

Electrosynthesis of Hydrogen Peroxide: Catalyst Design and Synergistic Optimization of Device Systems

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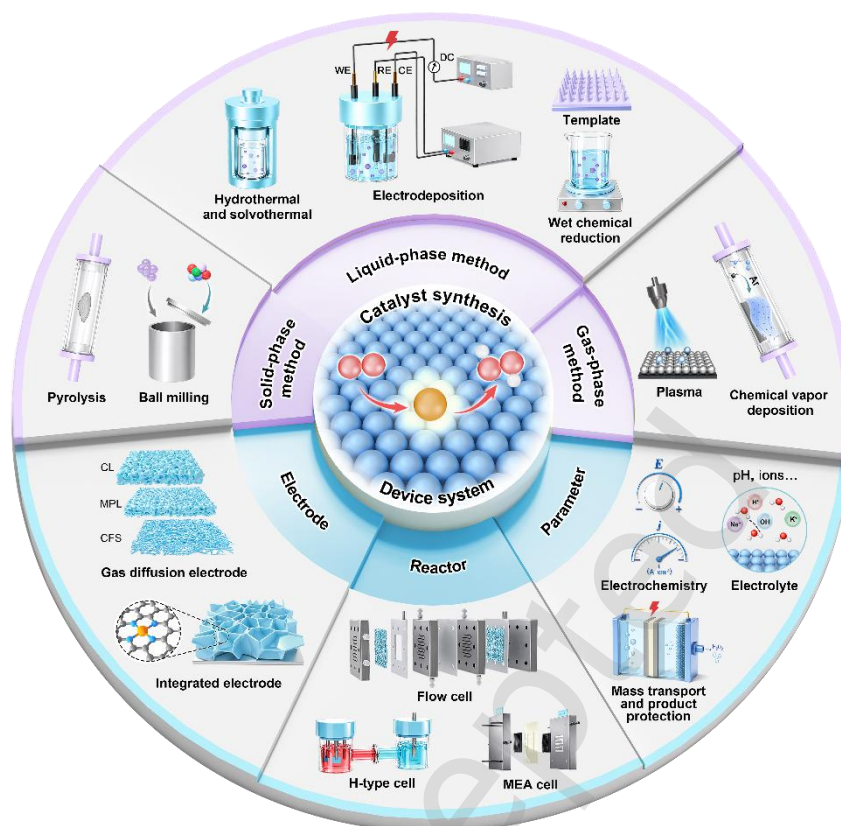
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Centered on synergistic optimization between electrocatalysts and devices, this review summarizes advances in H_2O_2 electro-synthesis via the 2e^- ORR. It encompasses reaction pathways, structure-performance relationship, various electrocatalyst categories, synthetic strategies, and modulation effects of device operational parameters. A multiscale coupling framework is proposed to accelerate the scalable industrial implementation of this green electro-synthesis technology.

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ABSTRACT: Hydrogen peroxide (H_2O_2) is a key green oxidant extensively used in chemical synthesis, wastewater treatment and medical disinfection. Electrosynthesis of H_2O_2 through the two-electron oxygen reduction reaction (2e^- ORR) features distinct merits including mild reaction conditions and environmental friendliness, rendering it a promising alternative to the traditional anthraquinone process. Currently, developing electrocatalysts with high activity, high selectivity, and robust durability, as well as realizing synergistic optimization of electrodes, electrolytic devices, and operational parameters, constitute critical bottlenecks restricting the large-scale deployment of this technology. Accordingly, this review comprehensively summarizes recent progress on H_2O_2 electrosynthesis via the 2e^- ORR. We first elaborate fundamental reaction mechanisms and catalyst design strategies. Afterwards, the modulation effects of integrated device systems on catalytic activity, selectivity, and stability are analyzed from the aspects of electrode structure, reactor configuration, and key operational parameters. Finally, the challenges and prospective opportunities facing H_2O_2 electrosynthesis systems are proposed, offering insights to facilitate the further development of this emerging field.

KEYWORDS: 2e^- ORR, H_2O_2 electrosynthesis, electrocatalyst design, device-system optimization, synergistic regulation

1 Introduction

Against the backdrop of the global carbon peaking and carbon neutrality goals, the innovation and scalable implementation of green low-carbon technologies have emerged as a core driving force for energy transition and sustainable industrial development. As an eco-friendly powerful oxidant, hydrogen peroxide (H_2O_2) finds widespread applications in chemical synthesis, pulp bleaching, medical disinfection, and many other fields, endowing it with irreplaceable industrial value [1–4]. Market forecasts suggest that the global H_2O_2 market reached around USD 1.75 billion in 2025. With a compound annual growth rate of 5.60% expected over 2026 to 2035, the market size is anticipated to hit USD 3.02 billion by 2035, demonstrating continuously rising industrial demand [5].

Currently, industrial H_2O_2 production predominantly relies on the anthraquinone process, which is based on the successive hydrogenation and oxidation of anthraquinone species. Nevertheless, this technique suffers from inherent limitations, including complex process, high operational expenditure, prominent safety hazards and considerable environmental contamination. These issues greatly hinder the green and economic development of the H_2O_2 industry

and impede compliance with sustainable development targets [1, 6, 7]. In addition to the traditional anthraquinone process, alternative routes for H_2O_2 generation include direct synthesis, photocatalysis, and electrocatalysis. Direct synthesis uses hydrogen and oxygen (O_2) as feedstocks for one-step H_2O_2 production, featuring high atom economy and a short process route. Nevertheless, its large-scale implementation is severely constrained by the requirement for Pd-based catalysts and safety risks arising from high-pressure hydrogen environments [8–10]. Photocatalysis relies on semiconductor materials to generate excited electron-hole pairs under light irradiation, driving either O_2 reduction or water (H_2O) oxidation toward H_2O_2 formation. While it benefits from solar-driven operation and environmental compatibility, severe photogenerated-charge recombination generally leads to low energy-conversion efficiency, hindering practical large-scale scaling [11, 12]. Electrocatalysis stands out as the most industrially promising green strategy for H_2O_2 synthesis, thanks to its mild reaction conditions, tunable driving force, and native compatibility with renewable electricity. Based on reaction mechanisms, electrocatalytic H_2O_2 production falls into two categories: anodic two-electron water oxidation (2e^- WOR) and cathodic two-electron oxygen reduction (2e^- ORR). The

$2e^-$ WOR pathway produces H_2O_2 directly via water oxidation without O_2 consumption, but it suffers from formidable bottlenecks originating from the competitive oxygen evolution reaction, together with insufficient catalyst selectivity and long-term operational stability [13,14]. By contrast, H_2O_2 electrosynthesis via the $2e^-$ ORR uses O_2 as the feedstock to produce H_2O_2 under the combined effect of an electric field and electrocatalysts. Endowed with inherent safety, low energy consumption, environmental benignity, and mild operating conditions, the $2e^-$ ORR represents a promising green substitute for the conventional anthraquinone process [15, 16]. Accordingly, this review provides a systematic overview of H_2O_2 electrosynthesis via the $2e^-$ ORR route. The key challenge of this technology is boosting reaction selectivity while suppressing the competitive $4e^-$ ORR pathway toward water formation [17, 18]. Electrocatalysts play a pivotal role in modulating reaction energy barriers and steering the reaction pathway toward target H_2O_2 production [19]. Meanwhile, electrodes, reactors and other device components govern gas-liquid mass transfer, ion migration kinetics, and three-phase interface stability, acting as critical supports to fully unlock the intrinsic catalytic performance [20]. Therefore, developing high-performance electrocatalysts and optimizing integrated device systems constitute essential prerequisites to advance the large-scale practical deployment of H_2O_2 electrosynthesis.

In recent years, significant progress has been made in the electrosynthesis of H_2O_2 via the $2e^-$ ORR. Nevertheless, numerous challenges persist in this field regarding both catalyst optimization and catalyst-device matching. Among catalyst materials, noble metal alloy-based systems such as Pt-Hg alloys represent some of the most effective catalysts. Unfortunately, their high cost and scarcity severely hinder large-scale deployment [21, 22]. Single-atom catalysts (SACs) feature well-defined coordination structures and high atom utilization efficiency. However, prolonged operation under acidic conditions or concentrated H_2O_2 media frequently triggers dissolution of metal centers, resulting in gradual loss of selectivity [23–26]. Although strategies including heteroatom doping and coordination structure regulation have been adopted to boost stability [27, 28], such modifications simultaneously alter the geometric and electronic structure of active sites, rendering the concurrent optimization of activity, selectivity, and durability difficult to realize. Metal-organic frameworks (MOFs) have been widely explored as precursors for carbon-based catalysts, yet the pyrolysis process frequently induces metal agglomeration and structural collapse [29, 30]. Even ionic-liquid-assisted pyrolysis, which improves precursor homogeneity [31], precise identification of active sites and batch-to-batch reproducibility remain challenging. Furthermore, carbon-based catalysts can attain high H_2O_2 selectivity in alkaline media via surface oxygen-containing functional groups (OFGs). These functional groups, however, are prone to reduction and hydrolysis under acidic conditions, leading to rapid performance degradation [32, 33]. From an industrial perspective, reducing metal loading can physically isolate active sites and suppress the competing $4e^-$ pathway. However, this approach inevitably lowers active site density

and thus fails to deliver industrially relevant current densities above 300 mA cm^{-2} . In short, isolated modification of catalysts is insufficient to overcome the existing technological bottlenecks. Multiple challenges also exist at the device level. Gas diffusion electrodes (GDEs) facilitate direct gas-phase O_2 transport through hydrophobic porous structures, effectively mitigating mass transport limitations in liquid electrolytes. During long-term operation, electrolyte penetrates the porous channels and induces electrode flooding, destabilizing the gas-liquid-solid three-phase interface [34, 35]. Approaches such as raising the polytetrafluoroethylene (PTFE) content, introducing a microporous layer, or constructing gradient wettability can alleviate flooding to some extent [36, 37], yet these tactics cannot fundamentally address interface instability and may incur extra mass transfer resistance. A more critical issue lies in the scale mismatch between catalysts and devices. The identical catalyst may deliver nearly 100% H_2O_2 selectivity in an H-type cell, whereas selectivity declines drastically when implemented within a membrane electrode assembly (MEA). This phenomenon originates from localized pH gradients, retained H_2O_2 near electrode surface, and inhomogeneous potential distribution. Clearly, neither catalyst-only optimization nor unilateral improvement of device configurations can fundamentally tackle industrial obstacles. Therefore, it is imperative for this research area to establish a multiscale synergistic regulation system integrating catalyst, electrode, reactor and operational parameters.

Therefore, this review focuses on the synergistic optimization of catalyst design and integrated device systems toward H_2O_2 electrosynthesis via the $2e^-$ ORR (Fig. 1). To bridge the existing divide between catalyst exploration and device engineering, we systematically sort out the core fundamental of the field and construct a correlative framework connecting catalyst microstructure, macroscopic devices configuration and overall performance. This work offers systematic guidance for designing high-performance catalysts, developing efficient device systems, and realizing favorable catalyst-device matching, thus advancing the industrialization of $2e^-$ ORR-based H_2O_2 electrosynthesis technology. Specifically, we first elaborate on the reaction mechanism of $2e^-$ ORR-based H_2O_2 electrosynthesis, catalyst structure-activity relationships, and fundamental theories governing the synergistic optimization of device systems. Next, the merits and limitations of nonmetallic, transition-metal and noble metal electrocatalysts are categorically discussed, with special attention devoted to the mechanisms, pros and cons, and regulation strategies of mainstream synthesis approaches, including solid-phase, liquid-phase, and gas-phase methods. We further analyze device optimization from three dimensions: electrode structure optimization, reactor configuration, and operational parameters. Moreover, the synergistic logic, matching principles, and regulatable strategies for catalyst-device integration are elucidated. Finally, current bottlenecks in the field are outlined, and prospective directions for future developments are proposed.

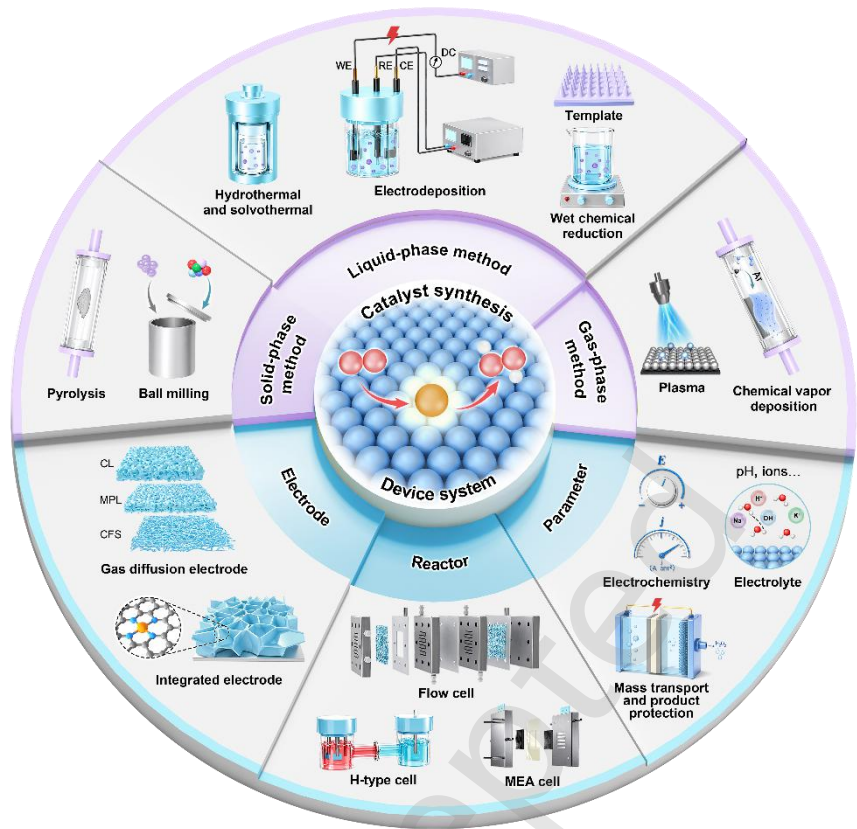


Figure 1 Schematic illustration of rational catalyst construction and synergistic optimization strategies of device-system toward H₂O₂ electrosynthesis.

2 Fundamental theories

2.1 Reaction mechanism of the ORR toward H₂O₂ electrosynthesis

The ORR proceeds via two competing routes, the 2e⁻ pathway and the 4e⁻ pathway. The 2e⁻ pathway for H₂O₂ electrosynthesis relies on selective electron-proton coupled transfer of O₂ at the catalyst surface, while the 4e⁻ pathway

yields H₂O. Competition between these two routes directly determine the H₂O₂ selectivity and production yield. Accordingly, it is essential to favor the target pathway via rational catalyst design and modulation of operational parameters [1, 18, 38]. The specific reaction mechanism of ORR varies with the pH of the reaction system, as detailed in Tables 1 and 2. Notably, unless otherwise stated, all potentials discussed in this review are referenced to the reversible hydrogen electrode (RHE).

Table 1 Reaction mechanism of ORR in acidic media

4e ⁻ ORR pathway	2e ⁻ ORR pathway
$O_2+4e^-+4H^+\rightarrow 2H_2O$ ($E^0=1.23\text{ V}$)	$O_2+2e^-+2H^+\rightarrow H_2O_2$ ($E^0=0.70\text{ V}$)
$O_2+e^-+H^+\rightarrow *OOH$	$O_2+e^-+H^+\rightarrow *OOH$
$*OOH+e^-+H^+\rightarrow *O+H_2O$	$*OOH+e^-+H^+\rightarrow *+H_2O_2$
$*O+e^-+H^+\rightarrow *OH$	/
$*OH+e^-+H^+\rightarrow *+H_2O$	/

Table 2 Reaction mechanism of ORR in alkaline media

4e ⁻ ORR pathway	2e ⁻ ORR pathway
$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$ ($E^0 = 1.23$ V)	$O_2 + 2e^- + H_2O \rightarrow HO_2^- + OH^-$ ($E^0 = 0.76$ V)
$O_2 + e^- + H_2O \rightarrow *OOH + OH^-$	$O_2 + e^- + H_2O \rightarrow *OOH + OH^-$
$*OOH + e^- \rightarrow *O + OH^-$	$*OOH + e^- \rightarrow **HO_2^-$
$*O + e^- + H_2O \rightarrow *OH + OH^-$	/
$*OH + e^- \rightarrow ** + OH^-$	/

From the above competing pathways of the ORR, the reduction of O_2 on the catalyst surface shares a common initial step: O_2 combines with one proton-electron pair to form adsorbed $*OOH$. Subsequently, if the O–O bond of $*OOH$ is retained and further combines with a second proton-electron pair, H_2O_2 is generated and desorbed from the catalyst surface, the reaction follows the 2e⁻ pathway. Conversely, if the O–O bond of $*OOH$ is cleaved, it dissociates into $*O$ and $*OH$, which are further reduced to H_2O , thus following the 4e⁻ ORR pathway. Therefore, whether the O–O bond is preserved is the core factor determining reaction selectivity, and the preservation of the O–O bond is closely related to the adsorption configuration of O_2 on the active sites of the catalyst [39]. Currently, three O_2 adsorption models are widely recognized: the Pauling model, the Griffiths model, and the Yeager model, as shown in Fig. 2a. Among them, the Pauling model corresponds to end-on adsorption, the Griffiths model to side-on adsorption, and the Yeager model to bridge-type adsorption. Different adsorption modes alter the bonding state of the O–O bond and the distribution of electron cloud. For Pauling-type end-on adsorption, only one oxygen atom of O_2 bonds to the

catalytic active site. Electron back-donation from catalyst d-orbitals to the O_2 molecule is predominantly localized on this bonded oxygen atom, and only a small fraction of electrons populate the π^* antibonding orbital of the O–O bond. Under such circumstances, the O–O bond order is largely retained, the adsorption energy is typically lower than -0.1 eV, and the energy barrier for O–O bond cleavage is high. As a result, the generated $*OOH$ intermediate tends to desorb from the surface, favoring the 2e⁻ pathway toward H_2O_2 production. In contrast, both the Griffiths side-on adsorption and the Yeager bridge adsorption involve orbital coupling between catalytic sites and both oxygen atoms of O_2 . Substantial electrons from catalyst d-orbitals are delocalized and populate the π^* antibonding orbitals of the O_2 molecule. The adsorption energy reaches -0.5 to -2 eV, which greatly reduces the O–O bond order and remarkably elongates bond length, accompanied by a sharp drop in the cleavage energy barrier. Once O–O bond scission occurs, $*O$ and $*OH$ intermediates are generated, switching the reaction toward the 4e⁻ reduction pathway for final H_2O formation (Fig. 2b) [10, 20, 40–42].

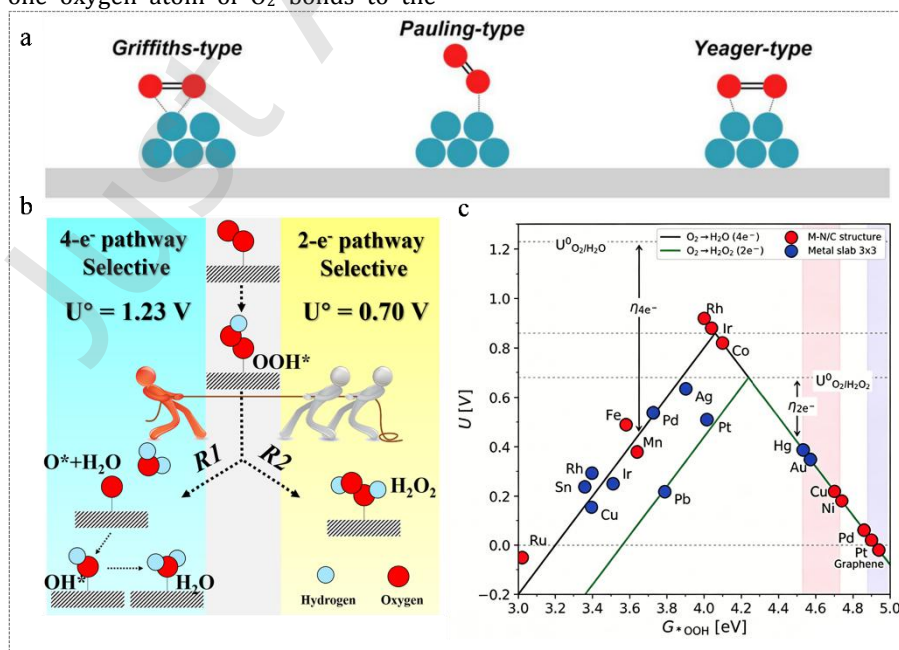


Figure 2 Reaction mechanism of 2e⁻ ORR for H_2O_2 electrosynthesis. a) Adsorption models of O_2 . Reproduced with permission from Ref. [10], © Springer Nature 2023. b) Schematic illustration of the ORR pathways and equilibrium potentials. Reproduced with permission from Ref. [43], © American Chemical Society 2019. c) Volcano-type relationship curve constructed as a function of the adsorption Gibbs free energy of $*OOH$ (ΔG^*_{OOH}). Reproduced with permission from Ref. [44], © Wiley-VCH GmbH 2025.

In addition to the adsorption configuration, the ΔG^{*OOH} serves as another critical descriptor dictating the reaction pathway. According to the volcano plot theory (Fig. 2c), the optimal ΔG^{*OOH} for the $2e^-$ ORR is approximately 4.2 eV [44, 45]. When $^{*}OOH$ adsorption is too strong, the residence time of $^{*}OOH$ on the active sites is prolonged, and the surface atoms of the catalyst continuously back-donate electrons to the antibonding orbitals of $^{*}OOH$, thereby reducing the O–O bond order and stretching the bond length. Once the energy barrier for O–O bond cleavage becomes lower than the desorption energy of H_2O_2 , $^{*}OOH$ will irreversibly decompose into $^{*}O$ and $^{*}OH$, which are then further reduced to H_2O , leading to a sharp decline in H_2O_2 selectivity. Conversely, if $^{*}OOH$ adsorption is too weak, the formation of $^{*}OOH$ becomes the rate-determining step; even if the O–O bond is not prone to cleavage, the overall reaction rate remains extremely low and cannot meet practical yield requirements. Therefore, the binding energy of $^{*}OOH$ should be moderate, precisely tuned to the vicinity of the volcano peak, so as to achieve rapid desorption while ensuring that the O–O bond is not broken [46].

2.2 Fundamentals of catalyst structure-performance relationship

As the core of the $2e^-$ ORR, the catalytic performance of a catalyst is determined by its intrinsic structural features. Clarifying the structure-activity relationship is therefore a critical prerequisite for achieving rational catalyst design and performance enhancement. The type, number, and exposure of active sites directly influence the adsorption configuration of O_2 and the binding strength of the $^{*}OOH$ intermediate, thereby governing the competition between the $2e^-$ and $4e^-$ pathways. For instance, Sun et al. [18] prepared a carbon-wrapped copper oxide catalyst (Cu-800@C) and found that the exposed metallic Cu sites tended to induce the $4e^-$ ORR pathway. Through encapsulating the Cu sites with a carbon layer, the active centers were transformed into carbon sites with the introduction of trace oxygen vacancies. As a result, end-on O_2 adsorption and accelerated $^{*}OOH$ formation were achieved, thereby boosting the H_2O_2 selectivity to 98%. The electronic structure of the catalyst modifies the surface electron cloud density, which affects the electron-proton coupled transfer rate and significantly regulates the reaction activity. For example, precise control of the surface adsorbed oxygen concentration in Fe-doped ZnO can optimize ΔG^{*OOH} , achieving a high H_2O_2 selectivity of 96% [47]. Similarly, tuning the degree of p-d orbital hybridization can regulate the coordination environment of Al-modified Ni, thereby adjusting the $^{*}OOH$ adsorption strength [48]. The morphology and pore structure of the catalyst determine the mass-transfer capability of the reaction system. A well-designed pore architecture can facilitate O_2 diffusion, accelerate H_2O_2 desorption, reduce side reactions caused by product accumulation, and simultaneously enhance the structural stability of the catalyst. For example, Du et al. [49] designed N/O co-doped hierarchical porous carbon nanoreactors (N/O-HPCNs), which rely on the hierarchical pore structure to enhance O_2 transport and shorten the residence time of H_2O_2 . This catalyst achieved an H_2O_2

production rate of $17.3 \text{ mol g}^{-1} \text{ h}^{-1}$ at an industrial-grade current density of 200 mA cm^{-2} , and maintained a Faradaic efficiency (FE) above 80% after 100 h of continuous operation. All of the aforementioned microstructural features are realized through appropriate synthesis methods and precise control of operational parameters. By selecting appropriate synthesis methods and precisely optimizing reaction conditions, targeted construction of active-site types, electronic structures, morphology, and pore architectures can be achieved, thereby regulating key processes such as O_2 adsorption, $^{*}OOH$ adsorption strength, and interfacial mass transfer, ultimately enabling precise optimization of catalytic performance.

