



Review

# Proton exchange membrane fuel cell from low temperature to high temperature: Material challenges

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## Abstract

Proton exchange membrane fuel cell (PEMFC) is considered as one promising clean and highly efficient power generation technology in 21st century. Current PEMFC operating at low temperatures (<80 °C) encounters several difficulties, such as CO tolerance, heat rejection, which can be, to a great extent, surmounted at higher temperatures (120–150 °C). However, the higher temperature conditions are much more challenging to implement, particularly with regards to the durability of the cell component materials. This paper overviews the drivers behind the interest in high-temperature PEMFC, and the challenges in developing novel materials to enable high-temperature PEMFC, including cell component durability (catalysts, polymer, bipolar plates, etc.), candidate polyelectrolytes for the electrode catalyst layer, and material compatibility in novel membrane electrode assembly (MEA), and provides an insight into the material research and development for PEMFC.

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**Keywords:** High-temperature proton exchange membrane fuel cell; Electrocatalysts; Polymer electrolyte; Bipolar plates; Durability; Material compatibility

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## 1. Introduction

Fuel cells are of great recent interest in our society today due to their high efficiency and potential for low emissions. Among all the various kinds of fuel cells [1,2], proton exchange membrane fuel cell (PEMFC, see Fig. 1 for general knowledge) is believed to be the most promising for transportation applications because of its fast startup and immediate response to changes in the demand for power and its tolerance to shock and vibration due to plastics materials and an immobilized electrolyte. They have also shown great promise for mobile applications such as portable electronics. In the energy market, the transportation sector is the main oil consumer, for example, in the U.S., transportation consumes about two-thirds of the nation's oil, and this figure is expected to remain essentially constant through 2020 [3]. Many efforts have been devoted into the research and development (R&D) of PEMFC for transportation. In the past decades, great advances have been achieved for PEMFC. The state-of-the-art advances in PEMFC have been described in detail by several recent reviews [4,5], on special topics such as electrodes [6] and catalysts [7–14], membrane [15–20], etc.

Current PEMFCs typically run at  $\leq 80^\circ\text{C}$  because of the working temperature limitation of the polyelectrolyte membrane (usually DuPont's Nafion). The primary reason is that the proton conductivity of Nafion membrane drops off very quickly

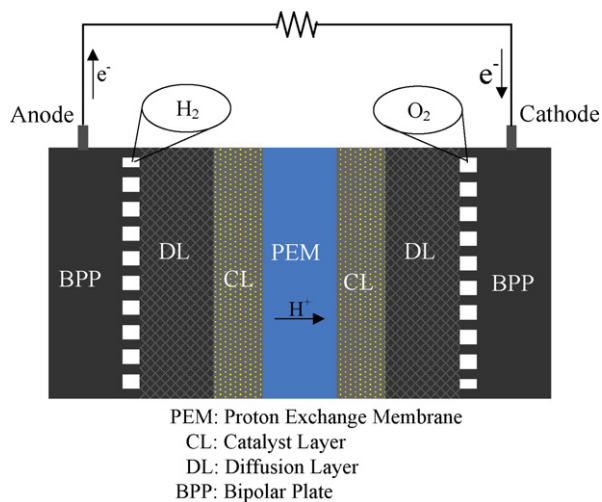


Fig. 1. displays the structure of a PEMFC and how it works. Proton exchange membrane (PEM), sometimes also called polyelectrolyte membrane works as the separator to prevent the reactants ( $\text{H}_2$  and  $\text{O}_2$ ) from mixing, it also transports protons from the anode to the cathode. Catalyst layer (CL) consists of carbon supported platinum or platinum alloy nanocatalysts (Pt/C) and the binder (usually Nafion), the later also works as electrolyte to extend the formation of the electrochemical triple-phase boundary (TPB). Diffusion layer (DL), also called gas diffusion layer, is mainly PTFE-hydrophobized carbon paper or carbon cloth, through which the reactant transport to CL and the product ( $\text{H}_2\text{O}$ ) flows out (at the cathode side). Bipolar plate (BPP) consists of gas-impermeable carbon plate or metal plate coated with protective layer. It works as the current collector. Between the BPP and DL is the so called flow field, which consists of gas channels grooved on the surface of BPP. When PEMFC is running, hydrogen is electrochemically oxidized at the anode, the resultant  $\text{H}^+$  transports across the PEM; oxygen is electrochemically reduced at the cathode, and combined with protons from the anode to form  $\text{H}_2\text{O}$ . Electrons transport through the external circuit, so a close circuit is formed and the electric power is generated.

