

Proton Exchange Membrane Fuel Cells: Focused on Organic-Inorganic Nanocomposite Membranes

Soheil Jalali¹, Mir Mohammad Seyedghayem¹, Fahimeh Hooriabad Saboor^{1*},
Aishwarya Venkatramani², Mehرداد Asgari^{2,3}

¹ Department of Chemical Engineering, University of Mohaghegh Ardabili, Daneshgah Street, 56199-11367 Ardabil, Iran

² Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, CB3 0AS Cambridge, UK

³ Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Rue de l'Industrie 17, CH-1951 Sion, Switzerland

* Corresponding author, e-mail: f.saboor@uma.ac.ir

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Abstract

The application of organic-inorganic nanocomposite membranes allows for a synergy between the desirable thermal and mechanical properties of inorganic materials with the reactivity, dielectric properties, durability, flexibility, and processability of the polymeric materials. Proton exchange membrane fuel cells (PEMFCs) suffer from some problems including water content management, carbon monoxide poisoning, hydrogen reformate, and fuel crossover through the membrane. Herein, specific solutions have been proposed to the above-mentioned problems using organ-inorganic nanocomposites. These solutions include doping proton conductive inorganic nano-particles in the proton exchange membrane, preparing nanocomposites via the sol-gel method, covalence bond of inorganic compounds with the polymer structure, and acid-based proton exchange nanocomposite membranes. Furthermore, hydrogen production with low carbon monoxide content using the ethanol steam reforming method, as well as the effect of CO in the hydrogen feed of PEMFC are explained and discussed. Finally, desirable conditions for achieving the maximum power density in exchange membrane cells (EMFCs) are discussed.

Keywords

proton exchange membrane, organic-inorganic nanocomposite, fuel cell, hydrogen

1 Introduction

1.1 The importance of fuel cell application

Despite two main global challenges including climate change and energy issues, fossil fuels are still the dominant energy source. Hydrogen as a clean and renewable energy source is a promising alternative to fossil fuel. The heavy demand for energy in the 21st century on one hand and the necessity of observing environmental considerations for energy generation, on the other hand, have prompted extensive studies on energy convertors such as fuel cells (FCs) [1].

Most of these studies have addressed the development and economical manufacturing of hydrogen fuel cells. The main challenge is still to reduce the need for hydrocarbon fuels and mitigate pollution [2].

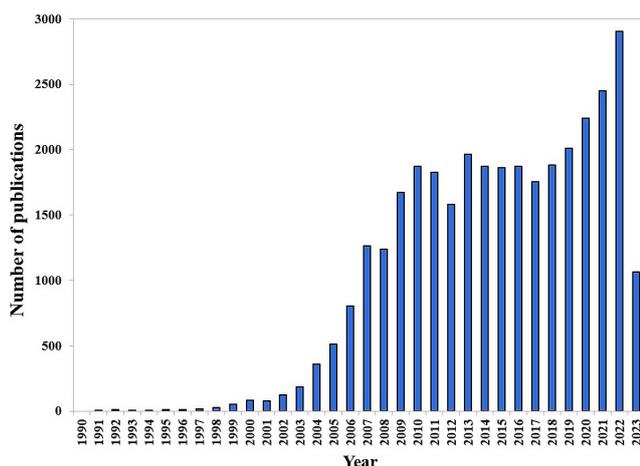
Fuel cells are normally categorized based on different factors including type of fuel, oxidizing agent, the type of fuel reformer (i.e., external, or internal reformer), type of electrolyte, operational temperature, etc. The most common classification of fuel cells is based on the type of

electrolyte used, which may include alkaline, molten carbonate, phosphoric acid, solid oxide, polymer, and methanol fuel cells. Another commonly used classification is based on the temperature at which the fuel cell operates [3]. Table 1 displays the temperature at which different types of fuel cells operate alongside the type of electrolyte and their abbreviations [4].

Among various types of fuel cells, the proton exchange membrane FC, in which hydrogen and oxygen are used as the fuel and the oxidant, respectively, is one of the most applicable fuel cells. This is due to the unique characteristics of proton exchange membrane fuel cells (PEMFCs) such as high-power density, facile movability, and low working temperature. Therefore, PEMFC has the potential to be implemented as an electrical generator in various applications such as automobiles and portable/stationary devices [5]. Fig. 1 displays the number of publications on proton exchange membrane fuel cells between 1990 and

Table 1 Different types of fuel cells based on the operational temperature [4]

Type of fuel cell	Operational temperature (°C)	Power density (mW/cm ²)	Fuel efficiency (chemical to electric)	Lifetime (h)
Polymer fuel cell (PEM)	80–200	350–600	40–60	>40000
Alkaline fuel cell (AFC)	80–100	100–300	55–60	>10000
Phosphoric acid fuel cell (PAFC)	150–220	350	45–60	>40000
Molten carbonate fuel cell (MCFC)	600–700	100–200	60–65	>40000
Solid oxide fuel cell (SOFC)	600–1000	240–300	45–60	>40000
Direct Methanol fuel cells (DMFC)	50–120	200–400	40	>20000


Fig. 1 The number of publications on PEMFCs between 1990 up to April 2023 (adapted from Scopus database [6])

2023. Based on this trend, it is clear that PEMFCs are still among hot topics for research and development of fuel cells.

Fuel cells based on polymer electrolyte membrane cells were extremely expensive with a short lifetime, due to the oxidation of divinylbenzene-polystyrene sulfonate copolymer membranes. Then, the Nafion membrane with chemical, mechanical, and thermal stability as well as high proton conductivity was introduced by DuPont company [7]. These membranes are costly with fuel permeability and decreased performance in dehydrated conditions at high temperatures. To overcome these disadvantageous, several studies conducted on the preparation of hydrocarbon polymers as a proton-exchange membrane such as polystyrene (PS), polybenzimidazole (PBI), polyether ether ketone (PEEK), polyether sulfone (PES), etc. The other widely studied strategy is the fabrication of organic-inorganic nanocomposite membranes to enhance thermal, structural, and chemical stability and suppress the fuel crossover in proton exchange membranes (PEMs) [8].

Here, we carried out an adapted approach for reviewing proton-exchange membrane FCs regarding fuel cell performance and utilization of organic-inorganic nanocomposite PEMs. Accordingly, we studied the relevant literature on the fabrication and application of hybrid mem-

branes by incorporating various materials such as clay, carbon nanotube (CNT), metal-organic frameworks (MOFs), Ionic liquid (IL), graphene oxide (GO), metal/metal oxides in polymeric membranes. We briefly discussed fuel cell classification, energy generation mechanisms, and hydrogen production from ethanol. A comprehensive discussion on the fuel cell components, H₂-air system, gas flow field designs, water management, fuel cross-over, and carbon monoxide poisoning in PEMFCs have been presented. In the following, the future outlook of proton-exchange membrane FCs is discussed.

