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Progress in Self-humidifying Technology of Proton Exchange Membrane Fuel Cells: A Comprehensive Review of Multi-scale Structure Design and Material Modification

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ABSTRACT

The performance and lifetime of proton exchange membrane fuel cells (PEMFC) are highly dependent on the wetting state of the membrane, and the phenomenon of "membrane drying" can lead to serious problems such as decreased proton conductivity, increased heat production and even membrane tearing. In order to reduce the dependence on external humidification system, self-humidification technology at the battery level has become a research hotspot in recent years. This paper systematically reviews the methods of self-humidification by adjusting the structure of internal components (flow field, membrane, catalytic layer, gas diffusion layer) and material modification, including the key progress in the past five years. The results show that the water distribution uniformity can be significantly improved by optimizing the flow field design (such as bionic flow field and porous metal foam flow field). The introduction of inorganic/organic additives (such as CeO_2, MOF) or the use of bipolar membrane design can effectively improve water retention and proton conductivity; The functional modification of the catalytic layer and gas diffusion layer (such as oxide load and gradient pore structure) further enhances the operating stability under low humidity conditions. Although self-humidifying technology has advantages in reducing system volume and cost, it still faces challenges such as material compatibility, long-term durability, and inadequate water management for high current density. Future research should focus on multi-scale collaborative optimization, the development of new materials and the performance verification under actual working conditions to promote the wide application of PEMFC in portable devices and new energy vehicles.

KEYWORDS

PEMFC; Water Management; Humidification; Self-humidification.

1. INTRODUCTION

Fuel cells as an efficient and environmentally friendly energy source, have gained widespread attention. They are chemical devices that directly convert the chemical energy of fuel into electrical energy. Since fuel cell convert the Gibbs free energy portion of the fuel's chemical energy into electrical energy through electrochemical reactions, they achieve high conversion efficiency. Fuel cell can be classified based on the type of electrolyte and operating temperature. Low-temperature fuel cell include alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), and proton exchange membrane fuel cell (PEMFC). High-temperature fuel cell include solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) [1]. PEMFC are widely regarded as the most promising type of fuel cell due to their advantages, such as low-temperature operation, high specific energy, short startup time, strong load-following capability, wide range of applications, and high efficiency [1-3].

They are primarily used in distributed power generation, portable power supplies, and new energy vehicles.

As shown in Fig. 1, the stable operation of a PEMFC typically requires the coordination of various systems, including water management, thermal management, power generation, control, electrical, fuel supply, and oxidant supply systems. The purpose of the water management system is to maximize the fuel cell's efficiency through effective water management while ensuring long-term stable operation. During the operation of PEMFC, water is continuously produced. It can exist within the fuel cell in the form of gaseous water, liquid water, and membrane-bound water. Membrane-bound water is usually present in the electrolyte, keeping the electrolyte membrane hydrated. The membrane exhibits high proton conductivity when hydrated, which enhances the performance of the fuel cell. However, excessive water content within the cell can lead to flooding issues [4]. Flooding in the gas diffusion layer and flow field obstructs the transport of gas reactants to the reaction sites, and the catalytic surface area is reduced due to water coverage. This significantly increases PEMFC activation losses and concentration losses, potentially leading to shutdowns. On the other hand, insufficient water content can cause membrane drying issues. Membrane drying increases resistivity, leading to greater heat generation during PEMFC operation, which further decreases energy conversion efficiency and exacerbates membrane drying issues, potentially even causing membrane tearing, thereby severely affecting output performance and remaining lifespan [5].

Therefore, proper humidification is very important in the operation of PEMFC. In order to realize the humidification of PEMFC, people put forward different humidification methods, this paper mainly describes the self-humidification level of the battery level. This paper mainly summarizes the humidification methods and technologies of PEMFC published in recent 5 years, including their principles, advantages and disadvantages and practical applications. At the same time, it provides effective guidance for humidity management of fuel cells, and promotes its optimization and development in different application scenarios. In the future, researchers can identify key challenges that need to be addressed to guide further innovation and optimization efforts.

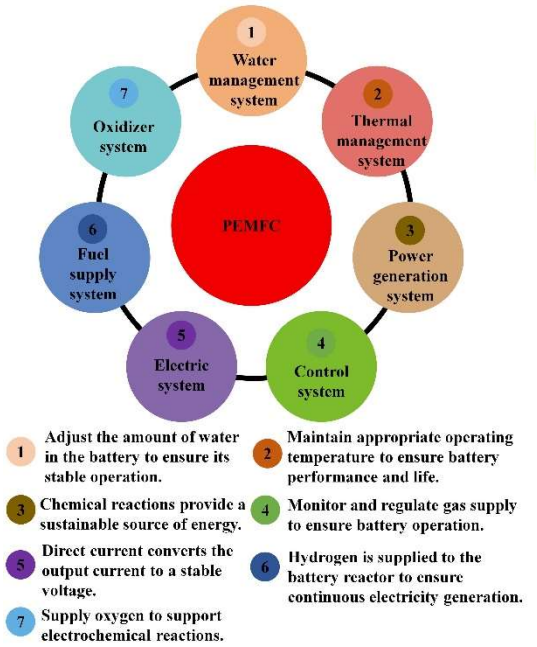

Fig. 1. Composition of PEMFC system;

Self-humidification at the battery level is to change the system structure (flow field, membrane, CL, GDL) without obtaining water from the outside world, such as designing a new flow field structure, adding various additives to the membrane components, etc. The structure of PEMFC is shown in Figure 2. PEMFC is mainly composed of a membrane electrode (MEA), including a proton exchange membrane (PEM) in the middle, a catalyst layer (CL) and a gas diffusion layer (GDL) on both sides. Fuel cell humidification mainly by changing its internal component structure or composition to achieve its own water regulation, this method does not require external humidification is also known as self-humidification. In order to be consistent with the literature, this paper refers to battery level humidification as "self-humidification". According to the changed components, self-humidification is divided into flow field, membrane, catalytic layer (CL) and gas diffusion layer (GDL).

