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Current Status and Development of Key Hydrogen Fuel Cell Technologies

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Abstract. As society continues to progress, hydrogen energy's status in the energy sector continues to rise. Hydrogen fuel cells, as a key clean energy technology for achieving the carbon peaking and carbon neutrality goals, face limitations in large-scale application due to issues such as high costs, poor stability of cathode catalysts, and insufficient performance of proton exchange membranes. This paper first reviews the challenges in adapting oxygen reduction reaction catalysts to acidic, alkaline, and other environments. Subsequently, the paper examined the effects of different elemental doping on catalyst performance, optimization mechanisms, and preparation strategies, citing examples of catalysts composed of precious metals in their single-atom form. Finally, this paper systematically reviews the research progress and performance characteristics of different types of proton exchange membranes. It aims to provide clear directional guidance and theoretical support for future breakthroughs in key hydrogen fuel cell technologies, thereby contributing technical assistance to advancing the global energy transition toward green and low-carbon solutions.

Keywords: Hydrogen Fuel Cell, Oxygen Reduction Reaction, Catalyst, Proton Exchange Membrane

1. Introduction

With the continuous advancement of urbanization and rapid social development, humanity's demand for energy continues to grow, making the global energy crisis increasingly prominent. As the primary energy sources today, the excessive use of fossil fuels like coal and oil leads to severe environmental issues such as excessive carbon emissions, global warming, and rising sea levels. This means the consumption of fossil fuels cannot grow indefinitely. Consequently, it is imperative to seek a new energy source to reshape the existing energy landscape.

Hydrogen energy holds immense potential for utilization due to its abundant resources, high energy density, and environmentally friendly, pollution-free byproducts. Hydrogen fuel cells, closely linked to hydrogen energy, are environmentally friendly and pollution-free, with near-zero carbon emissions throughout their entire lifecycle. They also boast high energy density, efficient energy conversion, and broad application scenarios, naturally offering boundless application prospects. In recent years, significant research achievements have been made in the field of hydrogen energy utilization both domestically and internationally. Sun Zhiqiang's team discovered that an atomic-level Ni catalyst system featuring coexisting single atoms and nanoclusters exhibits optimal

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hydrogen production performance at 550°C. It maintains excellent stability even after 120 hours of continuous operation, achieving enhanced hydrogen atom utilization efficiency through synergistic catalysis between single atoms and nanoclusters [1]. Tae-Ho Kim's team has successfully developed a hydrophilic patterned titanium-based porous transport layer that significantly enhances the performance of regenerative fuel cells. This material not only effectively increases the round-trip efficiency (RTE) of the cell to 25.7% but also simultaneously boosts the current density to 2 A/cm², providing a practical technical solution for optimizing the performance of key components in regenerative fuel cells. This breakthrough offers a novel pathway for optimizing hydrogen energy storage systems [2]. At the Shanghai Advanced Research Institute of the Chinese Academy of Sciences, a high-quality, active Pt-based high-entropy intermetallic oxygen reduction catalyst has been developed, achieving a mass activity of 0.65 A mg^{-1} Pt (5.4 times that of commercial Pt/C). After 20,000 cycles, its activity decayed by only 27%. These findings provide a new strategy for designing low-platinum catalysts [3].

Although hydrogen fuel cells hold promising prospects for development, they remain constrained by issues such as the susceptibility of cathode oxygen reduction catalysts to poisoning, high costs [4], and relatively low efficiency of proton exchange membranes. Based on this, this paper will examine the current application status of key hydrogen fuel cell technologies from the perspectives of both catalysts and proton exchange membranes, aiming to lay the groundwork for the widespread adoption of hydrogen fuel cells.

2. Oxygen reduction reaction catalyst

2.1. Performance of oxygen reduction reaction catalysts under different conditions

In the core electrochemical reactions of hydrogen fuel cells, the Hydrogen Oxidation Reaction (HOR) is the primary reaction at the anode, while the Oxygen Reduction Reaction (ORR) exclusively occurs at the cathode. Together, these two reactions form the central mechanism for energy conversion within the cell. In electrochemical reaction systems, the hydrogen oxidation reaction (HOR) occurring at the anode exhibits rapid kinetic characteristics, classifying it as a fast reaction process. Conversely, the oxygen reduction reaction (ORR) at the cathode requires multiple-step electron transfer processes coupled with proton transfer. This series of complex steps significantly slows the kinetic process, resulting in a reaction rate that is five orders of magnitude slower than that of the HOR. Therefore, the ORR reaction rate limits the power output of hydrogen fuel cells [5]. Currently, precious metal Pt and its alloys remain the optimal catalysts for the hydrogen evolution reaction (HOR) and oxygen reduction reaction (ORR). However, due to Pt's high cost, limited reserves, and susceptibility to poisoning, it struggles to meet large-scale commercial demands in terms of catalyst cost, battery efficiency, and stability. Therefore, further cost reduction, addressing the slow kinetics of ORR, and enhancing catalyst durability are critical for hydrogen fuel cell catalyst development.

