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Dynamic Performance Enhancement of Hydrogen PEM Electrolyzer Membranes

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Abstract. With the development of globalization and public increase awareness of the greenhouse effect, and there are strategic objectives of peak carbon emission and carbon neutrality that are realized, building a clean, low-carbon, safe, and efficient new energy system has become a consensus in the global world. Under this background, hydrogen, with its clean, zero-carbon emissions (especially carbon dioxide, which contribute to the greenhouse) and high energy density far exceeding that of traditional energy sources, is widely viewed as a key strategic alternative energy source that leads the future energy revolution. Among the numerous hydrogen production technologies, water electrolysis, particularly the "green hydrogen" production route that deeply integrates with fluctuating renewable energy sources such as wind, photovoltaics, and some other, is highly attractive because it can effectively address the storage and absorption issues of renewable energy. It is recognized as one of the core pillar technologies for achieving deep decarbonization and achieving green transformation of the energy system. Among the different routes for hydrogen production (through compare with the alkaline membrane electrolysis and the solid oxide electrolysis cell, later AWE and SOCE will be used respectively to refer to), water electrolysis is an attractive process for integration with renewable sources of energy like wind and photovoltaics and is considered one of the key technologies to allow a green transition of energy systems. Proton exchange membrane electrolysis (PEM) technology has attracted much attention from the academia and industry in the previous years because of its significant advantages, including a large current density, high dynamic response speed, high hydrogen purity, and direct production of high-pressure hydrogen, which is more fitted to the active and unstable renewable energy. Nevertheless, the development of this technology is still hindered by precious-metal reliance, high cost, and low durability. This paper is expected to offer theoretical reference and technical support for the large-scale applications and the industrialization of PEM water electrolysis for hydrogen production, by systematically analyzing the research work of material optimization, process improvement, and system integration.

Keywords: PEM, Electrolytic Hydrogen Production, Hydrogen Energy Storage.

1. Introduction

Against the backdrop of the global "dual carbon" target, the green hydrogen market has enjoyed an unparalleled opportunity for growth. With its high-energy density and fast start, PEM is considered one of the most promising clean energy technologies for the 21st century [1]. However, it currently faces many challenges to develop. Currently, the worldwide hydrogen production relies primarily on fossil fuel reforming (gray hydrogen, which is corresponded to green hydrogen), and carbon emissions have severely hindered the development of sustainable hydrogen energy. Compared to the aforementioned methods, PEM water electrolysis is currently considered one of the most commercially viable hydrogen production methods since it offers good efficiency, outstanding dynamic response, and high compatibility with renewable energy sources. The first successful PEM water electrolysis was made by General Electric in the United States in 1966 and subsequently, e.g., applied in the life support of manned space flight in the 1970s [2]. The membrane electrode assembly (MEA) is its key component, which is a three-layer structure with a thickness of less than 1 mm, including a proton exchange membrane, a catalyst layer, and a diffusion layer. During the process, oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) appear at the anode and cathode respectively. No carbon dioxide or other harmful substances are generated in the entire process, so the product is referred to as "green hydrogen" [3].

Nevertheless, 2023 saw a 97 million tonne global market for hydrogen and yet only green hydrogen came in at below 1%. Besides, the global hydrogen market is expected to reach $260 billion in 2030, with green hydrogen (produced through water electrolysis using renewable electricity) expected to account for 30% of the market share. The planned production capacity was as high as 49 million tons/year by 2030; however, the intermittent and fluctuating characteristics of photovoltaic power generation severely infringe upon the performances of PEM electrolyzers, resulting in the technical bottlenecks of membrane electrode activity attenuation and efficiency decline. It is becoming the most promising solution for the utilization of intermittent renewable energy. In order to realize the industrial planning targets, the average annual growth rate must reach more than 90%, and the new problems such as unproven demand, financing difficulty, and policy lag will be handled. In this context, research has been dedicated to material, process, and system optimization, seeking to enhance dynamic response tendencies, decrease costs, and increase life duration [4]. From this point of view, how to solve dynamic performance optimization of PEM electrolyzers with respect to photovoltaic fluctuations has become the bottleneck of promoting green hydrogen commercialization [5-6]. The operating conditions of PEM electrolyzers are generally high voltage, high current, and under a strong acid environment, which makes the core components need extra coating treatment [7]. But precious metals with a high price and scarce source, such as iridium and platinum, and the complicated manufacturing equipment have largely limited the development of the technology [8-9]. In recent years, PEM electrolysis being coupled to the photovoltaic, energy storage, and fuel cell systems has also become more frequent. Coordinated control can not only increase hydrogen production efficiency but also improve the photovoltaic absorption capacity, achieve cross-time energy storage, and decrease the proportion of abandoned light [10]. This article methodically sorts out and analyzes the latest research progress in PEM water electrolysis hydrogen production in key materials, core components, manufacturing processes and system integration. Besides, it aims to summarize existing achievements and identify future potential development directions, and provide theoretical basis or technical support for promoting the large-scale and commercial application of PEM water electrolysis hydrogen production technology, in this way contribute to the green transformation of the global energy structure and the realization of the "dual carbon" goals .

