Nafion-Based Membrane

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Nafion, a perfluorosulfonic acid proton exchange membrane (PEM), has been widely used in direct methanol fuel cells (DMFCs) to serve as a proton carrier, methanol barrier, and separator for the anode and cathode. A significant drawback of Nafion in DMFC applications is the high anode-to-cathode methanol fuel permeability that results in over 40% fuel waste.

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1. Introduction

Immense consumption of unsustainable and non-renewable fossil fuels for a variety of purposes, including transportation, generation, and conversion, has greatly reduced the availability of existing energy resources such as petroleum, coal, or natural gas [1]. The usage of fossil fuels also contributes to environmental degradation due to the high amount of greenhouse gas emissions. As energy demands rise and environmental concerns grow, it is imperative that long-term renewable energy sources be developed. However, renewable sources such as solar, wind, or geothermal are limited by the weather conditions. Thereby, in the present juncture of energy and economic insecurity, the fuel cell has emerged as a potential alternative to conventional energy sources due to the numerous advantages it offers. Particularly, fuel cell establishes high energy density, lower emission of pollutants such as SO_X, NO_X, CO, and CO_2, and has the benefit of being portable.

The fuel cell is an electrochemical device that supplies energy continuously in one step by converting chemical energy into electrical energy as long as the external supply of fuel and oxidant is maintained [2]. Thus, fuel cells are able to provide power continuously without requiring long charging times or the replacement of new energy generators. Presently, there are several types of fuel cells, such as alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC), solid oxide fuel cells (SOFC), and proton exchange membrane fuel cells (PEMFC), which are classified based on the type of electrolytes used and operating conditions [3]. Electrolytes such as alkaline solution, acidic solution, molten carbonate salt, ceramic ion, and solid polymer are used in AFC, PAFC, MCFC, SOFC, and PEMFC, respectively. Moreover, fuel cells differ by the reactants used, the type of ions transported, the structure of the fuel cell system, and their application in different fields. Among all these fuel cells, PEMFC has been actively researched owing to its low operating temperature of less than 100 °C, high power density, low corrosion, facile infrastructure (no moving parts), and quiet operation [4]. Generally, PEMFC can operate on a variety of fuel sources, for instance, hydrogen, formic acid, or alcohol.

The direct methanol fuel cell (DMFC) is one of the PEMFCs, which uses methanol directly as fuel to generate electricity without fuel combustion. DMFC has gained much attention as it is a simple and compact system that eliminates the need for auxiliary units, as well as has a fast start-up time under ambient conditions [5][6]. Moreover, liquid methanol is low cost, environmentally friendly, easy to distribute, and stores and handles under standard conditions. Methanol also has a high energy density [7][8]. According to Joghee et al., the energy density of methanol is 15 times higher than lithiumion batteries [9]. As a result, it benefits portable devices, especially when conventional batteries are unable to meet growing energy demands, as people nowadays expect more functions that require a continual supply of power. In addition, methanol is intriguing as it can be produced from biomass, which is considered a cleaner energy source for long-term usage.

The basic configuration of a single DMFC consists of a fuel reservoir, bipolar current collectors, and a membrane electrode assembly (MEA). MEA is made up of a solid polymer electrolyte membrane (PEM), which is the core component of DMFC, sandwiched between two catalyzed electrodes. The electrode comprises two layers, namely the catalyst layer and the gas diffusion layer (GDL). Carbon-supported PtRu and carbon-supported Pt catalyst are widely used in anode and cathode to speed up the methanol oxidation reaction (MOR) and oxygen reduction reactions (ORR), respectively [7]. However, due to the scarcity and high cost of Pt, much effort has been expended on producing low-cost and efficient dual-role electrocatalysts for MOR and ORR [10]. On the other hand, GDL, which is placed in intimate contact with the catalyst layer, works to conduct electrons from the catalyst layer to the current collector, as well as a supportive or protective layer for the catalyst by offering suitable mechanical strength [11]. Typically, GDL is made to establish necessary hydrophobic characteristics for carbon dioxide to escape from the anode and to retain water within PEM, preventing it from drying up [9].

PEM is an ion-exchange membrane with a fixed charge; it is responsible for transporting oppositely charged ions from anode to cathode during electrochemical reactions. With that said, a cation exchange membrane is composed of a negatively charged group with a free proton ion and serves as a cation carrier and a barrier to anion [12]. Thus, in DMFC, PEM is also known as the proton exchange membrane, as it is used to transport protons from anode to cathode. Apart from its function as a proton transporter, the PEM provides a barrier for methanol fuel and electrons, enabling current to flow in the external circuit. As a result, PEM has crucial effects on the efficiency and performance of DMFC.

