



The proton exchange membranes for fuel cell applications - A Review

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Abstract: PEMFCs (proton-exchange membrane fuel cells) are a promising technology for producing safe and effective electricity in the twenty-first century. The primary components in a fuel cell system are proton exchange membranes (PEMs). The aim of the researchers was to develop a proton exchange membrane with high proton conductivity, low electronic conductivity, low fuel permeability, low electroosmotic drag coefficient, good chemical/thermal stability, good mechanical properties, and a low cost. The "iron triangle" of efficiency, durability, and cost is used to classify these. The current PEMFC technology is based on costly perfluorinated proton-exchange membranes (PEMs) that only work when completely hydrated. There is a lot of interest in lowering membrane costs and expanding the operating window of PEMs because of the applications. The creation of 'water-free' electrolytes that do not need hydration could minimize the complexity of PEMFC systems. It also allows the PEMFC to work in 'warm' conditions (above 100°C), improving its performance even more. Since fewer Pt could be used in colder climates, capital costs could be further reduced. This paper provides an overview of the main requirements for proton exchange membranes (PEM) in fuel cell applications, as well as a review of the existing membrane materials and their ability to meet these requirements. This paper examines and discusses a variety of potential alternative candidates. Some new products, innovations, and research directions are also explored in order to meet the PEM fuel cell industry's demanding efficiency and durability requirements. Alternative PEMs are divided into three categories: modified Nafion® composite membranes, functionalized non-fluorinated membranes and composite membranes derived from them, and acidebase composite membranes. In the sense of composite membranes, many widely used inorganic additives are discussed. Finally, general methods for calculating and analyzing proton exchange membrane properties, such as proton conductivity, ion exchange potential, water absorption, gas permeability, methanol permeability, longevity, thermal stability, and fuel cell efficiency testing, have been investigated.

Keywords: Polymeric electrolyte, Proton exchange membrane Fuel cell, Nafion , Composite membranes

1. INTRODUCTION

Fuel cells are on the brink of causing a massive disruption in the world of electricity due to their unique properties. By definition, a fuel cell is an electrochemical device that converts chemical energy from fuel into electrical energy without burning it. As a result, the chemical energy associated with the electrochemical reaction of the fuel with the oxidant is directly converted into water, electricity, and heat in a fuel cell device. H₂, methanol, gasoline, and other fuels have traditionally been used in fuel cells. In conclusion, the reactions that occurred in a fuel cell can be explained as follows: The hydrogen in the anode electrode transforms into a hydrogen ion, releasing electrons. The electrical current is generated by electrons moving through a foreign circuit towards the cathode. The following anodic and cathodic reactions were performed in the PEM fuel cell with H₂ gas in the anode:

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 feature and, in other words, the fuel cell's integral heart is the membrane electrode assembly (MEA), which is made up of two parts: electrocatalyst and



membrane. In this part, the electrical current step (electrochemical reaction) will be processed. The purpose of the membrane between electrodes is to conduct emitted protons from anode to cathode [1]. Current ions travel through the electrolyte membrane to the cathode, where they contain water and heat with free electrons. In Figure 1, the primary compartments of the PEM fuel cell are depicted. Fuel cells have the following advantages over other forms of energy-producing equipment: better reliability, lack of mobile parts and therefore lack of sonic pollution, and no emissions of environmentally polluting gases such as SO_x, NO_x, CO₂, CO, and others. The only drawback of fuel cells, in contrast to their advantages, is their higher cost, which can be overcome by using modern technology and mass manufacturing of these fuel cells. Fuel cells can be categorized in a variety of ways depending on the standards used, which are usually based on various factors relating to operating conditions and fuel cell construction. The type of electrolyte used in fuel cells, the type of ion transferred through the electrolyte, the type of reactants (e.g. main fuels and oxidants), the working temperature and pressure, the active and indirect use of primary fuels in fuel cell systems, and ultimately the primary and regenerative systems are all factors in fuel cell systems. Fuel cells are commonly classified and designated based on the quality of the electrolyte used in the fuel cell. Therefore, based on this classification, fuel cells include the following different types: (1) alkaline fuel

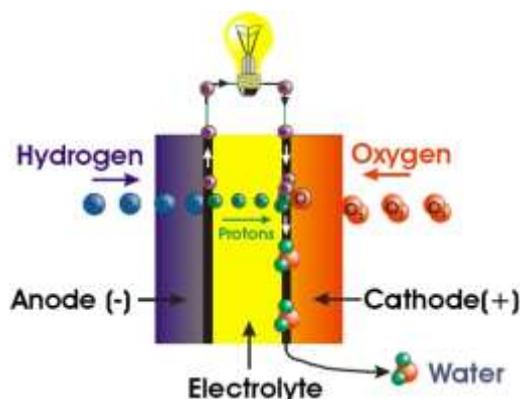


Fig. 1 e Schematic design of the PEM fuel cell.

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].

Ion-exchange membranes have been used in a variety of industrial processes, including electro-dialytic concentration of seawater to produce edible salt, as a separator for electrolysis, electro-dialysis desalination of saline water, electro-dialysis separation of ionic materials from non-ionic materials, electro-dialysis recovery of acid and alkali from waste acid and alkali solution, and electro-dialysis separation of ionic materials from non-As discussed in the previous part, solid polymeric electrolytes with proton-transfer capabilities will be used in PEM fuel cells. The gel-like polymeric compounds that were severely swollen and carried fixed positive and negative charges are among the ionic polymer electrolytes. This polymer do not have the ability to move proton in dry environments and only have this property in a saturated state, so increasing the amount of water within them would improve the ionic conductivity. Dupont first developed a chemically stable cation-exchange membrane based on sulfonated polytetrafluoroethylene as Nafion® in the 1970s, which led to widespread use of the membrane in the chlor-alkali industry and energy storage or conversion systems (fuel cells) [4]. The DuPont Co.'s fluorinated sulfonic acid Nafion membrane was used as a reference membrane for polymeric electrolyte fuel cells. Figure 2 depicts the various forms of ion exchange membranes as well as the progression of their growth since their first introduction. Traditionally, ion exchange membranes are classified into anion exchange membranes and cation-exchange membranes depending on the type of ionic groups attached to membrane matrix. Cation exchange membranes contain negatively charged groups, such as eSO_3^-



, $eCOO^-$, ePO^{2-} , ePO_3H^- , $eC_6H_4O^-$, 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 eNH_3^+ , $eNRH_2^+$, eNR_2H^+ , eNR_3^+ , ePR_3^+ , eSR_3^+ , etc., fixed to the membrane backbone and allow the passage of anions but reject cations [5,6].

Type of Fuel Cell	Operating Temp. (°C)	Power Density (mW/cm ²)	Fuel Efficiency (Chem. Elec.)	Lifetime to (hr)	Capital Cost (\$/kW)	Area of Application
AFC [2]	60e90	100e200	40e60	>10,000	>200	Space, Mobile
PAFC	160e220	200	55	>40,000	3000	Distributed Power
PEMFC	50e80	350	45e60	>40,000	>200	Portable, Mobile, Stationary
MCFC	600e700	100	60e65	>40,000	1000	Distributed Power Generation
SOFC	800e1000	240	55e65	>40,000	1500	Baseload Power Generation

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 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. Materials that can speed up the commercialization of fuel cells are the focus of today's study. This paper is a study of past and current research in the field of proton exchange membrane production for fuel cells in order to improve efficiency, longevity, and cost. 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]. Many advancements have been made in recent years, but there are still technological and economic barriers to the commercialization of fuel cells. Many attempts have been made in this regard to grow PEMFC membranes with improved efficiency and longevity.

