Research Status of Platinum-Based Catalysts for Hydrogen Fuel Cells

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Abstract: The global focus has shifted towards new energy sources in recent years. With the increasing severity of environmental pollution and climate change, countries and enterprises are seeking sustainable energy solutions. Hydrogen fuel cell technology has emerged as a promising clean energy alternative, offering significant potential in reducing carbon emissions and improving energy conversion efficiency. This technology has garnered attention for its environmentally friendly characteristics and long-term energy strategy implications, attracting the interest of scientists and engineers. Among the technical aspects of hydrogen fuel cells, the role of platinum-based catalysts is particularly crucial. This paper provides an overview of the most recent research advancements in the composition, structure, and carrier of platinum-based catalysts used in hydrogen fuel cells. It delves into methods for enhancing the anti-poisoning capabilities and stability of catalysts through doping and surface structure control. Additionally, it discusses approaches to enhance carbon carriers by regulating the level of graphitization and oxidation.

1 INTRODUCTION

The global focus on energy issues has increased significantly in recent years. With economic development and population growth, the demand for energy has risen rapidly. It is predicted that global energy demand will continue to increase, reaching 23 TW in 2030 and potentially 30 TW in 2050. The reliance on non-renewable energy sources like coal and oil has led to environmental pollution, the greenhouse effect, and resource depletion. In 2016, renewable energy sources such as wind power, biomass, and solar photovoltaic power accounted for only 20.5% of global energy consumption. This heavy reliance on fossil fuels has caused environmental problems and contributed to global warming. Therefore, there is a critical need to prioritize research and application of renewable energy for sustainable development (Zhu et al., 2019).

Hydrogen energy, characterized by being zero-carbon, pollution-free, renewable, high in energy density, and diverse in acquisition methods, is considered a promising alternative to traditional fossil energy sources. Clean, renewable, and efficient hydrogen power generation technology is seen as the key to achieving a hydrogen economy. Hydrogen fuel cells, known for their high efficiency, cleanliness, and sustainability, are considered an ideal energy conversion method without pollution and carbon emissions. The only byproduct of hydrogen fuel cells is water, and they do not involve the Carnot cycle, resulting in high energy conversion efficiency. Therefore, the development of catalysts with high activity, stability, durability, and low cost has become a focus of hydrogen fuel cell research (Wei et al., 2019).

Platinum (Pt) catalysts are widely recognized as efficient electrocatalysts for the hydrogen oxidation reaction (HOR). They exhibit fast reaction rates, particularly in acidic conditions, where the kinetics are extremely rapid, with an exchange current density of about 10^2 mA/cm²Pt. (Durst et al., 2014) Despite their excellent performance, Pt catalysts have drawbacks such as high cost, scarcity, susceptibility to impurities, and unsatisfactory surface structure and composition of catalyst carriers. These factors can reduce catalyst activity, significantly impacting the efficiency of hydrogen fuel cells in practical applications. Therefore, current research on Pt-based catalysts for hydrogen fuel cells primarily focuses on regulating the composition and structure of the catalyst particles and improving the catalyst carriers. This article provides a summary of the current research progress on Pt-based catalysts for hydrogen fuel cells in terms of composition, structure, and carriers, and proposes future research directions for hydrogen fuel cell catalysts.

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2 CATALYST PARTICLES

In hydrogen fuel cells, the primary goal of continuously optimizing catalyst particles is to enhance catalytic activity, reduce costs, improve durability and anti-poisoning performance, and optimize the catalytic reaction path and mass transfer efficiency. By introducing different elements, the electronic structure and chemical properties can be adjusted to enhance its anti-poisoning ability and stability. Surface regulation technology optimizes particle size, shape, and distribution, increases active sites, and improves the adsorption and mass transfer behavior of reactants. This helps in reducing the amount of precious metals while maintaining high performance, leading to economical and efficient catalyst design. In the application process of platinum catalysts, the negative hydrogen effect generated at the anode can lead to catalyst poisoning, which is a challenging issue to completely avoid in practical applications. In hydrogen fuel cells, the negative hydrogen effect refers to the presence of toxic gases such as carbon monoxide (CO) and hydrogen sulfide (H_2S) on the anode. These toxic gases will adsorb on the surface of the platinum catalyst, hinder the hydrogen oxidation reaction, reduce active sites, and subsequently decrease the rate of hydrogen oxidation reaction, thus affecting battery performance. Therefore, current research focuses on solving the problem of catalyst poisoning by optimizing catalyst particles (Wang et al., 2020).

