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# *Research Progress on the Corrosion and Degradation Mechanism of Carbon Carriers in Proton Exchange Membrane Fuel Cells under Start-Stop Conditions*

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***Abstract.*** With the rapid development of modern society, the global dual carbon goals and hydrogen energy have been vigorously promoted by the state. Proton exchange membrane fuel cells (PEMFC) have received extensive attention because they can be widely applied in hydrogen vehicles and energy storage systems. Catalytic systems with carbon as the carrier face significant challenges, especially in terms of durability, as the carbon carrier is highly prone to corrosion when the fuel cell is frequently switched on and off. This paper conducts a systematic study on the corrosion and failure behavior of carbon-based catalyst carriers in PEMFC, mainly focusing on the intrinsic connection between the carbon corrosion mechanism and the structural stability and electrochemical performance degradation of the catalyst. Based on the representative literature on carbon black, graphene, and carbon nanotubes, in recent years, this study systematically summarizes the structural characteristics, the electrochemical stability of different carrier materials, and their effects on the dispersion and catalytic activity of platinum nanoparticles through literature review and comparative analysis. The results show that Carbon corrosion under high potential cycling and start-stop conditions leads to the destruction of the carbon skeleton structure, the shedding and agglomeration of platinum nanoparticles, and even causes rapid attenuation of the output power density. However, by constructing a carbon/non-carbon hybrid structure, one can enhance the durability of the catalyst. The research in this paper provides an important theoretical basis for the design and optimization of high-durability PEMFC catalyst carrier materials.

***Keywords:*** PEMFC, Carbon carrier corrosion, Start-stop decay, Catalyst durability

## 1. Introduction

As the global carbon peaking and carbon neutrality goals continue to advance, the energy system is accelerating its transformation towards clean and low-carbon [1]. Among them, Hydrogen energy is regarded as one of the important energy sources for sustainable development in the future because it has high energy density and zero carbon emission [2]. Proton exchange membrane fuel cells (PEMFCs) [3-4] represent the core technology for the efficient utilization of hydrogen energy, occupying an important position in fuel cell electric vehicles [5] and stationary energy storage

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systems. Their advantages include high energy-to-energy conversion efficiency, low operating temperature, and fast start-up response [3,6,7]. Despite the outstanding application prospects of PEMFCs [8], there are still many challenges in large-scale commercialization. For example, issues such as the durability of platinum-based catalysts and carbon carriers [1], costs [2], and the rapid decline in lifespan caused by the frequent start-stop operation of vehicles [5] during actual use are considered core problems that prevent large-scale commercialization. Under actual operating conditions, repeated start-stop can also cause sharp fluctuations in electrode potential, thereby accelerating material aging and performance degradation.

At present, most studies have focused on enhancing the reactivity of catalysts through. Material design, while less attention has been paid to the intrinsic mechanisms of corrosion and failure of the carbon materials that carry the catalysts under long-term operating conditions. Given the importance of carbon carriers in maintaining the structural stability and electrochemical performance of catalysts, this paper will conduct a systematic analysis of carbon carrier-related issues in PEMFC to provide an important theoretical reference for improving the durability of fuel cells [6,9,10].

## 2. The basic working principle and membrane electrode structure of PEMFC

The basic working principle of a PEMFC is the redox reaction at the cathode and anode by consuming hydrogen and oxygen [4]. The purpose is to convert the chemical energy of the fuel into electrical energy through the redox reaction. Additionally, at the anode, hydrogen is oxidized under the action of a catalyst to produce protons and electrons [7]. The protons are transferred through the exchange membrane to the cathode, and then the electrons form a current output through an external circuit. At the cathode, oxygen reacts with protons and electrons to form water and release heat, completing the energy conversion process [4,11].

