

Research Progress in Proton Exchange Membrane Fuel Cell

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Abstract. The massive combustion of non-renewable fossil fuels causing global warming has raised concerns. However, fuel cells, including proton exchange membrane fuel cells, face challenges such as short lifespan and high cost, hindering their large-scale commercialization. The objective of this paper is to explore the growth, practical utilization, concerns, and enhancement techniques of proton exchange membrane fuel cells, which are a promising source of renewable energy. Research indicates that the lifespan of Proton Exchange Membrane fuel cells (PEMFC) is influenced by the conditions of the reaction environment. The high expenses associated with these cells can be largely attributed to the inflammability and explosiveness of hydrogen, the primary raw material, which can present transportation challenges. Moreover, the use of precious metals as reaction catalysts can result in poisoning, which restricts their application to a narrow spectrum. In conclusion, further improvements are necessary for the future application of PEMFC. More innovations are needed to expand the application areas by using more efficient and safe materials that are easier to transport. To broaden the way for the future development of green new energy. This paper is a valuable resource for improving proton exchange membrane fuel cell technology.

Keywords: Proton exchange, membrane fuel cell, hydrogen energy, lifetime.

1. Introduction

The carbon dioxide produced by the massive combustion of oil extracted from fossil fuels, which is a non-renewable resource, has led to the worsening of global warming, and new energy fuel cells, which were proposed in the 20th century, have begun to receive a great deal of attention again. Green and environmentally friendly hydrogen as raw material for new energy battery technology is developing rapidly, and its application is also widespread. Its green and clean advantages make people feel at ease at the same time, the high energy conversion rate, high power, and safety of the generated material are also extremely convenient and also be regarded as the future of the automobile power source. However, the problems of difficult transportation and the high cost of hydrogen energy have also come to light. This has caused people to reduce the use of new green energy, but it has also exacerbated the problem of environmental pollution, forming a vicious circle.

To maximize the solution to this problem, the proton exchange membrane as an important component in fuel cells has become one of the hot spots in new energy research. Countries have also provided the basis in terms of the upcoming progression of PEMFC. For example, China has formulated policies related to modern energy systems in the 14th Five-Year Plan, as well as the 2020 Long-Term Plan for the Development of the Hydrogen Energy Industry and the Strategic Plan for Hydrogen Energy, which provides guidelines currently engaged in the advancement of PEM fuel cells.

This article aims to improve the efficiency and security of proton exchange membrane fuel cells., which are crucial components of new energy technology. Firstly, it reviews the current development of proton exchange membrane fuel cells and their various applications, including the Nafion series of membranes. Additionally, it outlines some of the challenges associated with fuel cells, such as hydrogen transportation, metal poisoning, and membrane degradation due to water content. Lastly, the article proposes potential solutions for future improvements, including organic/inorganic nanocomposite plasmonic exchange membranes, extending membrane lifespan, and developing self-humidification proton exchange membranes.

2. PEMFC's Development

PEMFC has its origins in the early 1960s when NASA proposed it as a reliable and efficient energy system. The issue of environmental pollution and global warming continues to deteriorate, people are increasingly focused on environmental protection and sustainable development. The world recognizes that new energy fuel cells are an important way to protect the environment in the future, and they are an essential and significant part of the clean energy system. The application of renewable energy sources such as hydrogen, wind, and solar can decrease reliance on traditional sources of energy. Hydrogen is safer, more efficient, and sustainable, and the technology for its application is now more mature. Furthermore, the high energy density and conversion efficiency of PEMFC make it a powerful source for automobile transportation, resulting in improved range capability. As a result, PEMFC is now commonly utilized in power research and development within the transportation industry.

The state has implemented policies to support the development of hydrogen fuel cells, the growth of the hydrogen energy industry, and the commercialization of fuel cell applications. However, the current domestic proton exchange membrane is still in the experimental testing phase and only produced in small batches, unable to meet the demands of industrialization. Increased basic research efforts are necessary. Developing proton exchange membrane fuel cells is a long road due to technical, financial, and environmental challenges. According to the Medium and Long-term Plan for the Development of Hydrogen Energy Industry (2021-2035) and China's Hydrogen Energy and Fuel Cell Industry White Paper, it is projected that by 2025, China's hydrogen fuel cell vehicle ownership will range from 50,000 to 100,000. Furthermore, the widespread adoption of hydrogen energy and fuel cell vehicles is anticipated to occur between 2030 and 2035 [1].