2.1 Transition Metal and Oxide Doping

Doping serves as an effective strategy for mitigating platinum-based catalyst poisoning. By introducing small quantities of other elements or compounds to the catalyst, its catalytic performance can be fine-tuned. This approach is widely employed in the modified synthesis of platinum-based catalysts. The introduction of new elements or components generates electronic or bifunctional effects, allowing for the optimization of the proportion, type, and content of doping elements to maximize the catalyst's resistance to CO poisoning (Zhang et al., 2021).

Incorporating oxygen-philic metal elements such as ruthenium (Ru), iron (Fe), cobalt (Co), and nickel (Ni) into platinum-based catalysts can enhance the adsorption of surface hydroxyl groups (OH) through bifunctional effects. This promotes the desorption of CO oxidation to carbon dioxide (CO2) and improves the CO tolerance and hydrogen oxidation reaction activity of platinum-based catalysts. Notably, platinum-ruthenium alloy catalysts have garnered attention due to their exceptional resistance to CO poisoning. The synergistic effect between platinum and ruthenium reduces the oxidation potential of CO, making it easier to be oxidized under low potential conditions. Consequently, platinum-ruthenium alloy catalysts generally exhibit superior CO tolerance. Currently, PtRu catalysts are the most widely studied and applied in the field of anti-CO poisoning. The synergistic effect between Pt and Ru can reduce the CO oxidation potential, making it easier to be oxidized at low potentials. Therefore, PtRu catalysts usually have better CO tolerance. Studies have shown that the higher CO poisoning resistance of PtRu/C catalysts comes from the oxidation and removal of CO adsorbed on its surface, including direct electrochemical oxidation and water-gas shift reaction.

The water-gas shift reaction usually occurs at 180°C~350°C, so during the operation of the fuel cell, the oxidation of CO on the catalyst surface is usually dominated by electrochemical oxidation. For other element doping, the high tolerance of CO is not only due to the electrochemical oxidation process of surface CO, but also the process of Mo catalyzing CO and H_2O in the water-gas shift reaction further improves its anti-CO poisoning performance. Therefore, the catalyst also has ideal HOR catalytic activity in H_2/CO (100 μmol/mol), and the cell voltage only drops by 100 mV at a current density of 1 A/cm^2, which is about 0.4 times that of the Pt/C catalyst (Min, Kim and Jung, 2019).

To enhance the anti-CO poisoning performance of Pt-based catalysts, it is vital to utilize the electronic and bifunctional effects through doping. This enhancement relies on the reasonable regulation of several key factors, including the proportion, number, and type of doping elements. Traditional alloys are typically limited to combinations of two or three elements. In contrast, high-entropy alloys, a new type of alloy composed of no fewer than five metals, have emerged in recent years. High-entropy alloys offer high entropy effects, hysteresis diffusion effects, lattice distortion effects, and cocktail effects, allowing for the adjustment of metal components to achieve improved stability and catalytic activity compared to traditional alloys.

2.2 Surface Structure Control

Doping strategies have limitations in optimizing the anti-poisoning performance of catalysts. Regulating the surface structure of Pt-based catalysts offers a new way to improve their performance further. Different surface structures of crystals at the microscopic level affect the adsorption characteristics of CO on the catalyst surface. At the macroscopic level, core-shell catalysts are a common means of surface structure regulation. These catalysts consist of a single or multi-layer Pt shell layer that plays a catalytic role and a supporting core structure. By adjusting the core type, surface Pt atomic coverage, or the number of Pt shell layers, the center position of the surface metal d band can be changed, thus affecting the HOR activity and anti-poisoning ability of the core-shell catalyst (Liang et al., 2020).

When the coverage of the Pt monolayer on the surface of the catalyst core is less than 1, it acts as a sub-monolayer core-shell catalyst. A low Pt coverage results in a lower CO adhesion coefficient, and the surface structure will affect the gas adsorption on the metal surface, thus influencing the catalytic reaction. Making reasonable changes in the coverage can reduce the CO adsorption energy and improve the anti-poisoning ability of the Pt-based catalyst. Controlling the number of Pt shell layers has a significant impact on the activity in the hydrogen oxidation reaction (HOR) and the tolerance to carbon monoxide (CO). Recent experiments demonstrated that synthesizing two layers of Pt AL on PtCo/C resulted in the formation of a Pt_{2AL}-PtCo/C catalyst. This catalyst was then tested using reformed hydrogen as the experimental gas to assess its durability. The findings indicate that the presence of the Pt double layer prevents the core Co atoms from corroding, leading to significantly improved stability. Additionally, the CO adsorption on the Pt_{2AL}-PtCo/C catalyst is reduced, resulting in enhanced area specific activity and durability of the catalyst in CO-rich environments (Wang et al., 2018).

