

Review

Recent Approaches to Achieve High Temperature Operation of Nafion Membranes

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Abstract: A proton exchange membrane fuel cell (PEMFC), as an efficient energy conversion device, has many advantages, such as high energy conversion efficiency and environmentally friendly zero emissions, and is expected to have great potential for addressing the uneven distribution of global green energy. As a core component, the performance of the proton exchange membrane (PEM) directly affects the overall output of the fuel cell system. At present, Nafion membranes with good, comprehensive properties are the most widely used commercial proton exchange membrane materials. However, Nafion membranes demonstrate a great inadaptability with an increase in operating temperatures, such as a rapid decay in proton conductivity. Therefore, enhancing the overall performance of Nafion membranes under high temperatures and low relative humidity (RH) has become an urgent problem. Although many efforts have been made to solve this problem, it is difficult to find the balance point between high-temperature conductivity and overall stability for researchers. In this paper, we summarize the recent approaches to improving the operating temperature of Nafion membranes from the following two perspectives: (1) using different materials for the modification of Nafion membranes, and (2) applying different modification methods to the Nafion membranes. Based on the structural and functional characteristics of Nafion, the non-destructive targeted filling of fillers and the efficient synergy of the two-phase region are two vital research directions for the preparation of high-performance composite membranes.



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Keywords: Nafion membranes; proton conductivity; modification materials and method; fuel cell; relative humidity

1. Introduction

Throughout the development of human society in the past century, traditional fossil energy, including coal, oil, and natural gas, became an important driving force for social development [1]. However, the consumption of traditional fossil energy is the main source of greenhouse gases, and its large-scale use has caused the current, serious global environmental crisis. Presently, with the promotion of the sustainable development model and harmonious co-existence between humanity and nature, an increasing number of clean energy sources are attracting attention, such as solar, wind, geothermal, microbial cell, and hydrogen energy [2–5]. However, some renewable energies are unstable and intermittent during the power supply generation, and it is therefore difficult for those generators to provide valuable electricity for the grid in a continuous and stable manner. Hence, the additional employment of energy storage/generators is needed to improve the utilization rate and stability of renewable energy. Therefore, as an efficient energy conversion device, fuel cells have great potential to address the uneven distribution of global green energy. Moreover, the operation of fuel cell power generation is obviously simpler. After a long-term of technological accumulation, hydrogen technology has made great progress and

has been applied in some fields. Meanwhile, as efficient energy conversion devices, fuel cells play an important role in the practical application of hydrogen energy. For the last 30 years, fuel cells have been used primarily to replace internal combustion engines and to supply power for stationary and portable applications [6]. However, the history of research on the fuel cell does not only span 30 years; the investigation spans nearly two centuries. Since the first scientific report on the principle of fuel cells was written in 1838 by German chemist Christian Friedrich Schonbein [7], several types of fuel cells have been developed, including the alkaline fuel cell (AFC) [8–10], proton exchange membrane fuel cell (PEMFC) [11–13], phosphoric acid fuel cell (PAFC) [14–16], molten carbonate fuel cell (MCFC) [17–19], and the solid-oxide fuel cell (SOFC) [20–22], shown in Figure 1. Since 1970, the development of fuel cells have had the following characteristics: a reduced catalyst cost, an improved performance, and a prolonged service life. At present, the PEMFC has the most potential as an alternative generator to the traditional internal combustion engine. Currently, PEMFCs have an energy conversion rate of 60%: three times that of on-board internal combustion engines (~20%). PEMFCs have become one of the keys to the future “hydrogen economy” [23].

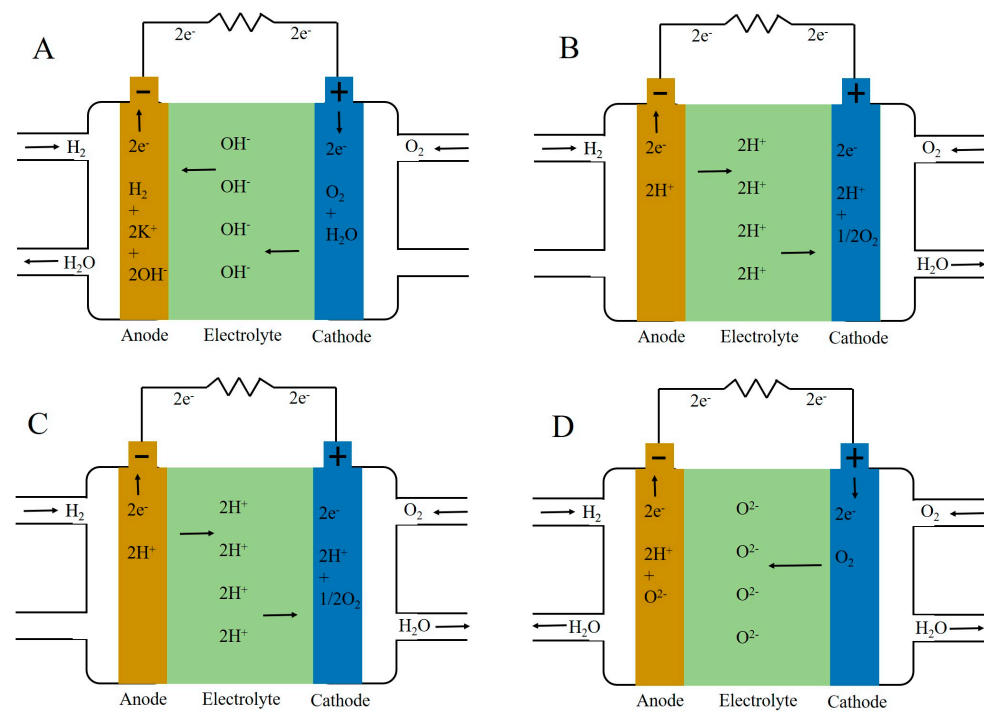


Figure 1. Principles of operation of an alkaline fuel cell (A), proton exchange membrane fuel cell (B), phosphoric acid fuel cell (C), and solid oxide fuel cell (D) [7].

