Research Progress on Oxygen Reduction Catalysts for Hydrogen-Oxygen Fuel Cells Cathode

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Abstract. Developing effective and sustainable energy conversion technologies is of vital importance in addressing the increasingly serious environmental and energy issues. Due to its high energy density, rapid startup, and zero emission characteristics, proton exchange membrane fuel cells (PEMFCs) have shown great potential in the transportation and distributed energy sectors. However, in practical applications, the performance of PEMFCs is severely limited by the slow reaction rate of the cathode oxygen reduction process (ORR). Therefore, the development of effective and stable ORR catalysts is of vital importance for advancing the development of PEMFC technology. This article and its related content conduct a comprehensive analysis of fuel cell catalysts, covering both noble metal catalysts and non-noble metal catalysts. Additionally, it elaborates in detail on how advanced modification strategies can enhance the performance and stability of catalysts, and provides an outlook on the future design direction of catalysts that possess high activity, long lifespan, and economic efficiency.

1 Introduction

Traditional fossil fuels have seriously contaminated the environment due to the rising need for energy worldwide. By directly converting hydrogen and oxygen into electricity through electrochemical reactions, Proton Exchange Membrane Fuel Cells (PEMFCs) are an effective energy conversion device that produces only water and emits no emissions. However, PEMFC performance in real-world applications is severely limited by the slow kinetics of the cathode oxygen reduction process (ORR), hence the creation of effective and stable ORR catalysts is essential to the advancement of PEMFC technology.

Fuel cell catalysts are primarily classified into noble metal catalysts and non-noble metal catalysts based on compositional and structural differences. Platinum (Pt)-based alloys remain the most widely used ORR catalysts due to their superior catalytic activity and electrochemical stability. Nevertheless, the scarcity and high cost of noble metals severely hinder the large-scale commercialization of PEMFCs [1]. To address this, transition metal-

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nitrogen-carbon materials have garnered research attention, though challenges persist in their catalytic activity and durability.

Therefore, this review and other aspects have conducted in-depth reviews of fuel cell catalysts, covered the two main categories of noble metal catalysts and non-noble metal catalysts, and detailed introduced the characteristics, research progress of improvement strategies, and challenges of various catalysts.

2 Precious metal catalysts

In the early stage of the development of fuel cell technology, platinum black was commonly used as the catalyst for ORR due to its relatively good catalytic properties. However, platinum black exposed obvious drawbacks in practical applications. Because the Pt particles in platinum black have relatively large sizes, this large particle size leads to a low utilization rate of platinum atoms. However, platinum, as a precious metal, is scarce in resources and expensive, and such a high loading made the catalyst cost prohibitively high, which severely limited the widespread application of fuel cells in real life.

In 1986, a significant breakthrough was achieved in the field of fuel cell catalysts. Van Zee and other researchers innovatively adopted carbon-supported platinum (Pt/C) catalysts [2]. The specific surface area of carbon materials is quite distinctive as it allows creating a large space of attachment on which platinum particles can be attached. Simultaneously, platinum particles may be produced in the size of nanoparticles by sophisticated methods of preparation and attain a high degree of dispersion on the carrier of carbon. This geometrical property allows the increased exposure of platinum atoms on the surface which contributes to a high surface utilization rate of platinum atoms.

Later, Norskov and other scientists [3] were able to provide important theoretical assistance in the construction of fuel cell catalysts when the theoretical study was being conducted and further examined. Using density functional theory (DFT), they precisely determined the adsorption energy of the intermediate products on the surface of the ORR. They produced an estimate of the catalytic activity of the metals in the relationship of the oxygen adsorption energy to the volcano graph after a good deal of computation and data analysis.

This is an important scientific accomplishment of this theoretical result that shows the inherent relationship between catalytic activity of various metals in ORR reaction and adsorption energy of oxygen. Based on this theory, platinum was confirmed to be effective in successful catalytic activity in the ORR reaction, since it is capable of having a moderately low oxygen adsorption energy, which made it the ideal ORR catalyst.

3 Non-precious metal catalysts

Since the precious metals are scarce resources within the crust of the earth, their mining and purification are tedious and expensive, which further leads to expensive costs of precious metal-based catalysts.

In the realistic implementation of hydrogen fuel cells, in order to guarantee that their performance is in line with the requirements, many precious metal catalysts are usually required, exacerbating the cost pressure further, and making hydrogen fuel cells disadvantaged in the competition with other traditional energy technologies, and seriously limiting the popularization of hydrogen fuel cells in many areas including transportation and energy storage.