3. Application of PEMFC

Extensive research has enabled the proton exchange membrane fuel cell to be widely used in practical applications. This kind of green new energy battery can not only reduce people's over-dependence on the use of fossil energy but also reduce the pollution of the environment. PEMFCs have a variety of applications, including powering cell phones, large-scale power stations, backup power, as well as transportation such as cars, underwater submarines, and drones. Nowadays, most of the proton exchange membranes have been characterized by high proton conductivity, low fuel crossover, good thermal stability, and good chemical and mechanical structural stability. In addition to this, the low preparation cost of proton exchange membranes is one of the reasons why they have been put into mass use. At present, most of the commercialized proton exchange membranes at home and abroad are composed of perfluorinated polymer main chains with sulfonic acid side chains, and the most representative of them are Nafion series membranes. Perfluorinated sulfonic acid membranes are highly stable chemically, conductive at high humidity, and have high current density at low temperatures. With the continuous advancement of fuel cell technology, the range of available proton exchange membranes (PEMs) is increasing. These membranes can be classified according to the level of fluorine content within the polymers. The three primary categories include perfluorinated sulfonic acid proton exchange membranes, partially fluorinated proton exchange membranes, and non-fluorinated proton exchange membranes [2]. However, due to the difficult preparation, and high cost, fluorine and the waste product are not easy to deal with and the proton conductivity and membrane water content are closely related to the design of the humidification membrane complexity and other shortcomings, restricting the perfluorosulfonic acid membrane in the PEMFC in the commercial application of a large number of scientific researchers began to make improvements, began to develop a more efficient, lower-cost environmentally friendly non-fluorinated proton exchange membrane [3].

According to the International Energy Agency (IEA) report, the global fuel cell system is expected to reach 4 million units in the next ten years and will increase at an annual growth rate of 30% [4]. Increasingly, people are turning their attention to alternative and sustainable energy sources, while

also investigating the potential of batteries such as PEMFCs. These innovative batteries have the capacity to supplant the use of fossil fuels, which are currently a major contributor to the problem of climate change. As a result, they can be employed in a wide range of practical applications.

4. Problem and Measure

4.1. Problem

The primary substance used in proton exchange membrane fuel cells is hydrogen, which is typically stored and transported through low-temperature liquid storage, high-pressure liquid storage, and metal hydride storage methods. However, hydrogen is highly flammable and explosive, which poses a significant safety risk to individuals if leaked. Additionally, hydrogen has a high permeability rate, which means that traditional containers are unable to fully prevent leaks. Maintaining stability at high pressure also adds to the complexity and cost of hydrogen storage and transportation, contributing to the failure of hydrogen energy to be widely used.

Proton exchange membranes doped with phosphoric acid are currently the most advanced materials available. However, there have been some challenges with the introduction of new groups. While basic groups can enhance phosphate uptake through acid-base interaction, they may also compromise the mechanical strength of the membrane. Modifying the membrane structure to create porosity can boost phosphate uptake, but it can also reduce mechanical properties and increase the risk of phosphoric acid leakage, which can pose serious hazards such as poisoning.

Meanwhile, most of the proton exchange membrane fuel cells use precious metals as catalysts in the process. However, there are many poisoning factors of precious metals as catalysts: thermal poisoning, adsorption poisoning, poisoning of toxic agents, and poisoning of active sites, which can cause catalyst deactivation. For example, under high-temperature conditions, sintering, and melting may occur on the surface of the precious metal catalyst, which will lead to the loss of active centers and deactivation of the catalyst, resulting in higher reaction costs. Secondly, during the use of precious metal catalysts, the poisoned catalysts may release harmful substances, such as heavy metals or some volatile organic compounds, which will cause pollution to the environment and make the originally clean new energy batteries cause environmental pollution problems again.

