy by polymeric membrane in terms of kJ per gram of polymer is grafting (1 kGy = 1 kJ/gr membrane). The irradiation rate is defined by kGy in hour or kGy/hr. Radiation-induced graft polymerization is a well-known method for the modification of the physicochemical properties of materials, and is of particular interest for achieving specifically desired properties as well as excellent mechanical properties [39]. The mass-based degree of grafting DG_m is defined as percent of the weight difference between polymeric films before and after of the grafting action which is calculated according to:

$$DG_m = \frac{(W_g - W_0)}{W_0} \times 100 \quad (1)$$

where W_0 and W_g are the weights of the film before and after grafting, respectively [35].

5.2. *Crosslinking method*

As in previous sections mentioned, perfluorosulfonic acid membranes such as Nafion are used as a proton exchange membranes for fuel cell applications [40]. Nafion has excellent proton conductivity, but it has been found that over 40% of methanol can be lost in direct methanol fuel cell (DMFC) across the membrane due to excessive swelling [41]. To improve the

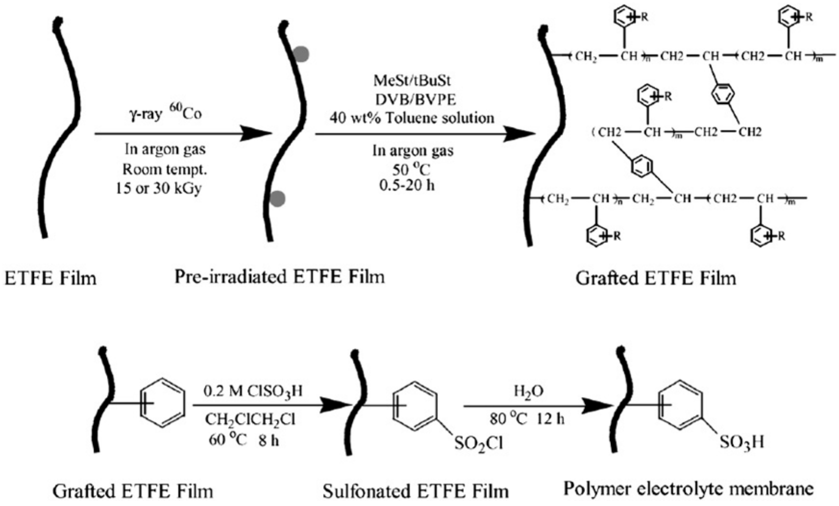


Fig. 10 – Preparation of the new polymer electrolyte membranes by irradiation grafting method (reprinted with permission from [38]).

performance of a DMFC, it is necessary to reduce the loss of fuel and methanol crossover across the polymer electrolyte membrane in the fuel cell [42–43]. It is lead to increase of the proton conductivity of the proton conductive polymer membranes and as a result the produced voltage per consumed current density increase in the unit fuel cell. Therefore, from the crosslinking method can be used to obtain three dimensional networks in membrane structures in order to reduce the methanol crossover through membrane [44]. In the crosslinking method for preparation of the proton exchange membranes, the membranes without charged sites are changed into proton exchange membranes by crosslinking in presence of the organic charged groups. The creation of crosslinking caused to improve the chemical and thermal stability of ion exchange membrane. Fig. 11 shows the proposed reaction mechanism of PVA and PSSA MA for preparation of the crosslinked proton exchange membranes [45].

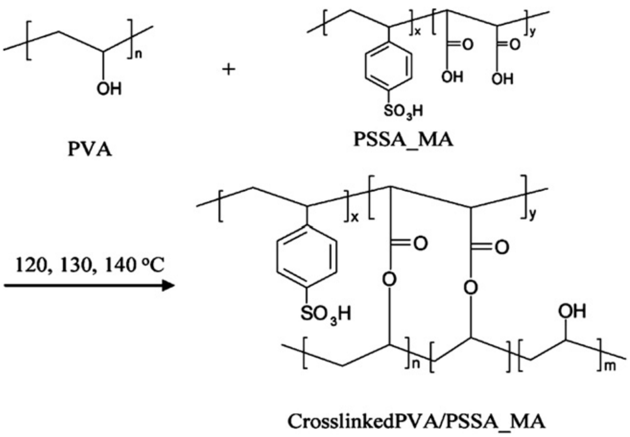


Fig. 11 – Possible reaction mechanism of PVA and PSSA MA (reprinted with permission from [45]).

5.3. *Plasma grafting polymerization method*

The grafting polymerization by plasma is one of the methods for preparation of proton exchange membranes for applications in miniaturized fuel cells. Plasma polymerized films exhibit a high degree of crosslinkage and are pinhole free even for films of only a few hundred nanometer in thickness, in contrast to conventionally polymerized films. Hence, a sharp reduction of the methanol permeability and a decrease in the resistance of a fuel cell electrolyte membrane is achieved by using plasma polymerized electrolytes. The overall membrane resistance also will be reducing by plasma polymerization method due to the lower thickness of the ion exchange membrane (in about 1 μm) [46]. By increasing the plasma energy in this polymerization, ionic conductivity of membrane will be reduce due to the higher degree of crosslinking, because the transferring of water molecules is so hard. The plasma polymerized electrolyte membranes have been developed by using tetrafluoro ethylene to generate the polymeric backbone of an ion-conductive membrane and vinylphosphonic acid to incorporate acid groups, which are responsible for the proton conductivity [47]. In Fig. 12 has been shown the major differences between a monomer, a conventional polymer and the polymer prepared by plasma polymerization. The structure of the prepared polymer in plasma polymerization is a quietly dense which this matter caused to severely reduction of the methanol crossover in the usage of this polymer as a membrane in direct methanol fuel cells.

5.4. *Sol–gel method*

The sol–gel method provides the easier introduction of pure inorganic phase into polymeric matrix (mostly in composite membranes). In sol–gel chemistry, molecular pre-materials will change into particles with nano sizes. This colloidal suspension form or sol, leads to formation of the gel networks. Gel will change into different materials with the different properties by the various drying techniques. The sols have

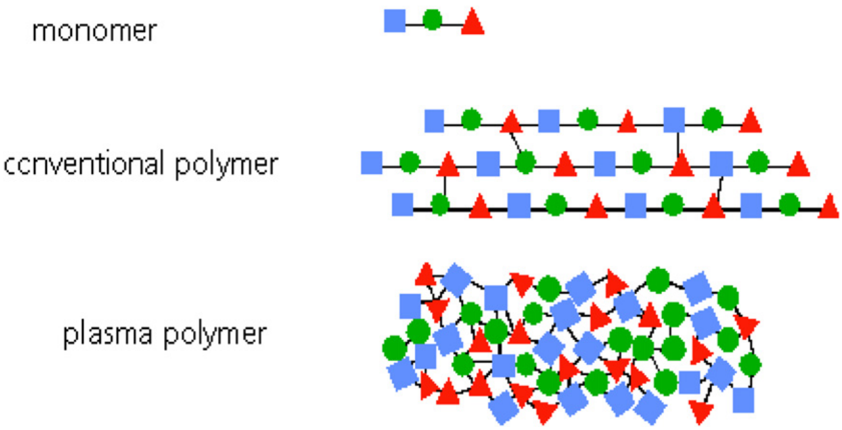


Fig. 12 – Differences between a monomer, a conventional polymer and the polymer prepared by plasma polymerization.

been formed from dispersing colloidal particles (with the size about 1–100 nm) in liquid and gel from rigid and continuous network with pores under micrometer size and polymer chains which have the average length greater than micron too. The sols are usually prepared by using of the metallic alkoxides. With regard to this, the metallic organics are insoluble in the water, but these alkoxides solved in the alcoholic solution. The polymerization reaction begins by adding of water in sol. This process will be done by two main reactions as hydrolysis and condensation. These reactions are as follows:

Hydrolysis reaction: $M-O-R+H_2O \rightarrow M-OH+R-OH$

Condensation reactions: $M-OH+HO-M \rightarrow M-O-M+H_2O$

$M-O-R+HO-M \rightarrow M-O-M+R-OH$

In this above reactions, R is the alkyl groups such as methyl, ethyl, propyl, etc [48]. Fig. 13 shows the general scheme of the hydrolysis and condensation processes.

5.5. *Direct polymerization of monomers method*

Direct polymerization of monomers is a new and traditional method of preparing proton exchange membranes and can be also used to prepare fuel cell membranes, a special category of proton exchange membranes. The membranes are prepared directly from the polymerization of possible monomers such as styrene and di-vinyl benzene, followed by sulfonation. The polymerization mostly takes place in an inert matrix through monomer soaking or pore can filling. It has been noted that sometimes, the polymerization is directly conducted from sulfonated monomers without the post-sulfonation step [49].

6. Modification of the proton exchange membranes in fuel cell applications

Recently, the modification of the fluorinated membranes such as Nafion and non-fluorinated membranes such as sulfonated polyether ether ketones, sulfonated polyether sulfones, sulfonated polyether imides and other types of proton exchange membranes have been studied and investigated in fuel cell applications. It is clear that Nafion® and related polymers are still being intensely examined in view of the complex cell requirements of high proton conductivity and outstanding chemical stability combined with longevity of 60,000 h at 80 °C. The major disadvantages of these PFSA materials are: the high cost of membrane amounting to US$ 700 per square meter [49], requirement of supporting equipment [50–51], and temperature related limitations. Degradation of PFSA membrane properties at elevated temperatures is

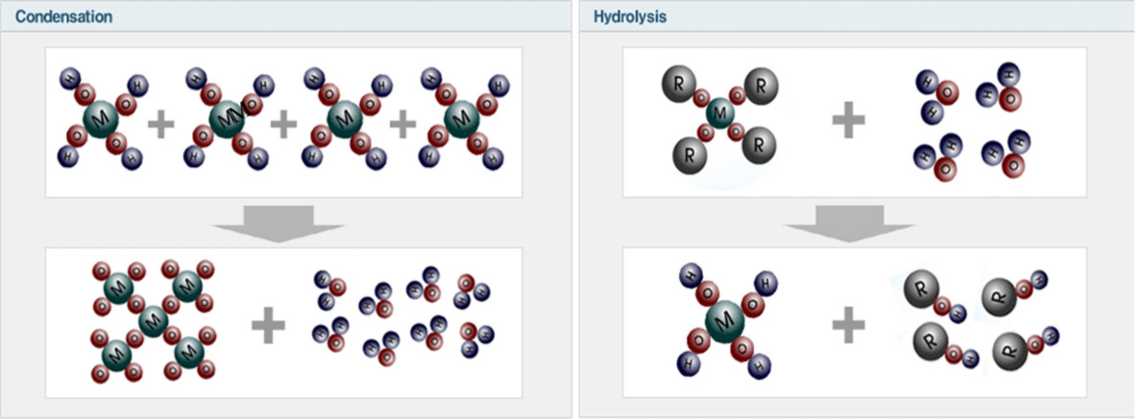


Fig. 13 – General scheme of the hydrolysis and condensation processes (reprinted with permission from [49]).

another serious drawback. Conductivity at higher temperatures (up to 100 °C) is reduced than lower temperatures [12]. Also, the phenomena related to membrane dehydration, reduction of ionic conductivity, decreased affinity for water, loss of mechanical strength due to softening of polymer backbone and increased parasitic losses through high fuel permeation are observed at temperatures above 80 °C. With regard to the application in direct methanol fuel cells (DMFC), Nafion® exhibits a high methanol permeability greater 80,000 Barrers at 80 °C, which drastically reduces the DMFC performance and renders it unsuitable for DMFCs [52]. Efforts are directed to eliminate the disadvantages such as crossover problems and loss of hydration above 100 °C. Despite its shortcomings, Nafion® is still the polymer of choice for most PEFC and DMFC applications. However, it is likely that Nafion® will be replaced by an alternative membrane in the future [53]. In order to overcome few of the disadvantages of the PFSA membranes enumerated above, the authors are also carrying out research work to identify promising alternatives [54–55].

Basically, there are two ways to enhance the properties of proton exchange membrane: Polymeric blend membranes and polymer/inorganic composite membranes. The latter is easier to fabricate. This type of composite can be configured in a number of ways:

- Both polymer and inorganic components can be ionically conductive;
- Ionic polymer with inorganic filler for mechanical support;
- Ionic polymer with water-retaining inorganic filler;
- Ionically conductive inorganic additive with supporting polymer [56].

This partial list only covers a few of the possible combinations. Polymer inorganic composite membranes are interesting because many of the inorganic additives used are able to operate at much higher temperatures than the pure polymers. Some of the possible advantages of incorporating inorganic compounds into composite membranes include, enhanced proton conductivity, water retention at high temperatures, and mechanical support [57]. Rikukawa and Sanui [12] suggest that in order to produce materials that are less expensive than Nafion, some sacrifice in material lifetime and mechanical properties may be acceptable, provided the cost factors are commercially realistic. Hence the use of hydrocarbon polymers, even though they had been previously abandoned due to low thermal and chemical stability, has attracted renewed interest. Therefore, the efforts to develop these higher temperature membranes include modification of the conventional host polymers, e.g., via incorporation of various hygroscopic inorganic nanosized particles or by developing alternate new polymer systems [58–70]. The most important goals of modification of the proton exchange membranes in PEM fuel cells can be mentioned such as preparation of the proton exchange membranes with lower cost compared to the fluorinated membranes, the desirable water uptake and retain in the elevated temperatures, desirable proton conductivity in the higher temperatures, the lower extent of the reactant gaseous and methanol crossover through the membrane, improved thermal stability, higher mechanical and chemical strength and also creation of the self-humidity of the membranes in elevated temperatures.