After undergoing high-potential cycling in acidic media, carbon materials readily form surface oxides. These oxides not only increase the double-layer capacitance but also induce platinum poisoning, leading to severe loss of oxygen reduction reaction activity. This significantly compromises the performance stability of the associated electrochemical system. In contrast, low-potential cycling in acidic media exhibits minimal oxygen reduction activity loss, primarily attributable to Ostwald ripening of platinum, without causing significant changes in double-layer capacitance [6].

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Research by senior scientists has revealed that the high efficiency of hydrogen fuel cells can only be sustained over extended periods when using ultra-pure hydrogen (purity exceeding 99.97%); otherwise, impurity gases such as ammonia typically cause poisoning. In alkaline membrane fuel cells, commercial platinum-carbon catalysts are highly susceptible to poisoning by ammonia in the fuel, leading to significant degradation of catalytic activity. Simultaneously, the hydrogen oxidation reaction (HOR) kinetics of these platinum-based catalysts are inherently slow, hindering efficient reaction progression. The synergistic effect of these two issues further accelerates overall cell performance decline, significantly impacting the long-term stable operation of the fuel cell [7].

2.2. Study on the performance of precious metal catalysts for the oxygen reduction reaction

To better investigate the effects of two different metal dopants—molybdenum and gold—on the stability of platinum-nickel alloy catalysts, Huang et al. established a complete platinum-nickel-based nanowire (NWs) model catalyst. The study revealed that molybdenum primarily suppresses outward diffusion of nickel atoms, while gold mainly stabilizes the surface platinum coverage. Based on these findings, a PtNiMoAuNWs catalyst with dual heterometallic doping of molybdenum and gold was synthesized. Compared to catalysts with single heterometallic doping, it exhibited the highest mass activity and specific activity [8].

Addressing the core challenges of high cost and low durability in platinum-based catalysts for hydrogen fuel cells, Professor Yu's team proposed an innovative synthesis strategy. By precisely controlling the reaction process, nitrogen was effectively incorporated into platinum-cobalt alloys, offering a new pathway for optimizing catalyst performance. This newly developed platinum-cobalt alloy is characterized by its ordered platinum-cobalt structure both on the surface and internally, along with exceptional structural stability achieved through cobalt-nitrogen bonds. This effectively prevents cobalt dissolution, significantly enhancing the alloy's durability [9].

To address the low catalytic activity and selectivity of atomically dispersed platinum electrocatalysts caused by unfavorable oxygen adsorption conditions, researchers loaded platinum atoms onto an α-Fe_2O_3 support, constructing a catalyst with dispersed PtFe diatomic sites that exhibits high resistance to deactivation and destruction. Under alkaline conditions, this catalyst exhibits outstanding electrochemical performance: its onset potential reaches 1.15 V, with a half-wave potential of 1.05 V. At a test potential of 0.95 V, it achieves a mass activity of 14.9 $A \cdot mg^{-1}$Pt. Furthermore, after 50,000 cycles, its activity shows minimal decay. This fully demonstrates the catalyst's promising catalytic potential in alkaline systems. In the latest two tests, this catalyst also significantly outperformed 20% Pt/C catalysts in terms of energy density and Pt utilization [10].

2.3. Strategies and examples for preparing single-atom catalysts based on noble metals

When the precursor solution of the active component comes into sufficient contact with the carrier under specific conditions, the metal ions in the precursor solution gradually dissociate from the solution phase, selectively enriching and stably adsorbing onto the carrier surface. After undergoing processes such as filtration, drying, and calcination, the corresponding single-atom catalyst can be obtained. The impregnation method primarily achieves single-atom loading through interactions between the metal active component and the support. Consequently, the strength of these interactions directly influences the loading amount of the active component, which in turn affects the catalyst's performance. Zhang et al. employed glucose as the graphene precursor and sodium chloropalladate as the metal precursor to prepare a graphene-supported Pd single-atom catalyst via

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an impregnation method, achieving a Pd loading of 2.3% to optimize the selective hydrogenation process [11].

High-temperature atomic capture utilizes elevated temperatures to induce thermal migration of atoms on metal surfaces, thereby forming individual metal atoms that deposit onto the carrier surface. Through interactions with the carrier, this process synthesizes single-atom catalysts. The method's essence lies in the "reverse Ostwald ripening" phenomenon occurring in metal nanoparticles under oxidizing or inert atmospheres, coupled with the "riveting" effect exerted by the substrate on the formation of metal single atoms. The Nie research group employed this method to prepare Pt single-atom catalysts supported on CeO_2, achieving both low-temperature CO oxidation activity and outstanding hydrothermal stability [12].

Atomic layer deposition (ALD) primarily utilizes self-limiting surface chemical reactions. Different precursors are alternately pulsed into the reaction chamber, where they undergo chemical reactions, and byproducts are purged. This deposition cycle forms a single atomic layer. Repeating this cycle ultimately builds the desired thin-film structure precisely onto the substrate. Inspired by this approach, Yan's team ultimately synthesized Pt single-atom catalysts supported on graphene, which were then utilized in the 1,3-butadiene addition reaction. Their study revealed that the catalyst exhibited 100% selectivity and a high 1,3-butadiene conversion rate of 95%, while also demonstrating excellent durability [13].

