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Progress in the Application of PtCo Alloy Catalysts in Oxygen Reduction Reactions for Fuel Cells

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Abstract: Proton Exchange Membrane Fuel Cells (PEMFCs) are considered an effective way to address energy shortages and environmental pollution due to their high efficiency, low-temperature operation, and environmental friendliness. However, the oxygen reduction reaction (ORR) at the cathode in PEMFCs is very slow and needs rare and expensive Pt-based catalysts, which limits their commercialization process. To reduce costs while maintaining efficient catalytic performance, researchers have developed various technological strategies, among which PtCo alloy catalysts have garnered widespread attention due to their excellent ORR catalytic performance. This article reviews the latest progress and current status of PtCo alloy catalysts in PEMFC oxygen reduction catalysis, discusses the impact of catalyst component control, particle size regulation, crystal face regulation, doping, and other regulatory strategies on the catalytic activity of fuel cells, and provides a detailed introduction to the most promising PtCo alloy structures, such as polyhedra, core-shell, nanoframes, and ordered intermetallic structures. At the same time, the research on catalyst supports is discussed, and the challenges and future prospects of PtCo alloy catalysts in their applications are pointed out.

Keywords: PtCo alloy, electrocatalyst, oxygen reduction reaction, proton exchange membrane fuel cell

1. Introduction

With the intensification of the global energy crisis and the increasing severity of environmental pollution issues, the search for clean and efficient energy conversion technologies has become particularly important. Proton Exchange Membrane Fuel Cells (PEMFCs), as a clean and efficient energy conversion device, are considered the preferred power source for future applications in fields such as aerospace, military, electric vehicles, portable power supplies, and regional power stations due to their high energy conversion efficiency, large energy density, low operating temperature, environmental friendliness, ease of operation, and ease of mass production [1-7]. In the energy conversion process of PEMFCs, the oxygen reduction reaction (ORR) at the cathode plays a key role, but it is limited by a high reaction energy barrier and slow kinetic process, necessitating reliance on catalysts. Current catalysts are primarily high-loading carbon-supported platinum group metal (PGM) catalysts, which are expensive and scarce. Additionally, PGMs are prone to migration, agglomeration, dissolution, redeposition, poisoning, and detachment on carbon supports, leading to a decrease in both catalyst activity and stability, which hinders the further commercial application

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of PEMFCs. This article also summarizes the preparation methods and catalytic activity performance of PtCo alloy catalysts with different structures (such as polyhedra, core-shell, nanoframes, and ordered intermetallic compounds). Furthermore, the article analyzes the impact of supports on PtCo alloy catalysts and points out the current technological challenges and future development directions, which is of great significance for promoting the industrialization process of fuel cells and advancing the development of fuel cell technology.

2. Research progress on PtCo Alloy catalysts

2.1. PtCo catalyst regulation strategies

In the study of PtCo alloy catalysts, regulatory strategies are key to improving catalyst performance [8]. The following are some specific regulatory strategies.

2.1.1. Component regulation

Component regulation involves adjusting the ratio of Pt to Co to optimize the catalyst's performance. The latest research indicates that by precisely controlling the ratio of Pt to Co, the electronic structure and surface activity of the catalyst can be significantly affected. For example, by using atomic layer deposition (ALD) technology, the atomic ratio of Pt and Co in the alloy can be precisely controlled to achieve the best ORR activity [9]. Furthermore, with X-ray absorption spectroscopy (XAS) technology, researchers can gain a deeper understanding of the electronic structural changes in alloys with different component ratios, providing a theoretical foundation for the design of high-performance catalysts.

2.1.2. Particle size regulation

Particle size regulation is another important research direction. By controlling the size of PtCo alloy nanoparticles, their surface area and the number of active sites can be adjusted. The latest research shows that using high-temperature pyrolysis can synthesize PtCo alloy nanoparticles of specific sizes, which exhibit excellent activity and stability in ORR. Additionally, with transmission electron microscopy (TEM) and dynamic light scattering (DLS) technologies, researchers can monitor the growth process of nanoparticles in real-time, thereby precisely controlling their size [10].

2.1.3. Crystal face regulation

Crystal face regulation is about improving the catalyst's activity by selectively exposing specific crystal faces. For example, PtCo alloy nanocrystals synthesized by electrochemical deposition can preferentially expose the 111 crystal face, which shows higher activity in ORR. With X-ray diffraction (XRD) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) technologies, researchers can analyze the crystal face structure of catalysts, providing experimental evidence for crystal face regulation.