with relative humidity (RH) decreasing and cannot yield sufficiently high membrane conductivity ( $>0.1 \text{ S cm}^{-1}$ ) without an external humidification subsystem in a fuel cell system at high temperature ( $>80^\circ\text{C}$ ) [21,22]. The membrane will also loss its mechanical and dimensional stability at high temperature due to its low glass transition temperature ( $T_g$ ) ( $80\text{--}120^\circ\text{C}$ ) [15]. Working at low temperatures, i.e.,  $\leq 80^\circ\text{C}$ , brings about several challenges for PEMFC [16,23], especially for application in transportation, such as fuel impurity ( $\text{CO}$ ,  $\text{H}_2\text{S}$ , etc.) tolerance ( $<20 \text{ ppm}$ ) and heat rejection (see below). So efforts have strived to increase the working temperature of PEMFC. The desirable temperature is generally believed to be  $120\text{--}150^\circ\text{C}$ . The prohibitive cost of present PEMFC system is another challenge.

Operation at an increased temperature ( $120\text{--}150^\circ\text{C}$ ) causes greater challenges for PEMFC [24]. Novel materials that can give high performance and high durability under such conditions are prerequisite for high-temperature PEMFC, among which alternative electrolyte membranes that can work at high temperatures ( $120\text{--}150^\circ\text{C}$ ) and low relative humidities ( $\text{RH}=25\text{--}50\%$ ) are one of the most important. Many current research efforts are devoted to the development of alternative electrolyte membranes [24], including non-fluorinated hydrocarbon polymer [17], inorganic-polymer composite [18,20,25], anhydrous proton conducting polymers [26] (e.g., PBI/ $\text{H}_3\text{PO}_4$  [27–30], Nafion/ $\text{H}_3\text{PO}_4$  [31]). For example, since year 2000, the U.S. Department of Energy has established “The High Temperature Membrane Working Group” to advance the R&D of high temperature membranes for PEMFC. Great advances have been obtained in this field [15,16,32–34]. Comparatively, little effort has been devoted to material durability and compatibility issues of high-temperature PEMFCs.

In this article, the reasons for high-temperature PEMFC are at first summarized and analyzed. The material challenges (durability, compatibility, etc.) for high-temperature PEMFC are described. We do not want to give a thorough review on literature, but an insight into the R&D of high-temperature PEMFC, based on selected research reports from peer-reviewed journal publications.

## 2. Why high temperatures?

The theoretical analysis and experimental investigations have shown that working at high temperatures ( $120\text{--}150^\circ\text{C}$ ) can provide the following advantages for PEMFC [16,23,35]:

### 2.1. Electrode reaction kinetics

The overall electrochemical kinetics of a PEMFC is determined by the slow oxygen reduction reaction (ORR) [24]. Due to the sluggish ORR kinetics [8,36], the over-potential at the cathode (ORR electrode) accounts for the major voltage loss of PEMFC and remains a major focus of PEMFC research [8,24,37]. The reaction kinetics of hydrogen oxidation and ORR will be both enhanced at high temperature, especially for ORR [24,38]. Of course, there is also a counter balance from the simultaneous loss of thermodynamic driv-

ing force (reversible cell voltage) at improved temperatures [24,37].