1. Proton exchange membranes for fuel cell applications

Membrane is the central component of the PEM fuel cell, as previously said. The polymeric membrane has three functions in PEM fuel cells: charge carrier for protons, separator of reactant gases, and electrical insulator to prevent electrons from flowing through the membrane (due to the negative charge of SO₃⁻ and electron repelling). DuPont produced a perfluorosulfonic acid dubbed "Nafion®" in the 1970s that increased the membrane's basic conductivity by two orders of magnitude while also extending its lifespan by four orders of magnitude (10⁴e10⁵ h). This soon became a standard for PEMFC and remains so till today. The Dow Chemical Company and Asahi Chemical Company synthesized advanced per fluorosulfonic acid membranes

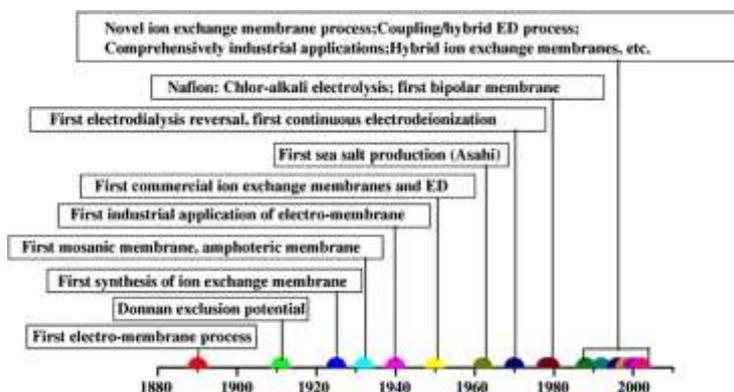
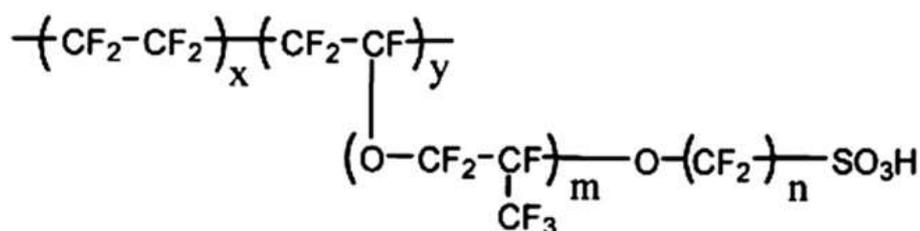


Fig. 2 e Types of the ion exchange membranes based on their development time (reprinted with permission from [8]).

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 is made up of a copolymer of fluoro 3,6-dioxo 4,6-octane sulfonic acid and polytetrafluoroethylene (PTFE). The Teflon backbone of this structure gives the membrane its hydrophobic appearance, and hydrophilic sulfonic acid groups ($\text{HSO}-3$) have been chemically grafted into the backbone. The polymer's ionic groups also allowed it to absorb a significant amount of water, resulting in hydration. As a result, the degree of hydration and thickness of a suitable proton exchange membrane affect its performance, which is a key factor in deciding whether it is suitable for use in a fuel cell [11]. The proton conductivity of the proton exchange membrane was linked to its effectiveness, and the proton conductivity was also linked to the humidity of the membrane. A higher humidity level results in better proton conductivity.



Nafion [®] 117	$m \geq 1, n=2, x=5-13.5, y=1000$
Flemion [®]	$m=0, 1; n=1-5$
Aciplex [®]	$m=0, 3; n=2-5, x=1.5-14$
Dow membrane	$m=0, n=2, x=3.6-10$

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

1. The degree of the proton conductivity of the proton exchange membrane was related to its efficiency, and the proton conductivity was also related to the membrane's humidity. The greater the humidity level, the higher the proton conductivity. Reduced membrane thickness is one way to prevent water drag or water crossover, allowing for better fuel cell efficiency.. Reduced membrane thickness also has other benefits, such as lower membrane resistance (and thus improved membrane conductivity), lower cost, and quicker hydration. Due to difficulties with stability and fuel by-pass, however, there is a limit to how much membrane thickness can be decreased. The polymer electrolyte as membrane must have the following attractive properties in order to achieve high efficiency in fuel cell applications: 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. Processes of proton conduction in proton exchange membranes Proton conduction is a key feature of proton exchange membrane fuel cells, and it's normally the first thing people look for when deciding which membranes to use. High conductivity is needed for the required efficiency, particularly at high current density, and resistive loss is proportional to the membrane's ionic resistance. Proton transfer in hydrated polymeric matrices is generally defined on the basis of one of two main mechanisms: (1) "proton jumping" or "Grotthus mechanism" and (2) "diffusion mechanism" with water as the vehicle or "vehicular mechanism".In proton hopping mechanism protons hop from one hydrolyzed ionic site to another across the membrane with intended application [10].

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	e	0.15	e	0.0071
Flemion	Perflourinated	e	0.15	e	e
Ionac Chemical Company, Sybron Corporation, USA					
MC 3470	e	1.5	0.6	35	0.0075
MC 3142	e	1.1	0.8	e	0.0114
Ionics Inc., Watertown, MA 02172, USA					
61AZL386	e	2.3	0.5	46	0.0081
61AZL389	e	2.6	1.2	48	e
61CZL386	e	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

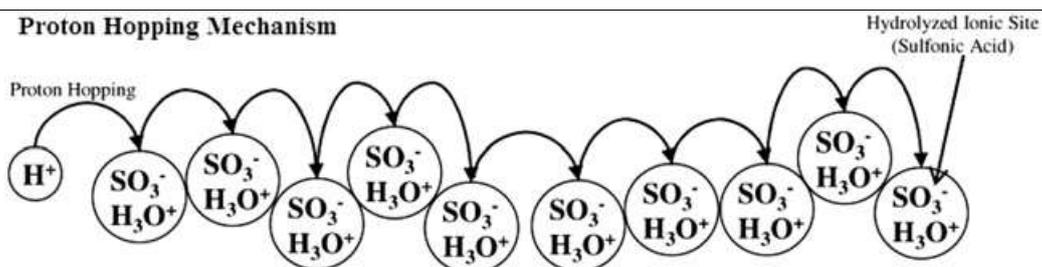


Fig. 4 e The simple scheme of the hopping mechanism (reprinted with permission from [16]).



exchange membrane which allow the transferring of the hydrated protons through the membrane. The vehicular mechanism of proton conduction in pristine and nanocomposite membranes is depicted schematically in Fig. 5. (a,b). Electroosmotic drag and concentration gradient-driven diffusion (which occurs as self-associated clusters: $(H_2O)_y$) are two other possible transport pathways for water. The hydrophobic nature of

Teflon backbone facilitates the water transfer through the membrane because the surfaces of the hydrophobic holes. A provisional hydronium ion is formed when a proton emitted by hydrogen oxidation in an anode binds to a water molecule, and another proton from the same hydronium ion binds to the other water molecule. In the presence of water, ionic clusters swelled and formed the percolation process for proton trans- ferring. In Fig. 4 [16], the hopping process is represented in a simple scheme. The hopping mechanism has no effect on conductivity in perflourinated sulfonic acid membranes like Nafion..

A vehicular mechanism is the second mechanism. In this mechanism, the electrochemical difference causes hydrated proton (H_3O^+) to diffuse through the aqueous medium. The electroosmotic drag causes the water-connected protons ($H(H_2O)_x$) to bring one or two molecules of water through the membrane and to be exchanged with them in the vehicular mechanism. The major function of the formation of the vehicular mechanism is the existence of the free volumes within polymeric chains in protentend 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 tempera- ture. 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.

