Enhancing Catalyst Performance in Fuel Cells: Challenges and Innovations

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Abstract: The research of this study is to explore methods and innovations to improve the performance of fuel cell catalysts. The oxygen reduction reaction (ORR) in the fuel cell is a critical step. Traditionally, platinum-based catalysts were the best choice. However, their high cost limits the wide application. Therefore, this research aims to find more cost-effective alternatives to improve the viability of fuel cells. This study divided electrocatalytic materials into two parts which are platinum-based catalysts and non-noble catalysts for further compare the different characteristics of various catalysts, including platinum-based catalysts, transition metals oxides, transition metals nanomaterials, and single-atom catalysts. At the same time, the advantages and disadvantages of electrocatalytic materials and non-metallic materials are compared, and the methods that describe how to solve the research problems are proposed. This research also compares platinum-based catalysts with transition metal catalysts and compares transition nanomaterials with traditional nanomaterials which have different characteristics. In terms of environmental protection and sustainable development, non-noble catalysts are more available and environmentally friendly than precious metal catalysts with complex mining techniques. In the future, non-metal catalysts will have a wide range of commercial potential in various applications and are expected to replace electrocatalytic materials.

1 INTRODUCTION

Proton Exchange Membrane Fuel Cells (PEMFCs) are emission-free energy converters for various applications, including stationary devices. They convert chemical energy from hydrogen oxidation and ORR into electrical power. These two reactions also need the catalyst. However, hydrogen oxidation and oxygen reduction need a catalyst, especially the ORR which has naturally slow kinetics in PEMFCs and requires electrocatalysts.

Platinum-based catalysts have been the preferred choice owing to their superior efficiency in facilitating ORR (Bai et al., 2022), with Pt-C catalysts renowned for their exceptional electron and proton mobility (Li et al., 2023). However, the exorbitant cost associated with platinum has hindered its widespread adoption, prompting a quest for more cost-effective alternatives to enhance the feasibility of PEMFCs

In response to this challenge, researchers have turned their attention towards exploring alternatives to platinum-group metals (PGMs) that offer stable cell performance at a reduced cost (Snitkoff et al., 2021). Among these alternatives, first-row transition metals have emerged as promising candidates for metal-based catalysts, primarily due to their affordability relative to platinum.

In this study, we compare many styles of catalysts and their characteristics (eg: platinum-based catalyst, transition metals oxides catalyst, transition metals nanomaterials, and Single atom catalyst. Additionally, researchers have begun incorporating heteroatoms into catalysts to enhance their performance and transition from platinum to first-row transition metals as cost-effective alternatives.

2 ELECTROCATALYTIC MATERIAL

Due to the expensive cost of platinum-based catalysts, the wide application of platinum-based catalysts in fuel cells is limited, so many researchers aim to find more cost-effective catalysts. Compare the characteristics of platinum-based catalysts with non-noble metals

The studies gradually add heteroatoms into the electrocatalyst to improve the activities of the

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catalysts. At the same time, researchers switch the catalysts from platinum-based catalysts to the less costly catalysts transition metal catalysts.

2.1 Platinum-Based Catalyst

Recent studies revealed that Platinum-based catalysts are becoming the most common catalyst in PEMFCs, especially in oxygen reduction reactions. Based on recent studies, Platinum-based catalysts have different diameters. Platinum-based catalyst activity became worse when the size of platinum nanoparticles increased. When the diameter of the platinum nanoparticles-based catalyst is 3nm, the activity of the platinum nanoparticles-based catalyst becomes maximum (Chen et al., 2022). The high temperature also has a certain degree of influence on the platinum-based catalyst. The interaction between platinum and sulfur atoms doped in a carbon matrix can inhibit the sintering of nanoparticles at 1000℃ so that the average particle size of platinum-based nanoparticles can be controlled within 5 nm at high temperatures which can maintain the activity of platinum-based catalyst (Han et al., 2022).

Firstly, silicon and lithium can form a variety of alloys, such as $Li_{12}Si_7$, $Li_{13}Si_4$, Li_7Si_3, $Li_{15}Si_4$, $Li_{22}Si_5$, etc., which not only have high capacity, but also have de-embedded lithium potentials lower than 0.5 V vs. Li/Li^+, with $Li_{22}Si_5$ having a capacity of up to 4200 mAh/g.

In addition to Si-Li alloys, there are other silicon-based alloy materials. Mukanova et al. (2017) achieved a facet capacity of 80 mAh/cm² by forming a three-dimensional composite anode with silicon thin films on graphene-coated nickel foam by chemical vapour deposition and magnetron sputtering. Ding et al. (2020) prepared a binder-free anode with bilayer graphene-coated silicon nanoparticles (SiNPs) embedded in the porous nickel current collector, and although a respectable face capacity was achieved, the performance of the interfacial layer still needs to be improved. In view of this, Tzeng et al. (2023) proposed thick and porous silicon-based anodes, and constructed porous anodes with electrical conductivity on nickel foam by mixing SiNPs, phenolic resin binder, and the conductive agent Super P, which exhibited excellent cycling performance and charge storage capacity. Experiments shown that the 80 nm nickel foam nanoporous silicon-based anode maintained excellent performance after a total of 50 cycles, where the current density was 4 mA/cm^2, retaining a retained area capacity of up to 6.5 mAh/cm², which provided a charge storage capacity of 23.4 C for an anode area of 1 cm² at a current rate of 4 mA.