As mentioned in above, Nafion®, the conventional proton conducting polymer electrolyte membrane is expensive, mechanically unstable at temperatures above 100 °C, and conductive only when soaked in water, which limits fuel cell operating temperatures to 80 °C, which in turn results in lower fuel cell performance due to slower electrode kinetics and low CO tolerance [71]. Thus, the development of membranes which are mechanically and chemically stable at higher temperatures (above 100 °C) is an active area of research for producing economical fuel cells. A wide range of the fillers such as SiO_2, zirconium phosphate, phosphotungestic acid [72–73], molibdophosphoric acid, suspending SiO_2, organically modified silicates, silane based fillers and zeolites are used for the preparation of the Nafion-based composite proton exchange membranes. Composite membranes are shown the promising characteristics such as lower H_2, O_2 and methanol crossover, good thermal stability, increased proton conductivity, and higher water uptake. In the following sections, the types of the modified proton exchange membranes in the PEM fuel cells are investigated.

6.1. *Modified Nafion membrane with inorganic oxides MO_2 ($M = Ti{-}Si{-}Zr$)*

An increase of the cell temperature produces enhanced CO tolerance in PH-PEFC, faster reaction kinetics and reduced heat-exchanger requirement. The main problem for PEFC operation above 100 °C is the loss of proton conductivity of the perfluorosulphonic electrolyte due to the lower-water content with a consequent decrease of the cell performance. For all these reasons, great interest has been focused on the development of alternative membranes able to work above 100 °C. Several approaches have been used to overcome this problem, such as the use of thermally resistant polymers or the introduction of a hygroscope and/or proton conductor material as filler in the polymeric perfluorosulphonic matrix. In the latter case, the inclusion of inorganic fillers improves the mechanical properties, the membrane water management and also contributes to inhibiting the direct permeation of reaction gases by increasing the transport pathway tortuousness [48,74]. Modified Nafion® membranes containing inorganic fillers such as SiO_2, TiO_2, ZrO_2 [60,75–80] and other compounds characterized by water retention capacity or by proton conduction as hetero-poly-acids (PWA, PMoA, SiWA) or layered zirconium phosphate [58,81–85] are valid materials to use as polymer electrolytes in a medium temperature PEFC. Therefore, in general, the so-called ‘high-temperature membranes’ can be developed via modification of the polymer host membranes with (1) hygroscopic oxides such as SiO_2 and TiO_2 to increase water uptake; (2) inorganic solid acids such as ZrO_2/SO_4^{2-} to increase the water uptake as well as the concentration of acid sites; and (3) inorganic proton conductors such as hetero-poly-acids to enhance further proton conductivity using inorganic-assisted proton transport together with high water uptake and high acid concentration in the membrane [86–89]. The method of preparation of the ZrO_2, SiO_2 and TiO_2 composite proton exchange membranes was based on the in situ sol–gel synthesis methods [67]. In this procedure, the host

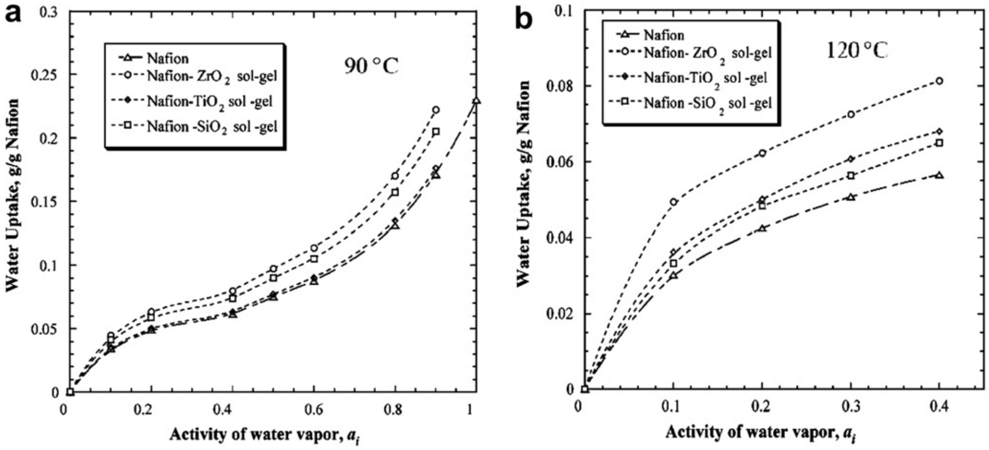


Fig. 14 – Water uptake vs. activity of water vapor for nanocomposite of Nafion® - MO_2 and Nafion® membrane at temperatures a) 90 °C and b) 120 °C (reprinted with permission from [90]).

proton exchange membrane serves as a template that directs the morphology, particle growth, and size of the oxide in the PEM matrix, resulting in nanosized particles. Fig. 14 shows the water uptake measurements for the nanocomposite membranes at 90 and 120 °C, respectively. At both temperatures, all Nafion®-MO_2 nanocomposite exhibited better water uptake at a given relative humidity (RH) than unmodified Nafion® membrane. The enhanced water uptake can be attributed to the hydrophilic nature of the acidic inorganic additives within the pores of Nafion® membrane and the increased acidity and surface areas of nanoparticles. The basic sorption trend at both temperatures was similar, with water uptake increasing from silica to Titania to Zirconia nanocomposites. This is in order of increasing acid strength. Higher water uptake and enhanced acidity result in greater proton conductivity, which would presumably result into better fuel cell performance under hot and dry conditions [90].

Fig. 15 shows the conductivity measurements for the nanocomposite membranes at 90 and 120 °C, respectively, as compared to Nafion® membrane. At both temperatures, Nafion® ZrO_2 sol–gel nanocomposite showed higher conductivity than Nafion® for over the complete range of water activity. The increase in the conductivity of Nafion® - ZrO_2 sol–gel nanocomposites is the combined result of higher water uptake as well as acidity. Hence, from water uptake, ion exchange capacity and conductivity results, it is evident that higher water uptake does not inevitably result into higher conductivity. It is not only the total water uptake, but also the distribution of water between surface and bulk that determines conductivity [88]. Bulk water is much more effective in proton conduction. The fuel cell performance of a single cell with all four types of membranes under fully humidified and dry conditions is shown in Fig. 16. Since sulfated zirconia is acidic, it causes higher water sorption in the nanocomposites [90]. Composite membranes have a lower resistivity than Nafion under fully humidified conditions and give better I-V performance in fuel cells. Also, water sorption into Nafion-based membranes increases with increased temperature [91].

6.2. *Modified Nafion membrane with types of clays*

Among the inorganic compounds suitable for the organic matrix, the clay family is a promising candidate. Indeed, layered silicate, like smectite clays, show attractive

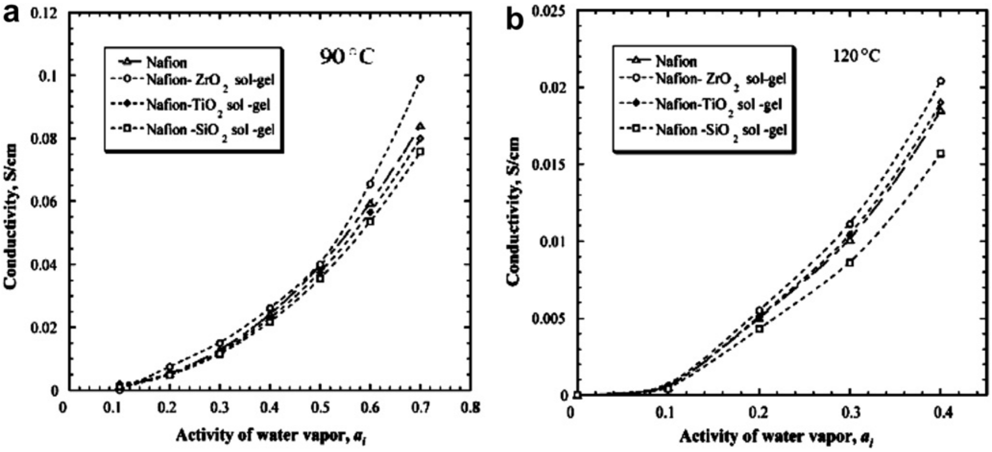


Fig. 15 – Conductivity vs. activity of water vapor for nanocomposite Nafion® - MO_2 and Nafion® membrane at temperatures a) 90 °C and b) 120 °C (reprinted with permission from [90]).

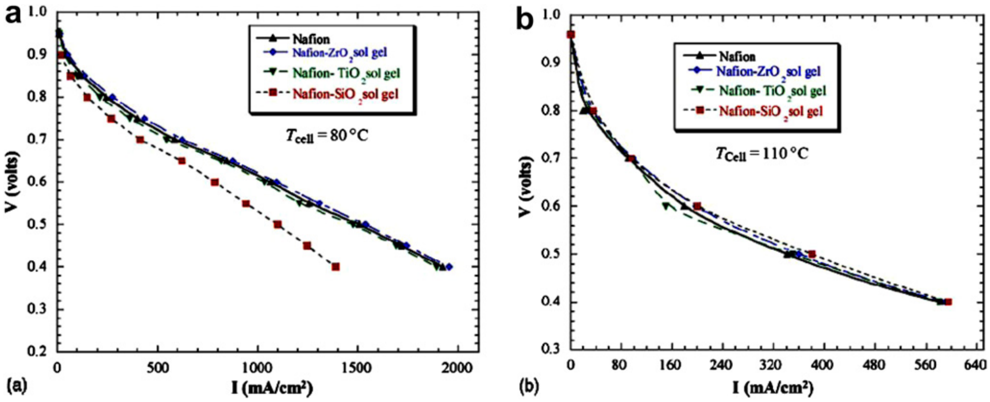


Fig. 16 – The cell performance of Nafion®-112 vs. Nafion® - MO$_2$ sol–gel, composite membrane. Oxygen and Hydrogen at 2.0 and 1.3 times stoichiometric flows, respectively, P = 1.0 atm, $T_{Humidifier}$ = 80 °C, under a) fully humidified condition at 80 °C and b) dry condition at 110 °C (reprinted with permission from [90]).

hydrophilic properties and good thermal stability at high temperature [92,93]. The layered silicates commonly used for PEM fuel cell applications are Laponite (Lp) or Montmorillonite (MMT) made of silica tetrahedral and alumina octahedral sheets which have advantageous hygroscopic properties [95–99]. Indeed, the monovalent ions located between the clay layers allow the absorption of polar solvent, like water, with good retention capacity. The smectite clays are so usually named "swelling" clays. These synthetic (Lp) or natural (MMT) inorganic materials incorporated into a polymer membrane help to prevent the loss of the hydration water at high temperature but also under low relative humidity environment. Nevertheless, the addition of clay, which is a poor proton conductor, inside Nafion®, which is highly proton conductive, can lead to a reduction of the global proton conductivity of the membrane [100]. If a comparison is made with commercially available Nafion® membranes, the addition of a small amount of montmorillonite salts to perfluorosulfonic acid (PFSA) membranes leads to the reduction of the methanol crossover and, concurrently, a decrease of conductivity [98]. Organic modification was done with the following objectives: (1) to have a better compatibility with the polymer, i.e., to have a good interface bonding between polymer and silicates/Aerosils; [101] (2) to decrease methanol permeability; (3) to aid the proton conductivity of the whole composite membrane system [102]. Table 4 reports the water uptake, and the thickness of the dry (T_d) and fully hydrated (T_w) states of hybrid membranes filled with Laponite type of the clay. As shown clearly in Table 4, the water uptake is higher with composite membranes (87 and 70%) than with the perflourinated membranes (50% for recasted Nafion® and 30% for Nafion®-117) while the thickness expansion stays comparable (18 ± 2%). This relevant difference in water uptake is due to the high water adsorption capacity of this kind of Laponite [100].

This observation suggests that the water retention of the inorganic phase is responsible for the improved water retention of the hybrid membranes. Because proton conduction is directly related to the water content, it is important to determine, for membranes presenting some interesting water retention capacities, the dependence of their proton conductivity with the environment conditions, like temperature and humidity level. Fig. 17 shows the results of conductivity measurements for different relative humidity conditions (from 50 to 100% RH) at 25 °C for Nafion®-115 and for hybrid membranes. From Fig. 17, it can be noted that the proton conductivity of the Nafion®/Lp-g membrane is higher than the one of the Nafion®-115 whatever the relative humidity conditions, and is higher than the one of the Nafion®/Lp between 70 and 98% RH. The decrease of the proton conduction with relative humidity is faster for commercial membrane than for hybrid ones [107]. The improvement of the composite membrane behavior has been previously evidenced by ex situ analysis and has to be evidenced now in fuel cell. Then, Nafion®/Lp-g hybrid membranes are tested in a fuel cell test station at different operation conditions, changing for example, the cell temperatures (80–120 °C), the reactant gases (H_2/O_2 and H_2/air), and the gas pressures (3–4 bar) in order to

Table 4 – Thickness in dry and wet states (T_d and T_w) and corresponding thickness expansion and water uptake (W_{ut}) for Nafion® and for hybrid membranes at room temperature.