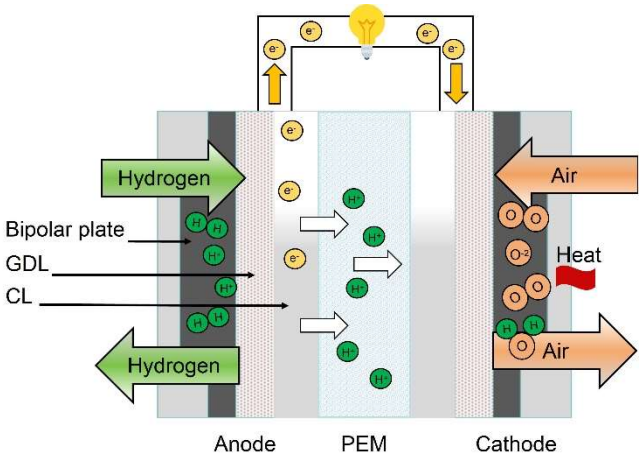

Fig. 2. PEMFC structure diagram.

2. CHANGE THE FLOW FIELD STRUCTURE

The optimization of the flow field is mainly aimed at the uneven distribution of the generated water in the electrode, some areas (such as the area near the flow field outlet) may be flooded, while other parts (such as the area near the flow field entrance) may be in a dry state. Self-humidification is realized by optimizing the flow field and redistributing the water generated by the electrochemical reaction.

2.1. Flow Field Distribution

In research on flow field configurations, co-flow setups often lead to lower moisture levels near the air inlet, whereas counter-flow configurations can avoid this problem. In counter-flow configurations, the membrane near the gas inlet is humidified by hydrogen gas containing all the water expelled from the anode. Wang et al. [7] demonstrated that counter-flow configurations could significantly increase current density by 21.21% compared to co-flow setups. Although counter-flow configurations enhance inlet air humidity, they can also cause flooding at the inlet if it is already adequately humidified. Tong et al. [8] designed a cross-flow field and analyzed its water-thermal distribution and performance at various locations. They found that the water distribution in the cross-flow channels was more uniform, preventing membrane drying within the PEMFC. Wang et al. [9] further indicated that the cross-flow channel configuration not only enhanced the uniformity of water distribution but also increased water concentration, enabling self-humidification under appropriate conditions.

In terms of flow field shape, the geometric parameters of the flow field significantly affect the water accumulation process. Improving the flow field shape can lead to better water distribution. The most

commonly used traditional flow fields in PEMFC are parallel flow fields, serpentine flow fields [10], and wavy flow fields [11-13]. These channel designs are simple and easy to manufacture, but there is still much room for improvement in gas uniformity, pressure drop, and water management. Recently, biomimetic flow fields have received widespread attention. Trogadas et al. [14] inspired by the lungs, designed biomimetic flow fields with different branching patterns to achieve more uniform reactant distribution and minimize entropy generation in the system. Under conditions of 50% RH and a current density above 0.8 A/cm², these fields show a 20% improvement in performance compared to serpentine flow fields. Xie et al. [15] inspired by spider webs, proposed a novel spider web-type flow field and compared it with the serpentine flow field. The polygonal structure and multi-layered spiral design of this flow field increase the rib and total flow field area, resulting in more uniform water distribution. With similar voltage and current density to the serpentine flow field, the pressure drop in these fields is half that of the serpentine flow field. Additionally, there are snowflake-shaped flow fields [16] and leaf-shaped flow fields [17], which have advantages in water retention at low humidity and water removal at high humidity due to their complex structures. However, these biomimetic flow fields mainly address issues related to reactant distribution and excessive pressure drop in traditional designs, so this paper will not discuss them in further detail.

Inspired by the mixed wettability surface of desert beetles, Zhao et al. [18] designed a bio-inspired multifunctional surface (BMS) within the flow field, consisting of superhydrophobic coatings and superhydrophobic grooves. Under low current and low humidity conditions, the superhydrophobic grooves mitigated the increase in internal resistance caused by membrane drying. Under high current and high humidity conditions, the superhydrophobic coating reduced voltage fluctuations and pressure drops caused by flooding. Due to the dual function of BMS, the peak power density of the cell was 26.3% higher than that of a conventional cell, providing a new approach based on mixed wettability methods.

Adding various shapes of baffles in the channels can enhance the diffusion of fuel gases, water management, and the uniformity of temperature distribution in fuel cell [19-21]. Recently, Yang et al. [22] proposed an improved method based on the concept of longitudinal vortex-enhanced heat and mass transfer by adding rectangular plates in the serpentine channels of the cathode. This rectangular plate method generates longitudinal vortices, allowing more fuel gas to be transported from the channel to the gas diffusion layer, improving the uniformity of water distribution by 10.87%. Increasing pressure or decreasing temperature and relative humidity can enhance the fuel cell's power density. Additionally, various designs such as flow field distributors, auxiliary flow fields, and trap flow fields have been explored [23-28]. These innovative flow fields, along with various baffle and trap structures, contribute to better water management. However, at higher temperatures, sulfonic acid groups can easily lose water, making self-humidification challenging. While these designs can mitigate the negative effects of backpressure compensation temperature, achieving self-humidification and high performance under various operating conditions may require the integration of other methods.