A PEMFC consists of several main parts: a proton exchange membrane (PEM), catalytic layer (CL), gas diffusion layer (GDL), bipolar plate (BPP), and the outermost end plate (EP) [24,25]. Together, the proton exchange membrane, catalyst, and gas diffusion layer form the membrane electrode assembly (MEA) in which the electrochemical reactions take place. PEMFCs are fed by hydrogen/oxygen and are catalyzed mainly by precious metal alloy compounds containing Pt [26]. Based on these characteristics, PEMFCs have many advantages. Firstly, the separator of the anode and cathode is a solid polymer membrane (planar structure), and the cell operates at relatively low temperatures, so aspects such as handling, assembly, or tightness are less complex than in most other types of cells. Additionally, PEMs are usually non-corrosive polymer materials [12]. This improves safety by avoiding the need to handle acids or any other corrosive substances in the fuel cell. Additionally, the disposal of waste electrolytes is also easier to handle. Finally, the cell system adapts well to the low pressure of reactants (1 or 2 bar) and CO₂, allowing for the

direct use of the atmosphere. On the other hand, many disadvantages also hinder the further application of PEMFCs. The chemical reactions of the anode and cathode require the assistance of precious metal catalysts; these catalysts are not only expensive, but also have a poor tolerance to CO and H₂S. Moreover, catalyst poisoning will reduce the efficiency of electrode reactions in the fuel cell. Most importantly, conventional membrane materials, such as Nafion membranes, are highly dependent on water, and their performance deteriorates severely under high-temperature and low-humidity conditions [27–29]. As a result, a water management component needs to be added, which further increases the complexity of the fuel cell system [30]. These problems must be solved if further applications of fuel cells are to be realized in light electric vehicles and portable electronic equipment.

Depending on the operating temperature of a PEMFC, researchers classify it as a low-temperature proton exchange membrane fuel cell (LT-PEMFC, <100 °C) or a high-temperature proton exchange membrane fuel cell (HT-PEMFC, >100 °C) [31]. As research on PEMFC progressed, researchers found it important to raise the operating temperature of the fuel cells to improve their performance during operation. The research has shown that raising the operating temperature of a PEMFC to above 100 °C can solve the “two-phase flow” problem caused by the coexistence of two gas–liquid phases in the fuel cell system [32,33]. At the same time, a high operating temperature is helpful for improving the dynamics of the related chemical reactions; a high temperature can improve the catalyst’s tolerance to carbon monoxide, hydrogen sulfide, and other toxic gases and simplify the hydrothermal management components of the fuel cell system [34–36]. These properties also imply a reduced Pt loading in fuel cells, allowing even non-Pt catalysts to be used [37]. As a result, HT-PEMFCs are expected to achieve large-scale applications in hydrogen fuel vehicles and combined heat and power systems [38].

Although increasing the operating temperature is beneficial to the overall output performance of PEMFCs, it also raises some key issues that hinder the further development of HT-PEMFCs. These problems include: (1) possible corrosion and a decrease in the mechanical stability of the bipolar plate under high-temperature conditions [39,40]; (2) a performance decrease and an insufficient high-temperature resistance of the catalysts [41–43]; and (3) low proton conductivity and a lessened stability of PEM materials under high-temperature conditions [44–46]. Overall, HT-PEMFCs need to reach the three major objectives of low cost, high performance, and excellent durability for further commercial system development. To achieve these goals, the research on the optimization of the core component—PEM—is essential. In other words, PEM needs to meet at least two requirements: (1) have a high proton conductivity under high-temperature and low-humidity conditions; and (2) have a comprehensive stability that can maintain long-term operation, including good mechanical properties, a high chemical stability, and so on.

On the anode catalytic layer side of the proton exchange membrane in a PEMFC system, the hydrogen breaks into electrons and protons on the surface of the catalyst. On the cathode catalytic layer side, the oxygen then splits into oxygen ions to produce water and protons, followed by a wasting of heat. As a result, the PEM should be specially designed for the rapid and selective diffusion of the H⁺ generated at the anode to the cathode. The main membrane material categories for HT-PEMFC applications include the following four: (1) sulfonated, hydrocarbon-based polymer membranes, such as sulfonated polyether ether ketone (SPEEK) and sulfonated polyether sulfone (SPES), which generally has good mechanical stability, fine thermal resistance, and high water absorption over a wide temperature range [47–49]. However, the main issue of membrane degradation is poor thermal stability at high temperatures. At the same time, water absorption and desorption can also cause catalyst-stripping and membrane-thinning problems [50]. (2) Phosphoric acid-doped polybenzimidazole (PBI) membranes: this type of membrane material is inexpensive and maintains good chemical and thermal stability in the temperature range of 100–250 °C [15,51]. Most importantly, the proton conduction of an acid-doped PBI membrane has nothing to do with water molecules and can achieve efficient proton conduction without humidification. However, hardware corrosion and performance degradation

caused by phosphoric acid leakage should not be ignored [52–54]. (3) Acid–base membranes: an acid–base proton exchange membrane uses non-aqueous solvents such as acidic proton ionic liquid to replace water as a proton carrier [55–57]. Meanwhile, some solid materials can also function as proton-conducting mediums. Therefore, acid–base membranes have high thermal stability and proton conductivity under low humidity and even dry conditions [58–60]. (4) Modified perfluorinated sulfonic acid membranes (PFSA): PFSA, with highly developed technology and wide commercial application, exhibit a high proton conductivity and good chemical and mechanical stability at low temperatures [61–63]. At present, the most representative PFSA is the Nafion membrane produced by DuPont. Although it has many drawbacks under high-temperature conditions, we cannot ignore its inherent, excellent, comprehensive performance and the vast scope of its performance improvement space. However, comprehensive review papers on this subject are still very limited. In this paper, we will review this topic from three perspectives in combination with the recent research: (1) proton conduction mechanisms and the structural characteristics of Nafion membranes; (2) the modification materials used in the refinement of Nafion membranes, including hygroscopic materials, high-temperature proton conductive materials, materials modified by functional groups, and proton conductor materials; and (3) the modification methods used in the improvement of Nafion membranes, including the solution-cast method and swelling-filling method. In addition, we propose future directions for the high-temperature modification of Nafion membranes.

2. Proton Conduction Mechanism and Structural Characteristics of Nafion Membranes

In order to improve the proton conduction in Nafion membranes, the first step is to understand the mechanism of proton conduction in the membrane. The mechanism of proton conduction in the membrane is shown in Figure 2. Taking hydrogen fuel as an example, H_2 loses its electron to form a proton when it hits the catalyst. Since there is no electron layer around the proton, it is easier to generate electrostatic attraction with the outer electrons of surrounding atoms or ions to form hydrogen bonds: this is an important basis for proton transmission in the membrane [64–67]. Currently, there are two widely recognized mechanisms for proton conduction in Nafion membranes: The first is the “Vehicular mechanism”. As the transport medium, water molecules will first form H_3O^+ with H^+ , which is then transported through the channel of hydrophilic clusters formed by sulfonic acid or through the free volume inside the membrane under the action of the concentration gradient. This transport mechanism, which shows a strong dependence on water molecules, is the dominant mode of proton conduction at medium and low temperatures [68–70]. Another conduction mechanism is the “Grotthus mechanism”. In this mechanism, protons form H_3O^+ with water molecules or otherwise form hydrogen bonds with other groups (sulfonic acid groups). Then, driven by electrostatic attraction and potential difference, H^+ transitions from H_3O^+ or $-SO_3H$ to the adjacent H_2O or $-SO_3$. During this process, protons complete the process of passing through the membrane [71–73]. When compared with the “Vehicular mechanism”, proton conduction through the “Grotthus mechanism” tends to have a higher energy barrier. Therefore, the “Grotthus mechanism” is more active under high-temperature and low-humidity conditions. At the same time, the free path of proton jumping is usually smaller than the distance between the carriers, so protons need to be transferred into the hydrated proton network prior to jumping to the next carrier. The participation of water molecules in the “Grotthus mechanism” is still required. As a consequence, water molecules are an important medium for proton conduction. Furthermore, water evaporation caused by a high operating temperature is the main reason for the decay of proton conductivity.