Sample	Dry State, T_d (μm)	Fully hydrated state		Thickness Expansion (%)
		T_w (μm)	W_{ut} (wt.%)	
Nafion® 117 [100]	185	205	30	11
Recasted Nafion®	102	120	50	18
Nafion®/Lp (90/10, w/w)	121	140	87	16
Nafion®/Lp-g (90/10, w/w)	117	140	70	20

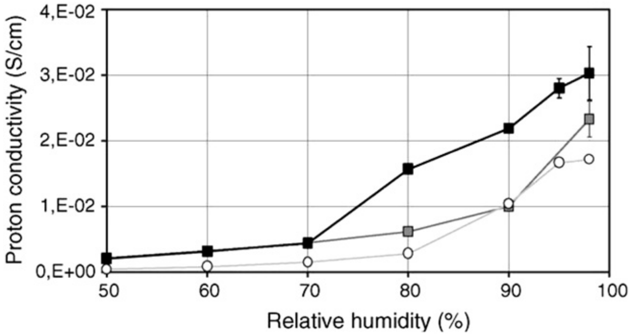


Fig. 17 – Variation of proton conduction at 25 °C with relative humidity for Nafion®-115 (○) and hybrid Nafion® containing 10 wt.% of unmodified Laponite (Nafion®/Lp (□)) and containing 10 wt.% of grafted Laponite (Nafion®/Lp-g (■))(reprinted with permission from [100]).

determine the benefit brought by the particular formulation of the material. The comparison of the two membranes performances is made directly on the corresponding polarization curves.

The corresponding polarization curves are represented in Fig. 18 for Nafion® and for composite membrane of Nafion® for the two working conditions. In the optimal operation conditions, the humidity level in the cell is good. As seen in Fig. 18, the use of Nafion® enables to reach about 600 mA cm^{-2} of electronic current produced at 0.6 V, while the use of a Nafion®/Lp-g membrane leads to the production of about 720 mA cm^{-2} at the same voltage. This difference corresponds to a 20% improvement in power density (430 mW cm^{-2} versus 360 mW cm^{-2}) [100]. The improvement of the power density produced in the cell with the hybrid Nafion® is then interesting even for the optimal operation conditions of Nafion®. The difficult operation conditions, corresponding to higher temperature (120 °C instead of 80 °C), dilute cathode gas (air instead of O_2) and lower gas pressure (3 bar instead of 4 bar), induce a drastic dehydration effect in the cell. Then, the sensitivity of the membrane to humidity can easily be observed with this procedure. In those conditions, a Nafion® membrane can deliver 390 mA cm^{-2} of current at 0.6V while the composite one (Nafion®/Lp-g) can reach 500 mA cm^{-2}, as seen in Fig. 18. Then, composite Nafion® presents a better behavior than the commercial Nafion®, whatever the operation conditions. Nevertheless, the gain in power density is always more significant under difficult humidification conditions. This improvement in fuel cell work has to be related to the good water retention of the inorganic filler while the sulfonic acid groups grafted to the particles surface enhance the global proton conductivity of the material [100].

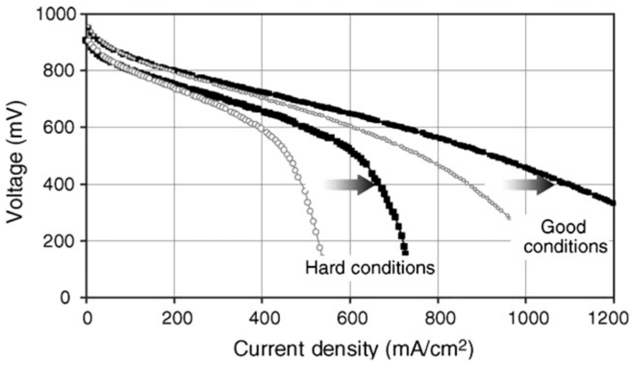


Fig. 18 – Polarization curves for Nafion®-115 (○) and hybrid membranes (Nafion®/Lp-g (90/10, w/w)—symbol (■)) under good operation conditions (80 °C, H_2/O_2, 4 bar) and hard operation conditions (120 °C, H_2/air, 3 bar) (reprinted with permission from [100]).

Fig. 19 presents the methanol permeability and proton conductivity of membranes fabricated with various proportions (0–6 wt.%) of montmorillonite clay modified with the POPD400-PS in Nafion® membrane. The methanol permeability decreased rapidly as the amount of MMT-POPD400-PS added to Nafion® increased. Indeed, several studies have demonstrated that adding montmorillonite nanofiller can improve the barrier properties of Nafion® membrane towards methanol, because the length-to-width ratio of the additive is high [98,103–106]. The methanol permeability of the composite membranes that contained 6 wt.% MMT-POPD400-PS was 1.2 × 106 cm^2 S^{-1}, 60% of that of pristine Nafion®. The proton conductivity of the composite membranes increased with added MMT-POPD400-PS. The proton conductivity of the composite membranes generally declined from that of pristine Nafion® membrane as the inorganic filler content increased [61,98,103–107]. However, the cause may involve various mechanisms of proton transportation. We suggest two mechanisms that improve proton transportation in the composite membrane: (1) hopping mechanism is promoted by the intercalating agent (POPD400-PS) with a long chain and (2) the vehicle mechanism is accelerated on the surface of the introduced clay network oxide [108]. Three to five weight percent MMT-POPD400-PS is tentatively concluded to be the optimum level of inorganic filler in the composite electrolyte membrane for DMFCs [109].

Fig. 20 plots cell potential versus current density and power density versus current density of the DMFC membrane electrode assembly (MEA) with an MMT-POPD400-PS and pristine Nafion® composite membrane. Indeed, the suppression of the methanol crossover results in higher OCV at lower current

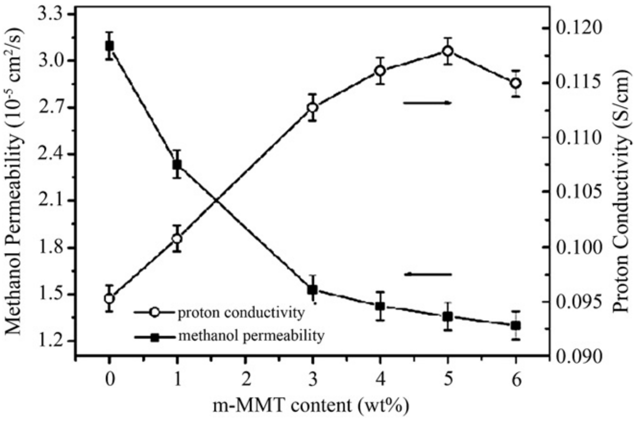


Fig. 19 – The proton conductivity (○) and methanol permeability (■) of the pristine Nafion® and composite membranes fabricated with different amounts of MMT-POPD400-PS (reprinted with permission from [109]).

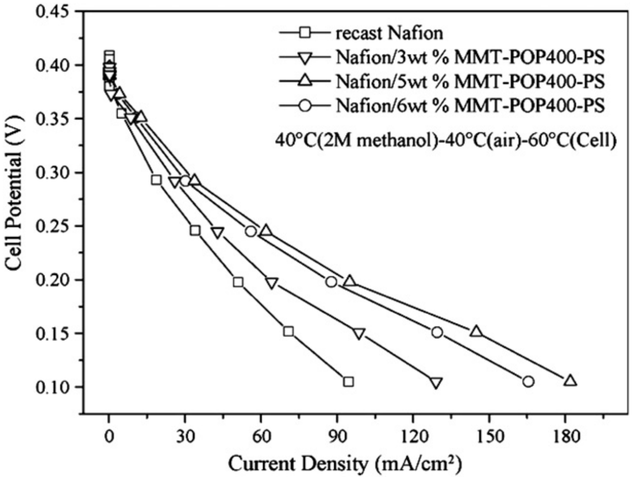


Fig. 20 – Polarization curves for the MEA made with pristine Nafion® membrane and composite membranes operated at 313 K (reprinted with permission from [109]).

densities [110]. The composite membrane with 5 wt.% MMT-POPD400-PS outperformed pristine Nafion®. The current densities measured with composite membranes that contained 0, 3, 5 and 6 wt.% MMT-POPD400-PS, were 51 and 64, 95 and 88 mA cm^{-2}, respectively, at a potential of 0.2V. Meanwhile, the membrane with 6 wt.% inorganic loading does not outperform that with 5 wt.%, perhaps because the proton conductivity at 6 wt.% inorganic loading is reduced, as plotted in Fig. 19. However, all of the composite membranes that contain MMT-POPD400-PS outperform pristine Nafion® at high current densities [109].

As a result, The Nafion®/MMT-POPD400- PS composite membranes exhibit a higher selectivity than pristine Nafion®, perhaps because of the increased proton conductivity and decreased methanol permeability of the composite membranes. The high selectivity reveals that the composite membrane is suited to DMFC applications. The combination of these effects substantially improved the properties of Nafion®/MMT-POPD400-PS composite membranes, which are appropriate for DMFC applications [109].

6.3. *Modified Nafion membrane with types of zeolites*

Zeolites are a class of crystalline aluminosilicates, which form a framework of SiO_2 and AlO_4 tetrahedra and contain exchangeable cations on the extra-framework to maintain the electrical neutrality. The ion exchange of cations often changes the chemical and physical properties of zeolites, such as a thermostability, adsorption capacity, amount and strength of acid site [111]. Therefore, zeolites can potentially be a candidate for novel ion-conducting materials, since the cation is mobile in the framework structure, which has been materialized as ion exchangers in an aqueous phase [112]. However, membranes made of pure zeolites are plagued by defects, such as cracks or gaps and exhibit poor mechanical properties, such as brittleness and fragility [113]. Moreover, these membranes are expensive to manufacture [114]. A zeolite–polymer composite membrane represents a compromise between the nonselective polymeric films and the brittle zeolite film. The composite combines the highly selective solid state proton conductor with the flexibility of a polymer matrix [115]. For zeolites at 100% relative humidity, the higher temperature of the higher ion conductivity is up to

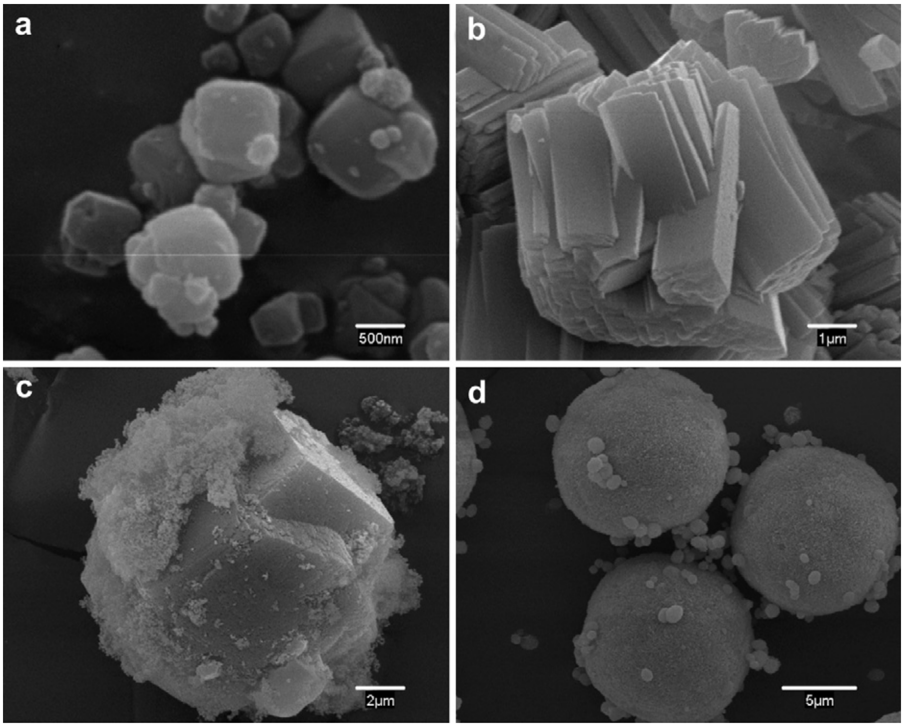


Fig. 21 – SEM micrographs of the surface zeolite powders: (a) NaA zeolite, (b) Mordenite, (c) ETS-10 and (d) Umbite (reprinted with permission from [119]).

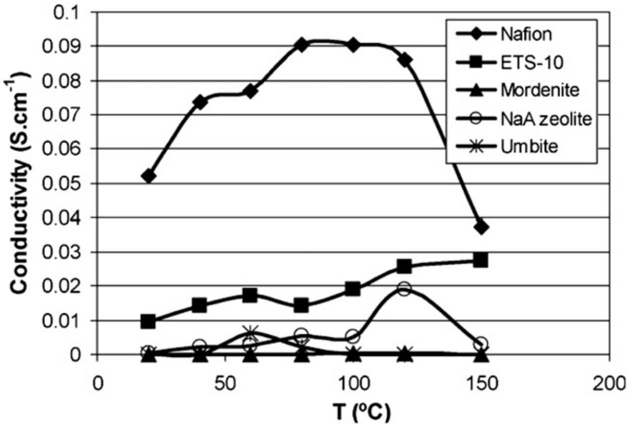


Fig. 22 – Proton conductivity versus temperature curves for all of the samples are plotted for R.H. 100% up to 150 °C (reprinted with permission from [119]).

100 °C [116]. Above this value, conductivity in zeolites is strongly influenced by the amount of adsorbed water [117–118]. SEM micrographs of the zeolite powder used in the preparation of the polymer - zeolite composite membranes are presented in Fig. 21. It can be seen that umbite shows a different morphology compared with the other ones. The spherical geometry can be a drawback because the higher inter-grain void volume and the lower contact surface than the other three zeolites that are prism in shape [119].

In Fig. 22, conductivity versus temperature for all the samples are plotted for RH 100% up to 150 °C. Although lower values than Nafion were measured, zeolite–polymer composites show a more stable performance at high temperatures. Ionic conductivity in solids, zeolites included, increases with temperature mainly due to higher ion mobility and the bigger quantity of adsorbed water. From 100 °C, Nafion drops sharply due to the dehydration process. However, NaA zeolite continues increasing conductivity up to 120 °C and ETS-10 up to 150 °C. Moreover, ETS-10 was subjected at several warning–cooling cycles and did not present hysteresis. Umbite and Mordenite presented the worst results. Umbite behavior can be due to the morphology as it was seen in SEM micrographics. Mordenite conductivity was 1.86×10^{-5} S cm^{-1} at room temperature and 100% R.H. after 24 h in the cell. This value is similar to that obtained by Hibino et al. [111], 1.07×10^{-5} S cm^{-1}, for the same conditions [119].