2.2. Use of New Porous Flow Fields

Besides modifying flow field distribution, porous metal foams (PMF) are valued for their lightweight, high strength, and good rigidity. Consequently, PMFs are considered ideal media for heat transfer or thermal management in the new energy sector [29]. Murphy et al. [30] were the first to use two types of flat porous metal foams-nickel and expanded titanium-as flow fields embedded in anodes and cathodes. The high porosity of metal flow fields [31] improves the uniformity of temperature and humidity within the fluid. Furthermore, PMF's large contact area and small ribs enhance mass transfer and reduce ohmic resistance, thereby improving PEMFC performance and achieving higher power density at lower costs [32]. This optimized foam flow field has demonstrated the highest performance reported to date. Ahn et al. [33] compared the performance of PEMFC with copper foam and serpentine flow field bipolar plates. The results showed that PMF flow fields exhibited about a 7%

higher current density under pressurized and low humidity conditions compared to serpentine flow fields. As shown in Fig. 3b, Wu et al. [34] used neutron radiography to study the characterization of water molecules in PMF, finding that fuel cell with PMF achieved a voltage increase of about 50% compared to those with serpentine flow field designs. This is attributed to the water being "stored" in the pores of the metal foam, leading to better humidification.

Porous flow fields offer better removal of anode water and utilization of cathode water compared to conventional flow fields, and they help avoid complete blockage of the flow field, reducing water accumulation [35]. This results in improved membrane hydration. Zhang et al. [36] investigated the dynamics of droplet behavior in different channel sizes within porous flow fields and their impact on PEMFC performance. They found that PEMFC with porous flow fields could achieve optimal performance even without air humidification. Subsequently, Lian et al. [37] introduced a novel porous flow field on the cathode side, which utilizes metal fibers to create a continuous capillary channel network, as shown in Fig. 3c. Their experimental results demonstrated that, under low humidity conditions, the fiber flow field exhibited the best performance at 50°C. Additionally, increasing backpressure significantly improved the fuel cell's performance. They further optimized the structure [38], leading to a 15.21% increase in peak power density and average output current of the fiber porous self-expanding flow field. However, the dense and unorganized structure of this porous flow field caused substantial pressure loss and could potentially result in severe water retention within the porous flow field.

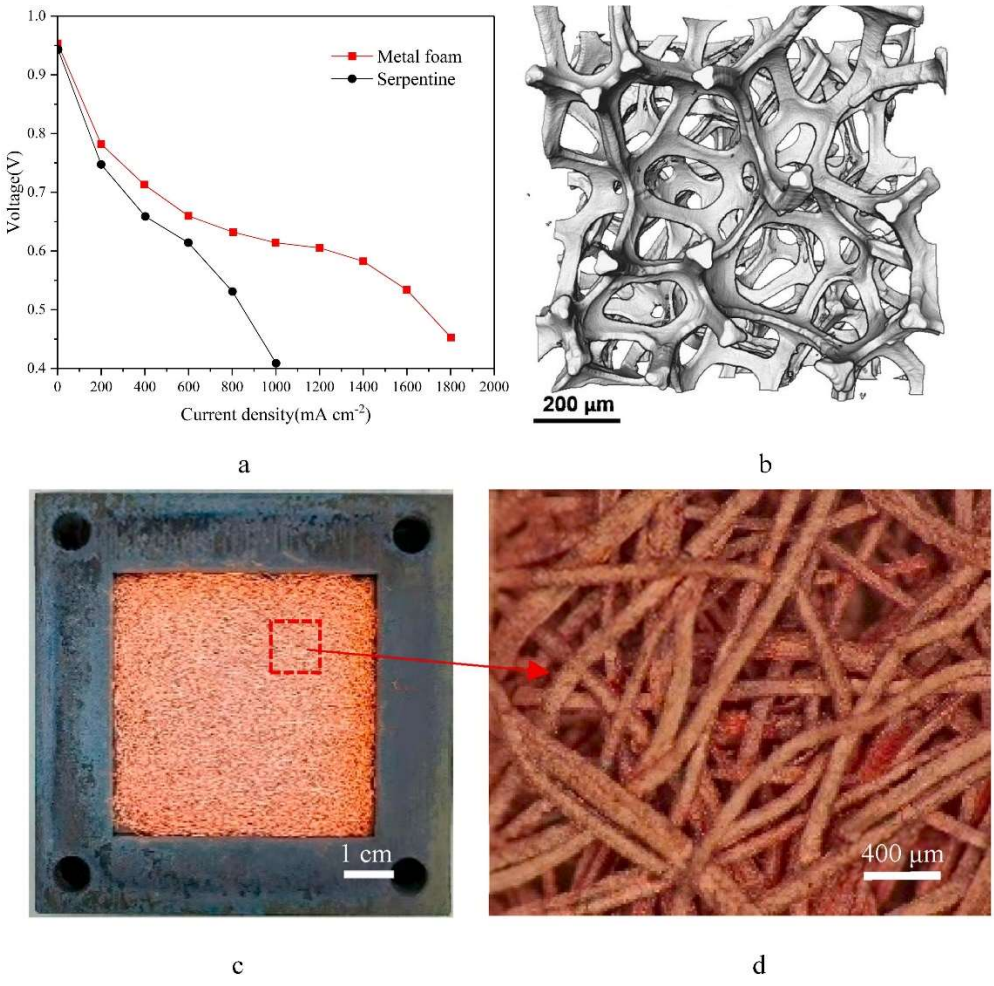

Fig. 3. a. Polarization curves for metal foam flow-field and conventional serpentine flow-field; b. SEM micrograph of the compressed metal foam [34]; c. Sintering mold; d. Porous Copper Fiber Sintered Sheet (PCFSS) [37].