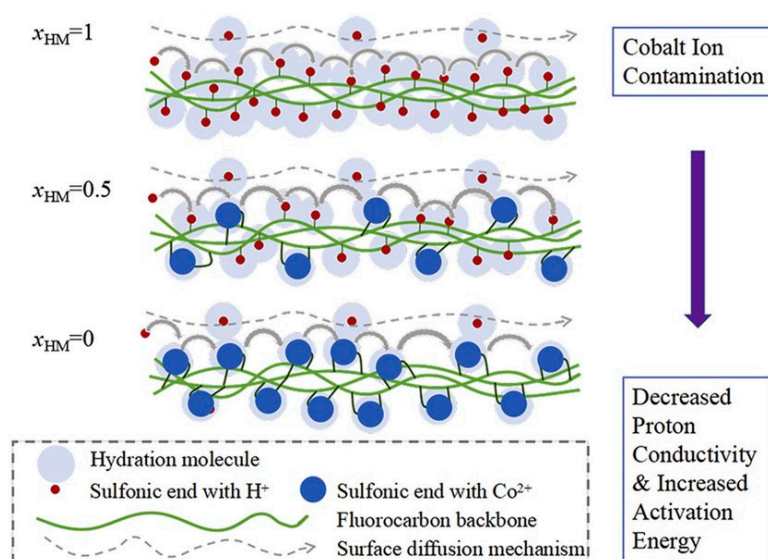


Figure 2. The schematic diagram of proton conduction mechanism for ultrathin Nafion film [70].

In fact, various possible proton conduction mechanisms in Nafion membranes are directly related to their unique microstructures [67]. Nafion is a perfluorosulfonic acid proton exchange membrane material, and its macromolecular structure has a strong, hydrophobic, fluorine-containing main chain and a strong, hydrophilic sulfonic acid group [66]. Therefore, a clear hydrophilic/hydrophobic phase separation can be observed in Nafion membranes. As is shown in Figure 3, sulfonic acid groups form hydrophilic, spherical micelle clusters in Nafion membranes. Based on the observation and estimation, the diameter of each cluster is approximately 4–6 nm, and the spacing between clusters is approximately 5 nm. There is also a connecting channel, which has a diameter of approximately 1 nm, between each cluster [74–76]. This is the strong hydrophilicity of sulfonate, which provides water molecules for proton conduction. Although the hydrophobic region formed by the fluorine-containing main chain has a limited contribution to the proton conduction, it is the basis of the good mechanical and chemical stability of Nafion membranes and plays a key role in maintaining the overall stability of the membrane materials.

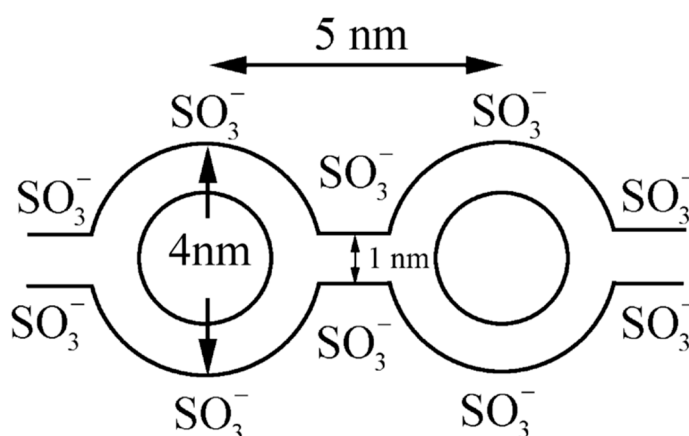


Figure 3. The schematic diagram of spherical micelles formed by a sulfonic acid group.

According to the transport mechanism of protons in a Nafion membrane and the structural characteristics of the Nafion membrane, the main approaches for improving the high-temperature proton conductivity of Nafion membranes are as follows: (1) improve the proton exchange capacity, i.e., increasing the number of sulfonic acid groups. This is the most direct and common method for improving the proton conductivity under low-temperature conditions. However, with the increase in working temperature, the thermal

stability of sulfonic acid becomes worse, and the proton conduction efficiency is greatly reduced due to water loss. Therefore, the improvement of the proton exchange capacity on the conductivity of high-temperature proton is very limited. (2) Another approach is to improve the water retention performance of the membrane materials. Since water loss is the main cause of high-temperature conductivity attenuation, improving the water retention performance of the membrane materials will effectively enhance the high-temperature proton conduction. This is one of the most effective high-temperature modification strategies for preparing composite membranes, involving using Nafion as the matrix and choosing fillers with good moisture retention properties. (3) A third approach to improving the high-temperature proton conductivity is to utilize a high-boiling-point proton conductor. As an important proton transport conductor in Nafion membrane, water is extremely volatile at high temperatures due to its low boiling point, resulting in the attenuation of proton conductivity. If a proton conductor with a high boiling point is selected, the influence of the high-temperature environment on proton conduction will be greatly reduced. At present, phosphoric acid, phosphotungstic acid, and other low-volatility conductors are widely used. Based on the above modification approaches, different modification materials and strategies will have different effects on proton conductivity, mechanical and chemical stability, and fuel cell performance.

3. Modifying Agent

The high-temperature modification of Nafion membranes should first consider improving the proton conductivity while reducing or avoiding the influence of the modifier on the stability of the membrane material. Therefore, the modifying agent should meet the following requirements: (1) have good hygroscopicity to improve the water-retaining capacity of the Nafion composite membrane under high-temperature and low-humidity conditions; or (2) demonstrate good high-temperature proton conductivity and thermal stability, both of which can improve the proton conduction efficiency in a Nafion membrane; (3) be composed of functional-group-modified materials, so that it may form rich hydrogen bonding with Nafion matrix; (4) as a proton transport conductor, have no or low dependence on water molecules and maintain a high proton conduction efficiency under high-temperature conditions; and (5) have good compatibility with the Nafion matrix.