The membrane electrode serves as the core component of a PEMFC, which consists of a catalytic layer, a gas diffusion layer, and a proton exchange membrane [3,11]. Among them, the catalytic layer is where the electrochemical reaction takes place, and the gas diffusion layer is responsible for transporting the reaction gas, removing the product water, and conducting electrons, while providing mechanical support for the electrode [12]. The bipolar plates are responsible for gas distribution, conduction, heat dissipation, and connection of the battery cells [9]. The performance of PEMFCs is usually judged by power density, current density, and electrochemical activity density, the size of the ohmic internal resistance, and mass transfer Resistance also has a significant impact on output performance.

## 3. Carbon-based catalyst support materials in PEMFC

Carbon materials are widely used in PEMFC catalyst carrier systems due to their good electrical conductivity, high specific surface area, and relative stability in acidic environments. The traditional carbon black carrier is currently the most mature technology and was first used because of its low cost [2]. However, due to the disordered structure and high defect density of the carbon black carrier [10], electrochemical corrosion is prone to occur under high potential conditions, leading to gradual degradation of the carrier structure and instability of the catalyst. To enhance the stability of the carrier, researchers have attempted to introduce some highly structured, ordered carbon materials [1] (graphene, carbon nanotubes, etc.). These materials do bring about significant changes. Graphene, with its high degree of graphitization and excellent electron transport capacity, helps to build a stable conductive network. At the same time, carbon nanotubes, with a bunch of structures and strong mechanical properties, show certain advantages in maintaining the structural integrity of the

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catalytic layer. In addition, porous carbon materials can significantly improve gas transport conditions by regulating pore size distribution and specific surface area, but structural defects still limit their corrosion resistance.

The structural defect changes come from improvements in heteroatom-doped carbon materials in recent years. By adding elements such as nitrogen, sulfur, or phosphorus to the carbon skeleton, scientists can effectively regulate the electronic structure of carbon materials, enhance the interaction between platinum nanoparticles and the carrier, thereby improving the dispersion of platinum and inhibiting its migration and agglomeration during operation. There are significant differences in platinum dispersion, conductivity, and long-term stability among different types of carbon carriers [1,10], which directly affect the electrochemical performance and durability of PEMFCs [8,12].

## 4. Platinum and platinum alloy electrocatalysts supported on carbon carriers

In the cathode oxygen reduction (ORR) reaction of PEMFC, platinum-based catalysts perform exceptionally well in an acidic environment. They not only have high catalytic activity but also high reaction stability. Therefore, platinum-based catalysts remain an irreplaceable part in current commercial operations. Although some non-precious metal catalysts have made certain progress in laboratory research, their activity and durability still do not meet the long-term operation requirements in actual fuel cell conditions, so Pt/C catalysts still dominate at present [12,13].

Platinum is too expensive to be fully commercialized on a large scale. To reduce platinum usage and improve catalytic performance, researchers have developed a variety of platinum alloy catalyst systems, such as Pt-Co, Pt-Ni, and Pt-Fe. By regulating the electronic structure and surface strain effect of platinum, these alloys can optimize the adsorption energy of oxygen intermediates, thereby significantly improving the ORR reaction kinetics [13]. However, alloying, while enhancing catalytic activity, brings a lot of problems, such as dissolution and structural rearrangement of alloying elements under acidic valence adjustment.

In this process, the carbon carrier plays a significant role, not only supporting the entire framework but also influencing the electronic structure and stability of platinum and its alloys through interfacial interactions. Studies have shown that the structure and surface chemical properties of the carrier can significantly affect the stability of the alloy catalyst under conditions of high potential cycling and contamination by harmful substances, thereby intensifying the contradiction between catalytic activity and long-term durability.

## 5. The mechanism of high potential formation under start-stop conditions

During the actual operation of fuel cells [9,14], PEMFCs [8] do not remain in a stable working state all the time, but frequently experience start-up and shutdown processes. During the start-stop phase, as the reaction gas cannot be supplied immediately, hydrogen will be exhausted in some local Spaces and air reverse osmosis will occur frequently, and there will be significant fluctuations in the potential distribution inside the electrode [4,7]. Current studies have shown that during shutdown or the initial stage of startup, the cathode potential can instantly rise to levels far above the normal operating range, even exceeding 1.2V (vs. RHE).