3. CHANGE THE MEMBRANE STRUCTURE

To achieve self-humidification, various modification techniques are used to enhance membranes, allowing them to generate and retain water under dry conditions and improve proton conductivity. Key methods include adding various additives to the membrane and surface modification.

3.1. Membrane Composition

This section divides membrane additives into inorganic and organic materials.

3.1.1. Inorganic Material Fillers

The concept of "self-humidifying PEM" was first proposed by Watanabe et al. [39], who added moisture-retaining silica or titanium dioxide to Nafion solutions to create self-humidifying PEM membranes. These inorganic fillers form a dynamic hydrogen-bond network within the composite membrane, allowing it to store water and retain water that diffuses back, exhibiting lower ohmic resistance under high loads. Other common inorganic oxide fillers include zirconia (ZrO_2) [40], alumina (Al_2O_3), and tungsten trioxide (WO_3) [41]. However, these hygroscopic fillers do not have proton conductivity, and weak interactions between these fillers and Nafion can reduce filler dispersion, potentially decreasing the mechanical strength of the PEM. Cerium dioxide (CeO_2) has gained widespread attention due to its excellent moisture-retaining properties and antioxidant capabilities, which help mitigate the chemical degradation of PEM. Recently, Choi et al. [42] introduced dendritic CeO_2 into membranes, finding that CeO_2 nanoparticles enhanced the membrane's moisture retention under low humidity conditions, thereby improving membrane performance. Ce elements effectively scavenge free radicals, enhancing PEMFC durability and minimizing reductions in membrane ionic conductivity. Vinothkannan et al. [43] first aminated carbon nanotubes (CNT) with 3-Aminopropyltriethoxysilane (APTES) to obtain ACNT, then synthesized a dual-functional filler CeO_2-ACNT using cerium nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$] and sodium hydroxide (NaOH). This filler was incorporated into Nafion membranes using a solution casting method. The presence of ACNT improved Nafion's mechanical strength and proton conductivity, while CeO_2 helped alleviate Nafion membrane chemical degradation. The proton conductivity under 20% low humidity reached 12.2 mS cm^{-1}, which is five times that of conventional membranes.

To prevent chemical degradation of the PEMFC and achieve performance under low humidity conditions, You et al. [44] mixed trivalent metal oxide lanthanum titanate (LTO) with Nafion to create porous lanthanum titanate nanostructured membranes and studied the effects of different structures (cubic, spherical, and tubular) on the membrane. Lanthanum exhibits excellent physicochemical properties and high surface hydroxyl affinity. The tubular morphology of LTO-T facilitates water diffusion from the cathode to the anode through the Nafion/LTOT membrane. Enhanced moisture retention due to LTO-T's porous surface and the creation of proton conduction pathways allowed the cell to achieve a power density of 504 mW cm^{-1} at 80°C and 30% RH. Wang et al. [45] prepared a novel bionic Nafion (Bio-Nafion) membrane by electrospinning bio-functional silica (Bio-SiO_2) nanofibers and Nafion matrix. The presence of different polar groups from amino acids improved Nafion's thermal stability, water absorption, dimensional stability, and proton conductivity. This method also provides a new direction for expanding the use of inorganic material fillers.

In summary, inorganic material fillers are widely used in membrane modification. Besides hygroscopic inorganic oxides, materials such as zeolites [46] and clays [47, 48], known for their excellent moisture retention properties, can also serve as additives in self-humidifying membranes. Additionally, various inorganic acids like zirconium phosphate [49], phosphotungstic acid [50], copper phthalocyanine tetrasulfonic acid tetrasodium salt [51], and phytic acid [52] are utilized. Carbon nanomaterials such as carbon nanotubes (CNT) [53], graphene oxide (GO) [54], and carbon nanofibers (CNF) [55] are also employed.

However, many of these inorganic materials face limitations in practical applications due to issues such as incompatibility with the membrane, lack of electrical conductivity, and inability to prevent chemical degradation of Nafion membranes caused by free radical attacks generated by the PEMFC.

3.1.2. Organic Material Fillers

Table 1. The advantages of adding different materials to the membrane.