2.3 Synergistic optimization of device-system

In the $2e^-$ ORR electrosynthesis system for H_2O_2 , the device serves as the reaction platform and is deeply coupled with the catalyst. Both components collectively determine the overall reaction efficiency and H_2O_2 yield [50, 51]. For example, Ji et al. [51] pointed out that the excellent intrinsic activity of M–N–C SACs can only be fully exploited in a highly compatible electrochemical reactor, and that the optimization of the catalyst electronic structure and the enhancement of mass transfer in the reactor are inseparable. Synergistic optimization of the device-system refers to the coordinated regulation of electrodes, reactor configuration, and operational parameters based on the reaction mechanism, in order to resolve the trade-offs among components and achieve synergistic enhancement, thereby improving overall performance. The electrode serves as the direct support for the catalyst; its electrical conductivity, gas permeability, wettability, and catalyst loading directly affect electron conduction, O_2 diffusion, and the state of the gas-liquid-solid three-phase interface [52, 53]. The reactor configuration determines the mass-transfer pathway, O_2 utilization efficiency, and H_2O_2 separation efficiency of the reaction system. For example, Cao et al. [54] constructed a novel electrochemical reactor using 3D printing technology; by optimizing the internal flow-channel geometry to enhance turbulence, they significantly improved the hydrodynamic behavior between the electrolyte and the GDE. This device used exactly the same electrode, proton exchange membrane, and electrode spacing as a conventional flow cell, with only the reactor structure being different. The test results showed that the new reactor achieved a FE of 90% and an energy consumption as low as 13 kWh kg^{-1} , far outperforming the conventional device. This further reveals the critical importance of device design for electrochemical performance. Even when the catalyst, membrane material, and operating conditions are identical, an inappropriate reactor configuration can severely limit catalytic performance, whereas a well-designed device can substantially enhance reaction efficiency. Operational parameters precisely govern the reaction kinetics and interfacial mass transfer, and are key to ensuring the full expression of catalyst activity and selectivity. Zhao et al. [50] conducted scale-up tests on a porous solid electrolyte (PSE) reactor and found that the performance degradation during scale-up was not mainly due to catalyst deactivation, but rather to the failure in device-catalyst coupling caused by the

non-uniformity of the laminar flow field in the reactor. Based on this finding, the research team optimized the structure and successfully developed a 12-unit modular electrode-stacked reactor, which operated stably for over 400 h, produced 2.5 kg of pure H_2O_2 per day, and achieved energy costs significantly lower than the market price. It is thus evident that the electrode, reactor, and operational parameters interact with one another; improvement in a single dimension is insufficient to achieve a breakthrough in overall performance. Only through synergistic regulation can the full potential of the catalyst be unleashed, enhancing the efficiency and stability of H_2O_2 generation and providing support for the industrial application of ORR electrosynthesis of H_2O_2 . Detailed optimization strategies will be elaborated in the following sections.

3 Electrocatalyst construction

3.1 Categories of electrocatalysts

Regarding catalyst construction, the catalysts currently used in 2e^- ORR-based H_2O_2 electrosynthesis can be classified into three major categories according to the elemental composition and electronic structure of the active centers: metal-free, transition-metal, and noble-metal catalysts [55]. Metal-free catalysts represent a core research focus in the field of 2e^- ORR-based H_2O_2 electrosynthesis. Typical examples include heteroatom-doped (N, O, S, P, B, etc.) carbon materials, intrinsic carbon defects, and porous carbon frameworks [56, 57]. The primary advantages of this class of catalysts lie in the abundance of raw materials, the simplicity and controllability of the synthesis process, and the low preparation cost. In addition, the carbon-based skeleton offers a high specific surface area and tunable porous structures [58–60]. By precisely controlling the type and amount of heteroatom dopants as well as the concentration of carbon defects, the electronic distribution on the carbon surface can be effectively optimized, and the adsorption energy barriers of reaction intermediates can be tuned. Under suitable reaction conditions such as appropriate applied potential and electrolyte environment, exceptionally high H_2O_2 selectivity can be achieved, effectively suppressing the competing 4e^- ORR pathway [58, 61, 62]. For example, Wang et al. [63] prepared nitrogen-doped carbon materials (N-C_{800}) by tuning the pyrolysis temperature of ZIF-8. In this material, the carbon atoms adjacent to graphitic nitrogen serve as the primary active sites, effectively weakening the $^*\text{OOH}$ adsorption strength to an optimal energy window that facilitates desorption. As a result, an H_2O_2 selectivity of approximately 95% was achieved in neutral simulated seawater (0.5 M NaCl). In addition, defect-rich graphene and porous biomass-derived carbon materials constructed by high-temperature etching can significantly promote the 2e^- ORR pathway through edge defects and vacancy sites, representing typical low-cost materials for H_2O_2 production [64, 65]. However, this class of catalysts has inherent performance limitations. The active sites are primarily derived from heteroatom dopants, carbon edge defects, and vacancy sites. Compared with metal-based catalysts, the effective active site density is generally low, making it difficult to achieve efficient H_2O_2 production at ultra-high current densities [66]. Moreover, the carbon-

based functional structures are susceptible to framework corrosion and defect reconstruction in strongly acidic or strongly alkaline electrolyte media. During prolonged electrolysis, active sites are gradually lost and the surface structure undergoes irreversible collapse, leading to continuous decay in catalytic activity and product selectivity. Thus, the cycling stability and operational adaptability of these materials require further improvement [67, 68].

Transition-metal catalysts represent a research hotspot and a key breakthrough direction in the current field of 2e^- ORR catalysis, mainly encompassing non-noble metal SACs, metal oxides, metal hydroxides, and metal organic complexes based on Co, Fe, Ni, Mn, and other transition metals [69–73]. The core advantage of these catalysts originates from the unique outer electron configurations of transition metals. Their rich and variable d-electron configurations, multi-dimensional orbital energy level distributions, and flexible switchable redox valence states enable precise regulation of the adsorption, binding, and desorption behavior of the key $^*\text{OOH}$ intermediate during electrocatalysis [74, 75]. Among them, SACs feature atomically dispersed active centers, well-defined coordination structures, 100% atomic utilization, and precisely tunable coordination environments. These advantages effectively overcome the agglomeration and uneven active sites of traditional metal nanoparticle catalysts, rendering them the most promising transition metal catalytic system at the current stage [76–80]. For example, Tian et al. [81] anchored Co single atoms onto a hierarchically porous carbon support rich in edge defects. The edge sites induced a downshift of the d-band center of the Co centers, moderately weakening $^*\text{OOH}$ adsorption and preventing over-reduction of the intermediate. This catalyst achieved an H_2O_2 selectivity of approximately 95% and a production rate of $1.72 \text{ mol h}^{-1} \text{ g}^{-1}$ in alkaline media. Nevertheless, transition-metal catalysts still face unavoidable application bottlenecks. Among them, the stability limitations of Fe and Co-based mainstream single-atom and composite systems are particularly pronounced. During long-term electrolysis, the metal active centers are highly prone to leaching and dissolution, leading to a significant decline in catalytic activity. Meanwhile, the dissolved Fe and Co metal ions can react with the H_2O_2 generated in the reaction system through Fenton or Fenton-like reactions, triggering the generation of reactive oxygen species. These not only continuously decompose H_2O_2 , reducing the yield, but also damage the coordination structures on the catalyst surface and the support skeleton, further deteriorating the cycling stability of the catalytic system [82, 83].

Noble-metal catalysts are primarily represented by Pd, Au, and their binary and multi-component alloys. These catalysts possess exceptionally high intrinsic catalytic activity, superior electrical conductivity, fast electron transfer kinetics, and excellent chemical structural stability. During electrocatalytic reactions, they are not prone to structural corrosion or component leaching, and their electrochemical reversibility and reaction stability far exceed those of other catalyst types [84, 85]. In addition, by precisely tuning the alloy composition, particle size, and

surface morphology, the adsorption strength of the $^*\text{OOH}$ intermediate can be accurately optimized, and the competing reduction side reactions can be effectively suppressed. In some optimally designed noble-metal catalytic systems, the H_2O_2 selectivity can approach the theoretical ideal value [86, 87]. For instance, Zhang et al. [88] developed an ultrafine Au nanoparticle catalyst (APES-Au/PC) via a carbon-nanosheet-driven spontaneous deposition strategy. By modulating the interfacial electronic structure between the Au nanoparticles and the porous carbon support, an H_2O_2 selectivity of nearly 95% was achieved under weakly alkaline conditions (0.1 M KOH). Tian et al. [89] constructed AuPd alloy catalysts by precisely tuning the atomic ratio of Au to Pd. The catalyst leverages the bimetallic electronic synergistic effect to precisely optimize the d-band center and d-band width of the Au active sites, thereby finely tuning the adsorption and desorption behavior of the $^*\text{OOH}$ intermediate and effectively suppressing the $4e^-$ reduction side reaction, achieving both high activity and high selectivity. However, this class of catalysts also suffers from a critical limitation that impedes large-scale application: the scarcity and high market price of noble metals such as Pd and Au result in extremely high catalyst preparation costs. Moreover, noble-metal materials are difficult to load and regenerate at low cost on a large scale, which greatly restricts their industrial application [90–92]. Overall, the three classes of catalysts differ in their applicable scenarios and limitations. How to leverage their respective strengths while compensating for their weaknesses to improve overall performance remains an important research topic. Based on the above classification, the following sections will focus on the synthesis methods of these catalysts.

3.2 Synthesis strategies for electrocatalyst

Generally, the structural characteristics of a catalyst directly determine its catalytic performance, and synthesis strategies are the core means of constructing such structures. Typically, based on the physical state of the reactants, catalyst synthesis strategies can be categorized into three major classes: solid-phase methods, liquid-phase methods, and gas-phase methods.

3.2.1 Solid-phase methods

(1) Pyrolysis method

The pyrolysis method involves high-temperature treatment of precursors in an inert atmosphere (N_2 , Ar, He) to promote decomposition, carbonization, doping, or phase transformation, thereby yielding materials with specific structures and catalytic activities [93]. It offers advantages such as simple operation, controllable cost, and easy scalability, and catalytic performance can be further enhanced by adjusting process parameters like precursor composition and pyrolysis temperature. For example, Lim et

al. [94] used NiAc_2 and 1,10-phenanthroline as precursors, loaded the mixture into the channels of SBA-15, and added trace amounts of solvents with different vapor pressures (acetone, ethanol, deionized water) to promote confined coordination. Then they synthesized Ni-based atomically dispersed catalysts ($\text{Ni-N/C}_{3\text{X}}$) by pyrolysis at 800°C under flowing N_2 . By varying the phenanthroline-to-Ni molar ratio (1:1, 2:1, 3:1) and the solvent type, they could tune the relative proportion of Ni nanoparticles and Ni-N_4 single-atom sites in the product, as well as the degree of planar geometric distortion of the Ni-N_4 sites. When deionized water was used as the solvent and the molar ratio was 1:1, ligand deficiency led to the simultaneous formation of Ni nanoparticles and Ni-N_4 sites; at ratios of 2:1 and 3:1, only isolated Ni-N_4 sites were generated after pyrolysis, without Ni nanoparticles. However, the Ni-N_4 structure at the 2:1 ratio exhibited a higher degree of distortion, and its $2e^-$ ORR activity was significantly lower than that of the 3:1 sample. In systems using acetone, ethanol, or no solvent, incomplete coordination resulted in products with a large number of Ni particles (Fig. 3a). Nevertheless, this work still relied on complex SBA-15 template confinement and subsequent etching with a mixed HF/HCl acid, making the procedure cumbersome and unfavorable for large-scale production.

During pyrolysis, precursors often suffer from uneven mixing, which leads to agglomeration of active sites. Therefore, homogenizing the precursor components becomes particularly important. Tian et al. [31] developed a zwitterionic-liquid-assisted pyrolysis strategy. Specifically, they mixed a boron-containing zwitterionic liquid with dicyandiamide and performed two-step pyrolysis under flowing N_2 to obtain a B, N-co-doped carbon catalyst with a turbostratic structure (CNB-ZIL 8). Taking advantage of the low viscosity and high miscibility of the zwitterionic liquid, this strategy pre-dispersed the B and N sources at the molecular level within the carbon precursor, thereby forming a large number of highly dispersed interfacial B–N–C structures during pyrolysis, rather than aggregated inert hexagonal BN particles. X-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure characterization confirmed that B and N atoms in CNB-ZIL 8 mainly existed as BNC_2 and BN_2C moieties, with no large *h*-BN domains (Fig. 3b). When applied in alkaline media, this catalyst achieved an HO_2^- production rate of $1787\text{ mmol g}^{-1}\text{ h}^{-1}$ and a selectivity as high as 85% at a flow-cell voltage of -1.4 V , significantly outperforming the control samples (CNB-ZIL 9/10) that tended to form *h*-BN agglomerates under high-temperature pyrolysis. This work demonstrates that molecular-level pre-dispersion using ionic liquids can effectively overcome the bottlenecks of uneven heteroatom distribution and low active-site density in conventional pyrolysis doping, offering a new route for the precise construction of active sites in high-performance catalysts.

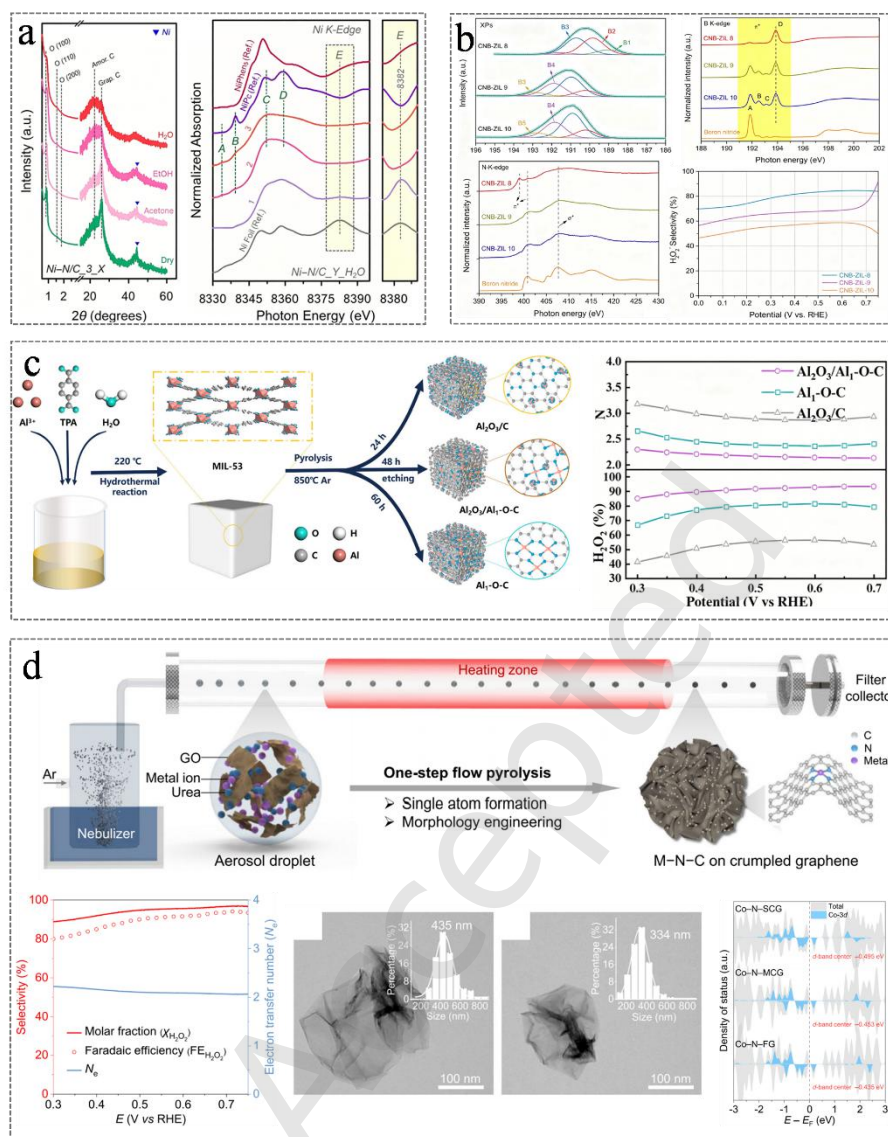


Figure 3 a) X-ray diffraction (XRD) patterns of Ni-N/C₃X catalysts, Ni K-edge x-ray absorption near edge structure spectra and their enlarged spectra in the peak a region. Reproduced with permission from Ref. [94], © The Royal Society of Chemistry 2024. b) XPS spectra of CNB-ZIL 8, CNB-ZIL 9, and CNB-ZIL 10, B and N near-edge x-ray absorption fine structure spectra, and H₂O₂ selectivity of the CNB-ZIL samples. Reproduced with permission from Ref. [31], © Wiley-VCH GmbH 2022. c) Schematic illustration of the synthesis of Al₂O₃/C, Al₂O₃/Al₁-O-C and Al₁-O-C, the electron transfer number and H₂O₂ selectivity. Reproduced with permission from Ref. [95], © American Chemical Society 2025. d) Schematic illustration of the synthesis of M-N-CG via continuous-flow spray pyrolysis, electron transfer numbers and H₂O₂ selectivity of Co-N-FG, Co-N-MCG, and Co-N-SCG, transmission electron microscopy (TEM) images of Co-N-MCG and Co-N-SCG, total density of states (gray) and cobalt d-band density of states (blue) for the Co-N-FG, Co-N-MCG, and Co-N-SCG systems. Reproduced with permission from Ref. [96], © Wiley-VCH GmbH 2026.

In addition to precursor composition, pyrolysis temperature is often a key factor for enhancing catalytic performance. For example, Li et al. [95] pyrolyzed MIL-53(Al) precursors at 750, 850, and 950 °C for 6 h under an Ar atmosphere, followed by alkaline etching to synthesize Al₂O₃/Al₁-O-C tandem catalysts (Fig. 3c). By adjusting the pyrolysis temperature, they optimized the ratio of Al₂O₃ nanoparticles to Al single-atom sites and their electronic interaction. The catalyst obtained at 850 °C exhibited H₂O₂ selectivity of 85–93.4% in the potential range of 0.3–0.7 V. Density functional theory (DFT) calculations revealed that Al₂O₃ sites promote H₂O decomposition to generate *H, while adjacent Al-O₄ single-atom sites are responsible for reducing O₂ to *OOH; the synergistic effect of the two enables an efficient 2e[−] ORR pathway. Different from the

conventional static pyrolysis described above, He et al. [96] recently developed a continuous-flow spray pyrolysis process (Fig. 3d). Through extremely short residence times and rapid gas-liquid interfacial heat transfer, they achieved simultaneous control over the carbon support morphology and the electronic structure of single atoms. Specifically, they atomized a mixed solution containing graphene oxide, cobalt salt, and urea to form aerosol droplets, which were then spray-pyrolyzed at 750 °C under an Ar flow to obtain Co single atoms supported on crumpled nitrogen-doped graphene (Co-N-SCG) in one step. By varying the pyrolysis temperature (300 °C, 750 °C), they altered the degree of crumpling of the graphene substrate, which in turn induced geometric distortion and electron deficiency at the Co-N₄ sites. The catalyst pyrolyzed at 750 °C achieved H₂O₂ mole

fractions exceeding 90% over a wide potential range of 0.30–0.75 V. DFT calculations confirmed that the lattice compression caused by crumpling shifted the Co d-band center downward and weakened *OOH adsorption, thus promoting the 2e⁻ ORR pathway. This work also provides new insights for precisely tuning the geometric and electronic structures of SACs.

(2) Ball milling

Ball milling is a typical mechanochemical synthesis method that utilizes the mechanical force generated by high-energy ball milling to trigger chemical reactions or structural reorganization among solid reactants. Compared with conventional liquid-phase synthesis, ball milling offers outstanding advantages such as simple operation, solvent-free conditions, and suitability for large-scale production [97, 98]. In the field of 2e⁻ ORR, ball milling can enhance catalyst performance by introducing defects and functional groups through mechanochemical effects. For example, Gao et al. [99] used peanut-shell-derived biochar as the raw material to prepare a series of carbon-based electrocatalysts (MBC-X) via mechanical ball milling. Owing to the mechanochemical effect of ball milling, a large number of carbon defects and

OFGs (C–O, –COOH, C=O, O–C=O) were in situ introduced into the carbon skeleton (Fig. 4a). Among these, carbon defects strengthen O₂ adsorption and charge transfer, while OFGs provide key active sites for the 2e⁻ ORR. Their synergistic effect enabled the MBC-2 catalyst to achieve a H₂O₂ electrosynthesis activity 4.2 times higher than that of pristine biochar, with an H₂O₂ selectivity of 87% in a 50 mM Na₂SO₄ neutral electrolyte at –0.7 V vs. Ag/AgCl. Similarly, Han et al. [100] adopted a mechanochemical ball-milling strategy to treat graphite raw material, simultaneously exfoliating graphite and generating a large number of edge dangling bonds, which were then selectively oxidized with CO₂ or dilute O₂ to precisely construct OFGs such as quinone groups and –COOH at the edges of carbon nanosheets, yielding quinone-enriched graphitic nanosheet catalysts. The synergistic effect of ball-milling-induced edge defects and targeted functional groups enabled this catalyst to achieve an H₂O₂ selectivity as high as 97.8% at 0.75 V in 0.1 M KOH (Fig. 4b). DFT calculations further reveal that the edge quinone groups can effectively tune ΔG^*_{OOH} to approach the theoretical optimum, fully verifying the effectiveness of ball milling in enhancing catalytic performance.

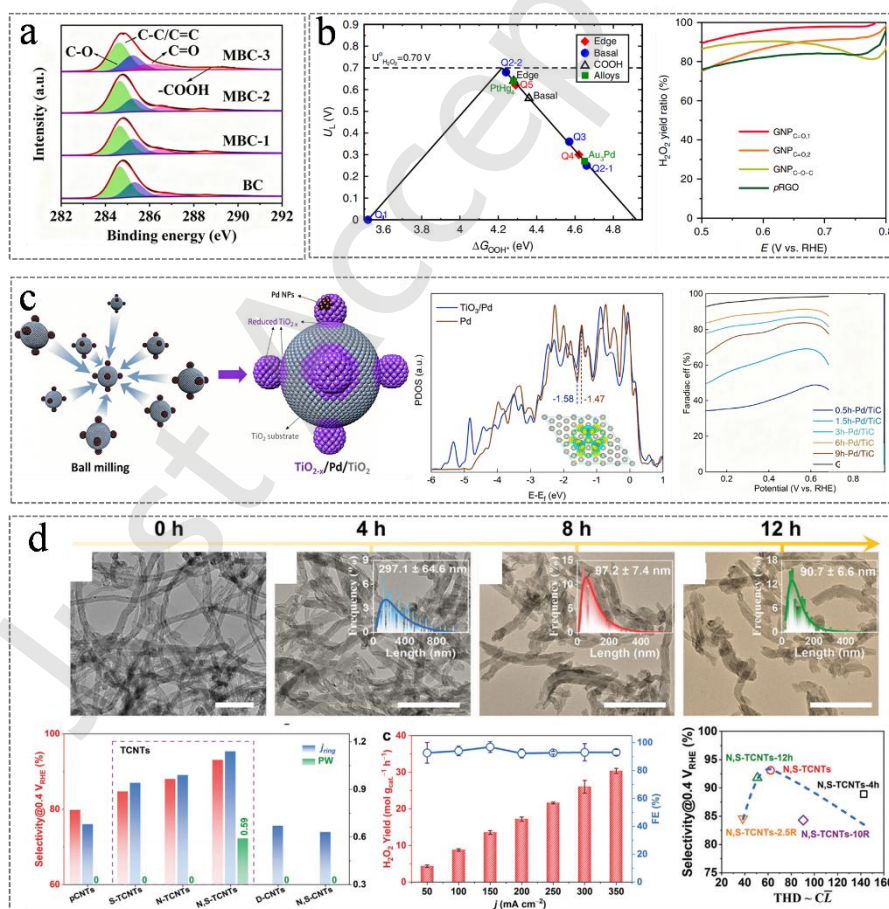


Figure 4 a) C 1s XPS spectra of MBC-X. Reproduced with permission from Ref. [99], © Elsevier 2022. b) DFT volcano plot and H₂O₂ selectivity of the samples. Reproduced with permission from Ref. [100], © Springer Nature 2020. c) Schematic illustration of the synthesis of Pd/TiC with strong metal-support interaction (SMSI), H₂O₂ FE and d-band center. Reproduced with permission from Ref. [101], © American Chemical Society 2022. d) TEM morphology, H₂O₂ selectivity, flow cell productivity and thermodynamic descriptor volcano plot of N, S-co-doped carbon nanotubes (N, S-TCNTs). Reproduced with permission from Ref. [102], © Wiley-VCH GmbH 2023.

In addition to improving catalyst performance through defect introduction, ball milling can also precisely optimize

catalyst structure and performance by adjusting process parameters such as rotational speed, ball-to-powder ratio,

milling time, and atmosphere. For example, Zhang et al. [101] successfully synthesized Pd/TiC electrocatalysts based on SMSI via ball milling (Fig. 4c). They tuned the milling time (0.5–9 h) and atmosphere (air, Ar, O₂) during the mechanical ball-milling process. The results showed that the sample milled for 6 h formed a TiO_{2-x} encapsulation layer of moderate thickness, which downshifted the d-band center of Pd and optimized the adsorption energy of *OOH, thereby promoting the 2e⁻ ORR pathway. Rotating ring-disk electrode (RRDE) tests further demonstrated that the Pd/TiC catalyst delivered H₂O₂ selectivity exceeding 90% within the potential window of 0.1–0.7 V in 0.1 M KOH, with an onset potential as high as 0.877 V. Too short a milling time (0.5 h) failed to form the encapsulation layer, while too long a time (9 h) led to an overly thick coating that hindered mass transfer. Milling in a pure O₂ atmosphere suppressed the SMSI effect, whereas milling in Ar or air with low oxygen partial pressure promoted the formation of the reductive coating layer. Unlike the above approach that tuned milling time and atmosphere, Long et al. [102] tuned not only the ball-milling time but also the feeding ratio during ball-milling to boost catalytic performance. Specifically, they successfully synthesized N, S-TCNTs via ball milling, utilizing the mechanical force during milling to fracture the carbon nanotubes and preferentially dope heteroatoms at the fractured tips rather than on the sidewalls. By adjusting the milling time (4–12 h) and the mass ratio of thiourea to CNT, they found that the sample milled for 8 h with a thiourea-to-CNT mass ratio of 3:1 possessed a moderate heteroatom density at the tips, enabling precise tuning of *OOH adsorption energy to an optimal state, thereby maintaining an H₂O₂ selectivity > 90% over a wide potential window of 0.19–0.78 V and achieving a high production rate of 30.37 mol g⁻¹ h⁻¹ at a current density of 350 mA cm⁻² (Fig. 4d). Insufficient or excessive milling time and improper precursor ratios all led to performance degradation. This work clearly demonstrates the fine-tuning capability of ball-milling parameters such as time and precursor ratio on the local environment of catalysts at the atomic scale.