Electrochemical selectivity (β), defined in Eq. (2) as the proton conductivity divided by the methanol permeability, allows a comparison of the new membranes with each other and with the Nafion benchmark.

$$\beta = \frac{\sigma}{P} \tag{2}$$

In the past, this goal was taken to imply high proton conductivity. However, while the current standard fuel cell membrane Nafion 117 has a very high conductivity, its selectivity is compromised due to high methanol permeability. If another membrane had higher selectivity, but lower conductivity, the membrane conductance could be kept large by making the membrane thin [115]. As shown in Fig. 23, the components are chosen so that protons are transported through both the dispersed phase and the polymer matrix. If the dispersed material is impermeable to methanol, protons will have a more direct and shorter path compared to methanol. This membrane could enhance the proton selectivity, while reducing methanol crossover. Choice of zeolites as the dispersed membrane phase because their regular pore size promises selective separations based on molecular size and shape (Coronas and Santamaria, 1999). For example in the case of including a mordenite as the zeolite phase and polyvinyl alcohol (PVA) [120] as the polymer, the hydrophilic nature of both PVA and mordenite prevents the formation of nonselective voids at the polymer-zeolite interface, while also exploiting the selectivity of the mordenite. Mordenite is one of the most stable zeolites in existence (Breck, 1974), and is one of the most highly conducting (10^{-3} s/cm) and widely studied (Knudsen et al., 1988). In the best case, a PVA membrane containing 60% mordenite by volume demonstrates a mere two-fold increase in selectivity over Nafion. The substantial decrease in methanol permeability is not offset by the decrease in proton conductivity, yielding better selectivity. The most successful result by far is a PVA membrane containing 50% mordenite by volume. Compared to Nafion, this membrane demonstrates a 200-fold decrease in methanol permeability, with only an order of magnitude decrease in proton conductivity, which results in ~20-fold increase in selectivity [115].

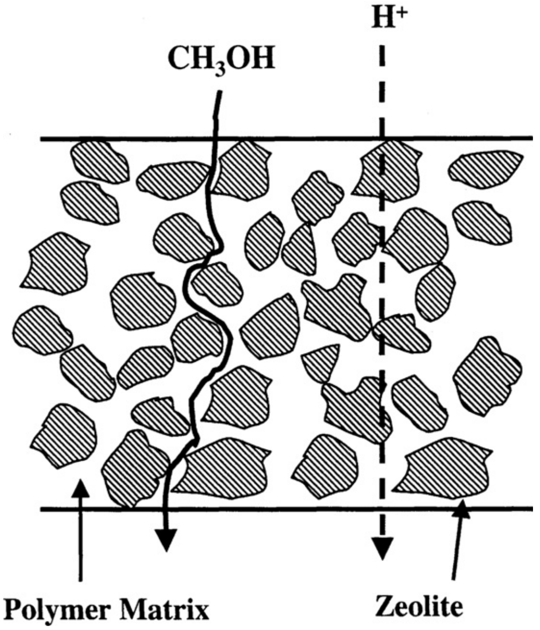


Fig. 23 – H$^+$ and methanol ions passing way in the polymer matrix of the filled membranes with zeolite (reprinted with permission from [115]).

6.4. *Modified Nafion membrane with conductive polymers such as polyaniline*

Several research groups have used various methods and strategies to decrease methanol crossover, e.g., operating a cell with relatively low methanol concentrations <2 M [121]

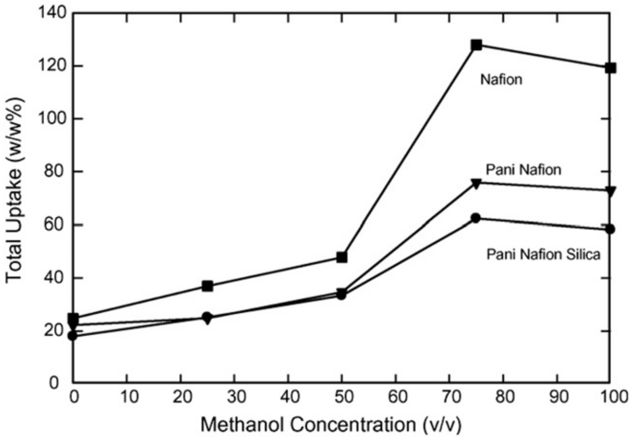


Fig. 24 – Solvent uptake of Nafion and Nafion/PANi composite membranes (reprinted with permission from [139]).

and limiting temperatures below 70 °C. Another strategy is to carry out structural modifications of Nafion membranes. These includes: (1) grafting of styrene monomer [122]; (2) pore-filling type PEM using Teflon as a substrate and acrylic acid-vinyl sulfonic acid copolymer as the proton conductive matrix [123]; (3) modification with polyvinyl alcohol [124] or polypyrrole [125]; (4) silicon dioxide–Nafion composites [126]. All these studies have achieved a considerable reduction of methanol permeation, but at the same time an undesirable decrease in proton conductivity. Tan and Belenger [127–128], carried out extensive characterization of composite Nafion/polyaniline films for proton conduction. The results showed that protonic transport is dependent on the amount of polyaniline disrupting the ionic pathways with potential application in fuel cell technology. Polyaniline is a well-known intrinsically conductive polymer. It can be easily obtained by chemical or electrochemical oxidation of the monomer aniline [129–131]. The electrical conduction in polyaniline may be ionic (charge carriers are ions), electronic (charge carriers are electrons) or mixed [132–133]. The Nafion/silica and sPEEK/silica membranes were synthesized by in situ condensation of TEOS as described elsewhere [134–136] to yield a silica content of 3.8 wt.%. In this technique, silica nanoparticles were embedded into the hydrophilic clusters of the perflourinated membrane by means of a sol–gel process. Nafion 117 and the Nafion/silica composite membranes were modified with polyaniline by a redox polymerization process [137]. The membranes are hereinafter identified as Nafion/PAni-X or Nafion/silica/PAni-X, where PAni stands for polyaniline and X represents the aniline solution immersion times. Polyaniline modification was evident because of the dark-green colouration of the Emeraldine salt due to the protonation of polyaniline by the sulfonic groups of Nafion [138].

The results obtained from methanol/water uptake experiments are given in Fig. 24. All the uptake results indicate that the polyaniline layer on the Nafion surface reduces water absorption (less hydrophilic), which prevents the methanol from diffusing into the bulk of the Nafion structure. For Nafion/silica membranes, the data suggest that the silica nanoparticles provide structural stability to Nafion, but no further benefits. The XRD patterns of Nafion measured dry and after immersion in methanol/water solutions of different methanol concentrations are presented in Fig. 25. These show that the crystallinity of the Nafion Teflon backbone drops dramatically when immersed in methanol solution, and the backbone character peak almost disappears in 50 vol. % methanol solutions. The XRD data give strong evidence to suggest that the low hydrophilic polyaniline layer provides a barrier on the Nafion and therefore prevents to large degree methanol diffusion through the membrane whilst maintaining the integrity and crystalline structure of the Nafion. These results suggest that the polyaniline modification layer restrains Nafion swelling, and thus reduces methanol uptake [139].

The influence of temperature on proton conductivity for all membranes tested in a fully hydrated condition is given in Fig. 26. Both polyaniline modified membranes show conductivities 3–5 folds below that of Nafion. The low the proton conductivity values are probably the result of two effects. First, the polyaniline molecules have a strong interaction (chemical bond) with Nafion, via the positive charged imine/amine groups and the negatively charged sulfonic groups

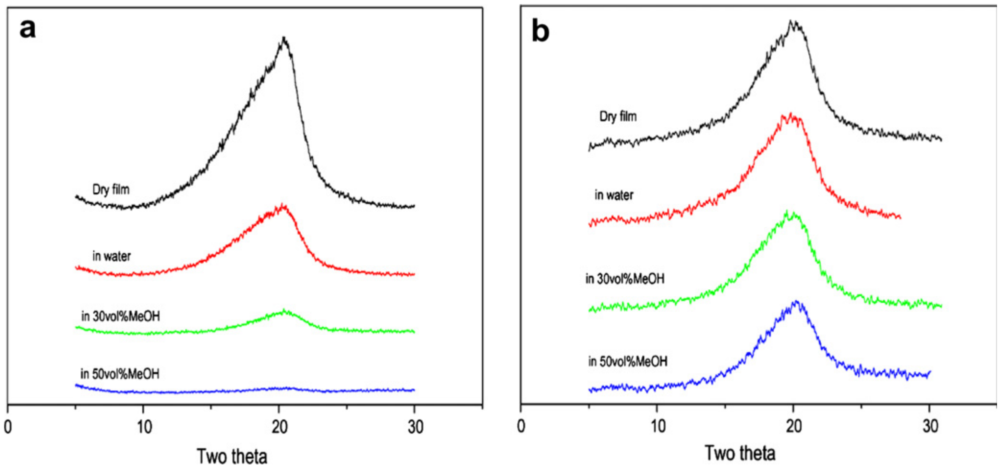


Fig. 25 – X-ray diffraction patterns (XRD) of (a) Nafion and (b) Nafion/PANi-5 composite membranes measured after immersion in different methanol concentrations (reprinted with permission from [139]).

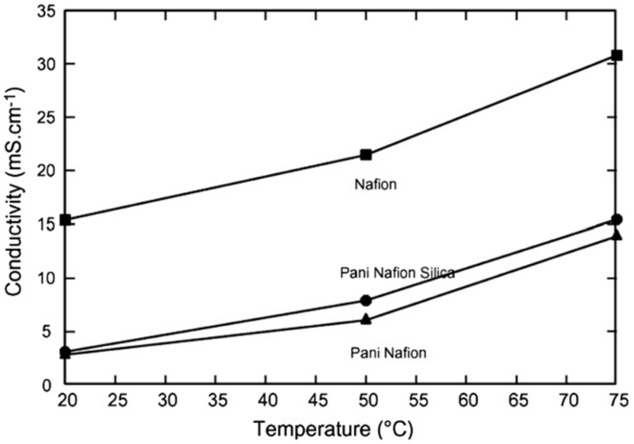


Fig. 26 – Proton conductivity of Nafion and Nafion/PANi composite membranes measured at different temperatures (reprinted with permission from [139]).

[140–142], thus interfering with essential elements of the proton transport mechanisms. The second cause for the reduction of proton conductivity of Nafion is the lower hydrophilic properties of the polyaniline layer. The polyaniline layers therefore restrict not only methanol diffusion but also water permeability into the membrane and thereby result in low conductivities [139].

The polarization curves in 2 M methanol solution and air operation mode are shown in Fig. 27. The results of the curves show that polyaniline modified membranes have higher open-circuit voltage (OCV) values but lower polarization curves compared with Nafion-117. The results strongly suggest that the large interfacial resistance value in polyaniline modified Nafion membranes provides the possible reason for low performance output. These observations clearly justify the findings discussed above in that polyaniline adds lower hydrophilic properties to the composite membrane whilst also having a strong interaction with the sulfonic groups. As a result, the interaction of aniline with the sulfonic groups of Nafion causes a restriction of protonic pathways. In addition, the polyaniline hydrophilicity is low, and further impedes proton transport via the Grotthus mechanism and the global proton conductivity of composite membrane comes down. Membrane modification with polyaniline caused to decrease the proton conductivity of the composite membrane about 3–5 fold lower than that of Nafion. The polyaniline modification also allows the membrane to become less hydrophilic, which explains the lower proton conductivity. On a positive note, methanol crossover is reduced by over two orders of magnitude, as verified by crossover limiting current analysis. Thus, in general, modification of the Nafion membranes caused to improve the selectivity and performance of the direct methanol fuel cells [139].

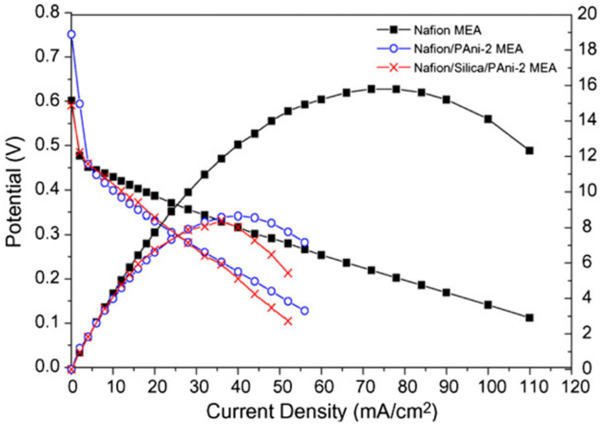


Fig. 27 – Polarization curves of DMFCS with Nafion or Nafion/PANi composite membranes at 20 °C (reprinted with permission from [139]).