## 2.2. CO tolerance

Trace CO in hydrogen feed gas can significantly depress the performance of PEMFC due to the strong adsorption of CO on Pt electrocatalysts [39–41]. The adsorption of CO on Pt will be weakened at high temperatures, thus CO tolerance will be enhanced [23], for example, the CO tolerance is 10–20 ppm at 80 °C, 1000 ppm at 130 °C, and up to 30,000 ppm at 200 °C [42], which will also offer cost advantage for hydrogen production and perhaps no requirement for the CO cleanup in fuel processing system.

## 2.3. Heat management

Even though PEMFC is a very efficient system, there is still 40–50% of the energy produced as heat [43]. The produced heat in a working PEMFC stack must be removed quickly from fuel cells, otherwise the fuel cell system will overheat. It is well known that the rate of heat transport is proportional to the temperature difference between PEMFC and the environment. For PEMFC working at low temperatures ( $\leq 80$  °C), the heat rejection rate of the state-of-the-art automotive radiators is insufficient to reject continuous full power waste heat [21]. It requires a novel complex cooling system with a large dimension and weight, for example, the cooling system in the state-of-the-art fuel cell cars accounts for about 50 wt.% of the total fuel cell system. Increase of PEMFC working temperature to  $>120$  °C will make the cooling system in present internal combustion engine (ICE) vehicles possible in fuel cell vehicles and thus will greatly increase the weight- and mass-specific energy densities and increase the total energy efficiency [16,21]. Under high temperatures, the heat can be recovered as, e.g., steam, which in turn can be used for direct heating, steam reforming or for pressurized operation. If the operational temperature is elevated to, for example, 200 °C, water steam of up to 15 atm can be produced from a fuel cell stack [16]. In this way the overall system efficiency will be significantly increased.

## 2.4. Water management

PEMFC working at temperatures  $\leq 80$  °C under atmospheric pressure often involves a dual-phase water system, i.e., liquid water/water vapor; when the humidification is too high, water condenses and the electrodes are flooded, which makes water management difficult [16,44,45]. However, if a PEMFC is running at atmospheric pressure and above 100 °C, only single water phase, i.e., water vapor, exists in PEMFC [16,24]. So the transport of water in membrane, catalyst layers and diffusion layers will be easier to balance. Transport of reactants ( $H_2$  and  $O_2$ ) in the electrode layers is also expected to be enhanced, and no flooding problem in cathode [46]. Additionally, the reduction in the amount of liquid water will increase the exposed surface area of the electrocatalysts and improve the ability of the reactants to diffuse into the reaction layer [47].

## 2.5. Non-platinum catalysts

With the increase of working temperature, the electrode reaction kinetics will be greatly enhanced, thus make it possible to use non-platinum catalysts, reducing the total cost of PEMFC [12,48].

The above mentioned advantages of high-temperature PEMFC are extraordinarily attractive, which has spurred interest in this area.

## 3. Durability of materials

PEMFC works under harsh conditions [49,50]: low pH, high water content, high electrode potential (cathode, 0.6–1.2 V versus reversible hydrogen electrode, RHE), high oxygen concentration and ORR intermediate  $H_2O_2$ . It is well established that the durability problem of materials will become more severe with the increase of working temperature [51,52]. The following are the main materials in PEMFC that are liable to degradation.

### 3.1. Catalysts and supports

Carbon supported Pt and its alloys are the catalysts widely used in present PEMFCs. The durability of the catalysts and their supports has been investigated in real or simulated low-temperature PEMFC condition [49,53–62]. It is found that the electrochemically active surface area of the electrodes will be decreased during PEMFC running [36,59,63–65], which contributes to the main performance degradation of PEMFC [51,64]. Pt or Pt alloy nanoparticles that are deposited on carbon black can agglomerate through diffusion on carbon surface to form larger particles during PEMFC operation or under the accelerated aging test [36,49]. Pt will also dissolve into the acidic operating environment, followed by hydrogen reduction and then staying in Nafion membrane in PEMFC or by precipitating onto larger Pt particles [54,59]. The dissolution phenomenon of non-platinum metals in Pt alloys is still more severe because of their poor resistance to corrosion [53].