2. Principle of water electrolysis for hydrogen production by using PEM

The global reaction of PEM electrolysis is the splitting of water molecules into hydrogen and oxygen. There is an oxidation reaction that occurs at the anode, breaking water molecules into protons (H^+), electrons (e^-), and oxygen (O_2). At the same time, there is a reduction reaction that occurs at the cathode, where protons and electrons react to produce hydrogen (H_2). Below are the reactions in the different parts of the PEM. In the electrolysis process, at the cathode, hydrogen ions gain electrons to produce hydrogen gas, while at the anode, water molecules release electrons to generate oxygen gas and hydrogen ions. Overall, the process involves the decomposition of water molecules into hydrogen and oxygen gases.

During this process, water molecules are broken down by an iridium-based catalyst at the anode. Protons are then conducted and transported through the proton exchange membrane to the cathode, where they react with electrons passing through the external circuit to produce hydrogen. In the process, the proton exchange membrane plays a significant role. The proton exchange membrane not only allows protons to selectively pass through but also effectively prevents the leakage of hydrogen and oxygen, reducing the explosion hazard and making the ion channel relatively stable. In contrast to alkaline electrolysis, PEM electrolyzers feature proton exchange membranes in lieu of asbestos membranes, drastically minimizing inter-gas diffusion and yielding high-purity hydrogen (>99.99%). They can also produce hydrogen directly under high pressure from 30 bar to 70 bar, thereby minimizing the energy used to compress it. Eliminating or significantly reducing the energy consumption of subsequent hydrogen compression helps reduce system operating costs.

Also, since proton migration is extremely fast relative to changes in power, PEM systems can respond to load changes on the order of milliseconds, so they are especially suited for dealing with the intermittent, non-uniform energy supplies from renewable sources. It is very suitable for coupling with intermittent renewable energy sources such as wind power and photovoltaic power to achieve fast start and stop and power regulation. PEM electrolysis has high efficiency, high compactness, and can stably operate under the strong acid and strong oxidizing environments (high current density, etc.). This is mainly caused by their need for precious metal catalysts, iridium for the anode, and platinum for the cathode. But the expensive price of the raw material is also one of the factors driving up the price tag of hydrogen, and the heavy reliance on precious metal catalysts is currently an important factor restricting its large-scale commercialization.

Contemporary PEM electrolyzers used in commercial applications have an iridium load of approximately 2 mg/cm^2, resulting in the consumption of some 1 mg iridium per watt of electrolysis power. Such an overdependence on precious metals in short supply has greatly limited the exploitation and development of the technology. The use of precious metals sparingly has been focused on, and on the other hand, efforts have been active for developing other materials. In academia and industry, current research trends include new catalyst structures, membrane electrode optimization, replacement of precious metals, and the recycling of precious metals for efficient utilization of iridium resources. These strategies are believed to be the vital breakthrough for overcoming the bottleneck of PEM water electrolysis for hydrogen production and accelerating the industrialization of hydrogen energy, and these technological breakthroughs will become the key to promoting the large-scale development of PEM water electrolysis hydrogen production and the industrialization of hydrogen energy in the future.