1.2 The various types of fuel cells

1.2.1 Alkaline fuel cells

In alkaline fuel cells, oxygen and hydrogen are used as the re-actants and its electrolyte medium is usually consisting of potassium hydroxide solution [9]. The electrolyte based on nickel, silver, and noble metal oxides is normally a water-based solution that is kept inside a porous matrix made of asbestos [10]. One of the main advantages of alkaline fuel cell is its low cost of manufacturing, especially considering that the catalyst used in this type of fuel is normally less expensive than the catalysts in other fuel cells [11]. Because of probability of liquid electrolyte leakage and a high sensitivity to contamination, alkaline fuel cells are not suitable for transportation (mobile) purposes [12].

1.2.2 Molten carbonate fuel cells

The electrolyte of these fuel cells is a combination of molten carbonate salts including, a mixture of sodium carbonate / lithium carbonate, or potassium carbonate/lithium carbonate, kept inside a matrix made of LiAlO₂. Given high operating temperature for this type of fuel cell, nickel and nickel oxide are used as anode and cathode, respectively [13, 14]. In comparison to other high-temperature fuel cells, however, carbonate fuel cells have two main disadvantages: (a) the complexity of operation with liquid electrolyte; (b) the residuals of chemical reaction in molten carbonate fuel cell [15]. The high temperature of operation

of molten carbonate fuel cell has limited its application in large power generation plants. Even their application in household settings is not very straightforward [16]. An advantage of this type of fuel is the possibility of utilizing generated heat in other chemical processes or steam generation process. The generated steam can then be transferred to steam turbines for electricity generation [17].

1.2.3 Phosphoric acid fuel cells

Phosphoric acid fuel cells are the first type of commercial fuel cell the development of which began from the mid-1960s. Then, they were tested experimentally in 1970. The electrolyte utilized in this fuel cell is phosphoric acid with almost 100% pure [18]. The catalyst utilized in the phosphoric acid fuel cell is platinum, and the matrix that is used for maintaining acidity level is made of silicon carbide (SiC). The most commonly used fuel in phosphoric acid fuel cells is hydrogen, where the hydrogen ion plays the role of charge carrier. Supplying the hydrogen required for phosphoric acid fuel cells is done by applying an external reformer, in which the hydrocarbon fuel is converted to hydrogen [19]. The heat generated in phosphoric acid fuel cells can be used in hybrid heat and electricity applications. One of the most important and practical uses of phosphoric acid fuel cells is in on-site applications or non-concentrated power plants installed on-site [20].

1.2.4 Solid oxide fuel cells

Development of solid oxide fuel cells began from the late 1950s, and currently they have the highest temperature among different types of fuel cell [21]. This fuel cell has planar and tubular structures, where a thin ceramic solid electrolyte is used instead of liquid electrolyte [22]. Considering the high operational temperature of solid oxide fuel cells, powerplant applications of this type of fuel cell are of more interest. High operational temperature brings a series of advantages for this type of fuel cell including variety in the utilized fuels (for example gasification of coal, the gases resulting from industrial processes and other sources), the possibility of direct conversion of hydrocarbon fuels without any need to fuel reformer, high efficiency and the possibility of application in power and heat generators [23, 24]. Considering the high operational temperature of solid oxide fuel cells, this type of cell is employed in major powerplants as well as hybrid cycle plants [17].

1.2.5 Methanol fuel cells

In the early 1990s, methanol fuel cells were not to be considered suitable because of low efficiency and power density

as well as other problems [25]. The extent of power taken from this type of fuel cell is about 200 to 400 mW/cm². Methanol fuel cell is indeed a type of polymer fuel cell, with the difference that: (a) in this fuel cell, the structure of electrodes is somehow different with the structure of polymer fuel cells, and (b) liquid methanol is used as the fuel [26]. The main problem of this type of fuel cell is methanol diffusion through the polymer membrane. The low operational temperature and no need to fuel reformers have made them good candidates for small and average-sized uses such as cell phones and other similar products including automobile power generators. Low temperature of these cells makes the methanol to hydrogen ion and carbon dioxide oxidation demand more catalyst and its better activity, thereby causing increased price of these cells [27]. Since methanol is toxic, some companies have also been trying to develop ethanol fuel cells. Nevertheless, the ethanol types are half as efficient as the methanol type, though through further research their efficiency is expected to converge to each other [28].

1.2.6 Polymer fuel cells (Proton Exchange Membrane Fuel cells)

Proton exchange membrane fuel cells were first used in the 1960s for GEMINI program of NASA. This type of fuel cell is one of the most attractive ones considering their design and operation. The existing polymer electrolyte is in the form of a flexible thin sheet, which conducts hydrogen ions, and is placed between two porous electrodes. For obtaining a desirable efficiency, the electrolyte should be saturated with water [29]. Nafion is one of the most efficient electrolytes used in this type of fuel cell. This membrane is small and light, and operates at low temperature. In polymer fuel cells, oxygen reduction reaction is about three times slower than the hydrogen oxidation reaction. The catalyst used in this fuel cell often contains platinum. The amount of catalyst consumed in the electrodes for this type of fuel cell is more than the content utilized in other types of fuel cells. The fuel consumed in polymer fuel cells requires pure hydrogen. Thus, for converting methanol fuels or gasoline to hydrogen, there is a need for an external reformer [30]. In this type of fuel cell, CO causes catalyst poisoning. Because of the solidity of the electrolyte of this type of fuel cell as well as its flexibility, it is not very likely to break or even crack. In comparison to other types of fuel cell, for a certain volume and weight, polymer fuel cells generate more power. This type of fuel cell requires short time for running due to its low temperature, making it the best option in vehicle applications as an alternative for internal diesel combustion engines

and gasoline ones. Further, these systems have suitable applications in household generators, small plants, as well as transportation [31].

1.3 Mechanism of energy generation in fuel cells

In methanol fuel cells, hydrogen ions (i.e., protons) carries charge. In the anode, liquid methanol is oxidized with water, and generates carbon dioxide plus hydrogen ions. The hydrogen ions move towards the cathode through the electrolyte and electrons via an external circuit that generates electricity in the system. In the cathode, hydrogen ions and electrons react with oxygen, whereby water is generated; part of this water is sent toward the anode for consumption [32]. Fig. 2 shows different mechanisms of energy generation in various fuel cells.

In polymer fuel cells, the utilized fuel is hydrogen. The hydrogen molecule in the anode is ionized to proton and electron ions, whereby their electrons are separated. The hydrogen ions which are positively charged (i.e., protons) diffuse into a porous membrane surface and move toward the cathode. The separated electrons cannot cross this membrane; rather they cross an external circuit and cause electricity generation. In the cathode, electrons, hydrogen protons, and oxygen in the air are mixed together and form water [33].

In solid oxide fuel cells, at high operational temperatures, oxygen ions with negative charge cross a crystalline

network, that is typically a mix of zirconium oxide and CaO. In the cathode, oxygen molecules of the air are mixed with electrons. When a gaseous fuel containing hydrogen crosses the anode, a negatively charged flow including oxygen ions crosses the electrolyte in order to oxidize the fuel. The electrons created in the anode cross an external circuit and move toward the cathode. In this way, the electric circuit is completed and electricity is generated. Solid oxide fuel cells do not need an external reformer [33].

