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Materials for fuel cell membrane

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Abstract

Proton-exchange membrane fuel cell (PEMFC) continues to receive a great deal of interest as an energy source for many practical applications and in particular to those related to the automotive industry. Among the different research directions, developing inexpensive and high-performing membrane materials for PEMFC has been identified as a key approach for reducing the cost of the technology, increasing its applications, and satisfying the other technical and economic demands of the consumers. The membranes' material should possess a combination of complex features including high proton conductivity; good mechanical, thermal, and chemical stability, low gas permeability, and moderate prices. Despite being commercialised and widely used, Nafion-based membranes feature many drawbacks and researchers are still working actively to find alternative membrane materials that can provide an adequate balance between the performance and cost.

In this chapter, an overview of the different PEMFC membrane materials is given. The properties, performance, and challenges of the membrane materials were compared and the future research directions were outlined.

Keywords: Fuel cell, membranes, PEMFC, DMFC.

1. Introduction

Fuel cells are electrochemical devices that generate electricity from a catalytic aided reaction of a fuel, mostly hydrogen, with an oxidant, such as oxygen or air [1]–[3]. Over the past years, the fuel cell has been identified as a promising alternative to traditional power sources such as heat engines, i.e. internal combustion engines, with higher efficiency, lower noise, and minimal amounts of pollutants [3], [4].

The low-temperature type of the fuel cells namely proton exchange membrane fuel cell (PEMFC) is currently used to power wide range of applications from charging system of electronic devices to an electric motor of a fuel cell electric vehicle (FCEV). PEMFC uses proton-conducting membrane as the electrolyte sandwiched between a cathode and an anode.

The working principle of the PEMFC is shown in Figure 1. The hydrogen is ionized at the anode to form protons (H^+) and electrons (e^-) whereas oxygen is reduced at the cathode. The produced protons (H^+) pass through the proton conductive membrane to the anode and combine with the reduced O_2 to form water whereas the resulted electrons travel through the external circuit to produce electricity. The cathode reaction is exothermic which imposes the need to remove the generated heat and maintain the cell at a constant temperature [5].

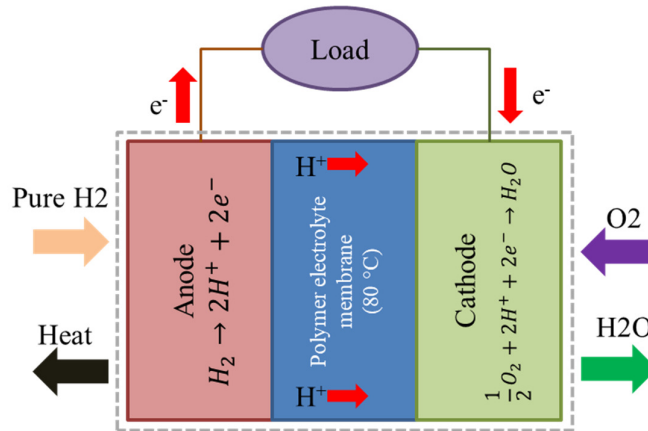


Figure 1: Working principles of PEMFC [3]

Direct methanol fuel cell (DMFC) is a subcategory of PEMFC in which energy-dense liquid methanol is used as the fuel instead of hydrogen. DMFC provide several advantages over

hydrogen fuel cell due to the ease delivery and storage of liquid methanol, lack of humidification requirement, and good stability and low cost of fuel [6]. The working principle of DMFC is very similar to hydrogen-fuelled PEMFC. When methanol enters the fuel cell at the anode, it is oxidized in the presence of water to produce carbon dioxide (CO_2), electrons (e^-) and hydrogen ions (H^+) [7]. The generated hydrogen ions cross the membrane while the electrons flow through the external electrical circuit to the cathode side. At the cathode side, the hydrogen ions, electrons, and oxygen react together and produce water (H_2O). Figure 2 summarizes the working principle of the DMFC.