Corrosion of the carbon support also occurs during PEMFC operation, which also leads to performance loss [49,55]. When carbon corrodes, some Pt and/or its alloy particles will peel from the electrode. Carbon corrosion will increase the electrode resistance by decreasing electric contact with the current collector [36]. Carbon corrosion will also accelerate the sintering of Pt by weakening the interaction between Pt and the support [49].

All these phenomena decrease catalytically active surface areas of the electrode, thus decrease the cell performance. Even worse, all of the above mentioned phenomena are aggravated with the increasing of working temperature [51]. The sintering of Pt may be reduced at low relative humidity but carbon corrosion be accelerated [66], the later may be due to the competition between the oxidation of carbon and water at high electrode potentials [51], especially at the reverse condition of a PEMFC [67]. Most of the researches of catalyst durability are carried out at low temperatures ( $\leq 80$  °C) and liquid electrolyte solutions or high humidity [63,64]. Some investigations are carried out at low humidity but low temperatures [68,69]. Few investi-

gations at high temperatures (120–150 °C) and low humidities (RH = 25–50%) reports are available. According to the state-of-the-art research reports, no catalysts have yet to satisfy the low-temperature PEMFC requirements for catalysts in terms of catalytic activity and durability [21,70], let alone that for the high-temperature PEMFC.

So many efforts should be devoted to answer at least the following questions: can Pt and/or Pt alloys supported on carbon materials (carbon black, carbon nanotubes, carbon nanofibers, etc.) with a desirable loading and a desirable catalytic activity survive from the high-temperature PEMFC conditions for a long lifetime, e.g., >5000 h for transportation application [1]? If the answer is no, what's the degradation behavior of carbon supported Pt and/or Pt alloy catalysts under high temperature and low humidity? What strategies can be employed to improve the durability? What materials can satisfy the requirements of catalysts for high-temperature PEMFC? A revolutionary breakthrough in science and technology on novel catalytic materials is needed, but not only evolutionary advances have thus far been reported [71].

Wang [72] and Shao [49] have reported that Pt nanocatalysts supported on multiwall carbon nanotubes showed a higher durability and a higher catalytic activity than that supported on other support materials (Vulcan XC-72 carbon black). This is due to the higher durability of the support and the specific interaction between Pt nanoparticles and the novel support [49]. Alloying Pt with other specific metals cannot only improve the catalytic activity [73], but also it can enhance the durability [21,53,60,71,74], which is due to the so called “anchor effects” [53,74]. It is recently reported that platinum (Pt) oxygen reduction fuel cell electrocatalysts can be stabilized by modifying Pt nanoparticles with gold (Au) clusters, which is attributed to the raised oxidation potential of Pt by Au [75]. Graphitization of carbon support produces a material which is highly resistant to oxidation and carbon corrosion, perhaps resulting in highly durable catalysts [76]. However, metal deposition on such graphitized supports is more difficult [36]. Some researchers observed an enhanced electrocatalytic activity and durability on nitrogen-doped [77–79] or boron-doped [80] carbon supported electrocatalysts for potential application in PEMFC. It is believed that the nitrogen-doping effect is due to the electron donor nature of nitrogen, which improves the ability of graphite to donate electrons to O<sub>2</sub> and makes the reaction of oxygen to water more easily. The electron donor nature of nitrogen enhances the delocalized  $\pi$  bonding of graphite layers in carbon support (CNT/CNF) [79], which makes strong the interaction between the support CNT/CNF and the catalyst metals. The enhanced CNT/CNF-metal interaction results in higher durability of catalysts. The investigation on carbides supported Pt [21,81,82] or non-Pt catalysts [83–86] is also carried out, but few reports are available on their durability.