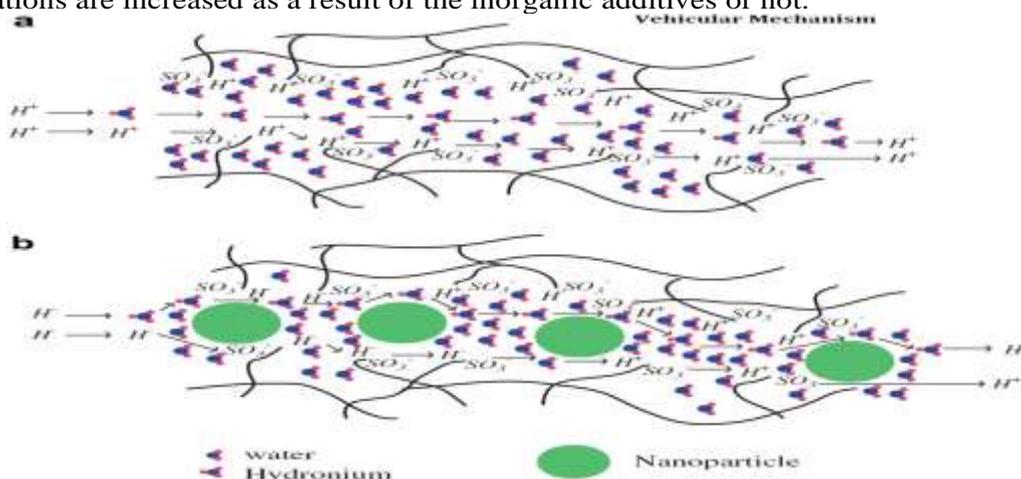


Fig. 5 e The Schematic design of the Vehicular Mechanism as proton conduction in (a) pristine membranes and (b) polymer/ nano-particle composite membranes (reprinted with permission from [13,17]).

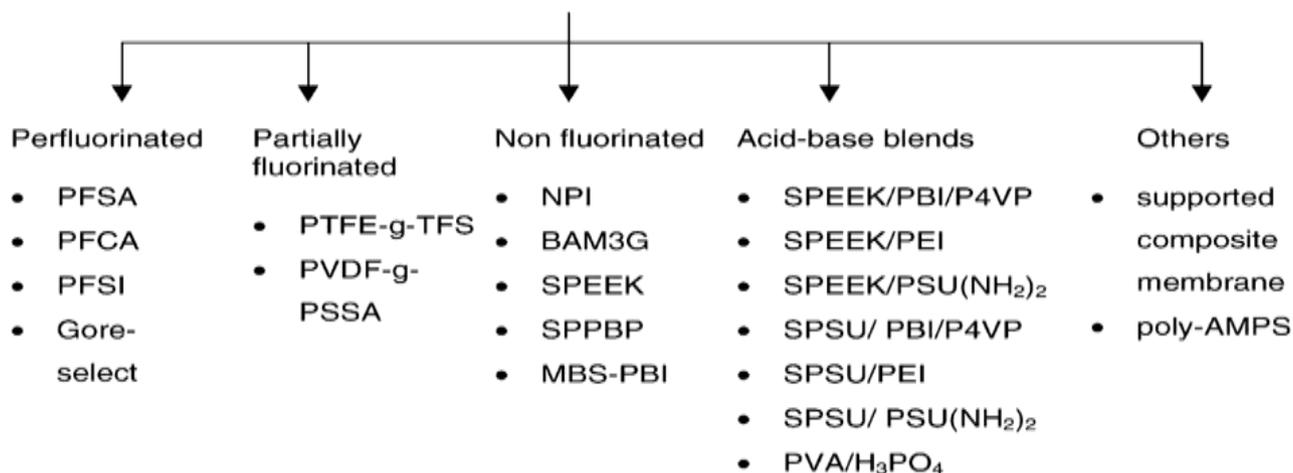


Fig. 6 e Classification of membranes based on materials (perfluorinated, partially fluorinated and non-fluorinated) and preparation method (acid-base blends and others) (modified with permission from [10]).

6 Classification of the materials used in proton exchange membranes synthesis

Perfluorinated ionomers (or partly perfluorinated), anti-fluorinated hydrocarbons (including aliphatic or aromatic structures), and acid-base complexes are the three broad categories of materials used in the fabrication of polymer electrolyte membranes. As seen in Fig. 6, membrane classification based on materials (perfluorinated, partly fluorinated, and non-fluorinated) and preparation methods (acid-base blends and others) has been shown [10].

Perfluorinated polymers have a tight C-F bond and low polarizability due to their limited size and high electronegativity of the fluorine atom. These polymers have been used in the chlor-alkali process and as proton exchange membranes for fuel cell applications due to their thermostability, chemical inertness, and increased acidity of the sulfonic acid group in eCF₂SO₃H [19]. These membranes are created by polymerizing monomers that contain a moiety that can be made cationic or anionic by further processing. DuPont produced these membranes, which are fluorocarbon-based ion-exchange membranes (Nafion) with good chemical and thermal stability. Figure 7 depicts the four-step synthesis process for membranes such as Nafion, which was introduced by DuPont in 1966. These perfluorinated membranes with a high equivalent weight (EW) have restricted their use in fuel cells due to their high power density [3]. Flemion®, made by Asahi Glass, and Aciplex-S®, made by Asahi Chemical, are similar polymers. Because of its high proton conductivity, chemical stability, and mechanical strength, the DuPont product is considered to be superior among the three main forms [20].

Non-fluorinated hydrocarbon polymers, which may be aliphatic or aromatic polymers with benzene ring structures in the polymeric backbone of the membrane or in the bulky pendant groups from this membrane polymeric backbone, are another kind of material used in proton exchange membrane synthesis. The use of hydrocarbon polymers for polymer backbones is currently one of the most promising routes to high-performance proton conducting polymer electrolyte membranes [12]. Hydrocarbon membranes have a number of benefits over perfluorinated membranes. They are less costly, commercially viable, and have a structure that allows polar sites to be introduced as pendant groups [10]. Water absorption is strong in hydrocarbon polymers with polar groups over a broad temperature spectrum, and the absorbed water is limited to the polar groups in polymer chains. Proper molecular design can slow down the decomposition of hydrocarbon polymers to some degree. Conventional methods for recycling hydrocarbon polymers are easy. Figure 8 [12] depicts the chemical properties of the hydrocarbon membranes. Aromatic hydrocarbons may be (a) inserted directly into the backbone of a hydrocarbon polymer to improve stability at high temperatures, or (b) polymers modified with bulky groups in the backbone to make them ideal for proton conduction [10,21]. Due to the existence of inflexible and bulky polyaromatic membranes, they are high temperature rigid polymers with T_g > 200 C.



[22] Classes of aromatic compounds Aromatic rings allow for both electrophilic and nucleophilic substitution. Main chain polyaromatics include polyether sulfones (PESF) [23e25], polyether ketones (PEK) with differing numbers of ether and ketone functionalities (such as PEEK, PEKK, PEKEKK, etc.), poly(arylene ethers), polyesters, and polyimides (PI) [26]. Since it is a hydrophobic polymer with a high glass transfer temperature (T_g 14 210 C), high mechanical power, and excellent hydrolytic stability, poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) can fulfill much of the specifications for use in PEMFCs. 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 compounds [27]. Polyaromatics are often preferred for fuel cell application due to their thermal stability. Also, the poly- aromatics from oxidant point of view are stable in the acidic medium.