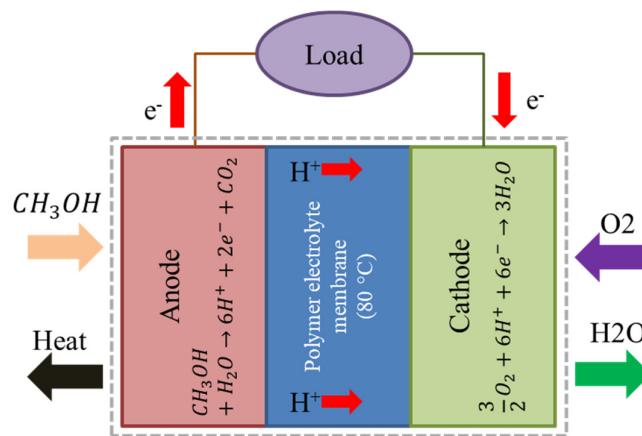


Figure 2: Working principles of DMFC

The membrane is the heart of the PEMFC and it plays a key role in the overall performance of the cell. The good membrane should be ionic conductive, impermeable to gases, durable, chemically stable under fuel cell operational conditions, resistant to chemical attack, and able to operate within a wide range of temperature.

In this chapter, an overview of the main membrane materials of the PEM fuel cell is presented. The main advantages and disadvantages of the different membrane materials are identified along with the main challenges.

2. Membrane material

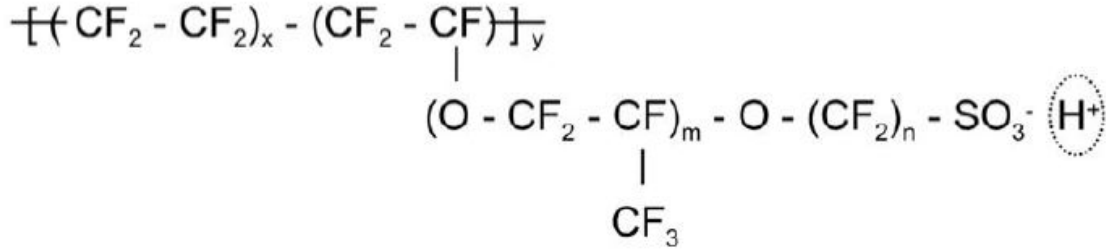
One of the most important features of a PEMFC membrane is its ability to conduct protons. This feature is determined by acid and water content of the membrane and it is also influenced by the

chemical structure and morphology of the membrane as well as its temperature. In addition to high proton conductivity, the membrane should possess adequate mechanical strength and stability as well as good chemical and electrochemical stability under PEMFC operating conditions [8]. Furthermore, the membrane material should be able to inhibit the reactants crossover through it in order to maximize the efficiency of the PEMFC. Additionally, the production costs of the membrane material should be as low as possible in order to increase the commercial feasibility of the PEMFC technology. The materials used for the PEMFC membrane can be categorised into three main groups including Perfluorinated and non-fluorinated membranes [8].

2.1 PFSA-BASED MEMBRANES

The most commonly used membrane material for low-temperature PEMFC is perfluorosulfonic acid polymer (PFSA) which includes a range of products from different manufacturers, under trade names of Nafion™ (DuPont), Flemion™ (Asahi Glass) and Hyflon™ (Solvay-Solexis) and Aquivion™ (Solvay) [9]. Nafion, which is the most commercialised PEMFC membrane, was invented by Grot [10] at DuPont by modifying Teflon which is the first synthetic polymer with ionic properties, i.e. ionomers. Nafion, as shown in Figure 3, is composed of perfluorinated backbones with sulphonic acid (HSO_3). The perfluoroether with the spaghetti-like chain molecules are responsible for the chemical stability of the membrane while the sulphonate side-chains are responsible for aggregating and facilitating hydration. When these membranes become hydrated, the protons become highly mobile in the hydrophilic regions of the sulfonic acid clusters which form channels through which H^+ ions can move freely under a potential gradient [9]. Thus, this material combines the proton conductivity of the hydrophilic micro-phase of the sulfonic acid chain; and the high mechanical strength of the hydrophobic polymeric phase of the perfluorinated backbones.

Furthermore, Nafion is very resistant to chemical attacks and release an extremely low rate of degradation products into the surrounding medium. Additionally, it exhibits high proton conductivity and a relatively high operating temperature range.



Nafion: m = 1-3, n = 2, x = 5-13, y = 1000-1200
 Others: m = 0, n = 1-5, x = 1-14, y = 800-1200

Figure 3: Structure of Nafion and its close polymers [11].

