Study of Cathode Oxygen Reduction Reaction (ORR) Catalysts for Proton Exchange Membrane Fuel Cells (PEMFCs)

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Abstract. With the increasing depletion of non-renewable energy sources, more and more attention is being paid to the development of sustainable energy sources. The paper outlines the fundamental ideas behind oxygen reduction reaction (ORR) catalysts and proton exchange membrane fuel cells (PEMFCs), discusses the various types of ORR catalysts, and examines the limitations of this technology. In this paper, three types of ORR catalysts, metal catalysts, non-precious metal catalysts, and non-metal catalysts, are introduced in turn, and the pros and cons of the three types of ORR catalysts are analysed. Among them, metal catalysts possess advantages such as high efficiency and controllability, but are expensive and difficult to commercialise widely. The second type of catalyst is usually made from more common and cheaper metals and is therefore less expensive to produce. However, the catalytic activity is lower, resulting in a slower reaction rate and therefore a higher amount of catalyst is required. Non-metallic catalysts are usually not dependent on rare metal resources and are therefore relatively low cost. In addition, non-metallic catalysts offer higher selectivity and controllability, but lower catalytic rates. This paper expects that with the growth of the hydrogen energy industry, proton exchange membrane fuel cells will gradually be widely used in the fields of transport and power supply, providing a cleaner and more efficient energy source for human beings.

Keywords: Electrochemical technology, PEMFCs, non-metal catalysts, metal catalysts, non-precious metal catalysts.

1. Introduction

As the demand for energy increases, and carbon emissions from fossil fuels contribute to global warming, the world has become more concerned about energy-related issues. This has led to an increased focus on energy-related issues around the world. As a result, greater emphasis has been placed in recent years on the development of renewable energy sources in the expectation that they may eventually replace a portion of oil and gas. As a renewable and clean energy source, the fuel cell has only electricity, heat and water as by-products [1]. It employs electrochemical reactions to turn the chemical energy held in the fuel into electrical energy on a continual basis. Therefore, the fuel cell is only a reactor that produces electricity so long as both oxygen and fuel are fed into it, necessitating the usage of an external fuel storage mechanism.

Fuel cells come in a wide variety of forms, including Alkaline Fuel Cells (AFC), Phosphoric Acid Fuel Cells (PAFC), Proton Exchange Membrane Fuel Cells (PEMFC), Solid Oxide Fuel Cells (SOFC) and others. The PEMFC, on the other hand, is one of the most appropriate for cars and mobile devices due to its quick start-up and high-power density, which makes them appropriate for usage in devices like cars that need quick response and high-power output. In addition to this, PEMFCs can operate in a relatively low temperature range (60°C-80°C), which reduces start-up time and energy loss. PEMFCs have a high energy density, which me·ans that they can generate more power in a relatively small space, which is advantageous for mobile devices where space is limited.

In contrast, a significant disadvantage of PEMFCs is their reliance on platinum as a catalyst. Its status as a precious metal adds significantly to the cost of PEMFCs, making them relatively expensive compared to other fuel cell technologies. In addition to this, PEMFCs have the disadvantage of low durability. These two factors pose a challenge to the realisation of wider commercial applications of PEMFCs as a clean energy solution. Efforts are underway to explore alternative precious metal materials to mitigate this cost issue and make PEMFCs more economically viable in the future.

As thus, developing novel oxygen reduction catalysts is an efficient strategy to cut the cost of fuel cells while also addressing the issue of reliance on costly metals such as platinum. In this paper, three types of oxygen reduction catalysts and their characteristics are briefly described. In addition, a forward-looking direction for a comprehensive evaluation of the three different oxygen reduction catalysts is proposed.

2. PEMFCs

A proton exchange membrane fuel cell is made up of the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR), two half-reactions. At the anode, hydrogen is subjected to oxidation in this process, as shown in equation (1) [2].

Anode:

$$2H_2 \rightarrow 4H^+ + 4e^- \tag{1}$$

While protons are passing through the solid polymer electrolyte (also known as proton exchange membranes), electrons are flowing into the cathode via a circuit that is external, producing a current of electricity. Water is created at the cathode when oxygen and protons combine, as shown in equation (2)-(3) [2].