In phosphoric acid fuel cells, the utilized fuel is hydrogen. The hydrogen ion plays the role of a charge carrier. As with polymer fuel cells, hydrogen in the anode is dissociated into proton and electron, where the proton through the electrolyte and electron through the external circuit are transferred to the cathode. In the cathode, electrons, hydrogen ions, and oxygen react with each other whereby water is generated. The usage of platinum catalysts can enhance the rate of anode and cathode reactions [18].

In molten carbonate fuel cells, conductive ions are carbonate. These ions are transferred from the cathode to the anode. In the anode, hydrogen reacts with these ions, whereby carbon oxide, water, and electron are formed. Electrons are transferred from the anode to the cathode using an external circuit, whereby electricity is generated. The oxygen of the air, the carbon dioxide recycled from the anode, and electrons react to create CO_3^{2-} ions, inundating the electrolytes with CO_3^{2-} ions. The generated heat

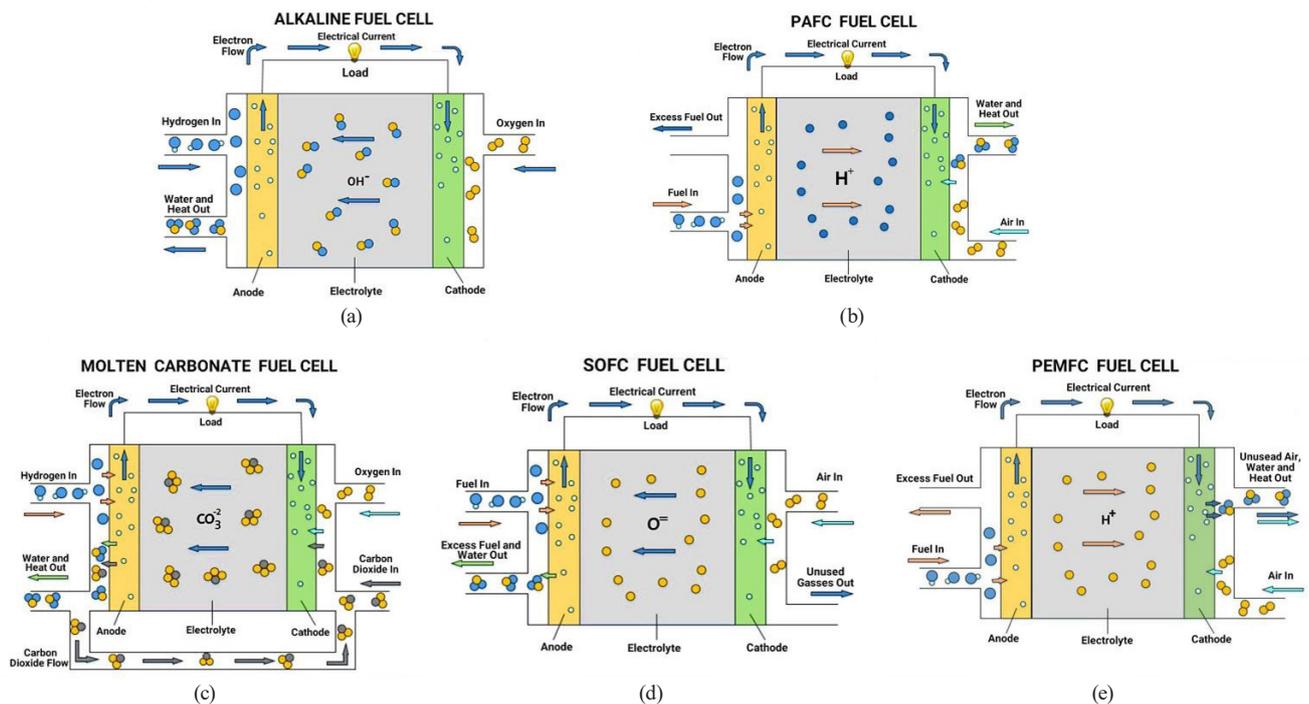


Fig. 2 Schematic representation of energy generation mechanism in various fuel cells; (a) alkaline fuel cell; (b) PAFC; (c) molten carbonate; (d) SOFC, (e) PEMFC

is used as a byproduct for high-pressure steam generation, which is very demand in industry [13].

In alkaline fuel cells, hydroxyl ions move from cathode to anode, react with hydrogen, and generate water plus electron. The electrons created in anode generate electricity through an external circuit. This external circuit delivers the electrons back to the cathode. The water generated in anode returns back to the cathode, where it reacts with electrons and oxygen, causing generation of more hydroxyl ions. These ions diffuse into the electrolyte, whereby the reaction continues. Therefore, the fuel cell generates electricity and heat as byproducts [11].

2 Hydrogen production from ethanol for application in proton exchange membrane fuel cells

Usage of hydrogen in fuel cells as a clean and efficient technology has advanced significantly in the 21st century. This can be due to development of hydrogen generation processes with carbon monoxide content. Ethanol steam reforming reaction is a renewable combination obtained from biomass, and is of great importance in developing mobile proton exchange membrane fuel cells [34]. Indeed, coupling ethanol re-forming process with ion exchange fuel cells can lead to minimal carbon emission cycle, though it should be noted that the generated carbon dioxide can be used for ethanol production [35].

The ethanol steam reforming reaction occurs in a catalytic reactor and with stoichiometric ratios of ethanol 1 mole and water 3 moles. The reaction product is 6 moles of hydrogen and 2 moles of carbon dioxide. It is an endothermic reaction and requires applying external energy. Byproducts and intermediate products generated by parallel reactions rarely form on the catalyst surface. Investigations have shown that the type and design of the catalyst have a very substantial effect on the maximum generation of hydrogen and carbon dioxide as well as minimum generation of carbon monoxide in this process. The low hydrogen efficiency in this reaction has been reported to be because of incidence of parallel reactions and generation of byproducts [35]. Various re-actions occur due to breakdown of the carbon-carbon bond in ethanol; these reactions require high temperatures within 350–650 °C [36]. Nevertheless, thermodynamically and using suitable catalysts, this reaction can also occur at lower temperatures of about 250 °C. Generally, temperature, pressure, composition, and flow rate of the reactants are the influential variables affecting the performance of this catalytic reaction.

Different catalysts lead to changes in the reaction path, where the catalyst is considered as the direct variable of this process, while the catalyst composition (i.e., the active phase and the support), precursors, and its preparation method are regarded as indirect yet important variables of the process. Presenting methods for purifying reformat and removing carbon monoxide from it for generating hydrogen fuel to be used in fuel cells has been studied extensively [12, 35]. Reactions such as water gas shift reaction and methanation are among the processes that can be used alongside hydro-gen production process and for purifying the generated hydrogen [37]. For example, a two-stage process has been explored involving one stage of ethanol steam reforming stage with Ni/Al₂O₃ catalyst and one stage of water gas shift reaction with Fe/Cr₂O₃ catalyst. To minimize the extent of generated carbon oxide, precise adjustment of the water/carbon ratio is suggested in this two-stage system [38]. Another solution to enhance the purity of the produced hydrogen is applying hydrogen permeable catalytic membranes in the methanol reforming reaction [12, 39].

