Recent Advances in Platinum Catalysts for Oxygen Reduction at the Cathode of Hydrogen Fuel Cells

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Abstract. For a long period of time the high cost and limited durability of platinum catalysts have been impeding the large - scale commercial progress of proton exchange membrane fuel cells. So then reducing the platinum quantity while maintaining excellent catalytic performance without spoiling catalyst functionality has become a crucial matter to concentrate on in this domain. This article hones in on the methods to achieve performance leaps for platinum-based catalysts delving into the recent research advancements in how to fabricate Pt catalysts and support engineering. As for the preparation strategies it focuses on the progress of the impregnation reduction method and the colloid method as well as the gradually developing technologies like atomic layer deposition and sol - gel synthesis; in terms of the support engineering this paper highlights the performance advantages of the three - dimensional structure of the graphene the MOF - derived carbon support and the ionic liquid - modified support and also their precursors. Finally, this article presents some insights concerning future industrial - scale production and sustainable development, aiming to offer a systematic reference for the prospect of preparing higher - efficiency, low - platinum catalysts and their supports.

1 Introduction

Energy is a vital resource and foundation for human survival. As issues such as the gradual depletion of fossil fuels and increasingly severe environmental pollution have come to the fore, calls for new energy sources have grown louder. At the same time, driven by global sustainable development goals such as “carbon peaking” and “carbon neutrality,” the transition from fossil fuels to clean energy is accelerating. A series of technological advancements that are based on hydrogen energy and are of great significance to sustainable development can assist human beings in getting rid of the dependence on fossil fuels and can also reduce environmental pollution. The proton exchange membrane fuel cell, which is an electrochemical device that can directly convert the chemical energy of combustion into electrical energy, is a highly efficient energy conversion device among traditional batteries, having advantages such as high energy conversion efficiency, fast load response, and small

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impact on the environment. Under the background of new energy vehicles and new energy infrastructure, they have already become a widely spread alternative that replaces the traditional fossil fuels.

A simple fuel cell has two half - cell reactions: the anodic reaction is a hydrogen oxidation reaction that occurs rapidly, and the cathodic reaction is an oxygen reduction reaction that takes place slowly. The oxygen reduction reaction at the cathode of fuel cells has characteristics such as long reaction cycles, slow kinetics and high overpotentials. These inherent characteristics make it the key factor that affects the efficiency of fuel cells and the further development of energy storage. Therefore, the development of the cathode oxygen reduction catalyst is a crucial step in overcoming the technical bottleneck of low fuel cell efficiency [1]. The ORR catalyst, which is the oxygen reduction reaction, is the type of material that is used in fuel cells to speed up the oxygen reduction reaction. Its core function, which is to reduce the energy consumption of reactions and enhance the battery's efficiency, makes it one of the core components of fuel cells.

The platinum - carbon catalyst that has excellent catalytic performance in the oxygen reduction reaction has attracted wide attention. However, platinum is scarce and costly, which causes the price of platinum-based catalysts to always be quite high. Also, when fuel cells operate for a long time, platinum particles are prone to agglomeration and dissolution, thus leading to the decline of the performance of platinum-carbon catalysts. To address this issue the industry has explored various methods from the perspective of preparation strategies methods like the impregnation reduction method and the colloid method are employed to enhance the catalyst performance from the material aspect different substrates are used to support platinum to develop new materials thereby improving the intrinsic activity of active sites.

2 Preparation strategy

2.1 Immersion reduction method

The impregnation - reduction method is a classic strategy for preparing platinum - based fuel cell catalysts. Its core principle is that by making use of the electrostatic adsorption or coordination interaction between the oxygen-containing compound functional groups on the carrier surface and the metal precursor ions, the precursor is evenly dispersed onto the carrier surface. Then, through gas-phase reduction or liquid-phase chemical reduction, the adsorbed metal ions are transformed into nanoparticles on the spot, and finally, a highly dispersed Pt/C catalyst is obtained.