6.5. *Modified Nafion blend membrane with sPEEK and polyacrylonitrile (PAN)*

Poly (ether ether ketone) (ICI: Vitrex® PEEK) is a semi-crystalline polymer possessing excellent thermal stability, chemical resistance, and mechanical properties. The electroosmotic drag coefficient and solvent (water and methanol) crossover of sulfonated PEEK (sPEEK) are lower than that of Nafion®. However, the general problem of sPEEK membranes is that they begin to swell too easily in operating temperatures between 60 and 80 °C and thus lose their mechanical stability. Different strategies is considered for swelling reduction that the most important cases can be mentioned blending of sPEEKs with basic N-containing polymers such as PBI to generate ionic crosslinking via acid–base interaction [40]. On the other hand, there are several promising investigations using blended membranes involving polyacrylonitrile (PAN) for fuel cells. Carter et al. reported that the addition of linear PAN into sulfonated polyphosphazene has several advantages including: (1) improved mechanical properties of the blended membrane, (2) easier membrane electrode assembly (MEA) fabrication during hot-pressing of the electrodes, and (3) a low methanol crossover due to the very low permeability of PAN to water and methanol [143]. The PAN addition allows the fabrication of polymeric blend membranes with superior mechanical properties as well as low methanol permeability [144]. Table 5 showed the effect of PAN content on membrane swelling ratios. The incorporation of thermally treated PAN reduces the swelling of membranes in water, as the swelling

Table 5 – IEC and swell ratios of composite membranes from sPEEK and commercial PAN (MW = 150,000).

Membranes[a]	IEC (m mol/gr)	Swell ratio (%)
sPEEK without heat treatment [145]	2.10	Dissolved in water
100:0	1.78	8.1
99:1	1.76	4.4
98:2	1.74	3.8
95:5	1.67	2.5
90:10	1.58	2.1
80:20	1.37	0.0
70:30	1.22	0.0

a Weight ratio of sPEEK against PAN.

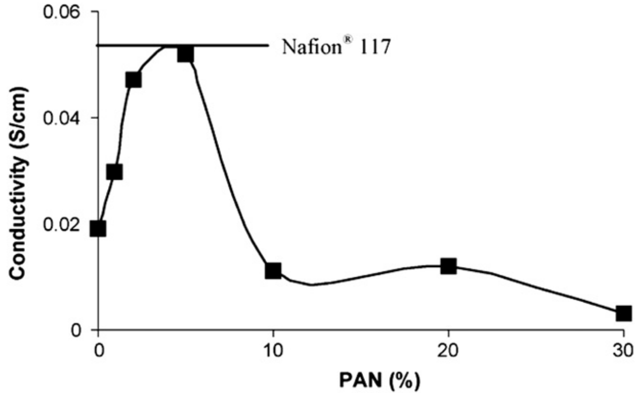


Fig. 28 – Proton conductivity versus PAN (MW = 150,000) in composite membranes (reprinted with permission from [145]).

ratio decreased with increasing of PAN content in blended membranes [145].

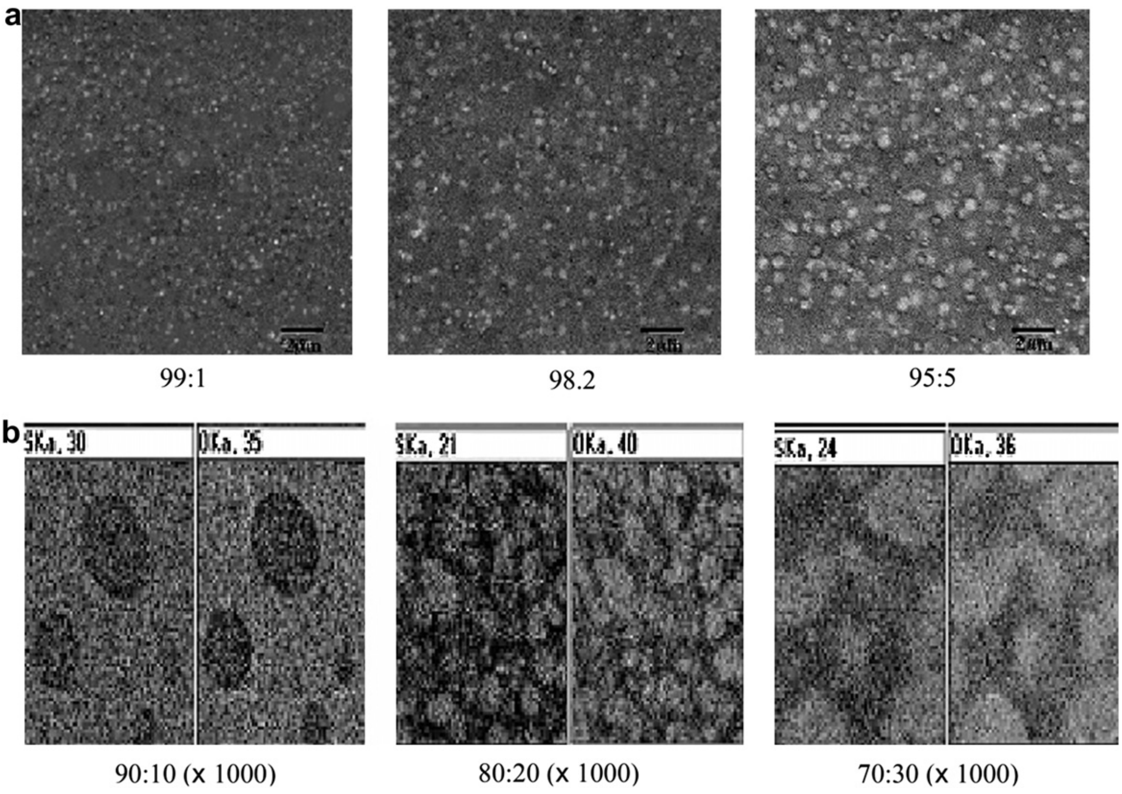
In Fig. 28, proton conductivity of blended membranes first increased with the addition of PAN. As shown in Fig. 28, above 5%, the conductivities decreased quickly. This could be due to larger PAN regions in the blended membranes blocking the proton transport. When PAN was 20 or 30%, there was a phase inversion between PAN and sPEEK, and PAN became the continuous phase. Therefore, proton conductivity would be further reduced. The dilution of sPEEK in blended membranes might be another reason for the drop of proton conductivities [145].

Table 6 – Methanol permeability of Nafion® –117 and composite membranes from sPEEK and commercial PAN (MW = 150,000).

Membranes[a]	Properties		
	Thickness (cm)	Slope ($\times 10^{-5}$ s^{-1})	Methanol permeability ($\times 10^{-7}$ cm^2 s^{-1})
Nafion® 117 [145]	0.022	1.444	27.4
100:0	0.0027	4.554	10.6
95:5	0.0035	1.802	5.4
80:20	0.0047	1.117	4.5
70:30	0.0047	0.419	1.7

a Weight ratio of sPEEK against PAN.

SEM images in Fig. 29 showed the microstructure change of these blended membranes. The size of the PAN regions increased with the content of PAN below 10%. At 20–30%, the phase inversion was clearly observed through the elemental distribution maps. In the maps, the bright white region corresponded to the sulfur/oxygen rich phase, i.e. sPEEK. At 20 and 30%, the bright white region was isolated by the darker PAN phase. Methanol permeability of these membranes are listed in Table 6 and compared to Nafion®-117. The sPEEK membrane without PAN displayed methanol permeability of 39% of Nafion®-117. The blended membranes with thermally treated PAN resulted in lower methanol permeability because the microsized dispersion of rigid ladder PAN chains



99:1
98.2
95:5

90:10 (x 1000)
80:20 (x 1000)
70:30 (x 1000)

Fig. 29 – (a) SEM of composite membranes with 1, 2 and 5% PAN (MW = 150,000). (b) Elemental distribution maps through SEM of composite membranes with 10, 20 and 30% PAN (MW = 150,000) (reprinted with permission from [145]).

Table 7 – Methanol permeability of composite membranes from sPEEK and PAN with different MW (sPEEK:PAN = 80:20).

Membranes[a]	Properties		
	Thickness (cm)	Slope ($\times 10^{-5}$ s^{-1})	Methanol permeability ($\times 10^{-7}$ cm^2 s^{-1})
3500 [145]	0.0068	0.114	0.67
7500	0.01	0.109	0.94
35,000	0.0075	0.195	1.26
150,000	0.0047	1.117	4.5

a M_W of PAN.

prevented methanol from transferring through the membrane. At 5 wt.% PAN, the methanol permeability was only 20% of that of Nafion®-117 while the proton conductivity was similar. Hence, methanol permeability and hot water swelling of blended membranes were significantly reduced while proton conductivity was increased to be competitive to Nafion®-117. These properties would make it a candidate as a possible low cost alternative to Nafion®-117.

As shown in Table 7 we found that the methanol permeability increased with PAN molecular weight (MW). The possible reason is that there are more molecular chains in PAN with lower MW than in PAN with higher MW at the same weight. Thus, the amount of ladder chains formed during heat treatment is greater and occupies larger space, which results in a stronger effect of blocking methanol [145].

6.6. *Modified Nafion membrane with proton conductive materials (heteropolyacids)*

The proton exchange membranes (PEMs) currently used in fuel cells, such as Nafion® membranes, are highly proton conductive and chemically and physically stable at moderate temperatures [40,147]. However, these preferable properties are deteriorated above their glass transition temperature (T_g) ca. 110 °C. Additionally, they require adding water to humidify the fuel and oxygen in order to maintain the membrane's proton conductivity. The humidifier will make the whole system complex and large. Therefore these needs promote the research and development self-humidifying membranes for PEMFC [3]. Up to now, many materials such as Pt, metal oxides, Pt/SiO_2, hetero-poly-acid, and $ZrHSO_4$ were highly dispersed into Nafion or sulfonated poly (ether ether ketone) (sPEEK) resin to fabricate self-humidifying membranes [75,148–152]. Heteropolyacids (HPA) with Keggin anion structures have received the most attention due to their simple preparation and strong acidity in development of composite membranes for PEMFCs [153,81,58]. But the major factor limit the performance of Nafion®/HPA composite membranes is the extremely high solubility of the HPA additive in aqueous media [81,155]. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is insoluble in water and organic solvents and has micro and mesopores with a high surface area. The $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ particles which were expected to increase the proton conductivity of the membrane and catalyze the recombination of H_2 and O_2. The single cell (electrode area = 5 cm^2) with these proton exchange membranes exhibited better performance than that with the commercial Nafion® (NRE-212) membrane under fully humidified and dry conditions. Fig. 30 shows the EDX results of the cross-section of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ -SiO_2/Nafion membrane. It can be seen that the Si and Cs elements were dispersed homogeneously along the cross-section of the membrane (Fig. 30). It means that the $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ particles were uniformly dispersed in the membrane [156].

Fig. 31 shows the polarization curves of cells with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-$SiO_2$/Nafion – proton exchange membrane and Nafion® NRE-212 membrane operated under fully humidified condition with the cell temperature at 60 and 80 °C, respectively. The cell performance with the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-$SiO_2$/Nafion was better than that with the NRE-212. Fig. 31 shows the effect of $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ particles addition into Nafion matrix in composite membrane than the pristine Nafion. From the Tafel slope of the polarization curves, the conductivity of the composite membrane was greatly improved by the addition of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ particles [156]. Fig. 32 shows the polarization curves of H_2/O_2 fuel cells with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-$SiO_2$/Nafion and Nafion® NRE-212 membrane operated under fully humidified and unhumidified conditions at 60 °C. The fuel cell performance were decreased when the fuel cell were operated with dry gas compared to that operated with fully humidified gas. The decrease of the cell performance with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-$SiO_2$/Nafion is slighter than that with NRE-212 membrane. The cell performance under dry gas conditions was obviously improved which is because of the addition of $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ as hygroscopic material dramatically increased the water content in the membrane, and increase the proton conductivity as well. Meanwhile, the SiO_2 particles play an important role in maintenance the water produced in the self-humidifying membrane in situ at high temperature due to their hygroscopic property and to release the water once the proton exchange membrane needs it. The new self-humidifying membrane was considered to be a very promising membrane for PEM fuel cells [156].

6.7. *Modified Nafion membrane with polymeric acid–base complexes*

The typical membranes (DuPont's Nafion series or other perfluorosulfonic acid membranes) only perform properly below 100 °C because that the membranes dehydrate at higher temperature and the proton conductivity decays sharply [157–158]. Therefore, many different approaches have been carried out to develop novel PEM membranes for high temperature operation. The novel composite membrane was synthesized according to the acid–base polymer complexes concept developed by Kerres et al. [157], which consists of

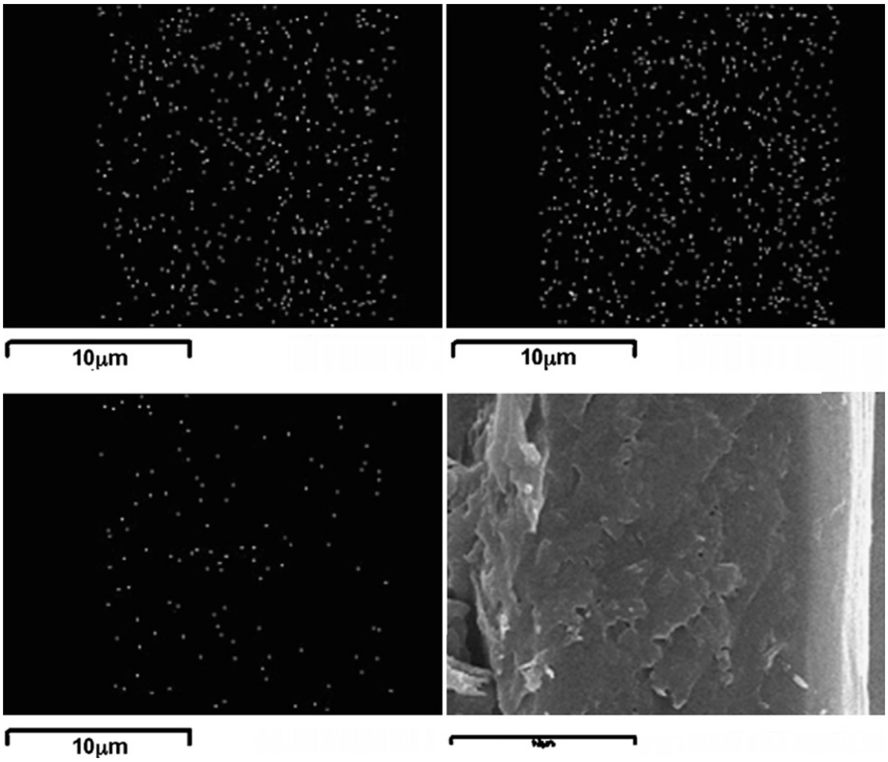


Fig. 30 – EDX analysis result of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-$SiO_2$/Nafion membrane: Si element (top left); S element (top right); Cs element (bottom left); the region used for the EDX analysis (bottom right) (modified with permission from [156]).