Fig. 3 indicates a schema of the two-stage process for producing hydrogen with very high purity for fuel cell applications. As shown in Fig. 3, palladium-based membranes have been employed for purifying the output flow of the reforming process and separating hydrogen from gas residuals [40].

3 Proton exchange membrane performance

Usage of proton exchange membranes for separating the fuel and oxidizer is the heart of fuel cell technology. These membranes are such that they can only allow crossing of the proton. In comparison to other types of fuel cells, they are inexpensive and high efficiency. They function well at low temperatures (80 °C) and are suitable for vehicle and household uses. Nevertheless, the necessity of applying pure fuel and employing the expensive catalysts of platinum are two challenges of this type of fuel cell. Proton

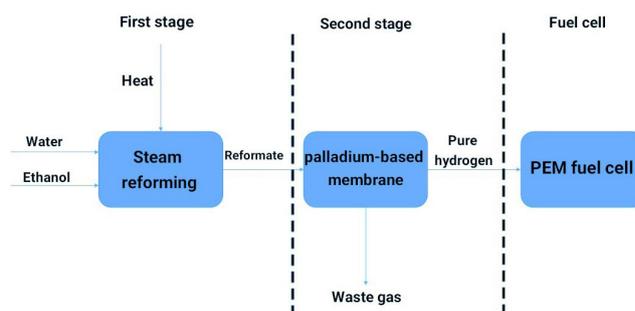
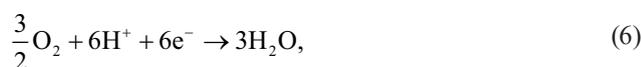
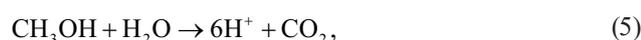
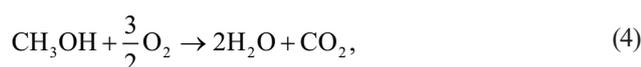
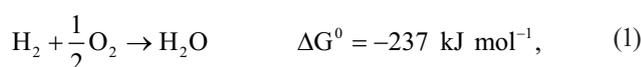


Fig. 3 Scheme of the two-stage process of pure hydrogen production [40]

exchange membrane fuel cells can be categorized into hydrogen and methanol fuel cells [41, 42].

At the interface between the platinum metal catalyst and electrolyte, the fuel is converted to proton and electron. As explained in Section 2, only protons cross the membrane, while the electrons are conducted through an external circuit and return to the cathode side after doing useful work. Chemical reactions in both types of fuel cells, i.e., hydrogen and methanol fuel cells, are as follows in Eqs. (1)–(6) [17]:



The cell voltage is obtained through changes of Gibbs free energy of chemical reaction, as shown in the following relation (Eq. (7)):

$$\Delta G = -nFV, \quad (7)$$

where n represents the number of reaction electrons, F is the Faraday constant, and V denotes the cell voltage for thermodynamic equilibrium [17].

3.1 Fuel cell components

A polymer fuel cell belongs to low-temperature fuel cells. Considering its low-temperature operation, high-efficiency catalysts should be used in its electrodes. The most important catalyst utilized in this cell is platinum. One of the best ways for reducing the amount of platinum catalyst is to apply a thin layer of catalyst metal with the maximum possible surface area. The electrode is porous so that gas could diffuse through any electrode thereby reaching the catalyst surface. Platinum and carbon substrate are suitable conductors for electrons [43].

Proton conductor membrane is the heart of a polymer fuel cell which should have properties including inexpensiveness and availability. It should not have partial and total solubility in water, nor should it be permeable

to reactant gases. It should also have suitable ion conduction under fuel cell operational conditions [44]. Up to 120 °C and above, it should have high thermal and chemical stability. It should also possess chemical stability against acids, free radicals, and oxidizers; it should have at least up to 5000 hours of useful operation and transportation applications; and it should enjoy the necessary and suitable mechanical strength [45]. The most common type of material used as the polymer membrane belongs to fluorinated polymer family with the commercial name of Nafion. These polymers can absorb large amounts of water thereby increasing the ion conductivity. The operational lifetime of Nafion membranes is high and as long as 50,000 hours [46]. The proton conductive membrane has a thickness between 50 and 200 microns. This low thickness should function as an effective separator of reactant gases in the anode and cathode and could well keep hydrogen away from oxidizing materials. Note that in spite of ion conductivity, the mentioned membrane is not electrically conductive, i.e., it does not pass electrons. This results from the organic nature of the membrane structure, changing them to electric insulators [47].

The anode electrode/membrane/cathode electrode combination is known as the membrane-electrode assembly or MEA. The power density generated by the cell has increased from about 0.5 A to 15 A for every milligram of platinum. The membrane thickness in each MEA is variable depending on the type of membrane used [48]. The thickness of the catalyst layers depends on the platinum content in each electrode. In a catalyst layer containing 0.15 g catalyst, the thickness is about 10 μm that is less than half of the thickness of a paper sheet. Such a MEA with the total thickness of about 200 micron or 0.2 mm can generate more than 0.5 A of current per each cm² with the voltage of 0.7 V [49].

Gas diffusion layers, one of them being around the anode and the other around the cathode, have been usually made of carbon porous sheets or carbon fabrics, with a thickness of between 100 and 300 microns. These layers should be made of materials such as graphite carbon so that they could conduct the electrons leaving anode and entering the cathode. The porous nature of the gas diffusion layer guarantees easy diffusion and effective absorption of any reactant gas on the catalyst used in the MEA [50]. Diffusion refers to flow of gas molecules from a high concentration region to-wards the low concentration region, where the gas is consumed. Usage of suitable materials in application of the gas diffusion layer allows achieving suitable amount of water flow from the anode electrode to the MEA, so that

the membrane is constantly saturated. It also allows out-flow of the water generated in the cathode to prevent turbulent flow in the cell [51]. The gas diffusion layers are often protected against humidity with certain percentage of Teflon, so it is ensured that at least some pores do not become completely clogged because of water [52].

3.2 Hydrogen–air system in PEMFCs

As shown in Fig. 4, in a hydrogen-air fuel cell system hydrogen flows from a storage tank to a fuel cell stack. Airflow receives from a fan or blower. The generated electricity current by the fuel cell is used as a direct current (DC) to power a vehicle's electrical motor. The stack size and weight can be reduced using a battery or capacitor in the system. Metal hybrids or high-pressure bottles are usually applied for hydrogen storage at a pressure of 1 MPa or 35 MPa, respectively. Stainless steel, carbon fiber- or glass fiber-reinforced aluminum are utilized in hydrogen bottles. To enhance safety, a relief valve is used to open at over-pressure conditions, and an H_2 sensor is applied to detect hydrogen leakage. The vehicle's driver can monitor the fuel cell stack and battery condition through a control system that regulates the hydrogen and air flow rates into the stack. In stack overheating or H_2 leakage conditions, the control system shuts down the fuel cell system. Reactants humidification before entering the stack improves the performance and running time of PEMFCs [53].