It should be noted that the early Pt/C catalysts prepared through the traditional impregnation process generally have a low platinum loading (approximately 1 weight percent), which makes it difficult to meet the requirements of the proton exchange membrane fuel cell for a highly active catalyst layer. If the total amount of platinum in the catalyst layer remains unchanging all the time, then increasing the platinum loading on the catalyst support can greatly reduce the needed catalyst mass, which can then make a thinner catalyst layer and also reduce the resistance of oxygen mass transfer, which is quite beneficial for enhancing the power density and durability of the fuel cell. Therefore, the research and development of platinum-based catalysts with high loading and high dispersion has turned into a key means for performance optimization.

To handle this challenge, a "double - carrier" cascade loading strategy is put forward: Firstly, TiO_2 nanospheres are dispersed into the aqueous phase, and then polyvinylpyrrolidone (PVP) is introduced as a stabilizer, and ascorbic acid is used as a green reducing agent, so that the platinum precursor is in - situ reduced on the surface of TiO_2 and uniformly nucleated [2]. By controlling the number of deposition cycles, Pt/TiO_2 intermediates with different platinum loadings (marked as Pt/ TiO_2 - 1 to - 3) are precisely prepared; then, the obtained composite material is loaded onto the Vulcan XC - 72 carbon black carrier by the secondary impregnation method, and a Pt/ TiO_2/C ternary composite catalyst is constructed. This design not only allows for the controlled enhancement of platinum loading but also makes use of the remarkable metal-support strong interaction (SMSI) between TiO_2 and Pt to strengthen the anchoring of nanoparticles, while suppressing migration and agglomeration, thus creating a new approach for the rational design of high-loading and highly-stable catalysts indeed.

Shown in Table 1, Ioxy/IC represents the ratio of the total intensity of oxygen-containing functional groups to the total carbon signal intensity. A lower value indicates the reduced existence of acidic oxygen-containing compounds - like hydrogen peroxide - and such substances will suppress the efficiency of the oxygen reduction reaction (ORR); in other words, the higher-efficient oxygen reduction reaction (ORR) comes into existence. The result shows that Pt/ TiO_2 - 2 has a moderate content of Pt and the lowest Ioxy/IC value, which can effectively inhibit the generation of hydrogen peroxide and then increase the ORR current density as stated in [2].

Table 1. Pt Content in Different Catalysts and Ioxy/IC [2].

Catalysts	Pt content (wt%)	Ioxy/IC (%)
Pt/TiO_2 -1	2.01	26
Pt/TiO_2 -2	3.10	25
Pt/TiO_2 -3	3.84	27

The advantage of the impregnation reduction method is that the loading amount and particle size of platinum can be controlled by adjusting reaction conditions; this relatively simple process that requires the fewest equipment is also quite suitable for large-scale production. However, a problematic thing is that the reaction makes use of a liquid medium, and this can cause nanoparticles to clump together quite easily. Moreover, the high surface tension of the solution can lead to the high - surface - area porous carrier structure breaking apart. Also, because the carbon support is water - repellent, even if one can make it more water - loving through surface oxidation, that will result in the support having a shorter lifespan. Thus, it restricts the making of the catalyst on a large scale at high concentrations.

2.2 Colloidal method

The colloid method, which is a classic liquid - phase synthesis strategy, will introduce surfactants, polymers or organic ligands into the reaction system to function as stabilizers and shape regulators. Combined with reducing agents the metal precursors are reduced to monodispersed nano-colloids and then through steps like loading and washing carbon black-supported catalysts (such as Vulcan XC-72) are then produced.

Based on the differences in reaction media and reduction mechanisms the colloid methods have mainly led to technical approaches like oil-in-water methods DMF solvothermal methods and microemulsion methods. However, because there are obvious differences in the standard reduction potentials between platinum and the inorganic salt precursors of transition metals like cobalt and nickel in the coordination system of chloride ions and nitrate ions ($\Delta E°$ greater than 0.5 volts), it is rather difficult to achieve simultaneous reduction at that time [3].