These are only primary investigations and only incremental advance for durable and high-activity catalysts for PEMFC. Investigations on non-platinum catalysts have made advances recently [12,48,87], but their durability under high temperature needs further study.

### 3.2. Bipolar plates

The development of bipolar plates for PEMFC in recent years has been reviewed by several researchers [88–91]. In most designs, the bipolar plates should have the following functions [88,90]: (1) to distribute the fuel and oxidant within the cell which requires it being impermeable to reactant gas (H<sub>2</sub> and O<sub>2</sub>); (2) to facilitate water management within the cell; (3) to separate individual cells in the stack; (4) to carry current away from the cell and to facilitate heat management, which require it being a good conductor for the heat and the electron transport. Bipolar plates are under a corrosive environment: low pH, with one side exposed to the reductive gas (H<sub>2</sub>), which works as the anode in one cell, and the other side to the oxidative gases (O<sub>2</sub>), which works as the cathode in another cell. Therefore, bipolar plates should also be of great resistance to chemical and electrochemical corrosion. This limits the materials that can be used for manufacturing bipolar plates [88], which include nonporous graphite carbon, composites, metals. Traditionally, nonporous graphite carbon is the most commonly used bipolar plate material because of its high chemical and electrochemical stability to survive the fuel cell environment and its high conductivity. However, the cost of both nonporous graphite carbon raw materials and the manufacturing to introduce flow field grooves is prohibitive for application in PEMFC [90]. Carbon based composite (carbon–carbon and carbon–polymer composites) bipolar plates are developed as an alternative to graphite carbon. But for carbon–carbon composites, the poor mechanical strength is inherent [90]; the carbon–polymer composite bipolar plates encounter the problem of high resistivity [88]. Metal (usually coated a protective layer) plates are used as another alternative by some developers [92–94]. Due to the consideration of the cost, specific weight, mechanical properties, gas impermeability, electrical and thermal conductivities, and so on, metal plates are preferred [1,41,89,95], especially for transport vehicle PEMFC application. Metals investigated include aluminum, stainless steel, titanium and nickel. There is also the corrosion problem for metal bipolar plates under PEMFC conditions [95]. Coating a protective layer on the surface of metal bipolar plates can only alleviate, but not completely eliminate, the corrosion problem [41]. Coated layer sometimes increase the interfacial resistivity of the bipolar plates [24]. Furthermore, metal ions dissolved from metal bipolar plates (both the from the bulk and the coated protective layer) can contaminate the polymer electrolyte membrane [90], which is harmful for PEM's life and conductivity property [95,96]. The present investigations on bipolar plates are focused on novel materials and the corrosion behavior under low-temperature PEMFC conditions. So what's the corrosion behavior of metal bipolar plate under the high temperature and low humidity conditions, i.e., the targeted high-temperature PEMFC working conditions? However, to our best knowledge, no reports are available on this topic. In addition to novel material development, many efforts should be devoted to investigate the behavior of the materials and the resultant bipolar plates under high temperatures and low humidity conditions.

### 3.3. Membrane durability

Membrane durability has been widely investigated for both Nafion and novel alternative membranes. It is generally believed that  $\text{H}_2\text{O}_2$  and its intermediates generated during oxygen reduction and the chemical combination of  $\text{H}_2$  and  $\text{O}_2$ , reduce the lifetime of PEMs by attacking both end-groups and side chains of membrane polyelectrolyte, but there are still controversies in their degradation mechanism and model [52,97]. Several reviews on the state-of-the-art of PEMs [15,16,19,20,32–34,98] and their future development [99] have been published recently, we will not iterate it. We only want to point out that the operation of PEMFC at higher temperature and lower relative humidity results in even faster degradation rate for membrane [19,51]. But unfortunately again, few investigations have been carried out at high temperatures and low relative humidities.