Although ball milling shows significant potential for regulating catalyst structure, it still faces several obstacles. Coupled parameters are difficult to optimize independently, the structural evolution under mechanical force remains unclear, forcing catalyst design to rely largely on empirical trial and error. In addition, reproducibility between runs and uniformity in structure and activity during scale-up have not been adequately addressed, which seriously hampers its industrial applicability.

3.2.2 Liquid-phase methods

(1) Hydrothermal/Solvothermal method

Hydrothermal/solvothermal methods leverage high-temperature and high-pressure liquid media in closed systems to enable precursors to undergo dissolution, nucleation, and crystallization under subcritical or supercritical conditions. Owing to its advantages of mild reaction conditions, high product crystallinity, and strong tunability of morphology, it has become one of the mainstream approaches for controlling the microstructure of 2e⁻ ORR catalysts. By adjusting parameters such as

reaction temperature, time, precursor ratio, and additive types, the hydrothermal/solvothermal method can precisely control the size, dimensionality, and even the exposed crystal facets of the products. For example, Liu et al. [103] prepared hierarchical hollow SmPO₄ nanosphere catalysts via a two-step hydrothermal method. By systematically varying the phosphating time (1, 12, 24 h), they found that the reaction time determined the extent of ion exchange and dissolution-recrystallization. At 1 h, only a small number of nanorods were attached to the surface. At 12 h, a well-defined hollow sphere structure with uniformly dense nanorods on the surface was formed; while at 24 h, excessive growth led to shell thickening and a decrease in specific surface area (Fig. 5a). Among these, the hollow structure of the 12 h sample was the most favorable for mass transfer, achieving an H₂O₂ selectivity as high as 96% at 0.45 V in 0.1 M KOH, far exceeding those of the 1 h (88%) and 24 h (85%) samples. XRD Rietveld refinement reveals that the hexagonal SmPO₄ crystals possess adjacent Sm atoms distances exceeding 4 Å and intrinsic proton/ion channels of approximately 5 Å in diameter. DFT calculations further demonstrate that this unique geometry significantly optimizes $\Delta G^{\circ}_{\text{OOH}}$ and lowers the kinetic energy barrier. Similarly, Zhang et al. [104] synthesized Sn-doped BiOCl nanosheet electrocatalysts via a one-step hydrothermal method. By adjusting the amount of SnCl₄·5H₂O added (2–10 mol%), the surface morphology and the degree of fragmentation of the nanosheets were controlled. XPS and Raman analyses revealed that Sn⁴⁺ doping induced an electron-deficient state at the Bi sites, shortened the Bi–O bond length, and significantly enhanced the electrical conductivity. At a Sn doping level of 6 mol%, the specific surface area of the catalyst increased from 0.2976 m²/g to 3.9373 m²/g, and the highly active (001) facets were preferentially exposed, resulting in an H₂O₂ selectivity of 92.9% at 0.4 V in 0.1 M KOH.

In addition to morphology control, the high-temperature and high-pressure enclosed environment of the hydrothermal/solvothermal method enables the in situ construction of intimate heterointerfaces, facilitating nanoscale contact between different components and significantly improving the utilization efficiency of active sites. For example, Nie et al. [71] grew Ni(OH)₂ nanosheets in situ on the surface of oxidized carbon nanotubes (O-CNTs) via a one-step hydrothermal method (180 °C, 12 h). Without subsequent treatment, this approach achieved nanoscale integration of the highly conductive CNT framework with the active Ni(OH)₂ component, constructing a composite heterostructure of CNT-supported Ni(OH)₂ nanosheets. In this structure, the CNT reduced charge transfer resistance, while the unsaturated Ni atoms at Ni(OH)₂ edges and oxygen vacancies act as the primary active centers. Electron paramagnetic resonance and x-ray absorption spectroscopy confirmed that the oxygen vacancies formed during hydrothermal treatment reduced the Ni coordination number to 5.7, enhancing O₂ adsorption and activation. DFT calculations indicated that the proton migration energy barrier on the Ni(OH)₂ surface was only 0.35 eV, far lower than the 1.21 eV of NiO, confirming its efficient water dissociation and proton transfer capability (Fig. 5b).

Benefiting from this structural design, the catalyst achieved an H_2O_2 production rate of $30.86 \text{ mol g}^{-1} \text{ h}^{-1}$ in 1 M NaCl with

a FE exceeding 80%.

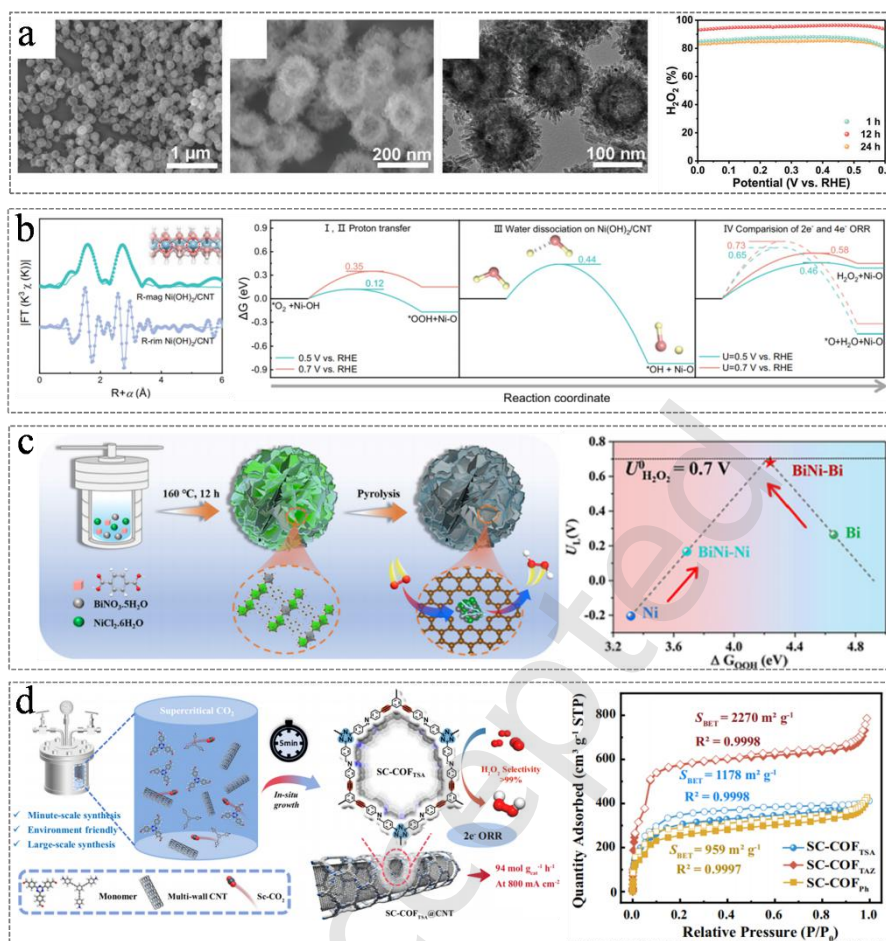


Figure 5 a) Scanning electron microscopy image, TEM image and H_2O_2 selectivity of $\text{SmPO}_4\text{-12}$. Reproduced with permission from Ref. [103], © Wiley-VCH GmbH 2025. b) Extended x-ray absorption fine structure fitting results obtained in R-space based on the Ni-O and Ni-Ni scattering path models; proton transfer process at 0.5 V and 0.7 V (I); water dissociation on the outer surface of $\text{Ni}(\text{OH})_2$ and the optimized geometries of the initial state, transition state, and final state (II, III); and the *OOH protonation process for the 2e^- ORR and the *OOH dissociation process for the 4e^- ORR in the $\text{Ni}(\text{OH})_2$ system at 0.5 V and 0.7 V (IV), where pink represents O atoms in H_2O and yellow represents H atoms in H_2O . Reproduced with permission from Ref. [71], © Springer Nature 2025. c) Schematic illustration of the preparation process of BiNi/C and the corresponding activity volcano plot. Reproduced with permission from Ref. [105], © American Chemical Society 2025. d) Schematic illustration of the supercritical CO_2 -assisted solvothermal synthesis of ORR electrocatalysts and the N_2 adsorption-desorption isotherms of SC-COFs. Reproduced with permission from Ref. [106], © Springer Nature 2025.

The hydrothermal/solvothermal method also exhibits good method compatibility and is often combined with post-treatment calcination or pyrolysis strategies to achieve further functionalization based on the pre-established morphology and structure, thereby obtaining catalysts that are difficult to prepare by a single method. For instance, Wu et al. [107] first synthesized $\text{Ni}(\text{OH})_2$ nanosheets via a hydrothermal method (100°C , 6 h), and then calcined the product under vacuum (0.1 Pa) at 400°C for 30 min. The hydrothermal step introduced PVP as a structure-directing agent, yielding nanosheet morphologies. The vacuum calcination promoted the removal of lattice oxygen, forming a high concentration of oxygen vacancies. DFT calculations revealed that the oxygen vacancies shifted the Ni d-band center from -1.942 eV to -1.614 eV , converting the O_2 adsorption configuration from the Yeager-type, which is unfavorable for the 2e^- ORR, to the Pauling-type, which favors H_2O_2 generation. As a result, the H_2O_2 selectivity

increased from 21% for pure NiO to 95%. Similarly, Liu et al. [105] first prepared Ni/Bi-MOF precursors via a hydrothermal method (160°C , 12 h), ensuring atomic-level uniform distribution of Bi^{3+} and Ni^{2+} in the MOF framework, followed by pyrolysis (675°C , 2 h) to form BiNi alloy nanoparticles (Fig. 5c). DFT calculations confirmed that Bi in the alloy plays a dual regulatory role of physical isolation and electronic isolation. On one hand, it increases the Ni-Ni interatomic distance and induces electron transfer from Ni to Bi, weakening the excessively strong *OOH adsorption on pure Ni. On the other hand, it enhances the electron density of Bi itself, enabling the Bi sites to achieve a moderate $\Delta G_{\text{*OOH}}$ (4.24 eV) that compensates for the weak adsorption of pure Bi. Benefiting from this synergistic electronic and geometric regulation, the catalyst achieved an H_2O_2 selectivity as high as 98% under alkaline conditions.

Notably, significant breakthroughs have been made in recent years regarding the reaction efficiency of

hydrothermal/solvothermal methods. Traditional organic solvothermal synthesis of covalent organic frameworks (COFs) typically requires over 72 h, high temperatures above 120 °C, and complicated freeze-pump-thaw cycles, severely limiting large-scale applications. To address this bottleneck, Song et al. [106] developed a supercritical CO₂-assisted rapid solvothermal method. By leveraging the excellent gas diffusivity and liquid solubility of supercritical fluids, they completed the polymerization of triazine-based COFs and their in situ growth on CNTs within 5 min (Fig. 5d). Compared with conventional methods, this strategy not only reduced the reaction time from days to minutes but also yielded products with higher crystallinity and larger specific surface areas. The resulting COF@CNT composite achieved an H₂O₂ production rate of 94 mol g⁻¹ h⁻¹ at 800 mA cm⁻² with a FE exceeding 95%, outperforming analogous materials synthesized by conventional methods. This work provides a new route for the efficient and scalable preparation of 2e⁻ ORR catalysts. However, it should be noted that the supercritical CO₂ method currently still relies on high-pressure equipment, and the recycling of CO₂ in large-scale production has not been fully resolved, leaving its industrial competitiveness to be further validated.

(2) Wet chemical reduction method

The wet chemical reduction method involves the addition of a reducing agent to a liquid-phase system to reduce catalyst precursors to metallic elements, alloys, or low-valence metal oxides, thereby preparing catalysts. This method offers mild reaction conditions and simple operation, enabling precise control over particle size, composition, and surface properties. It is widely used in the preparation of noble-metal and transition-metal catalysts. By selecting appropriate reducing agents and reaction conditions, catalysts can be finely designed across multiple dimensions. For example, Bharathan et al. [108] used PdCl₂ as the palladium source and NaBH₄ as the reducing agent to first reduce the Pd precursor and load it onto a CeO₂/C composite support in aqueous solution, followed by air annealing to obtain isolated PdO clusters. When the Pd loading was reduced to 0.027 wt%, the formation of Pd ensemble sites was effectively suppressed. The catalyst achieved an H₂O₂ selectivity as high as 97% at 0.7 V in 1 M KOH (Fig. 6a). In this system, in addition to relying on low loading to isolate Pd sites, the SMSI between Pd and CeO₂ directly modulates the electronic structure of the Pd active centers, synergistically enhancing selectivity.

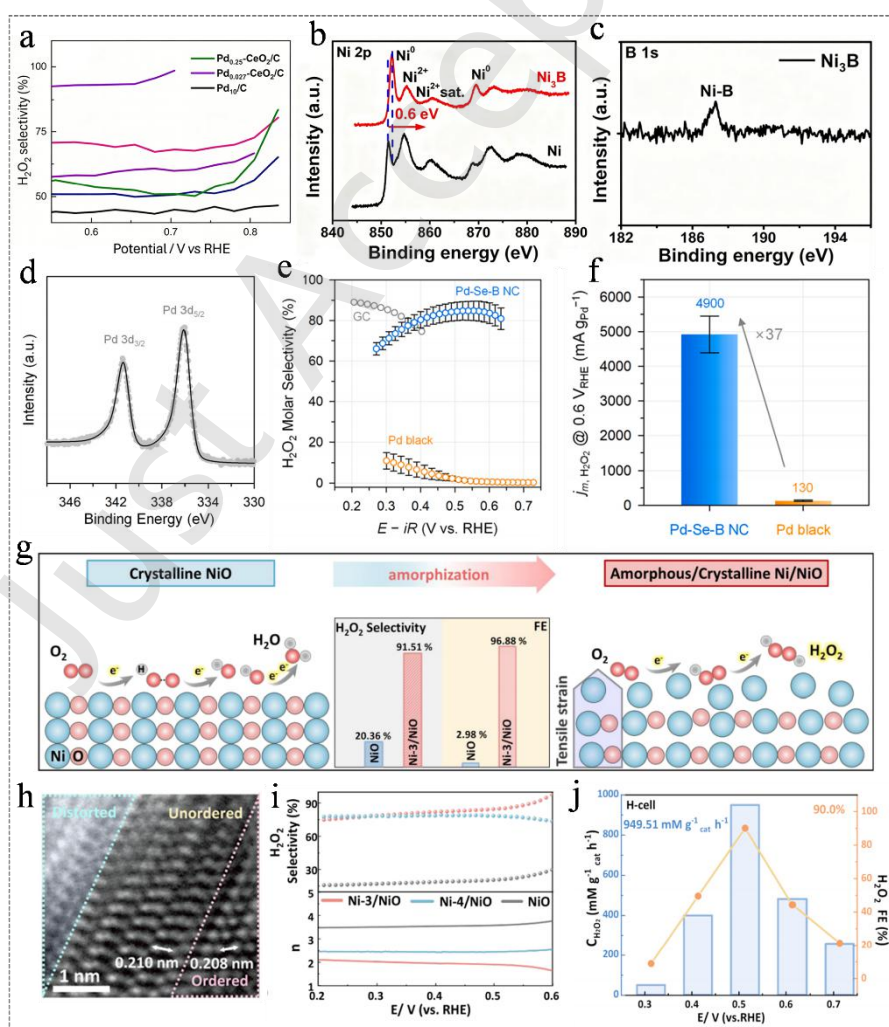


Figure 6 a) H₂O₂ selectivity of Pd_x-CeO₂/C with different Pd loadings. Reproduced with permission from Ref. [108], © The Royal Society of Chemistry 2025. b) Ni 2p spectra of Ni and Ni₃B. c) B 1s XPS spectrum of Ni₃B. Reproduced with permission from Ref. [109], © Elsevier 2020. d) Deconvoluted Pd 3d XPS spectra. e) Molar H₂O₂ selectivity of P-Se-B nanocomposite, Pd black electrode, and glassy carbon electrode. f) Mass activity of H₂O₂ per unit

Pd at 0.6 V. Reproduced with permission from Ref. [110], © Elsevier 2022. g) Schematic illustration of the $2e^-$ ORR mechanism at the amorphous-crystalline Ni/NiO heterointerface. h) Inverse fast fourier transform image showing the coexistence of ordered, distorted, and disordered regions in Ni-3/NiO. i) H_2O_2 selectivity and electron transfer number of NiO and Ni-x/NiO ($x = 3, 4$). j) H_2O_2 yield and corresponding FE of Ni-3/NiO in an H-type cell. Reproduced with permission from Ref. [111], © American Chemical Society 2025.

Compared with relying on low loading and metal-support interactions to tune electronic structure, non-metal doping offers a more direct route for electronic structure optimization. For example, Ma et al. [109] used KBH_4 simultaneously as a reducing agent and a boron source to reduce Ni^{2+} in tetraethylene glycol in one step, synthesizing Ni_3B nanoparticles. XPS analysis showed that the Ni 2p peak shifted positively by 0.6 eV compared with pure Ni, while the B 1s peak shifted negatively by 0.3 eV compared with pure B, confirming the strong electronic interaction between Ni and B (Fig. 6b, c). DFT calculations indicated that the high electronegativity of B reduced the density of states of the Ni 3d orbitals near the Fermi level, bringing the *OOH binding energy closer to the optimum, achieving an H_2O_2 selectivity exceeding 90% and a mass activity of $16.5 A g^{-1}$. On this basis, introducing two non-metal elements simultaneously during the reduction process can further regulate the geometric arrangement of active sites while modifying the electronic structure. Lee et al. [110] co-reduced $Pd(acac)_2$ and H_2SeO_3 with $NaBH_4$ in tetraethylene glycol to prepare $Pd_{17}Se_{15}Pd_3B$ composite catalysts in one step. XPS analysis revealed that the Pd 3d_{5/2} binding energy (336.1 eV) fell between that of metallic Pd (335 eV) and PdO (336.7 eV), indicating that the incorporation of Se and B modulated the electronic structure of Pd (Fig. 6d). The Se and B atoms in the two phases acted as spacer units, disrupting the Pd-Pd-Pd ensemble sites and converting the side-on adsorption of O_2 to end-on adsorption, which favors the preservation of the O-O bond. The catalyst achieved an H_2O_2 selectivity of $85 \pm 5\%$ in 0.1 M KPi near-neutral electrolyte at pH 8, with a Pd-based mass activity 37 times that of commercial Pd black at 0.6 V (Fig. 6e, f). It is worth noting that the above studies all focused on crystalline materials. Extending the regulatory dimensions of the wet chemical reduction method from composition and geometric structure to phase and strain states promises more significant performance breakthroughs. For example, Wang et al. [111] used $NaBH_4$ to partially reduce NiO nanospheres, achieving a gradual transition from crystalline NiO to amorphous/crystalline Ni/NiO heterojunctions by precisely controlling the reduction time (Fig. 6g). TEM imaging revealed that the NiO interplanar spacing in the strained regions increased from 0.208 nm to 0.210 nm, corresponding to a 1.13% tensile strain (Fig. 6h). DFT calculations showed that the interfacial

tensile strain upshifted the Ni d-band center by 0.23 eV, thereby enhancing O_2 adsorption while moderately weakening the *OOH binding strength, shifting the ORR pathway from the $4e^-$ to the $2e^-$ route. The Ni-3/NiO catalyst achieved an H_2O_2 selectivity of 91.78% at 0.5 V and a FE as high as 97.47% at 0.68 V. In a three-electrode H-cell, the catalyst achieved an H_2O_2 production rate of $949.5 mM g^{-1} h^{-1}$ (Fig. 6i, j).

(3) Electrodeposition method

Electrodeposition is a catalyst synthesis method characterized by mild conditions and high controllability, enabling uniform loading of active components on electrode surfaces and structural regulation [112]. This method offers advantages such as controllable preparation processes, precise loading of active components, and strong bonding between the catalyst and electrode, which effectively reduces active component detachment, enhances cycling stability, and enables in-situ catalyst preparation, making it suitable for the construction of integrated electrode-catalysts. For example, Liu et al. [113] directly deposited carbon black (CB) on nickel foam via constant-voltage electrodeposition and further impregnated it with PTFE to form a gas diffusion electrode. This electrode integrates the catalytic layer and diffusion layer into one, and was directly assembled in an electrolyzer, achieving an H_2O_2 concentration of 897.73 mg/L at $12 mA cm^{-2}$, with significantly superior cycling stability compared to non-GDE electrodes (Fig. 7a). They also investigated the effects of deposition time, deposition cycle number, and electrolyte CB concentration, finding that excessively short deposition time leads to insufficient CB loading and scarce active sites; overly long deposition time causes continuous increase in circuit current, leading to electrolyte heating or even boiling, which is detrimental to uniform catalyst loading. Insufficient deposition cycles result in discontinuous CB coverage on the substrate surface, while excessive cycles may cause over-accumulation of active components, blocking the porous channels of the nickel foam. When the CB concentration in the electrodeposition solution is too low, the catalytic layer becomes too thin, limiting the reaction area; when too high, CB tends to aggregate, hindering O_2 transport to the catalytic interface.

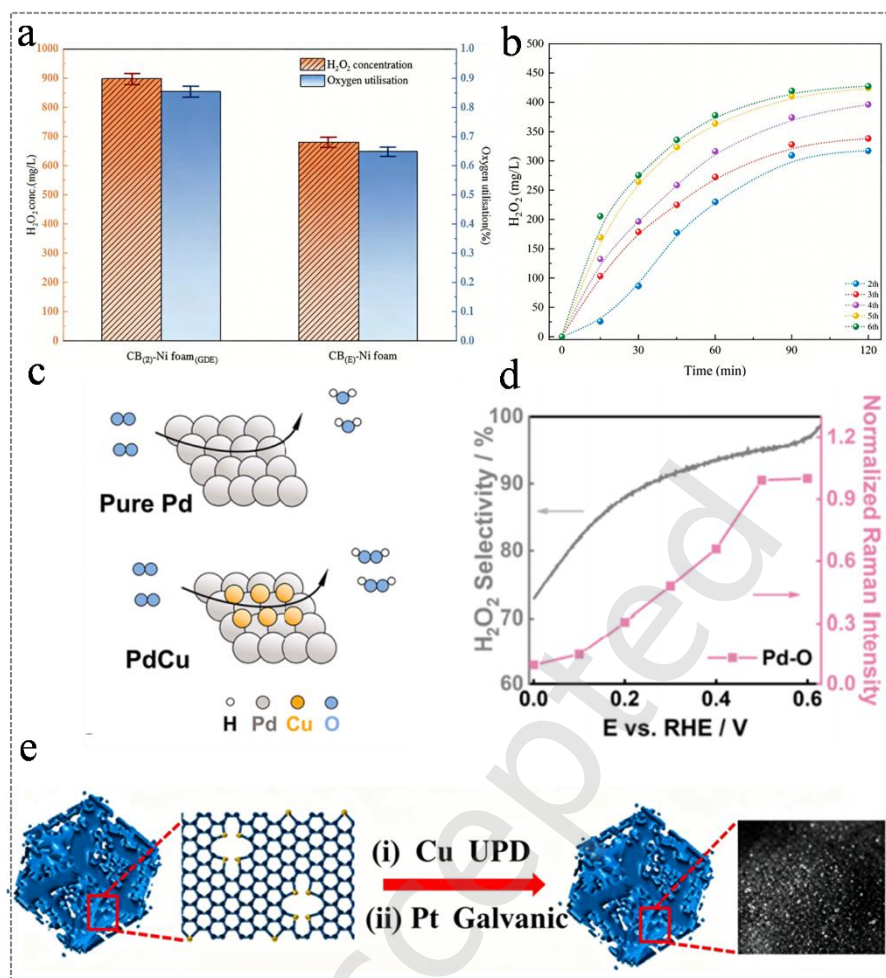


Figure 7 a) H_2O_2 yield. Reproduced with permission from Ref. [113], © Elsevier 2024. b) Effect of electrophoretic deposition frequency on H_2O_2 production. Reproduced with permission from Ref. [114], © Elsevier 2024. c) Schematic illustration of the ORR on different surfaces. d) H_2O_2 selectivity of PdCu NWs/C ORR catalyst and normalized Raman intensities of Pd-O. Reproduced with permission from Ref. [115], © American Chemical Society 2023. e) Flowchart of the preparation process for the $\text{Pt}_1\text{-meso-S-C}$ catalyst via Cu underpotential deposition and Pt galvanic replacement. Reproduced with permission from Ref. [116], © American Chemical Society 2021.

In addition to tuning deposition time, cycle number, and electrolyte concentration, deposition frequency is also commonly adjusted in electrophoretic and pulsed electrochemical deposition methods to enhance catalyst performance. Yang et al., [114] when preparing CB-CF cathodes via electrophoretic deposition, systematically examined the effect of deposition frequency (2–6 cycles) on catalytic performance. They found that as deposition frequency increased, the loading of active components on the electrode surface gradually increased, and H_2O_2 production rose correspondingly, with optimal catalytic performance achieved at a deposition frequency of 5 cycles. However, excessive frequency led to uneven accumulation of active components, inhibiting mass transfer efficiency (Fig. 7b).