2.2.1 Oleamide method

Oleylamine which is a high - boiling organic solvent approximately at 350 degrees Celsius has carbon - carbon double bonds in its molecular structure. It shows relatively weak reducing property under high-temperature conditions and can also act as a reaction medium as well as a mild reducing agent. Moreover, its terminal primary amino group ($–NH_2$) can coordinate with metal ions, effectively regulating the oxidation - reduction potential of metal species, thus promoting the synergistic co - reduction of different metal precursors. Because there is a rather large difference in the standard reduction potentials between platinum and transition metals like cobalt and nickel, it is often difficult to produce alloy nanostructures with uniform compositions when directly reducing them together; hence, organic ligands (acetylacetonates) are often introduced to narrow the potential difference so as to make the reduction more synchronous.

In an experiment, taking acetone - platinum and acetone - cobalt as precursors, oleylamine is made to act as both a solvent and a reducing agent, and at 300 degrees Celsius, the co - reduction of platinum and cobalt is realized to produce alloy nanoparticles; then these particles are loaded onto the carbon black support, and then high - temperature heat treatment is carried out in a H_2/Ar mixed atmosphere to make the partial formation of an ordered $L1_0$ phase structure. First, the surface non-noble metals are removed via pickling, and then secondary heat treatment is carried out, finally resulting in a high-performance PtCo/C catalyst. After 30,000 aging cycles, the activity decay of this material is only 19%, while the activity decay of the commercial Pt/C catalyst in the same period is as high as 85%, and compared with the commercial benchmark, the overall performance is obviously much better indeed [4].These results show that the high - temperature synthesis strategy which is based on the oleylamine system has obvious advantages in developing highly active and stable platinum alloy catalysts yet the problems of high energy consumption and complex operation still need to be resolved when it is applied on a large scale.

2.2.2 DMF solvent-thermal method

In recent years compared with the traditional high - boiling - point solvent amines the N,N - dimethylformamide (DMF) which has a low boiling point (153 ℃) strong reducibility moderate toxicity and is liquid at room temperature and easy to use has gradually become a more preferred medium when carrying out the solvothermal synthesis of platinum - based nanocatalysts. This method usually makes it possible to effectively reduce metal precursors at relatively lower temperatures. Using DMF as both a solvent and a reducing agent, with platinum acetylacetonate and nickel acetylacetonate as precursors, PtNi nanooctahedra with uniform morphology were successfully prepared through a 42-hour hydrothermal reaction at 120 ℃ in a PTFE-lined reactor; After being supported on a carbon carrier, the resulting PtNi/C catalyst exhibited a mass activity of 1.45 A mg_{pt}^{-1} for the oxygen reduction reaction at 0.9 V [5].

However, due to DMF’s low boiling point and the need for a sealed, pressurized reaction system, this synthetic strategy typically requires a pressure-resistant reactor. It still faces engineering challenges in scale-up production, such as safety, solvent recovery, and environmental sustainability, necessitating process optimization to facilitate practical application.

2.2.3 Micellar emulsion method

Introducing amphiphilic surfactants into an immiscible oil-water two-phase system can create a thermodynamically stable microemulsion system. When the aqueous phase is dominant, an oil-in-water (O/W) structure forms, in which tiny oil droplets encapsulated by surfactants are dispersed in a continuous aqueous phase; conversely, under conditions of excess oil phase, a water-in-oil (W/O) reverse microemulsion forms, in which nanoscale water cores are stabilized by a surfactant interfacial film and dispersed in a continuous oil phase.

Watanabe et al. [6] successfully prepared PtM/C alloy catalysts with uniform particle size and stable composition using diphenyl ether and 1,2-tetradecane-1,2-diol as a mixed solvent, and acetone-platinum and transition metal salts as precursors. A Pt shell structure was formed through heat treatment in a hydrogen atmosphere, and 2–3 layers of Pt atoms were deposited via liquid-phase chemical reduction. Performance tests indicate that the oxygen reduction activity of the resulting PtCo/C catalyst is 2.5 times that of commercial Pt/C; it retains 68% of its initial activity after 30,000 accelerated aging cycles, whereas the activity retention rate of commercial Pt/C drops to 20% after 10,000 cycles.

3 Vector engineering

3.1 Graphene materials

Due to its unique single-layer two-dimensional structure, extremely high theoretical specific surface area, excellent electrical conductivity, and chemical stability, graphene is regarded as an ideal next-generation catalyst support. However, the strong π-π stacking interactions between the layers of raw graphene and the weak interaction between its chemically inert surface and platinum particles hinder further improvements in graphene-based electrocatalysts [7]. Therefore, modifying graphene has become a key focus for achieving breakthroughs.