There are also durability problems for other part materials of PEMFC [24], such as the materials used for sealing [100] and gas diffusion layers. All the durability problems will change with working conditions, especially will become more severe at high temperatures [24]. Furthermore, the investigation on the durability of materials is time-consuming. To test the durability of materials in a real normally working PEMFC is inefficient, if not impossible, because the life requirement for PEMFC, thus its materials, is, for example, >5000 h for transportation and >40,000 h for stationary application [1]. Therefore, the so called accelerated degradation test (ADT) is developed [53,54,57,62]. Most of the ADT methods are ex situ ones, so how and to what extent the ex situ methods can simulate the real working condition of PEMFC is still in question, for example, as the widely used method for screening novel alternative polymer membrane materials, Fenton's reagent test sometimes cannot work well (see the following section) [17]. Time-effective and reliable methods for material durability investigation are indispensable, especially with the testing condition of high temperatures (120–150 °C) and low relative humidities (20–50%). The open-circuit voltage test may be the only simple screening method, so far, to predict membrane lifetime [21,68], which can be easily extended to various humidities and high temperature. The open-circuit voltage testing condition is also in close similarity with real fuel cell working environment.

### 4. Polyelectrolyte in catalyst layers

The amount of polyelectrolyte used in catalyst layers is not as large as that in membranes, however, it is also important [85], because it is closely related to the electrode performance, Pt utilization, and MEA durability [101]. In current PEMFCs, Nafion ionomers are employed in the catalyst layer as a binder and the proton conducting electrolyte to extend the electrochemical triple-phase boundary (TPB) formation [6]. The later is important for obtaining a desirable Pt utilization and thus a high performance of MEA. In the catalyst layer, the transport of reactants, protons and electrons, i.e., the formation of TPB, can be illustrated in Fig. 2 [22].

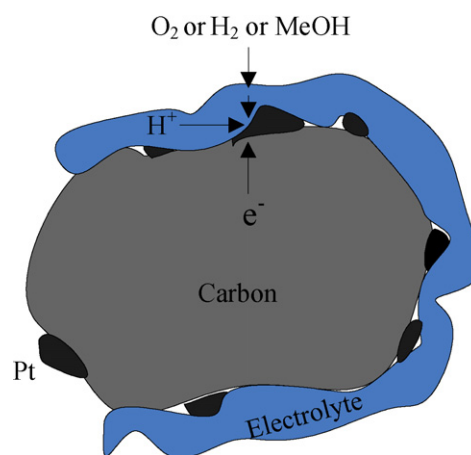


Fig. 2. Schematic of the reactant, proton and electron transport in catalyst layer of PEMFC electrode, i.e., the formation of the electrochemical triple-phase boundary.

It can be seen that the reactant must transport through the proton conducting electrolyte before it arrives at the reaction sites and then takes part in the electrode reactions. So the electrolyte in the catalyst layer must be reactant-permeable, otherwise it might cause reactant mass transport limitations [102]. This is completely different from the polyelectrolyte used in membranes which requires no or much less reactant permeability [15,16]. The other problem is that, for most alternative proton conducting polyelectrolytes which are mainly aromatic hydrocarbon and more hydrophilic than Nafion [101], liquid water is more easily to form in the electrode which might block the transport of reactants (fuel and oxidant).