In particular, the eutectic reaction takes place throughout the melting procedure because the melting points of Cu and Si are slightly different. This makes it simpler for Si to create the Cu_3Si alloying phase and evenly disperse it on the Si matrix resulting in greater suppression of the volume growth. Zhang et al. (2021) first prepared Si-Cu_3Si composite with a capacity of 1000 mAh/g after 300 cycles, while Li et al. (2023) prepared P-doped Si-Cu alloys by the vacuum melting method, which improve the electrical conductivity and lower the Li^+ diffusion barriers to significantly enhance the electrochemical performance, Among these, the $P_{0.5\%}$Si-Cu alloy had a significantly lower R_{ct} value than the undoped Si-Cu alloys, with a capacity of 1048 mAh/g after 60 cycles.

In addition, Si-Sn alloy anode has sparked much interest because of its unique lithium embedding ability and buffering effect on volume change. Tian et al. (2021) successfully prepared a novel anode material consisting of tin nanowires (SnNWs) embedded with SiNPs by solid-gas reaction method, which exhibited a high and stable capacity at both room and low temperatures.

Although silicon alloy structure has significant effect in solving the swelling problem of silicon-based anode, its preparation process is complicated and costly, which limits its mass production application. Therefore, researchers have turned to the strategy of compositing nanosilicon and carbon materials to seek performance enhancement and cost reduction.

2.2 Non-Noble Metal

Compared to platinum-based which belongs to precious metals, non-noble metals are abundant on Earth. These allow non-noble metal catalysts to have a lower cost compared with platinum-based catalysts wide appliance in the production process, which is conducive to large-scale production and application. In terms of environmental protection and sustainable development, the process of precious metals may cause pollution to the environment, while non-noble metals are relatively environmentally friendly.

The activities of catalysts of non-noble metal catalysts can be adjusted by changing their composition and structure. This makes non-noble metal catalysts have a wide range of applications and prospects.

The researchers used the comparative study method. The activities of catalysts of platinum-based catalysts and transition metal catalysts were compared. At the same time, transition metal nanomaterials and traditional nanomaterials were also compared. The studies divided the single-atom catalyst into five categories based on the difference in the supporting materials.

2.2.1 Transition Metals Oxides

Chevrel-phase-type compounds unveil Ruthenium-centered catalysts as viable non-noble metal alternatives for ORR in acidic environments (Vante, 2010). Ruthenium-based catalysts employed in these reactions yield H_2O_2, a trend observed to decrease with increasing electrocatalyst loading. Studies indicate that metal center activities, at equivalent loadings, follow the sequence Fe < Co < Ru < Pt, as depicted in Figure 1. Further analysis, correlating oxygen-binding energies with RRDE experiments measuring H_2O_2, underscores the pivotal role of electrocatalyst loading (Vante, 2010).

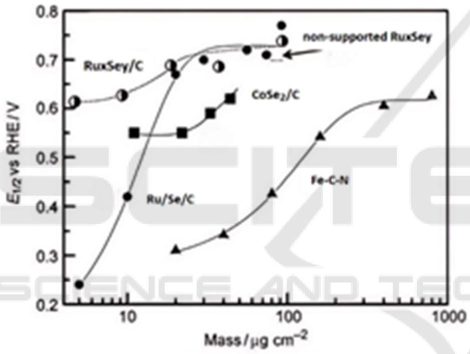

Figure 1: The curve of E1/2 with Mass. Chalcogenides: non-supported RuxSey (1), RuxSey/C (2), and Ru/Se/C (3); CoSe2/C (4); and Fe-C-N (5) (Vante, 2010).

In alkaline environments, corrosion-resistant non-noble metals such as Fe, Co, and Mn exhibit notable activity in oxygen reduction reactions. Graphene oxide catalysts based on non-noble metals feature stable spatial crystal structures and high corrosion resistance, contributing to their favorable activity in these reactions (Tao et al., 2024). The catalytic activity of Mn oxide catalysts varies with different valence states. Zhang et al. (2020) observed enhanced catalyst activity during the high-potential or hypervalent state of Mn.

In addition to the advantages of transition metal oxides in acidic and alkaline media, there are these three characteristics. The first characteristic is the hydroxyl groups inserted on the surface of transition metal oxides can be further functionalized. The second is to maintain crystal structure and prevent metal particles from agglomeration. The last characteristic is Transition metal oxides have better alkali corrosion resistance than carbon-based materials in precious metals. For instance, Meng Sun and co-workers found graphene/graphene oxide supported single transition metal oxides show good oxygen reduction reaction performance and long-term durability. The reason is the rich functional hydroxyl groups, stable spatial crystal structure, and good alkali corrosion resistance (Sun et al, 2015).

