Recent Advances in Electrochemical H2O2 Production Via Oxygen Reduction Reaction: Fundamentals and Catalyst Design

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Abstract. The electrochemical synthesis of hydrogen peroxide (H_2O_2) through the two-electron oxygen reduction reaction ($2e^-$ ORR) presents a promising alternative to the conventional anthraquinone oxidation method. The successful commercialization of electrochemical H_2O_2 production depends critically on the fabrication of efficient cathode catalysts that exhibit high catalytic activity, selectivity, and stability. However, achieving significant H2O2 yields with advanced electrocatalysts remains challenging. This paper presents a systematic review of the latest advancements in the design, synthesis, and application of electrocatalysts for H_2O_2 production, with a focus on noble metals, transition metals, and carbon-based catalytic systems. In addition, strategies for enhancing electrocatalytic activity and selectivity are also discussed, aiming at developing cost-effective, high-performance catalysts for the $2e^-$ ORR. Finally, we summarize critical challenges in this field, providing a comprehensive reference to guide future research and development efforts in improving electrochemical H_2O_2 production technologies. By addressing these challenges and encouraging innovative approaches, the electrochemical production of H_2O_2 may advance toward more efficient and sustainable industrial applications.

Keywords: Electrocatalysis, oxygen reduction reaction (ORR), electron transfer, catalyst design, H_2O_2 production.

1. Introduction

Hydrogen peroxide (H_2O_2) is a widely used chemical that plays a significant role in various industries, including bleaching, mining, metal processing, textiles, wastewater treatment, and organic synthesis.[1-3] Currently, over 95% of industrial H_2O_2 is manufactured using the anthraquinone oxidation/reduction method (AQ), which involves four critical steps: hydrogenating anthraquinone, oxidizing anthrahydroquinone, extracting the H_2O_2 solution, and purifying and concentrating the final product.[4,5] While this production approach effectively supports the widespread manufacturing of concentrated H_2O_2, it suffers from several significant challenges, such as high energy consumption, significant by-products generation, and substantial safety hazards during the transport and storage of concentrated H_2O_2.[6]

The advancement of electrochemical technology has enabled the efficient and safe production of H_2O_2, which can be generated in situ under ambient conditions via the two-electron reduction of oxygen molecular ($2e^-$ ORR) in an aqueous medium.[7-9] This electrochemical method is economically attractive for H2O2 production, as it requires only water, oxygen, and electrical energy. Generally, there are three main pathways for the: (1) a $4e^-$ reduction producing H_2O, (2) a $2e^-$ reduction yielding the desired H_2O_2, and (3) a single e^- transfer pathway that facilitates the generation of *OOH intermediates.[10] The complexity of the ORR, which involves proton-coupled multi-electron transfers along with several reaction pathways, poses a significant challenge for efficiently and selectively producing H_2O_2. In particular, the competition between $4e^-$ and $2e^-$ reduction pathways underscore the need for selecting suitable catalysts to maintain high selectivity.[11]

To effectively produce H_2O_2 via the $2e^-$ ORR, it is essential to attain both high selectivity for H_2O_2 and a high current density. Most research efforts on the electrochemical synthesis of H_2O_2 have been

dedicated to the development of active catalysts, which initially focused on noble metals like Pt and Pd.[12,13] In recent years, there has been a shift toward exploring alternative catalysts that are economically and environmentally sustainable, reducing reliance on expensive and potentially hazardous metals. These alternatives include transition metal-based catalysts and carbon-based catalysts.[14-16] For instance, modifications such as introducing single metal sites or specific defects on carbon surfaces have been investigated to boost both the activity and the stability of these carbon-based catalysts for electrocatalytic H_2O_2 synthesis.[17] Significant progress has been made in developing cost-effective catalysts with excellent catalytic performance. However, significant gaps still exist before these advancements can be utilized in industrial applications.

Given the growing interest in electrochemical H_2O_2 synthesis, it is crucial to review the recent advancements in catalytic materials for H_2O_2 synthesis via $2e^-$ ORR. This review begins by addressing the fundamental principles underlying the design of electrochemical $2e^-$ ORR catalysts. Then, it summarizes the latest developments in design strategies, preparation methods, and the practical applications of electrocatalysts specifically aimed at H_2O_2 synthesis. Finally, we explore the significant challenges and potential opportunities that exist in this field. This review aims to provide valuable perspectives on designing and developing high-performance ORR electrocatalysts, thereby promoting the practical application of electrochemical H_2O_2 synthesis technology.