Battery life is also a major problem found in the use of proton exchange membrane fuel cells, the reaction environment will have an impact on the nature of the battery material. The service life of the proton exchange membrane is affected by a variety of factors, and its acid and alkali resistance and high-temperature resistance are more important factors in the selection. The working environment of the fuel cell is usually high temperature and high pressure, which will lead to the aging and degradation of the membrane at a faster rate, The structure is also changing, and the performance of the membrane decreases until it fails, resulting in the shortening of the service life of the cell. At the same time, too high or too low moisture content will hurt the life of the membrane. Excessively high moisture content will cause deformation of the membrane after swelling, while excessively low moisture content will lead to phenomena such as drying and hardening of the membrane [5]. The catalyst's poor durability contributes to the short lifetime of proton exchange membrane fuel cells.

4.2. Measure

4.2.1. Organic/inorganic nanocomposite plasmonic exchange membranes

By improving the water retention capacity of the membrane as a way to expand the operating temperature of the fuel cell, it can also extend the service life of the proton exchange membrane. In 2009, Fei, 20Guoping et al. used sulfonated polysulfone, phosphotungstic acid, and silica sol as the raw materials to prepare an organic-inorganic composite proton exchange membrane such as nanoparticle-modified Nafion membrane nano-structural schematic diagram (Fig. 1) [3]. The conductivity of this membrane at 80°C was higher than the previously used Nation membrane proton conductivity, and the methanol permeability coefficient was much smaller than that of the Nation

membrane [6]. Back in 2017, Ying Ou et al. prepared an organic/inorganic nanocomposite plasmon-exchange membrane [7]; and it wasn't until 2022 that Cuicui Dong et al. proposed a nanosheet layer filler with alkaline functional groups on the surface and a sulfonated polyarylether ether sulfone consisting of a proton exchange membrane [8]. The proton conductivity and modification methods of different plasmon exchange membranes are shown in Table 1.

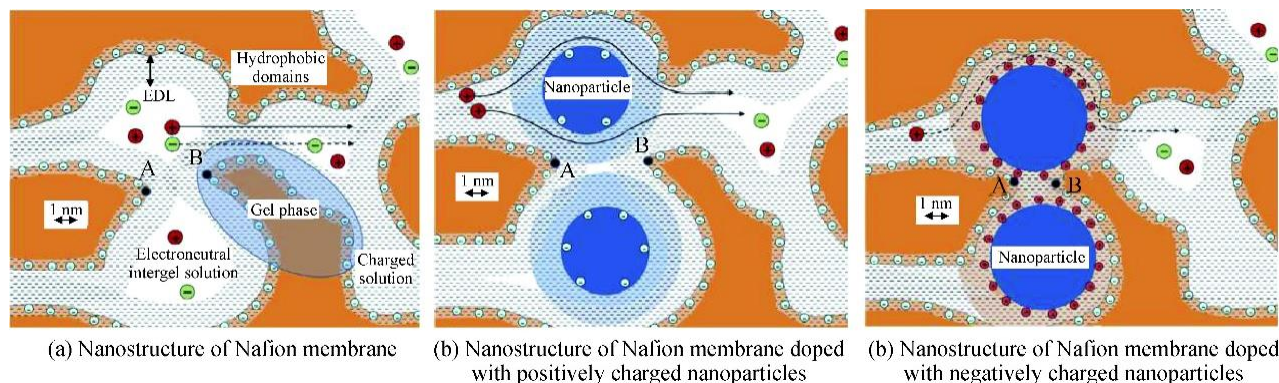


Figure 1. Schematic diagram of nanostructure of Nafion membrane modified by nanoparticles. <https://kns.cnki.net/KXReader/Detail?invoice=KFnHo8DCTM39zo8AYcILJGJatpnF8h8%2Fdaf2WBKqg0YRQREWCiBQn%2Fj6Yz5bUOIYLARAUGmaHx%2F1Hm%2FKRd8lnze0JERUR9dvDgk7cUXM3bk%2F5uuWOeVkkUwxRVA0GBYCY32aWc6sZxrtxNJOOfmRHDWraFvt1%2BIVsGfw4kJ5400%3D&DBCOD=CJFD&FileName=GSYT202209031&TABLEName=cjfdlast2022&nonce=58A74AE03252434AB853E62A990F5DEC&TIMESTAMP=1692435922865&uid=>

Table 1. Proton conductivity of PEMs.