mixing polymeric acid with polymer bearing basic sites. Phosphoric acid-doped polybenzimidazole (H_3PO_4/PBI) and H_3PO_4/PBI/silica nanocomposite membranes have been investigated intensively and used more successfully [160–161] in high temperature PEMFC because of the excellent thermo-chemical stability, lower gas permeability [162] and mechanical property of PBI, and good proton conductivity after doped with H_3PO_4 at elevated temperature (200 °C) [163,164]. The formation of acid–base polymer complex presented in this study was shown in Fig. 33. The sulfonic acid groups of Nafion interact with the N-base of PBI either by formation of hydrogen bridges or by protonation of the basic N-sites. In the polymer complex, Nafion not only plays as a crosslinking agent but also improves the chemical stability of the polymer matrix. The transformation of Nafion resin from H^+ form to Na^+ form was the most important step for the composite membrane fabrication. Nafion–Na in the Nafion–PBI composite membrane was protonated and then interacted with PBI component

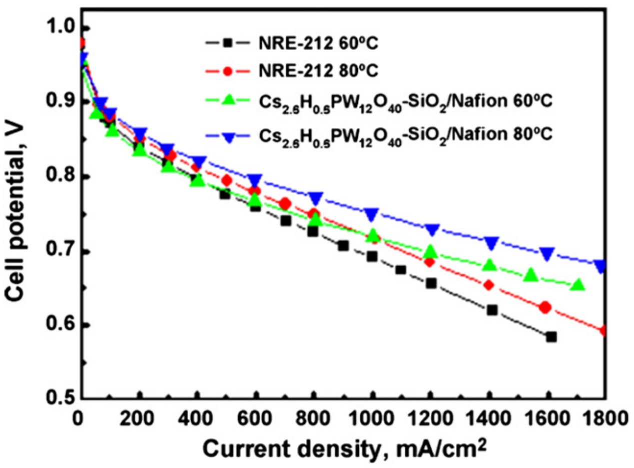


Fig. 31 – Fuel cell performance of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-$SiO_2$/Nafion self-humidifying membrane and NRE-212 at 60 and 80 °C under fully humidified conditions (modified with permission from [156]).

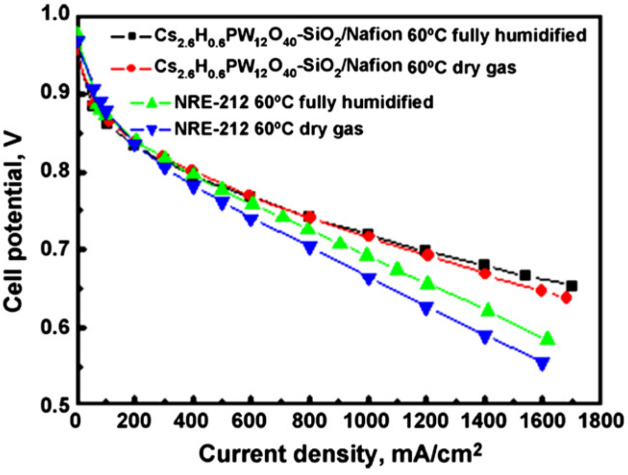


Fig. 32 – Fuel cell performance of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-$SiO_2$/Nafion self-humidifying membrane and NRE-212 at 60 °C under fully humidified and un-humidified conditions (modified with permission from [156]).

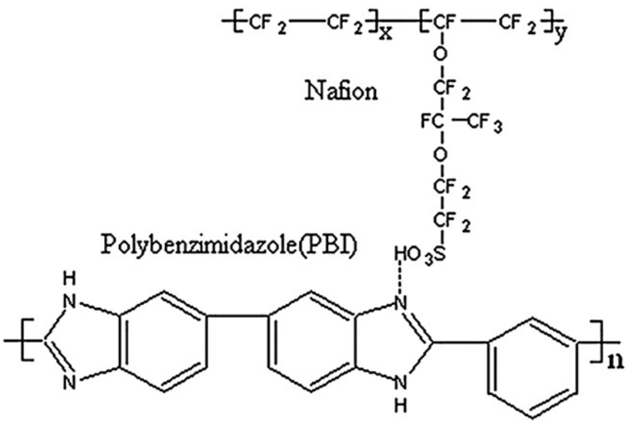


Fig. 33 – Acid–base complex formation mechanism between the sulfonic acid group of Nafion and the imidazole nitrogen of PBI (reprinted with permission from [165]).

formed Nafion–PBI crosslinked complex. In this step, the composite membrane was also doped with H_3PO_4 [165].

The acid doping level of H_3PO_4/Nafion–PBI composite membrane was lower about 8% than that of the H_3PO_4/PBI membrane, which accorded with the molar ratio (about 7%) of $-SO_3H$ to PBI repeat unit. This result indicated that the reaction, as shown in Fig. 33, occurred certainly between the sulfonic acid group of Nafion and the imidazole nitrogen of PBI. The polarization curves of the H_2/O_2 single cell with the composite membrane were shown in Fig. 34. It is obvious that the performance of the single cell reached its maximum at 60 h, and then degraded a lot during the following test, for example, the voltage of the single cell at 1000 mA cm^{-2} fell from 0.55 V at 60 h to 0.45 V, at 540 h, but it increased a little again at 720 h. After about 60 h, the single cell reached its maximum performance. The degradation in the single cell performance during the test was results of the degradation of the electrocatalyst and membrane [165]. The little increase at 720 h was due to the increase in the membrane proton conductivity, which was a result of the increase in permeability of membrane [166].

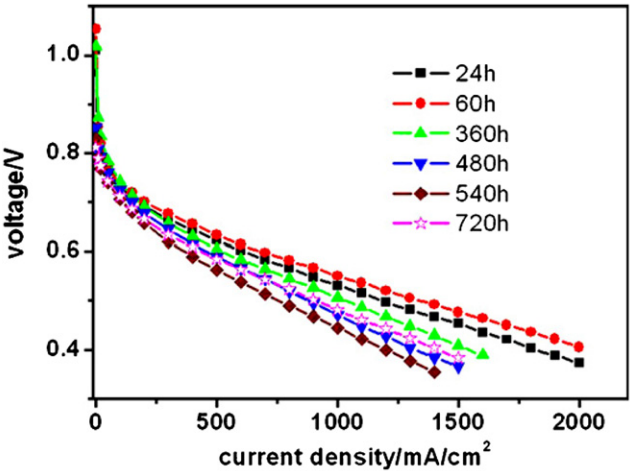


Fig. 34 – The polarization curves of the H_3PO_4/Nafion–PBI composite membrane single cell at different test time (reprinted with permission from [166]).

The performance at constant current (700 mA cm^{-2}) and the open current voltage (OCV) of the H_2/O_2 single cell with the composite membrane were shown in Fig. 35(a), as a contrast, those of the H_2/O_2 single cell with the H_3PO_4/PBI membrane were shown in Fig. 35(b). Comparing the steady performance curves of the two single cells, it is definite that the stability and durability of the H_3PO_4/Nafion–PBI composite membrane is much higher than that of the H_3PO_4/PBI membrane in high temperature PEMFCs. The results of proton conductivity investigations of H_3PO_4/Nafion–PBI composite membranes indicated that the introduction of Nafion had not reduced the proton conductivity of the H_3PO_4/PBI membrane. The results of the mechanical tensile properties (Not shown in here) can be seen that even after the 760 h durability test, the composite membrane hold still better mechanical strength than the 500 h-tested H_3PO_4/PBI membrane. All above results implied the H_3PO_4/Nafion–PBI composite membrane also had more mechanically robust than the H_3PO_4/PBI membrane and therefore the novel H_3PO_4/Nafion–PBI composite membrane is a better candidate in high temperature PEMFC for achieving longer cell lifetime [165].

As mentioned in the previous sections, Nafion® as a fluorinated proton exchange membrane, the conventional proton conducting polymer electrolyte membrane is expensive, mechanically unstable at temperatures above 100 °C, and conductive only when soaked in water, which limits fuel cell operating temperatures to 80 °C, which in turn results in lower fuel cell performance due to slower electrode kinetics and low CO tolerance [71]. Thus, the development of membranes which are mechanically and chemically stable at higher temperatures (above 100 °C) is an active area of research for producing economical fuel cells. Similarly, the non-fluorinated proton exchange membranes such as aliphatic or aromatic structures as polymeric backbone in membranes (e.g. sPEEK, sPES, sPEI,...) has been studied and investigated. The modification of these polymers with wide range of the fillers such as MO_2 (e.g. SiO_2, TiO_2, ZrO_2, ...) [167–174], zirconium phosphate [175–177,155,66], phosphotungestic acid [178], boron phosphate [179], phenolic resins [180–181], organically modified silicates (clays) [73,182–183], silane based fillers [184] and zeolites [1] have been done for the preparation of the non-fluorinated based composite proton exchange membranes in fuel cell applications. Composite membranes are shown the promising characteristics such as lower H_2, O_2 and methanol crossover, good thermal stability, increased proton conductivity, and higher water uptake. In this section, the types of the modified non-fluorinated proton exchange membranes in the PEM fuel cells are investigated.

7. Measurement and investigation methods of the proton exchange membranes properties

In this section, methods of evaluation and characterization of proton exchange membrane includes proton conductivity measurement, ion exchange capacity (IEC), water uptake, ion exchange capacity, methanol permeability, gas permeability,

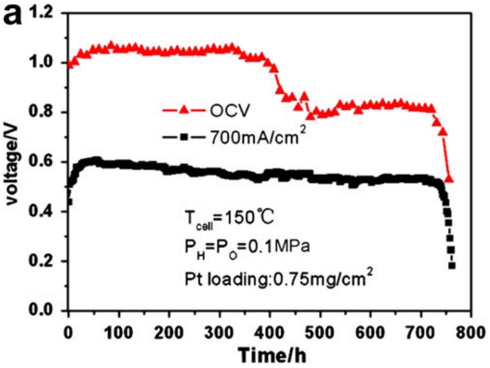


Fig. 35 – The steady state performance and open current voltage (OCV) variations of single cell with H_3PO_4/Nafion–PBI composite membrane (a) and H_3PO_4/PBI membrane (b) during life test (reprinted with permission from [165]).

durability, thermal stability and fuel cell performance of the membrane were presented.

7.1. *Membrane proton conductivity measurement with electrochemical impedance spectroscopy (EIS)*

Proton conductivity of the proton exchange membranes measure by the electrochemical impedance spectroscopy method over the frequency range of 10 Hz–10 MHz with 50–500 mV oscillating voltage in the particular conductivity cell. The proton conductivity of the membrane was measured by AC impedance technique using a Solartron impedance-gain phase analyzer. Membrane sample was equilibrated in deionized water for 24 h at room temperature prior to testing. Then, the surface water was removed, and the swollen membrane was rapidly placed between two stainless-steel electrodes in a conductivity cell (this cell is used to host the sample). The water content of the membrane was assumed to remain constant during the short period of time required for the measurement. All impedance measurements were performed at room temperature and relative humidity 100%. The membrane resistance (R) was obtained from the intercept of the impedance curve with the real-axis at the high-frequency end (obtained from a Niquyist plot). Then, proton conductivity of membrane, σ (Siemens per centimeter (S/cm)), was calculated according to Eq. (3), where σ is defined as the reciprocal of R and L and S are the thickness and area of the membrane, respectively [185].

$$\sigma = \frac{L}{R \cdot S} \tag{3}$$

High temperature conductivity measurements were conducted in water vapor. The conductivity cell was placed above liquid water in the head space of a sealed vessel. This experimental setup allowed the membrane to equilibrate with saturated water vapor at the desired temperature. The temperature was controlled by a wrap-around resistance heater and feedback temperature controller [185].

Ionic conduction in a solid material is due to a thermally activated process. Proton conductivity obeys either a simple Arrhenius law or a Vogel-Tamman-Fulcher (VTF) equation. At temperatures below the glass transition temperature, T_g, the conductivity obeys generally an Arrhenius-type law [186]:

$$\sigma = \frac{A}{T}\exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

A is a constant proportional to the number of charge carriers, E_a is the activation energy and R is the ideal gas constant. Above glass transition temperature (T_g), the conductivity usually follows the VTF formula [18,187]:

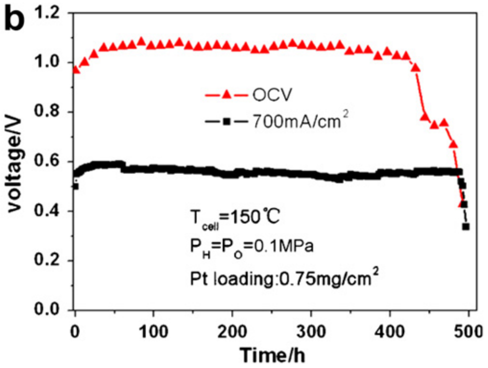
$$\sigma = \frac{A}{\sqrt{T}}\exp\left(-\frac{B}{T-T_0}\right) \tag{5}$$

B is a pseudo activation energy related to the segmental motions of the polymer and T_0 is called equilibrium glass transition temperature. The VTF behavior describes conductivity in polymers where the segmental motions contribute to the proton transport. As a consequence, amorphous polymers exhibit a higher conductivity above glass transition temperature than below. Typically, three distinct conductivity behaviors can be observed in polymer electrolytes:

1. VTF behavior is observed above glass transition temperature (T_g) of the polymers.
2. Arrhenius-type behavior at low temperatures and VTF at high temperatures.
3. Arrhenius-type behavior throughout the whole temperature range with a clear decrease of the activation energy around T_g. This is the behavior of polymers with an extremely rigid structure; thus, the contribution of segmental motions is low [18].