To deal with the aggregation problem of two - dimensional graphene and the low - conductivity problem of reduced graphene oxide, the development of three - dimensional porous graphene network structures is another important research direction [8]. The open and interconnected pore channels in three-dimensional graphene can enable the rapid diffusion of reactants and products and also expose more active sites on the inner and outer surfaces. It is shown in the research that the PtCo@3DG composite material prepared by loading PtCo nanoparticles onto three-dimensional graphene exhibits a mass activity as high as 0. At zero there is a value of 801 milligrams raised to the power of negative 1. Between nine volts and six volts. Its activity is 8 times that of commercial Pt/C, and even after 10000 cycles, the loss of activity is extremely small [9]. This three - dimensional framework not only provides a very sturdy support for the platinum particles but also has a continuous conductive network that can ensure the rapid transmission of electrons during the reaction.

Generally speaking the graphene - based carrier through modifications like heteroatom doping surface functionalization and three - dimensional structure construction effectively adjusts the size dispersion and electronic structure of platinum nanoparticles thus enhancing the activity and durability of the catalyst in oxygen reduction. However, the control of the defect density and graphitization degree of the graphene still remains a challenge, and under the present circumstances it has to be dealt with.

3.2 MOF-derived materials

Unlike the materials mentioned above the greatest value of MOFs which is often in their use as precursors can be transformed into nitrogen - doped carbon - based materials through controlled pyrolysis and such materials are those that combine high electrical conductivity and a large number of active sites together. When undergoing engineering treatment, MOF materials can be transformed into composite carriers that have high conductivity, abundant pore structures and active sites, and with such composite carriers, even at extremely low platinum loading levels, the performance that surpasses commercial platinum carbon catalysts can be achieved [10].

Specifically speaking, there actually exists a successful approach which is to use the MOF - 74 based on copper as the supporting substance. Researchers encapsulated ultra - low - content platinum nanoparticles into its pores and then carbonized the material at 900 degrees Celsius, successfully synthesizing for the first time a platinum - copper bimetallic catalyst containing only 1 weight percent of platinum. Electrochemical tests show that this optimized catalyst has reached 1. Approximately several volts or so and the half-wave potential is 0. Reaching 88 volts in an alkaline medium, both of which are superior to the commercial platinum-carbon catalysts [11].

Another study has put forward a method which takes ZIF - 67 as a template to stabilize nitrogen - doped carbon. This approach which first obtains cobalt/nitrogen-doped carbon intermediates through high - temperature pyrolysis and then forms platinum - cobalt alloy nanoparticles in - situ through displacement reaction results in a catalyst with an extremely low platinum content, only 0. Please provide the specific sentence that needs to be rewritten. Well its half - wave potential still reaches 0. The voltage of 87 volts surpasses the voltage of the 20% commercial Pt/C catalyst utilized for comparison. It is worthy of being noted that this catalyst shows extremely good methanol tolerance, with no obvious decrease in activity in the existence of methanol, whereas the commercial Pt/C catalyst is rapidly poisoned and deactivated. This then manifests the unique function of the MOF-derived nitrogen-doped carbon support in terms of regulating reaction pathways and enhancing anti-poisoning ability as well [10].

The catalyst support made by using MOFs as the precursor, which has the resulting porous carbon matrix and the heteroatom doping effect, can realize the efficient dispersion and electronic structure regulation of the ultra-low concentration platinum nanoparticles. This not only greatly reduces the amount of precious metals needed but also notably improves the oxygen reduction activity, long-term operation stability, and methanol poisoning resistance ability of the catalyst. However, at the present time, MOF materials still encounter challenges such as poor electrical conductivity and low ion transport efficiency, as well as issues like metal node agglomeration and the destruction of the porous structure during pyrolysis, all of which still need to be resolved.

