



Coupling oxygen reduction and water oxidation for concerted H_2O_2 production: a sustainable paired-electrosynthesis strategy

Xia Lu^{1,3,4}, Shu-Guo Han^{3,*}, Dong-Dong Ma⁵, Wenbo Wei², Qi-Long Zhu^{2,3,*} 

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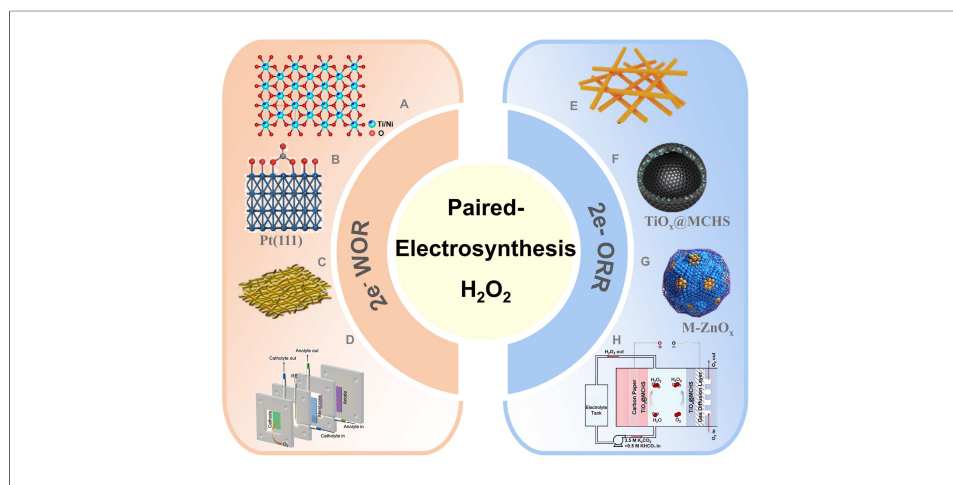
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Abstract

Hydrogen peroxide (H_2O_2) is an important green oxidant for clean energy and environmental technologies, yet its dominant anthraquinone process relies on complex, fossil-based and energy-intensive operations that are incompatible with distributed, low-carbon production. Electrocatalytic synthesis via the two-electron oxygen reduction (2e^- ORR) and water oxidation reactions (2e^- WOR), powered by renewable electricity, offers a sustainable route to on-site H_2O_2 generation from O_2 and/or H_2O . However, conventional electrolyzer setups typically employ only one of these half-reactions for H_2O_2 production, leading to substantial energy losses and limited overall Faradaic efficiency (FE). In this context, coupling 2e^- ORR and 2e^- WOR to produce H_2O_2 simultaneously at the cathode and the anode has emerged as a promising paired-electrosynthesis strategy.



¹College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 350117, Fujian, China.

²School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, Zhejiang, China.

³State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), Fuzhou 350108, Fujian, China.

⁴Fujian College, University of Chinese Academy of Sciences, Fuzhou 350002, Fujian, China.

⁵Hubei Key Laboratory of Low Dimensional Optoelectronic Materials and Devices, Hubei University of Arts and Science, Xiangyang 441053, Hubei, China.

***Correspondence to:** Prof. Shu-Guo Han, State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), No. 8, Gaoxindao Road, Minhou, Fuzhou 350108, Fujian, China. E-mail: hanshuguo@fjirsm.ac.cn; Prof. Qi-Long Zhu, School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, Zhejiang, China. E-mail: qlzhu@fjirsm.ac.cn

Dual-electrode concerted H_2O_2 production could surpass the efficiency ceiling of single-electrode systems by avoiding sacrificial counter reactions, lowering the cell voltage and theoretically pushing the overall FE towards 200%. However, the practical realization is still hampered by 2e^- ORR and 2e^- WOR kinetics mismatch, competitive side reactions, H_2O_2 crossover and degradation, and insufficient catalyst and electrode durability under oxidative operation. This review summarizes recent progress in the paired H_2O_2 electrosynthesis via 2e^- ORR//WOR, covering the thermodynamic and kinetic fundamentals, coupling modes and cell architectures, performance metrics and benchmarking protocols. Finally, we highlight the challenges and opportunities in low-carbon paired-electrosynthesis H_2O_2 manufacturing.