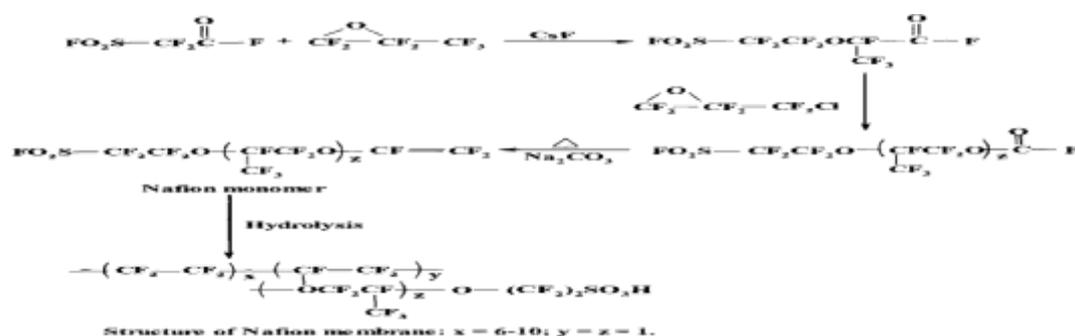


Fig. 7 e Nafion membrane and its preparation scheme (reprinted with permission from [3]).
Acidebase complexes

Acidebase complexes have been proposed as a potential substitute for membranes that can sustain high conductivity while avoiding dehydration symptoms at high temperatures. The acidebase complexes, in general,

The insertion of an acid portion into an alkaline polymer base to facilitate proton conduction is being considered for fuel cell membranes [10]. Figure 9 depicts the configurations of well-known acidic and basic polymers and their complexes. The phosphoric acid-doped polybenzimidazole (PBI/H₃PO₄) membrane seems to be the most active high-temperature PEMFC device so far, ideally under atmospheric strain. It has sparked substantial research into polymer synthesis, membrane casting, physicochemical characterization, and fuel cell developments in recent years. Acid-doped PBI

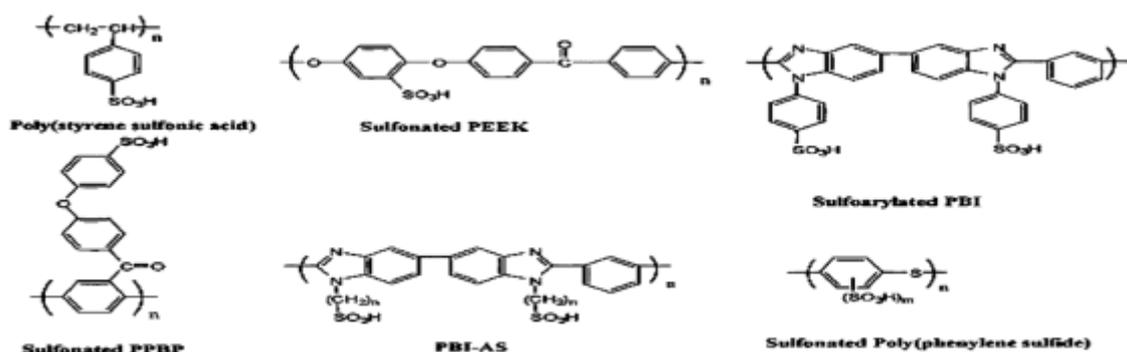


Fig. 8 e Chemical structure of polymer electrolyte membranes based on hydrocarbon polymers (reprinted with permission from [16]).

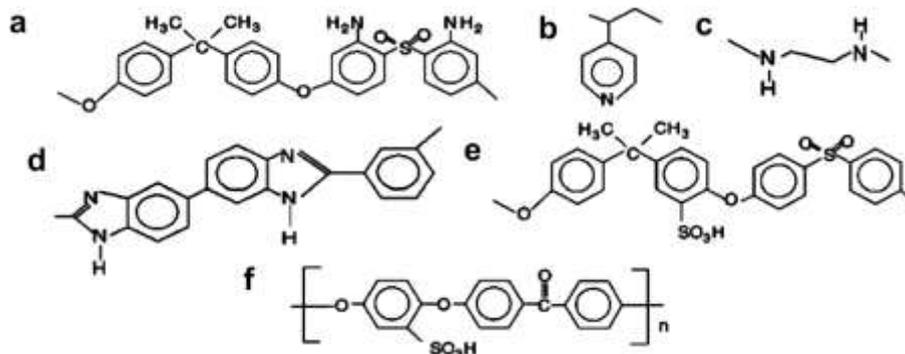


Fig. 9 e Structure of basic polymers (aed) and acidic polymers (e, f) (reprinted with permission from [10]).

membranes have been extensively characterized. Related fuel cell technologies have been developed, and a high temperature PEMFC has been successfully demonstrated at temperatures up to 200 degrees Celsius at atmospheric pressure. In comparison to Nafion cells, no gas humidification is needed, allowing for the removal of a complex humidification system. The PBI cell also has simple control over air flow rate and cell temperature (over a larger range) [28]. Many experiments have been conducted to date in order to produce alternative membranes that have good fuel cell capacity and are low in cost. Acidebase polymer blends are a promising substance among these alternatives. Ionic crosslinking (electrostatic forces) and hydrogen bonding bridges, which occur between acid and base polymers, play a significant role in controlling membrane swelling while maintaining flexibility. As a result, these membranes have a low water absorption, low crossover, strong proton conductivity, excellent thermal stability, and high mechanical versatility and strength [29]. A sequence of hybrid acidebase polymer membranes for use in fuel cells were generated by solegeling sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (sPPO) with 3-ami- nopropyl) triethoxysilane (A1100). The acidebase interaction increases not only membrane homogeneity and thermal stability, but also mechanical strength and flexibility, according to experiments [29]. Acidic sulfonated polymers (sPPENK, sPPESK, and sPBEEK) and simple polyetherimide (PEI) membranes were prepared and demonstrated excellent swelling resistance, thermostability, hydrolysis resistance, and oxidative resistance, as well as high proton conductivity. Accordingly, they are expected promising fuel cell proton exchange membrane materials in the future [30].

The conductivity of the PBI membrane, for example, was around 4.6×10^{-2} S/cm at 450 percent doping and 165°C . The conductivity was also found to exceed 0.13 S/cm at very high levels of doping (around 1600 percent). At 190°C and atmospheric pressure, a fuel cell with a doped PBI/ H_3PO_4 membrane produced a power density of 0.55 W/cm^2 and a current density of 1.2 A/cm^2 [30]. Kerres et al. generated sPEEK/PBI membranes with the acidic compound sulfonated poly(etheretherketone) sPEEK and the simple compound poly (benzimidazole) PBI. At ion-exchange capacities IEC of 1, the membranes showed strong proton conductivities and excellent thermal stabilities (decomposition temperatures $>270^\circ\text{C}$). The membranes were also put to the test in an H_2 membrane fuel cell, where they performed admirably. Vargas MA et al. created a new protonic conductor gel (PVAL/ $\text{H}_3\text{PO}_2/\text{H}_2\text{O}$) with PVAL (polyvinyl alcohol) and H_3PO_2 (hypophosphorous acid) as the primary chemicals and water as the common solvent. The gels have excellent mechanical properties and are translucent. They also achieved the highest electrical conductivity in this kind of substance in the literature (in the range of $10^{-1} \text{ S cm}^{-1}$) using this device at ambient and subambient temperatures. The effect of temperature and acid concentration on electrical conductivity was investigated. At 23 degrees Celsius, the maximum open fuel cell voltage was 435 millivolts. The performance of the fuel cell improved when it was fed with humidified hydrogen.