Materials	Advantage	References
SiO_2, TiO_2, Al_2O_3, WO_3	Retain water	[39], [64]/ [65]/ [40]/ [66]/ [41],[67]
CeO_2	Retain water; Antioxidant.	[42], [68]
HfO_2	Retain water; Improve mechanical strength and proton conductivity.	[69]
CeO_2-ACNT	Retain water; Antioxidation; Improve mechanical strength and proton conduction.	[43]
LTO-T	Retain water; Improve proton conductivity and stability.	[44]
Bio-SiO_2	Absorb water; Improve thermal stability, mechanical strength and proton conductivity.	[45]
Zeolite	Absorb water; Improve thermal stability and proton conductivity.	[46], [70]
Clay	Absorb water; Improve thermal stability and mechanical strength.	[47], [48]
Zirconium phosphate	Absorb water; Improve the mechanical strength of the film.	[49], [71]
Phosphotungstic acid	Absorb water; Improve proton conductivity and stability.	[50], [72]
Copper phthalocyanine tetrasodium sulfonate salt	Absorb water; Increase proton conductivity	[51]
Phytic acid	Absorb water; Improve mechanical strength and conductivity.	[52]
CNT	Retain water; Improve mechanical strength and dimensional stability.	[53]
GO	Absorb water.	[54]
MOF organic blend (UiO-66-SO_3H+UiO-66-NH_2)	Retain water, improve proton conductivity and durability.	[62]
MOF organic blend (CS/A+B)	Water retention at high temperatures; Increase proton conductivity.	[63]

Organic material fillers primarily include small organic compounds and organic polymeric materials. The use of organic fillers enhances the beneficial properties of the membrane and offers a convenient, efficient, and cost-effective approach, making them a popular subject of research. Small organic

compounds mainly include covalent organic frameworks (COFs) [56,57] and hydrogen-bonded organic frameworks (HOFs) [58]. Organic polymers include polyvinylidene fluoride (PVDF) [59], polyvinyl alcohol (PVA) [60], and sulfonated poly (arylene ether ketone) (SPAEK) [61]. By combining these organic materials with various moisture-retaining substances, the modified membranes show excellent performance in both proton conductivity and moisture retention.

In recent years, functionalized fiber network scaffolds and metal-organic framework (MOF) have gained attention. The introduction of these scaffolds can direct the rearrangement of hydrophilic and hydrophobic regions and enhance the overall performance as modifiers. The resulting composite proton exchange membranes exhibit strong moisture retention, higher power output, and better durability. Zhuang et al. [62] prepared three types of membranes by incorporating UiO-66-SO_3H, UiO-66-NH_2, and their mixture into Nafion matrices. They found that the water absorption rate followed the order: mixed-doped membranes > single-doped membranes > Nafion membranes. This improvement is due to the synergistic effect of the mixture forming more continuous hydration channels, which facilitates rapid proton transport. The mixed-doped membranes show better performance. Dong et al. [63] incorporated acidic and basic isomorphous MOF into a low-cost chitosan (CS) polymer to create a proton-conducting hybrid membrane (CS/A+B). Due to the synergistic effect between acidic and basic MOF and the CS matrix, the proton conductivity reached 3.78×10^{-3} S cm^{-1} at 120°C under anhydrous conditions. This performance surpasses that of single-component (A, B, and CS) or solely acidic/basic MOF-filled membranes (CS/A and CS/B), potentially advancing the future application of these MOF in fuel cell.

By adding various materials and their mixtures, the membrane's moisture retention, ionic conductivity, porosity, mechanical properties, and thermal strength can be significantly improved. Table 1 lists various organic and inorganic additives and their advantages. Membrane modification provides a promising alternative for membranes or proton exchange membranes in various energy applications.

3.2. Bipolar Membranes (BPM)

Recently, the concept of bipolar membrane (BPM) has garnered significant attention. In BPM design, the membrane comprises two layers: an acidic membrane and a basic membrane. This configuration allows for in-situ water generation, providing a potential solution for passive humidification, and ensuring high ionic conductivity and low ohmic losses. Additionally, the inherent faster kinetics of the alkaline cathode opens up the possibility of using non-precious metal catalysts.

As shown in Fig. 4a, Peng et al. [73] designed a membrane fuel cell with a combination of an anion exchange membrane (AEM) and a proton exchange membrane (PEM). Utilizing the self-humidifying property of BPM, they achieved an output power of 327 mW cm^{-2} under dry air supply conditions at 50°C. They further investigated the BPM's interface model [74], exploring the water formation process and self-humidification mechanism through water flux streamlines. They found that the thickness of the AEM in BPM affects the amount of water needed at the PEM-AEM interface, impacting the effective diffusion of water to both electrodes. Water generated at the BPM interface and diffused to the anode and cathode formed a bell-shaped distribution, with higher moisture content at the interface and decreasing towards the cathode and anode sides.

In Fig. 4b and 4c, Peng et al. [75] studied the water distribution behavior of four different alkaline polymer electrolytes (BPMFC-$QAPSF_{95}$, BPMFC-$QAPSF_{105}$, BPMFC-QAPPB, BPMFC-QAPPT) based on their previous theory. They established a positive correlation between the water diffusion rate (Dw), water distribution, and output current density. The results indicated that increasing the Dw of alkaline polymer electrolytes enhances the amount of water generated at the interface and rapidly transports it to the cathode, thus improving ion conductivity and ORR kinetics. This approach achieved a breakthrough in the peak power density of BPMFC, reaching 1.06 W cm^{-2} without external humidification.