Despite their wide-spread use, there are still many drawbacks of using Nafion-based membranes. The proton conductivity of Nafion depends on the water content so a humidification equipment is normally needed to provide the required level of humidity. Also, the Nafion-based membrane might experience swelling and shrinking during humidity and thermal cycles due to changes in water uptake. Additionally, Nafion shows very poor performance at high temperature and chemical degradation over long term operation within PEMFC. The chemical degradation of Nafion is due to the formation of peroxy and hydroxyl radicals that attack the sulfonic acid clusters and decompose the polymer chain [12]. Furthermore, Nafion is a high-cost material and its manufacturing process is complicated and releases various toxic intermediates and waste products [13]. Another drawback of Nafion membranes is the poor conductivity at low relative humidity.

Considerable research efforts were made to address the aforementioned drawbacks and to develop cheaper and less water-dependent Nafion membrane.

The main approaches for improving the mechanical and chemical stability of a Nafion membrane are through reinforcement of the membranes with an inert matrix such as polymer structure or an

inorganic matrix. Generally speaking, the inorganic matrix is used for improving the membrane's chemical and temperature stabilities while polymer structures, such as polytetrafluoroethene (PTFE), are used for enhancing mechanical stability [14]. The introduction of a reinforcing matrix may negatively affect the conductivity and permeability of the reinforced membrane [14]. This is mainly because part of Nafion is replaced with the matrix material in the composite membrane. However, different additives, such as phosphotungstic acid, can be used to enhance the proton conductivity of the reinforced Nafion membranes.

Thin porous polytetrafluoroethene (PTFE) foils were used to reinforce the Nafion membrane and create composite membrane [15][16]. The developed membrane was very thin and has high proton conductivity and excellent mechanical stability.

Nanocomposite membranes were suggested as a solution to tackle the dehydration issue of the Nafion membrane. In this approach, the Nafion membranes were modified using micron or submicron inorganic and organic antioxidant additives such as ZrO₂ [17], TiO₂ [18], TiSiO₄ [19], silica [20], and benzoquinone [12]. Such additives offer a high water retention capability, which enables the membrane to maintain its proton conductivity when the fuel cell operates at high temperature. They also improve the physical properties of the membrane such as elastic modulus, tensile strength and hydrophilicity. Additionally, these antioxidants significantly improve the chemical durability of the electrolyte membrane by inhibiting attacks from radicals.

The thickness, hydration, and proton conductivity of the membrane are the main features that determine the overall performance of PEMFC [21]. Reducing the thickness of the membrane enhances its proton conductivity [21]. Using a reinforcing matrix can increase the overall conductivity of the membrane as the reinforced membrane is substantially thinner than the Nafion membrane [14].

Partially fluorinated membranes, such as sulfonated copolymer incorporating α,β,β -trifluorostyrene monomer, were suggested as a cost-effective replacement of Nafion-based membranes. Upon testing in single-cell hydrogen/air fuel cell at 85 °C with an active area of 50

cm², these membranes showed high efficiency and long operation lifetime of around 15000h [22]. However, this membrane is still in the development stage and no information is available on its durability, stability, and gas permeability [22].

2.2 Non- fluorinated membrane

Significant research efforts were made to produce low-cost membrane through replacing the Nafion-based membranes by more cost-effective and less water-dependent polymers such as sulfonated polymers (sulfonated PEEK (SPEEK), polystyrene, polyimides, and polyphenylenes), and acid-base polymer (phosphoric acid (PA)-doped Polybenzimidazole (PBI)) [23].

In fact, the development of non-fluorinated membrane started before considering the fluorinated ones. Polystyrene-sulfonic acid (PSSA) membranes were the first commercial PEMFC membranes. In early 1959, General Electric (GE) prepared a phenolic membrane through the polymerization of phenol-sulfonic acid with formaldehyde. The developed membrane exhibited low mechanical strength, short lifetime of around 300–1000 h, and a fuel cell power density in the range of 0.05–0.1kWm⁻² [8]. Later, an attempt was made by GE to improve the power density by developing partially sulfonated polystyrene sulfonic acid membranes which showed a better water uptake and higher power density than the phenolic membranes but they suffered brittleness in the dry state. Another development was undertaken by GE in which they prepared cross-linked polystyrene-divinylbenzene sulfonic acid membrane/polymer in an inert matrix. The developed membrane showed an operational life of up to 10000h and power density of up to 0.8kWm⁻². However, the proton conductivity of all the developed membranes by GE was very low which negatively affected the resulting power density. Generally, PSSA membranes are unstable under practical operational conditions of PEMFC. The main reason for the degradation of PSSA is the peroxide attacks at the hydrogen atoms within the polymer chain of PSSA, shown in Figure 4 [14].