3.1. Hygroscopic Materials

The preparation of inorganic–organic hybrid membranes with hygroscopic materials is the most direct and effective way to improve the high-temperature proton conductivity of Nafion membranes. After introducing the hygroscopic materials into the Nafion matrix or filling in the proton transport channel, the water retention capacity and the high-temperature proton conductivity of the composite membranes are significantly improved. Meanwhile, due to the physical barrier effect of the fillers, the methanol resistance performance of the composite membranes is also enhanced. Modification materials with good hygroscopic properties mainly include SiO_2 [77–79], TiO_2 [80–82], ZrO_2 [83–85], and other inorganic oxides.

Ke et al. [86] prepared Nafion/ SiO_2 composite membranes and studied the effects of different particle sizes of SiO_2 on the performance of the composite membranes and fuel cells. When compared with pristine Nafion membranes, the water retention capacity of the composite membranes was significantly improved, mainly because the SiO_2 nanoparticles themselves have good hygroscopic qualities. The results showed that the composite membrane had the highest proton conductivity when the particle size of SiO_2 was 10 nm. In a single cell test at 110 °C and 59% RH, the performance of the composite membrane was significantly enhanced in the medium-to-high current density range. Sacca et al. [87] prepared a composite membrane using TiO_2 powder and Nafion solution which showed better single-cell performance under the test conditions of 80–130 °C. Vincenzo et al. [88] prepared Nafion/ TiO_2 composite membranes and applied them to high-temperature direct methanol fuel cells. At 145 °C, the power density of the composite membranes with 5%

mesoporous titania reached 335 mW/cm². Santiago et al. [81] prepared a Nafion/TiO₂ composite membrane and tested it using electrochemical impedance spectroscopy (EIS). They found that the adding TiO₂ improved the water management, lowered polarization resistance, and enhanced the performance of fuel cells under high-temperature and low-humidity conditions. At the same time, the addition of the inorganic phase was helpful in improving the overall thermal stability of the composite electrolyte, enabling it to work at higher temperatures. In Figure 4, Janchai et al. [89] studied the effect of a quantitative silica addition on the microscopic properties of Nafion composite membranes using a molecular dynamics simulation. Under high-temperature or low-humidity conditions, the addition of silica can greatly affect the diffusion coefficient of water molecules or the proton conductivity. In addition to particles or powders, nanofibers of such inorganic materials are also commonly used in the high-temperature modification research of Nafion membranes. Wang et al. [90] synthesized a series of biofunctionalized silica nanofibers and further prepared composite membranes with Nafion. Their results showed that the addition of nanofibers can effectively improve the proton conduction efficiency in the composite membranes. Xu et al. [91] prepared Nafion composite membranes using silica nanofibers prepared by electrospinning. The addition of silica nanofibers not only improved the high-temperature conductivity of the composite membrane but also significantly enhanced the mechanical stability of the composite membrane.

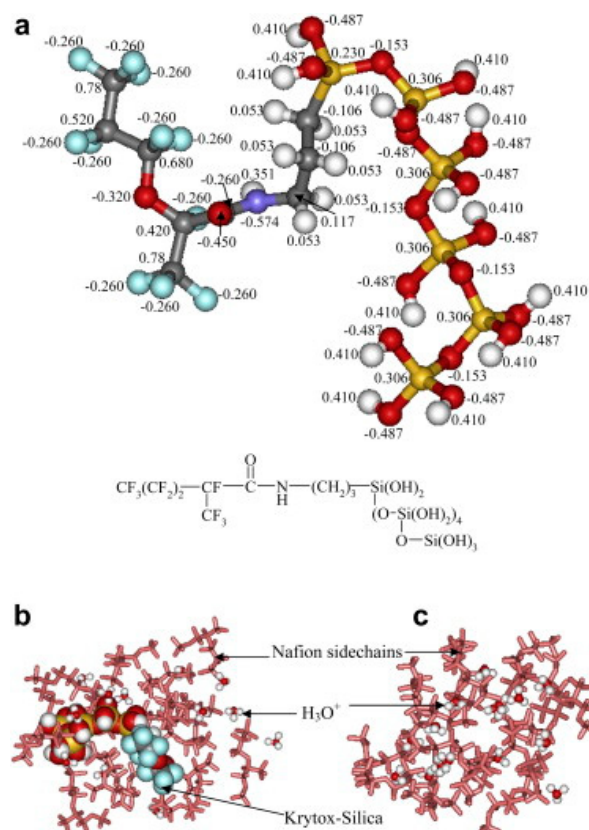


Figure 4. Initial structures of (a) Krytox-Silica molecule and charges, (b) 5% wt of Krytox-Silica in Nafion system, and (c) pure Nafion system [89].

To summarize the above work, it can be seen that the addition of highly hygroscopic inorganic oxides such as SiO₂ and TiO₂ can significantly improve the high-temperature water retention performance of Nafion composite membranes. Additionally, a physical barrier of inorganic particles can reduce the penetration of fuel. By adjusting the filling ratio reasonably, the composite membrane can obtain excellent comprehensive performance.

In addition to the single component modification, the preparation of a composite membrane through the modification of two components is another common strategy. The

synergistic effect of the two components is conducive to further improving the comprehensive performance of the modified composite membrane. Considering the convenience of functionalization and preparation, SiO₂-TiO₂ nanoparticles are commonly used as two-component modifications, which have the following advantages: (1) Two components tend to have a higher thermal stability than one component [92]; (2) due to the unbalanced charge distribution on the Si-O-Ti bond, more acidic sites are exposed on the surface of the binary nanoparticles, which is conducive to efficient proton transport [93]; and (3) in binary nanoparticles, one component may affect the alignment of another component, thereby adjusting the particle size, increasing the surface area, and facilitating the absorption of water molecules [94]. Therefore, the two-component system provides more possibilities for functional modification [95]. Sayeed et al. [96] prepared a sulfonated TiO₂-SiO₂, reinforced Nafion composite membrane for which the water retention capacity and methanol resistance of the composite membranes were significantly improved. Yin et al. [97] synthesized SiO₂-TiO₂ nanoparticles by a one-step method. The binary nanoparticles were further treated with sulfonation and amino functionalization. The strong interaction between nanoparticles and the Nafion matrix led to a new phase-separated structure in the composite membrane, and the nanoparticles modified with acid–base functions were more likely to form hydrogen bonds with water. There were two modes of proton conduction in the composite membrane: “transport” and “jump”. The activation energy of proton conduction decreased. At 80 °C and 26.1% RH, the proton conductivity reached 0.0137 S/cm. When compared with the recast, pristine Nafion membrane, the maximum power density of a single cell at 60 °C was increased by 51.3%. Lee et al. [98] prepared a high-temperature composite proton exchange membrane using phosphoric-acid-modified TiO₂-ZrO₂ nanofibers, which improved the high-temperature performance and durability of the composite membrane.

