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Recent Advances in Electrochemical Synthesis of Hydrogen Peroxide

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Abstract: Hydrogen peroxide stands as a valuable, eco-friendly, versatile oxidizing agent that is widely used in chemical synthesis, industrial product bleaching, and wastewater treatment. At present, the anthraquinone method is the main method for synthesizing H_2O_2 in large quantities in industry. However, this method has the disadvantages of high cost, excessive energy consumption, intricate procedures, and significant emissions of pollutants are notable. It is not suitable for on-site preparation on demand, and the products prepared by the anthraquinone method are not suitable for on-site preparation. Safety hazards are prone to occur during storage and transportation. Using electrocatalysts to synthesize H_2O_2, attainable via either the two-electron oxygen reduction reaction or the water oxidation reaction On-site on-demand preparation of hydrogen peroxide. It is a promising alternative method that has attracted attention in recent years. This article briefly introduces the reaction mechanism, catalyst design, and application development of electrochemical synthesis of H_2O_2.

Keywords: Hydrogen Peroxide; Electrocatalytic; Electrochemistry; Synthesis; Catalyst

1. Introduction

Hydrogen peroxide, denoted as H_2O_2, stands as an eco-friendly and highly reactive oxidant [1], ranking among the vital chemicals globally. Renowned for its versatility and environmental benefits, H_2O_2 finds extensive applications in both industrial and household settings, encompassing uses such as sterilization and disinfection [2], wastewater and exhaust gas treatment [3], chemical synthesis, textile bleaching, and for semiconductor cleaning and liquid fuels, etc. [4,5]. In addition, the only products of H_2O_2 decomposed during the reaction are water and oxygen [6] and no other harmful chemical residues are produced, so H_2O_2 is safer than other oxidants.

The prevalent method in industrial hydrogen peroxide synthesis is the current method for hydrogen peroxide production is the anthraquinone process, known for its dual characteristics of being energy-intensive and intricate. [7]. However, the traditional synthesis method of anthraquinone has some inevitable shortcomings, such as involving hydrogenation reactions (mixing hydrogen and oxygen can cause an explosion), high energy consumption, and environmental pollution. Thus, an immediate requirement exists to devise methods for the efficient, cost-effective, and environmentally friendly preparation of H_2O_2, along with investigating their practical applications. [1]. In recent years, photocatalytic and electrocatalytic H_2O_2 preparation has attracted widespread attention from scientific researchers. Recently, advanced electrochemical oxidation processes for water purification have emerged. In such procedures, H_2O_2 is generated through the two-electron reduction of introduced oxygen, demonstrating its efficacy as an oxidant for water treatment [8]. Electrochemistry, which generates H_2O_2 from water and oxygen through electrolysis, is a more effective strategy for the development of water purification in developing countries. In addition, electrolysis will all be driven by renewable electricity (such as wind or solar energy) to create equipment that operates sustainably and environmentally friendly to avoid environmental pollution [9]. Some studies have shown that the synthesis of H_2O_2 through oxygen reduction electrochemical reaction provides a simpler and more sustainable method to maximize the use value of this important chemical [10-12].

In order to promote the development of cutting-edge research on electrochemical synthesis of H_2O_2, it is important to review and summarize its latest research progress in a timely manner. Therefore, this article, based on previous literature, discusses the basic principles of photocatalytic production of H_2O_2, catalyst design, reaction medium control, as well as its engineering application status and future development trends.

2. Reaction Mechanism of Electrochemical Synthesis of H_2O_2

Using a simple electrochemical device, H_2O_2 is prepared through the 2e-electrochemical oxygen reduction reaction process ($2e^-$ORR), which is actually the electrochemical catalysis to produce H_2O_2 [13]. The electrochemical two-electron oxygen reduction pathway can achieve continuous and dispersed production of H_2O_2 under mild conditions [14]. Berl et al. [15] first reported the use of electrochemical oxygen reduction to synthesize H_2O_2 in 1939.