3.3 Gas flow field in PEMFCs

In a fuel cell stack, reactants flow through channels of a bipolar plate, entitled as flow field in PEMFCs. As shown in Fig. 5, four common designs for a gas flow field include

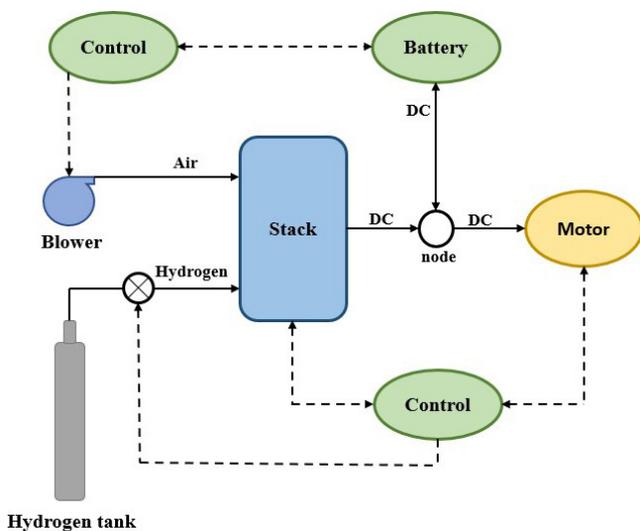


Fig. 4 Schematic of hydrogen-air fuel cell [53]

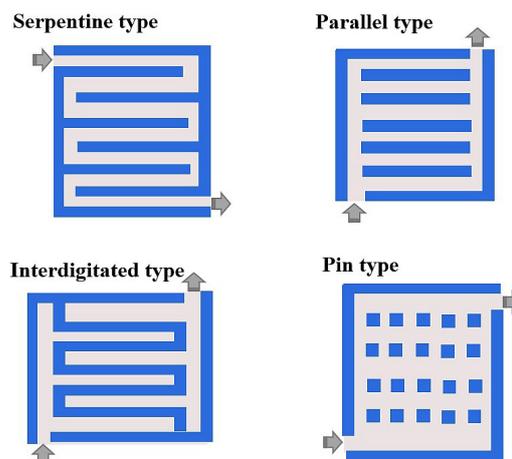


Fig. 5 Different flow field designs in PEMFCs [5]

straight parallel-, serpentine-, pin-, and interdigitated-type [54]. The gas flow field is essential to isolate the gaseous reactants and spread them to the catalyst layer. The flow field also functions to transfer current to the external circuit [55]. Moreover, the gas flow design can influence heat and water control as well as reactants dispersion and voltage stability in a fuel cell [56].

4 Challenges and solutions in PEMFCs

Despite the enormous advantages of proton exchange membrane FCs, long-term applicability, as a critical issue, strongly depends on the durability of the fuel cell stack, especially the electrocatalyst and gas diffusion layer.

One of the most effective parameters on fuel cell durability is the working temperature. Even in high-temperature PEMFCs, working at high temperatures destroys the PEM and the cell performance since it results in hydrogen flow through the electrolyte membrane toward the cathode side. Moreover, working at very low temperatures, even at negative temperatures results in damage to the membrane, and gas diffusion layer due to the ice-formation and extra cell pressure [57].

4.1 Management of water and heat in proton exchange membrane fuel cell

Water plays an important role in fuel cell operation. Water as a reactant in the anode side is used for producing proton, for membrane hydration for enhancing the proton transfer towards the cathode, and as the protons' reaction product on the cathode side. The water flow towards the anode causes development of a state called "water flooding" [58]. Thus, an equilibrium should be established between membrane hydration and prevention from the flooding. The water flux is determined by electroosmosis

factor. This factor represents the ratio of water molecules to proton molecules that cross. This coefficient is 2.5 for Nafion membrane. Effective humidity is essential for the cell and oxidant. In order to prevent water flooding, high gas flow is used on the cathode side.

Another issue is the heat management for commercialization of PEMFCs [59]. The amount of heat loss in fuel cells depends on the output electric power, which limits the energy efficiency of 50%. PEMFCs often function within 70–80 °C, in order to prevent membrane dehydration. Temperatures below 60 °C cause condensation of water and water flooding on the electrode side as well as voltage drop. Heat generation in proton exchange membrane fuel cells includes reaction heat, irreversible electrochemical reactions, Ohmic resistance, and water condensation [60, 61]. The extent of heat generated is higher in the direct methanol type compared to the ion exchange membrane, which is due to its lower energy efficiency (20–25% in 0.0–3.4 V). At higher cell temperatures, methanol oxidation reaction increases, and its crossover rate also rises, causing diminished fuel cell efficiency and energy density [16].

4.2 Fuel cross-over, oxidation and carbon monoxide poisoning

There are two technical challenges regarding direct methanol as well as proton exchange membrane fuel cells [62, 63]:

1. methanol cross-over (6–10 mol/cm s) and its reaction with platinum on the cathode side and reduction of the cell efficiency (50–2100 mA/cm²);
2. poor activity of the anode catalyst and in turn high potential drop in the direct methanol type (i.e., 350 mV) compared to the proton exchange membrane (i.e., 60 mV). The slow kinetics of anode because of the crossing of methanol leads to decreased energy density by 3–4 times in the direct methanol type compared to the proton exchange membrane type, which uses pure hydrogen fuel. Various metals have been evaluated. Presence of carbon monoxide in fuel causes platinum catalyst poisoning and blockage of the active sites [62]. As observed in Fig. 6, three methods have been presented for mitigating the poisoning effects, including use of platinum metal alloys, elevating the fuel operating temperature, and adding oxygen to the gas fuel.

The poisoning effects are temperature dependent and diminished at higher temperatures. In proton exchange membrane fuel cells, in order to prevent poisoning, pure

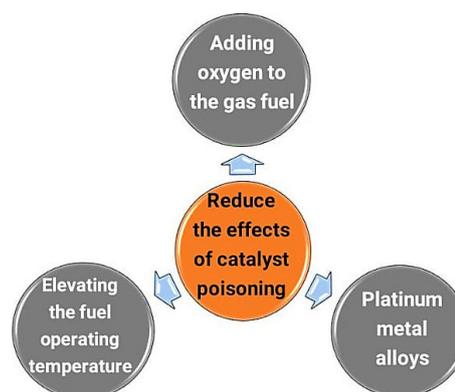


Fig. 6 Different methods for preventing or decreasing catalyst poisoning

hydrogen should be used, and for the direct methanol type, high-temperature operation is a suitable solution. In addition to the above points, other factors also affect the function of fuel cells including membrane dehydration, decreased conductivity, and mechanical stability of the membrane. Also, under oxidation conditions, free radicals (oxygen, hydroxide, and peroxide) attack alkyl chains of the polymer, leading to decreased functional groups and membrane performance. Thus, fuel cell membrane should have high stability in oxidizing media as well as thermal and mechanical stability in a wide range of pHs [17].