3.3 Ionic liquid carrier

The concept of ionic liquids (ILs) was first put forward by Paul Walden when he was synthesizing ethylammonium nitrate (EAN). Ionic liquids that are molten salt substances composed of organic cations and inorganic or organic anions and stay liquid at room temperature have the characteristics of non-volatility, good thermal stability as well as high ionic conductivity. Different from traditional carriers the ionic liquids having adjustable cation - anion structures can adjust the electronic structure and microscopic environment of catalytic materials at the molecular level thus enhancing the oxygen reduction reaction performance of platinum - based catalysts.

Ionic liquids which play an important part in structural regulation and can serve as ideal precursors for heteroatom doping. By pyrolyzing ionic liquids that specifically contain elements like nitrogen and phosphorus, carbon materials that are doped with heteroatoms can be directly synthesized. The doped atoms, which can effectively adjust the electron distribution of the carbon matrix, will create numerous active sites for anchoring platinum nanoparticles [12]. In a certain research, nitrogen-phosphorus co-doped carbon materials were successfully synthesized by using polymerizable imidazole phosphate ionic liquids as precursors. This kind of material that has fairly good electrocatalytic performance in the oxygen reduction reaction under alkaline conditions has an initial potential as low as around 0. At 92 volts which is near the level of commercial platinum-carbon catalysts [13]. In another research a homogeneous mixture of melamine and 1-butyl-3-methylimidazolium hexafluorophosphate is made and then pyrolyzed resulting in a mesoporous carbon material doped with nitrogen phosphorus and fluorine. This material not only shows a quite good oxygen reduction catalytic activity but also has a rather good tolerance to methanol cross - contamination, thereby giving rise to new insights for the design of anti - poisoning catalysts of direct methanol fuel cells [14]. A carbon support having inherent catalytic activity can be constructed by utilizing ionic liquids as precursors, which is beneficial for the dispersion of platinum.

When ionic liquids are adopted as surface modifiers as carriers, by designing anions and cations, the electronic structure and surface microenvironment of platinum active sites can be adjusted, thereby significantly enhancing the activity of platinum catalysts and their tolerance towards methanol. However, these materials have high preparation costs and also poor stability, which then indeed hinders their further development and improvement.

3.4 Summary

Generally speaking, different catalyst supports for oxygen reduction reactions respectively have their own unique characteristics in terms of performance and application. Conventional carbon carriers that are of relatively low cost and have favorable electrical conductivity are thus suitable for large-scale application in fuel cells; however, their stability and inherent activity are limited. Graphene-based materials that have a large specific surface area and excellent electrical conductivity are frequently used in high-performance fuel cells and electrochemical sensors; yet, they are prone to the situation of agglomeration. MOF-derived materials that have adjustable structures and high precious metal utilization rates are suitable for low-platinum and efficient catalytic systems but their preparation processes are quite complicated; ionic liquid interfaces that are designable and have high intrinsic activities are suitable for specific electrochemical environments yet they are relatively expensive and lack sufficient stability. Therefore, in the actual application, one needs to select an appropriate carrier in line with the requirements of the equipment and then further enhance its overall performance through methods like synthesis and modification and the like.

4 Conclusion

This paper conducts a systematic review on the research progress of low - platinum and highly stable oxygen reduction catalysts for fuel cell cathodes, with the emphasis being placed on preparation strategies and support engineering. At present although the liquid - phase synthesis process has greatly enhanced the utilization rate of platinum the cost and the scalability still are the obstacles to large - scale industrialization in terms of the carrier the graphene carrier effectively alleviates the agglomeration and conductivity problems and the carbon material derived from metal - organic frameworks (MOF) achieves high platinum dispersion and low loading through adjustable pore structures the modification of ionic liquids enhances the interfacial activity and methanol tolerance however key challenges such as insufficient structural stability of MOF under high potential and the leaching tendency of ionic liquids have not been well solved yet. In future research, the coordinated optimization of carriers and processes ought to be highlighted as the key point: taking the precise structural design and the enhanced stability of MOF-derived carbon materials as the core breakthrough points, and then combining with the simplification and the large-scale promotion of green and controllable preparation processes, the promotion of high-performance platinum-based catalysts from the laboratory to large-scale application can be realized, which can then offer real support for the actual development of fuel cells.

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