Electrodeposition can also be combined with doping, compositing, and other strategies to further optimize catalytic performance. Du et al. [115] realized controllable modification of Cu with different coverages (34.3%, 40.6%, 49.0%) on Pd surfaces via underpotential deposition, forming PdCu composite structures (Fig. 7c). They found that the introduction of Cu stabilizes Pd-O species and optimizes the adsorption energy of *OOH intermediates,

thereby enhancing 2e^- ORR performance. Based on this mechanism, they further synthesized PdCu nanowires via liquid-phase co-reduction, achieving an H_2O_2 selectivity exceeding 85% and a production rate of $1.866 \text{ mol g}^{-1} \text{ h}^{-1}$ in 0.1 M HClO_4 (Fig. 7d). Through the strategy of combining underpotential deposition with displacement reactions, catalytic sites can be precisely designed at the atomic scale, enabling efficient regulation of reaction selectivity. Yin et al., [116] leveraging the strong affinity between sulfur-doped mesoporous carbon and metals, achieved adsorption and deposition of isolated Cu single atoms in the underpotential region above the thermodynamic equilibrium potential of Cu. Subsequently, utilizing the reduction potential difference between Cu and Pt precursors, a spontaneous displacement occurred, yielding atomically dispersed Pt SACs ($\text{Pt}_1\text{-meso-S-C}$) in situ on the carbon support (Fig. 7e). Further studies revealed that the Pt precursor concentration in the displacement system can precisely regulate the dispersion state of Pt species: catalysts prepared with low precursor concentrations feature isolated Pt single atoms as active sites, with an electron transfer number of approximately 2. Increasing the Pt precursor concentration results in the appearance of a small amount of Pt clusters, raising the

electron transfer number to 2.25–2.41, where some active sites trigger $4e^-$ side reactions, leading to a notable decline in H_2O_2 selectivity.

(4) Template method

The template method is a class of synthetic strategies that utilizes pre-designed templates to construct porous materials, with its core principle lying in replicating the morphology or pore structure of the template into the target product. Owing to its precise control over pore structure, morphology, and spatial confinement effects, the template method has become an important synthetic strategy for constructing high-performance $2e^-$ ORR catalysts. Depending on the nature of the template, it can be classified into hard-templating and soft-templating methods.

The hard-templating method employs pre-synthesized nanostructures or macroscopic frameworks as molds. Its primary advantage lies in the accurate replication of the template's microscopic morphology, thereby constructing hollow or hierarchical porous structures that increase specific surface area, expose active sites, and accelerate mass transfer. For example, Yan et al. [117] used Sb_2S_3 nanorods as a hard template, coated them with a carbon layer, and then removed the template via sublimation under vacuum after high-temperature pyrolysis, successfully synthesized N, S co-doped hollow carbon nanofiber catalysts anchored with Sb single atoms (Sb-NSCF) (Fig. 8a). The hollow structure formed during template removal significantly increased the specific surface area ($445\text{ m}^2/\text{g}$) and mesopore volume of the catalyst. In a 1 M KOH three-phase flow cell, Sb-NSCF achieved a yield of $7.46\text{ mol g}^{-1}\text{ h}^{-1}$ at 0.55 V under a high current density of 50 mA cm^{-2} and operated stably for 75 h, demonstrating excellent potential for industrial applications. Wang et al. [118] adopted a self-sacrificial strategy in the hard-templating derivative method, using Co-glycerate

spheres as templates, followed by pyrolysis at different temperatures and acid washing to remove large Co particles, yielding Co nanoparticle-embedded open carbon nanocages (P-Co@C-X). These template-derived carbon nanocages possess abundant nanocavities and mesoporous channels. Combined with the synergistic electronic modulation between Co nanoparticles and surface $-C-O-C$ groups, P-Co@C-700 achieved an H_2O_2 selectivity of 94% at 0.6 V in 0.1 M $HClO_4$. Notably, in contrast to the one-dimensional nanorod morphology of the Sb_2S_3 template, the Co-glycerate sphere template constructed a three-dimensional hollow cage structure. The latter not only provided a larger internal cavity volume but also anchored Co nanoparticles within the carbon walls through confinement effects, preventing particle migration and agglomeration, reflecting another layer of value offered by the hard template.

Unlike the spherical self-sacrificial template adopted by Wang et al., Xu et al. [119] employed a three-dimensional melamine sponge as a monolithic hard template. After adsorbing Ni^{2+} and boric acid, the composite was directly pyrolyzed in one step to synthesize a composite material with Ni nanoparticles encapsulated in B, N co-doped carbon nanotubes (Ni@B/N-CNTs-MS) (Fig. 8b). The three-dimensional interconnected monolithic framework of the sponge template suppressed the excessive growth of Ni particles through physical confinement while catalyzing the in-situ growth of CNTs. The B, N co-doping brought its ΔG_{OOH} close to the theoretical optimum at the volcano plot apex, achieving an H_2O_2 selectivity of 90% in 0.1 M KOH and a yield of $690\text{ mmol g}^{-1}\text{ h}^{-1}$ at 0.2 V. Notably, this template not only provided a more open interconnected network but also endowed the material with a macroscopic monolithic morphology while confining the metal, facilitating scalable preparation and electrode processing in practical applications.

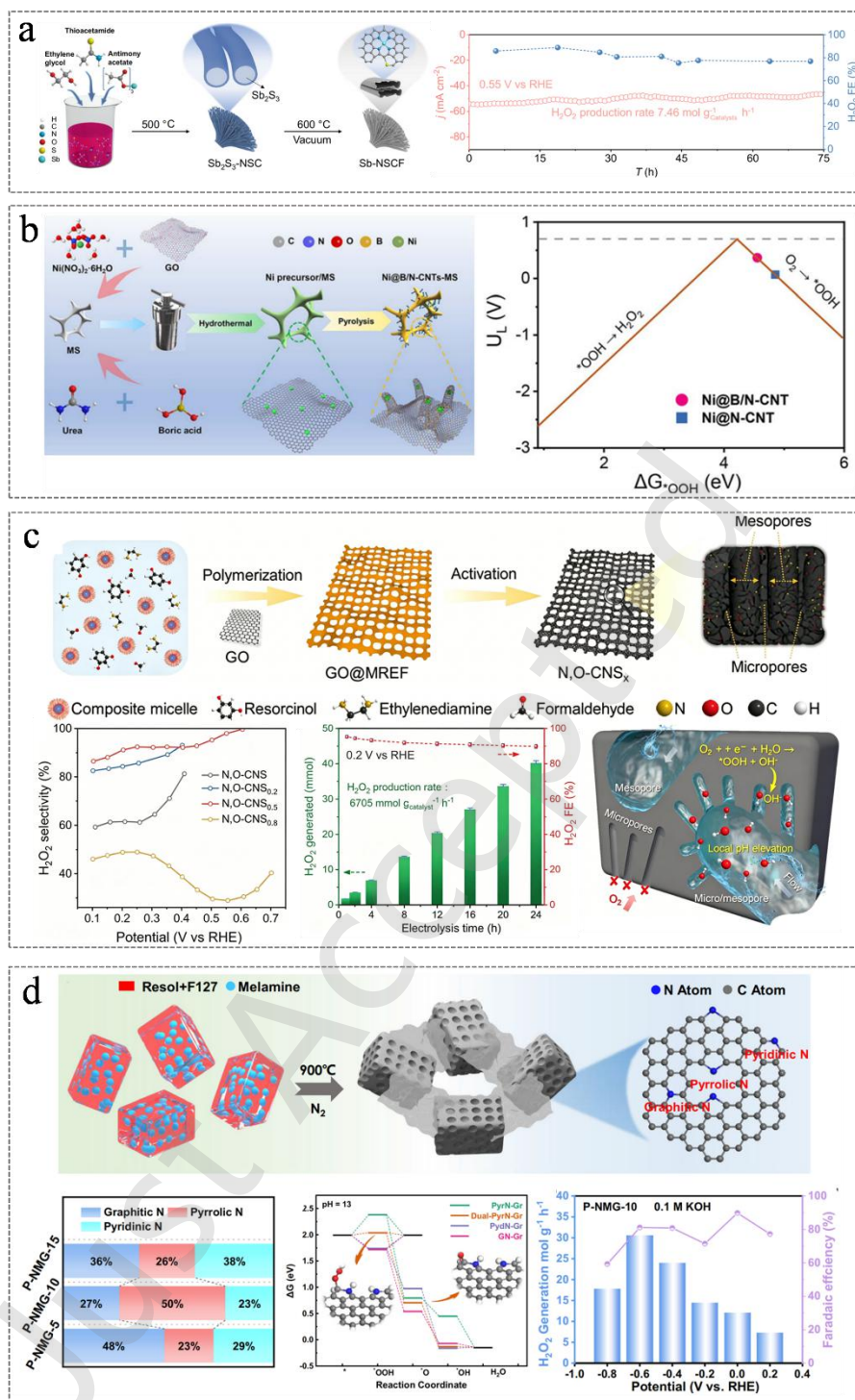


Figure 8 a) Schematic illustration of the preparation process of Sb-NSCF; chronoamperometric stability test for H₂O₂ generation at 0.55 V and the corresponding FE of Sb-NSCF. Reproduced with permission from Ref. [117], © Springer Nature 2023. b) Synthesis method of Ni@B/N-CNTs-MS and the simulated activity volcano plot for the 2e⁻ ORR pathway toward H₂O₂ generation. Reproduced with permission from Ref. [119], © The Royal Society of Chemistry 2023. c) Schematic illustration of the preparation of N,O-CNS_x catalysts; H₂O₂ selectivity; H₂O₂ yield during four consecutive cycles and the corresponding FE over time; schematic of local pH increase in the micro/mesopore model. Reproduced with permission from Ref. [120], © Wiley - VCH GmbH 2024. d) Schematic illustration of the synthesis of P-NMG-X; relative contents of graphitic N, pyrrolic N, and pyridinic N species in the materials; free energy profiles of the 2e⁻ and 4e⁻ ORR pathways at 0.7 V on different N-doped graphene models; H₂O₂ selectivity and productivity of P-NMG-10 at different potentials. Reproduced with permission from Ref. [121], © Springer Nature 2023.

Unlike the exogenous nature of hard templates, the soft-templating method utilizes micelles formed by the self-assembly of amphiphilic surfactants as pore-directing agents. Its advantage lies in the in-situ introduction of ordered mesopores into carbon materials, along with mild template

removal conditions. For example, Jing et al. [120] used F127 as a soft template and 1,3,5-trimethylbenzene as a swelling agent to self-assemble a mesoporous template on the surface of graphene oxide. After carbonization, N, O co-doped mesoporous carbon nanosheets were obtained (Fig. 8c).

Subsequently, micropores were created on the mesopore walls through ZnCl_2 activation, ultimately yielding a hierarchical porous catalyst (N, O-CNS_{0.5}) with both micropores and mesopores. This material achieved an H_2O_2 selectivity > 90% within the potential window of 0.2–0.6 V in 0.1 M K_2SO_4 , with a flow-cell yield as high as $6705 \text{ mmol g}^{-1} \text{ h}^{-1}$. Finite element simulations and experiments confirmed that the micro/mesoporous hierarchical structure can enrich O_2 and elevate the local pH, forming an alkaline-like microenvironment that accelerates the intrinsically sluggish 2e^- ORR kinetics in neutral media. This work reveals that the soft-templating method can not only create physical space but also alter the local reaction environment through pore confinement, achieving a functional coupling of structure creating microenvironment, which cannot be easily achieved by hard templates that merely replicate external morphology.

The combined template strategy can integrate the complementary advantages of different templates to achieve more complex hierarchical pore structures and specific morphologies. For example, Peng et al. [121] employed F127 as a soft template to induce mesopore formation, while simultaneously utilizing C_3N_4 generated from the pyrolysis of melamine at high temperatures as a self-sacrificial template to guide the in-situ growth of graphene nanosheets. Through this dual-template synergistic strategy, they prepared a graphene/mesoporous carbon composite catalyst (P-NMG-10) (Fig. 8d). The pyrrolic N content in P-NMG-10 reached as high as 4.7 at%. DFT calculations showed that the synergistic effect between adjacent pyrrolic N sites optimized the $^*\text{OOH}$ adsorption configuration, significantly reducing the reaction energy barrier of the 2e^- ORR. Electrochemical tests demonstrated that P-NMG-10 achieved a H_2O_2 yield of $30 \text{ mol g}^{-1} \text{ h}^{-1}$ at -0.6 V in alkaline medium (0.1 M KOH). Notably, in this work, C_3N_4 served both as a nitrogen source and a self-sacrificial template. This dual-purpose design reduced the synthesis steps, while the self-sacrificing nature of the hard template eliminated the need for additional template removal operations, highlighting the superiority of the combined template strategy in process simplification and functional integration.

3.2.3 Gas-phase methods

(1) Vapor deposition methods

Vapor deposition methods is a preparation method that utilizes gas-phase reactions to decompose and deposit precursors under high-temperature or plasma conditions, forming catalyst films or nanoparticles on substrate surfaces. Based on the mechanism, it can be divided into physical vapor deposition and chemical vapor deposition (CVD). Physical vapor deposition has very limited application in the 2e^- ORR field, and current mainstream research predominantly employs CVD. Unlike traditional pyrolysis methods that directly mix metal salts with carbon sources,

which readily cause metal agglomeration at high temperatures, CVD uses high-purity gaseous or volatile solid precursors to complete decomposition and deposition in a sealed atmosphere. This approach not only ensures high product purity without foreign impurities but also effectively suppresses metal agglomeration through gas-phase molecular-level mixing and simultaneous nucleation, achieving atomic-level uniform dispersion of active components.

For example, Hu et al. [122] employed a separation chemical vapor deposition (SCVD) strategy, placing the nitrogen/carbon source upstream and the CNTs pre-adsorbed with Co^{2+} ions downstream, utilizing the gaseous species decomposed upstream to in situ construct atomically dispersed Co–N–C SACs ($\text{Co}_{\text{SA}}\text{-N-C/CNTs}$) on the downstream CNT surface. Distinct from traditional pyrolysis where cobalt salts mixed with carbon sources readily aggregate into metallic cobalt nanoparticles upon heating, SCVD fundamentally avoids the migration and agglomeration of Co^{2+} through gas-phase mass transfer and stepwise heating (Fig. 9a). XRD and TEM confirmed that the SCVD-derived samples exhibited no diffraction signals or aggregates of metallic Co nanoparticles, showing only isolated single-atom bright spots; in contrast, the products from conventional pyrolysis contained numerous Co nanoparticle impurities. Benefiting from this, the catalyst achieved over 90% Faradaic efficiency for H_2O_2 in 0.1 M HClO_4 at 0.1 V. Moreover, this strategy exhibits universality, successfully preparing other SACs such as Fe, Cu, and Ni. Similarly, Lu et al. [123] employed a CVD method to prepare Co single-atom carbon-nitrogen materials, followed by oxidation to introduce epoxy groups, yielding CoNC-O. TEM confirmed that Co atoms were atomically dispersed without particle agglomeration. In acidic media, the catalyst achieved an H_2O_2 selectivity of 88.5% and a production rate of $622.5 \text{ mmol g}^{-1} \text{ h}^{-1}$ in an H-type cell.

Beyond supporting metal single atoms, the CVD strategy is also applicable to metal-free catalysts, enabling highly uniform distribution of multiple elements. Bao et al. [124] adopted a CVD-like method, placing PVP-K30 and melamine phosphate in different temperature zones, and prepared carbon-oxygen co-doped phosphorus nitride catalysts (COPN-3) through stepwise volatilization and pyrolysis (Fig. 9b). Energy-dispersive x-ray elemental mapping revealed that the C, O, N, and P elements were highly uniformly distributed in the product without any phase separation. The COPN-3 catalyst achieved 93.2% H_2O_2 selectivity within the potential window of 0.0–0.6 V in alkaline 0.1 M KOH electrolyte. When assembled in a flow electrolytic cell with neutral 0.5 M Na_2SO_4 solution, it delivered an ultrahigh H_2O_2 production rate of $25758 \text{ mmol g}^{-1} \text{ h}^{-1}$ at a current density of 130 mA cm^{-2} , corresponding to a FE of 99%. In a separate potentiostatic stability test in 0.1 M KOH alkaline system at 0.4 V, the catalyst operated continuously for 90 h with almost no decay in H_2O_2 selectivity throughout.

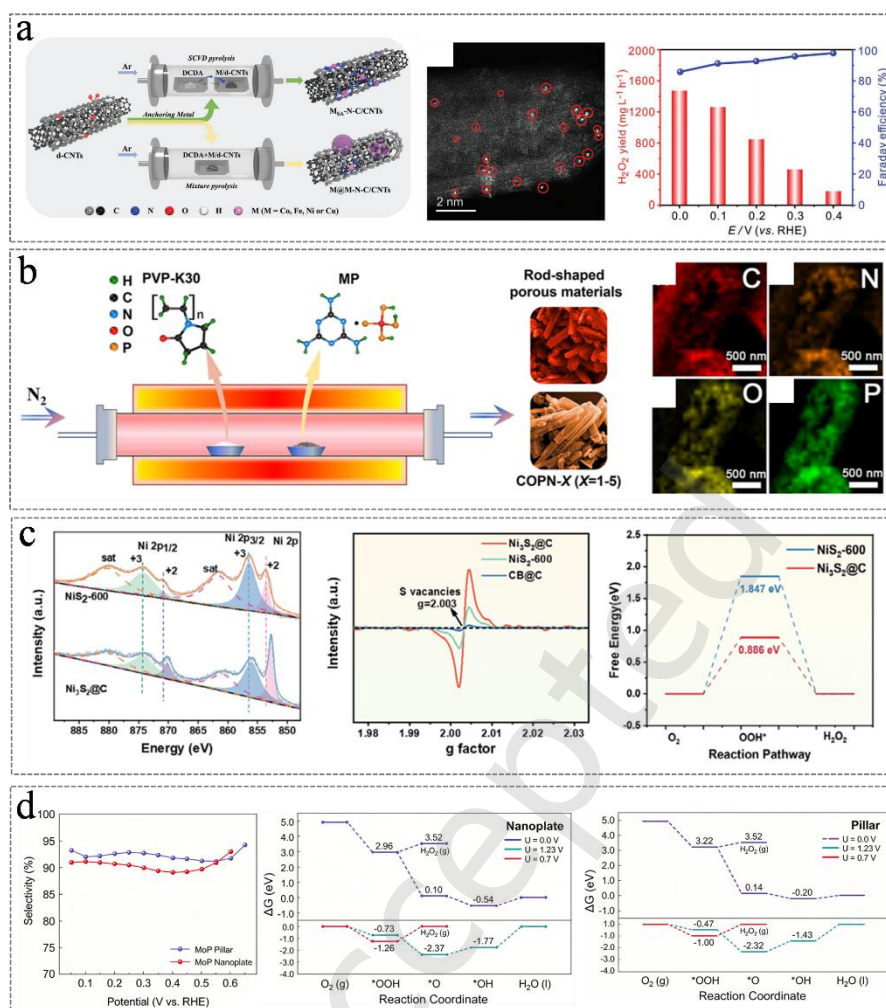


Figure 9 a) Comparison of the synthesis processes between SCVD and conventional mixing pyrolysis; TEM image of CoSA-N-C/CNTs ; H_2O_2 productivity and corresponding FE of CoSA-N-C/CNTs at different applied potentials in 0.1 M HClO_4 . Reproduced with permission from Ref. [122], © Wiley-VCH GmbH 2024. b) Schematic illustration of the synthesis of rod-like porous COPN-X; Energy-dispersive x-ray elemental mapping of C, O, N, and P elements in the COPN-3 catalyst. Reproduced with permission from Ref. [124], © American Chemical Society 2023. c) Schematic illustration of the formation of defect-rich carbon-coated Ni_3S_2 ($\text{Ni}_3\text{S}_2\text{@C}$); XPS Ni 2p spectra of $\text{NiS}_2\text{-600}$ and $\text{Ni}_3\text{S}_2\text{@C}$; electron paramagnetic resonance spectra of $\text{NiS}_2\text{-600}$, $\text{Ni}_3\text{S}_2\text{@C}$, and CB@C ; free energy diagrams of the $2e^-$ ORR at 0.70 V for all models. Reproduced with permission from Ref. [125], © Wiley-VCH GmbH 2024. d) H_2O_2 selectivity of MoP nanosheets and MoP pillar structures; Gibbs free energy diagrams of the $2e^-$ and $4e^-$ reaction pathways. Reproduced with permission from Ref. [126], © Wiley-VCH GmbH 2025.

Stability has always been a critical challenge hindering the practical application of electrocatalysts. CVD can construct robust chemical bonding interfaces between catalysts and substrates, thereby significantly enhancing long-term cycling stability. For example, Liu et al. [125] used anhydrous ethanol as the carbon source to in situ deposit a porous carbon layer on the surface of NiS_2 via CVD, simultaneously achieving phase transformation and defect regulation, successfully preparing the $\text{Ni}_3\text{S}_2\text{@C}$ catalyst. XPS revealed a clear negative shift in the Ni 2p binding energy, indicating the formation of strong electronic interactions between the carbon layer and the inner core. Benefiting from this strong bonding interface, $\text{Ni}_3\text{S}_2\text{@C}$ achieved an H_2O_2 production rate of $3860 \text{ mmol g}^{-1} \text{h}^{-1}$ in an alkaline 0.1 M KOH flow cell at a current density of -50 mA cm^{-2} . Furthermore, electron paramagnetic resonance tests revealed that CVD induced the formation of a high concentration of sulfur vacancies. DFT calculations comparing the vacancy-free $\text{NiS}_2\text{-600}$ model with the sulfur-

vacancy-rich $\text{Ni}_3\text{S}_2\text{@C}$ model demonstrated that the high sulfur vacancy concentration optimized the Gibbs free energy of $^*\text{OOH}$ adsorption from 1.874 eV to 0.886 eV, significantly reducing the energy barrier of the $2e^-$ ORR (Fig. 9c). This also reveals that CVD not only provides a physical protective layer but also modulates the electronic structure through interfacial chemical bonding and generates defects in situ, which is difficult to achieve with conventional coating methods. Notably, Kim et al. [126] recently combined CVD with liquid-metal-assisted growth technology to prepare MoP single-crystal catalysts with controllable crystal facets. By adjusting the growth temperature (700–900 °C), they achieved a continuous morphological transition from (10 $\bar{1}$ 0)-faceted nanopillars to (0001)-faceted nanoplates. The (10 $\bar{1}$ 0)-faceted electrode achieved an H_2O_2 selectivity of 92% at 0.45 V, and DFT calculations revealed an $^*\text{OOH}$ adsorption energy of 1.00 eV for the (10 $\bar{1}$ 0) facet, outperforming the (0001) facet at 1.26 eV (Fig. 9d).

(2) Plasma method

The plasma method is a dry processing technique that utilizes high-energy particles (ions, radicals, and electrons) to bombard material surfaces, inducing physical etching and chemical modification. It offers advantages such as rapid reaction rates, mild conditions, no pollutant generation, and precise tunability of catalyst defect structures, making it suitable for rapid catalyst preparation and modification [127, 128]. Unlike traditional pyrolysis, which requires several hours of high-temperature treatment, the plasma method can generate a large number of surface defects within a short time at room temperature, with almost no damage to the bulk material, demonstrating significant superiority in defect introduction. For example, Dong et al. [129] used H_2 plasma to treat TiO_2 for only 20 min at room temperature, successfully introducing a high concentration of oxygen vacancies and preparing defective TiO_{2-x} catalysts. Electrochemical tests showed that this catalyst achieved an H_2O_2 selectivity of 94% at 0.2 V in 0.1 M KOH alkaline medium, far superior to untreated TiO_2 . More interestingly, by combining in situ Raman spectroscopy and DFT calculations, the authors found that the actual catalytically active sites were not the surface oxygen vacancies, which are easily repaired by reaction intermediates, but rather the

subsurface or near-surface oxygen vacancies. These defects remained stable during the reaction, continuously providing highly active reaction sites.

To overcome the limitations of standalone plasma treatment, recent efforts have combined it with other methods to enhance defect generation efficiency. Peng et al. [130] developed a plasma-assisted ball milling technique by integrating plasma with mechanical ball milling. They mixed PTFE powder with CNTs and processed them in a PBM device. Utilizing instantaneous high temperatures and mechanical shearing, they fractured the C-F bonds in PTFE, partially stripped F atoms, and generated abundant defects, while simultaneously anchoring the defect-rich PTFE segments onto the CNT surface via C-C bonds, forming dense C-F_{2-x} active sites (Fig. 10a). The resulting PTFE@CNTs composite achieved an H_2O_2 selectivity exceeding 95% at -0.6 V in 0.1 M KOH alkaline medium, with a yield above 35 mol g⁻¹ h⁻¹. By combining mechanical force assistance with plasma treatment, this strategy overcomes the limitations of conventional plasma processing, enhances defect generation efficiency, and preserves the mild operating conditions, thereby enabling higher active site density without sacrificing selectivity and opening a new route for preparing high-performance electrocatalytic materials.