5 Organic-inorganic ion exchange membranes

5.1 Ion-exchange membrane features and drawbacks

The important features that should be considered for all ion exchange membranes are as follows:

- high proton conductivity,
- low electron conductivity,
- low fuel and oxidant permeability,
- low water transfer through diffusion and electroosmosis,
- stability against hydration and oxidizing agent,
- good mechanical stability in both dry and humid states,
- low cost, and
- potential to be embedded in the membrane-electrode assembly.

Because of the high-water absorption in the membrane, mechanical stability and water transfer are two key parameters in PEMFCs. Developing proton transfer systems with low water content or no water is the major challenge in the fabrication of new membranes [64, 65]. The innovation of ion exchange membranes is polymers that are based on perfluorinated hydrocarbons (Nafion). This type of fluorocarbon polymers was different from other types that had been synthesized by then; unlike Teflon, it also showed interactivity

with the surrounding environment, exactly in contrast to per-fluorinated polymers with neutral nature [66]. Given the Teflon structure, it shows longest stability in oxidative-reductive environments (more than 60,000 h). Fully hydrated Nafion membrane (Nafion 117) shows proton conductivity of about 0.1 s/cm and power density 750 mA/cm² with membrane voltage drop of about 150 mV [17, 67]. In addition to Nafion, other polymers such as polyvinylidene fluoride (PVDF), poly-ether ether ketone (PEET), polytetrafluoroethylene (PTFE) have also been used.

The most important downsides of Nafion membrane are low conductivity, poor performance at low humidity, drying at high temperatures (above 90 °C), and high methanol permeability. To overcome these challenges, different types of Nafion nano-composite membranes have been presented with metal layers or organic-inorganic hybrids. Studies are focusing on preparing inexpensive functionalized aliphatic/aromatic membranes without fluorine [7]. Indeed, aromatic groups are used to enhance the thermal stability of the membrane polymer matrix. Since high extent of functionalization, for enhancing the ion exchange, causes severe swelling of the membrane even at ambient temperatures, cross-linked membranes (covalence, ion or ac-id-based) and membranes mixed with organic materials have been studied.

Several types of hydrocarbon-based polymers have been employed for proton exchange membranes, including sulfonated block copolymer of butylene-styrene/styrene-ethylene or sulfonated aromatic polymers based on PEEK, polyimide (PI), PES, and PBI. Nevertheless, to achieve suitable conductivity values, the extent of sulfonation should be increased. This causes considerable swelling of the membrane in response to hydration. The fuel diffusion and displacement (i.e., methanol) from the anode to cathode causes decreased efficiency of the voltage and performance of the fuel cell. Both features of proton conductivity and water absorption of the polymer membrane are a function of the extent of its ionic groups. These groups are often sulfonic acid. Meanwhile, high density of ions causes severe swelling of the membrane as well as decreased mechanical stability and durability of membrane. Thus, it is observed that the basic properties of ion exchange membranes (ion exchange capacity, water absorption, and proton conductivity) should be optimized concurrently and in the reaction medium. In this regard, organic-inorganic nanocomposites can well improve these properties and resolve the mentioned downsides.

5.2 Synthesis of organic-inorganic membranes

There are various methods for synthesizing organic-inorganic nanocomposites [68]. As observed in Fig. 7, organic compounds can be added in three forms including precursor (monomer or oligomer), premade linear polymer (as molten, solution, or emulsion), and polymer network cross-links physically (pseudo-crystalline linear polymers) or chemically (thermosets, elastomers). The inorganic compound can also be used as precursor (such as Tetraethyl orthosilicate (TEOS)) or pre-synthesized nanoparticles. In case of presence of organic or inorganic precursor, organic or inorganic polymerization is required [69, 70]. Moreover, numerous parameters affect the efficiency of fuel cells as shown in Fig. 8.

Organic-inorganic hybrid materials are very suitable candidates for use as proton exchange membranes. In hybrid materials, the inorganic parts confer high mechanical and thermal stability, while also providing magnetic and electric activity. On the other hand, the organic parts contribute to flexibility, multifunctional reactivity, machining, and processability at low temperatures. Also, due to synergistic effects, hybrid compounds have far better properties compared to single materials [71]. Organic-inorganic hybrid materials can be categorized into two groups:

1. Hybrids with van der Waals, ionic, or hydrogen bonds between organic and in-organic phases. The examples

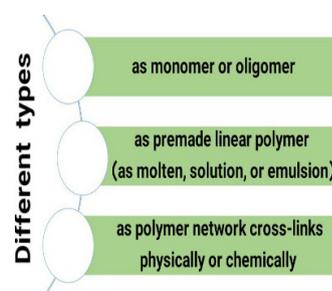


Fig. 7 Different methods of organic phase addition into the organic-inorganic nanocomposite membranes

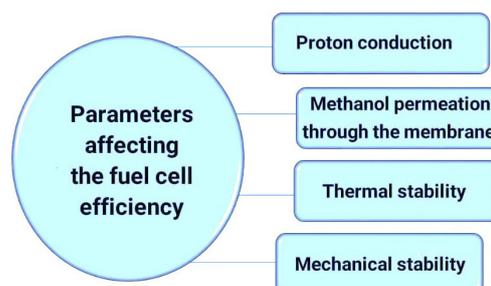


Fig. 8 Parameters affecting the fuel cell efficiency

include organic monomers entrapped in the porous matrix, inorganic particles in the polymers, polymers filled with inorganic particles via in-situ method, simultaneous formation of organic and inorganic framework, and organic dyes in the inorganic matrix.

- Hybrids with strong covalent bonds or ionic-covalence bonds such as silicon alkoxide improved with organic compounds, consecutive organic and inorganic networks, alkoxy-silanes with several functional groups, alkoxy-silane-functionalized polymers, and hybrids based on transition metal oxide networks.

Various methods have been presented for preparation of nanocomposites including blending inorganic precursors (monomer or oligomer) and linear or cross-linked polymer matrix. In case of applying monomer precursor, polymerization and cross-linking of organic and inorganic parts are required. Overall, blending, sol-gel, and in-situ polymerization are the main methods of preparation. Fig. 9 represents different methods for synthesis of organic-inorganic ion exchange membranes, including:

- blending the inorganic material in the organic polymer matrix,
- doping or diffusion of precursors and inorganic nanoparticles,
- hydrolytic and non-hydrolytic sol-gel, and
- self-assembly and layer by layer self-assembly methods.

