

# High Temperature Proton Exchange Membrane Technology Improvement based on Improved Melt Extrusion Method

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**Abstract**—High temperature proton exchange membrane is the bottleneck of fuel cell technology at present. The development of high temperature proton exchange membrane can make fuel cell technology mature and play a decisive role in solving energy crisis, environmental pollution and greenhouse effect. In this paper, two feasible methods of high temperature proton exchange membrane technology are compared and analyzed, and an improved melt extrusion method is proposed to improve high temperature proton exchange membrane technology.

**Index Terms**—fuel cell, high temperature proton exchange membrane, hydrogen bond

## I. INTRODUCTION

Increasing the working temperature of fuel cell is one of the effective measures to solve water management and catalyst poisoning. It is known that when the temperature exceeds 120°C, the influence of CO on the catalyst is obviously reduced, and at this time the water discharged from the battery exists in the form of gas, thus the drainage system is greatly simplified, simultaneously the reaction rate between the anode and cathode is increased, and further the working efficiency of the battery is improved [1]. The currently used Nafion membrane of perfluorosulfonic acid type uses water as the proton conduction medium, and the water in the membrane evaporates after the working temperature is below 80°C and more than 100°C, causing the proton conductivity to drop sharply. Therefore, it is necessary to increase the operating temperature of the proton exchange membrane first to increase the operating temperature of the battery.

At present, there have been many experiments to raise the working temperature of proton exchange membrane. For example, Tao Rong et al. have synthesized a quaternized poly (arylene ether ketone) polymer with excellent film forming property and good thermal stability [2]. Shuaiyuan Han et al. have made good progress in the study of high temperature proton exchange membrane based on phosphoric acid group [3]. There are two more feasible methods among these methods. One is to use high boiling point protic solvent instead of water as proton conducting medium. He et al. used phosphoric acid as PBI membrane of protic solvent under the conditions of 200°C and relative humidity 5%,

and a conductivity of 0.068s/cm was obtained [4]. The other is to add hydrophilic inorganic solid oxide into the membrane to enhance the water retention capability of the membrane. Mauritz research group and Osborn research group have successively proposed Nafion membrane doped with nano-silica [5, 6].


Based on this, this paper analyzes the essence of proton transfer between the two methods is the same, the difference is that the former is a liquid medium and the latter is a solid medium. The former has the advantage of high proton conductivity, but the disadvantage is that the liquid medium will lose water with the reaction, resulting in the membrane not working. The latter has the advantages of stability, no loss of conductive medium, and the disadvantage of low proton conductivity. Aiming at the shortcomings, this paper puts forward corresponding improvement measures.

## II. HIGH TEMPERATURE PROTON EXCHANGE MEMBRANE TECHNOLOGY IMPROVEMENT

### A. Proton Transfer Principle and Internal Structure of Traditional Nafion Membrane

Gierke and Hsu et al. put forward the ion cluster network model on the basis of small angle x-ray diffraction. It is believed that there is a certain loose type between fluorocarbon skeleton, ions and solvents, thus reverse micelles inside the material are formed and spherical structures with diameters of about 3-5nm are aggregated into. The specific size is determined by the hydration degree. These spherical structures are connected by short narrow channels with a diameter of 1-2nm, thus formed a network and provided channels for ions [7-9].

In Fig.1, the ion cluster is composed of water molecules. Hydrogen bonds OH-----O exist between water molecules, bringing water to cluster together, because hydrogen bonds  $R-SO_3H \cdots H_2O$  are also

formed between  and  $R-SO_3H$ , and sulfonic acid groups are connected to the polymer matrix through covalent bonds. Therefore, ion clusters composed of water molecules are fixed on the inner wall of the channel.  $H^+$  forms to Hydrogen bonds with water molecules and becomes hydrated hydrogen ions to be

transported in the membrane.  $H_2O + H^+ \rightleftharpoons H_3O^+$ . Thus, the essence of water as a transport proton is that hydrogen bonds can be formed by protons. In the process of hydrogen bonds breaking and forming,  $H^+$  is transferred from one water molecule to another, thus the function of proton exchange is realized through the inner channel of the membrane.

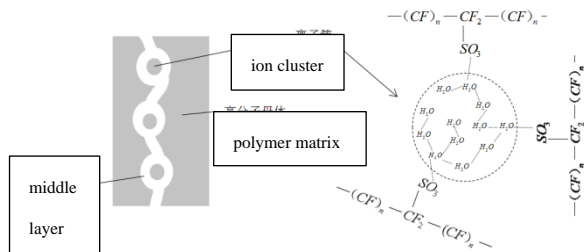


Figure 1. The ion cluster structure

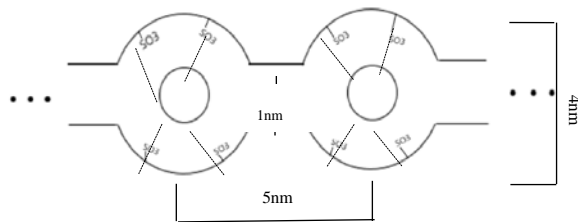


Figure 2. Microstructure of perfluorosulfonic acid membrane

**B. Comparative Analysis of High Temperature Proton Exchange Membrane Technology**

Two kinds of technical ideas are mentioned in the introduction to raise the working temperature of proton exchange membrane. First, the former one is that imidazole, phosphoric acid and other high boiling solvents are used to replace water as the medium of proton transfer. Take imidazole as an example (see Fig. 3).