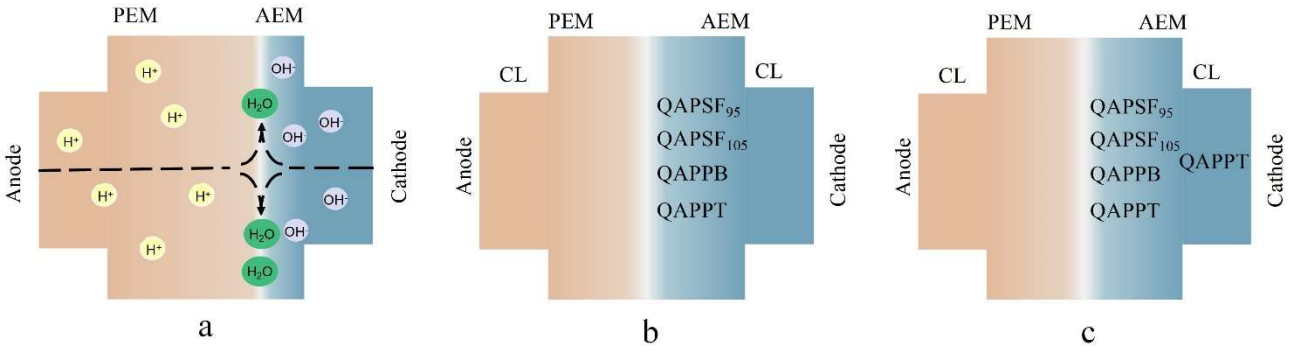

Fig. 4. a. Typical structure and principal mechanism of a BPMFC; b. The MEA of BPFMC with the same alkaline polymer electrolyte as AEM and AEI; c. The MEA of BPFMC with different alkaline polymer electrolytes as AEM and QAPPT as AEI.

For BPMFC, mass transport limitations (MTL) can significantly impact power output. Seeberger et al. [76] studied BPMFC with Fe-N/C cathode catalysts and found that the amount of deposited AEM material directly affects the rate at which water enters the cathode catalyst layer (CCL). Thinner AEM layers exhibit lower fluid transport resistance and better water absorption, resulting in stronger and more stable BPMFC performance, consistent with the findings of Peng et al. [74].

In addition to the BPMFC's inherent structure, the preparation method of the bipolar membrane significantly impacts the performance of the fuel cell. Daud et al. [77] utilized a hot-pressing technique to manufacture BPMFC and analyzed the effects of hot-pressing conditions on BPM adhesion and performance. By employing a numerical optimization method from central composite design (CCD), they determined the optimal hot-pressing conditions for BPM layers, achieving excellent power density, low fuel permeation, effective self-humidification, and outstanding durability with $_{S}$PEEK/PES$_5$-cQAPEEK$_{72h}$.

While this BPM design can achieve self-humidification and provides significant insights for achieving high power without external humidification, there are risks associated with BPM, such as the potential for delamination under high current densities. Additionally, beyond preventing delamination, degradation, and ion leakage, BPM must incorporate measures to reduce ohmic losses. Although reducing the membrane thickness is an effective strategy, insufficient membrane strength can lead to hydrogen and oxygen leakage. Furthermore, most middle-layer catalysts are suited for reverse bias and lack research on how to accelerate the formation of hydrogen and hydroxide ions at the kinetic level.

4. CATALYST LAYER (CL)

In the CL of PEMFC, ionomers serve as adhesives and conduction media for protons traveling from the reaction sites to the membrane. Under dry conditions, not only does membrane dehydration occur, but ionomer binders in the CL can also lose water at high temperatures, increasing proton conduction resistance. To address this, the concept of adding moisture-retaining materials to the CL to achieve self-humidification and maintain high proton conductivity under high-temperature operating conditions has been explored. Aristatil Ganesan et al. [78] synthesized platinum (Pt) supported on manganese oxide (MnO_x) catalysts and studied their self-humidification performance in PEMFC. The results showed that hydroxyl groups formed on MnO_x facilitated proton and electron transfer. The flower-like morphology of MnO_x exhibited dual functionality: it absorbed more water and improved the back-diffusion of water from the cathode to the anode. This increased the electrochemical stability of the fuel cell, achieving a peak power density of 0.65 W cm² under dry conditions. Angayarkanni et al. [79] applied a silica (SiO_2) composite layer onto Pt/C catalyst layers, resulting in a membrane

electrode assembly (MEA) with an impressive power density of 0.9 W cm² under dry gas conditions. Involves the hydrophilic nature of SiO_2 particles enhancing the water absorption capacity of the composite layer, aiding proton hydration, and facilitating water transfer from the Pt surface to the adjacent membrane electrolyte. They found that performance remained consistent in both dry and humid conditions, indicating that the SiO_2 composite layer did not adversely affect H_2 oxidation reactions. Dhanasekaran et al. [80] developed an optimal level of silica-decorated carbon as an alternative and highly stable support for platinum catalysts through a one-pot synthesis method. The results showed that this silica could retain water at the triple-phase boundary of a single cell, maintaining stable operation for 200 hours without external humidification. This demonstrated the excellent moisture-retaining properties of the composite catalyst and the overall performance and stability of the fuel cell stack.

These advancements in CL materials contribute to the development of PEMFC with enhanced self-humidification capabilities and improved performance under varying operational conditions.

Although adding these water-retaining oxides can achieve self-humidification, they do not have electron or proton transfer capabilities, which can lead to higher cell resistance. Additionally, these hydrophilic oxides have poor compatibility with Nafion ionomers, which may worsen the interface contact between the Nafion membrane and CL. Also, since these oxide particles are not fixed or bonded in the CL, they can easily aggregate or be lost.