2. Principles of H2O2 electrosynthesis

The electrochemical reduction of molecular oxygen (O_2) occurs primarily via two distinct reaction pathways, each characterized by different electron transfer processes and leading to different final products. The four-electron transfer pathway ($2e^-$ ORR) facilitates the direct formation of H_2O ($O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$, $E°$ = 1.229 V versus RHE), while the two-electron transfer pathway ($2e^-$ ORR) specifically generates H_2O_2 ($O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$, $E°$ = 0.695 V versus RHE).[4] The formation of superoxide intermediate, along with subsequent reactions, is less thermodynamically favorable compared to the complete reduction to water, making it a major challenge for catalysts to maintain selectivity toward the $2e^-$ ORR.

The four-electron reduction to H_2O comprises four elementary steps, while the two-electron reaction to form H2O2 involves two steps. The reactions can be summarized as follows:[18]

$$O_2 + 4(H^+ + e^-) \rightarrow 2H_2O \qquad E^0 = 1.229 \text{ V vs RHE} \tag{1}$$

$$* + O_2 + (H^+ + e^-) \rightarrow OOH* \tag{1a}$$

$$OOH* + (H^+ + e^-) \rightarrow H_2O + O* \tag{1b}$$

$$O* + (H^+ + e^-) \rightarrow OH* \tag{1c}$$

$$OH* + (H^+ + e^-) \rightarrow H_2O + * \tag{1d}$$

$$O_2 + 2(H^+ + e^-) \rightarrow H_2O_2 \qquad E^0 = 0.695 \text{ V vs RHE} \tag{2}$$

$$* + O_2 + (H^+ + e^-) \rightarrow OOH* \tag{2a}$$

$$OOH* + (H^+ + e^-) \rightarrow H_2O_2 + O* \tag{2b}$$

Where * represents an unoccupied reactive site on the surface of catalyst, and OOH^* indicates the adsorbed intermediate. Both pathways involve *OOH as an intermediate. Indeed, the interaction of *OOH with the surface reactive site, along with the subsequent cleavage of the O−O bond are critical factors in determining the final reaction products (H_2O or H_2O_2) (Figure 1).

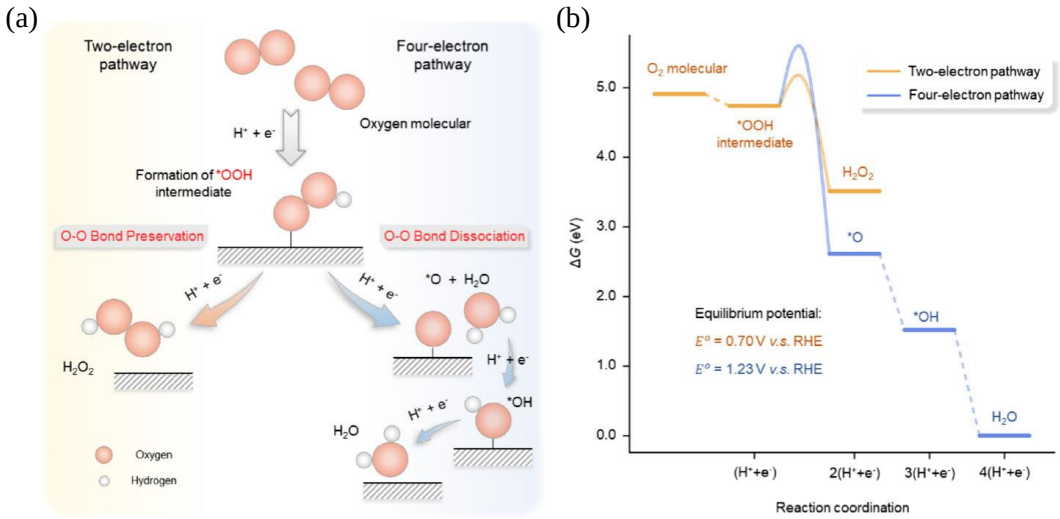

Figure 1. Electrochemical mechanism of ORR. (a) The ORR occurs via $2e^-$ and $4e^-$ pathways in acidic media. (b) A free energy diagram illustrates the $2e^-$ and $4e^-$ ORR pathways. Reprinted with permission.[19] Copyright 2018, American Chemical Society.

To effectively synthesize H_2O_2, stabilizing *OOH intermediate is crucial since its binding strength on active sites directly affects the selectivity and activity of the catalyst. Under optimal conditions, electrocatalysts should display a strong affinity for O_2 to promote the formation of *OOH. However, the binding strength of *OOH must remain moderate to prevent its immediate reduction to water.[20] Catalysts that bind oxygen too strongly tend to favor the break of the O−O bond in the *OOH intermediate, leading to water production rather than H_2O_2.[21] Therefore, achieving high selectivity for H_2O_2 requires minimizing barriers to *OOH dissociation while inhibiting its further reduction to *O and *OH species.