2.1.4. Doping

Doping involves introducing a third element to regulate the electronic structure and surface properties of the PtCo alloy. The latest research indicates that doping with elements such as Ni and Fe can significantly enhance the ORR activity and stability of PtCo alloys. With X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations, researchers can gain a deeper understanding of the impact of doping elements on catalyst performance.

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2.2. PtCo catalyst configurations

The configuration of PtCo alloy catalysts has a significant impact on their catalytic performance. Here are some specific configurations in the following sections.

2.2.1. Polyhedral structures

Polyhedral-structured Pt-based metal nanocrystals, due to their unique morphology and precise structure-reactivity control, are beneficial for enhancing the catalytic performance and stability of the oxygen reduction reaction (ORR). The latest research indicates that PtCo polyhedral nanocrystals synthesized via a template method possess high refractive index facets and negative curvature, demonstrating higher activity and durability compared to convex polyhedra. Through TEM and XRD techniques, researchers can analyze the morphology and facet distribution of polyhedral structures in detail, providing experimental data for optimizing catalyst design.

2.2.2. Core shell structures

Core-shell structured catalysts significantly reduce the loading of Pt and improve its utilization rate, achieving maximum efficiency of the catalyst. The latest research shows that PtCo core-shell structured catalysts synthesized via layer-by-layer self-assembly technology can alter the interaction between the core and shell by controlling the composition of the core and the morphology of the shell, modulating the electronic state of surface Pt, thereby enhancing ORR activity and stability. Through XPS and XRD techniques, researchers can analyze the composition and structure of core-shell configurations, providing theoretical support for the design of core-shell structured catalysts.

2.2.3. Nanoframes

Nanoframes (NFs) are a typical open three-dimensional nanostructure composed of cellular structures with nano- and microcrystalline lattice frameworks. The latest research indicates that PtCo nanoframes synthesized via the sol-gel method, due to their unique and stable framework structure, high specific surface area, and high-density active sites, can significantly increase the electrochemically active surface area (ECSA), resist harsh reaction environments, and enhance ORR activity and stability. Through TEM and nitrogen adsorption-desorption isotherms (BET) techniques, researchers can analyze the structure and specific surface area of nanoframes in detail, providing experimental evidence for the design of nanoframe catalysts.

2.2.4. Ordered intermetallic structures

Ordered intermetallic structures, due to the ordered arrangement of metal atoms and strong interactions between them, possess higher binding energy, the highest Co diffusion energy barrier, and more stable structures compared to disordered metal structures. The latest research indicates that PtCo-ordered intermetallic structured catalysts synthesized via high-temperature annealing methods, when catalyzing ORR under high potential and harsh acidic conditions, can slow down the dissolution, migration, and redeposition of metals, demonstrating excellent catalytic activity and durability. Through XRD and XAS techniques, researchers can analyze the atomic arrangement and electronic structure of ordered intermetallic structures, providing a theoretical basis for the design of ordered intermetallic structured catalysts.

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2.3. Catalyst supports

Catalyst supports provide an effective surface and additional active sites for Pt in catalytic reactions, enhancing the electrochemically active surface area (ECSA) and catalytic activity of the catalyst. Secondly, they anchor and confine the active metal Pt, dispersing metal nanoparticles (NPs) and effectively reducing their tendency to migrate and aggregate, thereby improving the stability of the catalyst.

2.3.1. Carbon supports

Carbon supports, due to their high specific surface area, excellent electronic conductivity, and low cost, have become the most widely used supports for current PtCo catalysts. The latest research indicates that carbon nanotubes and graphene, synthesized via chemical vapor deposition (CVD) technology and used as supports for PtCo catalysts, can provide excellent electronic conductivity and specific surface area, thereby enhancing the activity and stability of the catalyst. Through Raman spectroscopy and BET technology, researchers can analyze the structure and specific surface area of carbon supports, providing experimental data for the design of carbon supports.

2.3.2. Doped modified carbon supports

Introducing elements such as N, P, S, or metal compounds like TiO_2 to dope and modify carbon supports can effectively alter the carbon surface state and enhance the binding strength between the support and catalytically active metal atoms, thereby improving the stability of the catalyst. The latest research shows that doped modified carbon supports synthesized via high-temperature thermal treatment can significantly enhance the stability and activity of PtCo catalysts. Through XPS and XRD technology, researchers can analyze the surface state and structure of doped modified carbon supports, providing theoretical support for their design.

2.3.3. Non-carbon supports

Non-carbon supports such as polypyrrole (PPy), zeolitic imidazolate frameworks (ZIFs), and SnO_2 have garnered widespread attention due to their high corrosion resistance. The latest research indicates that non-carbon supports synthesized via the sol-gel method can provide excellent corrosion resistance and specific surface area, thereby enhancing the stability and activity of the catalyst. Through XRD and BET techniques, researchers are able to analyze the structure and specific surface area of non-carbon supports, providing experimental evidence for the design of non-carbon supports.