Cathode:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{2}$$

Overall:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{3}$$

Because the cathode's ORR kinetics are significantly slower than the anode's HOR dynamics. Consequently, improving ORR kinetics is crucial for improving PEMFC performance. Commercial Pt-based catalysts are often employed in cathode ORR, although PEMFCs cannot be widely commercialised due to the high cost of these catalysts.

3. Oxygen Reduction Reaction Catalysts

3.1. Metal Catalysts

Due to their outstanding efficacy in the oxygen reduction process, nanoparticles based on platinum (Pt) are ideal electrocatalysts for PEMFCs. The widespread commercialization of PEMFCs is currently hampered by excessive Pt loading, high cost, and inadequate durability. The metal catalysts with the highest ORR activity are made of platinum. The ideal catalyst material was created by lowering the binding energy of Pt-O by near 0.2 eV using theoretical data and calculation by DFT [3]. One of the most promising fabrication approaches is the inclusion of transition metals into Pt, which not only reduces production costs but also retains excellent catalytic activity. A crucial interplay between electrical and geometrical factors can alter the platinum's d-band centre with respect to its Fermi energy, decreasing or enhancing the binding energy of oxygenation intermediates. This interaction is what causes the increase in activity.

To further develop high activity ORR catalysts, two alternative approaches have been taken into account. To increase natural activity comes first. Compressive strain created by the addition of a transition metal with an atomic radius smaller than platinum increases the intrinsic activity by reducing the distance between the two platinum atoms. Maximising the number of active surface sites is another option. For instance, modifying the structure and architecture of nanoparticles can increase the number of active surface sites [3]. However, manufacturing cost remains the most fatal drawback of platinum-based catalysts, which greatly limits the possibility of being able to be widely used.

3.2. Non-Precious Metals Catalysts

The transition metal elements of the periodic table, such as iron, cobalt, nickel, copper, tungsten, chromium, and tin, are non-precious metals. They are all catalysts for ORR and are frequently found as transition metal complexes in catalysts. Since most of the platinum-based catalysts are currently used commercially, this greatly increases the cost of PEMFCs. As less expensive options, non-precious metal ORR catalysts have drawn a lot of interest. However, non-precious metal catalysts still operate inadequately in acidic conditions compared to platinum-based catalysts [4].

Due to the enormous diversity of non-precious metal catalysts, just a few of them are mentioned in this article. To replace high-cost, platinum-based precious metal catalysts, researchers have developed a variety of non-precious metal catalysts. An example is the Fe-N-C catalyst (FEC), which is considered the most likely potential replacement for platinum-based catalysts [5]. This is because it has a low-cost advantage over platinum-based catalysts and can reduce fuel cell manufacturing costs. It also has advantages such as higher power density. However, there are still some challenges that need to be improved. Examples include lack of stability and low durability.

Several studies have shown that Co-N-C catalysts (COC) have better stability compared to Fe-N-C catalysts, especially in acidic media. It was because iron ions can catalyse the Fenton reaction to produce highly reactive free radicals, which attack the carbon matrix in the PEMFC to decompose the membrane [6]. Cobalt is resistant to radical oxygen species (ROS), so COC help maintain high catalytic activity in long-cycle applications. However, the electrocatalytic activity of COC is not as good as that of Fe-based catalysts.

In contrast to COC and FEC, MoS_2 has a layered structure resembling graphene, with the atoms of molybdenum and sulphur stacked on top of one another by weak van der Waals interactions in each layer [7]. However, since most of the region of MoS_2 consists of catalytically inert substrates, only the boundaries contain active sites, which results in the inability to expose the edge sites. As a result, as compared to Pt-based catalysts, pure MoS_2 has substantially lower ORR electrocatalytic activity and conductivity. However, MoS_2 has some corrosion resistance in some acidic and alkaline environments and is suitable for catalytic reactions under some specific conditions [7].

3.3. Non-metallic Catalysts

3.3.1. Nitrogen-doped carbon nanotubes

Carbon materials are an important class of electrocatalytic materials due to their high electronic conductivity and tuneable porous structure. Doping heteroatoms is an effective approach for altering the electrical structure of carbon-based materials to boost electrocatalytic activity [8]. The catalytic process can be promoted by the charge precipitation caused by heteroatoms, which can produce highly active sites with appropriate adsorption strengths for the reaction substrates or intermediates.