Nafion, also known as perfluorinated sulfonic acid (PFSA) membrane, was developed by DuPont and is currently the most widely used and accepted PEM. It consists of a hydrophobic polytetrafluoroethylene (PTFE) backbone and a hydrophilic perfluorinated vinyl ether pendant side chain that is ionically bonded to a sulfonic acid group ($-SO_3H$) [13]. The negatively charged group (SO_3^-) of Nafion will block anions but enable cations to pass through. This ionic hydrophilic group also takes up water to keep the membrane hydrated, which assists in proton migration. When water is absorbed by the sulfonic acid groups, the hydrophilic ion-cluster domains and water bridges are formed to act as proton migration channels, enhancing the proton transfer [14]. The proton conductivity of the Nafion membrane can approach 0.1 s/cm when fully hydrated and at room temperature [15]. As for the PTFE backbone, it consists of high electronegativity small-sized fluoride atoms connected by a strong C-F bond, which contributes to the suitable mechanical properties of Nafion in a water-swollen state and its chemical stability [1][16]. As a result, Nafion may function in a fuel cell for more than 60,000 h, providing an outstanding lifespan for Nafion [17].

Given the vital significance of PEM in DMFC, discovering and developing suitable PEMs is a critical aspect of DMFC commercialization. To date, numerous review articles [1][13][18][19] have been published that outline the various types of membranes developed for use in PEMFCs. However, discussions of developing PEM, particularly for DMFC, have not been widely published thus far. With the increased attention and tremendous advancement that DMFC has seen in the last several years, a comprehensive and up-to-date review of the Nafion membrane, which is the most often used in DMFC, is important.

2. Functional Requirements

DMFC has been extensively examined and tested with various membranes. These membranes were designed to fulfill multiple functions at the same time. Hence, this section focuses on the functional needs of membranes that can be used in DMFCs.

2.1. High Proton Conductivity

A membrane with excellent proton conductivity can prevent ohmic loss and promote mass transport of protons, which is advantageous for supporting high current densities. For DMFC operation, the proton generated from the methanol oxidation at the anode should be able to migrate effectively through the membrane. The proton-conducting functionalities such as sulfonic acid ($-SO_3H$), phosphonic acid ($–PO_3H$), carboxylic acid (–COOH), or amine ($–NH_2$) within the polymer chains are responsible for the formation of ionic clusters for proton migration by forming bonds with the hydronium ion, to which the proton is provisionally attached [20]. Therefore, a high density of proton-conducting groups ($–SO_3^-$, $–PO_3^-$, $–COO^-$, or $–NH_2$) will facilitate proton transportation. Solid acids such as heteropolyacids (HPA), including phosphotungstic acid (PWA) and silicotungstic acid (SiWA), zirconium phosphate (ZrP), or cesium salts of HPA, have been reported to enhance proton conductivity by increasing the concentration of acid functional groups [19]. External factors, for instance, operating temperature and relative humidity (RH), may also have a plausible effect on proton conductivity. The conductivity of the proton was shown to increase with temperature [21]. Water content in the membrane also contributes to proton conductivity, as water forms swollen and connected ionic clusters that allow proton hopping and diffusion. However, the humidity of PEM is temperature-dependent. Under high-temperature operating conditions, the membrane may dehydrate. Thus, numerous approaches have been explored to improve the water retention capacity of membranes for use at high temperatures, including the addition of amphiphilic and hydrophilic fillers to membranes, such as silica and poly (vinyl alcohol) [22][23]. Additionally, the structure of PEM, such as ionic cluster size, the density of acidic functionalities, the tortuosity, as well as the interaction between the filler and polymer, all will influence the proton conductivity.

2.2. Low Methanol Permeability

Another important property of a membrane suitable for use in DMFCs is its suitable resistance to methanol. Methanol diffuses concurrently with protons by means of a bulk transport mechanism that uses free water molecules as transport agents inside the polymer matrix. According to Ahmad et al., the crossing of methanol from anode to cathode in Nafion wastes over 40% of the methanol fuel in DMFC. Methanol crossover also has a detrimental effect on the performance and durability of DMFC [24]. It leads to a reduction in fuel efficiency and open-circuit voltage, as well as poisoning the electrode due to direct oxidation of methanol at the cathode [6][25]. Therefore, extremely low methanol permeability is necessary to maximize fuel consumption and coulombic efficiency. According to reports, methanol permeability increases with temperature and is concentration-dependent [26]. The permeability of methanol also depends on the current density. Methanol crossover rate decreases as current density increases, as more methanol is consumed at high current density, reducing the concentration gradient in the system. Additionally, the alignment, orientation, and local packing density of the membrane matrix all affect methanol permeability, as reported by [27].

2.3. High Electrical Resistivity

PEMs for DMFCs should be capable of rejecting electron transport and driving them to an external circuit for electricity generation. For every proton that is transferred via the electrolyte, an equal amount of electrons must be transported through the external circuit, where they combine at the cathode to form water.