The current solution out of this dilemma is the gradual focus on the non-precious metals catalytic systems, by the research community, rather than the traditional precious metal

catalytic system. Researchers are in pursuit of the study and development of alternative materials that have low cost and high stability in the hope of decreasing the total prices of hydrogen fuel cells with the usage of such novel catalysts and contributing to the wide commercial use and popularization of hydrogen fuel cells.

Most catalysts of non-precious metals are today in existence and they have been developed with great success, two of them are transition metal oxide catalysts and transition metal - nitrogen - carbon (M-N-C) catalysts, two examples of non-platinum group metal catalysts. The unique electronic structure, as well as the chemical properties of transition metal oxide catalysts demonstrates a degree of activity in the catalytic reaction, including reducing oxygen. Indicatively, Zhang et al. [4] catalytically optimized the catalytic properties by covering manganese dioxide on carbon nanotubes (CNTs), with the highest power density of the fuel cell being the MnO_2/CNTs cathode to 210 mW/m^2 (2.3 times the catalytic capability with the traditional Pt /C cathode (229 mW/m^2). Nevertheless, these catalysts are not yet completely applicable in practice, due to such shortcomings of the materials as low conductivity and low stability, eliminating the possibility of their further development and implementation.

In contrast, M-N-C catalysts outperform many non-precious metal candidate materials in terms of catalytic performance. Strong chemical interactions between transition metals and nitrogen atoms in the M-N-C catalysts give several active sites where the oxygen reduction reaction can take place, enabling the catalyst to catalyze the reaction effectively. In addition to having a large specific surface area and good conductivity to facilitate the fast flow of electrons, the carbon material also acts as a carrier, facilitating the adsorption of reactants and the desorption of products, which improves the catalytic reaction. As an illustration, Li et al. [5] had created Fe-Co dual sites by laying Co on N-doped porous carbon, and such catalyst has an initial potential equivalent on the Pt/C counterpart, and the primary maximum energy density of PEMFCs was 0.98 W/cm^2, and (Fe, Co)/N-C is better than the majority of reported non-Pt catalysts using H_2-O_2 and H_2-air conditions. The dual-site arrangement of the system, as predicted by the density functional theory, indicates an advantage of using the configuration in the activation of the O-O bonds, as the four-electron oxygen reduction reaction requires.

Based on these advantages, transition metal - nitrogen - carbon (M-N-C) catalysts are regarded as the most promising technological direction to replace platinum-based catalysts at present.

4 Advanced catalyst improvement strategies

Researchers are actively exploring innovative improvement strategies to enhance the overall performance of the catalysts and accelerate the commercialization process of fuel cell technology. Common modification strategies include: alloy treatment, construction of carriers, construction of stable interfaces, interface modification and defect engineering, etc.

Several effective strategies exist for catalyst enhancement. Alloy treatment, for instance, not only increases the number of active sites by forming a new lattice structure but also modifies the electronic structure, thereby enhancing energy conversion efficiency and reducing costs. Using the dissociation energy properties of alloys as an example, in certain alloy, the reaction between the various atoms will alter the electronic distribution and the chemical bond parameters of the media, hence, the dissociation energy. An example of this is the $Pt_{20}Pd_{20}Cu_{60}$ alloy model which has a dissociation energy that is high compared to models of pure Cu and Pt. This large dissociation energy allows this alloy catalyst to be more active in catalytic reactions, whereby the dissociation and activation of reactant molecules become much easier; and its corrosion resistance and longevity are as well enhanced greatly. Not only was this catalyst able to pass 20000 possible cycle tests, the quality activity (1.66

A/mg Pt) was also highly effective and the activity showed good durability - with the 50000 potential cycle tests being done, the activity was not lost and instead the performance was maintained throughout in a complex working environment over an extended duration which indirectly reduces the cost of usage after all [6]. Besides the above alloy materials, it has also been found that more alloy catalysts of non-precious metals are extensively researched and utilized. As an illustration, the PtCoNi@NCNTs catalyst produced through incorporation of cobalt/nickel in the platinum network and incorporation with nitrogen-doped carbon nanotubes has good stability activity at the potential of 0.9 V. Due to this high efficiency catalyst, a fuel cell had a platinum utilization rate of 10.22 W /mg Pt cathode-1 and quality activity of 8.11 A/mg Pt cathode-1 at 0.7 V of voltage [6]. This distinctive composite construction takes advantage of all the strengths of the component element to its maximum. The fundamental catalytic active center is the platinum lattice, the electronic structure is governed through the embedding of cobalt/nickel, which increases the catalyst activity, and the catalyst is facilitated by carbon nanotubes that use nitrogen. Thus, the whole process is superior.