3.2. High-Temperature Proton Conductor Materials

As the proton conduction medium, high-temperature proton conductors can make up for the attenuation of proton conductivity of a Nafion membrane under high-temperature and low-humidity conditions, playing an auxiliary role. However, they cannot completely replace the proton conduction of the Nafion membrane itself. The majority of proton conductors are heteropoly acids such as silotungstic acid and phosphotungstic acid (PWA). Among these options, PWA has been studied more. Heteropoly acid materials, represented by PWA, usually have strong Bronsted acidity (being more acidic than 100% sulfuric acid and Nafion) [99], high proton conductivity (0.02–0.1 S/cm) [100], and good thermal stability. In addition to enhancing the high-temperature proton conductivity of the Nafion membrane, heteropoly acid materials are also widely used to improve the methanol resistance and water retention capacity of membrane materials [101–104]. due to its good proton conductivity, PWA has great value in the field of proton transport, especially under high-temperature conditions. Lu et al. [105] used PWA and mesoporous silica to prepare a novel, inorganic membrane material with a proton conductivity of 0.045 S/cm at 150 °C. Shao et al. [106] prepared a PWA-doped, Nafion-based composite membrane and found that, when compared with pristine Nafion, the crystallinity, thermal stability, and water absorption of the composite membrane were improved, and while the conductivity of the two were comparable under low-temperature conditions, the composite membrane had higher conductivity under high-temperature conditions. Although it has become a general consensus among researchers that PWA enhances the high-temperature conductivity of Nafion membranes, there is still a serious problem in Nafion/PWA composite membranes—the leakage of PWA. Due to its good water solubility, PWA dissolves and leaks during the actual operation of the fuel cell, which not only affects the performance of the composite membrane but, more seriously, the overflowing PWA corrodes the fuel cell plate and other components, directly affecting the service effect and life of the fuel cell. Therefore, in addition to realizing the efficient doping of PWA in the Nafion/PWA composite membrane, it is more important to improve the stability of PWA and avoid the harm caused by PWA dis-

solution. At present, in order to improve the stability of PWA in composite membranes, the most studied method is to introduce materials such as porous silica, carbon nanotubes, and other materials into the composite system to limit the molecular movement of PWA. There are two possible mechanisms of action: (1) the introduction of silica with an appropriate pore structure and carbon nanotubes with an appropriate scale. The pore structure of silica locks the PWA in carbon nanotubes, restricting its movement and reducing its dissolution. The other method (2) involves the introduction of silica by an in situ sol–gel method, in which silica is coated on the surface of PWA to improve its stability. Xu et al. [107] prepared a Nafion/silica/PWA composite membrane by the sol–gel method, and the test results found that the stability of PWA in the composite membrane was significantly improved. As PWA is catalyzed in the hydrolysis of silica precursor, the resulting silica immobilizes the PWA molecule. Therefore, the PWA is not easily dissolved and leaked. Bose et al. [103] prepared a silica-fixed PWA packing using the sol–gel method and then introduced the fillers into the Nafion membrane and catalytic layers, respectively. The results showed that, under high-temperature and low-humidity conditions, the water retention capacity of the MEA was enhanced, which enhanced proton conduction and charge transfer. The addition of PWA/SiO₂ will not poison the catalyst. Mohammad et al. [108] filled PWA into one-dimensional carbon nanotubes to form efficient proton transport nanowires, and further prepared composite membranes with Nafion. They believed that the free H on PWA in proton transport nanowires could improve the proton conduction efficiency of Nafion. At the same time, the proton conduction in the nanowires is affected by temperature. The higher the temperature is, the more active the proton conduction will be. The maximum output power of the prepared composite membrane was almost four times that of the pristine Nafion membrane at 120 °C and 40% RH. In addition to the common silica and carbon nanotubes, the stability of PWA in composite membranes can also be improved by loading PWA on the nanofibers prepared by electrospinning. Through hydrogen bonding between the PWA and Kevlar nanofibers, Yang et al. [109,110] prepared composite membranes with Kevlar nanofibers supported by PWA and Nafion. The loading of PWA on the nanofibers can effectively avoid the agglomeration of PWA molecules.

3.3. Functional-Group-Modified Materials

The functional-group modification of material is different from the direct doping of the above-modified materials. Generally, the characteristic groups with proton transport are grafted onto the support in the form of chemical bonds. The use of the proton transport of functional groups, combined with the relevant characteristics of the carrier material, are used for the high-temperature modification of the Nafion membrane as a whole. Common functional group modifications include sulfonic acid or phosphorylation, amongst others. These materials usually have high proton conductivity; commonly used carrier materials are mainly carbon-based materials, including graphene oxide (GO), carbon nanotubes (CNT), and graphene quantum dots (GQD), which have good thermal stability. As is shown in Figure 5, Zhang et al. [111] prepared high-temperature Nafion composite membranes with phosphoric-acid-functionalized GO. GO prepared by the Hummers method was coated with polydopamine, and the phosphate functional group was grafted onto the surface of GO. Phospho-functionalized GO doped into the composite membrane can not only provide more proton transport sites but also improves the water absorption and retention capacity of the composite membrane. At the same time, the phosphate groups are evenly distributed on the surface of GO, and the unique layer structure of GO helps to form new proton transport channels, especially under high-temperature and low-humidity conditions. Finally, the proton conductivity of the composite membrane was 6.6 times that of the pure Nafion film at 80 °C and 40% RH. Ahmed et al. [112] prepared Nafion/GO composite membranes and tested them at high temperatures (100–120 °C) in fuel cells. The results showed that the composite membranes demonstrated better water absorption and mechanical stability. The single-cell performance and battery durability were significantly improved. Yin et al. [113] made use of sulfonated carbon nanotubes (Su-CNTs) and Nafion to prepare a composite

membrane, shown in Figure 6. When the sulfonated carbon nanotubes were doped into the Nafion matrix, the microstructure in the membrane changed, forming a large number of proton transport channels, especially under the conditions of high temperature and low humidity. Carbon nanotubes effectively connect isolated, water-containing clusters, greatly improving proton transport efficiency. Wu et al. [114] used graphene quantum dots (GQD) and other quantum dot materials to modify the hydrophilic and hydrophobic regions of Nafion membranes, respectively, at the molecular level. The modification of the hydrophobic backbone by graphene quantum dots reduced the crystallinity and increased the water absorption of the composite membrane. Aiming for the commonly used phosphorylation and sulfonic acid modification at high temperature, Firouz et al. [115] studied the synergistic effect of sulfonic acid groups and phosphoric acid groups on the proton conductivity and the performance of high-temperature fuel cells. Theoretical calculations found a synergistic effect of the amphoteric and hygroscopic properties of the phosphoric acid group on the conductivity of the sulfonic acid groups. Meanwhile, the highly sulfonated side chain could improve the free volume in the membrane and form a hydrophilic channel.