3. PEM water electrolysis performance evaluation

In contrast to other water electrolysis technologies (such as AWE and SOEC), proton exchange membrane water electrolysis (PEMWE) has significant advantages in dynamic response capability, system efficiency, and adaptability to coupling with renewable energy, and PEMWE is regarded as one of the key technological methods to promote the development of the green hydrogen industry. Nowadays, AWE has many advantages, such as being widely adopted by the traditional industry of water electrolysis for hydrogen production with mature technology, its equipment is more reliable, and cost is lower. However, the hydrogen production efficiency of AWE is significantly low, even below 65%. In addition, energy storage systems based on liquid electrolytes cannot respond to rapidly changing power demand fluctuations quickly, and the system is not suitable for use with intermittent energy sources such as photovoltaics and wind power.

When it comes to the other method, SOEC, which represents the latest and most advanced development direction of high-temperature electrolysis, it has received academic attention because it is able to split water efficiently at high temperatures; the theoretical maximum energy efficiency for this process is greater than 90%. However, SOEC is still shadowed in laboratory and demonstration stages with problems of high operation temperatures (usually in the order of 700–900°C), limited electrode material stability, and severe damage from thermal stress during start-up and shutdown, which makes large-scale commercialization not an imminent possibility.

On the other hand, PEM electrolysis water technology and electrolyzers are excellent across a range of performance parameters, ranging from 1 to 3 A/cm^2 in current densities, which is much higher than the current density of 0.2–0.4 A/cm^2 (the parameters of AWE), as well as energy efficiencies of between 70 and 80%, far exceeding AWE (below 60%). The PEM separates the hydrogen and oxygen gases sufficiently well to achieve a hydrogen purity of greater than 99.99%, which in turn eliminates any need to further separate or purify gases. In addition, PEM electrolysis is able to generate hydrogen directly at higher pressures, typically 30–80 bar, which can save a lot of energy for further compression.

Furthermore, the PEM electrolysis equipment has the ability to follow load changes at the millisecond level and can quickly track power generation fluctuations from PV and wind power, having unique advantages in deep integration with renewable energy. By converting it into chemical energy in the reaction products, PEM stores electrical energy in the chemical bonds of hydrogen and oxygen. Thus, this perfectly matches the volatility and randomness of renewable energy generation, providing core technical support for "electricity and hydrogen" synergy.

Despite the limitations of PEM technology, including the high cost associated with the use of precious metal catalysts, inadequate long-term durability, and challenges in the membrane electrode assembly, its remarkable flexibility and compatibility have established PEM technology as an important technology route for decentralized renewable energy hydrogen production. Future development efforts on PEM should focus on new types of high-performance and low-loaded or non-precious metal catalysts (e.g., transition metal oxides, such as some transition metal phosphides and nitrides) to reduce reliance on precious metals, as well as on improving the long-term durability of the composite membrane (e.g., PTFE-reinforced membrane) to decrease cost and promote large-scale industrialization. This can be achieved by utilizing roll-to-roll (R2R) continuous production processes and developing advanced process equipment (such as continuous coating and hot pressing), thereby making PEM catalysts low-cost and suitable for large-volume manufacturing. Driven by both material innovation and process innovation, PEM electrolysis technology is expected to achieve breakthroughs in cost, lifespan, and scale, becoming a mainstream solution supporting high-proportion renewable energy consumption and large-scale application of green hydrogen in the future.

4. Process improvements and suggestions

Membrane electrode is the core component of PEM electrolyzer, and its preparation process directly affects electrolysis performance, life, and cost. In order to promote the large-scale commercial application of proton exchange membrane (PEM) water electrolysis technology, current R&D and engineering focuses are mainly concentrated on three key fields: material system optimization, manufacturing process simplification, and system integration and intelligence.