The catalytic performance and selectivity are predominantly influenced by the adsorption energies for O_2 molecules as well as the *OOH intermediate on the catalyst surface, which are deeply associated with the electronic characters of the catalysts.[22,23] Studies indicate that O_2 molecules exhibiting strong adsorption typically orient parallel to the catalyst surface, whereas those with weaker bonds arrange vertically.[24] A parallel configuration of O_2 enhances the likelihood of dissociation due to lower energy barriers, while a perpendicular alignment increases the barrier for cleaving the O−O bond, thereby favoring the generation of $2e^-$ ORR products.

Modifying catalyst materials can significantly adjust the binding strengthen of the HOO* intermediate, represented as ΔG_{*OOH}. Since the ORR proceeds via a proton-coupled electron transfer process, ΔG_{*OOH} serves as an effective descriptor of catalytic performance under both acidic and basic conditions, independent of the proton source.[17] A lower ΔG_{*OOH} value indicates stronger binding of the *OOH species, which may result in a shortened O–O bond within *OOH, thus *facilitating a sequential* $4e^-$ transfer *process that generates water molecules.* Conversely, *a higher* ΔG_{*OOH} *v*alue implies weaker binding, which generally promotes *OOH desorption of and enhances H_2O_2 formation.[13] Therefore, an effective catalyst should exhibit robust adsorption of molecular O_2 to promote the formation of *OOH, while simultaneously maintaining moderate adsorption of the generated *OOH to prevent its further reduction to water.

To enhance the reaction efficiency of $2e^-$ ORR catalysts, meticulous design and synthesis of active site structures are imperative. A profound understanding of the mechanistic pathways associated with both the $2e^-$ and $4e^-$ ORR processes is essential for rational catalyst development. Nevertheless, accurately predicting selectivity towards the desired ORR pathway remains challenging; catalysts that promote H2O2 production could inadvertently encourage its decomposition.

3. Electrocatalysts for H2O2 production

3.1. Noble-metal-based electrocatalysts

Due to the exceptional stability and efficiency, noble metal-based electrocatalysts have become a focal point of research and development. Optimizing the structure of noble metal catalysts can facilitate the $2e^-$ ORR. For instance, introducing secondary metals during the alloying process can enhance catalytic selectivity. These secondary metals can significantly influence catalytic behavior by adjusting the binding strengths of intermediate species (electronic effects) or altering the spatial arrangement of binding sites (geometric effect). [25]

Platinum-based catalysts are particularly favored for the ORR, attributed to their high catalytic activity, durability, and low over-potential. However, most Pt-based electrocatalysts favor the four-electron pathway, resulting in water production rather than the desired H_2O_2. This preference arises from the intense interaction between the peroxo intermediate (HOO*) and Pt atom, which inhibits the hydrogenation process necessary for H_2O_2 formation.[26] To facilitate H_2O_2 production, it is essential to prevent O−O bond cleavage, which can be achieved through an "end-on" adsorption configuration that allows only a single oxygen atom to interact with the surface of Pt-based catalyst. Recent studies by Rossmeisl and Stephens highlighted the potential of tuning HOO* binding by adjusting catalyst composition. They designed various noble metal alloy catalysts for H_2O_2 production. By electrodepositing mercury onto the platinum surface, they achieved enhanced selectivity for H_2O_2, attributed to the isolation of active sites, which restricts access to ensemble metal sites (Figure 2).[7] This approach effectively focuses the modification on the surface layer of the platinum nanoparticles, thereby reducing reliance on toxic mercury.