3. Evaluation technology standardization and improvement

Since electrocatalysts work in fuel cells as part of a membrane electrode assembly (MEA), the requirements for electrocatalysts are a combination of catalyst and catalyst layer design requirements. Currently, researchers have provided many effective methods and strategies to improve the ORR catalytic activity, stability, and durability of catalysts and have developed many excellent Pt-Co bimetallic ORR electrocatalysts. However, these performances do not fully represent or translate into actual fuel cell performance. The latest research indicates that through electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) techniques, the performance of catalysts in actual fuel cells can be more accurately assessed [11]. In addition, accelerated stress tests (AST) that simulate actual working conditions can be used to evaluate the long-term stability and durability of catalysts. The development and standardization of these evaluation technologies are crucial for the practical application and commercialization of catalysts.

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3.1. Stability and durability

Catalysts operate in harsh environments, such as alkaline or acidic conditions, including increased battery temperatures and the generation of active free radicals, which can lead to the degradation, leaching, atomic migration, particle migration, and aggregation of the second-phase metal Co under corrosive electrochemical conditions. This can cause the complex nanostructures of the catalyst to deform and collapse, while dissolved metal cations hinder proton conduction and the diffusion and permeation of oxygen, accelerating the disintegration of the membrane and catalytic surfaces. The latest research indicates that by introducing stable metal oxides such as CeO_2 and ZrO_2, the stability and durability of catalysts can be significantly improved [12]. These metal oxides can act as protective layers to prevent the degradation and leaching of metal Co. Through XPS and XRD techniques, researchers can analyze changes in the surface state and structure of the catalyst, providing experimental evidence for improving catalyst stability and durability.

3.2. Mass production

At present, apart from Pt/C and some PtCo bimetallic catalysts that can be mass-produced and widely commercially applied, most catalysts, such as morphologically controlled catalysts, are only produced in small reactors with harsh synthesis conditions, only achieving milligram-to-gram-scale preparation, and encountering difficulties and obstacles in scaling up production. The latest research indicates that continuous flow chemical synthesis technology can enable the mass production of PtCo catalysts. This technology can provide uniform synthesis conditions, resulting in high-quality catalysts. By optimizing reaction conditions and process control, catalyst production can be achieved from the gram scale to the kilogram scale. The development of these technologies is of great significance for the commercialization and large-scale application of catalysts.

4. Conclusion

This review summarizes the progress of PtCo alloy catalysts in the oxygen reduction reaction (ORR) of proton exchange membrane fuel cells (PEMFCs). The article begins by emphasizing the importance of PEMFCs as a clean energy conversion technology, highlighting the crucial role of Pt-based catalysts and addressing their associated cost challenges. It then provides an in-depth discussion on strategies for optimizing the performance of PtCo alloy catalysts, including composition control, particle size control, facet control, and doping. Furthermore, the article examines the structural advantages of PtCo alloys, such as polyhedra, core-shell, nanoframes, and ordered intermetallic configurations. It also explores the application of both carbon supports and non-carbon supports in catalysts and identifies key technical challenges in practical applications. These challenges include the need for standardized evaluation techniques, improving the stability and durability of catalysts, and addressing mass production bottlenecks.

In conclusion, Pt-Co alloying is shown to effectively adjust the position of Pt's d-band center, optimize the electronic structure, and increase active sites, thereby enhancing catalytic activity and stability. By controlling parameters such as composition, particle size, facets, and doping, as well as selecting the appropriate support, the performance of PtCo catalysts can be further improved. However, this article primarily provides a comprehensive analysis of PtCo alloy catalysts without delving into specific experimental data or direct performance comparisons. Future improvements could focus on analyzing the long-term performance and stability of different PtCo alloy structures in actual PEMFCs. Additionally, more environmentally friendly and cost-effective preparation methods should be explored to promote the commercialization of PtCo catalysts.

Future research directions include the development of new control strategies, such as machine learning-assisted design, to predict and optimize catalyst performance. and studying new non-noble

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metal alloy catalysts to further reduce costs. And strengthening the stability and durability research of catalysts under simulated actual working conditions to enhance their commercial application potential should be further investigated. Moreover, future studies could explore new support materials, especially those that provide better electronic conductivity and chemical stability, to improve the overall performance of catalysts. Through these research directions, the development of PEMFC technology can be further advanced, providing more effective solutions to energy and environmental issues.

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