This anomaly is also one of the key factors that induce electrochemical corrosion of carbon carriers. Because under high potential conditions, the carbon material that would otherwise work stably will gradually deteriorate the carbon carrier structure due to oxidation reaction kinetics, which adversely affects the long-term stability of the catalyst layer.

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## 6. Electrochemical corrosion reactions of carbon carriers under high potential conditions

It is necessary to know the corrosion reaction process of the carbon carrier under high potential conditions, since it is clearly known that the start-stop condition will cause an abnormal increase in the cathode potential. In a high-potential environment, irreversible electrochemical oxidation occurs on the carbon carrier, which is why the durability of PEMFC catalysts deteriorates. The process occurs when carbon reacts with water to produce carbon dioxide and releases protons and electrons, which leads to an oxygen reaction [3,10,11]. Although the reaction can occur thermodynamically at lower potentials, it is very slow under steady-state operating conditions; However, when the electrode potential rises above 1.2V (vs. RHE), the rate of carbon oxidation increases sharply, leading to the continuous degradation of the carbon carrier structure.

### 6.1. The principle of carbon skeleton collapse

In the high-potential environment induced by start-stop conditions, the corrosion of the carbon carrier often does not occur uniformly, and the corrosion begins at the higher energy and more chemically reactive parts of the current structure. These areas are usually defects on the surface of the carbon material, edges, and places where heteroatoms are mixed. As the carbon oxidation reaction continues, local carbon atoms are gradually oxidized to carbon dioxide and removed from the framework, and the originally continuous carbon grid breaks, thereby weakening the overall structural integrity of the carrier. As the degree of corrosion deepens, the carbon framework changes from a continuous structure to a porous one. This not only disrupts the conductive pathways within the catalytic layer but also reduces the support capacity of the carrier for platinum nanoparticles, resulting in a decrease in overall stability [1,10].

### 6.2. Shedding, migration, and agglomeration behavior of Pt nanoparticles

Based on this, the carbon carrier is less likely to continue supporting the platinum nanoparticles, which leads to a greater tendency for the platinum nanoparticles to shed in situ and migrate and agglomerate on the surface of the catalytic layer, resulting in an increase in particle size and a decrease in dispersibility. This process directly reduces the exposed active sites and the microstructure stability of the fabric catalytic layer.

### 6.3. ECSA and power density attenuation caused by carbon corrosion

The shedding and agglomeration of platinum nanoparticles significantly reduce the electrochemically active surface area (ECSA), which results in platinum nanoparticles having less effective area to react with oxygen for reduction. At the same time, the carbon carrier [1], corrosion also disrupts the conductive network and mass transfer channels within the catalytic layer, further amplifying the activity loss effect, which ultimately results in a sustained decline in the output power density and operational efficiency of the PEMFC.

## 7. Conclusion

Overall, carbon-based materials remain the most commonly used materials in PEMFC catalyst systems, but the corrosion problem of them under start-stop conditions has become a key technical bottleneck restricting the durability of fuel cells. There is still room for improvement in this paper. For instance, in-situ or quasi-in-situ characterization and analysis of the carbon carrier corrosion

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process under start-stop conditions have not been conducted, nor has the quantitative relationship between high potential distribution and carbon corrosion kinetics been deeply explored in combination with multi-scale modeling methods. Future research needs to enhance the structural stability of carbon materials while ensuring high electrical conductivity. At the same time, it is necessary to promote the study of non-carbon carriers and carbon/non-carbon composite carrier systems to reduce the usage of precious metals, achieve long-term commercialization, and ensure the long-term stable operation of PEMFC.

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