It is intended to increase the catalytic activity and stability of PEMFC catalysts by the investigation of new carbon structures used as support materials. Due to its exceptional characteristics in this area, nanotubes of carbon have shown to be a reliable material for support. It has a large surface area, excellent mechanical characteristics, and superior electrical conductivity, among other advantages.

Numerous studies have shown the advantages of nitrogen doping on materials containing carbon, particularly on the oxygen reduction process. Some studies looked at the connection between the nitrogen content of nitrogen-doped carbon nanotubes (N-CNTs) and the catalytic activity of the ORR, and they came to the conclusion that more nitrogen can be added to the stock solution during the synthesis of N-CNTs to increase the oxygen reduction reaction activity. Studies have also compared the durability and catalytic activity of conventional Ag/C and Pt/C catalysts with synthetic multi-walled N-CNT products for the ORR process using cyclic voltammetry (CV). Through the results of the experiments, it was discovered that N-CNT could compete with Pt/C catalysts and that it could maintain its stability in an alkaline environment even after being subjected to 3500 potential cycles in a saturated oxygen electrolyte [9].

3.3.2. Nitrogen-doped graphene

Given its varied structure, graphene has a potential future in the power sector. Graphene exhibits good optoelectronic properties, such as high thermal conductivity (~5000 W/mK), high electrical conductivity, high electricity conductivity and high specific surface area, among others. Doping enhances the optical and electrical properties of graphene. Whereas one of the most frequently used elements for doping graphene is nitrogen, nitrogen can also be incorporated into the structure of the material or grafted onto its surface utilising a variety of methods when a nitrogen precursor is present. Nitrogen-doped graphene is created by doping or functionalizing nitrogen or nitrogen molecules into graphene, which enhances its catalytic and oxygen reduction activities.

Nitrogen-doped graphene can be prepared by three different methods, namely wet, bombardment and high thermal techniques [10]. Each method contains a number of synthetic routes as shown in Fig. 1. Wet methods are mainly prepared under low temperature conditions and in liquid phase. Using liquid phase to prepare graphene surface is a better method. Because it can synthesize environmentally friendly nitrogen-doped graphene at low temperature, low cost and large scale. Another method is high heat treatment, a technique that includes pyrolysis. Then there is rearrangement of carbon and nitrogen atoms, and fusion between them is achieved by intercalation or chemical vapour deposition of nitrogen atoms under the influence of high temperatures. The last method, known as irradiation bombardment, usually involves the introduction of nitrogen atoms, rather than carbon or oxygen atoms, into the carbon network. The ability to adjust the quantity and position of nitrogen atoms put into the graphene sheet is the method's most crucial characteristic [10].

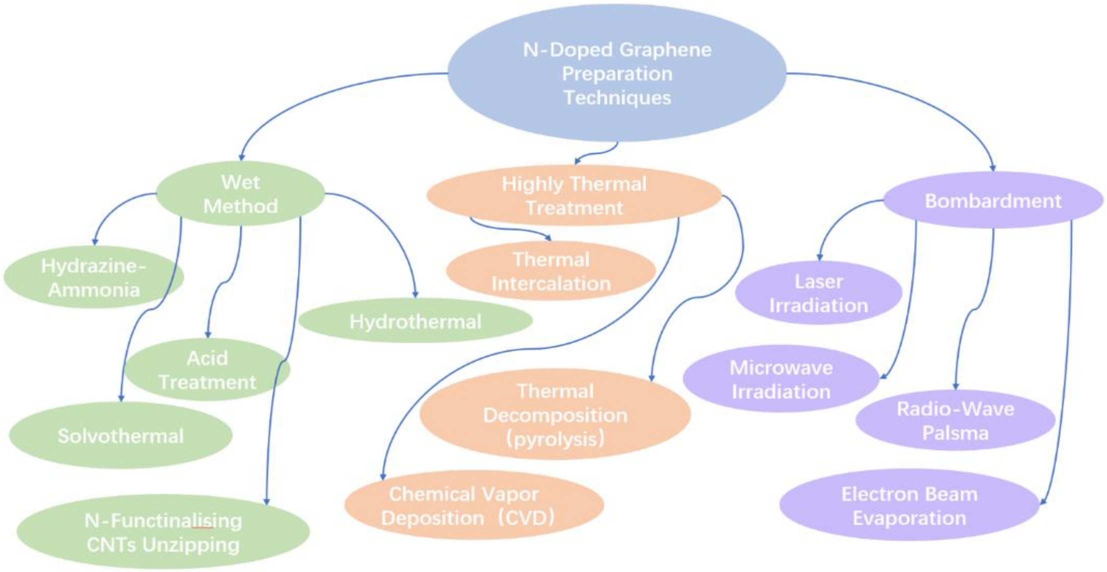

Figure 1. N-Doped Graphene Preparation Techniques. (Photo/Picture credit: Original)