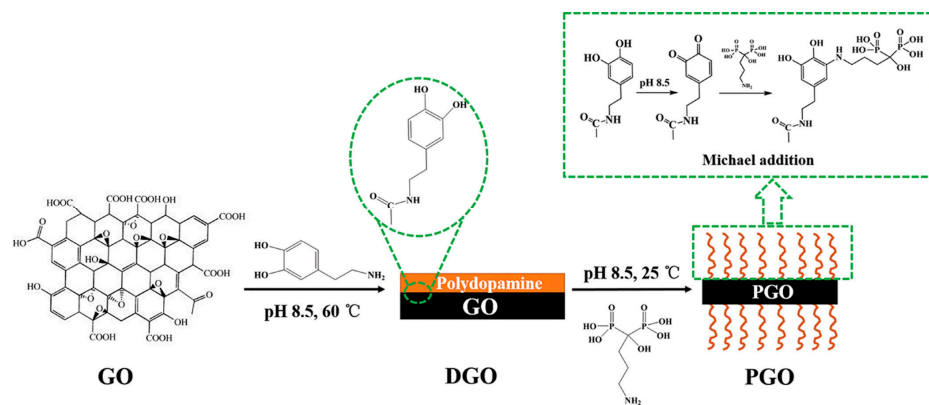


Figure 5. Synthetic process of DGO (polydopamine modified GO) and PGO (phosphonic acid functionalized GO) [111].

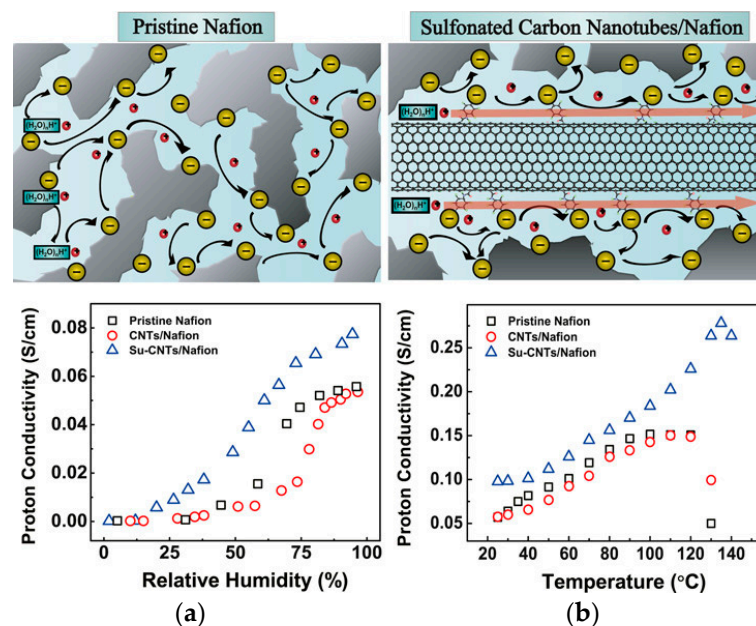


Figure 6. Schematic illustrations of proton transportation in water-hydrated (a) pristine Nafion membranes with tortuous proton pathways and (b) Su-CNTs/Nafion membranes with proton highways along Su-CNTs [113].

In addition to carbon-based materials, other functional-group-modified materials are often used in the high-temperature modification of Nafion membranes. Maiti et al. [116] prepared a Nafion composite membrane using an imidazole ionic liquid functionalized by dihydrogen phosphate. The thermal stability of the composite membrane was improved, and its proton conductivity reached 0.061 S/cm at 110 °C without humidity. Its maximum output power was 13 times that of the commercial Nafion117 membrane. Klose et al. [117] prepared Nafion composite membranes with high durability using sulfonated polyether ketone nanofibers prepared by electrospinning. The current density of the nanofiber-reinforced composite membranes did not increase appreciably in the humidity cycle test while an open circuit voltage was maintained. The degradation rate of the nanofiber-reinforced composite membrane was about 1.0 mV/h in the chemical accelerated stress test (90 °C, 30% RH).

3.4. Promote Proton Conduction Materials

Promote proton conduction materials usually have the following characteristics: (1) they may have a proton conduction capacity; or (2) the proton transport channel can be reconstructed through a special treatment or structural design. Phosphoric acid and some ionic liquids have been investigated among this type of material.

Yan et al. [118] studied the proton conductivity of Nafion composite membranes doped with phosphoric acid by molecular simulation. The calculated results showed that phosphoric acid is a good solvent to promote the proton ionization of the sulfonic acid group, and only two phosphoric acid molecules were needed for the dissociation of a sulfonic acid group. The transfer of protons between phosphoric acids is called the “jumping mechanism”. When the concentration of phosphoric acid is lower than the swelling concentration in the Nafion membrane, the phosphoric acid cannot form a continuous sub-phase in the membrane and the proton jumping path is interrupted; therefore, the proton conductivity of a composite membrane is lower than that of the original phosphoric acid. As the concentration of phosphoric acid is further increased, the main chain of hydrophobic polytetrafluoroethylene (PTFE) tends to gather to form a hydrophobic phase. Phosphoric acid and hydrophilic sulfonic acid groups can form a continuous proton transport channel, and the proton can be transferred uninterruptedly, such as in pure phosphoric acid, which is expected to obtain a high proton conductivity. Molecular dynamics studies also show that phosphoric acid and sulfonic acid anions have similar hydrogen bond characteristics. In the high-temperature modification of Nafion with phosphoric acid, PBI is usually introduced to prepare a binary composite membrane. Aili et al. [119] prepared a series of phospho-doped Nafion, PBI, and Nafion/PBI binary composite membranes. The experimental results showed that when the mass fraction of Nafion was 88%, the adsorption capacity of the composite membrane on phosphoric acid was at its minimum. The authors suggested that this may be related to the complete ion cross-linking between Nafion and PBI polymers. Polymers with a high viscosity show a very high swelling resistance. Since Nafion is more acidic than phosphoric acid, the ionic interaction between Nafion and PBI would not be affected by phosphoric acid. Therefore, the complex formed by Nafion and PBI remains intact. Zhai et al. [120] prepared a phosphorus-doped Nafion/PBI binary composite membrane and conducted a study on the durability of the composite membrane in high-temperature fuel cells. The study showed that the existence of Nafion enhanced the mechanical properties of the composite membrane, so the durability of the composite membrane was also improved. Kim et al. [121] systematically studied the high-temperature properties of Nafion/phosphoric acid composite membranes containing imidazoles (e.g., benzimidazole, 1,2,3-benzotriazole, pyrazole, and isopyrazole) with a proton conductivity of 0.23 S/cm at 150 °C. Yin et al. [122] loaded phosphoric acid molecules into the covalent organic frameworks (COFs) and prepared a composite membrane with Nafion. The acid–base pairs formed between the phosphoric-acid-loaded COF material and the Nafion can optimize the interface interaction and the hydrophilic region. Phosphoric acid provided abundant proton transfer sites and the proton transfer energy barrier was further