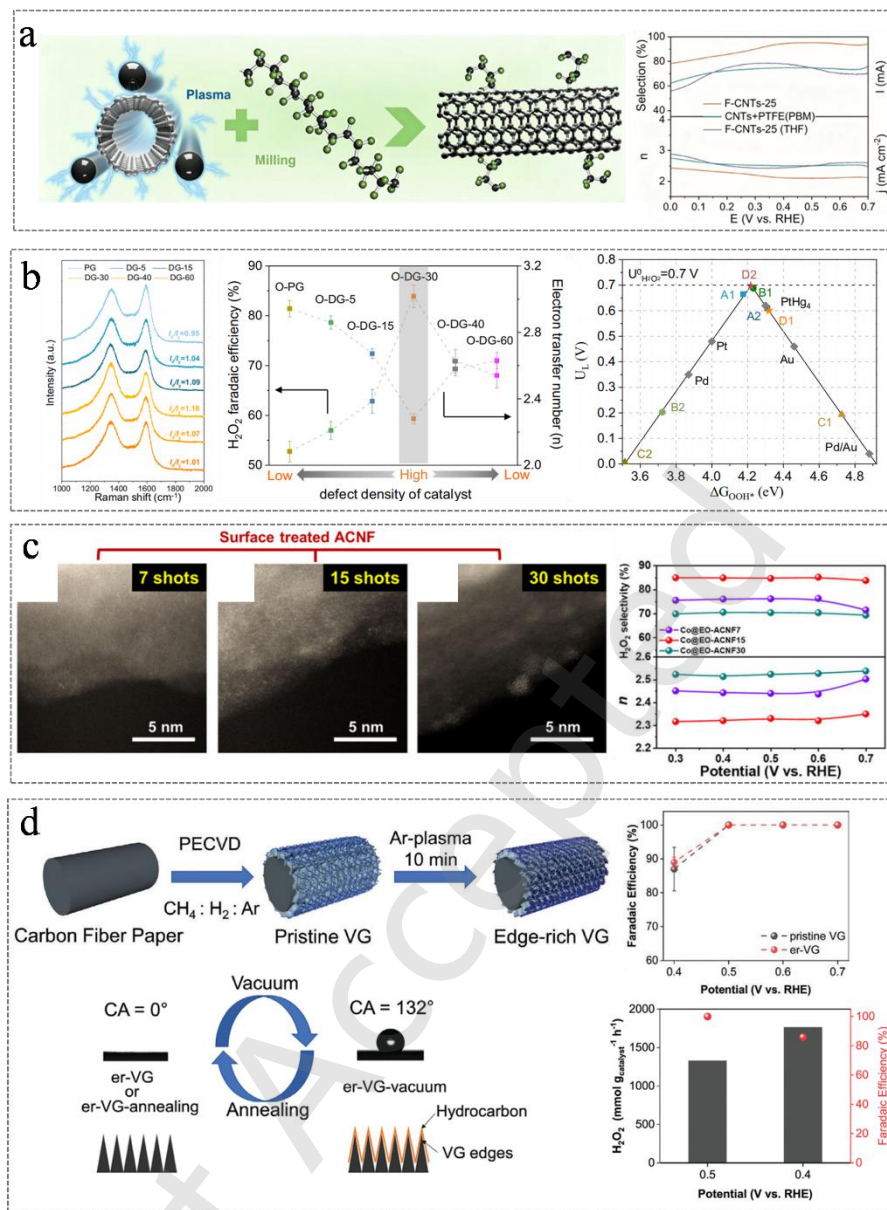


Figure 10 a) Schematic illustration of the synthesis process of F-CNTs-X; H_2O_2 selectivity and electron transfer number of the control samples. Reproduced with permission from Ref. [130], © Wiley-VCH GmbH 2024. b) Raman spectra of defect-free graphene and defect-engineered graphene with different Ar plasma treatment times; H_2O_2 FE of oxygen-modified defective graphene (O-PG), O-DG-5, O-DG-15, and O-DG-30 at 0.55 V; theoretical activity volcano plot. Reproduced with permission from Ref. [64], © Springer Nature 2023. c) TEM images of Co@EO-ACNF7, Co@EO-ACNF15, and Co@EO-ACNF30; H_2O_2 selectivity and electron transfer number. Reproduced with permission from Ref. [131], © 2024. d) Schematic illustration of the synthesis process of pristine vertical graphene (VG) and edge-rich vertical graphene (er-VG); FE at different applied potentials after 10 h of stability testing; schematic diagrams of water contact angles on er-VG (or annealed er-VG) and er-VG under vacuum, along with the reversible wettability regulation achieved through vacuum and annealing processes; H_2O_2 productivity normalized by catalyst loading at 0.5 V and 0.4 V, and the corresponding FE of the er-VG vacuum system. Reproduced with permission from Ref. [132], © Wiley-VCH GmbH 2021.

Furthermore, the plasma method features highly controllable process parameters. By adjusting parameters such as treatment time or pulse number, catalytic performance can be directly optimized. Wu et al. [64] used Ar plasma to treat graphene, precisely tuning the defect density by controlling the plasma treatment time (5–60 min); subsequent oxidation yielded (O-DG). As the plasma treatment time increased from 5 to 30 min, the defect density of graphene gradually rose, and the H_2O_2 FE of the resulting catalyst in 0.1 M KOH at 0.55 V increased from 52.94% to 84.93%. When the treatment time exceeded 30 min, excessive etching caused pore coalescence and

structural collapse of the carbon framework, leading to decreased catalytic performance, exhibiting a clear volcano-shaped trend (Fig. 10b). This result not only clarified the quantitative structure-activity relationship among plasma treatment time, defect density, and catalytic selectivity, but also revealed the moderation principle of plasma etching, providing guidance for precisely regulating catalyst defects and active sites through process parameters. Similarly, Hwang et al. [131] employed arc plasma deposition technology to achieve sub-monolayer-precision controllable loading of Co active species onto electrochemically oxidized aligned carbon nanofiber self-supporting membranes (EO-

ACNF) by precisely adjusting the pulse number (7, 15, 30 pulses). Combined TEM, XPS, and extended x-ray absorption fine structure confirmed that Co atom existed in atomically dispersed form after 7 and 15 pulses, whereas 30 pulses induced Co aggregation into clusters. In 0.1 M KOH electrolyte at 0.6 V, the 15-pulse sample achieved over 85% H₂O₂ selectivity (Fig. 10c). This countable deposition capability allows independent regulation of active-site density without changing other parameters, enabling systematic establishment of the structure-activity relationship between site density and catalytic performance, fully demonstrating the unique advantage of pulse parameters as a precise tuning dimension. Recently, Zhang et al. [132] combined the plasma method with subsequent vacuum treatment to achieve reversible regulation of surface wettability, providing new inspiration for integrated electrode design. Specifically, they used Ar plasma to post-treat VG, producing er-VG, which was directly used as a binder-free self-supporting electrode (Fig 10d). In 0.1 M KOH electrolyte at 0.5 V, this catalyst achieved a H₂O₂ FE of

100%. After vacuum treatment (0.03 Pa, 2 h), the material surface changed from superhydrophilic to superhydrophobic, with the contact angle shifting from 0° to 132°, significantly enhancing O₂ diffusion flux, and the productivity further increased to 1767 mmol g⁻¹ h⁻¹ at 0.4 V. This demonstrates that plasma treatment not only modulates surface chemical composition, but subsequent vacuum treatment can reversibly transform surface wettability. The entire process is completed in situ on the carbon paper substrate, without slurry coating or binders, avoiding active-site coverage and additional mass-transfer resistance. This integrated mode of in-situ preparation for direct use significantly shortens the translation path from material development to device application.

After reviewing the above-described synthetic approaches for electrocatalysts, we summarize in Table 3 the core advantages, inherent drawbacks, key regulating factors, and applicable catalyst types for these synthetic strategies.

Table 3 Comparison of synthesis methods for 2e⁻ ORR electrocatalysts.

Synthesis methods	Advantages	Disadvantages	Regulating factors	Applicable catalyst types	Refs.
Pyrolysis	Simple process; cost controllability; suitable for doping, carbonization and phase transformation.	High energy consumption; high-temperature-induced agglomeration and structural collapse; poor batch-to-batch reproducibility.	Precursor composition; pyrolysis temperature, time, atmosphere, and heating rate.	M–N–Cs; heteroatom-doped carbon; MOF/COF-derived catalysts.	[133–136]
Ball milling	Simple operation; solvent-free or low-solvent; large-scale preparation; facile introduction of defects.	Strong parameter coupling; poor structural homogeneity and reproducibility.	Ball milling time; rotational speed; ball-to-material ratio; atmosphere	Carbon materials; supported metals and alloys.	[97, 137]
Hydrothermal/Solvothermal	Mild conditions; high product crystallinity; tunable morphology and crystal facets; favorable for heterogeneous interface construction.	Long reaction time; requirement of sealed high-pressure equipment.	Reaction temperature, time, pH, solvent, etc.	Metal oxides, hydroxides, and phosphates; heterostructure.	[133, 138]
Wet chemical Reduction	Mild conditions; simple operation; facile tuning of composition and particle size.	Sensitivity to reduction/nucleation kinetics; prone to particle agglomeration; mandatory stabilizer assistance.	Type and concentration of reducing agent; precursor ratio; pH; temperature; etc.	Noble-metal nanoparticles, alloys, borides; heterostructure.	[139, 140]
Electrodeposition	Direct growth on substrates; controllable loading; suitable for integrated electrodes.	Limited large-area uniformity; pore clogging caused by excessive deposition.	Applied potential/current; deposition time; electrolyte concentration; deposition frequency, etc.	Metals/alloys, metal oxides.	[138, 141, 142]
Template	Tunable pore structure and morphology; large specific surface area;	Mandatory hard template removal; complicated synthesis; limited scale-up; possible structural collapse.	Template type, size and filling ratio.	Porous carbon, heteroatom-doped carbon, SACs and confined-metal	[143, 144]

	confinement effect suppresses agglomeration.			systems.	
Chemical vapor deposition	High purity; uniform atomic dispersion; strong interfacial bonding	High-equipment requirement; sensitive processing conditions; limited selection of gaseous precursors.	Precursor species; deposition temperature and time; gas flow rate; substrate position.	Heteroatom-doped carbon, SACs, metal-compound thin films.	[141, 145]
Plasma	Fast reaction kinetics; low-temperature treatment, low thermal damage; environmental compatibility; good universality.	Limited penetration depth; dominated by surface modification; complicated parameter optimization; possible framework damage upon excessive treatment.	Gas species; power; treatment time; pulse cycles, etc.	Carbon-based catalysts, SACs, metal oxides.	[146,147]

4 Optimization of device-system

The optimization of device-system serves as a critical bridge connecting the intrinsic performance of catalysts with macroscopic reaction efficiency. In the preceding sections, we have systematically reviewed the design principles and synthesis strategies for catalysts. However, the high activity and high selectivity achieved in laboratory-scale RRDE tests are often difficult to replicate in real electrolysis devices [148, 149]. The underlying reason lies in the coupled effects of mass transfer, ohmic drop, and interfacial microenvironment at the device level, which exert non-negligible influences on reaction pathways [150]. Therefore, this section systematically elaborates on the mechanisms through which device systems influence the mass-transfer efficiency, product selectivity, and long-term stability of H_2O_2 electrosynthesis via the 2e^- ORR, from three aspects: electrode structural design, reactor configuration innovation, and regulation of key operating parameters. It further reveals the synergistic and trade-off relationships among these factors, thereby laying a foundation for the collaborative optimization of catalysts and devices.

4.1 Design of electrode architectures

In the field of 2e^- ORR, electrodes act not only as carriers for electron transfer, but also as core platforms for reactant transport, construction of three-phase interfaces, as well as generation and migration of target products. Under practical device operating conditions, mass transport behavior at the electrode scale frequently emerges as the decisive factor governing reaction activity and selectivity. For this reason, electrode design has evolved from a simple catalyst loading substrate into a core regulator of reaction processes, whose essence resides in fabricating stable and efficient gas-liquid-solid three-phase reaction interfaces. A wide variety of electrodes have been adopted for H_2O_2 electrosynthesis at present, with mainstream categories consisting of powder-coated electrodes, GDEs and integrated electrodes [151–153]. For electrolytic systems targeting large-scale H_2O_2 electrosynthesis, GDEs and self-supported electrodes represent the two most promising cathode configurations. By contrast, powder-coated electrodes are primarily utilized for fundamental performance testing in laboratory half-cells and will not be discussed in depth herein.

4.1.1 GDEs

GDEs enable O_2 to be directly transported from the gas phase to the catalyst-layer interface by constructing hydrophobic porous architectures, substantially shortening the gas-diffusion pathway and thereby overcoming the mass-transport limitations caused by the low solubility of O_2 in aqueous electrolytes [154]. Therefore, GDEs can enable efficient H_2O_2 generation at high current densities and are regarded as one of the most promising electrode architectures for practical applications [155]. A typical GDE generally consists of three layers: a gas diffusion layer (GDL), a microporous layer (MPL), and a catalyst layer (CL) [156]. However, GDEs face significant stability challenges during long-term operation. Under electrowetting conditions, the electrolyte gradually penetrates into the GDL, inducing electrode flooding, which disrupts the three-phase reaction interface, impedes O_2 mass transport, and ultimately leads to decreased H_2O_2 selectivity and continuous deterioration of catalytic performance [157]. To address this issue, hydrophobic modification of the electrode is commonly employed. For example, Zhang et al. [158] optimized the PTFE/CB mass ratio in the CL to 0.6, thereby constructing a superhydrophobic three-phase interface with a contact angle of 141° . Compared with conventional GDEs, this electrode increased the O_2 diffusion coefficient by 5.7-fold and achieved an H_2O_2 production rate of $101.67 \text{ mg h}^{-1} \text{ cm}^{-2}$ at a high current density of 240 mA cm^{-2} , demonstrating the effectiveness of optimizing PTFE content in improving O_2 mass transport. However, this strategy did not resolve the secondary reduction of H_2O_2 at the reaction interface. Zhao et al. [36] systematically investigated the long-term degradation behavior of CB-PTFE-based GDEs and confirmed the intrinsic limitations of passive modification strategies that rely solely on hydrophobic components, such as PTFE. During electrolysis, the coupled effects of CB oxidation, PTFE defluorination, and Na^+ intercalation reduced the water contact angle of the electrode from 150.2° to 99.3° , while increasing the porosity from 36.2% to 64.8%, ultimately leading to electrode failure due to flooding (Fig. 11a). This suggests that simply increasing the PTFE content is insufficient to meet the requirements for long-term stable operation. To overcome these limitations, interfacial microenvironment regulation has been further introduced. For example, Cui et al. [159] revealed a unique local microenvironment within hydrophobic CL. Because the liquid electrolyte cannot readily penetrate deeply into the

pores, proton supply fails to keep pace with the consumption caused by oxygen reduction, leading to interfacial OH^- enrichment up to 2.5 times that of the hydrophilic electrode. The enriched OH^- species electrostatically repel the dissociated HO_2^- intermediates, accelerating their desorption from active sites and thereby significantly mitigating the secondary reduction of H_2O_2 . Sun et al. [160]

introduced oxygen vacancies into ZnO via vacancy engineering, which maintained a superhydrophobic interface with a contact angle of 140.9° and enhanced O_2 adsorption, while lowering the reaction energy barrier from 1.0 eV to 0.6 eV, thereby achieving a cumulative H_2O_2 concentration of $1005.2 \text{ mg}\cdot\text{L}^{-1}$ in a self-breathing undivided cell (Fig. 11b).

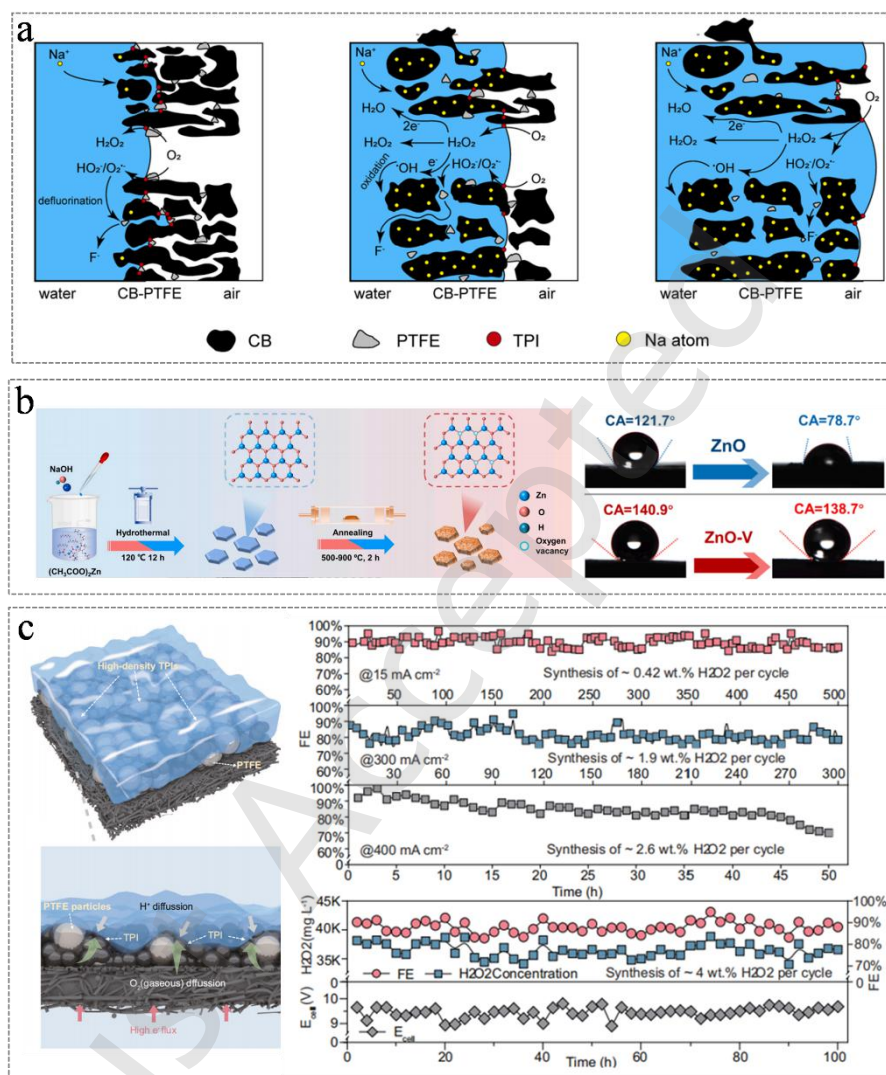


Figure 11 a) The progressive water intrusion, Na intercalation, PTFE defluorination, and electrode swelling during long-term H_2O_2 electrosynthesis. Reproduced with permission from Ref. [36], © Elsevier 2024. b) Schematic illustration of the ZnO-V synthesis and the corresponding variations in contact angle after ten consecutive runs. Reproduced with permission from Ref. [160], © Elsevier 2024. c) Catalyst layer with non-fused particulate-packed interface (PPE), magnified side view, long-term stability at 15, 300, and 400 mA cm^{-2} , and long-term stability test of the scaled-up system. Reproduced with permission from Ref. [37], © Springer Nature 2026.

Although physical hydrophobicity and chemically synergistic strategies substantially improve the initial performance, they still fall within the category of passive defense. Recently, Tian et al. [37] developed a gradient-wettability design based on a non-fused particulate-packed interface. Specifically, they first regulated the catalyst/binder interfacial structure to construct the PPE, in which PTFE existed as discrete particles uniformly mixed with CB, forming a three-dimensional interconnected porous network. This design avoided the encapsulation of active sites and pore blockage caused by PTFE wrapping around CB in the conventional melted segregated interface (Fig. 11c).

On this basis, they further designed a hierarchical CL with dual gradients in porosity and wettability. First, a dense hydrophobic bottom layer with a high PTFE content (PPE-D) was coated onto the GDL, forming a barrier against electrolyte intrusion. Subsequently, a non-fused particulate-packed top layer with a low PTFE content was deposited on top and treated with oxygen plasma to introduce OFGs, including $-\text{OH}$, $\text{C}=\text{O}$, and $\text{C}-\text{O}-\text{C}$. This treatment sharply decreased the contact angle of the top layer from 158° to 30° , thereby constructing a continuous wettability gradient from a superhydrophobic bottom layer to a hydrophilic surface layer (PPE-T). By combining three-dimensional

reconstruction, lattice boltzmann method simulations, and microfluidic visualization experiments, they confirmed that this gradient structure could harness capillary forces to drive the directional displacement of the electrolyte and guide the self-transport of H_2O_2 products toward macroporous regions, thereby preventing H_2O_2 over-reduction in electron/proton-rich zones. Electrochemical tests showed that PPE-T operated stably for over 300 h at 300 mA cm^{-2} while maintaining a FE above 85%. Furthermore, an integrated 400 cm^2 four-cell self-breathing stack enabled continuous H_2O_2 production without external O_2 supply, with a production cost as low as $\$0.381 \text{ kg}^{-1}$. This work marks a new stage in GDE interfacial regulation, shifting from passive resistance to flooding toward active guidance of fluid and product transport.

4.1.2 Integrated electrodes

Integrated electrodes generally refer to electrodes in which active materials are directly grown, anchored, or assembled onto a continuous conductive scaffold, or the material itself forms a three-dimensional network with mechanical stability and electronic conduction capability, allowing it to be used directly as a working electrode without relying on conventional powder-coating processes. Compared with powder catalysts, the advantages of integrated electrodes stem primarily from their structurally integrated configuration. The continuous conductive framework shortens electron-transport pathways and reduces the contact resistance between the catalyst and current collector, while open pores or oriented structures increase active-site exposure and enhance the diffusion of reactants and products within the electrode. Meanwhile, the reduced use of binders prevents polymers from blocking active sites and mass-transport channels, allowing the electrode surface to more closely represent the actual reaction environment and facilitating investigation of the effects of active sites, local pH, ionic effects, and the interfacial microenvironment on the 2e^- ORR pathway [161–163].

Based on the structural construction approach, integrated electrodes for H_2O_2 electrosynthesis can be categorized into two main types. Substrate-supported electrodes, which use commercial conductive substrates such as carbon cloth or carbon paper as the support for in-situ growth or deposition of active materials [33, 155, 163]. Self-supported framework electrodes, where the active material or precursor directly forms a continuous three-dimensional network without the need for an external substrate, allowing the electrode to function independently. These include thin-film electrodes, oriented fiber-network electrodes, and others. [152, 164]. Among them, substrate-supported electrodes based on carbon fiber and carbon cloth substrates possess a continuous carbon skeleton, which endows them with excellent mechanical strength, well-

developed porous structure and efficient electron-transport capability. They represent one of the most extensively investigated binder-free electrodes at present. For example, Cox et al. [33] rendered carbon-fiber paper hydrophilic through mild chemical treatment, introducing OFGs at graphitic carbon edge sites, and directly employed it as a binder-free electrode for the 2e^- ORR. This electrode avoided binder interference while retaining approximately 78% of the high porosity of the carbon fiber paper, and achieved an H_2O_2 FE of $(95 \pm 4)\%$ at 0.4 V in 0.1 M KOH with good long-term stability, demonstrating that carbon fiber paper can serve both as a binder-free reaction electrode and as a self-supported platform for studying the real electrode/electrolyte interfacial microenvironment. Zhang et al. [163] used carbon cloth as the supporting substrate and grew a three-dimensional hierarchical single-atom electrode with a Co-N_4 coordination structure in situ on its surface (Fig. 12a). The active nanosheets were tightly attached to the carbon-fiber surfaces, while open pores were retained between adjacent sheets, substantially improving electron transport and mass diffusion and effectively alleviating the poor conductivity and mass-transport limitations of conventional powder-based SACs. When assembled as the cathode of a flow electrolyzer, this self-supported electrode achieved an outstanding H_2O_2 production rate of $676 \text{ mol kg}^{-1} \text{ h}^{-1}$ at a cell voltage of roughly 1.6 V, with accumulated H_2O_2 concentration reaching 1840 mg L^{-1} within 4 h. Its charge transfer resistance (7.3Ω) was merely one-third that of the powder reference electrode (25.3Ω). Vertical graphene arrays also belong to the substrate-supported type, relying on oriented graphene nanosheets to construct open channels and abundant edge sites, thereby enhancing electron transport while forming hierarchical pores. For example, Lin et al. [155] reported a Co single-atom decorated vertical graphene self-supported electrode (CoN_4/VG) composed of vertically aligned graphene nanosheets with immobilized CoN_4 active sites. This architecture provided continuous electron-transport pathways and open hierarchical pores, ensuring sufficient exposure of the active sites and achieving nearly 100% H_2O_2 selectivity over the potential range of 0.3–0.5 V in an acidic H-type cell (Fig. 12b). Moreover, Wang et al. [165] grew a vertical graphene-array self-supported electrode in situ on a carbon-paper substrate. The interconnected graphene sheets formed a three-dimensional conductive network, while the vertically oriented structure fully exposed highly active graphene edge sites and created abundant gas-liquid-solid three-phase interfaces, ensuring a continuous O_2 supply at high current densities. The electrode achieved an H_2O_2 FE of up to 94% at 100 mA cm^{-2} , further demonstrating that arrayed carbon frameworks are beneficial for high-rate H_2O_2 electrosynthesis.