Different types of hybrids organic-inorganic proton exchange membranes include:

- ion exchange membrane based on perfluorinated organic-inorganic nanocomposite,

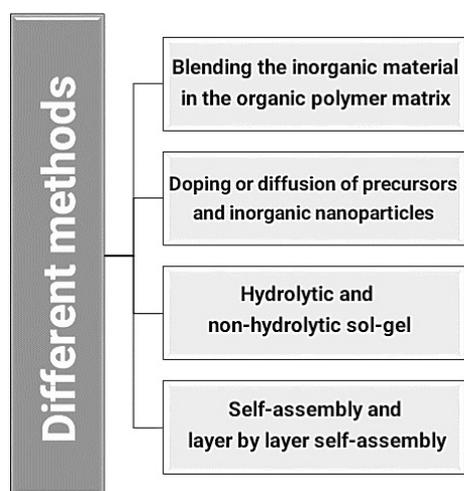


Fig. 9 Different synthesis methods for organic-inorganic proton exchange membranes

- ion exchange membrane based on partially fluorinated organic-inorganic nanocomposite,
- ion exchange membrane based on non-fluorinated organic-inorganic nanocomposite.

Meanwhile, Nafion-clay membranes, Nafion-CNT membranes, MOF-polymer membranes, and ionic liquid-polymer membranes have been investigated on proton exchange fuel cells.

5.3 Clay-polymer membranes

One of the most widely used nanomaterials in the synthesis of nanocomposite membranes is layered silicate or clay. Meanwhile, montmorillonite is a type of clay that has been examined extensively [17]. Electronic/ionic conductivity properties and biodegradation of polymer membranes show considerable improvement upon adding very trace amounts of clay. Clay often functions as nucleation agent for pseudo-crystalline polymers. Nevertheless, intercalated polymers to which clay has been added become amorphous [17, 67]. Layered nano-porous compounds are considered as an intermediate structure between layered materials and crystalline nano-porous structures. Layered silicates with a microporous three-dimensional structure can be used for catalytic, absorption, and ion exchange applications.

A nanocomposite membrane composed of poly(2,5-benzimidazole) polymer-grafted montmorillonite and sulfonated polyvinyl alcohol (PVA) was synthesized and applied for the high-temperature PEMFC with improved conductivity of 0.0075 S cm^{-1} at $140 \text{ }^\circ\text{C}$ without humidification [72]. CNT-smectite clay as a nanofiller was introduced in the Nafion membrane and showed improved conductivity of $7 \times 10^{-2} \text{ S cm}^{-1}$ at $120 \text{ }^\circ\text{C}$ and 30% RH compared with pristine Nafion [73]. A nanocomposite membrane composed of polyvinyl alcohol, polystyrene sulfonic acid, and montmorillonite was fabricated by solution casting method with an ion-conductivity of $2.07 \times 10^{-3} - 6.69 \times 10^{-3} \text{ S cm}^{-1}$ and maximum power density of 65.23 and 90.70 mW cm^{-2} at 25 and 50 $^\circ\text{C}$, respectively [74]. Sulfonated polyvinylidene fluoride-clay nanocomposite exhibited a power density of 33 mW cm^{-2} that was 3 times higher than the power density of the Nafion membrane [75].

By adding clay to polymer membrane, three cases may occur including:

- Microcomposites: in this case silicate layers have not been intercalated by polymer chains,
- Intercalated nanocomposites: in this case incorporation of polymer chains into the silicate structure

occurs in a crystalline and organized form, regardless of the polymer/silicate ratio and with organized nanometer distances, and

- Exfoliated nanocomposites: in this case individual layered silicate has been separated in the polymer matrix with average distances that depend on the extent of layered silicate loading [17, 67, 76, 77].

5.4 Carbon nanotube-polymer membranes

Carbon nanotubes have a unique atomic structure, high length-to-diameter ratio, and very high mechanical stability. Nanotubes can also improve the electric properties of the nanocomposite. Meanwhile, one of the disadvantages of carbon nanotubes is the probability of development of short-circuit, created by an electrolyte that is not electrically isolated. The second problem of CNTs is their tubular form. For direct methanol fuel cell, methanol permeation from the membrane is the major problem, where tubular form is less suitable than the planar shape. Thus, effective dispersion of the nano tube inside the polymer matrix can effectively reduce methanol permeation while maintaining membrane stability. Preparing a polymer/CNTs composite membrane with uniform dispersion depends on strong bonds at the interface between compounds. Fabrication of a nanocomposite without any negative effects and damage to the carbon nanotube is the main aim for preparing conductive composites. So far, studies for preparing nanocomposites with nano tube content of more than 5 wt% have had problems. Because of strong van der Waals forces, nanotubes tend to remain in close as strong bundles. Thus, they have low solubility in solvents and poor dispersion in the polymer matrix [78, 79].

The high proton conductivity is one of the most important characteristics of Nafion membranes for usage in fuel cells. The main challenge in this regard is fabricating a membrane with high conductivity under dry condition [80]. With increase in the membrane humidity, proton conductivity also increases. Nevertheless, in case of applying humid membranes, there is possibility of water flooding on the cathode side and decrease of the oxidation reaction rate plus swelling of Nafion membrane because of electroosmotic drag coefficient (EODC). Drag coefficient is a quantitative criterion for measuring membrane hydration and is defined as the crossed water-to-proton ratio. Studies have shown that this coefficient is independent of the type of Nafion membrane and is a function of water content [7]. The notable issue regarding fuel cells is high energy density and very low degradation. The leading solution is fabricating membranes with high thermal stability.

5.5 MOF-polymer membranes

In the past decades, MOFs have attracted a lot of attention and have been used in various applications due to their various advantages. The porous structure of MOFs is different from traditional porous materials, which has made them better compatible and changeable. These materials have good thermal and chemical stability, which is one of the key points of their use in fuel cells. Some MOFs have weak points such as processability and flexibility, which can be solved by adding polymer to this structure [81]. The proper functioning of PEMFCs depends on the effectiveness of PEM. It is believed that the proton conduction mechanism throughout the PEM is based on the Grotthuss mechanism and the vehicle mechanism [82, 83]. Also, these mechanisms help proton conduction in MOFs.

MOFs are not suitable for proton conductors due to their crystalline and porous nature, because of this, at first it seems that they are not a suitable option for use in proton-conducting membranes in fuel cells [84]. While after numerous analyses, promising results have been obtained that make MOFs one of the appropriate candidates for use in fuel cell membranes [85]. Currently, several groups have reported proton-conducting MOFs that act based on counter ions and guest molecules present in their pores [81, 85–87]. If there are counter ions in the channels of MOFs used in fuel cell membranes, which contain water, hydroxyl groups, acidic groups, or functional groups containing hydrogen atoms, they can help to conduct protons [81].

To date, various approaches have been used to improve and enhance the proton conductivity when using MOFs, such as hydrophobicity of the frameworks and coordination of proton conducting molecules that are placed in the pores and channels. Many advances have been made in the practical field, for example, we can point to MOFs, which have a significant conductivity similar to Nafion and with better advantages. But the long-term efficiency of this method should also be investigated whether the use of MOFs in PEM has stable and acceptable conditions in the long term or not [88].

5.6 Ionic liquid-polymer membranes

Operating PAMFC at high temperatures brings significant advantages. For example, the water management system is better controlled, and the wasted heat can be used optimally. Meanwhile, proton conduction in Nafion membranes requires humid conditions and low temperatures (<100 °C). These conditions have disadvantages and to solve them, Nafion membranes should be replaced with membranes that can conduct proton at high-temperature and under anhydrous conditions [89].