reduced. The composite membrane showed an excellent proton conduction efficiency under low-humidity conditions. In recent years, ionic liquid materials as high-temperature electrolytes are often used to prepare composite membranes with Nafion due to their high proton conductivity, good thermal stability, and fine physical properties. Yang et al. [123] used 1-butyl-3-methylimidazole ionic liquid to prepare a Nafion composite membrane. Under the condition of 160 °C without humidification, the proton conductivity of the composite membrane reached 0.0109 S/cm and the tensile stress was 5.3 MPa. Lu et al. [124] prepared Nafion composite membranes with a series of methylimidazolide ionic liquids. The ionic conductivity was 0.006 S/cm at 130 °C without humidification. The authors believed that the ionic conductivity would be affected by whether the ionic liquids were evenly filled in the Nafion matrix, and the composite membrane would have better stability. Sunda et al. [125] used an amino ionic liquid and Nafion matrix to prepare a composite membrane. A molecular dynamics simulation was used to study the structure and kinetic characteristics of the composite membrane with different doping amounts of ionic liquid. The results showed that hydrogen bonding mainly existed between the amino cationic acid site N-H and the sulfonic acid group of the Nafion. The distribution of sulfonic acid groups around amino cations improved with the increase of the ionic liquid concentration.

4. Modifying Methods Applied to Nafion Membranes

As with modifying agents, different modifying methods also have different effects on the performance of composite membranes and even fuel cell systems. According to the different application environments and performance requirements of Nafion composite membranes, an appropriate modification strategy was selected. Modifying methods in many types of research can be summarized into two categories: the “solution-casting method” and the “swelling-filling” method.

4.1. The Solution-Casting Method

Solution-casting, also known as hybridization or blending, is the most common Nafion-membrane-modification method. In order to improve the performance of Nafion, composite membranes are usually prepared by modifying materials with certain characteristics and a Nafion matrix. Mixing the modified material and Nafion solution using the solution-casting method to prepare the composite membrane is the simplest and most effective modification approach. For example, in the high-temperature modification of Nafion with silica, materials with good hygroscopicity are usually used for the modified material, such as silica and titanium dioxide. These are directly added to the Nafion solution, mixed evenly, and directly cast to prepare a composite membrane. The water retention capacity of composite membranes is usually significantly enhanced, and the high-temperature performance is greatly improved. Lee et al. [126] prepared high-temperature composite membranes by mixing functionalized, mesoporous silica with a Nafion solution by the direct solution-casting method. The high-temperature conductivity of the composite membranes was significantly improved, and the output power of fuel cells was also greatly improved. Zhang et al. [127] prepared amino-functionalized, mesoporous silica by selective etching. The composite membrane was further prepared by solution casting. The proton conductivity of the composite membrane reached 0.175 S/cm at 180 °C without humidification. Ketpang et al. [128] prepared Nafion composite membranes by evenly mixing porous zirconia nanotubes with Nafion solution. The excellent water retention capacity and the tubular structure of the fillers made it easy for water to diffuse through the membranes. Thus, the proton conductivity of the composite membranes was significantly improved under both fully wet (100% RH) and anhydrous conditions. At 0.6 V, the fuel cell assembled with the composite membrane showed 1.2 times the power density at 50% RH when compared to the pristine membrane, and also demonstrated better durability.

In addition to the high-temperature modification of Nafion, the solution-casting method is also widely used in other aspects, such as the improvement of the methanol resistance of Nafion. The advantages of this method are that it is simple, efficient, and

targeted, without complex physical or chemical processing processes, and it can compensate for the defects of the membrane materials. However, after further study, it was found that the simple mixing of the filler and matrix (mostly physical mixing, as it is difficult to achieve blending at the molecular level) often caused a problem of poor compatibility between the filler and matrix, especially in the preparation of Nafion composite membranes with an inorganic filler. Due to the compatibility between matrix and filler, the composite membrane undergoes an obvious phase separation, which has adverse effects on the mechanical properties and thermal stability of the composite membrane and directly affects its practical application in the fuel cell system. Even in the modification operation, researchers consciously modify the inorganic filler, such as through sulfonation, which can avoid the compatibility problem between the matrix material and the filler to a certain extent. However, the distribution of the filler in the matrix is still worthy of attention. With simple stirring and ultrasonic mixing it is difficult to achieve the uniform distribution of the filler in the matrix, and some materials with small particle sizes are agglomerate easily, which has an important impact on the modification effect.

4.2. The Swelling-Filling Method

Compared to the traditional “solution-casting” method, the advantage of the “swelling-filling” method is that it can realize the non-destructive modification of the membrane material; that is, minimize the impact on the matrix material. For Nafion, this modification method can be divided into two processes: “swelling” and “filling”. Firstly, appropriate solvents, such as water, alcohols, and mixtures, are selected to cause the Nafion to swell in the solvent. By controlling the temperature and solvent ratio, the excessive swelling of the membrane material is avoided and the long chain structure is fully opened, but the molecular bonds are not broken. The filler molecules are then dispersed in the solvent to fill the Nafion membrane under the action of a concentration gradient. Finally, the solvent is dried, and the filling is evenly dispersed inside the membrane. The whole process does not destroy the original macromolecular structure of the Nafion membrane, which further avoids the separation of the hydrophobic and hydrophilic phases formed by recasting. The uniform distribution of filler molecules can not only improve the specific properties of Nafion membrane but also maintains the integrity of the original structure, so that the performance of the composite membrane in other aspects will not be affected. Therefore, a non-destructive, targeted modification of Nafion membranes can be achieved. Based on the above “swelling” and “filling” processes, using the special phase separation and cluster structure in Nafion membrane, fillers with certain special properties can be directionally filled into the Nafion membrane to achieve molecular-level filling and greatly improve the modification effect.