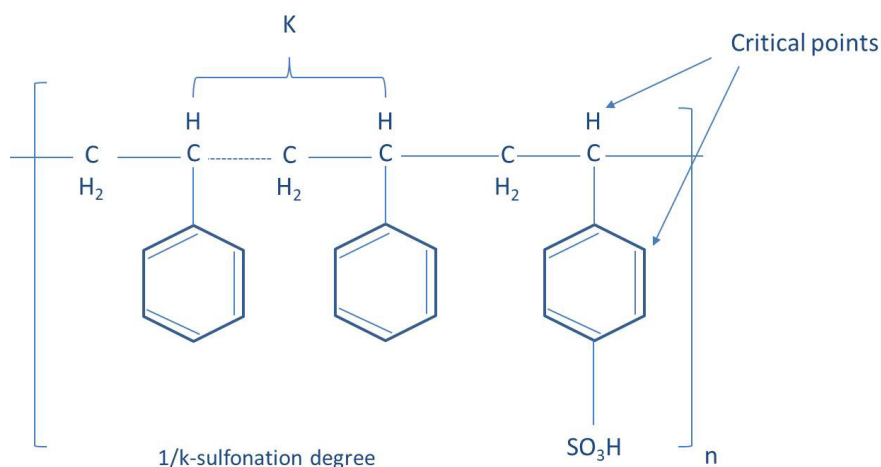


Figure 4: PSSA-based membranes for PEMFC [14]

Among the other non-fluorinated membranes, the arylene main-chain polymers, such as poly(phenylene), poly(ethersulfone), poly(etherketone), poly(phenylene oxide), poly(phenylene sulfide), and poly(thioetherketone)s exhibited good chemical stabilities within PEMFC environment [24]. Such membranes have shown exceptional performance for direct methanol fuel cell (DMFC) due to their lower methanol permeability compared to the perfluorinated [24].

Ballard Advanced Materials (BAM) developed two different types of PEMFC membranes. The first type was based on poly(phenylquinoxaline) (PPQ) polymers. The performance of this type of membrane was comparable to Nafion membranes but with significantly lower lifetime [22]. The second type of membrane was based on poly(2,6-diphenyl-4-phenylene oxide) which showed good mechanical properties in the dehydrated state and superior performance compared to Nafion and poly(phenylquinoxaline) (PPQ) based membranes. However, these membranes also showed low operation lifetime which was caused by the internal transfer of reactant gases across the membrane electrode assembly [22].

Sulfonated polyether ether ketone (SPEEK), i.e. poly(thioetherketone)s, has attracted increased attention for DMFC membrane applications due to its low cost, low methanol permeation, and very good mechanical properties [22]. However, the proton conductivity of SPEEK is relatively low but it can be increased by increasing the sulfonation levels [25]. Increasing sulfonation levels in SPEEK make it water-soluble and reduces its mechanical strength [25]. The material durability

of SPEEK membrane is generally lower than that of Nafion due to fact that SPEEK is susceptible to hydroxyl radicals attacks on non-sulfonated phenyl ether aromatic rings, as shown in Figure 5, during PEMFC operation [14].

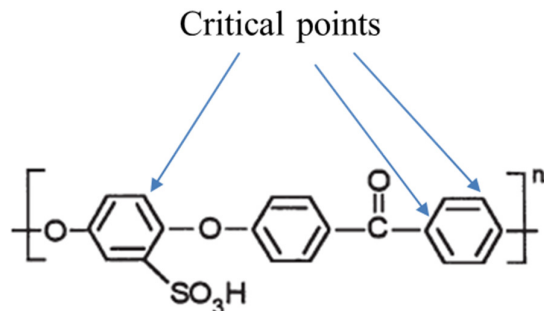


Figure 5: Chemical Structure of SPEEK with possible sites for radicals attacks (acquired from [22] and modified)

Sulfonated Polyimide (SPI)-based membranes, which use thermostable polymers, provide a combination of desirable membrane features such as high mechanical and thermal properties and durability against aggressive chemicals and heat [14]. These membranes are generally favourable for medium-temperature PEMFC operations as their water uptake and swelling ratio show minimal variation over a broad range of temperature [14]. Additionally, the methanol permeability of (SPI)-based membranes is significantly lower than that of Nafion-based membranes. Furthermore, the proton conductivity of SPI-graphene composite membrane may reach up to 1.67 S/cm at 120 °C [16] and 1.201 S/cm at 80 °C which are adequate conductivities for PEMFC. However, these membranes are unstable in hydrated states and are highly susceptible to hydrolysis which forms a major challenge towards adopting them for PEMFC applications.