Table 3 lists the most common blends used in the preparation of acid-base complexes. The key benefit of

using high-temperature specialty polymers is due to their predicted stability in oxidative, reducing,



and acidic conditions, rather than their thermal stability. strongly sensitive to the doping level of complexThe conductivity of acidebase complexes is generally affected by doping level and temperature. The amount of phosphoric acid doping in an alkaline polymer is measured in moles per repeating unit of polymer. The distance between clusters of acid sites decreases as doping increases, and the anion moieties promote proton hopping between imidazole sites. Bouchet et al. [30] also present data that support a Grotthus process for a PBI membrane doped with phos- phoric acid as an acidebase complex (PBI/H3PO4)

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7 Fabrication and preparation methods of proton exchange membranes

The production of low-cost, high-performance materials and components for the polymer electrolyte fuel cell (PEFC) is a critical step toward commercialization and industry acceptance 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 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 mate- rials are expensive due to the complex fluorine chemistry involved in the fabrication [30]. As a result, the production of membranes that are both low-cost and high-performing is needed. As a replacement for Nafion membranes, new membranes with hydrocarbon polymer matrixes, inorganic and organic hybrid membranes, acidebase complexes, and grafting membranes by irradiation are now available. The radiation grafting approach is intriguing and ideal for proton exchange membrane preparation in fuel cells and other electrochemical applicationsThe fabrication and preparation of proton exchange membranes can be accomplished in one of four ways: (1) grafting polymerization with g-ray irradiation, (2) grafting polymerization with plasma, (3) Crosslinking process, (4) solegel method, and (5) direct polymerization of monomers The methods described above are detailed in the sections that follow.



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 (300hr) yield comparable to Nafion 112	Higher voltages of tests 650 mV obtainable at High current densities of 1000 mA/cm ² for Hydrogen fuel cell
2	PVA/H ₃ PO ₄	Highly doped	Good mechanical Strength	With decreasing acid concentration, grotthus transport mechanism decreases 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 ₃ PO 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 [30]. As a result, the production of membranes that are both low-cost and high-performing is needed. As a replacement for Nafion membranes, new membranes with hydrocarbon polymer matrixes, inorganic and organic hybrid membranes, acidebase complexes, and grafting membranes by irradiation are now available. The radiation grafting approach is intriguing and ideal for proton exchange membrane preparation in fuel cells and other electrochemical applications. The fabrication and preparation of proton exchange membranes can be accomplished in one of four ways: (1) grafting polymerization with g-ray irradiation, (2) grafting polymerization with plasma, (3) Crosslinking process, (4) solegel method, and (5) direct polymerization of monomers. The methods described above are detailed in the sections that follow.

Irradiation grafting polymerization method

Graft polymerization, which can be accomplished using electron beam, g-ray, and ultraviolet (UV) light irradiation or plasma, is a convenient technique for preparing ion exchange membranes since it allows for the rapid forming of active sites on a suitable polymer matrix [26]. Nasef and Jegzey [27] have reviewed the radiation-grafted membranes. The lack of chemical initiators or catalysts, the ease of preparation from the already prefabricated base film, and the simple regulation of the degree of grafting and ion exchange ability of the membranes are all advantages of radiation-grafted membranes. The High-energy irradiation, such as g-ray, electron-beam, and swift heavy ions, will start the grafting process. The polymer electrolyte membrane's base film serves as a hydrophobic host, limiting membrane swelling in water while also providing mechanical strength and dimensional stability. Furthermore, the cost of commercial radiation-grafted membranes is said to be in the thousands of dollars.

[28] 50e100 US \$m—2. As shown in Fig. 10, the method for preparing the new polymer electrolyte membrane by irradiation grafting consists of three steps: The polyethylene tetrafluoroethylene (ETFE) films were first pre-irradiated in argon gas at room temperature in the first step.. In this step, ETFE films were triggered in a pre-irradiation step before being grafted with monomers in a corresponding



step (the substitution stage). To incorporate sulfonic acid groups into the membranes, the grafted ETFE films were sulfonated in a chlorosulfonic acid solution, accompanied by hydrolysis in distilled water. The new polymer electrolyte membranes were characterized using the Fourier transform infrared (FT-IR) and thermogravimetric analysis (TG-DTA) techniques. The dimensional unit of irradiation in the grafting method of preparing polymer electrolyte membranes is kGy, which is defined as the amount of energy absorbed by the polymeric membrane in terms of kJ per gram of polymer (1 kGy 14.1 kJ/gr membrane). The rate of irradiation is measured in kGy per hour or kGy/hr. Radiation-induced graft polymerization is a well-known technique for modifying materials' physicochemical properties, and it's particularly useful for achieving complex properties as well as excellent mechanical properties [29]. The mass-based degree of grafting, or DG_m, is defined as a percentage of the weight difference between polymeric films before and after grafting, as determined by:

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

where W_0 and W_g are the weights of the film before and after grafting, respectively [25].

Crosslinking method

Perfluorosulfonic acid membranes, such as Nafion, are used as proton exchange membranes for fuel cell applications, as discussed in previous sections [20]. While Nafion has excellent proton conductivity, it has been discovered that in a direct methanol fuel cell (DMFC), over 40% of the methanol can be lost through the membrane due to excessive swelling [21]. To improve the 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 causes the proton conductivity of proton conductive polymer membranes to increase, resulting in an increase in the emitted voltage per consumed current density in the unit fuel cell. As a result of the crosslinking process, three-dimensional networks in membrane structures can be obtained, reducing methanol crossover via membrane [24]. The membranes without charged sites are changed into proton exchange membranes by crosslinking in the presence of organic charged groups in the crosslinking process for proton exchange membrane preparation. The development of crosslinking improved the ion exchange membrane's chemical and thermal stability. The suggested reaction mechanism of PVA and PSSA MA for the preparation of crosslinked proton exchange membranes as seen in Fig. 11.

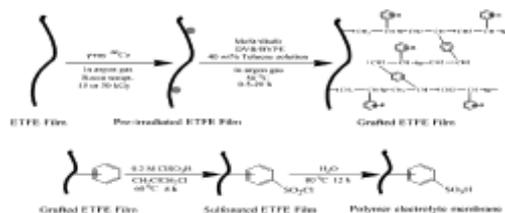


Fig. 10 e Preparation of the new polymer electrolyte membranes by irradiation grafting method

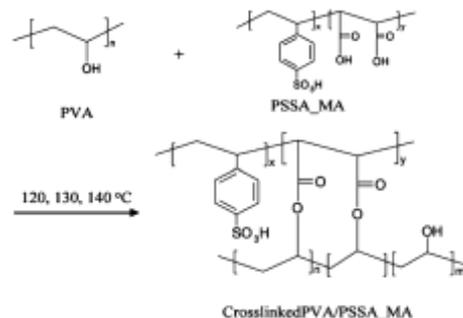


Fig. 11 e Possible reaction mechanism of PVA and PSSA MA (reprinted with permission from [45]).