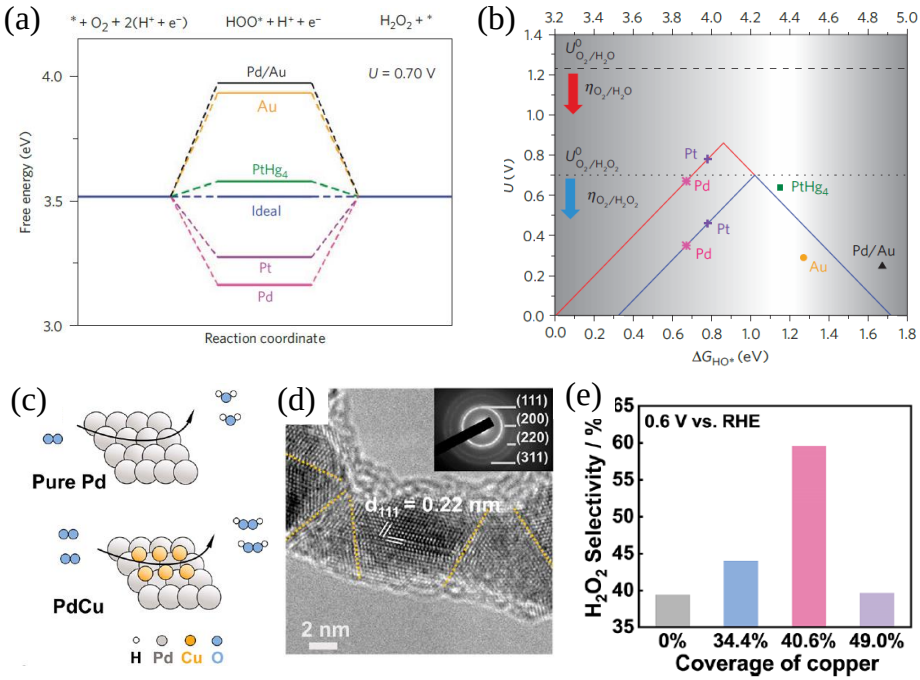

Figure 2. Strategies for optimizing the performance of noble metals. (a) Free energy diagram depicting the oxygen reduction reaction pathway to H_2O_2. (b) Volcano plot illustrating the relationship between the activity of various noble metal alloys for oxygen reduction to H_2O_2. (c) Schematic illustration showing ORR occurring on the modified Pd surfaces. (d) Structural characterization of PdCu nanowires. (e) Bar chart displaying the selectivity of H_2O_2 generation over the Pd-based nanocatalysts with varying Cu coverages. (a–b) Reprinted with permission.[7] Copyright 2013, Springer Nature. (c-e) Reprinted with permission.[30] Copyright 2023, American Chemical Society.

Au is another representative electrocatalyst. In contrast to Pt, Au-based catalysts demonstrate superior selectivity for H_2O_2 generation via ORR. Nevertheless, their catalytic performance is limited by low O_2 coverage on the Au surface and the weaker interaction of the HOO* intermediate with the surface. To counter this limitation, alloying Au with other noble metals, e.g., platinum (Pt), palladium (Pd), or rhodium (Rh) has shown favorable results.[27] For example, by controlling the Pd content, Au-Pd alloy nanocatalysts demonstrated improved selectivity for H_2O_2 production, benefiting from the ensemble effects produced by the finely dispersed Pd within the Au matrix.[28]

Pd has also been extensively studied as an electrocatalyst for the $2e^-$ ORR, which demonstrate strong selectivity and activity by manipulating its coordination environment. Although the performance of these catalysts still falls short of application demands, recent research has successfully developed bimetallic Pd-Au nanoframes through controlling the growth process. These alloy catalysts exhibited significantly enhanced onset potential, selectivity (over 90%), and stability for electrocatalytic H_2O_2 generation, surpassing the performance of Au and its alloy catalysts. DFT calculations suggested that the diluted Pd atoms in Pd-Au nanoframes improved the adsorption of key intermediate, *OOH, thereby boosting both reaction activity and selectivity.[29] Furthermore, geometric arrangement or ensemble effects associated with atom positioning on the surface of catalyst may also affect selectivity. For instance, Kang et al designed a model structure by depositing Cu on a Pd polycrystal surface, effectively enhancing the performance for H_2O_2 production. This design achieved high selectivity for H_2O_2 production (90%-99%) across an extensive potential span of 0.24 to 0.6 V, with an exceptional H_2O_2 production rate (Figure 2). In situ Raman spectscropy indicated that the incorporated copper atoms could stabilize Pd−O bonds. Density functional theory (DFT) calculations suggested that the Pd−O bonds on the catalyst surface optimized the interaction with *OOH on Pd sites.[30]

3.2. Transition-metal-based electrocatalysts

Transition-metals have also been widely studied in the electrocatalytic production of H_2O_2 due to their unique electronic structural properties. Metal porphyrins, especially those based on iron (Fe) and cobalt (Co), are one of the most common transition-metal based electrocatalysts used for ORR.[31] The catalytic performance of these metal complexes can be further improved when they are adsorbed onto conductive substrates, such as graphite electrodes. Inspired by metal porphyrins, researchers have developed metal-nitrogen-carbon (M−N−C) electrocatalysts by incorporating small amounts of transition metals, e.g., iron (Fe), manganese (Mn) , zinc (Zn), molybdenum (Mo), and cobalt (Co), into carbon-based materials.[32] These M−N−C electrocatalysts show excellent catalytic activity and selectivity towards the generation of H_2O_2 via $2e^-$ ORR pathway due to their unique geometric configurations. In these structures, reactive transition-metal atoms are highly complexed by the coordinating atoms, typically nitrogen (N) and carbon (C), which help to stabilize the reaction intermediates and inhibit O–O bond cleavage, thereby favoring H_2O_2 production.[33]

M−N−C electrocatalysts generally have around 1% weight of transition metals in atomic form, making them cost-effective while maximizing atomic efficiency. The metal center is critical, as it directly impact on the ORR pathway. Computational and experimental studies have displayed that Fe−N−C and Mn−N−C electrocatalysts predominantly reduce O_2 via a $4e^-$ transfer pathway, while Co−N−C catalysts are more selective for the $2e^-$ pathway leading to H_2O_2 production.[34] In M−N−C catalysts, the *OOH intermediate binds to the metal center at an atop position, highlighting the significance of the modulation of binding energy of *OOH in achieving selective $2e^-$ ORR to produce H_2O_2.[34]