7.2. *Water uptake measurement of the proton exchange membranes*

The performance of a membrane is dependent on proton conductivity, which in turn often depends on its water content. High proton conductivity is supported by high level of water uptake; at the same time, it is also a sign of low-dimensional stability as water influences the polymer microstructure and mechanical properties. Since water is also known to assist the mass transport of methanol and oxygen through the membrane, the water uptake measurements could serve as a quantitative measure of membrane performance for DMFC application as well. Gravimetric technique has been widely used for this purpose. Water uptake measurements due to gravimetric techniques are generally done by double weighing.



'Wet' weights (W_{wet}) of the membranes are first measured after equilibrating with water at different temperatures or upon exposure to water vapor at various pressures. The membrane samples are then dried at a temperature above the boiling point of water for a particular period of time and their 'Dry' weights (W_{dry}) measured. The total water content (W_{uptake}%) is determined from the difference between the wet and the dry mass of the membranes as follows [1]:

$$\text{Water Uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{6}$$

If t_w and t_d are the thicknesses of wet and dry membranes, respectively, the membrane swelling ratio may be calculated as:

$$\text{Swelling Ratio} = \frac{t_w - t_d}{t_d} \times 100 \tag{7}$$

The membrane water content parameter, 'λ', the number of moles of water per mole of acidic group can be calculated:

$$\lambda = \frac{N_{H_2O}}{N_{SO_3^-}}, \lambda = \frac{(W_{wet} - W_{dry})}{18 \times IEC \times W_{dry}} \tag{8}$$

IEC is the ion exchange capacity of the membrane. Water uptake curves are generally represented as number of water molecules per sulfonic acid group 'λ' versus thermodynamic water activity or relative humidity, which is the ratio of water partial pressure and saturation partial pressure of water (Fig. 36). The factors that affect the extent of the water uptake of a membrane are temperature, ion-exchange capacity, and pretreatment of membrane, the physical state of absorbing water, whether it is in liquid or vapor phase, and the elastic modulus of the membrane. A major objective in the nanocomposite and hybrid membrane research is to determine which chemical attributes of the composite membranes improve water level at elevated temperature and thereby improve PEMFC performance [15].

7.3. Ion exchange capacity measurement by using of the titration method

IEC or EW is the measure of relative concentration of acid groups within polymer electrolyte membranes. Proton conductivity and water uptake both rely heavily on the concentration of ion conducting units (most commonly sulfonic acid) in the polymer membrane. The ion content is characterized by the mass of dry membrane per molar equivalents of ion conductor and is expressed as EW with units of grams of polymer per equivalent or as IEC with units of milliequivalents per gram (mequiv. g^{-1} or mmol g^{-1}) of polymer. Varying the ion content of the membrane can control both its water uptake and conductivity. While it is desirable to maximize the conductivity of the membrane by increasing its ion content (decreasing equivalent weight), other physical properties must be considered. Too many ionic groups will cause the membrane to swell excessively with water, which compromises mechanical integrity and durability.

IEC of membranes is determined by titration at room temperature. The membranes in the acidic forms (H^+) are first converted to the sodium forms by immersing the membranes in NaCl solutions to exchange the H^+ ions for Na^+ ions by following equation:

$$R - H + Na^+ \rightarrow R - Na + H^+$$

the exchanged H^+ ions within the solutions are titrated with 0.01 N NaOH solutions. IEC values may be calculated from the titration result using the formula [188]:

$$IEC = \frac{\text{Consumed ml of NaOH} \times \text{Molarity of NaOH}}{\text{Weight dried membrane}} (\text{meguiv. } g^{-1}) \tag{9}$$

7.4. Methanol permeability measurement through the proton exchange membranes

The study of the methanol mass transport through DMFC membranes is very common due to its detrimental effect on the DMFC performance (reduced coulombic efficiency). Even if not accounting for the anode catalytic reaction and the electroosmotic drag mass transfer, the methanol permeability in the proton exchange membranes is usually evaluated by pervaporation and diffusion cell experiments [189]. For methanol permeability experiments, most researchers use

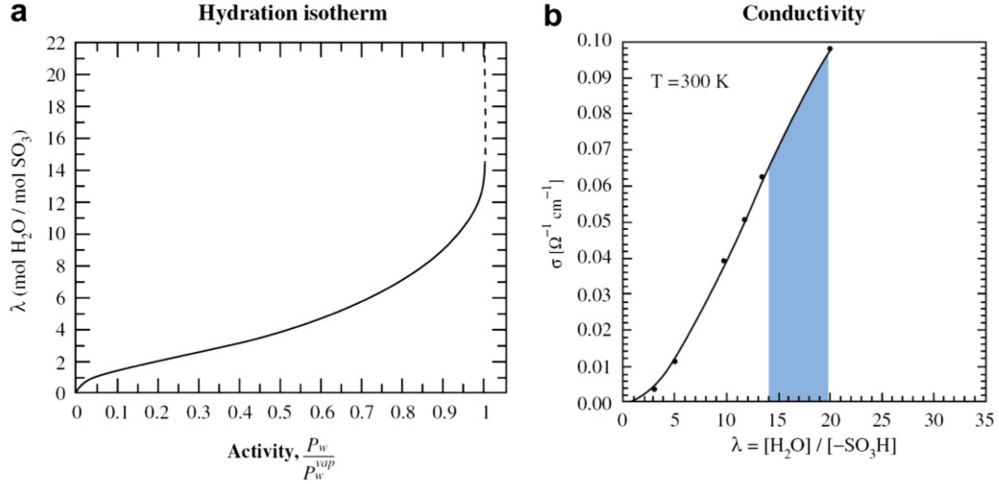


Fig. 36 – (a) Equilibrium water uptake or isotherm curve for Nafion at 300 K. The shaded line corresponds to coexistence with liquid water (λ = 22), (b) Conductivity vs. water-uptake curve at 300 K. The shaded area corresponds to coexistence with liquid water (λ = 22) (reprinted with permission from [15]).

a side-by-side diffusion cell, where the proton exchange membrane is sandwiched between donor (upstream side) and receptor (downstream side) compartments [16]. The donor compartment is charged with methanol (~1–2 M) and the concentration of methanol is measured on the downstream side as a function of time. The permeability can be determined from the slope of the early time data [190] where a variety of detection methods have been used, including gas chromatography [191] refractometry [192–194] and FTIR-ATR spectroscopy [190,195–197].

7.5. *Gas permeability measurement through the proton exchange membranes*

The gas permeability of the membranes was measured by means of a two chambers cell as shown in Fig. 37. A sample membrane was fixed by porous carbon plates with the membrane edges sealed by Viton® (DuPont) gaskets. During the measurement, a pressure difference of up to 1×10^6 Pa was applied to the membrane. The gas pressure of each side of the membrane was monitored via pressure sensors. The temperature was controlled with an oil bath by immersing the cell system in it. For the measurement of the gas permeability coefficient, $\mathcal{P}$, one chamber of the cell was filled with pressurized gases while the other was always kept under vacuum. The gas diffused through the membrane under the driving force of pressure. The mole number of the gas, n, passed through the membrane can be calculated from the decreased pressure P_d on one side of the membrane within a certain time (t in s) by using the equation:

$$n = \frac{P_d \cdot V}{R \cdot T}(\mathrm{mol}) \tag{10}$$

where R is the gas constant, T the temperature in Kelvin and V is the volume of the gas chamber. The gas permeability coefficient, $\mathcal{P}$, can then be calculated:

$$P = \frac{n \cdot L}{A \cdot t \cdot P_d}(\mathrm{mol\ cm\ cm^{-2}\ s^{-1}\ Pa^{-1}}) \tag{11}$$

where L (in cm) is the membrane thickness, A (in cm^2) the area of the membrane for gas diffusion and P_d (in Pa) is the pressure difference through the membrane. Before the measurement, the membrane was dried under vacuum at appropriate temperature for more than 1 h. All the measurements were performed when the other chamber of the cell was maintained under vacuum and the measured gas permeability is regarded as for dry membranes [198].

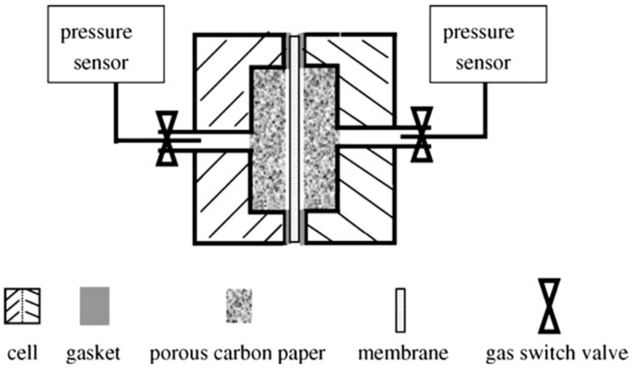


Figure 37

Fig. 37 – The Cell for gas permeability measurements (reprinted with permission from [198]).

7.6. *Durability measurement of proton exchange membranes*

Proton exchange membrane fuel cells (PEMFCs) are very promising as environment-friendly energy supplier. However, their durability and cost are the key issues that should be solved for practical applications. Now the research emphasis has shifted from improving the initial performance ("beginning-of-life") to enhancing fuel cell reliability and lifetime and to making fuel cell cost competitive. Proton exchange membranes (PEMs) are the key components in fuel cell system, which limit the lifetime of the whole PEMFCs. Thus enhancement of the durability of the PEMs is critical to the lifetime and commercial viability of the PEMFCs. In the last decade, the membrane degradation mechanism studies became the focus of attention. To sum up the recent published reports, the membrane degradations are mainly classified as chemical/electrochemical degradation and physical degradation. As for the former degradation, hydrogen peroxide and its decomposition intermediate products HO• and HO_2• with strong oxidative characteristics generated during the fuel cell operation have been considered as one of the important factors resulting in the membrane degradation. The formation of H_2O_2 has been confirmed using a microelectrode in an operating fuel cell [199] and detected in the outlet stream of the cell with Nafion membrane by Scherer [200].

Therefore, the membrane durability was evaluated by both ex situ Fenton test [201] and in situ OCV accelerated test [202]. Membrane samples were respectively immersed in 50 ml Fenton solution (3 wt.% hydrogen peroxide solution and 20 ppm Fe^{2+}). The durability tests were carried out at 80 °C for

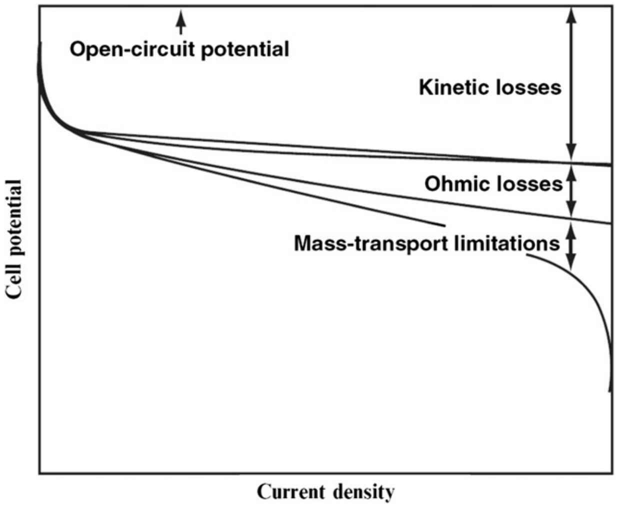


Fig. 38 – Example of a polarization curve showing the typical losses in a polymer-electrolyte fuel cell.

Table 8 – Advantages and disadvantages of the different modifications on Nafion as the perflourinated proton exchange membranes.

Modification Methods	Filler Type	Advantages	Disadvantages	Suitable Application
Inorganic Oxides, MO_2 (M = Ti–Si–Zr)	SiO_2, TiO_2, ZrO_2 [60,67,75–80,90,233] ZrO_2/SO_4^{-2} [86–89]	- Higher water uptake - Better fuel cell performance in higher temperatures - Higher membrane retention properties - Lower water Swelling	- Lower proton conductivity - Higher membrane cost	PEMFC
Clays	Laponite (Lp), Montmorillonite (MMT) [95–100] MMT modified with POPD400-PS [109]	- Lower methanol crossover - Lower membrane cost - Higher thermal stability - Higher membrane selectivity	- Lower proton conductivity	DMFC
Zeolites	NaA zeolite, ETS-10, Umbite, Mordenite [111,119]	- Higher thermal stability - Stable fuel cell performance in higher temperatures - Lower methanol crossover - Higher membrane selectivity	- Poor mechanical properties - Higher membrane cost - Lower proton conductivity	DMFC
Conductive Polymers	Polyaniline (PANi) [127–133,137–138] Polypyrrole (PPy) [125]	- Lower methanol crossover - Higher membrane selectivity	- Lower proton conductivity - Lower water uptake - Lower water swelling - Higher membrane cost	PEMFC, DMFC
Polymer Blend Membranes	sPEEK/PBI [40] Polyacrylonitrile (PAN)/ Polyphosphazene [143–144] sPEEK/PAN [145]	- Better mechanical properties - Easier MEA fabrication - Lower methanol crossover - Lower water Swelling - Improved thermal stability	- Lower proton conductivity - Higher membrane cost	DMFC
Proton Conductive Fillers	Pt/SiO_2, $ZrHSO_4$ [75,148–152] Heteropolyacid (HPA) [58,153–154,81,156]	- Higher proton conductivity - Self-humidifying properties - Better fuel cell performance in higher temperatures	- Higher leaching rate - Higher membrane cost	PEMFC
Acid–Base Complexes	PBI/H_3PO_4 [159] PBI/H_3PO_4/Silica [160–164] Nafion/PBI/H_3PO_4 [165–166]	- Better fuel cell performance in higher temperatures - Excellent thermo-chemical stability - Lower gas permeability - Better mechanical properties - Higher proton conductivity	- Higher membrane cost	PEMFC

150 h prior to fluorine ion characterization, the Pt wire was immersed into the analyte solution to decompose the residual hydrogen peroxide, which was to assure of the accurate and reproducible results.