Plasma grafting polymerization method

One of the techniques for preparing proton exchange membranes for applications in miniaturized fuel cells is plasma grafting polymerization. In comparison to conventionally polymerized films, plasma polymerized films have a high degree of crosslinkage and are pinhole free except with films as thin as a few hundred nanometers. Using plasma polymerized electrolytes, a sharp decline in methanol permeability and a decrease in the resistance of a fuel cell electrolyte membrane is achieved. Since the ion exchange layer is thinner, the total membrane resistance can be reduced by the plasma polymerization process (in about 1 mm). Since water molecules are difficult to transport, increasing the plasma energy in this polymerization reduces the ionic conductivity of the membrane due to the higher degree of cross-linking. Using tetrafluoro ethylene to create the polymeric backbone of an ion-conductive membrane and vinylphosphonic acid to add acid groups that are responsible for proton conductivity, plasma polymerized electrolyte membranes have been created. The main variations between a monomer, a conventional polymer, and a polymer prepared by plasma polymerization are seen in Fig. 12. The prepared polymer in plasma polymerization has a relatively thick structure, which has resulted in a significant decrease in methanol crossover in the use of this polymer as a membrane in direct methanol fuel cells.

Solegel method

The sol-gel process facilitates the incorporation of pure inorganic phases into polymeric matrixes (mostly in composite membranes). In sol-gel chemistry, molecular pre-materials transform into nano-sized particles. The gel networks are formed by this colloidal suspension type, or sol. By using various drying methods, gel can transform into various materials with various properties.

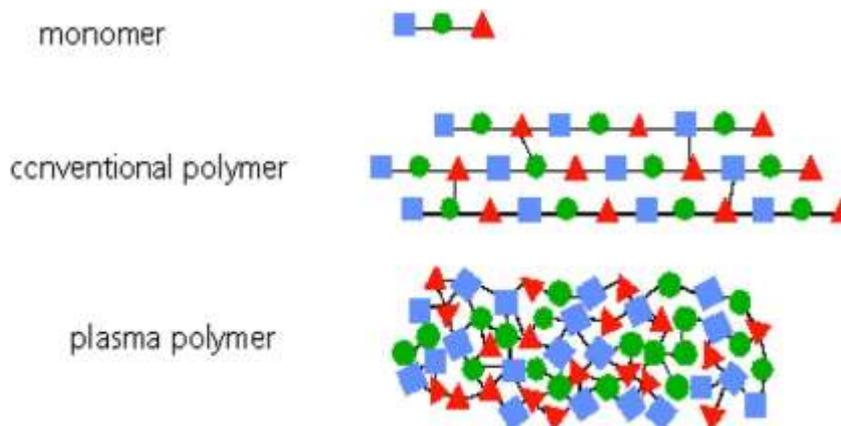


Fig. 12 e Differences between a monomer, a conventional polymer and the polymer prepared by plasma polymerization.

The sol is made from colloidal particles dispersed in liquid (size $1e100$ nm) and a gel made from a rigid and continuous network of micrometer-sized pores and polymer chains of an average length greater than a micron. The metallic alkoxides are commonly used to make the sols. In this case, the metallic organics are water insoluble, but the alkoxides dissolve in the alcoholic solution. The polymerization reaction starts with the addition of water to the sol. This can be accomplished by two primary reactions: hydrolysis and condensation. The following are some of the reactions: Hydrolysis reaction: $M e O e R \downarrow H_2O \nearrow M e OH \downarrow R e OH$ Condensation reactions: $M e OH \downarrow H O e M \nearrow M e O e$
 $M \downarrow H_2O$
 $M e O e R \downarrow H O e M \nearrow M e O e M \downarrow R e OH$ In this above reactions, R is the alkyl groups such as methyl, ethyl, propyl, etc. Fig. 13 shows the general scheme of the hydrolysis and condensation processes.



Direct polymerization of monomers method

Direct polymerization of monomers is a modern and traditional approach for making proton exchange membranes, and it can also be used to make fuel cell membranes, which are a subcategory of proton exchange membranes.

membranes for proton exchange The membranes are made by polymerizing a variety of monomers, such as styrene and di-vinyl benzene, and then sulfonating them. Monomer soaking or pore can filling are the most popular methods for polymerization in an inert matrix. It has been observed that polymerization can often be carried out directly from sulfonated monomers without the need for a post-sulfonation stage.

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

Modifications of fluorinated and non-fluorinated membranes, such as sulfonated polyether ether ketones, sulfonated polyether sulfones, sulfonated polyether imides, and other proton exchange membranes, have recently been

tested and investigated in fuel cell applications. In light of the complicated cell requirements of high proton conductivity and excellent chemical stability combined with durability of 60,000 hours at 80°C, it is apparent that Nafion® and associated polymers are still being thoroughly investigated.

The high cost of membrane, which can reach US\$ 700 per square meter, the need for supportive equipment, and temperature-related limitations are the main drawbacks of these PFSA products. Degradation of PFSA membrane properties at elevated temperatures is

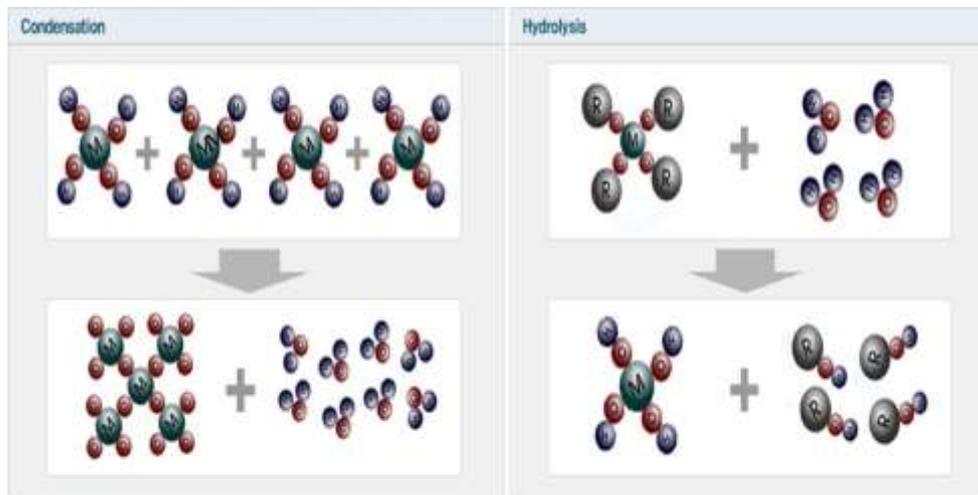


Fig. 13 e General scheme of the hydrolysis and condensation processes

another serious drawback. Conductivity at higher temperatures (up to 100 °C) is reduced than lower temperatures [12]. At temperatures over 80°C, membrane dehydration, reduced ionic conductivity, decreased tolerance for water, mechanical strength loss due to softening of the polymer backbone, and increased parasitic losses due to high fuel permeation are also observed. In terms of direct methanol fuel cells (DMFC), Nafion® has a high methanol permeability of greater than 80,000 Barrers at 80°C, which significantly decreases DMFC performance and makes it unsuitable for DMFCs. Efforts are being made to eliminate drawbacks such as crossover issues and hydration depletion above 100 degrees Celsius. Despite its flaws, Nafion® remains the preferred polymer for most PEFC and DMFC applications. However, it is likely that Nafion® will be phased out in the future and replaced by a different membrane. The authors are also conducting research to find promising alternatives to address a few of the drawbacks of the PFSA membranes mentioned



above. Polymeric mix membranes and polymer/inorganic composite membranes are the two most common approaches to improve the properties of proton exchange membranes. The second is less difficult to create. This form of composite can be built in a variety of ways, including:

- Ionically conductive inorganic additive with supporting polymer;
- Ionic polymer with inorganic filler for mechanical support;
- Ionic polymer with water-retaining inorganic filler;
- Ionically conductive inorganic additive with supporting polymer

This is just an incomplete list of the alternative combinations of countries. Many of the inorganic additives used in polymer inorganic composite membranes can act at much higher temperatures than plain polymers, which makes them interesting. Improved proton conductivity, water preservation at high temperatures, and mechanical support are some of the potential benefits of integrating inorganic compounds into composite membranes [7]. According to Rikukawa and Sanui [12], any sacrifice in material life-time and mechanical properties can be acceptable in order to manufacture products that are less costly than Nafion, as long as the cost factors are economically practical..