3.3.3. Boron-doped carbon nanotubes

Although boron as a dopant has received very little investigation to far, it offers a wide range of possible uses. By lowering the Fermi level into the valence band, boron doping of pure carbon nanotubes (CNTs) can change them from semiconductor tubes to metal tubes. Additionally, it can alter the CNTs' crystallinity and hardness. The number of defects in the CNTs' walls rises as a result of boron doping, raising their reactivity. As a result, boron-doped carbon nanotubes have a wide range of applications, including catalysis, oxygen reduction processes, and composites.

The first accepted method for creating carbon nanotubes and carbon nanotubes doped with boron was arc discharge. In this process, high-purity graphite is used for both the anode and cathode, and an inert gas environment is used throughout. Stephan et al. created the initial boron-doped carbon nanotubes using a modified arc discharge procedure [11]. It has also been shown that boron-doped carbon nanotubes can be laser-generated using a mixed paste of elemental boron and carbon and Co/Ni as a catalyst.

3.3.4. Sulphur-doped carbon nanotubes

It is commonly known that modifying the electrical characteristics of a CNT's sp^2 carbon can improve its capabilities, and recent years have seen significant advancements in all connected research in this field. In particular, substitution doping has been achieved by inserting heteroatoms into the CNT structure. These doped carbon nanotubes have been proposed for usage in a variety of applications including catalysis, optoelectronics, solar panels, and even energy storage. And according to related studies, sulphur-doped carbon nanotubes produce branched morphology. Compared to nitrogen doping, there are few research results describing the direct synthesis of S-CNTs.

Denis et al. in 2009 proved that it is possible to dope CNT with sulphur using calculations based on Density Functional Theory (DFT) [12]. They found that chemical vapour deposition (CVD) is an efficient method for synthesising such structures despite the fact that structural distortions are caused by the bigger size of the sulphur atoms compared to the carbon atoms and the longer C-S bonds compared to the C-C bonds. Zhou et al. described a one-step synthesis of S-CNTs from dimethyl sulphide over a Co/MgO catalyst at 1273 K [13]. The synthesized material is a mixture of sulphur-containing sheaths and carbon nanotubes with sulphur atoms in the structure. Instead of carbon nanotubes with sulphur atoms in their structure, however, the synthesized material appeared to be an aggregate of carbon nanotubes covered by sulphur-containing sheaths. Thus, it seems that the direct synthesis of sulphur-doped carbon nanotubes containing large amounts of sulphur remains challenging.

4. Conclusion

In the last decade, the gradual increase in global energy consumption has led to the scarcity of fossil fuel reserves and growing environmental problems. As a result, research on alternatives to fossil fuels is being carried out all over the world. Because of its great efficiency and environmental friendliness, PEMFC technology is one of the most prospective energy conversion technologies. In this paper, it is discussed that one of the main reasons for the inability of PEMFC to be widely commercialized is the fact that no oxygen reduction catalysts have been found that can simultaneously satisfy the characteristics of lower cost, high durability, and high catalytic activity. Most of the catalysts currently used commercially are platinum-based catalysts, which have the advantage of high catalytic activity but are limited in large-scale commercial application because of their high cost. Non-precious metal catalysts are relatively inexpensive to manufacture, but have lower catalytic activity than platinum-based catalysts. Although non-metallic catalysts have the advantages of low cost and sustainability, and even some non-metallic catalysts can compete with platinum-based catalysts at the experimental stage, the preparation of high-performance non-metallic catalysts requires complex synthesis and processing. In the future, people need to continue to address the above deficiencies, study more oxygen reduction catalyst materials, and develop more economical and efficient catalysts for large-scale commercial applications. This paper provides some suggestions for the large-scale commercial application of PEMFC and the further development trend of cathodic oxygen reduction catalysts.

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