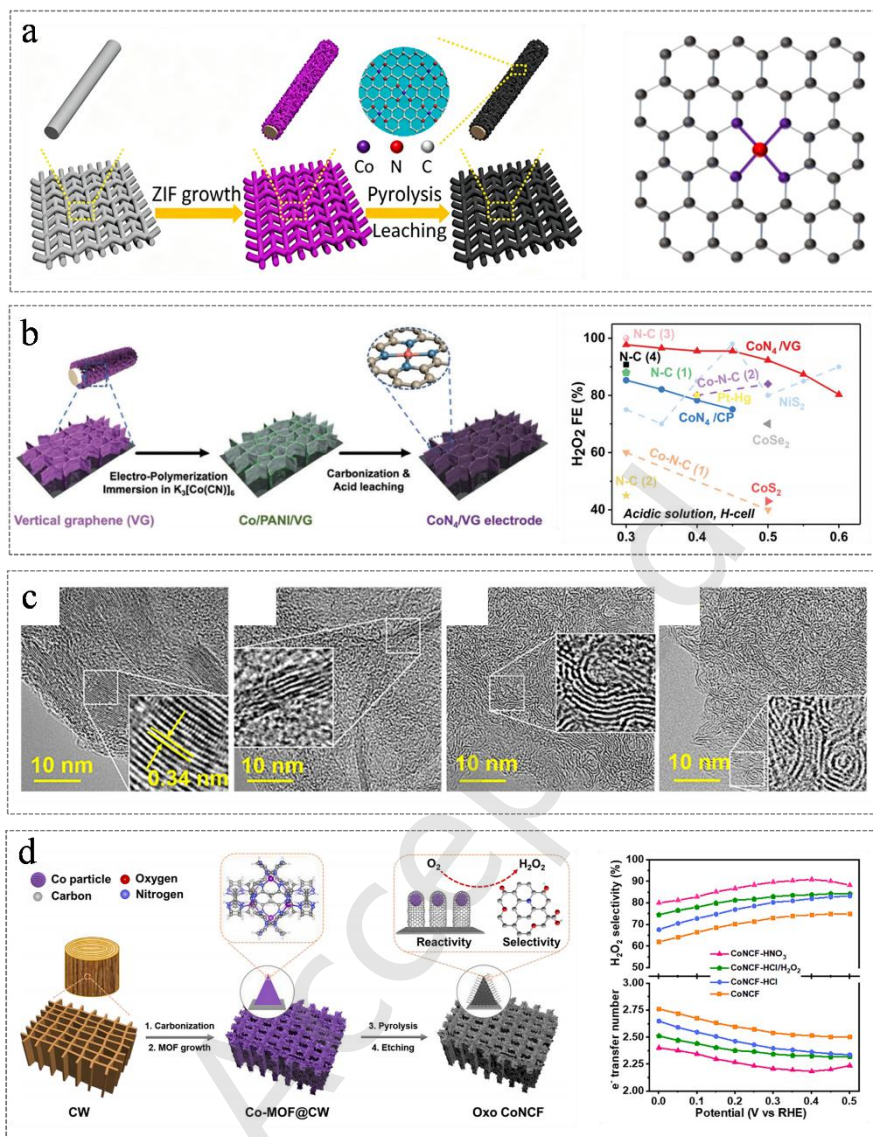


Figure 12 a) Schematic illustration of the preparation process of the hierarchical self-supported Co single-atom electrode and the Co-N₄ structural model. Reproduced with permission from Ref. [163], © Wiley 2019. b) Schematic illustration of the synthesis process of the CoN₄/VG electrode, H₂O₂ FE of CoN₄/VG and CoN₄/CP electrodes at different potentials, compared with previously reported H-type cell electrode systems. Reproduced with permission from Ref. [155], © The Royal Society of Chemistry 2022. c) TEM images of CM0, CM1, CM2, and CM3. Reproduced with permission from Ref. [152], © American Chemical Society 2023. d) Schematic illustration of the preparation process of the oxo CoNCF catalyst, along with H₂O₂ selectivity (upper panel) and electron transfer number (lower panel). Reproduced with permission from Ref. [164], © Elsevier 2022.

Self-supported framework integrated electrodes are constructed directly from active materials or precursors into continuous networks without the need for additional substrate supports, and their advantage lies in the excellent long-term structural stability conferred by the integrated scaffold. Chen et al. [152] prepared an integrated carbon-membrane electrode by carbonizing activated carbon and phenolic resin precursors and applied it in a flow-through electrochemical membrane reactor. The carbon membrane possessed high porosity, a large specific surface area, and abundant disordered carbon structures, including defects, edges, and sp³-C species. TEM (Fig. 12c) showed that with prolonged carbonization time under H₂ atmosphere, the microcrystalline structure of the carbon membrane gradually evolved from long-range ordered graphitic carbon to a complex structure with short-range order, rich curved graphene fringes, and interspersed disordered carbon

Among them, the CM3 sample treated with H₂ for 3 h exhibited the most pronounced disorder characteristics. These structures not only provided 2e⁻ ORR active sites but also enhanced reactant and product transport through the membrane pores, enabling continuous and stable H₂O₂ generation. Hwang et al. [131] first fabricated an aligned carbon-nanofiber self-supported membrane by electrospinning, introduced epoxy defect sites through electrochemical oxidation, and subsequently anchored atomically dispersed Co sites on the fiber surfaces using arc-plasma deposition, forming Co-N₂-O₂-coordinated active centers. In this integrated electrode, the one-dimensional aligned carbon-nanofiber framework created abundant three-phase interfaces and substantially improved macroscopic gas-liquid mass transport. Meanwhile, epoxy groups at the carbon edges synergistically regulated the electronic structure of the Co centers, precisely tuned the

adsorption energy of $^*\text{OOH}$, and directed the reaction toward the 2e^- ORR pathway, clearly demonstrating the synergistic catalytic effect between the ordered fibrous support and atomically coordinated active sites.

Building upon the above structural classification, the impact of modification strategies on the performance of integrated electrodes also deserves attention. The integrated scaffold primarily addresses electron transport and mass transfer, while the final selectivity still depends on the surface-active sites and interfacial microenvironment. Therefore, introducing single-atom sites, oxygen-containing functional groups, or tuning surface wettability on the integrated scaffold represents an important direction for constructing high-performance modified integrated electrodes. Coordination structures such as Co-N_4 , $\text{Co-N}_2\text{-O}_2$, and Co/N-C can regulate the $^*\text{OOH}$ adsorption strength and enhance 2e^- ORR selectivity; oxygen-containing functional groups can modulate the local electronic structure of the carbon scaffold, affecting O-O bond retention and H_2O_2 desorption. For example, Zhang et al. [132] developed an edge-enriched vertical graphene (er-VG) metal-free integrated self-supported electrode, and through electrochemical oxidation, thermal annealing, and oxygen plasma treatment, precisely distinguished the catalytic contributions of various edge oxygen-containing functional groups, confirming that the edge ether C-O-C moiety serves as the high-selectivity 2e^- ORR active center, while carbonyl groups are detrimental to H_2O_2 generation. Liu et al. [164] constructed a monolithic cobalt-nitrogen-carbon framework electrode using the open channels of carbonized wood, and achieved coupling of multiple active sites with porous channels by introducing Co/N-C active structures together with oxygen-containing functional groups (Fig. 12d). The HNO_3 -treated CoNCF-HNO_3 exhibited over 91% H_2O_2 selectivity in acidic media, with the electron transfer number decreasing from approximately 3.5 in the untreated sample to about 2.2.

In summary, the value of integrated electrodes lies not only in reducing binder usage, but also in the synergistic regulation of electron transport, active site exposure, mass transport, and interfacial microenvironment through structural construction and functional modification. Future design of high-performance integrated electrodes should focus on the synergistic optimization of the conductive scaffold, active sites, pore structure, and interfacial microenvironment.

4.2 Optimization of reactor configurations

In the electrocatalytic H_2O_2 system via 2e^- ORR, the reactor configuration not only determines the mode of O_2 supply and the pathways of ion migration, but also profoundly influences the local reaction microenvironment, interfacial reaction kinetics, as well as product transport and separation behavior. Therefore, the reactor should not be simply regarded as a supporting platform for catalysts and electrodes; rather, it should be understood as a system-level unit that regulates the entire reaction process. From the perspective of technological development, the evolution of H_2O_2 electrosynthesis reactors is essentially a process of continuously overcoming mass-transport limitations and

improving system integration. Early H-type cells were mainly used to evaluate the intrinsic activity of catalysts and verify reaction mechanisms. Subsequently, flow cells and microchannel reactors enabled high-current-density operation by strengthening O_2 supply and interfacial renewal. MEA systems further integrate reaction, mass transport, and product separation within a single device, advancing the system from reaction realization toward product engineering.

4.2.1 H-type cells

The H-type cell is the most commonly used basic configuration in H_2O_2 electrosynthesis research, characterized by the physical separation of the cathode and anode chambers, with ionic conduction achieved through a diaphragm or ion-exchange membrane [166]. Compared with subsequent flow-cell and MEA systems, the advantage of H-type cells lies not in achieving higher production rates or current densities, but in their simple structure and well-controlled variables, which provide a relatively clear environment for evaluating the intrinsic activity, reaction selectivity, and structure-activity relationships of catalysts. Therefore, this configuration is typically employed for active-site screening, reaction-pathway identification, and investigation of the adsorption behavior of the $^*\text{OOH}$ intermediate. It serves as an important foundational platform before transitioning from materials design to device optimization.

In specific studies, H-type cells are commonly used to confirm whether a catalyst possesses highly selective 2e^- ORR capability. For example, Lin et al. [155] verified in an H-type cell that the CoN_4/VG self-supported electrode achieved nearly 100% H_2O_2 selectivity in acidic media, confirming that isolated CoN_4 sites are favorable for maintaining the 2e^- pathway. Similarly, Liu et al. [167] used RRDE measurements in an H-type cell to screen cobalt-nitrogen co-doped CB catalysts, and found that they exhibited H_2O_2 selectivity exceeding 95% over a wide potential range of 0.45–0.75 V, confirming the highly efficient 2e^- ORR performance of this catalyst. In addition to selectivity validation, H-type cells are also commonly used to elucidate the influence of electrode geometry on reaction performance. For example, Tian et al. [168] prepared mesoporous carbon spheres with different internal structures, namely $\text{MHCs}_{0.1}$, $\text{MHCs}_{0.5}$, $\text{MHCs}_{0.7}$, and $\text{MCS}_{-0.5}$ (Fig. 13a), and evaluated their H_2O_2 electrosynthesis performance in an H-type cell. It was found that $\text{MHCs}_{0.5}$, with a moderate hollow fraction, achieved a FE exceeding 97% at 0.5 V and an accumulated H_2O_2 concentration of 40.3 mmol L^{-1} within 12 h, substantially outperforming the solid control sample and the control samples with excessively large or small hollow structures. In addition, when designing SACs for industrial current densities, Cao et al. [169] also relied on a combination of H-type system tests and theoretical calculations to assess $^*\text{OOH}$ adsorption energies and intrinsic reaction pathways. These findings indicate that, even when the ultimate goal is high current density and scalable operation, H-type cells still play an essential role in preliminary screening and mechanistic verification.

However, the limitations of H-type cells are also evident.

Because O_2 reaches the electrode interface mainly through dissolution and diffusion in the liquid phase, the system is readily constrained by the low solubility of O_2 and the long diffusion pathway, making it difficult to sustain continuous reactions at high current densities [170, 171]. Meanwhile, the generated H_2O_2 cannot be rapidly removed from the electrode interface in a static or semi-static solution, and is therefore prone to further reduction, decomposition, or indirect consumption at the anode. Therefore, H-type cells are more suitable as platforms for mechanistic studies and materials screening, but they cannot directly meet the requirements for high-throughput, high-concentration, and continuous production. These limitations have directly promoted the development of subsequent flow-cell and MEA systems, which transform the intrinsic performance of catalysts into truly productive capacity at the device scale by enhancing O_2 supply, shortening mass-transfer paths, and accelerating product removal.

4.2.2 Flow cells

To overcome the limitations of O_2 dissolution and diffusion in the liquid phase in H-type cells, flow cells have gradually become an important configuration linking fundamental electrochemical evaluation with continuous operation. Unlike H-type cells, which are mainly used to determine whether a catalyst possesses intrinsic $2e^-$ ORR activity, flow cells focus more on how the reactor enables the electrode to function continuously, uniformly, and stably under continuous operating conditions. Therefore, the core value of this type of configuration lies not only in increasing the O_2 supply, but also in reconstructing the reaction environment in which the electrode operates through flow-channel design, flow-pattern regulation, gas-liquid contact modes, and residence-time management, so as to establish a dynamic match among O_2 supply, interfacial reactions, and H_2O_2 removal.

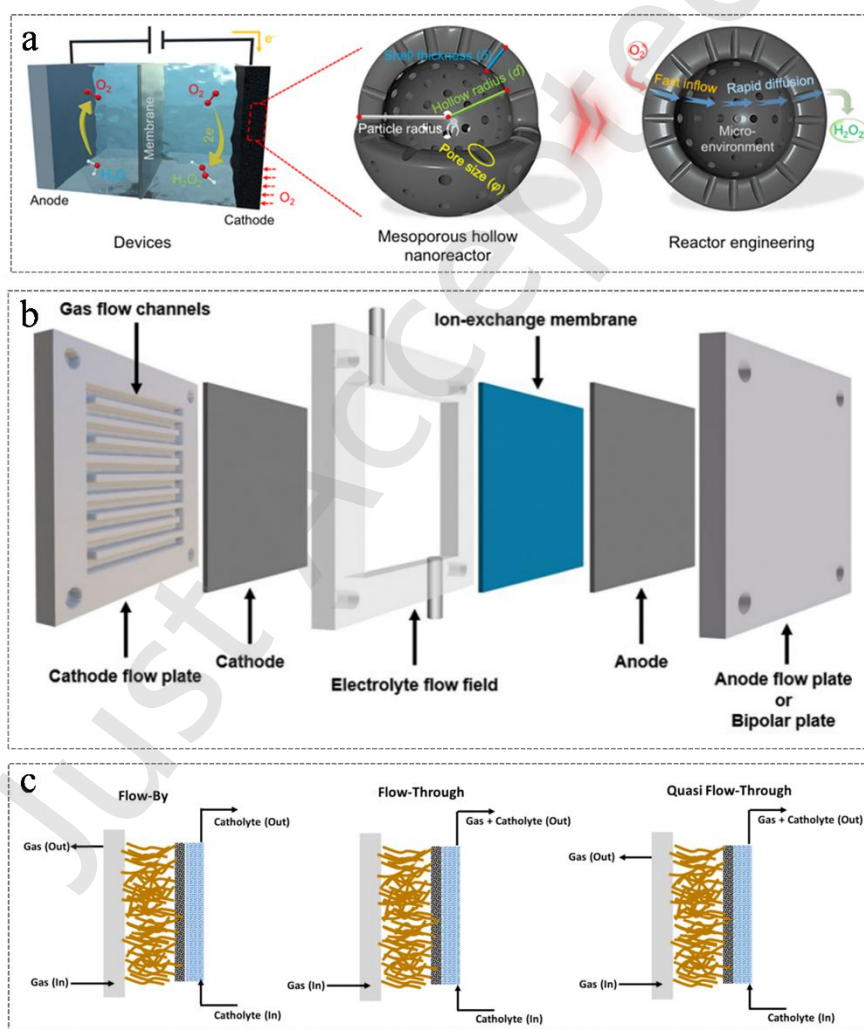


Figure 13 a) Schematic diagram of the nanoreactor design based on carbon spheres. Reproduced with permission from Ref. [168], © Springer Nature 2024. b) Key components of the flow cell. Reproduced with permission from Ref. [20], © The Royal Society of Chemistry 2024. c) Schematic diagrams of the operating modes of three types of GDEs: flow-through, flow-by, and quasi-flow-through. Reproduced with permission from Ref. [172], © Elsevier 2024.

A typical flow cell usually consists of a flow-field plate, a GDE, electrolyte flow channels, a diaphragm or ion-exchange membrane, and an anode chamber (Fig. 13b) [20]. Among these components, the flow-field plate determines the

distribution path of the electrolyte over the electrode surface, the gas-side channel governs the manner in which O_2 enters the electrode interface, and the liquid-phase flow is responsible for refreshing the concentration boundary layer

and carrying away the generated H_2O_2 . Thus, a flow cell is not simply a scaled-up version of the H-type cell; rather, it reorganizes the input pathways of reactants and the output pathways of products through reactor structure. In particular, when a GDE is integrated into a flow cell, O_2 no longer depends entirely on dissolution and diffusion in the electrolyte, but can instead be delivered directly to the vicinity of the CL through gas-phase channels, thereby shortening the mass-transport pathway. Cordeiro-Junior et al. [173] employed a Printex L6 carbon-based GDE in a flow-through reactor operated in batch mode, in which air was transported from the gas side through the porous structure of the GDE to the reaction interface, and investigated the effects of operating temperature and air supply on H_2O_2 generation. The results showed that, when O_2 was supplied through the GDE, H_2O_2 generation efficiency was no longer significantly dependent on the solubility of O_2 in the bulk electrolyte or on the associated temperature and pressure conditions. This finding indicates that this O_2 -supply mode can reduce the dependence of the reaction on dissolved oxygen transport in the liquid phase, thereby alleviating O_2 mass-transfer limitations. Furthermore, Bashir et al. [172] employed a GDE with a geometric area of 20 cm^2 and compared three gas-side operating modes: gas flow-by, flow-through, and quasi-flow-through (Fig. 13c). The gas flow-by mode achieved a peroxide FE above 95% during short-term operation, whereas switching to the flow-through or quasi-flow-through mode improved the long-term operational stability of the system. In particular, the quasi-flow-through mode operated stably for more than 20 h at 500 mA cm^{-2} and achieved a peak FE of 97%. These results indicate that flow-cell performance depends not only on the intensity of oxygen supply, but also requires coordinated regulation of gas/liquid flow rates, liquid/gas pressure differences, and gas transport modes to suppress electrode flooding and maintain stable mass transfer at high current densities.

The advantages of a continuous-flow system lie not only in maintaining a continuous input of reactants, but also in regulating the device operation through electrolyte circulation and product concentration management. Wei et al. [174] constructed a continuous-flow sulfite/air fuel cell, in which both the anolyte and catholyte were circulated by peristaltic pumps, and replaced the conventional oxygen-evolving anode with a sulfite-depolarized anode, achieving 100% H_2O_2 selectivity and low energy consumption at 100

mA cm^{-2} . Notably, through catholyte renewal experiments, this study demonstrated that after 10 h of continuous operation, simply replacing the catholyte reduced the cell voltage from -1.59 V to -1.29 V while the HO_2^- current efficiency remained at 100%, indicating that product accumulation at the cathode side significantly affects the device operation. Thus, the role of the continuous-flow system is not merely to increase the current density, but to sustain high efficiency and low energy consumption at relatively high current densities through the synergy of liquid-phase circulation, product concentration management, and anodic depolarization reactions.

Microchannel reactors can be regarded as a further refinement of flow cells in terms of channel dimensions, flow-pattern organization, and residence time control. Plutschack et al. [175] pointed out that microfluidic systems generally have higher surface-area-to-volume ratios because of their smaller reactor dimensions. In multiphase systems such as gas-liquid systems, the interfacial area between phases has an important influence on interphase mass transfer, while flow patterns such as bubble flow, slug flow, and annular flow are jointly governed by flow rate, viscosity, and channel properties. This indicates that the advantage of microchannel structures lies not simply in shortening diffusion paths, but in regulating gas-liquid interfacial distribution and mass-transfer processes through channel geometry and flow conditions. From the perspective of flow electrochemistry, Pletcher et al. [176] summarized that the rate of electrochemical conversion is limited by the mass transport of reactants to the electrode surface and that the current can be increased by increasing the reactant concentration, electrode area, or mass-transfer coefficient. At the same time, in a parallel-plate flow electrolyzer, a higher linear flow velocity enhances reactant mass transport to the electrode and increases the current, but shortens the residence time of the reactants within the electrode region and reduces the single-pass conversion. Therefore, flow-electrolysis systems need to balance mass-transfer enhancement, residence time, and conversion efficiency. Representative experimental performance data acquired under flow-cell conditions in recent years are compiled in Table 4, which provides reference for assessing practical application potential under industrially-relevant operating scenarios.

Table 4 Performance comparison of H_2O_2 electrosynthesis via 2e^- ORR in flow cell systems.

Catalyst	Electrolyte	Loading (mg cm^{-2})	FE (%)	Rate ($\text{mol g}^{-1}\text{ h}^{-1}$)	Stability	Refs
CoIn-N-C	0.1 M HClO_4	0.2	/	9.68	4 h (100 mA cm^{-2})	[177]
Ni-BTA	1 M KOH	0.1	> 80	34	40 h (0.2 V)	[178]
Co SA-AC(C-O-C)	0.5 M H_2SO_4	0.125	/	3.88	100 h (50 mA cm^{-2})	[179]
Se_2 -Pt NPs	0.1 M HClO_4	0.2 $\text{mg}_{\text{Pt}}\text{ cm}^{-2}$	/	4.16	400 h (250 mA cm^{-2})	[180]
Co-ZnO- O_3	1 M KOH	0.1	> 90	58.56	50 h (0.55 V)	[181]
ZnSA-ZnO/PC	1 M KOH	0.25	> 90	34.32	60 h (250 mA cm^{-2})	[182]
Co_2 DAC	0.1 M HClO_4	/	~ 100	11.72	100 h (400 mA cm^{-2})	[183]
Pd/MCS-8	0.5 M K_2SO_4	/	~88.7	15.77	24 h (0.2V)	[184]
In- N_2O_2 -P-mC	0.5 M K_2SO_4	/	> 95	22.54	24 h (100 mA cm^{-2})	[185]
Co-N-C	0.5 M NaCl	0.2	95.6	4.5	24 h (50 mA cm^{-2})	[186]
Ni(OH) $_2$ /CNT	1 M NaCl	0.1	> 80	30.86	156 h (200 mA cm^{-2})	[71]
Cu-SAO	1 M KOH	0.1	> 90	47.23	430 h (100 mA cm^{-2})	[187]
CoPc@OCW	0.1 M KOH	/	> 94	10.4	24 h (0.2 V)	[188]
Ni-BNC	1 M KOH	/	95.7	31.13	50 h (100 mA cm^{-2})	[90]
$\text{Ni}_3\text{V}_2\text{O}_8$ -NS	0.5 M Na_2SO_4	0.1	99.9	44.01	100 h (200 mA cm^{-2})	[189]

Co-N ₃ O/C	1 M KOH		> 96.1	12.8	120 h (100 mA cm ⁻²)	[80]
CoN ₄ -PC	1 M KOH	0.1	75	11.2	110 h (0.3V)	[21]
Mn CD/C	0.1 M KOH	/	> 80	8.68	50 h (200 mA cm ⁻²)	[190]
FeSAs/ACs-BCC	1 M KOH	0.2	89.4% ± 1.3	12.51 ± 0.18	/	[101]
Co-N-SCG	1 M KOH	/	92.5	23.78	120 h (0.1V)	[96]
Al ₂ O ₃ /Al ₁ -O-C	1 M KOH	0.167	87.9	39.4	100 h (100 mA cm ⁻²)	[95]
PVP-NiO _v	1 M KOH	1	91	15.12	/	[107]
Nb ₂ O ₅ -HD	1 M KOH	1	94	0.874	34 h (50 mA cm ⁻²)	[192]
F/Co-N-G	1 M KOH	0.05	~ 70	12.1	80 h (0.3V)	[193]
Co@EO-ACNF15	1 M KOH	/	84.45	15.75	48 h (100 mA cm ⁻²)	[131]
CoSA-N-C/CNTs	0.1 M HClO ₄	/	> 90	> 2	105 h (0.1V)	[122]
Utn-NiBDC	0.1 M KOH	0.25	92	13.7	100 h (200 mA cm ⁻²)	[194]
Sb-NSCF	1 M KOH	0.1	~ 80	7.46	75 h (0.55V)	[117]
Cl-PDC	0.5 M NaCl	0.2	~ 100	74.61	400 h (300 mA cm ⁻²)	[195]
TfpBQ	0.1 M K ₂ SO ₄	/	95.6	19.3	60 h (130 mA cm ⁻²)	[196]
COPN-3	0.5 M Na ₂ SO ₄	0.1	99	25.76	70 h (130 mA cm ⁻²)	[124]
S-mC-0.375	1 M KOH	/	~ 95	25	24 h (0.2 V)	[197]
SmPO ₄ -12	1 M Na ₂ SO ₄	/	> 90	4.56	12 h (150 mA cm ⁻²)	[103]
SC-COF _{TSA} @CNT-30	1 M KOH	0.15	> 95	94	8 h (200 mA cm ⁻²)	[106]
HG-CD-Ph	0.1 M KOH	/	98.01	9.14	/	[198]
B _n -C	1 M Na ₂ SO ₄	0.2	> 95	25.1	140 (300 mA cm ⁻²)	[199]
NFC	1 M KOH	0.2	~ 95	74.35	105 h (300 mA cm ⁻²)	[200]
S ₁₀ RG0	1 M KOH	0.6	~ 90.5	9.33 ± 0.19	40 h (300 mA cm ⁻²)	[61]
BN-C-1	0.1 M KOH	1.0	> 75	0.762	12 h (0.3V)	[136]
MCPs-0.2	0.1 M KOH	/	~80	17.38	50 h (200 mA cm ⁻²)	[201]
N/O-HPCNs	1 M KOH	/	92.8	17.3	100 h (200 mA cm ⁻²)	[49]
TFPTA-TTPE-COF	0.5 M K ₂ SO ₄	/	79.7	4.461	20 h (50 mA cm ⁻²)	[202]
NBO-GQDs/CNTs	0.1 M KOH	1	81	0.709	12 h (50 mA cm ⁻²)	[203]
TAM-CNT	1 M KOH	/	~ 95	28.97	800 h (300 mA cm ⁻²)	[204]

Overall, the role of microchannel reactors in H₂O₂ electrosynthesis should not be understood simply as shortening the diffusion distance or accelerating mass transfer, but rather as enabling fine control over the reaction interface and transport processes. Their core advantage lies in the coordinated design of channel scale, flow-pattern distribution, and liquid-phase flow velocity to regulate the gas-liquid interfacial area, the mass-transfer rate of reactants to the electrode surface, and the residence time of the fluid within the electrode region, thereby achieving a more appropriate balance among O₂ supply, ion migration, reaction efficiency, and single-pass conversion. For H₂O₂ electrosynthesis systems, this means that microchannel reactors can provide a more controllable reactor-design approach for mass-transfer enhancement and continuous operation at high current densities. However, their optimization should not focus solely on increasing the flow velocity, but rather on achieving an overall balance among mass-transfer efficiency, residence time, and product-generation efficiency.