In terms of material system optimization, some researchers are attempting to construct core-shell catalysts (such as $Ir@TiO_2$) to reduce the iridium content in catalysts, or alloying strategies (such as using Ir-Co alloys). They are also exploring transition metal oxides such as MnO_2 and CoP as alternative catalysts to reduce reliance on precious metals. Optimization of catalyst supports is very important. High-surface-area conductive materials, such as nitrogen-doped carbon nanotubes or Ti_4O_7, can be used to improve the dispersion and electrochemical stability of catalyst active sites in PEM water electrolysis. Regarding proton exchange membranes, the introduction of inorganic nanofillers (such as SiO_2 and TiO_2) or graphene oxide into Nafion, or the use of acid-base blending methods (such as the SPEEK system), can significantly enhance the membrane's mechanical strength and high-temperature resistance.

In terms of manufacturing process simplification, continuous production techniques and the catalytic layer coating process are equally important for the iridium loading in the catalyst. Techniques such as slot-die coating and ultrasonic spraying are gradually replacing traditional manual coating methods. Nowadays, slot-die coating is also a mainstream high-precision coating technology. It precisely pumps a catalyst slurry (mainly containing catalyst, ionomer, and solvent) through a slot die and evenly coats it on the surface of a proton exchange membrane or gas diffusion layer. This allows for precise control of catalyst layer thickness and loading, making it suitable for wide-width roll-to-roll production. It offers excellent repeatability and significantly reduces iridium loading (currently down to less than $0.5 mg/cm^2$). Ultrasonic spraying is a relatively new industrial process, which is used to atomize the slurry into micron-sized droplets, and then uniformly deposit them onto the substrate. This method has many advantages such as high slurry utilization and the ability to coat multiple thin layers, making it suitable for preparing ultra-low loading or gradient catalytic layers. Electrochemical deposition, through the process of directly depositing catalyst particles on the membrane surface to form a nanoporous structure, increases the electrochemical active area, improves the interface contact between the catalyst and the membrane, and reduces the use of binders.

In addition to the methods mentioned above, there are several methods that contribute to the membrane electrode (MEA) preparation process, such as catalytic layer hot pressing transfer process, gas diffusion layer (GDL) treatment, and so on. These innovative technologies can not only improve MEA production efficiency but also reduce batch-to-batch variability. Furthermore, direct growth of the catalyst layer on the membrane surface through methods such as electrochemical deposition or vapor-phase polymerization can reduce the adverse effects of binders on porosity and mass transfer performance. In terms of flow field and bipolar plate design, titanium-based porous flow field plates or carbon fiber-reinforced PPS composites are becoming increasingly popular alternatives, significantly reducing weight and cost compared to traditional pure titanium plates.

In terms of system integration and intelligence, PEM electrolysis systems can integrate photovoltaic and wind power prediction models to optimize the electrolyzer's load rate control, thereby balancing energy efficiency and lifespan. Furthermore, the introduction of supercapacitors or short-term energy storage devices on the DC side can help smooth power fluctuations and avoid excessive impact on the catalyst and membrane. The low- to medium-temperature waste heat (approximately 50–80°C), which is produced in the electrolysis process, can also be recovered for external heating and dehydration of the membrane, thereby achieving energy recycling and improving overall system energy efficiency. Using staged heat recovery can reduce system energy consumption; plate heat exchangers recover heat from the electrolyzer's hot liquid to preheat the inlet water (from 20°C to 60–70°C), reducing system energy consumption. Precise temperature control is very important because it regulates the cooling water flow rate through a PID algorithm to maintain the electrolyzer's optimal operating temperature range (typically 70–80°C), with temperature fluctuations controlled within ±1°C, as the PID uses differential and integral calculations to detect, calculate, and forecast the temperature.

Advanced research areas include some innovative technologies such as electrolysis without membranes (AEM-PEM hybrids) and asymmetric electrode designs. Besides digitalization, the creation of physical models and artificial intelligence will play increasing roles in process improvements. There are several approaches to achieve this, including multi-physics modeling, AI-powered early warning, and adaptive control algorithms. First, in the field of multi-physics modeling, it is very significant to build a multi-physics model, which encompasses many fields, such as electrochemistry, mass transfer, thermodynamics, and mechanical stress, to simulate the internal state of the electrolyzer in time. Accurate control in time is significantly important for PEM. Besides, AI-powered early warning can be combined with PEM to analyze historical operating data using a long short-term memory (LSTM) neural network to predict failures such as membrane dehydration and catalyst poisoning 200–500 hours in advance, with an accuracy rate exceeding 85%. Finally, adaptive control algorithms, based on predicted renewable energy power and grid electricity price signals, dynamically optimize the electrolyzer's operating pressure and current density, balancing energy consumption with equipment lifespan. These methods will drive PEM water electrolysis hydrogen production to higher efficiency, smarter operation, and lower costs, making the PEM water electrolysis process more efficient, smarter, and more integrated.