2.4. Suitable Chemical Stability

Chemical stability is also important for a PEM in DMFCs to be widely used and commercialized. The chemical durability of the membrane is a factor that affects the lifetime of fuel cells. In the operation of a fuel cell, the membrane will be subjected to a chemically oxidizing environment on the anode side and a chemically reducing environment on the cathode side. At the cathode, hydrogen peroxide is formed when oxygen is reduced through the two-electron pathway [28]. When hydrogen peroxide decomposes and reacts with metal ions (e.g., Fe^{2+}, Cu^{2+}, and Cr^{3+}) formed during the degradation of other components in the fuel cell (e.g., bipolar plate and sealing materials), intermediate products, such as hydroxyl radicals with strong oxidative characteristics are produced [29]. These radicals attack the polymer chain, causing defragmentation, unzipping, and thinning of the membrane [30][31]. Therefore, a stable membrane is required in DMFC to resist the chemical degradation caused by free radicals. The indirect approach to minimizing the effect of reactive radicals is to improve the membrane stability through the synthesis of short side-chain polymers or modification of hydrocarbon polymer electrolytes. While some publications also reported direct methods for mitigating free radical degradation, such as preventing the formation of hydrogen peroxide, destroying hydrogen peroxide, or incorporating free radical scavengers to suppress their reactivity and capture reactive oxygen radicals before they attack the membrane [16][30]. Cerium oxide, a metal oxide with valence electrons, is one of the materials used as a free radical scavenger in PEM.

2.5. Suitable Mechanical Stability

Mechanical strength is critical as it is closely related to the methanol crossover phenomenon, which affects DMFC performance. During fuel cell operation, the membrane undergoes dimensional changes due to the repeated swelling and shrinking processes [32]. The non-uniformly stress and compression exerted on the membrane lead to the formation of cracks and pinholes that have the potential to propagate widely across the membrane. Additionally, the presence of radicals arises from the decomposition reaction of hydrogen peroxide, resulting in the formation of local defects that speeds up mechanical damage to the membrane [30]. All these defects will further worsen methanol crossover issues. Therefore, a membrane with high flexibility and low rigidity is preferred to sustain mechanical stresses and prevent the membrane from breaking or perforating. Carbon nanomaterials are a type of filler material that has been used as reinforcing agents in polymer membranes due to their high mechanical stability. A packed structure is created within the polymer matrix, allowing it to withstand fatigue stress [33].

All of the above functional requirements have a big impact on the performance of the membrane and the whole DMFC system. Despite substantial research into alternative membrane materials that meet the requirements, Nafion remains the most widely used commercial membrane in DMFC. As such, this entry focuses on modifications to the Nafion membrane that improve its proton conductivity, methanol-blocking capability, and mechanical and chemical stability.

3. Proton Transport Mechanism in Nafion

Proton transportation across PEM is mainly carried out through surface diffusion, Grotthuss mechanism (hopping), or vehicular mechanism (diffusion) [34]. At the interface of a water-filled channel or pore wall, proton transfer occurs via surface diffusion, in which the proton hops between the adjacent sulfonic acid groups. In the context of the Grotthuss mechanism, protons jump in the percolation network formed by water molecules within the swollen hydrated ionic cluster [35]. Protons attached to sulfonic acid groups will provisionally bind to water molecules in the hydronium (H_3O^+) form. The protons are then transferred by breaking the hydrogen bond with one water molecule and forming a new hydrogen bond with another water molecule nearby [16][34]. Each water molecule works simultaneously to bond a free proton and release another in this process. Thus, increasing the water content within PEM facilitates Grotthuss proton transportation since protons can be transported faster to a closer water molecule [12]. On the other hand, vehicular diffusion, in which proton migrates together with a water molecule in the form of hydronium ion (H_3O^+), Zundel ($H_5O_2^+$), or Eigen ($H_9O_4^+$) is driven by the concentration gradient and electroosmosis drag [16][36]. In other words, protons diffuse across the membrane, with water molecules acting as the “vehicle”. Apart from that, the free volume within the polymer chains is also essential to the functioning of the vehicular mechanism.

Proton transportation, according to both Grotthuss and vehicular mechanisms, is highly dependent on the level of hydration, as water molecules participate in proton transport. However, membranes lose water at temperatures lower than 0 °C or higher than 100 °C [35]. At low degrees of hydration, the diffusion of water molecules is retarded, and connectivity between water molecules becomes poor, resulting in a low interaction of protons with the immobile sulfonic acid group [19][37]. Surface diffusion, in turn, dominates when there is insufficient water, as protons can only be transported by forming hydrogen bonds with sulfonic acid groups [11]. All in all, the proton conductivity depends on all three transport mechanisms, which are affected by the operating temperature, water content, and the inherent properties of the membrane.

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