4.2.3 MEA

On the basis of achieving efficient mass transfer in flow cells, the MEA system further couples reactions, ionic conduction, and product separation into a compact structure, representing an important trend in the adaptation of H₂O₂ electrosynthesis toward industrial-scale development. According to the use of ion-exchange membranes, MEAs currently employed for H₂O₂ electrosynthesis can be classified into three categories: single-membrane MEAs, dual-membrane solid-electrolyte MEAs, and membrane-free systems [205].

Among these, the single-membrane MEA is the most classical configuration, consisting of a GDE, an ion-exchange membrane, and a counter electrode. In a typical MEA design, the GDL and flow-field plate cooperatively regulate the mass-transport behavior of O₂, H₂O, and H₂O₂, while managing species exchange at the gas-liquid interface.

Owing to its simple structure and ease of assembly, this configuration is currently one of the most widely investigated reactor architectures for H₂O₂ electrosynthesis. However, in this configuration, the H₂O₂ generated at the cathode is in direct contact with the electrolyte flowing through the anode chamber. As a result, the product is inevitably contaminated by the supporting electrolyte in the anolyte, and additional separation and purification steps are required after product collection to obtain high-purity H₂O₂ solutions. The use of H-type cells and diaphragm-equipped flow cells can spatially isolate the cathodic product from the anolyte. However, H-type cells suffer from sluggish oxygen diffusion, restricting their current density to generally below 100 mA cm⁻². While diaphragm flow cells deliver moderate performance improvements, they still confront engineering hurdles including GDE flooding and ohmic resistance.

Dual-membrane solid-electrolyte MEAs form a sandwich-type structure by sequentially placing an anion-exchange membrane (AEM), a PSE layer, and a cation-exchange membrane (CEM) between the cathode and the anode. During operation under alkaline and neutral conditions, O₂ undergoes the 2e⁻ ORR in the cathode chamber to generate HO₂⁻, which permeate the AEM into the solid electrolyte layer. Meanwhile, H⁺ produced by the water oxidation reaction at the anode passes through the CEM into the same solid-electrolyte layer, where H⁺ and HO₂⁻ combine to form H₂O₂. The generated product is then carried out of the electrolyzer by high-purity deionized water flowing through the solid-electrolyte layer [206, 207]. This design enables effective separation of the product from the catholyte and anolyte, allowing salt-free, pure aqueous H₂O₂ solutions to be obtained directly and fundamentally resolving the product-contamination issue associated with single-membrane systems. For example, Xia et al. [208] constructed a sandwich-type configuration centered on the PSE, in which an AEM and the cathode were arranged sequentially outward on the cathodic side, while a CEM and the anode were arranged sequentially outward on the anodic

side. The H^+ generated at the anode and HO_2^- generated at the cathode recombined within the porous solid electrolyte layer to form H_2O_2 . Deionized water flowing through this layer could directly carry away pure H_2O_2 free of any ionic impurities, with the product concentration reaching up to 20 wt% without requiring subsequent purification steps (Fig. 14a). Notably, conventional dual-membrane solid-electrolyte MEA systems rely on AEMs as key components. However, AEMs suffer from poor chemical and mechanical stability during long-term operation. To overcome this limitation, Jang et al. [209] substantially modified the conventional dual-membrane solid-electrolyte MEA by introducing an ultrathin anion-exchange resin wafer of approximately 216 μm in situ between the cathode and the solid-electrolyte

layer. This wafer was designed to maintain a local alkaline microenvironment and suppress the competing hydrogen evolution reaction, thereby avoiding the chemical and mechanical degradation of a full AEM layer caused by long-term exposure to concentrated H_2O_2 (Fig. 14b). Experiments demonstrated that this reactor enabled stable H_2O_2 electrosynthesis for over one month at a high current density of 200 mA cm^{-2} . By regulating the flow rate of deionized water, it could produce H_2O_2 solutions with concentrations as high as 13.7 wt% while maintaining a FE of 91%. This strategy was also validated in other reactions, such as CO_2 reduction to formic acid, providing a new design paradigm for improving the long-term stability of solid-electrolyte reactors.

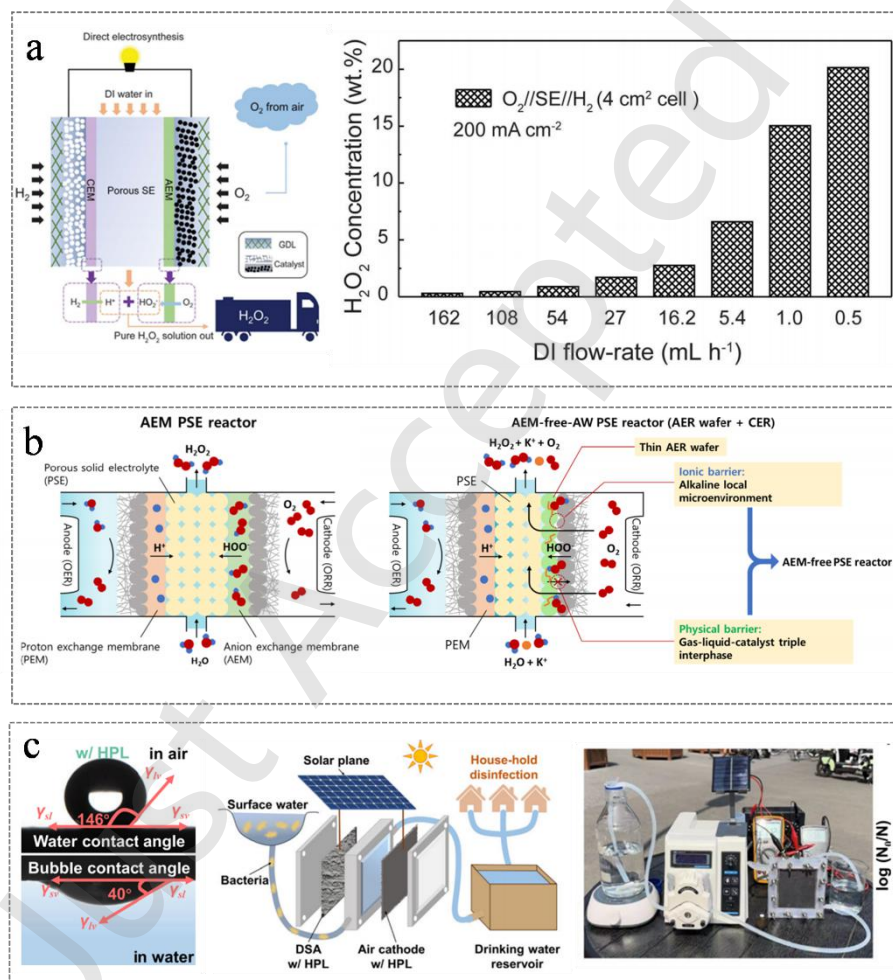


Figure 14 a) Electrosynthesis of H_2O_2 using pure H_2 and O_2 gas streams fed into the anode and cathode, respectively; the variation of H_2O_2 concentration with the flow rate of deionized water at a current density of 200 mA cm^{-2} is shown, enabling continuous production of a pure H_2O_2 solution with a concentration up to 20 wt% for on-site use. Reproduced with permission from Ref. [208], © American Association for the Advancement of Science 2019. b) Schematic illustration of the conventional AEM PSE reactor and AEM-free PSE reactor. Reproduced with permission from Ref. [209], © American Chemical Society 2026. c) Water contact angle and bubble contact angle measurements on the HPL-coated anode, where γ_{sv} , γ_{sl} , and γ_{lv} represent the surface free energies at the solid-gas, solid-water, and water-gas interfaces; the schematic diagram and digital images of a solar-driven membrane-free electrolyzer for H_2O_2 electrosynthesis and disinfection. Reproduced with permission from Ref. [210], © Springer Nature 2025.

Membrane-free systems completely eliminate ion-exchange membranes and rely solely on electrode-structure design and fluid management to achieve product separation and collection, thus offering the simplest architecture. However, under membrane-free conditions, the H_2O_2

generated at the cathode can migrate to the anode and be oxidized, leading to a substantial decrease in product yield. Yi et al. [210] proposed a bubble shielding strategy to suppress H_2O_2 degradation via reverse engineering of water-gas-electrode interfaces (Fig. 14c). This strategy uses low-

cost PTFE as a hydrophobic porous-layer coating on the anode. Owing to its hydrophobicity and aerophilicity, PTFE provides abundant bubble-nucleation sites, enabling oxygen-evolution bubbles to adhere to the electrode surface and form a physical barrier. This barrier shields H_2O_2 from contacting the active sites on the electrode, thus minimizing the anodic oxidative degradation of H_2O_2 . Using this strategy, the membrane-free electrolyzer produced $10.05 \pm 0.05 \text{ g L}^{-1} \text{ H}_2\text{O}_2$ within 5 h at a current density of 40 mA cm^{-2} , corresponding to an approximately 600% increase in H_2O_2 production compared with the system using an anode without bubble shielding. In addition, the team designed a solar-driven membrane-free electrolyzer for disinfection. Equipped with HPL-coated electrodes, this device enabled the in-situ inactivation of *E. coli* in surface water within 60 min, offering a low-cost and practical water-treatment solution for remote areas lacking access to electricity and sanitation facilities.

4.3 Regulation of operation parameters

In 2e^- ORR systems, device-level optimization has gradually shifted from improving the performance of individual catalysts to the synergistic regulation of multiple parameters. The core objective is to construct a stable and efficient reaction microenvironment, in which a dynamic balance can be achieved among O_2 supply, proton transfer, and product migration. From the perspective of regulation dimensions, electrolyte parameters, electrochemical parameters, and operational mass transport and product management jointly determine the overall system performance at three levels: the reaction environment, reaction driving force, and mass transport.

4.3.1 Modulation of electrolyte parameters

The electrolyte not only serves as an ion-conducting medium, but also directly participates in the formation and transformation of reaction intermediates. Its pH and ionic composition have a significant effect on the electrocatalytic system [211–214]. The effect of pH on the 2e^- ORR first arises from thermodynamic competition between reaction pathways. In acidic media, the equilibrium potentials of the 2e^- ORR and 4e^- ORR differ by 0.53 V, whereas under alkaline conditions, this difference decreases to 0.49 V. However, thermodynamic preference does not necessarily translate into a universal rule, as different catalysts exhibit markedly different responses to pH. Carbon-based metal-free catalysts usually show a strong dependence on pH. For example, Cox et al. [33] systematically investigated the ORR behavior of hydrophilic carbon-fiber paper under different pH conditions and found that, in 0.1 M KOH (pH = 13), the catalyst achieved a H_2O_2 FE of $95 \pm 4\%$ and a production rate of $49 \pm 4 \text{ mg L}^{-1} \text{ h}^{-1}$. Analysis of the RHE-referenced onset potentials revealed a pH dependence, indicating a non-proton-coupled electron-transfer mechanism. After conversion to the SHE scale, the onset potentials still varied with pH, further suggesting that the rate-determining step of the ORR remains proton-dependent. Combined XPS characterization and DFT calculations showed that ether, hydroxyl (C–O), and carbonyl (C=O) groups are thermodynamically stable at the reaction potential, whereas

carboxyl groups (–COOH), with a pK_a of approximately 4, undergo deprotonation and become unstable at $\text{pH} > 4$. At high pH, interfacial field effects induced by solvated K^+ ions further stabilize the deprotonated oxygen-containing sites, collectively enhancing the H_2O_2 production rate. Another study further confirmed the pH dependence of carbon-based catalysts. Yang et al. [206] found that a carbon-cloth-based GDE promoted O_2 enrichment through its microporous carbon layer (Fig. 15a), which induced an increase in the local pH at the electrode interface. Finite-element simulations together with electrochemical analyses showed that the locally elevated pH caused by O_2 accumulation could stabilize the key $^*\text{OOH}$ intermediate and suppress its over-protonation, enabling nearly 100% H_2O_2 FE under neutral conditions. SACs provide a more flexible platform for regulating pH adaptability. The conventional Fe– N_4 configuration tends to promote the 4e^- pathway under alkaline conditions. In contrast, Wu et al. [215] tuned the coordination environment of Fe from FeN_4 to FeN_2O_2 (Fig. 15b), which downshifted the d-band center and optimized $\Delta G_{^*\text{OOH}}$ from 3.51 to 4.27 eV. As a result, the catalyst achieved H_2O_2 selectivity above 95% in 0.1 M KOH and maintained selectivity above 82% in neutral 0.5 M Na_2SO_4 , demonstrating a significant enhancement in selectivity over a broad pH range. Moreover, Okazaki et al. [216] systematically investigated the behavior of GDEs under different pH conditions and found that, within the pH range of 1.0–10.0, the electrode potential remained stable during 5 h of galvanostatic operation at -40 mA cm^{-2} , with a FE above 80%. At pH = 1.0, the H_2O_2 concentration reached approximately 100 mmol L^{-1} . In contrast, when the pH increased to 13, the potential dropped abruptly within 3 h, accompanied by a decrease in the H_2O_2 production and a significant decline in FE (Fig. 15c). Further analysis revealed that the performance decay was not caused by catalyst degradation, but rather by GDE flooding. After the reaction, the contact angle of the GDE decreased with increasing pH, indicating enhanced hydrophilicity, which hindered gas-phase O_2 diffusion. Notably, after the used GDE was dried overnight at room temperature, its hydrophobicity and electrochemical performance were largely restored, suggesting that the flooding process was reversible. Long-term stability tests over 24 h further confirmed that acidic conditions ($\text{pH} \leq 2.8$) could effectively suppress flooding, whereas the electrode rapidly failed under neutral to alkaline conditions. Therefore, acidic electrolytes not only ensure the chemical stability of H_2O_2 , but also significantly enhance the flooding resistance of GDEs. Lu et al. [15] systematically summarized the combined effects of pH on catalyst-design principles and reaction mechanisms. They pointed out that, in acidic media, noble metals and SACs exhibit high H_2O_2 selectivity because they favor end-on O_2 adsorption, whereas carbon-based materials show limited activity under acidic conditions. In alkaline media, OFGs on carbon materials can serve as stable active sites. Neutral media provide a balance between catalyst compatibility and product stability; however, buffer solutions are required to maintain the local pH, and proton consumption can induce local alkalization at the electrode interface, which may alter the reaction pathway.

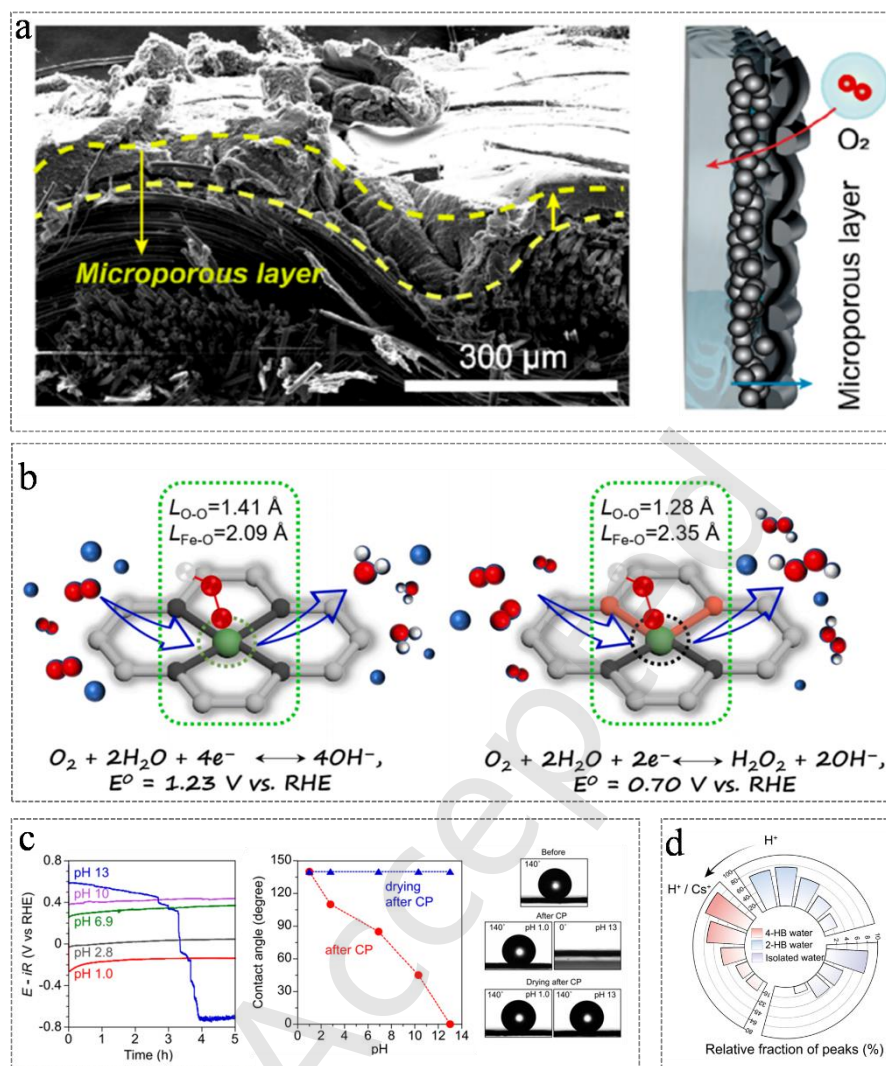


Figure 15 a) Cross-sectional and surface scanning electron microscopy images of bare CB, and schematic diagram of the GDE structure using CB. Reproduced with permission from Ref. [206], © American Chemical Society 2022. b) Different coordination configurations of single-atom Fe, with the left panel showing the FeN_4 configuration and the right panel showing the FeN_2O_2 configuration. Reproduced with permission from Ref. [215], © Elsevier 2022. c) Potential-time curves, contact angles, and corresponding photographs of the CoN_x/KB GDE after 5 h chronopotentiometry (CP) testing at -40 mA cm^{-2} . Reproduced with permission from Ref. [216], © American Chemical Society 2024. d) Cation-dependent contribution ratios of the bands at 3550, 3400, and 3200 cm^{-1} , where 3550 cm^{-1} corresponds to isolated water, 3400 cm^{-1} to doubly hydrogen-bonded water, and 3200 cm^{-1} to tetrahedrally hydrogen-bonded water. Reproduced with permission from Ref. [217], © Springer Nature 2026.

In addition to pH, the ionic composition of the electrolyte also exerts a significant influence on 2e^- ORR selectivity. Wang et al. [217] added 0.3 M Li_2SO_4 , Na_2SO_4 , K_2SO_4 , or Cs_2SO_4 to 0.5 M H_2SO_4 and found that the 2e^- ORR selectivity of the Co-CNT catalyst monotonically increased from 20% in pure acid to 80% in the presence of Cs^+ , while the H_2O_2 reduction current was suppressed by 50%. In situ ATR-SEIRAS combined with molecular dynamics simulations revealed that Cs^+ ions, through their strong hydration, reconfigured the hydrogen-bonding network at the electrode/electrolyte interface: the proportions of isolated water (3550 cm^{-1}) and doubly coordinated hydrogen-bonded water (3400 cm^{-1}) increased significantly, whereas that of strongly hydrogen-bonded, tetrahedrally coordinated water (3200 cm^{-1}) decreased (Fig. 15d). This interfacial water restructuring raised the energy barrier for proton hopping from water molecules to the active sites, thereby

suppressing the proton-excess-induced 4e^- pathway and H_2O_2 reduction. The promoting effect followed the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ and was positively correlated with the hydrated radius of the cations. In contrast to the cation effect emphasized by Wang et al., Rocha et al. [218] found that anion type also plays a critical role. Under identical pH and conductivity conditions, the H_2O_2 FE approached 100% when SO_4^{2-} was used as the supporting electrolyte, whereas it decreased to approximately 84% and 65% in the presence of NO_3^- and ClO_4^- . The authors attributed this behavior to the anodic formation of persulfate species from SO_4^{2-} , which promoted H_2O_2 generation through an autocatalytic pathway. In contrast, ClO_4^- is already in its highest oxidation state and therefore cannot participate in such a synergistic reaction. This anion effect complements the cation-induced interfacial water regulation mechanism reported by Wang et al., jointly revealing the profound influence of electrolyte ionic

composition on $2e^-$ ORR selectivity.

4.3.2 Tuning of electrochemical parameters

Electrochemical operating parameters directly govern the reaction rate and energy efficiency and therefore constitute critical constraints on efficient operation and scalable application. In general, current density is closely correlated with both H_2O_2 production rate and selectivity. In the low-current-density regime, mass transport is not limiting, and selectivity is governed primarily by the intrinsic catalytic activity. By contrast, at high current densities ($>200 \text{ mA cm}^{-2}$), O_2 consumption may outpace its replenishment through mass transport, resulting in local O_2 depletion and intensified side reactions. Cui et al. [159] systematically compared the performance of hydrophilic Nafion-bonded and hydrophobic PTFE-bonded GDEs over a range of current densities. The FE of the hydrophilic GDE decreased sharply to approximately 13.6% at 100 mA cm^{-2} , whereas the hydrophobic GDE maintained a relatively high FE at 150 mA cm^{-2} . Nevertheless, its selectivity also began to decline as the current density was further increased. This study demonstrates that mass transport limitations exert a decisive influence on selectivity at high current densities, and highlights that hydrophobic interfaces can mitigate this performance degradation by preserving gas-phase diffusion pathways. Furthermore, Ni et al. [219] demonstrated that in a two-compartment electrolytic cell, as the current density was increased from 100 mA cm^{-2} to 300 mA cm^{-2} , the steady-state electrolyte temperature gradually rose from 32.7°C to 49.3°C , while the H_2O_2 selectivity continuously decreased from an initial value of $>95\%$ to only 68.2% after 180 min of operation at 300 mA cm^{-2} . Further analysis revealed that the selectivity decay was not solely caused by catalyst deactivation, but rather stemmed from the elevated temperature exacerbating the disproportionation decomposition of H_2O_2 in the alkaline cathodic environment. DFT calculations showed that the Gibbs free energy of the spontaneous decomposition reaction of H_2O_2 decreased from -1.12 eV at 25°C to -1.47 eV at 65°C , indicating a significantly enhanced thermodynamic driving force. Moreover, even when the catholyte was adjusted to strongly acidic conditions ($\text{pH} < 3$), the decomposition at elevated temperatures remained unavoidable due to the strongly alkaline microenvironment (local $\text{pH} > 12$) generated at the interface under high current densities. After external forced cooling was applied to maintain the electrolyte temperature below 35°C , the H_2O_2 selectivity at 300 mA cm^{-2} recovered from 68.2% to 88.8%, indicating that thermal management becomes a critical issue under high-load operation.

In addition to the mass-transport and thermal management challenges associated with high current densities, the applied potential determines both the reaction driving force and the selective operating window of the $2e^-$ ORR [84, 220]. Lu et al. [221] prepared O-CNTs by nitric acid oxidation of commercial carbon nanotubes and compared the ORR behavior of CNTs and O-CNTs using a RRDE. The results showed that in 0.1 M KOH , O-CNTs exhibited a reduction in overpotential of approximately 130 mV at the same current density compared to unoxidized CNTs, while maintaining an H_2O_2 selectivity of about 90% in the

potential range of $0.4\text{--}0.65 \text{ V}$. In neutral electrolyte, the onset potential was positively shifted by about 150 mV, and the H_2O_2 selectivity increased from approximately 60% to about 85%. Furthermore, after loading O-CNTs onto PTFE-treated carbon fiber paper, this electrode achieved current densities of 20 and 40 mA cm^{-2} at 0.72 and 0.68 V in 1 M KOH , while still maintaining $>90\%$ H_2O_2 selectivity. This study demonstrates that lowering the onset overpotential of the $2e^-$ ORR, enabling the reaction to occur at milder potentials, is beneficial for balancing reaction rate and H_2O_2 selectivity. Furthermore, Chang et al. [222] employed a solution impregnation method to deposit partially oxidized amorphous $\text{Pd}\delta^+$ small clusters onto mildly oxidized CNTs, constructing the $\text{Pd}\delta^+$ -OCNT catalyst. This catalyst exhibited nearly 100% H_2O_2 selectivity in acidic electrolytes, with the $2e^-$ ORR onset potential positively shifted by approximately 320 mV relative to the OCNT substrate, and maintained 95–98% H_2O_2 selectivity over a wide potential window of $0.3\text{--}0.7 \text{ V}$, while achieving a mass activity of 1.946 A mg^{-1} at 0.45 V. These results indicate that a rational active-site structure can broaden the high-selectivity operating potential window, enabling the catalyst to simultaneously maintain high activity and high selectivity over a wide potential range. It is worth noting that the optimal electrochemical parameters are not fixed values but depend on the coupled effects of the electrolyte environment, electrode structure, and mass transport conditions. Therefore, the appropriate current density and potential window should be determined for each specific system to achieve optimal performance.