As a result, the use of hydrocarbon polymers, which had previously been discarded due to poor thermal and chemical stability, has resurfaced. As a result, attempts to improve these higher-temperature membranes include modifying traditional host polymers, such as by incorporating different hygroscopic inorganic nanosized particles or creating new polymer systems.

The most important goals of proton exchange membrane modification in PEM fuel cells include the preparation of proton exchange membranes at a lower cost than fluorinated membranes, desirable water uptake and retention at elevated temperatures, desirable proton conductivity at higher temperatures, and a lower extent of reactant gaseous and methanol crossing.

In addition, the membranes' self-humidity is generated when they are exposed to high 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. 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. The Nafion-dependent composite proton exchange membranes are made with a variety of fillers, including SiO₂, zirconium phosphate, phosphotungstic acid, molybdophosphoric acid, suspending SiO₂, organically adapted silicates, silane based fillers, and zeolites. Lower H₂, O₂, and methanol crossover, improved thermal stability, greater proton conductivity, and better water absorption have all been shown in composite membranes. The types of modified proton exchange membranes used in PEM fuel cells are investigated in the following pages.

Modified Nafion membrane with inorganic oxides MO₂ (M^{1/4} Ti/Si/Zr)

Increased cell temperature results in improved CO resistance, better reaction kinetics, and lower heat-exchanger requirements in PH-PEFC. The loss of proton conductivity of the perfluorosulphonic electrolyte due to lower water content is the key issue for PEFC activity above 100°C, resulting in a decrease in cell efficiency. For both of these causes, there has been a lot of interest in developing alternate membranes that can operate at temperatures above 100 degrees Celsius. The use of thermally tolerant polymers or the introduction of a hygroscopic and/or proton conductor material as filler in the polymeric perfluorosulphonic matrix have both been tried to solve this issue. In the above case, the addition of inorganic fillers increases mechanical properties, membrane water control, and helps to prevent reaction gas direct permeation by increasing the tortuousness of the transport pathway [4]. Modified Nafion[®] membranes containing inorganic fillers such as SiO₂, TiO₂, ZrO₂, and other compounds characterized by water retention capability or proton conduction as hetero-poly-acids (PWA, PMoA, SiWA) or layered zirconium phosphate are appropriate materials for use as polymer electrolytes in a medium temperature PEFC. As a result, the so-called "high-temperature membranes" can be produced by modifying the polymer host membranes with (1) hygroscopic oxides such as SiO₂ and TiO₂ to increase water uptake; (2) inorganic solid acids such as ZrO₂/ SO₂ to increase water uptake as well as the concentration of acid sites; and (3) inorganic proton conductors such as heteropoly-acids to enhance fusing. The method of preparation of the ZrO₂, SiO₂ and TiO₂ composite proton exchange membranes was based on the in situ solegel synthesis methods [6]. In this procedure, the host

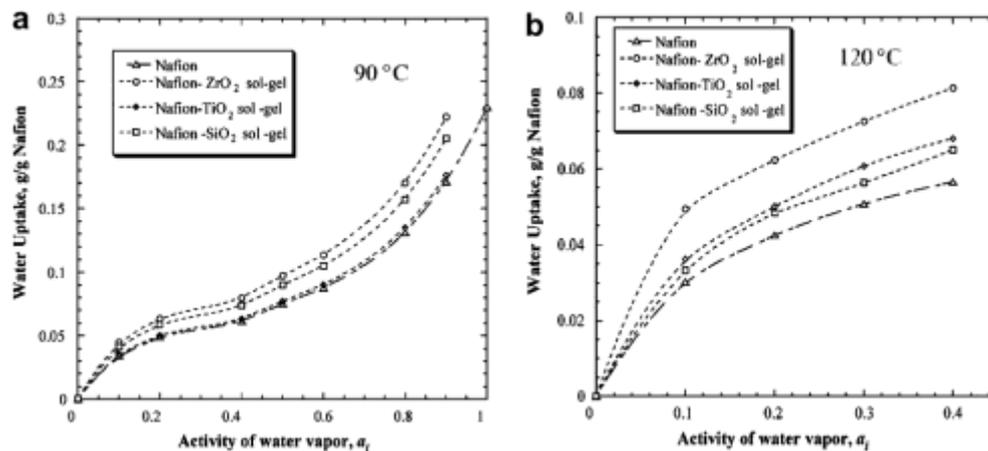


Fig. 14 e Water uptake vs. activity of water vapor for nanocomposite of Nafion® - MO₂ and Nafion® membrane at temperatures a) 90 °C and b) 120 °C.

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, both Nafion®-MO₂ nanocomposite membranes had greater water uptake than unmodified Nafion® membranes at a given relative humidity (RH). The hydrophilic aspect of the acidic inorganic additives within the pores of the Nafion® membrane, as well as the increased acidity and surface areas of nanoparticles, are responsible for the increased water absorption. At both temperatures, the basic sorption pattern was the same, with water absorption increasing from silica to Titania to Zirconia nano-composites. This is in ascending order of acid intensity. Higher water absorption and acidity result in higher proton conductivity, which can lead to improved fuel cell efficiency in hotter environments. In comparison to the Nafion® membrane, Fig. 15 indicates conductivity tests for nanocomposite membranes at 90 and 120 degrees C Nafion® ZrO₂ solegel nanocomposites demonstrated higher conductivity than Nafion® for across the whole spectrum of water temperatures at both temperatures. an operation Higher water absorption and acidity all contribute to the rise in conductivity of Nafion® - ZrO₂ solegel nanocomposites. As a result of the effects of water uptake, ion exchange capability, and conductivity, it is clear that higher water uptake does not always imply higher conductivity. Conductivity is determined not only by overall water absorption, but also by the distribution of water between surface and bulk Proton conduction is much more efficient with bulk water. Figure 16 depicts the efficiency of a single fuel cell with all four types of membranes under completely humidified and dry conditions. Since sulfated zirconia is acidic, it allows the nano composites to absorb more water. Under totally humidified conditions, composite membranes have a lower resistivity than Nafion and have improved I-V efficiency in fuel cells. Water sorption into Nafion-based membranes often increases as the temperature rises.