Li et al. [129] proposed the idea of “swelling-filling” reconstruction for the first time. Polymer materials with proton conductivity were filled in situ into a Nafion membrane, which realized the nanoscale filling of Nafion. The proton conductivity methanol resistance and direct methanol fuel cell (DMFC) performance were significantly improved. Li et al. [130] further used this method to nondestructively fill graphene quantum dots into the Nafion membrane skeleton structure to achieve the physical barrier effect of quantum dots on methanol molecules. The results demonstrated that the methanol resistance performance of the composite membrane was significantly improved. Based on the “swelling-filling” method, Li et al. [131,132] further investigated the influence of different particle sizes of silica and different forms of organic polymer materials on the application of Nafion composite membranes in DMFC. The “swelling-filling” modification strategy has been successfully applied to improve the performance of Nafion membrane in DMFC. However, it has not yet been tested in the high-temperature modification of Nafion membranes.

Xu et al. [133,134] further explored the high-temperature and low-humidity modification of Nafion based on the “swelling-filling” nondestructive modification strategy. In the composite membrane, the original, ordered nanophase separation in the Nafion mem-

brane was maintained, and the water retention capacity of the composite membrane was significantly improved. At 110 °C and 60% RH, the proton conductivity of the composite membrane reached 0.033 S/cm, which was 30% higher than that of the pristine Nafion membrane. At the same time, the mechanical stability of the composite membrane was also enhanced due to the rich hydrogen-bond attraction between the silica nanoparticles and Nafion chains. In the above work, although the uniform filling of silica in Nafion can be achieved, silica enters the Nafion framework structure when the Nafion membrane swells in the solvent and will be dispersed throughout the membrane. However, it is the hydrophilic region of the membrane material that plays a crucial role in the high-temperature conductivity of the composite membrane. Due to the evaporation of water molecules in the cluster structure at high temperatures, the conductivity of protons decreases rapidly. Therefore, if the cluster area can be filled accurately and directionally, the modification effect of the composite membrane will be greatly improved.

Based on this consideration, the targeted filling of Nafion membranes was proposed. Mauritz et al. [135,136] proposed an in situ sol–gel method with a sulfonic acid group on Nafion as the catalytic site. This was used to modify the Nafion membrane with inorganic fillers. Taking silica as an example, in this method, tetraethyl orthosilicate was used as a precursor of silica. Under the acidic catalysis of the sulfonic acid group, Tetraethyl orthosilicate was hydrolyzed in situ to produce silica. Xi et al. [137] prepared a Nafion/silica composite membrane using the in situ sol–gel method to reduce the permeability of vanadium ions in vanadium flow cells. Chen et al. [138] made Nafion/zeolite composite membranes with the same method, and the methanol permeability was significantly inhibited. However, there are two drawbacks that hinder the practical application of this method. First, silica easily grows on the surface of Nafion, which blocks the proton transport channel in Nafion, making the sol–gel reaction at room temperature uncontrollable. Secondly, an uncontrolled sol–gel process reduces the mechanical strength of Nafion. This is because many ethanol molecules are generated during the hydrolysis of silicon precursors (such as tetraethylorthosilicate) and Nafion chains are damaged by swelling. In order to overcome these shortcomings, Dresch et al. [66] tried to modify Nafion membranes by this “sol–gel” method using different ethanol solvents. However, the growth of silica particles was reported to occur in both the ionic and non-ionic domains of Nafion. This will destroy the original nanophase separation structure, and the mechanical strength may also be affected. Xu et al. [134,139–141] further realized the controllable filling of silica in Nafion membranes based on the “swelling and filling” and “sol–gel” strategies, shown in Figure 7. By controlling the in situ “sol–gel” reaction at low temperatures (0 °C), a tetraethoxysilane (TEOS) solution was used as a precursor of silica, which was employed to fill the Nafion skeleton with solvent and was introduced into the $-\text{SO}_3\text{H}$ ion clusters. Here, the $-\text{SO}_3\text{H}$ group was used as the catalyst for the hydrolysis of TEOS instead of the added acid. Thus, the silica network grew inside the ion cluster and was self-anchored as a “water reservoir” by the $-\text{SO}_3\text{H}$ group.

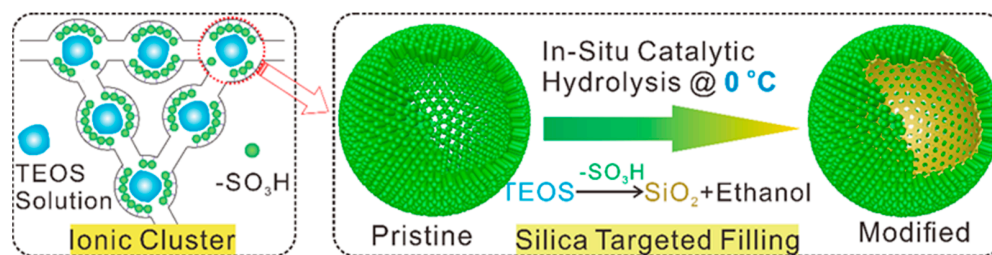


Figure 7. Schematic of the in situ, controllable sol–gel reaction of silica in the ionic cluster of the Nafion [134].

5. Summary and Outlook

It is difficult to enhance the overall high-temperature performance by improving the molecular structure or proton conduction mode individually. Therefore, the addition of

other components is an effective approach to further expanding the high-temperature application potential of Nafion membranes. However, the compatibility of the filler with Nafion matrix and the deterioration of the mechanical properties of the composite membrane still require attention. The surface functional-group modification of fillers in a multi-component composite and the application of nano-fiber materials effectively solve the above problems. Of course, the composite mode and modification efficiency still need to be further explored. In addition to the filler, the choice of modification method also has an important impact on the performance of the composite membrane. "Solution-casting" has the advantages of being a simple preparation process with an obvious modification effect, but it also has the disadvantages of destroying the original nanophase separation structure and proton transport channel. By employing the strategy of "swelling-filling", these problems can be avoided and doping at the molecular level can be achieved. The results have shown that the destruction of the original phase-separation structure will cause serious damage to the proton conductivity and mechanical properties of the composite membrane.

Based on the structural characteristics of hydrophilic/hydrophobic phase separation and the functional characteristics of different phases leading to different properties, the modified material was first filled in the hydrophilic cluster in situ to rebuild the proton transport channel. Fractional synergy enhances the proton conduction efficiency. Secondly, the non-destructive filling of modified material in the hydrophobic phase is achieved by the swelling-filling method, which further improves the comprehensive stability of the composite membrane. Finally, the efficient synergy of the two-phase region is confirmed by the chromatography technology, electrochemical measurements, and morphology.

Although the application of Nafion membranes has been extensive and highly developed, it is still necessary to continue studying the Nafion membrane itself, including relevant qualities such as cost control, environmental friendliness, glass transition temperature, and so on. Based on the material structure–performance relationship, the excellent Nafion or composite membrane can be prepared to achieve a long-term operation in an HT-PEMFC and promote the practical application of HT-PEMFC technology.

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