In addition to the core-shell structure, controlling the special surface morphology of materials is also a feasible method for surface structure control. By enhancing the electronic structure characteristics of bulk materials, more surface active sites are exposed, leading to improved performance of anti-poisoning catalysts. For instance, the synthesized three-dimensional network structure of PtBi nanorod catalyst enhances the utilization rate of Pt. Its interconnected pore structure increases the overall electrochemical active area of the catalyst. Additionally, the bimetallic structure introduces an oxygen-philic effect, which improves the CO tolerance of the PtBi nanorod catalyst.

3 CATALYST CARRIER

Platinum-based carbon catalysts (Pt/C catalysts) are commonly used as cathodic and anodic catalysts in hydrogen fuel cells. However, they are often negatively affected by harsh working environments, leading to degradation and loss of activity. The surface structure and composition of the carbon carrier play a crucial role in the electrocatalytic deactivation of these catalysts. An ideal carbon carrier should possess good electron conductivity, a reasonable pore structure, a large specific surface area, and excellent resistance to electrochemical corrosion. In traditional Pt/C catalysts, platinum nanoparticles (PtNPs) have a high specific surface energy, but their weak interaction with the carbon carrier makes them prone to migration and agglomeration. Furthermore, the surface of the carbon carrier contains a large number of defects and unsaturated bonds, rendering it susceptible to oxidative corrosion under long-term working conditions. This can result in the deterioration of the carrier and the shedding of Pt NPs, ultimately reducing the activity of the catalyst and leading to deactivation. To address these issues, researchers have modified the carbon carrier to effectively prevent its corrosion and enhance the interaction between Pt NPs and the carrier, thereby improving the performance and durability of the catalyst.

3.1 Graphitization of Carbon Catalysts

The graphitization degree of carbon carriers has a significant effect on its electrochemical corrosion performance. By increasing the graphitization degree, its anti-electrochemical corrosion ability can be effectively enhanced, thereby avoiding the structural collapse of the catalyst caused by carrier corrosion during long-term operation. Recent studies have shown that by precisely controlling the time and energy distribution of laser irradiation of ethylene, scientists have successfully synthesized a new type of laser-induced carbon material, called onion-like carbon (OLC). Raman spectroscopy characterization results confirmed that OLC has a significant degree of graphitization. In practical applications, Pt/OLC catalysts show higher catalytic activity than traditional Pt/C catalysts.

Compared with commercial carbon black (XC), OLC has a unique concentric graphite layer structure and σ - π bond hybrid structure, which significantly enhances its interaction with platinum (Pt) atoms. Such structural characteristics not only help to inhibit the surface migration of Pt atoms, thereby improving the durability of the catalyst under long-term working conditions, but also make OLC more stable in electrochemical reactions. In addition, the d-band center position of Pt on the OLC shell structure moves downward. This change in electronic structure reduces the adsorption strength of oxygen on the Pt surface, thereby enhancing the activity of oxygen reduction reaction (ORR). This shows that OLC has significant advantages in improving catalyst performance and durability, and provides new ideas and methods for the development of high-performance electrocatalysts (Muhyuddin et al., 2023).

3.2 Carbon Carriers Oxidation

The oxidation treatment method effectively alters the surface properties of the carbon carrier, promoting interaction between the surface groups and platinum nanoparticles (PtNPs). This treatment improves PtNP dispersion and resolves migration and aggregation issues during the catalytic process. Infrared spectroscopy (IR) characterization reveals that abundant functional groups are introduced on the carbon black surface after oxidation treatment, enhancing interaction with PtNPs and improving catalyst performance.

Transmission electron microscopy (TEM) characterization results show that carbon black treated with different oxidation methods has varying dispersion effects on PtNPs. H_2O_2 treatment demonstrates the best PtNP dispersion, followed by HNO_3 treatment, while untreated carbon black exhibits the worst dispersion. This indicates that H_2O_2 treatment is more effective in introducing functional groups, thereby improving PtNP distribution (Xia et al., 2021).