Besides alloy treatment, making an appropriate carrier to carry the catalyst is also a method that would enhance the catalyst performance. The carrier does not only give physical support to the catalyst; it also interacts and influences the electronic structure and chemical properties of the catalyst. In one instance, the loading of small nanoparticles of platinum containing the metal components of the intercalation compound was performed using sulfur-anchored porous sulfur-doped carbon carriers (Yang et al.). This system shows a high degree of chemical interaction between the platinum and the sulfur that highly deters the sintering of the nanoparticle at high temperatures and regulates the average size of the metal intercalation compound particles to be less than 5 nanometers. Agglomeration of nanoparticles occurs readily in high-temperature systems and hence, reduces the specific surface area and active sites, which influences catalytic functions. Because to the sulfur anchoring effect, the nanoparticles' mean particle diameter decreases, increasing their specific surface area and quality activity, which significantly improves the catalyst's performance. In single cell experiments, the quality activity of four metal intercalation compounds/platinum catalysts (PtFe, PtCo, PtNi, and PtCu three metal intercalation compounds) as cathode catalysts significantly outperformed that of platinum carbon catalysts. The accelerated durability tests verified the great stability of metal intercalation compound catalysts. The PtCo and PtFe i-NP catalysts were found to retain 77 and 79 percent of their initial mass activity after 30,000 AST cycles, respectively, in the accelerated stress test (AST) of PEMFC. Of special respect are the findings that the cathode of PtCo i-NPs that had the lowest platinum loading was 0.1 and had a maximum power density of 1.08 W/cm^2 under high stoichiometric conditions [7].

Furthermore, the construction of a stable interface is of great significance for preventing catalyst dissolution and migration, and further enhancing the service life of the catalyst. A stable interface can provide a relatively fixed reaction environment for the catalyst, reducing the loss and structural changes of the catalyst during the reaction process. The GenInoue team reports that, in comparison to pure Pt/C, the carbon-supported platinum catalyst with a silica intermediate phase (Pt/C(IJ)), known as SiO_2-Pt/C(IJ), has lower oxygen diffusion resistance, higher dispersion, and stability. To confirm the stabilizing effect of silica coating, the zeta potential of Pt/C(IJ) and SiO_2-Pt/C(IJ) was measured. After a week, the zeta potential of SiO_2-Pt/C(IJ) increased to -62 mV, higher than Pt/C(IJ), indicating that the Si-OH groups formed after silica coating improved the stability of the catalyst [8]. One of the key elements influencing the reaction rate in fuel cells' oxygen reduction process is oxygen diffusion resistance. Reduced oxygen diffusion resistance increases the rate at which oxygen reaches the catalyst active sites, hence increasing the effectiveness of the process. Increase in dispersion implies that catalyst active sites will be better exposed within the reaction system,

and there will be more availability of the reaction opportunities. Other substances like multi-walled carbon nanotubes, cerium dioxide and polythiophene have also been demonstrated to be useful in improving the stability of the catalyst besides silica and nitrogen-doped carbon. These materials possess distinctive physical and chemical characteristics, like high conductivity of multi-walled carbon nanotubes and high specific surface area, redox property of cerium dioxide, and chemical stability of polythiophene, and can react with the catalyst to create an interface structure, which is stable against the effect of the external environment [9-11].