INTRODUCTION

H_2O_2 is a versatile and relatively benign oxidant that supports key processes in pulp and paper production^[1,2], disinfection and medical sterilization^[3,4], wastewater treatment^[5], and fine chemical synthesis^[6], and is widely recognized as one of the most important industrial chemicals^[6]. With growing demands from energy and environmental technologies, there is increasing interest in sustainable, decentralized H_2O_2 supply^[7,8]. At present, however, global production is dominated by the anthraquinone oxidation process, which relies on noble-metal catalysts^[9,10] and fossil-derived organic working media in a multi-step loop^[11,12], and requires concentration, storage and long-distance transport of H_2O_2 solutions^[13]. The associated energy consumption, organic waste generation and safety risks are difficult to reconcile with the principles of green chemistry and carbon-neutral manufacturing^[14].

Electrochemical routes that convert O_2 and/or H_2O into H_2O_2 ^[15,16] using renewable electricity offer a fundamentally different paradigm, enabling on-site and on-demand production under ambient conditions^[17-19]. The two key half-reactions are the two-electron oxygen reduction (2e^- ORR): $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$ and the two-electron water oxidation reactions (2e^- WOR): $2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ ^[20], which in principle allow H_2O_2 generation from inexpensive feedstocks^[21]. In most conventional electrosynthetic configurations, only one of these half-reactions is exploited for H_2O_2 formation, while the counter electrode operates a kinetically sluggish, high-overpotential reaction such as the oxygen evolution reaction (OER)^[22]. The necessity to drive OER as a sacrificial process not only wastes electrical energy and reduces the overall Faradaic efficiency (FE_{cell})^[23], but also constrains cell design and limits the competitiveness of single-electrode H_2O_2 electrosynthesis^[24].

Therefore, coupling 2e^- ORR and 2e^- WOR in the same electrochemical cell to generate H_2O_2 simultaneously at the cathode and anode has emerged as a promising paired-electrosynthesis strategy^[25-29]. In this configuration, both half-reactions directly contribute to the target product, with an overall reaction $2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{H}_2\text{O}_2$, maximizing atom and charge utilization^[16,30] [Figure 1]. In principle, such 2e^- ORR//WOR coupling can surpass the energy-efficiency limit of single-electrode schemes, avoid low-value sacrificial reactions, reduce cell voltage, and push the overall H_2O_2 Faradaic efficiency (FE) towards 200%^[31,32], while being intrinsically compatible with modular, flow-type and membrane-based reactors driven by intermittent renewable power^[23]. In practice, however, 2e^- ORR//WOR paired systems are still at a nascent stage: efficient and selective 2e^- WOR catalysts remain scarce, leading to current density (j) and kinetics mismatch between the two electrodes^[33]. Meanwhile, both half-reactions compete with 4e^- pathways and with further reduction, oxidation or disproportionation of H_2O_2 ^[34], and mass-transport limitations, H_2O_2 crossover and harsh oxidative conditions impose stringent requirements on electrode, electrolyte and membrane stability^[35].

Existing reviews predominantly address single-pathway electrocatalysis, focusing on either 2e^- ORR or 2e^- WOR. This review focuses specifically on 2e^- ORR//WOR paired-electrosynthesis strategy for concerted H_2O_2 generation. We first clarify the thermodynamic and kinetic fundamentals of 2e^- ORR and 2e^- WOR and