The ORR reaction involves a multi-electron transfer process, mainly generation of H_2O_2 occurs through a two-electron pathway, specifically the 2e-ORR or producing water through a four-electron pathway ($4e^-$ORR). In the ORR reaction, the O_2 molecule adsorbed on the electrode surface first combines a proton (H^+) and an electron resulting in the creation of the *OOH intermediate [16]. When *OOH further combines with the proton, a $2e^-$ORR path occurs to generate H_2O_2; and When the O-O linkage within the *OOH intermediate is broken and dissociated into *O and *OH intermediates, and then combined with protons and electrons, the $4e^-$ORR path occurs to generate H_2O. From the above reaction mechanism, it can be seen that the retention of the O-O linkages in the reaction intermediate *OOH, along with the moderate binding energy of *OOH are the prerequisites for achieving $2e^-$ORR to generate H_2O_2. Among these, the decisive role in the oxygen reduction reaction (ORR) pathway is played by the manner in which O_2 molecules adhere to the catalyst surface [17].

3. Catalyst Selection for ORR Process

Generally speaking, the occurrence of the electrocatalytic ORR reaction involves three steps, namely, the process involves the adherence of oxygen molecules to the catalyst surface, the transfer of electrons between the interaction involving the catalyst and oxygen molecules, and the subsequent desorption of the reaction products [18]. The selection and use of different catalysts will directly affect the performance and application of H_2O_2 products, making it challenging to develop efficient, economical, and safe catalysts for electrocatalytic ORR to produce H_2O_2 [19]. Currently, the most common catalysts on the market are Carbon-based catalyst and Noble-metal-based catalysts, as well as other catalysts.

3.1 Noble-metal-based Catalysts

Materials composed of noble metals exhibit favorable catalytic activity and selective generation of H_2O_2 in the oxygen reduction reaction involving two electrons, often referred to as $2e^-$ORR, and are currently the most widely studied type of catalyst [14]. In terms of electronic effects, it's noteworthy that no entirely noble metal exhibits both adequate activity and selectivity pertaining to the two-electron oxygen reduction reaction ($2e^-$ORR) simultaneously. Even so, noble metals, particularly Pt and Pd, continue to be the most suitable candidates, because of their excellent ORR activity under acidic conditions. Discrete active metal atoms can change the O_2 adsorption mode, allowing it to specifically catalyze ORR to generate H_2O_2 [20].

Choi et al [21] found that factors such as the crystal structure, particle size, and active site distance of noble metals have an important impact on oxygen reduction activity and H_2O_2 selectivity. While it has been demonstrated that noble metal catalysts exhibit effective performance in the oxygen reduction reaction involving two electrons, commonly denoted as $2e^-$ORR, these factors combine with O_2. Metals with lower strength (e.g., Au, Ag, Hg) usually exhibit lower reaction rates and higher overpotentials in reactions [21]. Zhao et al.

[22] obtained PdAu bimetallic nanoframe (PdAu-nf) through a stepwise synthesis method and found that it has good 2e$^-$ORR performance in acidic systems. Fortunato et al confirmed that alloy strategies can improve and maintain high selectivity to H_2O_2 [23].

3.2 Carbon-based Catalyst

While noble metal materials like Au, Pt, Pd, Pt-Hg, Pd-Hg, and Au-Pd show excellent catalytic performance in 2e$^-$ORR reactions, the widespread utilization of metal materials is significantly impeded by their scarcity and elevated costs [14,24]. In recent years, non-metallic carbon materials extensive research has been conducted on them as an economical substitute to noble metal-based electrochemical catalysts.