3. Proton Exchange Membrane (PEM)

Among the membrane electrode assembly materials in hydrogen fuel cells, the PEM is the most critical component. Its primary function is to isolate the two electrodes during chemical reactions while facilitating the transfer of protons (hydrogen ions, H^+). The fundamental principle involves hydrogen ions binding to sulfonic acid groups on the PEM, then migrating from one sulfonic acid group to another until they ultimately reach the opposite side of the membrane. Meanwhile, electrons and anions cannot pass through. PEM can be classified into perfluorinated PEM, partially fluorinated PEM, and non-fluorinated PEM based on the type of material used in their formation [14].

Perfluorosulfonic acid (PFSA) proton exchange membranes are the most popular because of their ease of proton transmission and their resistance to deformation and damage under high heat and pressure. The chemical structure of PFSA molecules is relatively complex. The polytetrafluoroethylene (PTFE) backbone serves as the molecular skeleton, providing stable structural support. The perfluoroethylene side chains act as bridges connecting the backbone to functional groups. Sulfonic acid groups constitute the core units that confer specific physicochemical properties. Together, these three components form the fundamental structural framework of PFSA molecules. Better resistance of proton exchange membranes to high heat and pressure and to changes in the chemical environment depends on the hydrophobicity of the PTFE backbone. The superior proton permeability of PFSA PEM is attributed to the sulfonic acid end groups ($-SO_3H$) on the side chains. Benefiting from the strong electron-withdrawing effect of adjacent fluorine atoms, the electron density near the $-SO_3H$ group is significantly reduced. This allows it to ionize into $-SO_3^-$ and H^+ in aqueous media, greatly enhancing the proton conductivity of PFSA. PFSA membranes come in two types: long-side-chain (LSC) membranes and short-side-chain (SSC) membranes. Although more expensive than LSC PFSA, SSC membranes exhibit superior performance in membrane electrode assemblies, particularly under low humidity conditions, owing to their higher sulfonic acid group density. This situation further resulted in higher

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ionic conductivity and water absorption while maintaining comparable mechanical properties, and the glass transition temperature (Tg) was also elevated [15].

Radiation-induced grafting is the most commonly employed method for preparing partially fluorinated PEM. Additionally, methods for preparing partially fluorinated PEM also include blending or doping. The BAM series produced by Ballad Advanced Materials in Canada significantly enhances PEM stability while reducing fluorine content and lowering PEM costs [16]. Sahl Sadeghi et al. synthesized PVDF-g-PSSA membranes via one-step radiation grafting of sodium styrene sulfonate (SSA) onto powdered PVDF, followed by solvent evaporation [17]. The submicron structure revealed an ordered arrangement of ion channels, with proton conductivity increasing as the grafting level rose.

Non-fluorinated PEM materials are primarily non-fluorinated hydrocarbon polymers, which may be aliphatic or aromatic polymers featuring benzene ring structures either within the polymer backbone of the membrane or in bulky side chains derived from this backbone. In the field of high-performance proton-conducting polymer electrolyte membranes, hydrocarbon polymers offer advantages such as broader raw material availability, lower preparation costs, and greater molecular structural design flexibility. Incorporating hydrocarbon polymers into the polymer backbone is currently regarded as one of the most promising technological directions [18].

In current research, two primary approaches are employed to impart excellent proton conductivity to non-fluorinated hydrocarbon polymer proton exchange membranes: One involves synthesizing polymers containing sulfonic acid groups. For instance, Kyu Ha Lee et al. synthesized a series of sulfonated polyaryletherketone (SPAEK) block copolymers via polycondensation reactions. SPAEK membranes fabricated using solution casting exhibited superior proton conductivity [19]. Another approach to achieving high proton conductivity in polymer membranes involves incorporating acidic substances into the polymer matrix. Extensive research has focused on doping polybenzimidazole (PBI), polyether ether ketone (SPEEK), and polyimide (PI) with H_2SO_4 or H_3PO_4.

4. Conclusion

Although hydrogen fuel cells are regarded as one of the most promising new energy sources for the future, numerous challenges remain in areas such as oxygen reduction reaction catalysts. Against this backdrop, this paper reviews issues with oxygen reduction reaction catalysts in acidic and alkaline environments, investigates the influence of different elements on catalyst performance, introduces preparation strategies and examples for three commonly used noble metal single-atom catalysts, and provides an overview of proton exchange membrane classifications for hydrogen fuel cells. Looking ahead, leveraging advantages such as high atomic utilization, precious metal single-atom catalysts are poised to become the mainstream catalysts for hydrogen fuel cells. Consequently, achieving major breakthroughs in key technologies such as oxygen reduction reaction catalysts and proton exchange membranes for hydrogen fuel cells is no longer a distant prospect.

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