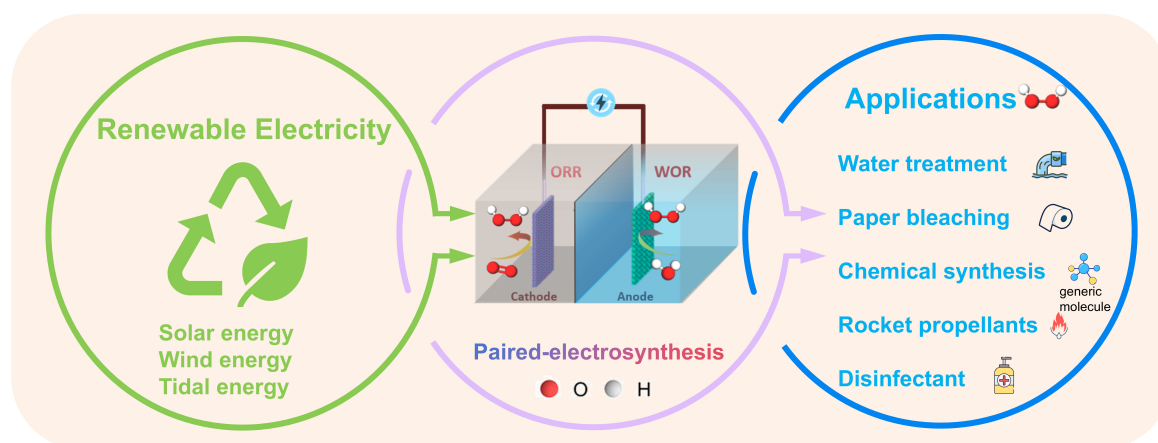


Figure 1. Schematic diagram of the on-site H_2O_2 synthesis by a sustainable paired-electrosynthesis strategy and its applications.

the rationale of $2e^-$ ORR//WOR pairing, and briefly introduce representative cell architectures and performance metrics. We then summarize recent advances in the paired-electrosynthesis strategy, categorized by asymmetric and symmetric catalytic electrode pairs, highlighting the structure-activity-stability relationships. Finally, we outline the key challenges and opportunities in catalyst design, equipment development, and mechanism research, aiming to guide the development of scalable, low-carbon H_2O_2 production technologies.

RATIONALE AND FUNDAMENTALS OF PAIRED H_2O_2 ELECTROSYNTHESIS

In paired H_2O_2 electrosynthesis, O_2 and H_2O serve as the feedstocks, and H_2O_2 can be produced concurrently through the $2e^-$ ORR at the cathode and the $2e^-$ WOR at the anode^[36–39]. Notably, because both electrodes can generate H_2O_2 simultaneously, the overall FE of paired H_2O_2 electrosynthesis could approach 200% when each half-reaction proceeds with high selectivity^[40–44]. Achieving such high electron utilization, however, requires precise regulation of both cathodic ORR and anodic WOR toward the $2e^-$ routes while suppressing competing multi-electron pathways and parasitic H_2O_2 loss reactions^[45–50]. Accordingly, mechanistic understanding has become central to advancing paired H_2O_2 electrosynthesis. In this section, we first establish the fundamentals of anodic $2e^-$ WOR and cathodic $2e^-$ ORR separately, focusing on their distinct reaction pathways, active-site motifs, and key activity/selectivity descriptors^[51–55]. We then overview typical electrolyzer configurations and standardized testing/quantification protocols, which are essential for reliably benchmarking paired H_2O_2 production across different studies and platforms.

The $2e^-$ ORR//WOR coupling concept

$2e^-$ ORR

In the reduction system of electrochemical synthesis of H_2O_2 , ORR is the core electrochemical process^[56–61]. The path specificity gives $2e^-$ ORR a unique advantage in the electrochemical synthesis of H_2O_2 , but in practical applications, its selectivity and activity have always been constrained by the inherent competition with the $4e^-$ ORR pathway^[62]. Therefore, in-depth analysis of the reaction mechanism of $2e^-$ ORR to avoid competition from the $4e^-$ ORR pathway^[63–65], and the interaction between oxygen and key intermediates has become the core prerequisite for the design of a high-efficiency electrocatalytic system^[66–68].