One of the ways to achieve this goal is to use protic ILs as proton conductors. One of the subgroups of acidic ILs are protic ILs, which can replace Nafions due to their high proton conductivity and high thermal and chemical stability [90, 91]. Protic ILs, after combining with polymers, can be used in PEMs used in fuel cells [89].

Moreover, poly ILs can be mentioned as one of the most promising classes of polymers that have a high potential for use in PEMs. Poly ILs have shown proper performance under anhydrous conditions and at temperatures above 100 °C [89]. For use in PEM, poly ILs combined with other polymers can be a more suitable option than ILs because of the better characteristics they show. They can keep some properties of ILs, such as proper structure, high thermal and chemical stability, high conductivity, etc., and address some issues such as the problem of leakage from the membrane structure [89–92]. Although in some cases the mechanical properties of poly ILs require extensive studies and efforts to be improved [93].

5.7 Graphene-polymer membranes

Graphene is a 2D nanostructure with incredible features such as high surface area, conductivity, thermal and mechanical stability, flexibility, and chemical resistance especially in corrosive media. Graphene-based materials are promising carbon-based support for PEMFCs electrocatalysts such as noble metals, non-noble metals, and metal-free catalysts. Due to the hydrophobic nature of pure graphene, modification of graphene to form graphene-based materials including graphene oxide, 3D graphene, or heteroatom-doped graphene is required to achieve high dispersion of metal catalyst particles, which results in reducing the catalyst loading. Moreover, graphene-based materials can be considered nanofillers in polymer electrolyte membranes. Several studies have been reported on the modification of polymeric membranes such as sulfonated poly(ether ether ketone) (SPEEK), PBI, polyaniline (PANI), sulfonated poly(arylene ether sulfone) (SPAES), Nafion, and poly(vinyl alcohol) (PVA) [94].

Facile hydration of GO due to the presence of oxygen-containing groups improves the proton conductivity in GO-PEMs. A nanocomposite membrane composed of SPEEK polymer and sulfonated GO was fabricated and exhibited high conductivity of 0.055 S cm⁻¹ and power density of 378 mW/cm² at 80 °C and 30% RH [95]. The addition of 5 wt% of polydopamine-functionalized GO into SPEEK polymer enhanced the proton conductivity and a power density of about 47% and 38%, respectively [96]. The presence of 3-mercaptopropyltrimethoxysilane functionalized

GO as nanofiller in Nafion composite membrane improved the proton conductivity by about 4 times [97]. PBI polymer containing 2wt% GO was treated with phosphoric acid for high-temperature PEMFC application without humidification. Phosphoric acid-doped PBI-GO nanocomposite exhibited a maximum power density of 0.38 W/cm², and a current density of 0.252 A/cm² [98].

5.8 Metal oxide-polymer membrane

Investigation of organic-inorganic nanocomposite membranes using various nonporous metal oxides such as SiO₂, TiO₂, Zr₂O, Fe₂O₃, etc., as fillers have been reported in Literature. SiO₂ as a low-cost inorganic filler with water retention properties is widely studied in PEMFCs. SiO₂-PBI membrane was fabricated using 40%–120% TEOS as silica precursor using the facile sol-gel method and showed improved mechanical stability and fuel cell performance [99]. TiO₂ as a hygroscopic filler facilitates the fuel cell performance at high working temperatures with high mechanical stability. The application of amine modified TiO₂ nanotubes improved the proton conductivity of Nafion membranes by about 4–5 times [100]. Sulfonated TiO₂-polybenzimidazole nanocomposite membranes have been synthesized using a solvent-casting method and evaluated in high temperature PEMFC application with a maximum current density of 0.89 A cm⁻² [101]. zirconia-silica incorporated Nafion membrane showed a performance of 610 mW cm⁻¹ at 120 °C, 50% RH [102]. Incorporating 5 wt% of Zr₂O into a phosphoric acid doped polyethylene imine and polyvinyl alcohol nanocomposite resulted in an ion-exchange capacity of 2.94 mmol/g⁻¹ and proton conductivity of 4.34 10⁻² S/cm⁻¹ [103].

6 Conclusion and future outlook

High-temperature proton exchange membranes are very important for industrial uses such as fuel cells. Nafion-based nanocomposite membranes are an important group of these proton exchange membranes. This article briefly reviewed proton exchange nanocomposite membranes and their applications in fuel cells. Different types of nanofillers as well as their preparation methods affect the thermal, mechanical, proton conduction properties, and methanol permeation in PEMs, and some of these changes cannot be achieved in conventional composites. The differences in the characteristics of organic and inorganic compounds such as solubility and thermal stability have limited usage of conventional synthesis methods. Nevertheless, in recent studies, simple methods have been presented for preparing nanocomposite PEMs. Surface

modification of these membranes can be divided into several major groups:

- improving membrane humidification,
- reducing electroosmotic drag and cross-over of fuel from the membrane,
- improving the mechanical and thermal properties without reducing the proton permittivity feature,
- improving proton conductivity through adding conductive organic solid compounds to the polymer matrix, and
- decreasing the drying rate of the proton exchange membrane and enhancing the humidity retention potential.

A better understanding of the relationship between the pseudo-crystalline morphology of Nafion and the transitional, thermal, as well as mechanical properties of Nafion would lead to the fabrication of membranes with better performance. Establishing a balance between the proton conduction ratio to methanol permeation is very important. Meanwhile, low conductivity and poor performance of per-fluoro sulfonate ion exchange membranes such as Nafion at low humidity and high temperature are considered the major problems of industrializing fuel cells. These have led to numerous attempts for modifying PEMs to enhance their efficiency. Synthesis of a new type of product such as membranes based on choosing a suitable polymer with appropriate functional groups for placement of inorganic compounds in the preparation of hybrid membranes seems to be essential. The current barriers ahead of PEMs can be mentioned as high proton conductivity at high temperatures (such as 120 °C and humidity 50%), as well as long stability and durability on their operational conditions in fuel cells.

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Materials functionalized with sulfonic acid have limitations of low conductivity under dry conditions. Accordingly, the synthesis of a new and functionalized compound for operation at high temperatures seems to be essential.

So far the design of new PEMs has been based on modifying the ratio of aliphatic/aromatic polymers, selecting suitable functional groups, and employing inorganic fillers to achieve features such as: (a) mechanical as well as dimensional stability of membrane under humid conditions and an average temperature of 80–130 °C, (b) maintaining water at high temperatures to keep humidity and proton conductivity. Generally, the problems regarding the development of nanocomposite membranes are as follows:

- determining suitable inorganic filler and its dispersion conditions for the polymer of interest,
- optimizing the amount of filler in the polymer matrix,
- determining the suitable synthesis and casting method for PEMs,
- precisely investigating the interaction of the filler/polymer matrix and solvent.

All of these issues have a great influence on the morphology, long-term stability, and electrochemical properties of the composite in fuel cells. Future research areas include attempts for achieving high content of functional groups for both organic and inorganic parts without affecting membrane stability.

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