Proton conductor	Polymer	Modification method	Relative humidity/%	Proton conductivity(S/cm)	Reference
Sulfonic acid	Nafion	Introducing hydrophilic SiO ₂	30	0.05	[9]
	SPSF180C	Optimization of hydrophilic channels	35	0.051	[10]
Phosphoric acid	IMPPO-M	Enhance acid-base interaction	0	0.1	[11]
Phosphonic acid	PBI2	Introducing sulfonic acid groups	30	0.126	[12]

Note: a is the upper operating temperature limit; b is the lower operating temperature limit; c is sulfonated poly (sulfide sulfone imide), SPSFI

4.2.2. Self-humidifying proton exchange membrane

The catalytic layer is the main place where chemical reactions occur in a proton exchange membrane fuel cell, i.e., improvements can be made in the catalytic layer to enable the cell to operate efficiently in low humidity environments [13]. Hydrophilic oxide particles, such as titanium dioxide and silicon dioxide, are doped into the self-humidifying proton exchange membrane material. The hydrophilic particles allow the membrane to absorb the water generated during the fuel cell reaction and maintain the membrane's humidity. After doping these hydrophilic oxides, according to different application environments and routes of use, the content and diameter of hydrophilic oxides can be changed to adjust the humidification performance of the membrane for application. In 2016, Yang et al. prepared a hydrophilic oxide-doped self-humidifying proton exchange membrane by introducing dispersed TiO₂ particles into Nafion membrane and found that a better humidification effect can be obtained after practice [14].

4.2.3. Improvement of PEMFC reaction ambient temperature

Enhancing the anti-CO poisoning capability of noble metal catalysts like Pt can improve the performance of PEMFC in high ambient temperatures, resulting in a reduced poisoning rate. Nonetheless, it is crucial to address the humidity issue effectively, as low humidity levels caused by the high temperature environment require attention.

5. Future development trends

To survive on Earth for a longer period, it is inevitable for people to focus on developing renewable and green energy sources. Among them, hydrogen fuel cells have already been developed and are being continuously explored for more permanent applications. When it comes to modifying the proton exchange membrane, doping can help the membrane adapt to different environments and improve its lifespan to a certain extent. However, this process also increases the manufacturing cost of the membrane. Further research and development is necessary before this approach can be widely implemented. The variety of noble metal catalysts for proton exchange membranes is limited to the Pt class, but researchers could explore other options for more possibilities.

Therefore, the design of new proton exchange membranes can be optimized by taking into account several factors. For low-temperature fuel cells, enhancing the hygroscopicity of the proton exchange membrane can further improve its practicality. Additionally, improving the stability of non-aqueous proton carriers can prolong the lifespan of proton exchange membranes in medium and high-temperature fuel cells. Perfluorinated material can also be used as a safer alternative for preparing proton exchange membranes, to ensure the safety of proton exchange membranes [15]. Fuel cells' utility can be enhanced by changing the ion types that pass through the exchange membrane while maintaining reactant separation.

6. Conclusion

The current development status, existing problems, and improvement methods of PEMFC are investigated. It is crucial to note that the genesis of PEMFC dates back to the early 1960s, with a gradual refinement of the membrane material and structure over time. As a result, PEM fuel cells have found increasing use in applications such as portable power supply, stationary power generation, and transportation. However, they are still undergoing experimental improvements, and further practical applications will be necessary to enable their widespread adoption. Numerous techniques are being researched to enhance the performance of proton exchange membrane fuel cells. These comprise utilizing composite materials, doping to alter materials, and selecting catalysts made of precious metals that are both efficient and secure. The goal is to elevate the mechanical characteristics and longevity of the proton exchange membrane, which will enable it to function in elevated temperatures and under reduced moderation states. PEMFC industrialization is still facing many problems, life and cost and other development bottlenecks still exist, but as science and technology continue to advance, the future application of fuel cells will certainly have further development. This paper provides ideas for the direction of the future enhancement of the proton exchange membrane.

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