There are two different pathways for the H_2O_2 generation and the free radical species: (1) generating at the cathode due to the electrochemical two-electron reduction of oxygen [203] or the chemical combination of crossover hydrogen and oxygen at the cathode (mechanisms 1–4) and (2) generating at the anode due to the chemical combination of crossover oxygen and hydrogen at the anode (mechanisms 4–7) [204,205].

(1) $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$
(2) $H_2O_2 + M^{2+} \rightarrow M^{3+} + HO^\bullet + HO^-$
(3) $HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$ (hydrogen peroxide radical attacks PEM)
(4) $H_2 + O_2 \rightarrow [O] + H$ (on Pt surface)
(5) $H_2 \rightarrow 2H^\bullet$ (via Pt catalyst)
(6) $H^\bullet + O_2$ (diffused through PEM to anode) $\rightarrow HO_2^\bullet$
(7) $HO_2^\bullet + H^\bullet \rightarrow H_2O_2$ (diffused into PEM)

Effective strategies should be taken to improve the membrane durability. The passive approach is to improve polymer stability, such as synthesis of short side chain polymers [206,207], novel hydrocarbon polymer electrolytes [208], or composite membrane with PTFE [209]. The active approach is to suppress the free radicals attack, such as avoiding H_2O_2 formation, destroying H_2O_2 [210–213] or scavenging the free radicals [214,215]. Trogadas and Ramani [211] prepared Pt/C/MnO_2 hybrid catalyst to minimize the effect of reactive oxygen species at fuel cell operation condition. Though the hybrid catalyst can mitigate the generation of hydrogen peroxide, the activity of the catalysts is poor at the same time. Zhao and et al. have been designed a multifunctional catalyst which can decompose H_2O_2 and scavenge the free radicals on the surfaces of the nanoparticles. Since the scavenging catalyst is nonconductive, the cell performance may reduce with the nanoparticles dispersion. Thus, the proton conductivity was also considered. In their study, they have been investigated the effects of the multifunctional catalyst composed of a metal oxide with variable valence, cerium nanoparticles,

Table 9 – Advantages and disadvantages of the different modifications on sPEEK as the non-fluorinated proton exchange membranes.

Modification Methods	Filler Type	Advantages	Disadvantages	Suitable Application
Inorganic Oxides, MO_2 (M = Ti–Si–Zr)	SiO_2 [225], TiO_2 [174], ZrO_2 [229]	- Higher thermal stability - Lower methanol crossover - Higher water uptake - Lower water Swelling	- Lower proton conductivity - Higher membrane cost	PEMFC, DMFC
Clays	Silica-SO_3H [224] Modified nano-silica [225] Organo modified MMT [226] Lapinte, MCM-41 [227] Modified MMT with Krytox [232]	- Higher chemical and mechanical stability - Lower methanol crossover - Lower membrane cost - Higher water retention properties	- Lower proton conductivity	DMFC
Zeolites	β-zeolite [221] Modified zeolite with ZrP [222] H-type of β-zeolite [223]	- Lower methanol crossover - Higher thermal stability - Better fuel cell performance in higher temperatures - Lower membrane swelling - Higher mechanical stability	- Lower proton conductivity - Higher membrane cost	DMFC
Conductive Polymers	Polypyrrole (PPy) [228]	- Lower methanol crossover - Better DMFC performance - Higher thermal stability	- Lower proton conductivity - Higher membrane cost	DMFC
Proton Conductive Fillers	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [155] Tungstophosphoric acid [220] *phosphatoantimonic acid* [230] Phosphotungestic acid [231]	- Higher proton conductivity - Better self-humidifying properties at high temperatures - Chemical and physical stability - Better fuel cell performance in higher temperatures - Higher water uptake - Higher IEC amounts	- Higher leaching rate - Higher membrane cost	PEMFC

and a solid acid, cesium substituted 12-tungstophosphoric, in PEMs [216].

7.7. *Thermal stability of measurement of proton exchange membranes*

One of the major issues to be addressed in the development of proton-conducting nanocomposite and hybrid membranes for fuel cell applications is their high temperature stability. It arises primarily due to the fact that the sulfonic acid side chains in backbone polymers such as Nafion and other sulfonated hydrocarbon membranes undergo desulfonation with increase in temperature. While the sulfonic acid groups in Nafion are stable up to a temperature of 280 °C in air [215,217,218], the degradation temperature of sPEEK is reported to be in the range of 240–330 °C. Desulfonation is in general studied by means of thermogravimetric analysis (TGA), differential thermal analysis (DTA), Fourier-transform infra-red spectroscopy (FT-IR) and TGA-mass spectrometry (MS). In Nafion-based composites this decomposition behavior is attributed to the loosening of sulfonic acid groups present in the unmodified Nafion membrane [219]. It was also observed that the temperature at which this decomposition occurs shifts with the nature of inorganic additive within the pores of Nafion membrane. For example, sharp thermal degradation of the unmodified Nafion occurs at about 325 °C, whereas for Nafion-ZrO_2, and Nafion-SiO_2 sol–gel membranes, degradation temperature shifts to about 360 °C and 470 °C, respectively [90]. The TiO_2 incorporated membranes on the other hand are reported to show not much improvement in thermal degradation temperature as compared with Nafion. A systematic investigation on the thermal behavior of nanocomposite and hybrid membranes would thus give more insights into their stability at high temperatures. Although informative, these thermal stability results can hardly be used to predict the long-term durability of these membranes. Therefore, the degradation of the proton exchange membranes mostly was investigated by Thermogravimetric analysis (TGA). The primary degradation in degradation mechanism of theses membranes is the degradation of polymeric backbone of membranes and the secondary degradation is the degradation of the pendant groups or inorganic compounds inside the membranes in higher temperatures than the primary degradation.

7.8. *MEA testing in fuel cell performance test system*

The development of new or modified PEMs with improved characteristics for fuel cell applications requires a quantitative determination of their electrochemical performance under relevant fuel cell conditions. The most straightforward approach for this is to construct a membrane electrode assembly (MEA) and measure the cell parameters in a single cell configuration. A membrane electrode assembly includes an anode, a cathode, a membrane disposed between the anode and the cathode and an extended catalyst layer between the membrane and the electrodes. The conversion efficiency of MEA depends on many factors including type and thickness of both membrane and gas-diffusion material, nature of binder used in the electrodes and the binder to catalyst ratio apart from the operation conditions (temperature, pressure, flow rates, humidification of reactant gases). In addition, the ability to collect data from an operating electrochemical system can be alluring. Single cell testing is relatively straightforward and operation conditions can be accurately monitored as it allows specific control over humidity, reactant flow and temperature. Cell performance is often described by the polarization curve, i. e., and cell voltage vs. current density. A typical curve is shown in Fig. 38. In general three main polarization losses can be identified: (a) activation overpotentials, arising from charge transfer and other reaction kinetics; (b) ohmic losses, arising from the electrical resistances of the cell materials and interfaces and (c) mass transport overpotentials, arising from the limitations of mass transport. At low current densities, the shape of the curve is primarily determined by activation polarization, which gives it the characteristic logarithmic shape. It plays an important role if the reaction rate on the electrode surface is restricted by sluggish electrode kinetics. Similar to a chemical reaction, the electrochemical reaction has to overcome an activation barrier. This barrier usually depends on the electrode material (electrocatalyst). When pure hydrogen is used as fuel, the activation losses of the anode are negligible, because the rate of the hydrogen oxidation reaction is orders of magnitude higher than the rate of the cathode reaction. Hence, the main source of activation overpotential is the cathode, which means the oxygen reduction. When current density increases, the shape of the curve becomes approximately linear, reflecting the effect of *ohmic losses*. This is caused by both the resistance due to the migration of ions within the electrolyte and the resistance due to the flow of electrons. It can be expressed by the product of cell current (I) and the overall cell resistance (R, including electronic, ionic and contact resistances). When current density is increased further, the curve begins to bend down due to mass transport overpotentials, which result from limitations in the availability of reactants at the catalyst surfaces. The main source of losses is the cathode side again, because the diffusivity of oxygen is significantly lower than that of hydrogen, due to the larger molecular size of oxygen.

Fuel cell efficiency on the other hand is directly proportional to the power density (in W cm^{-2}), which can be linked directly to the chemistry of the polymer membrane. Higher achievable power density directly translates to smaller, thus less expensive fuel cells. Thus, a swift comparison of the obtained data against those obtained with unmodified membranes will provide useful information on the influence of inorganic phase on the nanocomposite efficiency. Their effectiveness as a catalyst binder may be evident from an investigation on the interfacial effects of membrane on electrodes and catalysts. In the case of Class I membranes intended for high temperature operations, apart from I–V measurements, the methanol crossover flux vs. methanol feed concentration can be collected; the suitability of the membrane for DMFC applications may be accessed from these data. The long time stability of the membranes against different operating conditions may also be studied. In short, membrane electrode assembly (MEA) testing will be of great advantage to fine tune the hybrid membrane properties in order to give them commercial viability. However, a major technical challenge is up-scaling single cell performance to multi-cell stacks [197].

8. Conclusions

Today energy crises and environmental pollution has turned into a great problem for human. For solving these problems vast efforts to replace fossil fuels with other energy sources such as its connotation clean fuel have been taken. Fuel cells due to their particular properties are on the verge of creating a vast revolutionary change in the field of electricity. In the PEM fuel cells, from solid polymer electrolytes which have the ability to transfer of proton, has used as membrane. Ion exchange membranes especially proton exchange membrane, has an important role in the proton transferring in PEM fuel cells electrolyte. The desirable ion exchange membrane should be have the higher perm selectivity, suitable proton conductivity, good mechanical and chemical stability and the factors affecting the performance of the suitable proton exchange membrane are as follows: sufficient hydration and thickness of the membrane. Cation exchange membranes were obtained from the attachment of the acidic functional groups and the anion exchange membranes from the attachment of the alkaline functional groups into polymer backbone of membrane. The reduction of the membrane thickness caused to increase of the membrane proton conductivity but also leads to increase the fuel crossover through the membrane. The fluorinated membranes due to their high cost, low proton conductivity in higher temperatures and higher methanol crossover caused to develop the composite membranes. Therefore, the most important goals of modification of the proton exchange membranes in PEM fuel cells can be mentioned such as preparation of the proton exchange membranes with lower cost compared to the fluorinated membranes, the desirable water uptake and retain in the elevated temperatures, desirable proton conductivity in the higher temperatures, the lower extent of the reactant gaseous and methanol crossover through the membrane, improved thermal stability, higher mechanical and chemical strength and also creation of the self-humidity of the membranes in elevated temperatures. For example, the introduction of the metallic oxides such as MO_2 into polymer matrix of the proton exchange membrane caused to increase the water uptake and retention property and then increase the proton conductivity of membrane in elevated temperatures which this increase in the water uptake is related with the acidity of these oxides. The clays modified with sulfonic acid groups caused to increase the membrane IEC and then the proton conductivity and membrane performance increases in fuel cells at elevated temperatures. Although the polymer-zeolite composite membranes have the lower values of proton conductivity than Nafion, but polymer-zeolite composites show a more stable performance at high temperatures. Also, the lower extent of the methanol permeability of the polymer-zeolite composite membranes with their lower proton conductivities caused to increase their selectivity in direct methanol fuel cell applications. The incorporation of the heteropolyacids into polymer matrix of membranes not only caused to increase the composite proton conductivity, but also due to retention properties of the heteropolyacids, the composite membranes have self-humidity properties in the elevated temperatures. Tables 8 and 9 summarize the advantages and disadvantages of the different modifications on the perflourinated and non-fluorinated proton exchange membranes respectively, which have been discussed in this review paper. As a result from Tables 8 and 9, the proton exchange membranes modified with clays are suitable for DMFC applications of fuel cells and the fabrication cost of these composite membranes is low. However, these membranes don't have sufficient proton conductivity for PEMFC and the PEM fuel cell performance of these membranes is low. The using of the polyaromatic structures in proton exchange membranes such as sPEEK is suitable for high temperature fuel cells. The modification of these polyaromatic membranes with acidic oxides (MO_2) cause to increasing of membrane thermal stability in elevated temperatures. Therefore, for high temperature fuel cells the use of polyaromatic structures of membranes and self-humidifying additive cause to the improvement of fuel cell performance with dry reactant gases. For increasing of the fuel cell performance in PEMFCs, the proton conductivity of the membrane must be high. For reaching this goal, the using of the proton conductor materials such as heteropolyacids is recommended. Therefore, fuel cells with proton exchange membranes modified with proton conductors have a higher fuel cell performances compared with membranes modified other fillers.

Acknowledgments

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