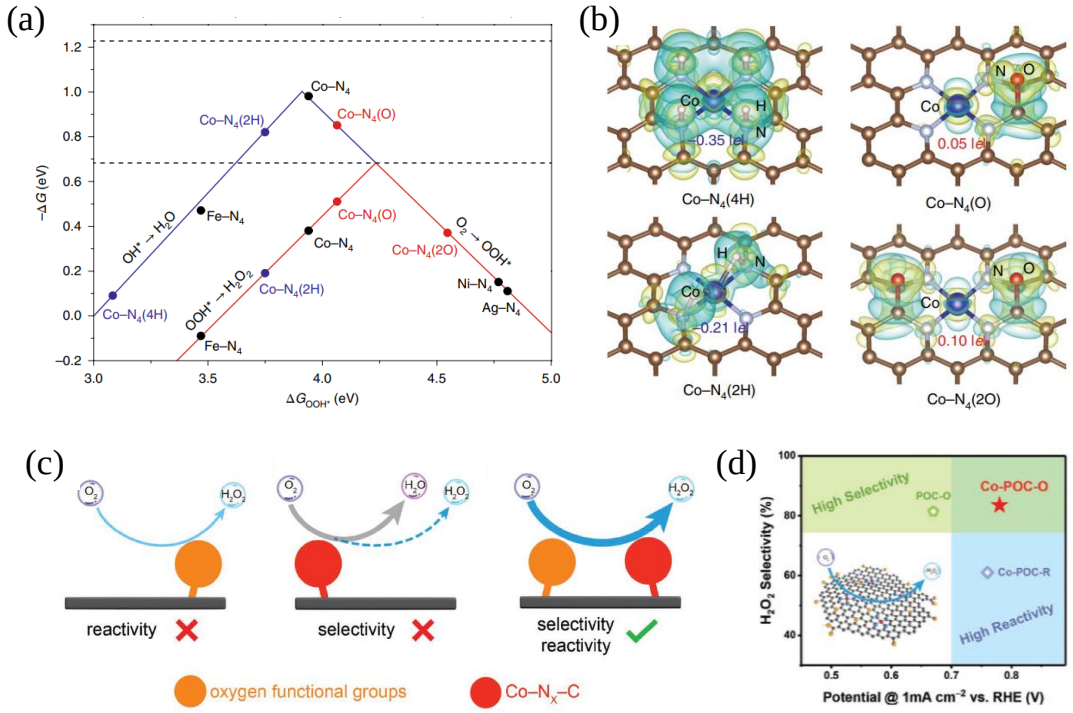

Figure 3. (a) Volcano plots of typical M-N_x electrocatalyst for ORR. (b) The differential charge densities of Co−N_4/graphene electrocatalyst post-adsorption of different intermediates around the Co active center. The yellow and cyan isosurfaces depict the regions of electron accumulation and depletion, respectively. (c) An illustration of the combined effect of Co−N_x−C active sites with oxygen-containing functional groups in electrocatalyticH_2O_2 generation. (d) A comparative analysis of electrocatalytic H_2O_2 production performances over different Co−POC catalysts. (a–b) Reprinted with permission.[35] Copyright 2019 Springer Nature. (c-d) Reprinted with permission.[36] Copyright 2023, Wiley-VCH.

Bidentate nitrogen ligands have been identified as optimal precursors for nitrogen-containing carbon materials, facilitating the formation of Co–N_2–C active sites during high-temperature calcination, which are active for selective H_2O_2 production. However, the distinct functions of various Co−N_x−C active sites remain a topic of debate (where x indicates the coordination number). Specifically, Co−N_4−C sites are generally believed to favor the $2e^-$ pathway for H_2O_2, while Co−N_2−C sites could potentially enhance the $4e^-$ pathway leading to water production (Figure 3).[35] Strasser et al. reported the evolution trends of various metal–N–C catalysts, including Co, Cu, Mn, Ni, and Fe, for electrocatalytic H_2O_2 generation. Among these catalysts, The Co−N−C catalyst exhibited the most suitable interaction with *OOH intermediate, resulting in substantial H2O2 productivity and selectivity, with minimal H2O2 reduction reaction activity.[32]