Generally speaking, pure carbon materials do not have intrinsic 2e$^-$ORR reactivity. Strategies such as heteroatom doping, construction of carbon defects, and enhance 2e$^-$ORR performance is achievable through the creation of oxygen functional groups. Implementing these approaches can induce alterations in the local electronic structure of the carbon-based material, thereby changing the adsorption characteristics of the carbon material for *OOH intermediates and the possibility of O-O fracture, thereby effectively promoting the generation of H_2O_2. At present, carbon-based catalysts have initially achieved catalytic efficiency on par with catalysts based on noble metals in alkaline media, but their low activity in acidic media still restricts their development [14]. Incorporating electronegative heteroatoms like nitrogen (N), boron (B), and sulfur (S) into the carbon-based material lattice preserves the integrity of the π-conjugated system in the he structure of carbon may be partially compromised, causing charge redistribution, thereby this alters the binding characteristics of *OOH intermediates on the surface of carbon in the oxygen reduction reaction, and ultimately regulating its 2e$^-$ORR performance [25]. In addition to heteroatom doping strategies, there are usually inherent defects in untreated carbon materials like graphite, graphene, and carbon nanotubes, and porous carbon, such as holes, edges, and hybrid carbon sites. These undoped carbon intrinsic defects the carbon material's electronic structure can be adjusted and its ORR activity can be significantly adjusted [26-28]. In addition, the presence of oxygen-functional groups on the surfaces of carbon-based materials also plays a crucial role in enhancing 2e$^-$ORR activity [14].

4. Application Development of Electrochemical Synthesis of H_2O_2

With the continuous development of electrochemical 2e$^-$ORR systems, H_2O_2 electrosynthesis technology has received widespread attention and applications span various fields, including: pollutant degradation, electrochemical energy storage, sterilization and disinfection, small molecule conversion, and energy [29].

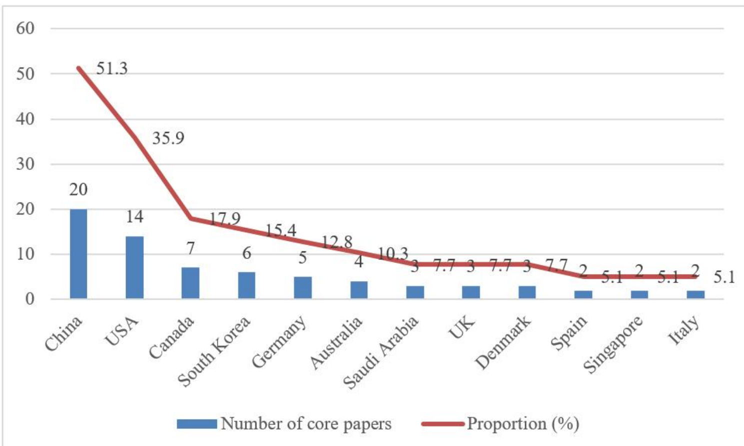

Figure 1: National Distribution of Core Papers on Electrocatalytic Synthesis of H_2O_2

At present, cutting-edge research in the field of electrochemical catalysis of H_2O_2 is mainly distributed in China, the United States, Canada, South Korea, Germany, Australia and other countries (as shown in Figure 1). Among them, hot research mainly focuses on the following three aspects: (1) Design of catalysts such as metal single atoms and carbon-based materials for redox reactions; (2) Development of equipment for electrocatalysis; (3) Exploration of the application performance of H_2O_2 products.

5. Conclusions

Electrochemical synthesis via $2e^-$ORR is an emerging technology for on-site and sustainable production of H_2O_2. Although electrochemical catalysis of H_2O_2 has been extensively studied in recent years and some breakthroughs have been made, it still faces great challenges and opportunities in actual industrial production. How to develop electrocatalysts with high activity, high selectivity and low cost, as well as how to design more stable and convenient electrocatalytic reaction equipment, will be the research trend in the fields related to electrochemical catalysis of H_2O_2 in the future. Through continuous efforts, the majority of researchers will gradually overcome the above challenges in the field of electrochemical catalysis of H_2O_2 and make concrete progress, bringing more assistance to family life and industrial development.

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