Electrochemical tests demonstrate that oxidation treatment significantly enhances the electrochemical stability of Pt/C catalysts. TEM analysis before and after durability cycling reveals that the average particle size of PtNPs on untreated and treated carbon supports increases from 2.5nm and 2.6nm to 5.3nm and 4.8nm, respectively. These results show that oxygen-containing functional groups introduced by oxidation treatment help connect with metal nanoparticles through oxygen atoms, reducing nanocatalyst agglomeration.

In summary, oxidation treatment notably improves PtNP dispersibility and reduces migration and aggregation by introducing oxygen-containing functional groups on the carbon support surface, which significantly enhances the catalytic activity and stability of the catalyst. This treatment method offers an effective approach to developing efficient and stable electrocatalysts.

3.3 Compound Doping Modification

The addition of semiconductor oxides, can significantly enhance the electrochemical corrosion resistance of the carrier and the overall performance of the fuel cell. To prove this, the researchers mixed carbon black XC-72 with anatase, loaded TiO_2 onto the surface of the carbon black through hydrolysis, and obtained a carbon powder (TiO_2-C) containing 5 wt% TiO_2 after drying. They then used photodeposition to deposit platinum nanoparticles (Pt NPs) on the TiO_2-modified carbon carrier to create the Pt/TiO_2-C catalyst.

Photodeposition is crucial in this process as it facilitates the efficient deposition of Pt. This is because under light conditions, the electron-hole pairs generated on the oxide surface can reduce the noble metal anions, resulting in more even distribution of the Pt NPs on the oxide sites. Electrochemical test results indicate that, compared to commercial Pt/C samples, Pt/TiO_2-C catalysts demonstrated superior thermal stability and electrochemical activity at different temperature ranges (298-343K).

Further fuel cell performance tests revealed that the power density of Pt/TiO_2-C catalysts increased with rising temperature. This effect is primarily due to the fact that the doping of TiO2 modifies the surface activation energy of the catalyst, changes the interaction between Pt NPs and the carbon carriers, and thus generates a synergistic effect. These findings demonstrate that the performance of Pt-based catalysts can be effectively enhanced by doping TiO_2 in carbon carriers, offering a viable approach for advancing fuel cell technology (Mobarakeh, 2017).

4 CONCLUSION

This article reviews the the latest research on platinum-based catalysts for hydrogen fuel cells. It focuses on the impact of catalyst particles, doping technology, and carrier modification on improving catalyst performance.

Firstly, by introducing transition metals and oxide doping, the catalyst's resistance to carbon monoxide (CO) poisoning and stability can be significantly improved. This method adjusts the electronic structure and surface chemical properties of the catalyst, allowing it to operate efficiently while reducing the amount of precious metals needed, thus achieving an economical and efficient design.

Secondly, controlling the surface structure, particularly the regulation of core-shell structures and special surface morphology, is crucial for enhancing the activity and durability of the catalyst. Core-shell structures can optimize the hydrogen oxidation reaction (HOR) activity and anti-poisoning ability by adjusting the core type, surface platinum atom coverage, or the number of shell layers, thereby changing the surface metal d-band center position. Special surface morphologies improve catalytic reaction efficiency by increasing active sites and enhancing gas adsorption characteristics on the metal surface.

Furthermore, studies on carrier modification have shown that increasing the degree of graphitization of carbon carriers and introducing oxidation treatment can significantly enhance the catalyst's resistance to electrochemical corrosion and overall performance. Graphitized carbon carriers offer better electronic conductivity and structural stability, helping to maintain the catalyst's structural integrity and high performance during long-term operation. Oxidation treatment, by introducing oxygen-containing functional groups on the carbon carrier surface, enhances the interaction between the carrier and platinum nanoparticles (Pt NPs), reducing issues related to nanoparticle migration and aggregation. Lastly, doping the catalyst with semiconductor oxides such as TiO_2 can enhance its thermal stability and electrochemical activity. This method modifies the catalyst's surface activation energy, improves the interaction between Pt NPs and the carrier. As a result, it increases the power density and the overall performance of the fuel cell.

In conclusion, future research should continue to focus on exploring new materials and methods to improve the performance and durability of hydrogen fuel cell catalysts. This will provide a solid scientific foundation for the development of hydrogen energy technology, promoting the widespread adoption of clean energy and sustainable development.

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