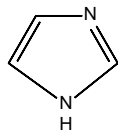
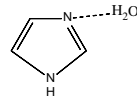


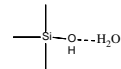
Figure 3. Imidazole structural formula

In Fig. 3, The N atom located in the upper right corner can easily attract  $H^+$  to form hydrogen bonds and the H atom below another imidazole molecule, so imidazole molecules can be clustered together in large numbers through hydrogen bonds. Thus, imidazole molecules behave similarly to water molecules in the membrane, so they can be used as a medium of transmission. Moreover, because imidazole has a high boiling point, the operating temperature of the exchange membrane using imidazole as a medium is also relatively high, reaching about 180°C. However, the problem of this method is also very serious. Imidazole molecules will form hydrogen bonds



with water molecules, and will be lost together with the water generated by the battery reaction.

In another method, Manritz research team doped nano-silica particles in Nafion films to improve the water retention of the films [3]. However, under high temperature conditions, because water becomes gaseous, most protons are not transported by water molecules in the membrane but are transported by hydrogen bonds



formed between silicon hydroxyl groups on the

surface of nano-silica particles and  $H^+$ . Although the silicon hydroxyl group can also be combined with water molecules through hydrogen bonds, and then  $H^+$  is transferred with water molecules, but most of  $H^+$  are transferred directly through the silicon hydroxyl group (see Fig. 4).

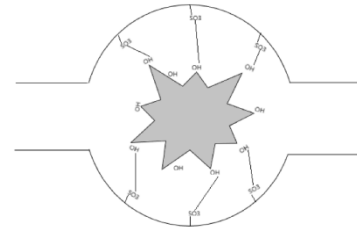


Figure 4. Microstructure of nanoparticles  $SiO_2$  in membrane

Because the nano-silica particles are solid, it seems that  $H^+$  can only be transported on the surface of the particles, while liquid clusters such as water and imidazole can be transported through the interior, which explains why the proton conductivity of the proton exchange membrane doped with nano-silica particles is much lower than that of the proton exchange membrane using liquid media under the same conditions. But also because it is solid, the media will not lose and will be relatively stable.

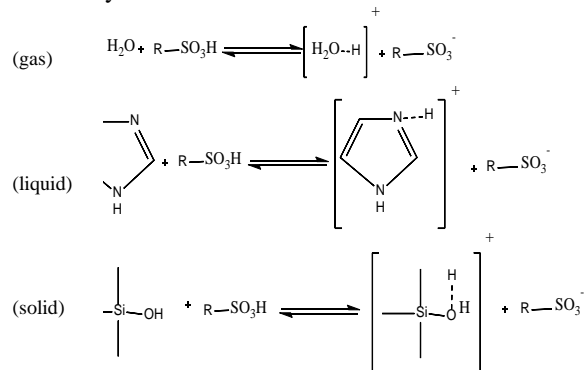


Figure 5. Hydrogen bond production of three media at 160°C

As can be seen from Fig. 5, transmitting  $H^+$  using these media is essentially the same, all through hydrogen bonds. At present, the problem of loss caused by the use of liquid media does not seem to be solved, while solid

media can improve proton conductivity by increasing the distribution density of silicon hydroxyl groups on its surface.

### C. High Temperature Proton Exchange Membrane Technology Improvement

There are a large number of silicon hydroxyl groups on the surface of silica gel, about a few to a dozen per square nanometer, far more than silica. In theory, the conductivity of the membrane doped with silica gel will be greater than that of the membrane doped with the same proportion of silica under the same conditions. In order to verify this conjecture, this paper makes a comparative experiment between the traditional membrane doped with silica and the traditional membrane doped with silica gel. However, before the comparison test, the problem of doping technology must be solved first.

According to Mauritz research group's experiments [5], the doped traditional membrane will cause local damage when operating in high temperature and low humidity environment due to the uneven distribution of silicon dioxide impurities in the membrane. Therefore, the doped membrane must be recast. According to Tang et al. [10], the impurity distribution of silicon dioxide in the recast membrane is uniform, and the diameter of silicon dioxide particles is confirmed to be about 3.0nm by projection electron microscopy experiments. However, this kind of recasting method requires molds, which is extremely expensive and cannot be produced in large quantities. At present, this kind of inefficient casting method is mostly used in China, while DuPont company in the United States uses melt extrusion method, which is extremely efficient and has always been monopolized by DuPont company. This method uses the principle that the melting temperature of perfluorosulfonic acid resin differs greatly from the initial decomposition temperature, and directly extrudes the resin from the extruder after melting [11]. However, due to the fact that the "pinhole" problem cannot be solved during the melt extrusion process in China, we have to turn to the mold casting method [12].

In this paper, an improved melt extrusion method is proposed to make membrane. First, the extrusion outlet of the extruder is lengthen. The extrusion outlet is made of two thin metal plates with two 30nm thick graphene sheets sandwiched between them. The outside of the extrusion outlet is covered with a condensing tube. Thus, the melted resin has been cooled and formed before being extruded into the air, so there will be no "pinhole" problem due to cooling and evaporation in the air. In the process of preparing the doped membrane, nano-silica particles or silica gel particles are directly put into the molten resin liquid, and then extruded and molded from the extruder. The experimental results show that the conductivity of the proton exchange membrane doped with silica is 0.016s/cm at 130°C, while the conductivity of the proton exchange membrane doped with silica is 0.073s/cm at the same temperature, which is obviously higher than that of the silica membrane. Therefore, it is presumed to be true.

### III. CONCLUSION

High temperature proton exchange membrane is very important to fuel cell technology and is the key factor to make it mature. Therefore, the research on fuel cells should focus on the research and development of high temperature proton exchange membranes.

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