To further increase the activity and stability, other elements or compounds can be added into the catalyst to modify the structure and chemical characteristics. This plan will be able to control the electronic state, surface characteristics, and crystal structure of the catalyst leading to optimization of its catalytic activities. Indicatively, Kucernak [12] and his colleagues succeeded greatly in loading the iron capacity. Their starting synthesis solution involved preparing a sacrificial material (zinc) in the first synthetic step to form a carbon-nitrogen skeleton and then substituted the iron onto this skeleton, and they succeeded in loading the iron amount of 7 wt.% in the form of single-atom Dead Sea-iron Fe-N_4 sites (Fe-NC). The 7 wt% high amounts of surface density iron loading facilitated the Fe -NC catalyst to show a good oxygen reduction reaction at 0.8 V voltage of 31.9A g^{-2}. A peak power density of 429 mW/cm^2 was attained at a current density of 145 mA/cm^2, a voltage of 0.55 V and an iR compensation voltage of 0.90 V; all under H_2-O_2 conditions. This special synthesis process allows to distribute the iron evenly in the carbon-containing nitrogen structure, creating an iron structure of high surface density. The surface density of the metal is high which offers more active sites of the catalytic reaction so that the catalyst can be highly active and efficiently enhances the catalytic reaction in the respective catalytic reaction. Also, such procedures as the interface change and defect engineering can be taken as the means of improving the activity and stability of non-precious metal catalysts.

Interface modification can optimize the electron transfer and reactant adsorption processes by adjusting the interfacial interactions between the catalyst and the support or other components. Defect engineering, on the other hand, increases the number and activity of active sites by introducing defects into the catalyst material and altering its local electronic structure and chemical properties. For example, a new kind of nitrogen-doped carbon thin-layer encapsulation structure with high defect density was created using techniques such high-temperature deposition in vapor phase deposition and ammonium chloride heat treatment. The Fe-N-C catalyst with nitrogen-doped carbon coating (referred to as Fe-AC-CVD) in this study demonstrated a decreased Fe site density following NH_4Cl treatment, suggesting that the introduction of intrinsic lattice defects increased the intrinsic activity associated to the conversion frequency (TOF). Fe-AC-CVD showed enhanced stability of over 300 hours in the membrane electrode assembly and under stress testing of 0.67 V voltage due to the conversion of rich-defect pyrrole nitrogen coordination FeN_4 sites to extremely stable pyridine nitrogen coordination FeN_4 sites.

Besides, the Fe-AC-CVD cathode showed higher electrochemical oxidation resistance in the high-voltage portion of the anoxic environment, which was consistent with the outcome of increased stability. The large concentration of defects in this structure gives the reaction more active centers and the nitrogen-doped carbon thin-layer encapsulation is able to protect the internal structure of the catalyst against external environmental damage hence, improving the stability of the catalyst [13].

On the same note, rational designing of the support can make a big contribution on the performance of the non-precious metal catalysts. The support does not only serve to offer physical support to the catalyst which influences the catalytic activity of the catalyst in a synergistic manner. For example, when carbon nanotubes are used as the support structure, the CoBi catalyst (henceforth referred to as CoBi/CNT) is built in a unique one-dimensional

structure of tubes and has a large specific surface area, which can provide sufficient attaching sites to the CoBi catalyst and increase its specific surface area.in contrast to CoBi, which has a mass activity of 5.86 $mA.mg^{-1}$. The CoBi/CNT catalyst has a maximal mass activity of 25.7 $mA.mg^{-1}$ Co [14]. Simultaneously, carbon nanotubes' high electrical conductivity can lower electron transfer resistance and accelerate electron transfer between the catalyst and reactants, improving the catalyst's mass activity and stability and allowing it to perform better in catalytic reactions.

5 Conclusion

This review has conducted a systematic and comprehensive overview of fuel cell catalysts from multiple aspects such as working mechanism, scientific issues, modification strategies, and application prospects. It covers the two main categories of noble metal catalysts and non-noble metal catalysts, and details the characteristics, research progress of improvement strategies, and challenges of each type of catalyst.

Based on in-depth research on fuel cell catalysts, the following design concepts for high-performance catalysts have been proposed: cost-effectiveness and environmental friendliness, feasibility of large-scale production and simplicity, compatibility with other components of the fuel cell, good dispersion, and excellent electrochemical stability.

Furthermore, with the rapid development of advanced technologies such as artificial intelligence, new opportunities and challenges have emerged in the design of fuel cell catalysts. Screening methods based on artificial intelligence can utilize big data and machine learning algorithms to quickly predict material properties, significantly shortening the development cycle of new high-performance catalysts; deep generative artificial intelligence frameworks can help optimize the nanostructure design of the catalyst layer, achieve precise control of the catalyst's microstructure, and improve catalyst performance. Although the research on intelligent materials and adaptive catalytic technologies has not yet been applied, they have pointed out the direction for the future development of fuel cell catalysts, promising more efficient and flexible energy conversion and pushing fuel cell technology to new heights.

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