4.3.3 Regulation of mass transport and product management

In addition to electrolyte composition and electrochemical driving force, mass transport and product management during operation are also critical factors affecting H_2O_2 generation efficiency and system stability. Unlike parameters such as pH, ionic composition, potential, or current density, operational mass transport primarily influences the local reaction microenvironment near the electrode by regulating O_2 supply, electrolyte circulation, bubble behavior, interfacial wetting state, and H_2O_2 residence time. Insufficient O_2 supply or untimely product removal can readily lead to concentration polarization, further decomposition of H_2O_2 , and interfacial destabilization. Therefore, this section will focus on the theme of continuous reactant supply, stable interfacial mass transport, timely product output, and suppression of side-reaction losses.

From the perspective of gaseous reactant input, the O_2 supply mode and gas flow rate directly affect the accessibility of reactants to the reaction interface and are key operating parameters for regulating H_2O_2 production rate, selectivity, and long-term stability. Particularly under high current density operation, the O_2 consumption rate increases significantly with electron flux. If O_2 cannot be continuously and effectively delivered to the reactive sites, O_2 deficiency near the electrode readily occurs, further exacerbating concentration polarization and causing the reaction to competitively shift toward the $4e^-$ ORR, hydrogen evolution, or further reduction of H_2O_2 . Xia et al. [223]

investigated the effect of underwater wetting states on H_2O_2 electrosynthesis using a superaerophilic CB-PTFE electrode. When the electrode was in the underwater Wenzel-Cassie state, the electrode surface could rapidly capture O_2 microbubbles generated by aeration, facilitating O_2 transport to the electrode interface through gas films, gas pockets, and three-phase contact lines. Meanwhile, the hydrophobic PTFE facilitated the detachment of generated H_2O_2 from the three-phase interface, thereby achieving high ORR current and H_2O_2 current efficiency. When the electrode transitioned to the fully wetted Wenzel state, O_2 transport relied primarily on dissolved oxygen diffusion, the three-phase interface disappeared, and both H_2O_2 production rate and current efficiency declined markedly. This study further pointed out that maintaining a stable Wenzel-Cassie state requires coordinating the O_2 bubbling rate with the O_2 consumption rate during ORR, indicating that O_2 supply optimization is not simply about increasing gas flow rate, but rather achieving dynamic matching among O_2 transport, interfacial wetting state, and reaction consumption. Furthermore, to address the electrowetting and flooding issues of GDEs under high current densities, Cui et al. [224] constructed an anti-electrowetting CB-PTFE carbon film electrode with interconnected microcracks (Fig. 16a). This structure can maintain local hydrophobic microchannels under an electric field, allowing atmospheric O_2 to spontaneously diffuse to the reaction interface and alleviating the O_2 starvation, three-phase interface destruction, and selectivity decline caused by electrowetting in conventional continuous carbon film electrodes. This electrode achieved high selectivity and long-term stable operation at industrially relevant current densities of $100\text{--}300\text{ mA cm}^{-2}$ in open air. Therefore, optimization of O_2 operating parameters should shift from simply adjusting gas flow rate to synergistic matching of O_2 transport rate, O_2 consumption rate, bubble/gas film status,

electrode wettability, and current loading. Only under conditions where a stable gas-liquid-solid three-phase interface is maintained and electrode flooding or O_2 deficiency is avoided can an efficient and stable 2e^- ORR process be sustained at relatively high current densities.

Regarding liquid-phase circulation and product management, the electrolyte or product flow rate should not be simply understood as a parameter that alters electrolyte properties, but rather as an operational variable for regulating product residence time, outlet concentration, and mass-transfer renewal. Ruggiero et al. [225] investigated the effect of SE compartment wash water flow rate on H_2O_2 electrosynthesis in a dual-membrane MEA solid-state electrolyte electrolyzer, finding that reducing the wash flow rate prolonged product residence time and increased outlet H_2O_2 concentration. However, at excessively low flow rates, some H_2O_2 remained trapped in the SE compartment, leading to underestimated FE and potentially exacerbated H_2O_2 degradation due to localized mass-transport limitations, causing the system to deviate from the ideal continuous operation state. Compared with relying solely on extremely low single-pass flow rates to obtain high-concentration products, the circulation mode can accumulate H_2O_2 gradually at relatively higher flow rates and achieve greater total product yield (Fig. 16b). This demonstrates that the core of liquid-phase circulation optimization is not simply reducing or increasing the flow rate, but rather achieving a balance among timely product removal, residence time control, and target concentration accumulation. Excessively low flow rates readily cause product retention and degradation, while appropriately increasing the flow rate or adopting circulation operation is more favorable for maintaining the stability and practicality of the continuous electrosynthesis process.

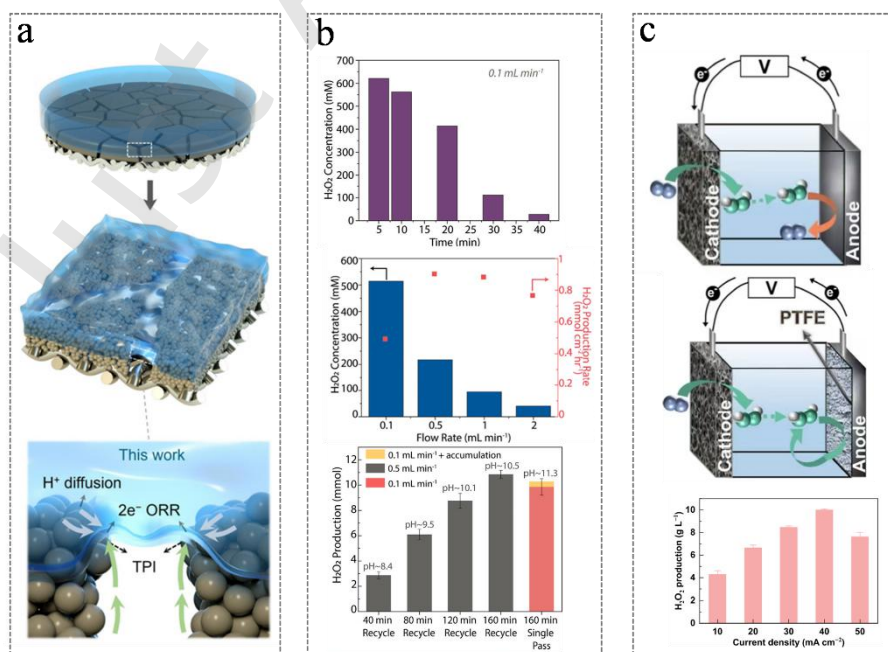


Figure 16 a) Discontinuous CB-PTFE film electrode and the corresponding underwater working mechanism for the 2e^- ORR under high current densities. Reproduced with permission from Ref. [224], © The Royal Society of Chemistry 2024. b) H_2O_2 concentration over time at a flow rate of 0.1 mL min^{-1} after electrolysis; H_2O_2 concentration and production rate; cumulative molar H_2O_2 yield under recirculating operation at 0.5 mL min^{-1} and single-pass operation at 0.1 mL min^{-1} . Reproduced with permission from Ref. [225], © Elsevier 2024. c) Schematic diagrams of the membrane-free

electrolyzer with uncoated and HPL-coated anodes; H_2O_2 accumulation in the membrane-free electrolyzer after 5 h of operation at different current densities. Reproduced with permission from Ref. [210], © Springer Nature 2025.

In addition to O_2 supply and liquid-phase circulation, product protection during long-term operation is also an important aspect of operating condition regulation. After generation, H_2O_2 does not remain stable in the system. It may either be further reduced to H_2O at the cathode side or oxidized to O_2 at the anode side. This issue is more prominent in membrane-free electrolyzers, as the absence of membrane isolation allows the product to more readily contact anodic active sites and undergo oxidative loss. To address anodic decomposition in membrane-free H_2O_2 electrolyzers, Yi et al. [210] constructed a PTFE hydrophobic porous layer on the anode surface, which created a shielding interface by inducing oxygen bubble formation, limiting H_2O_2 transport to anodic reactive sites and thereby significantly suppressing anodic oxidative loss (Fig. 16c). The results showed that compared with the uncoated anode, this bubble-shielding strategy increased H_2O_2 accumulation in the membrane-free electrolyzer by approximately 600%. The paired HPL electrode system also achieved an H_2O_2 concentration of $10.05 \pm 0.05 \text{ g L}^{-1}$ at 40 mA cm^{-2} while maintaining good operational stability. This study demonstrates that operating condition optimization for H_2O_2 electrosynthesis cannot focus solely on cathodic O_2 supply and 2e^- ORR rate, but should also incorporate product migration pathways and H_2O_2 oxidation/reduction losses into the overall regulation framework. For continuous systems, promoting H_2O_2 generation and suppressing H_2O_2 losses should be optimized simultaneously to improve the final product concentration and long-term operational stability.

In summary, the core of regulating mass transport and product management in operation is not the extreme optimization of a single variable, but rather establishing a synergistic balance among O_2 supply, liquid-phase circulation, interfacial stability, and product protection. Gas-phase input must ensure that O_2 transport rate matches current loading to avoid interfacial O_2 deficiency, electrode flooding, or three-phase interface destabilization. Liquid-phase circulation must balance timely product removal with target concentration accumulation, preventing product retention and degradation at excessively low flow rates while avoiding product dilution and increased energy consumption at excessively high flow rates. Product protection requires simultaneous attention to loss pathways including cathodic further reduction, anodic oxidative decomposition, and cross-interface migration. Thus, operating condition optimization for H_2O_2 electrosynthesis should shift from traditional single-factor adjustment to multi-parameter synergistic design, integrating reactant supply, mass-transfer renewal, bubble behavior, wetting state, product concentration, and long-term stability into a unified evaluation framework, thereby achieving comprehensive improvement in high selectivity, high concentration, low loss, and long lifetime operation.

5 Conclusions and perspectives

As a green and mild route to H_2O_2 production with potential

for distributed applications, the 2e^- ORR provides a new direction for replacing the conventional anthraquinone process. With the synergistic optimization of catalyst design and device-system as its central theme, this review systematically summarizes the reaction mechanisms, catalyst structure-activity relationships, and major synthesis strategies for H_2O_2 electrosynthesis via the 2e^- ORR, and further analyzes the effects of device-system on mass transport, selectivity, and stability from three perspectives: electrode structure, reactor configuration, and operating parameters. The field has gradually developed from the early pursuit of catalysts with high selectivity alone to a stage of comprehensive optimization involving activity, selectivity, stability, and device compatibility; device-system have also evolved from H-cells to flow cells and then to MEAs. However, several key challenges remain. First, catalyst active-site structures are complex, and the structure-activity relationships under realistic reaction conditions remain unclear. Second, highly selective catalysts in practical devices are readily affected by factors such as O_2 mass transport, local pH, potential distribution, and H_2O_2 retention, making it difficult to stably reproduce laboratory test performance at the device scale. Third, in situ characterization and diagnostic methods for coupled devices are insufficient, which prevents deciphering the intrinsic correlations among catalysts, microenvironments and performance degradation during operation and restricts our understanding of catalyst-device coupling mechanisms. Fourth, problems including electrode flooding, product decomposition, increased energy consumption, and insufficient long-term stability persist during operation at high current densities. Fifth, a complete engineering closed loop among catalyst preparation, reactor scale-up, and product separation has not yet been established. Therefore, the central question for future H_2O_2 electrosynthesis is no longer whether a highly selective 2e^- ORR can be achieved, but whether directly usable H_2O_2 can be produced over the long term, efficiently, and with low energy consumption under realistic device conditions. To address these challenges, future research should not remain limited to the optimization of a single catalyst or a single device structure. Instead, a multiscale synergistic design framework should be established through the precise construction of active sites, stabilization of electrode three-phase interfaces, enhancement of reactor mass transport, targeted product delivery, and coupled regulation of operating parameters, thereby advancing H_2O_2 electrosynthesis from laboratory performance validation toward an efficient, stable, and scalable green manufacturing technology.

5.1 Predictable catalyst design

Currently, many 2e^- ORR catalysts have exhibited high H_2O_2 selectivity in RRDE or small-scale electrolyzers, but their active-site structures are often heterogeneous and are prone to structural reconstruction, metal-center deactivation, or H_2O_2 decomposition under conditions of high current density, complex electrolytes, and prolonged operation.

Therefore, catalyst development urgently needs to shift from conventional empirical trial-and-error screening toward theory-guided, predictable, and precise catalyst construction. The establishment of this new paradigm requires systematic breakthroughs in three dimensions: descriptor development, high-throughput screening, and database platform construction.

In descriptor development, conventional volcano-plot descriptors relying solely on the $\Delta G^{\circ}_{\text{OOH}}$ barely meet multi-dimensional evaluation criteria covering activity, selectivity and stability. In recent years, researchers have devised new multi-dimensional descriptors to improve prediction capacity. For instance, Mok et al. [38] proposed the $\Delta\Delta G$ selectivity descriptor. By accounting for the free-energy difference between $\ast\text{O}$ and $\ast\text{OOH}$ adsorption, this descriptor enables the prediction of 2e^- ORR selectivity trends. Its validity was validated against 155 binary alloy systems, offering new insights to break the limitations of the traditional single $\Delta G^{\circ}_{\text{OOH}}$ descriptor. Meanwhile, deep coupling between DFT calculations and machine learning provides a feasible route for automatically identifying multi-dimensional key descriptors beyond the conventional volcano-plot framework. Wang et al. [226] combined DFT calculations with an SISO-based machine-learning model to systematically probe 42 SACs supported on Sc_2CS_2 MXene. They identified electronegativity, first ionization energy, valence-electron number, metal-sulfur bond length, electron affinity, and metal charge as core descriptors dictating 2e^- ORR performance. Furthermore, for non-planar SAC systems, Jia et al. [227] reported a novel descriptor $\Delta\text{ed-p}$. Built upon the classic d-band-center theory, this descriptor additionally accounts for the rearrangement effect between ligand N-p orbitals and metal d orbitals, which more accurately depicts the structure-activity relationship between catalytic performance and electronic structure for non-planar SACs. The above studies demonstrate that future descriptors will evolve from single adsorption-energy metrics toward multi-dimensional prediction systems.

From the high-throughput-screening perspective, machine-learning-driven virtual screening greatly broadens the chemical space for catalyst discovery. Yu et al. [228] integrated active-motif design with machine learning, expanding the chemical space through elemental substitution and achieving efficient screening. They discovered novel 2e^- ORR catalysts absent from existing databases, which exhibit superior stability to known materials. Ye et al. [229] established a workflow integrating high-throughput computations and machine learning. They constructed 78 theoretical models of edge-anchored SACs and adopting structural stability, catalytic activity and operando catalytic stability as screening metrics for systematic performance evaluation. Assisted by a machine-learning regression model, the top-five key descriptors governing catalytic activity were successfully recognized, offering critical guidelines for the theoretical design and expansion of edge-anchored SACs. These findings reveal that machine learning can substantially reduce the reliance of high-throughput screening on DFT calculations, but also effectively discover catalytic materials inaccessible to conventional rational design.

Regarding database-platform construction, high-quality catalytic databases constitute an essential data foundation for data-driven catalyst design. Nevertheless, dedicated large-scale databases comparable to mature systems such as CO_2RR are still lacking for 2e^- ORR-based H_2O_2 electrosynthesis. Widely used databases including Materials Project, OQMD, Catalysis-Hub, and Open Catalyst Project mainly supply material-structure, electronic-property, and catalytic adsorption. Although they provide fundamental data support for machine-learning models, they cannot comprehensively describe reaction selectivity, interfacial microenvironments, and device operating parameters involved in H_2O_2 electrosynthesis [230–233]. Therefore, it is urgent to construct dedicated databases for the 2e^- ORR system that integrate DFT calculations, experimental performance data and practical electrolyzer parameters. Such databases will enable predictable optimization spanning from material design to device performance and accelerate the large-scale application of H_2O_2 electrosynthesis technology.

5.2 Multiscale device synergy

The intrinsic activity of a catalyst can be fully realized only within an appropriate electrode interfacial structure and reactor environment. For H_2O_2 electrosynthesis via the 2e^- ORR, the development of GDEs, flow cells, and MEAs has essentially aimed to address the low solubility of O_2 , long mass-transport pathways, and product retention. Under high-current-density operating conditions, system performance is no longer determined by catalyst activity alone, but is jointly constrained by multiple factors, including O_2 supply, three-phase interfacial stability, local pH variations, ion migration, water management, heat accumulation, and H_2O_2 desorption and decomposition. Therefore, future optimization of device-system should shift from the improvement of individual structures toward multiscale synergistic design. At the electrode scale, stable gas-liquid-solid three-phase interfaces should be constructed through pore-structure regulation, optimization of catalyst-layer thickness, and a balance between hydrophilicity and hydrophobicity. At the reactor scale, rational flow-field design, membrane-structure selection, and optimization of product-removal pathways should be used to reduce concentration polarization and the likelihood of side reactions. At the process-parameter scale, an optimal operating window should be established for current density, electrolyte composition, O_2 flow rate, temperature, and circulation rate. In particular, the evaluation boundaries of H-type cells, flow cells, and MEAs should be clearly distinguished to avoid direct comparison of data obtained under different mass-transport conditions, reaction areas, product-collection methods, and operating durations. Thus, the key to device-system optimization lies not in independently improving a single mass-transport metric, but in achieving dynamic matching among catalyst activity, the electrode interface, and reactor operating conditions. Only by establishing multiscale correlations can performance mismatch in practical devices be avoided, thereby advancing H_2O_2 electrosynthesis toward continuous operation at high current densities with high stability.

5.3 In situ characterization and diagnostic methods for coupled devices

Substantial performance gaps across H-cells, flow cells, and MEAs highlight the demand for in situ characterization and diagnostic tools compatible with practical device architectures. Although conventional ex-situ characterization delivers information regarding catalyst composition and structure, it fails to capture the dynamic evolution of active sites, interfacial microenvironments, and reactant-product distributions under high-current-density operation [234]. Particularly within flow cell and MEA configurations, multiphase gas-liquid-solid transport, localized pH fluctuations, H_2O_2 accumulation, and electrode-wetting states are intricately coupled. Relying solely on pre- and post-reaction structural analysis is insufficient to rationalize the mismatch between intrinsic catalyst performance and device-level performance. Therefore, related research urgently needs to shift from static structural analysis toward interfacial evolution and device-process diagnostics under realistic working states.

Preliminary progress toward this goal has been reported. For example, Huang et al. [235] constructed a flow-cell electrolyzer equipped with a quartz window and employed operando Raman spectroscopy to capture surface O_2 and *OOH intermediates, thereby enabling direct tracking of the 2e^- ORR process under near-practical oxygen-supply conditions. Zhang et al. [236] performed operando Raman tests in a flow cell operating at 200 mA cm^{-2} , tracking the continuous accumulation of H_2O_2 and its interaction with KF through the evolution of O–O vibrational signals, indicating that dynamic monitoring of the reaction process is extending toward industrially relevant conditions. Meanwhile, mass-transport and two-phase behaviors at the device scale have attracted increasing attention. For instance, Cui et al. [159] adopted in situ electrochemical reflection-absorption imaging coupled with a GDE to resolve the two-dimensional distributions of H_2O_2 and OH^- on electrode surfaces in real time. Combined with electrolysis experiments and theoretical calculations, they revealed the influences of wettability and catalytic-layer structure on $\text{O}_2/\text{H}_2\text{O}_2$ mass transport and reaction selectivity. Kim et al. [237] employed high-speed imaging in a microelectrode model system to resolve interfacial bubble evolution and accordingly optimized fluid management and bubble removal in MEA. Nevertheless, dynamic diagnostics directly for practical flow cells and the internal working states of MEAs remain quite limited.

Future research should therefore extend the scope of in situ characterization beyond reaction mechanisms toward device-state diagnosis. On one hand, new characterization platforms need to be developed to tolerate high current densities, real gas feeds, complex electrolytes, and long-term operation, enabling simultaneous multiscale monitoring of reaction intermediates, local H_2O_2 concentrations, pH gradients, gas-liquid mass transfer, flooding, and bubble behavior. On the other hand, such localized microscale data should be quantitatively correlated with macroscopic performance metrics including cell voltage, FE, product concentration, and long-term stability, so that device-performance-limiting factors can be pinpointed. Such

advances will drive H_2O_2 electrosynthesis research away from post-mortem failure analysis toward real-time diagnosis and feedback-driven optimization, laying a solid foundation for stable scale-up of high-performance flow cell and MEA devices.

5.4 Energy efficiency and economic evaluation

The practical deployment of electrochemical H_2O_2 synthesis relies not merely on the selectivity and FE of catalysts in short-term tests, but more critically on energy consumption, service life, material costs and product throughput under continuous operation. Most existing studies still take H_2O_2 selectivity, production yield or FE as core evaluation metrics, yet these parameters cannot fully reflect the engineering feasibility of the whole system. For practical applications, factors such as cell voltage, energy efficiency, electrode area, catalyst loading, membrane-material cost, electrode lifetime, product concentration, and post-treatment costs are equally critical. For example, Gu et al. [238] pointed out through techno-economic analysis that H_2O_2 electrosynthesis becomes economically competitive only when the system achieves sufficiently high energy efficiency at 300 mA cm^{-2} . This work indicates that future evaluation criteria for electrochemical H_2O_2 synthesis should evolve from optimization of individual performance metrics to full-process practical viability. Raw material costs, scalable fabrication, device energy consumption and long-term stability should be simultaneously considered at the catalyst design stage. Particularly for industrial-oriented systems, key parameters including electrode area, operating time, H_2O_2 concentration, energy consumption, current density, stability and product purity ought to be uniformly reported. This practice improves comparability across different research works and provides reliable data support for subsequent techno-economic analysis and engineering scale-up. Therefore, establishing standardized performance reporting protocols and a unified evaluation system constitutes an essential foundation for assessing the industrial potential of various catalysts and device architectures.

5.5 Integrated reaction-separation systems

Compared with the centralized production model of the conventional anthraquinone process, the greatest application advantage of H_2O_2 electrosynthesis via the 2e^- ORR lies in its green, mild reaction conditions and the potential for distributed, on-site, and on-demand production. Most current researches only focus on H_2O_2 generation performance in electrolytes, while neglecting product morphology tuning, high-efficiency separation and purification, purity control and compatibility with downstream application scenarios. This limitation prevents the electro-synthesis technology from fully exerting its unique scenario-based advantages. The requirements for H_2O_2 products differ significantly among application scenarios. Scenarios such as water treatment and in-situ disinfection prioritize low-cost, continuous on-site preparation capacity; while high-grade oxidation applications including fine chemical synthesis and pulp bleaching impose stricter requirements on product

concentration, purity and output stability. Murray et al. [239] proposed a phase-transfer catalysis strategy, which utilizes disulfonated anthraquinone to shuttle redox equivalents between two phases, enabling continuous H_2O_2 generation and separation in electrolyte-free water streams and offering a novel route for coupled reaction-separation systems.

On the other hand, the construction of integrated systems involves not only the separation and purification of cathodic products but also the synergistic matching of anodic and cathodic reactions. Coupling suitable anodic reactions with 2e^- ORR to construct paired electrolysis systems that simultaneously produce value-added chemicals at both electrodes represents an important pathway to overcome the efficiency limitations of single-electrode reactions and enhance the overall atom economy of the system [2, 149, 240]. For instance, Zhang et al. [241] coupled cathodic 2e^- ORR with anodic 2e^- WOR, achieving simultaneous H_2O_2 production on both electrodes. The full-cell FE reached as high as 154.8 %, with a total production rate of $4.3 \text{ mmol h}^{-1} \text{ cm}^{-2}$, which fully demonstrates the tremendous potential of paired electrolysis for breaking single-electrode efficiency limits and achieving synergistic performance enhancement. Oh et al. [242] constructed a self-powered electrochemical system employing $\text{Bi}_{4/3}\text{@Pt}$ as the glycerol oxidation reaction (GOR) anode and O-CNT as the 2e^- ORR cathode. Leveraging the potential difference between GOR and ORR, this system enables spontaneous H_2O_2 synthesis without external electrical or solar-energy input. It delivers a production rate of $8.475 \text{ umol cm}^{-2} \text{ min}^{-1}$, alongside 74 % selectivity toward glyceric acid at the anode, while concurrently outputting renewable electricity. This work illustrates the dual potential of cathodic-anodic synergistic value-adding for boosting production efficiency and lowering energy consumption.

Accordingly, future reactor design should expand beyond a single electrochemical reaction unit toward an integrated generation-separation-application system. By coupling solid electrolytes, membrane separation, phase-transfer catalysis, or downstream oxidation modules, targeted H_2O_2 delivery and immediate utilization can be achieved. At the same time, attention should be paid to the coupled matching and synergistic optimization of cathodic and anodic reactions, incorporating low energy consumption, high selectivity, and high atom economy into a unified evaluation framework. Only when H_2O_2 can be continuously and stably delivered at the target concentration and target purity with low energy consumption can H_2O_2 electrosynthesis via the 2e^- ORR realistically be expected to replace conventional centralized supply models in on-site applications and serve the needs of distributed chemical manufacturing, environmental remediation, and on-site disinfection. Overall, the future development focus of this field should not be the continuous setting of new records for individual performance metrics, but rather the establishment of a closed-loop design framework linking catalysts, interfaces, reactors, and product output, thereby realizing the transition from reports of high-performance materials to verifiable technologies.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Q. S.: Validation, investigation, writing manuscript. H. X. X.: Investigation, writing manuscript. J. Y. W.: Conceptualization, methodology. W. Y. L.: Methodology, validation. J. L. S.: Validation. J. Y. W.: Validation. Q. C. W.: Funding acquisition, project administration, review. Y. Q. Z.: Funding acquisition, project administration, review. J. J. L.: Funding acquisition, project administration, writing-review & editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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