Moreover, introducing heteroatoms into the catalyst framework can further modify the electronic structure of the active sites, achieving ORR via $2e^-$ pathway selectively. For instance, incorporating oxygen-containing functional groups into Co−N_x−C catalysts has been shown to enhance both selectivity and activity for electrochemical H_2O_2 synthesis. In the absence of O atom, the Co−N_4 site tends to favor the $4e^-$ pathway due to the intense binding strength of *OOH. However, substituting nitrogen with oxygen or introducing epoxy groups could greatly alter the binding energy of *OOH on the catalyst surface by adjusting their surface electronic structure properties. Theoretical calculations indicated that the active sites gradually transfer from Co atom to adjacent carbon atoms. Such engineered CoNOC catalysts have demonstrated excellent activity for electrochemical H_2O_2 synthesis, achieving over 95% selectivity.[36]

Similarly, studies have shown that the carbon atoms adjacent to iron atom can also serve as catalytic sites, with its catalytic activity being modulated by the coordination of adjacent metalloid

atoms. Experimental results indicate that the selectivity of ORR is significantly related to the coordination configurations of the active sites. For example, while $4e^-$ reaction pathway tends to occur on Fe−N−C catalysts, the coordination of Fe with C and O atoms creates Fe–C–O motifs, which exhibited high selectivity towards the production of H_2O_2. The optimized Fe−C−O catalyst exhibited an ORR current density of 0.1 mA cm^{-2}, achieving over 95% selectivity for H_2O_2 production even under neutral pH conditions. Theoretical calculations revealed that Fe−C−O configuration reduced the adsorption strength of *OOH compared to Fe−N−C motifs, facilitating a transition from the $4e^-$ to the $2e^-$ pathway.[37] These findings highlight the potential for designing highly active sites in M−N−C catalysts, with their activity and selectivity for ORR being fine-tuned through careful control of the coordination environment.

3.3. Carbon-based catalysts

Carbon nanomaterials are becoming a promising low-cost catalysts for electrochemical H_2O_2 production. Typical carbon-based electrocatalysts include carbon quantum dots, carbon nanotubes, porous carbon, and graphene.[38,39] The electrochemical performance of these carbon-based materials is greatly influenced by their geometric and electronic structures.

Porous structures offer distinct advantages for H_2O_2 production by promoting mass transfer and providing more catalytic active sites. For instance, 3D crumpled graphene, which features controlled defect arrangements and oxygen content markedly enhances the electrochemical synthesis of H_2O_2. This material shows a remarkable selectivity of 92% to 100% for H_2O_2 production across a wide potential range of 0.05 to 0.7 V vs. RHE, with a remarkable H_2O_2 yield of 473.9 mmol g cat^{-1} h^{-1} (Figure 4). DFT simulations have highlighted the significant contributions of defect arrangements and oxygen-containing functional groups in graphene to the $4e^-$ ORR processes.[40]

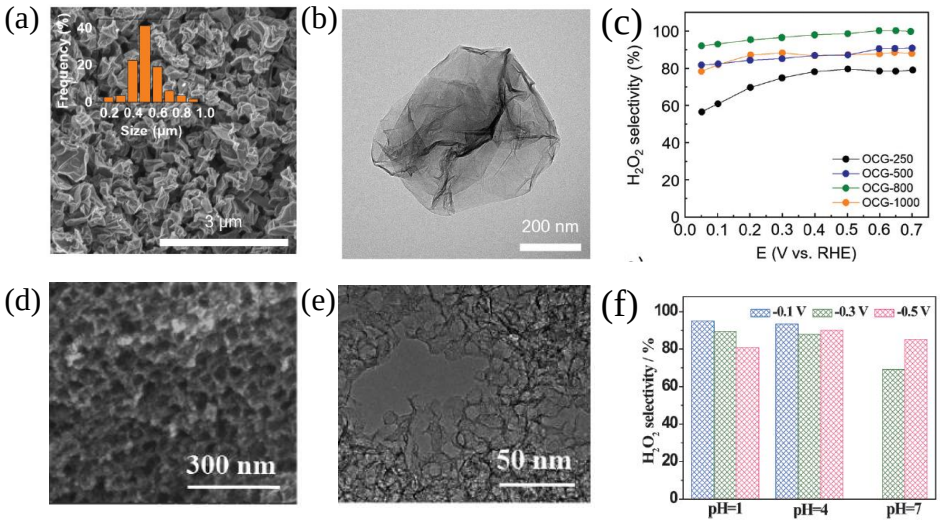

Figure 4. Two typical strategies for enhancing the electrocatalytic ORR performance of carbon-based catalysts. (a) SEM images of crumpled graphene synthesized at 800 °C The inset depicts the particle size distribution of oxidized crumpled graphene. (b) TEM images of the synthesized crumpled graphene. (c) The calculated selectivity for hydrogen peroxide (H_2O_2) production of the OCG catalysts. (d) SEM and (e) TEM images of hierarchically porous carbon derived from MOF-5. (f) The selectivity of electrochemical H_2O_2 production over the hierarchically porous carbon. (a–c) Reprinted with permission.[40] Copyright 2022, Royal Society of Chemistry. (e-f) Reprinted with permission.[43] Copyright 2015, Wiley-VCH.