Table1: Compares the Pt/C catalyst with Fe3/NG-800 in a different electrolyte by onset and half-wave potential.

	0.1M KOH		0.1M KClO4	
	Onset potential	Half-wave potential	Onset potential	Half-wave potential
Pt/C (Yan et al., 2023)	1.02V	0.85V	0.95V	0.82V
Fe3/NG-800 (Xiong et al., 2022)	1.03V	0.86V	0.92V	0.77V

2.2.2 Transition Metals Nanomaterial

Compared to conventional nanomaterials, the carbon material Vulcan XC-72 stands out as one of the most popular choices (Vante, 2010). It's well-known that Pt/C catalysts exhibit low activity and carbon instability, resulting in slow oxygen reduction rates. To enhance activity, scientists have turned to transition metal nanomaterials, which are cost-effective and readily available. Through pyrolysis and etching techniques, researchers synthesized Fe3/NG nanoparticles. Notably, the catalyst Fe3/NG-800 displays heightened activity at 800° C compared to other temperatures. Figure 2 illustrates the onset potential and half-wave potential of Fe3/NG-800 versus Pt/C (Xiong er al., 2022).

2.2.3 Single-Atom Catalysts

Unlike traditional catalysts and nanomaterial-based catalysts, where metal particle activity is typically concentrated at corners or edges, single-atom catalysts (SACs), as outlined by Zhang Tao's team, significantly reduce the energy barrier and exhibit more than an order of magnitude greater activity (Su et al., 2021).

Single-atom catalysts have witnessed rapid development in recent years, with a myriad of styles emerging over the past decade. Researchers have categorized them into five distinct types based on the support material: single metal atoms anchored on metals, metal compounds, non-metallic carbon-based supports, MOFs, and zeolites.

The activities of single-atom catalysis can be changed with the enhancement of coordination. In order to increase the activities of single-atom catalysis, the operator should carefully select the appropriate support while performing appropriate metal-carrier interactions (Li et al., 2019). For instance, Hutching and co-workers found that there are different activities of vinyl chloride monomers in Au single-atom catalysts. The reason is that the ratio of Au(I): Au(III) is caused by the different Au-Cl coordination (Malta et al., 2017).

Recent studies have demonstrated that single-atom catalysts can substantially enhance catalytic activity by achieving maximal atomic utilization and revealing ample active sites. Moreover, single-atom catalysts exhibit high selectivity, as evidenced by the comparison between desk current and ring current, showcasing reduced desk current and increased ring current. For instance, Yang and co-worker successfully used a single platinum atom catalyst which fixed on nanometer titanium nitride was prepared by using chlorine ligands. According to Figure 3. (a) which reveals high selectivity, transmission electron microscopy images showed that only TiN nanoparticles were present in 0.35wt% of the platinum-TiN sample, and no platinum nanoparticles were observed. However, Figure 3. (b) is the HAPtDF-STEM image, where the white dots are platinum nanoparticles.

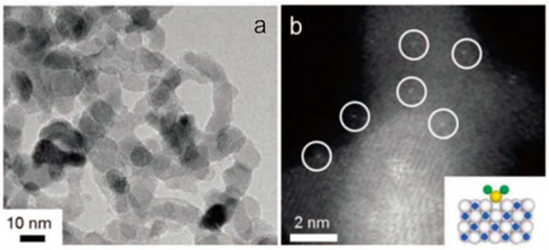

Figure 2: (a) Transmission electron microscope image. (b) HAPtDF-STEM image reveals 0.35 wt% Pt/TiN (Su et al., 2021).

3 CONCLUSION

According to a comparison of electrocatalytic material and non-metal material, they have different advantages and disadvantages. As an electrocatalyst material, platinum-based catalysts have high to be a barrier to wide use.

In contrast, non-metal materials like Ru hold promise for replacing Pt in oxygen reduction reactions in fuel cells under acidic conditions. Transition metal oxides exhibit high activity, ranking second only to platinum-based catalysts. Notably, Mn displays exceptional activity in alkaline environments due to its unique structure and varying valence.

Transition metals nanomaterials, a subset of non-metal materials, offer affordability and accessibility compared to traditional electrocatalytic materials. While traditional catalysts may lack sufficient activity and durability in real-world applications, single-atom catalysts show promise in overcoming these limitations during oxygen reduction reactions. However, their practical application remains limited.

Looking ahead, non-metal material catalysts hold potential for widespread commercial use, potentially replacing electrocatalytic materials in various applications. Moreover, the incorporation of rare earth elements into Proton Exchange Membrane Fuel Cells can enhance their localized characteristics, paving the way for further advancements in the field.

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