In the cathode catalyst layer, oxygen is electrochemically reduced to  $\text{H}_2\text{O}$ , and more or less  $\text{H}_2\text{O}_2$  is usually formed in the oxygen reduction reaction process, which has been confirmed on carbon supported Pt catalysts (Pt/C) and the formation of  $\text{H}_2\text{O}_2$  is enhanced with a decrease in agglomeration of Pt/C [103]. It is well known that  $\text{H}_2\text{O}_2$  is harmful to polyelectrolyte durability [19], even though there is still dispute on the formation sites of  $\text{H}_2\text{O}_2$  and the exact mechanism for  $\text{H}_2\text{O}_2$  to attack the polyelectrolyte [52]. Unlike polyelectrolyte in the membrane which is a little far from the reaction sites of ORR, polyelectrolyte in the catalyst layer are just touched with the sites where ORR takes place, at which the concentration of  $\text{H}_2\text{O}_2$  is expected to be much higher than that in membrane. The polyelectrolyte in the catalyst layer is more likely to be negatively affected by  $\text{H}_2\text{O}_2$  and has to be more chemically stable than membrane. The Fenton's reagent test, i.e., putting the polymer in hot 3%  $\text{H}_2\text{O}_2$ /1 ppm Fe(II) solution to test its chemical stability [17], is widely used for the stability evaluation and the screening of novel alternative polymer membrane candidates [15]. This screening method does not work well sometimes for membrane materials, for example, polybenzimidazoles cannot stand Fenton's reagent test at all, but the membrane has been demonstrated with a fuel cell lifetime over 5000 h at 150 °C by continuous operation [16]. It has also been shown that, whereas sulfonated poly(ether ether ketone) (SPEEK) membranes can function for hundreds to thousands of hours in a fuel cell, the similar membranes may become brittle with partial loss of their IEC after

4 to 8 h in Fenton reaction solutions at 68 °C [17]. Due to the relative high concentration of H<sub>2</sub>O<sub>2</sub> in the catalyst layer, it is expected that Fenton's reagent test can work well in evaluating the chemical stability of polyelectrolyte for application in catalyst layer.

It can be deduced that proton transport is also different from that in membrane. In PEMFC, proton transports through the direction vertical to the membrane surface plane [15]. The anisotropic proton transport property, in which the through-the-plane proton conductivity of the membrane is higher, is desirable for polymer membrane [104,105]. But this is not the case in catalyst layer, in which the proton transport is a little more unoriented.

The requirements for mechanical and dimensional stability of polymer membrane are very high [16,106]. But for polyelectrolyte in catalyst layer, it is perhaps not the case. In one word, the requirements of polyelectrolyte for the catalyst layer and for the membrane are quite different. So the conclusion can be drawn that different polyelectrolytes should be or be preferred to be employed in the catalyst layer and the membrane for PEMFC, respectively [101]. So far, the same polyelectrolyte, i.e., Nafion, is employed in the catalyst layer and membrane in most PEMFCs.

It is found that the catalytic activity of carbon supported noble metal catalysts for oxygen reduction is higher in Nafion electrolyte than, for example, in phosphoric acid, due to the nonadsorbing nature of the sulfonic acid anions on the Pt catalyst surface [107]. Oxygen reduction reaction kinetics in Nafion system is also higher than other sulfonic acid group containing polymers [108]. Permeability of hydrogen [109] and oxygen [110] are also found to be higher than novel alternative polyelectrolytes, for example, the oxygen permeability of Nafion is 1.5–3 times larger than that for sulfonated polyether sulfone membranes [111] and five times larger than that for SPEEK [112]. This is attributed to the lower oxygen solubility in the non-fluorinated backbone [112]. The backbone fluorination of Nafion is also expected to mitigate hydroperoxide formation [15]. Nafion also shows a desirable high chemical stability in a Fenton's reagent test and real PEMFC working conditions. The amount of polyelectrolyte used in catalyst layer is relatively small, as compared with that for membrane. The high cost of Nafion will not exert much influence on total cost of PEMFC. So Nafion is considered to be one promising candidate polyelectrolyte for catalyst layer of next generation PEMFC. But its performance as a membrane is not good enough [15]. Alternative polymer membranes are needed, which are being under intensive investigation by many research groups [15,16,85,101,113].

The investigations on the catalyst layer with novel alternative ionomers and its application in MEA have recently been reported [102,112,114]. It has been shown that novel alternative ionomers in catalyst layer can cause several challenges in MEA design [102,112], such as cathode flooding, mass transport limitations in catalyst layer. The application of various polyelectrolytes in catalyst layer and membrane brings about the problem of material compatibility [115]. This will be discussed in the following section.