Metal-organic frameworks (MOFs) represents another attractive functional materials for H_2O_2 production, which are characterized by their exceptional surface area and consistent porosity. Furthermore, MOFs are increasingly being explored as effective precursors for creating porous carbon structures.[41,42] For example, hierarchically porous carbon (HPC) was fabricated by subjecting

MOF-5 to direct pyrolysis in a hydrogen environment (Figure 4). This synthesized porous carbon demonstrates exceptional catalytic efficiency in the electrochemical ORR for H_2O_2 synthesis across pH 1−7. The impressive performance can be ascribed to the increased sp^3 carbon content, various defects within the structure, and effective mass transfer processes.[43]

In addition, the electronic structural characteristics of carbon-based catalysts could also be effectively modified through the introduction of heteroatoms, single metal dopants, defects, and oxygen-containing functional groups, representing another strategy to enhance electrocatalytic activity for H_2O_2 synthesis.[44,45] For instance, the binding energy of OOH* on the catalyst surface can be optimized by introducing oxygen atoms near the carbon atoms, thus facilitating efficient H_2O_2 generation. McCloskey et al. developed a reduced graphene oxide (RGO) based electrocatalyst for the reduction of O_2 to produce H_2O_2. This RGO-based catalyst displays exceptional selectivity and stability for peroxide formation at low overpotentials (below 10 mV), achieving nearly 100% selectivity under alkaline conditions.[46]

Besides incorporating oxygen functional groups, nitrogen doping has proven to significantly boost the ORR activity and selectivity of carbon-based catalysts. The higher electronegativity of the incorporated nitrogen atoms gives opportunities for regulating charge distribution within the π-conjugated system in carbon-based catalysts, thereby tuning the adsorption properties for reactive intermediates on the catalyst surface during ORR. The nitrogen atoms in carbon nanomaterials can occupy various sites, e.g., pyridinic-N, pyrrolic-N, and graphitic-N.[47,48] Among these, pyridinic nitrogen is particularly effective for $4e^-$ ORR pathway to generate water molecule, as its delocalized lone pair electrons facilitates the transfer of charge from the π orbitals to the antibonding orbitals of O_2, therefore weakening the O−O bond. Conversely, pyrrolic nitrogen could stabilize OOH* intermediates, thereby enhancing H_2O_2 production selectivity.[48] Thus, maximizing the proportion of pyrrolic nitrogen relative to other nitrogen types is crucial for achieving selective H_2O_2 production.

4. Strategies for Enhancing Selectivity and Activity

Electrochemical H_2O_2 synthesis is regarded as a sustainable method since it primarily requires water, oxygen, and electricity throughout the process. Nevertheless, significant challenges remain, particularly in developing scalable catalysts that are cost-effective, efficient, and exhibit excellent electrochemical stability.

4.1. Morphological structural engineering

Optimizing the morphological structure of electrocatalysts is an effective strategy for boosting H_2O_2 yield. Typical approaches in morphological structure engineering include applying carbon layers to the catalyst surface, creating isolated metal atom dispersions on supports, and modifying the catalyst composition (e.g., creating alloys that include both active and inactive metals). These modifications can regulate the binding of reaction intermediates, favoring a $2e^-$ pathway for O_2 reduction. Furthermore, constructing a porous internal structure within the catalyst is crucial. A well-designed pore network can facilitate the diffusion of reactants and products, improving selectivity by controlling the transport of reactants to active sites. For instance, mesoporous structures can promote the rapid release of produced H_2O_2, thus preventing its subsequent reduction to water.

4.2. Electronic structure engineering

The electronic structure of electrocatalysts is essential in modulating O_2 reduction pathway. A major challenge in synthesizing H_2O_2 is to minimize the breaking of the O–O bond in the *OOH species. As the sole intermediate in the $2e^-$ ORR process for H_2O_2 formation, *OOH species plays a critical role in determining selectivity for H_2O_2 production through its adsorption strength on the active sites. To improve the selectivity for electrochemical H_2O_2 synthesis, the electronic structure of electrocatalysts can be manipulated through coordination engineering, e.g., adjusting the coordination

type and number of the central metal atom, introducing guest groups that alter the local coordination environment.[49,50]

The local coordination environment significantly influences the electronic structural properties of reactive sites, which modulates the interaction strength of the intermediates on the catalyst surface, thus triggering distinct reaction pathways toward either the $2e^-$ or $4e^-$ ORR processes. Therefore, redirecting the reaction pathway toward the electro-synthesis of H_2O_2 by modulating the electronic structural properties of the catalyst, rather than producing water through the $4e^-$ ORR, has emerged as a viable strategy. For example, recent work by Wang et al. focused on anchoring single iron (Fe) atoms in in vacancies within carbon nanotubes to investigate their performance in H_2O_2 synthesis. The results indicated that the coordination patterns, specifically Fe−O−C motifs, led to increased selectivity for H_2O_2. In contrast, substituting O coordination with N coordination shifted the reaction toward the $4e^-$ pathway, demonstrating the critical role of the electronic microenvironment in influencing reaction selectivity.[37]