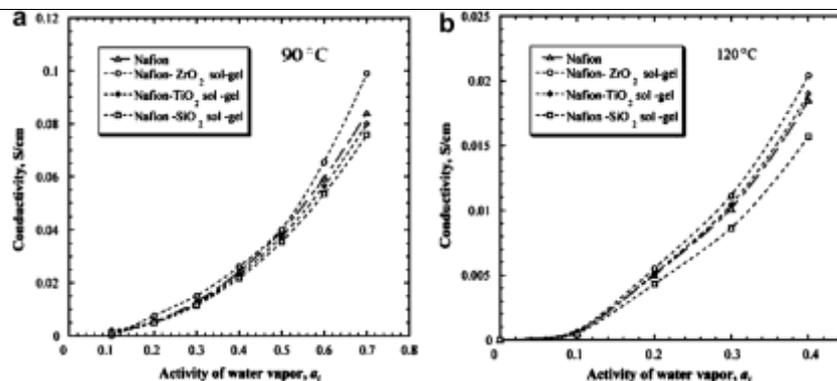


Fig. 15 e Conductivity vs. activity of water vapor for nanocomposite Nafion® - MO₂ and Nafion® membrane at temperatures a) 90 °C and b) 120 °C

hydrophilic properties and good thermal stability at high temperature. Laponite (Lp) or Montmorillonite (MMT), layered silicates consisting of silica tetrahedral and alumina octahedral



sheets with favorable hygroscopic properties, are widely used for PEM fuel cell applications. Indeed, the monovalent ions found between the clay layers allow for the efficient absorption of polar solvents such as water. Smectite clays are often referred to as "swelling" clays. This inorganic compounds, either synthetic (Lp) or natural (MMT), embedded into a polymer membrane, tend to avoid the depletion of hydration water at high temperatures and low relative humidity. The inclusion of clay, which is a weak proton conductor, within Nafion®, which is highly proton conductive, will, however, reduce the membrane's overall proton conductivity. When compared to commercially available Nafion® membranes, the addition of a small amount of montmorillonite salts to perfluorosulfonic acid (PFSA) membranes reduces the methanol crossing while also lowering conductivity. Organic improvement was carried out with the following goals in mind: (1) to improve polymer compatibility, i.e., to improve the interface bonding between polymer and silicates/Aerosils; (2) to reduce methanol permeability; and (3) to improve the composite membrane system's proton conductivity. Table 4 shows the water absorption as well as the thickness of hybrid membranes packed with Laponite clay in both the dry (Td) and completely hydrated (Tw) states. The water absorption, as seen in Table 4, is high.

Composite membrane thickness expansion is larger (87 and 70%) than perfluorinated membrane thickness expansion (50 percent for recasted Nafion® and 30% for Nafion®-117), though thickness expansion is comparable (18 T 2 percent). The high water adsorption potential of this form of Laponite explains the significant difference in water uptake. This finding shows that the inorganic phase's water preservation is responsible for the hybrid membranes' increased water retention. Since proton conduction is directly proportional to water content, it is critical to determine the dependency of proton conductivity on environmental conditions such as temperature and humidity level for membranes with interesting water retention capacities. Figure 17 displays the effects of conductivity measurements for Nafion®-115 and hybrid membranes at 25°C under various relative humidity conditions (from 50 to 100 percent RH). In Fig. 17, the proton conductivity of the Nafion®/Lp-g membrane is higher than that of the Nafion®-115 membrane regardless of relative humidity, and it is higher than that of the Nafion®/Lp membrane between 70 and 98 percent RH. Commercial membranes lose proton conductivity more than hybrid membranes as relative humidity rises. Ex situ experimentation previously demonstrated improved composite membrane activity, which must now be demonstrated in a fuel cell

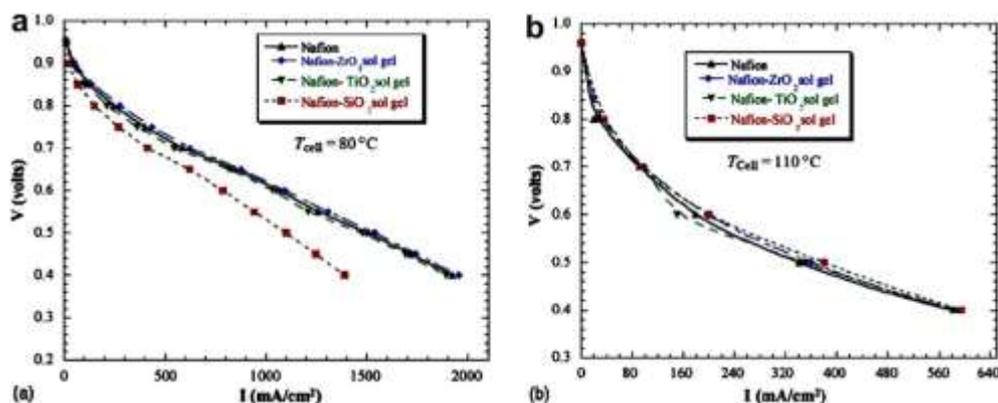


Fig. 16 e The cell performance of Nafion®-112 vs. Nafion®-MO₂ sole gel, composite membrane. Oxygen and Hydrogen at 2.0 and 1.3 times stoichiometric flows, respectively, $P \llcorner 1.0$ atm, $T_{\text{Humidifier}} \llcorner 80$ °C, under a) fully humidified condition at 80 °C and b) dry condition at 110 °C

8. CONCLUSIONS

Today, oil shortages and toxic degradation have been major issues for humans. To address these issues, extensive attempts have been made to substitute fossil fuels with alternative energy sources, such as clean power. Fuel cells are on the brink of causing a massive disruption in the world of electricity due to their unique properties. The membrane in PEM fuel cells is made of solid polymer electrolytes with the ability to transfer proton. Ion exchange membranes, especially



proton exchange membranes, play an important role in proton transfer in the electrolyte of PEM fuel cells. The ideal ion exchange membrane should have a higher perm selectivity, suitable proton conductivity, and good mechanical and chemical stability, with the following factors influencing the efficiency of the ideal proton exchange membrane: adequate hydration and membrane width. Cation exchange membranes were made by attaching acidic functional groups to the polymer backbone of the membrane, while anion exchange membranes were made by attaching alkaline functional groups to the polymer backbone of the membrane. Since the membrane thickness was reduced, the membrane proton conductivity increased, but the fuel crossover through the membrane increased as well. The fluorinated Due to their high cost, poor proton conductivity at higher temperatures, and higher methanol crossover, composite membranes were created. Therefore, the most important goals of proton exchange membrane modification in PEM fuel cells can be stated, such as lower cost of proton exchange membranes compared to fluorinated membranes, desirable water uptake and retention at elevated temperatures, desirable proton conductivity at higher temperatures, and lower extent of reactant gaseous and methanol.

The incorporation of metallic oxides such as MO₂ into the polymer matrix of a proton exchange membrane, for example, produced an increase in water absorption and retention, which then increased the proton conductivity of the membrane at elevated temperatures, with the increase in water uptake being attributed to the acidity of these oxides. At high temperatures, clays modified with sulfonic acid groups caused an increase in membrane IEC, followed by an increase in proton conductivity and membrane efficiency in fuel cells. Although the proton conductivity of polymer-zeolite composite membranes is lower than that of Nafion, the efficiency of polymer-zeolite composite membranes is more consistent. In addition, the polymer-zeolite composite membranes' lower methanol permeability, combined with their lower proton conductivities, increased their selectivity in direct methanol fuel cell applications. The integration of heteropolyacids into membrane polymer matrix resulted in an improvement in composite proton conductivity as well as retention.

The composite membranes have self-humidity properties at elevated temperatures due to the heteropolyacid properties. Tables 8 and 9 outline the benefits and drawbacks of the various changes to the perfluorinated and non-fluorinated proton exchange membranes that were explored in this review article. The proton exchange membranes modified with clays are ideal for DMFC applications of fuel cells, as seen in Tables 8 and 9, and the fabrication cost of these composite membranes is minimal. These membranes, however, lack adequate proton conductivity for PEMFC, and their PEM fuel cell efficiency is poor. High temperature fuel cells may benefit from the use of polyaromatic structures in proton exchange membranes like sPEEK. The addition of acidic oxides (MO₂) to these polyaromatic membranes increases their thermal stability at 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.

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