## 5. Material compatibility

If different polymers are employed in the catalyst layer and the membrane, respectively, there is the problem of the compatibility of the polymer membrane and the catalyst layer [115]. It has been found [101,114,116–118] that the interfacial resistance is larger for a MEA consisting of Nafion-based catalyst layers and non-Nafion membrane than all-Nafion one, and that the degradation rate for the former is much larger than the later. If the polymers in the catalyst layer and the membrane are the same one, regardless of it being, i.e., Nafion or non-Nafion, it seems that the interfacial resistance can be lowered to some extent [102,108]. The exact origin of the increased interfacial resistance between Nafion-based catalyst layers and non-Nafion membranes remains unknown, but it is reasonable to assume that Nafion, being a highly fluorinated tetrafluoroethylene-based material would tend to not bond intimately with a non-fluorinated copolymer. So the larger interfacial resistance is perhaps due to the different chemistry of the two polymers [115]. The larger degradation rate of non-Nafion-membrane MEA is due to the different rates of swelling/contraction of different polymers, which results in the delamination of MEA in the cycle of hydration–dehydration [112].

It has been reported [101,114] that modifying polyaromatic electrolyte membranes with fluorine and other functional groups can decrease the interfacial resistance in the MEA consisting of the Nafion-based catalyst layer and non-Nafion membrane. It is reasonable to assume that a fluorinated copolymer could be more compatible with highly fluorinated Nafion than a non-fluorinated copolymer [115].

It is reasonable to postulate that the chemical similarity of the polymers in the catalyst layer and in the membrane is important for a good binding of the two parts (the catalyst layer and the membrane) and thus lower interfacial resistance in the resultant MEA [115]. The following questions should be first stated. What influences the chemical similarity of two kinds of polyelectrolyte, the backbone and/or the functional group (side chains)? Do other properties of polyelectrolyte, such as hydrophobicity/hydrophilicity, influence the binding of the catalyst layer and the membrane? It should also be emphasized that if an alternative membrane material does emerge, considerable R&D will still be necessary to optimize and manufacture the new membrane electrode assembly (MEA). This development has taken many years for Nafion-type MEAs, although some of the expertise gained may be able to be transferred to the new system[1]. So many efforts are needed on the development of novel alternative materials for PEMs.

## 6. Conclusions and outlook

Operation of PEMFC at high temperatures (120–150 °C) brings about considerable advantages. However, many challenges for materials come with the advantages. The challenges in terms of material durability (catalysts, bipolar plates, and membrane), novel polyelectrolyte in the catalyst layer, and the material compatibility between membrane and electrodes, are

reviewed. Many efforts are needed in the R&D of novel materials for high-temperature PEMFC.

First, we should answer the question of the possibility of “high temperature” and “low humidity” and the pathway to get to the end. Some people have suggested to place emphasis on the strategy of “low relative humidity” at operating temperatures of 60–80 °C as the first step instead of “high-temperature” one [21].

Revolutionary breakthrough should be achieved in novel material development and the fundamental investigation on the fuel cell related properties. The properties of novel materials potentially used in high-temperature PEMFC should be investigated in-depth, in terms of their performance, durability, compatibility, and so on. A reliable and time-effective method should be developed for novel material screening. The emphasis should be placed on simulating real fuel cell working conditions and the relationship between the working conditions and the cell related properties. For example, it has been reported that the intrinsic oxygen reduction reaction kinetics in a PEMFC are independent of RH above 50–60%, but significant losses in ORR kinetics were observed at lower RH values, which is attributed to the reduced H<sup>+</sup> activity at low RH [119].

For examples, first principle calculation has proven to be a useful tool to novel catalyst design [120] and computational studies have been utilized to facilitate and develop understanding of PEMs [121–123]. It has shown a promising result in the effort to use computational tools to understand polymer morphology and properties [101], such as the state of adsorbed water and its transport in PEMs [121], and to the basis for understanding the mechanisms of proton conduction in PEMs [35].

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