Polybenzimidazole (PBI)-Based membranes, as shown in Figure 6, employ the phosphoric acid groups (H_3PO_4) instead of water as a proton transport medium and thus they are deemed to be appropriate for high-temperature PEMFC applications [14], [26]. The operational temperature range for this type of membranes is 160-220 °C. Development of PBI membranes has progressed well and CeltecL, CeltecP1000, and CeltecV from BASF are examples of commercialized PBI membrane [14]. Overall, the proton conductivity of (PBI)-Based membranes is directly proportional to acid content and greater content results in higher proton conductivity [14].

However, a significant increase of the acid content might lead to negative consequences on the other properties of the membrane such as tensile strength, homogeneity, and gas permeability; therefore a balanced acid content is extremely important to achieve membrane strength and conductivity. The PBI-membranes are also susceptible to attacks of OH• and OOH• radicals during fuel cell operation which impact its chemical stability. Generally, the chemical degradation rate of PBI is greater than that of Nafion and lower than that of lower molecular weight polymers [14]. Leaching of the free acid during fuel cell operation is another drawback of these PBI-based membranes which limit the application of these membranes below 150 °C [27].

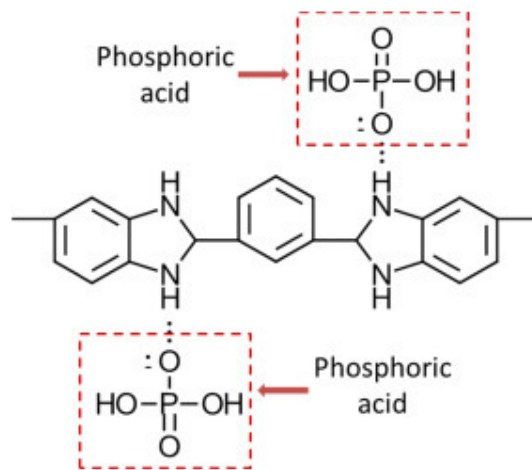


Figure 6: Chemical structure of a PBI/phosphoric acid membrane [26]

3. Summary

The membrane is a key part of PEMFC and it contributes significantly to the overall performance and cost of the device. Membranes separate the anode from cathode compartments of the fuel cell but they allow efficient transfer of protons from the anode to the cathode.

PFSA-based membranes are dominating the low-temperature PEMFC market. They generally provide long operational life, good stability, and high proton conductivity. However, the high cost and the loss of conductivity at high temperatures or low relative humidity are the main drawbacks of these membranes. Modification of PFSA membranes with various additives, such as inorganic

and organic compounds, was found to be a promising approach for addressing the dehydration issue of the PSFA membranes.

Significant advances have been made in the development of a broad range of polymers and membranes as alternatives to classical PFSA type. Generally, these materials are inexpensive and recyclable; have easier fabrication routes, and can operate within wider temperature range.

Sulfonated polyether-ether ketone (SPEEK)-based membranes are the most widely studied polymer after Nafion due to their high commercialization potential. PBI-based material, which can operate at a higher temperature and less relative humidity compared to PFSA-membranes, are also promising membranes for PEMFC due to their higher carbon monoxide tolerance and reducing the complexity of the stack. Despite that non- PFSA membranes are more cost-effective; they showed lesser conductivity, reduced mechanical and chemical stability compared to PFSA-based membranes.

Despite the dramatic developments made in the last few years, developing an inexpensive, proton conductive and durable membrane continues to remain a challenge for PEMFC technology. It is expected that the focus of future research will be on improving the water-free membranes such as PFSA-based composite membranes using polymer/inorganic additives; and polymer/acid blends such as PBI-based membranes. These membranes enable the PEMFC to run at a higher temperature allowing various advantages including higher catalysts activity, improved electrode kinetics, greater fuel impurities tolerance, easier integration with high-temperature hydrogen generators, and easier thermal management. Improving membrane materials should be conducted in parallel with enhancing the catalyst layers properties in terms of activity and stability in order to achieve the utmost outcome.

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