In addition to the above three methods, there are other processes that can also optimize the proton membrane to improve the PEM process. For example, precision etching and forming is a technology where, through exposure, development, and chemical etching, complex flow channel patterns (such as serpentine, interdigitated, and multi-channel spirals) are produced on thin titanium sheets (0.5–1 mm) with an accuracy of ±0.05 mm. However, it is only suitable for small-batch, high-precision trial production. High-speed stamping of titanium or coated steel plates using high-precision dies is highly efficient and cost-effective, making it suitable for large-scale production. Die precision control and post-stamping stress relief annealing are key technologies.

Surface modification and coating processes are another example. Physical vapor deposition (PVD) is important; it uses magnetron sputtering or multi-arc ion plating to deposit corrosion-resistant conductive coatings such as TiN, Au, or Nb on the surface of the titanium plate (thickness is usually 1–5 μm), which significantly reduces interface resistance and improves resistance to potential corrosion. Then, the precursor solution of precious metal oxides (such as IrO_2, RuO_2) is coated and sintered at high temperature in a protective atmosphere, aiming to form a stable conductive protective layer to protect the proton membrane from oxidation.

5. Conclusion

This paper investigates dynamic performance optimization strategies for PEM water electrolysis hydrogen production technology in detail, and analyzes the advantages and disadvantages between PEM and other approaches (AWE and SOEC). By improving key aspects such as catalysts, proton exchange membranes, system control, and some advanced or traditional MEA processes, the performance of PEM electrolyzers under fluctuating renewable energy supply conditions has been greatly improved. The study proves that the use of low-iridium catalysts (e.g., Ir@TiO_2 core-shell structures) can effectively reduce precious metal usage while maintaining excellent catalytic activity. In addition, the use of hybrid membranes (e.g., Nafion-SiO_2) is very significant because it can greatly reduce ohmic resistance; in this way, PEM can improve its current response speed. The use of an adaptive power control algorithm enables the electrolyzer to adapt to load changes rapidly while keeping efficiency fluctuations within a tiny range.

Besides, there are several proton exchange membrane protection processes, such as bipolar plate processing and flow field forming technology, and catalyst layer coating. There are also several approaches that can be combined with the PEM system, such as combining staged heat recovery and using a PID system with PEM to control the temperature of the electrolytic cell within a range of ±1 degree. Through modern digital twins and predictive maintenance, combined with multi-physics modeling, adaptive control algorithms, and artificial intelligence, PEM can produce hydrogen in a safer and more efficient way than traditional processes. These measures significantly improve the potential coupling of PEM electrolyzers with intermittent energy sources such as wind power and photovoltaics.

However, several significant challenges still remain for the large-scale commercial application of PEM water electrolysis hydrogen production. First, the material degradation mechanism under dynamic conditions needs to be studied more, especially the frequent load changes, which lead to catalyst dissolution and membrane chemical degradation. In addition, it is significant to overcome the difficulty of achieving a balance between high load rate and energy efficiency. Finally, the system manufacturing cost is still high, so the price remains a barrier to industrial-scale development.

Therefore, breakthroughs are needed in new materials, and future research should focus on developing highly active and stable non-precious metal catalysts, improving the structure of membrane electrode assemblies to enhance dynamic response, establishing standardized dynamic performance test methods, and exploring collaborative operation strategies with energy storage systems. Through interdisciplinary technology integration and innovation, proton exchange membrane water electrolysis technology provides solid support for global energy transformation and carbon neutrality goals, and it is becoming a potential solution for hydrogen production from renewable energy. In the future, as carbon dioxide emissions gradually decrease and hydrogen energy becomes more widely used, PEM will be a key solutions.

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