4.3. Scalable electrochemical devices

The ultimate goal of developing H_2O_2 electrocatalysts is to achieve their industrial application. While the performance of electrocatalysts is a key factor influencing the electrochemical production of H_2O_2, the development of the electrochemical reaction system is also vital. As above discussed, the generation of H_2O_2 is greatly influenced by reaction kinetics. Rapid mass transport of O_2 at the catalyst surface is essential for enhancing reduction current density, and the rapid separation of the generated H_2O_2 from the surface of catalyst is also crucial for maintaining the selectivity of ORR. In other words, the mass transfer processes of O_2 and H_2O_2 on the catalyst surface greatly impact the concentration of H_2O_2 that accumulates within the electrochemical device.

To address these challenges, gas diffusion electrodes (GDEs) have become a primary focus in research aimed at overcoming the oxygen mass transport limitations in electrocatalytic H_2O_2 production (Figure 5).[51] These electrodes achieve a gas-solid-liquid three-phase interface on the electrode surface by depositing catalytic active components on the gas diffusion layer surface, which could maintain stable transport of O_2 gas to the catalyst surface. Once the O_2 molecule diffuses to the catalyst surface, it undergoes rapid reduction since the mass transfer rate of O_2 in the gas phase usually outpaces that in the liquid phase, thus alleviating the inherent low solubility limitations of O_2 molecule in many liquid environments. Additionally, it is crucial to prevent the local accumulation of H_2O_2 around the electrode surface, as it may be further reduced to water molecule.[52] Studies have shown that using a continuous flow reactor can effectively inhibit the local accumulation of the produced H_2O_2 around the electrode surface due to the continuous flow of reactants and products.

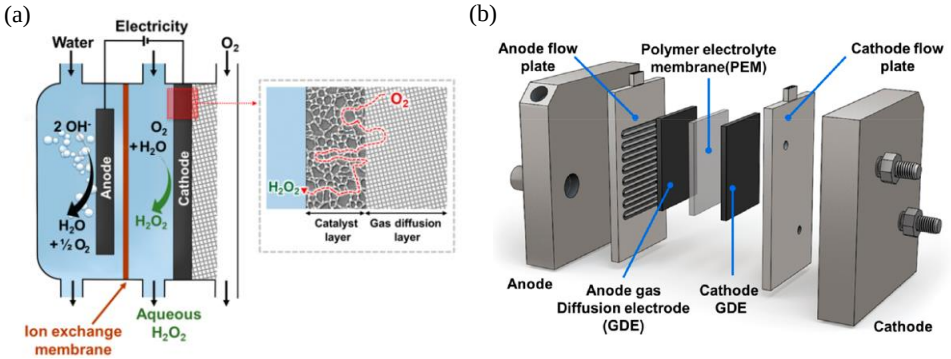

Figure 5. (a) Schematic representation of an electrochemical flow cell for H_2O_2 production based on gas diffusion electrode (GDE). (b) An illustration depicting an electrochemical flow reactor based on membrane electrode assembly (MEA), with MEA being sandwiched between current collectors designed with flow field patterns. (a) Reprinted with permission.[51] Copyright 2020, American Chemical Society. (b) Reprinted with permission.[52] Copyright 2018, American Chemical Society.

5. Summary and perspectives

The electrochemical synthesis of H_2O_2 emerges as a highly valuable and potentially sustainable technology. This paper reviews recent advancements in electrocatalysts specifically designed for $2e^-$ ORR to achieve H_2O_2 production selectively, including the development of noble-metal, transition-metal, and carbon-based electrocatalysts. However, significant challenges persist in achieving high selectivity for H_2O_2 synthesis with these electrocatalysts. Increasing the selectivity for H_2O_2 production via the $2e^-$ ORR requires effective suppression of the $4e^-$ ORR pathway, presenting challenges for the design and optimization of catalytic active sites. Additionally, there is a pressing need to develop in situ analytical techniques with high spatial resolution to explore the structural evolution of the catalytic sites during the electrocatalytic process. This understanding is vital for designing and synthesizing high-efficiency electrocatalysts.

While the research published thus far is promising, the practical application of electrocatalysts in industrial H_2O_2 production remains largely unexplored. Industrial electrochemical processes typically operate at significantly higher current densities and larger scales compared to laboratory-scale three-electrode systems. Addressing these challenges will promote the electrochemical H_2O_2 production, offering an environmentally friendly and energy-efficient solution to meet industrial demands.

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