Therefore, Su et al. [81] proposed using a Schiff base network (SNW) covalent organic framework (COF) loaded with phosphoric acid (PA) as an additive for the anode catalyst layer (CL). The unique polymer structure and immobilized PA of the COF network not only provide excellent water-retaining capabilities but also offer good proton transfer abilities. Under operating conditions of 60°C and 38% RH, the optimized COF-containing MEA achieves a maximum power density seven times that of conventional MEA.

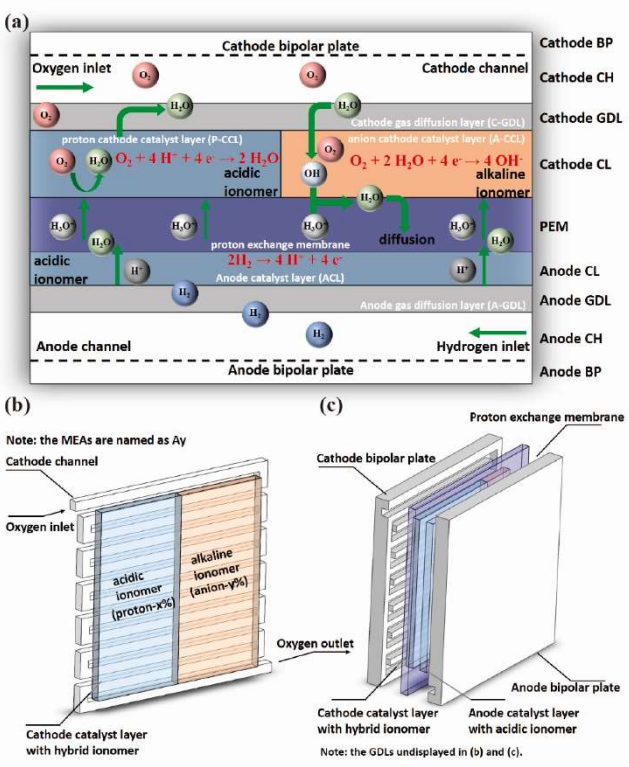

Fig. 5. a. Schematic diagram of the reactions based on an acid-alkaline patterned cathode catalyst layer; b. The relative position of the cathode catalyst layer and the flow channel; c. The hybrid cathode catalyst layer membrane electrode assembly in a single cell [83].

Subsequently, their team [82] investigated the optimal COF content in the CL, the effects of anode/cathode modification on performance, and the operating temperature of the PEMFC through electrochemical characterization and single-cell tests. The results showed that the optimal performance is achieved with 15 wt.% COF in the anode, reaching a power density of 690 mW cm^{-2} under dry conditions, which is nine times that of traditional MEA. Moreover, their 36-hour stability tests confirmed the practical reliability of this method in low-humidity environments, making COF a promising alternative for developing self-humidifying PEMFC.

In addition, Qiao et al. [83] recently proposed an acid-base mixed cathode method. As shown in Fig. 5, patterned acid-base catalyst layers are used for the cathode. The water produced by the acidic catalyst layer can quickly participate in reactions within the alkaline catalyst layer of the cathode, leading to a significant improvement in fuel cell performance under low humidity conditions. They reported that when the alkaline catalyst layer is patterned in the center of the cathode and constitutes 25% of the area, the peak power density (PPD) of the resulting fuel cell reaches 1.02 W cm^{-2} at 10% relative humidity, which is a 31.72% increase compared to cells without an alkaline catalyst layer. This approach provides a new perspective for self-assembling MEA and achieving low-humidity MEA, greatly advancing the development and application of fuel cell.

5. GAS DIFFUSION LAYER (GDL)

Similar to the principle of self-humidifying membranes, GDL self-humidification can be achieved through two main strategies: adding moisture-retaining materials to the GDL or altering the GDL structure.

5.1. Adding Moisture-Retaining Materials

In addition to traditional moisture-retaining materials like TiO_2 and SiO_2, some new oxide moisture-retaining materials have been explored. Ganesan et al. [78] prepared high-surface-area nanostructured manganese oxides (Mn_xO_x) clusters and electrodeposited platinum nanoparticles onto GDLs with Mn_xO_x layers. Due to the self-humidifying and durable properties of Pt/Mn_xO_x, the fuel cell achieved a peak power density of 650 mW cm^{-2} at 0.48V under dry air conditions and maintained a stable output for 150 hours at 0.8 A cm^{-2}.

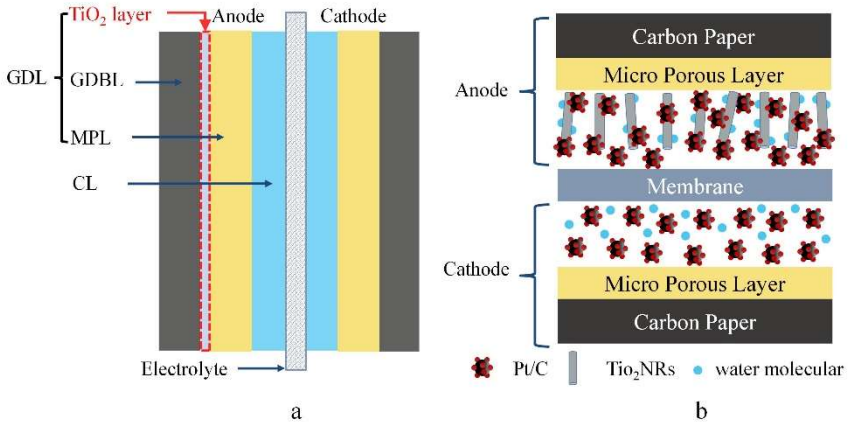

Fig. 6. a. Single crystal rutile titanium dioxide nanoarray (TiO2NRS) structure [84]; b. MEA structure with TiO_2 layer [85].

Additionally, special structures of metal oxides have gained attention. For example, titanium dioxide nanorod arrays (TiO_2NR_S) represent a form of TiO_2 that ensures uniform distribution and prevents

particle aggregation. This structure also helps retain water from the cathode's reverse diffusion, maintaining optimal water and gas transport pathways, and is widely used in catalyst layers. Recently, Wang et al. [84] uniformly grown single-crystal rutile-type titanium dioxide nanorod arrays (TiO_2NR_S) on GDL using a seed coating hydrothermal method, as shown in Fig. 6a. They investigated the impact of TiO_2 nanorods on MEA wettability, wear resistance, performance, and stability, and optimized its loading capacity. The results showed that due to the unique moisture-retaining ability of TiO_2NRs, a peak power density of 689.36 mW cm^{-2} was achieved under 21% relative humidity, which is comparable to performance at 100% RH.

5.2. Modifying GDL Structure

In addition to adding moisture-retaining materials, altering the structure of the GDL can also achieve self-humidification.

One approach is designing GDL interlayers. Hou et al. [85] developed a novel GDL with a hydrophilic TiO_2 layer coated on the gas diffusion backing layer (GDBL) using a hydrothermal method, as shown in Fig. 6b. The TiO_2 interlayer promotes hydration and reverse diffusion, achieving a current density of 1190 mA cm^{-2} at 12% RH and 65°C. This demonstrates the feasibility of using a mini-humidifier-like interlayer to create self-humidifying GDLs.

Single-walled carbon nanotubes (SWCNTs) have good wettability and pore structure, making them suitable as a water-storage layer to maintain PEM hydration. Zhang et al. [86] successfully prepared self-humidifying GDLs by controllably inserting SWCNT layers between hydrophobic MPL and GDS. They achieved a current density of 0.690 mA cm-2 at 26% RH, about four times higher than conventional MEA. Yin et al. [87] applied a buffer microporous layer (BMPL) with a structure similar to the anode catalyst layer onto the GDL. The BMPL's moisture-retention significantly improved water management in the membrane components and also achieved self-humidification.

While these interlayers can absorb and retain water to achieve self-humidification, potential issues include increased mass transport resistance and interlayer blockage at high current densities. Further research is needed to address these challenges for long-term operation and practical applications.

In addition to adding interlayers, Ren et al. [88] developed a reverse-gradient GDL using electrospinning technology, as shown in Fig. 7. This GDL features a gradually decreasing pore size from the catalyst layer to the flow field plate and was tested for breakthrough pressure and water saturation. The results indicate that the reverse-gradient GDL retains moisture better than both the regular gradient and uniform GDL, making it suitable for proton exchange membrane fuel cell under non-humidified conditions. Performance tests also confirmed that the reverse-gradient GDL offers superior moisture retention and higher power density at low humidity conditions. However, this reverse-gradient GDL is only suitable for conditions of 0-12% RH and may lead to "water flooding" issues at medium to high humidity levels.

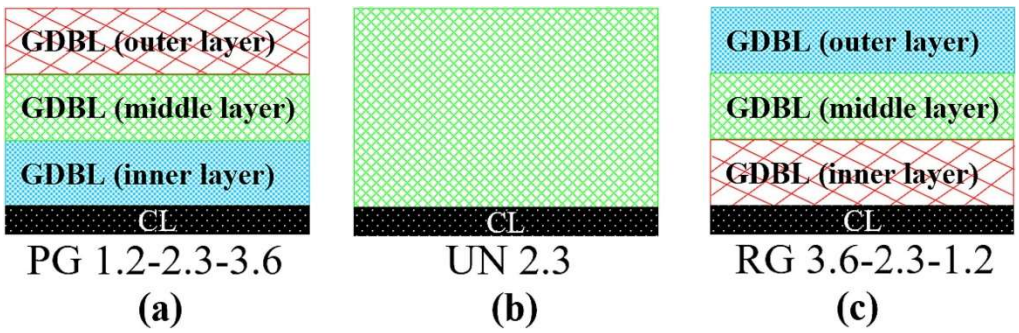

Fig. 7. Schematics of the electrospinning GDL with different pore size gradient structures: (a) PG 1.2–2.3–3.6, (b) UN 2.3, and (c) RG 3.6–2.3–1.2 [88].

6. CONCLUSION

The self-humidifying methods of PEMFC are reviewed in this paper. From the point of view of self-humidification, the self-humidification technology at the battery level does not need to rely on an external water source, but achieves the humidification effect by adjusting the structure of the battery components (flow field, film, CL, GDL). This self-humidifying technology has the advantage of simplifying the size and weight of the system and reducing manufacturing costs, while ensuring that the PEM remains moist while reducing the fuel cell volume and parasitic power. It is very attractive for compact applications such as portable devices, mobile devices and automobiles. Adding various materials to the membrane components can make the membrane components have better water production and water retention performance to achieve self-humidification. Continuous exploration of new materials for membrane modification can meet different needs, which is the most widely concerned technical direction at present and in the future. More reliable materials and more stable membranes are the direction of future exploration and development, and this addition to the membrane.

CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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