As shown in Figure 2, first O_2 is adsorbed on the catalyst to obtain $^*\text{O}_2$, and then protons to obtain $^*\text{OOH}$, which is a very important intermediate for electrocatalytic $2e^-$ ORR^[69–73]. There are many competitive reactions accompanied by the intermediate $^*\text{OOH}$ generation, such as the competitive reaction of $4e^-$ direct

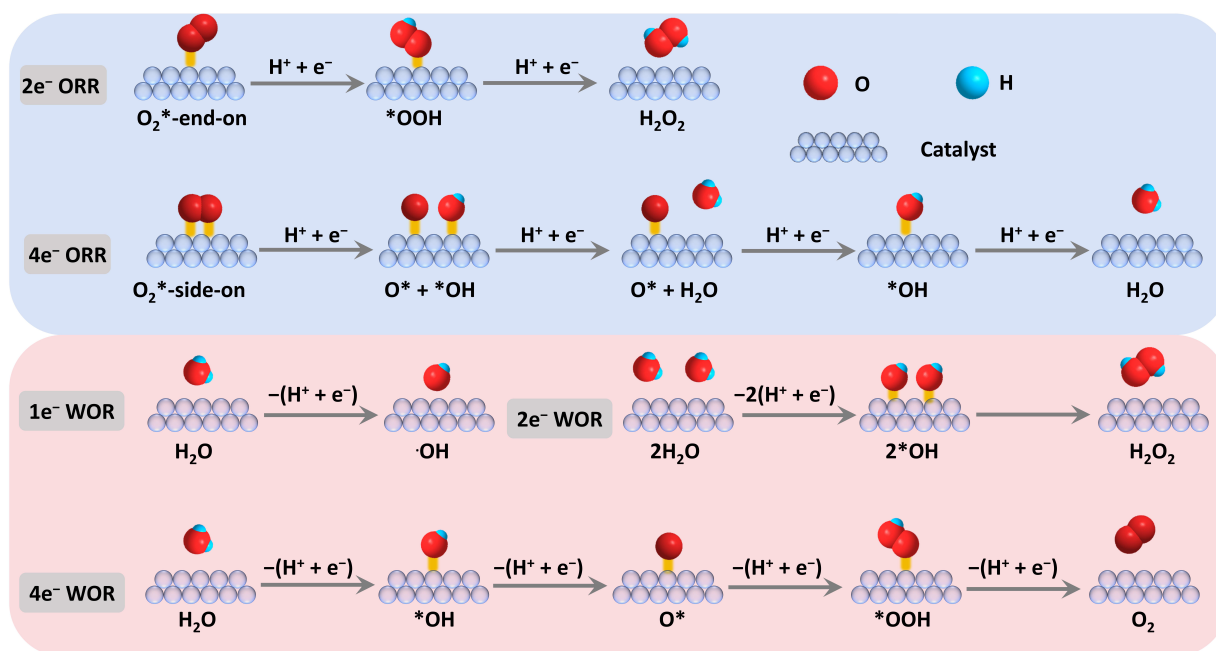


Figure 2. Illustration of ORR and WOR pathways.

or indirect ORR, which will affect the consumption of the intermediate $^*\text{OOH}$ ^[74–78]. Therefore, improving the effective utilization of $^*\text{OOH}$ has become the key to designing catalysts^[79]. The formation and stable adsorption of $^*\text{OOH}$ within the appropriate energy range have been proven to be an effective way to promote the $2e^-$ ORR process^[80,81]. The key to achieving this goal is whether the integrity of the O-O bond can be maintained throughout the catalysis process. Among them, the interaction of catalysts and oxygen species directly affects the cleavage of the O-O bond. For carbon catalysts, carbonyl and carboxyl groups exhibit relatively weak oxygen adsorption energy, which favors the formation of H_2O_2 . In contrast, hydroxyl and ether groups have strong oxygen adsorption, promoting O-O bond cleavage and leading preferentially to H_2O generation^[82]. Therefore, the catalyst design strategies that selectively preserve the O-O bond integrity is also critical for improving the efficiency of $2e^-$ ORR^[83–86].

$2e^-$ WOR

$2e^-$ WOR can realize the anodic electrosynthesis of H_2O_2 with water as the only reactant^[87,88]. $2e^-$ WOR involves three parallel and competing electrochemical paths, which together form the framework of its reaction mechanism. The reaction equations are presented as follows: Firstly, hydroxyl radical generation pathway: $\text{H}_2\text{O} - e^- \rightarrow \cdot\text{OH} + \text{H}^+$ ($E = +2.41$ V vs. reversible hydrogen electrode (RHE)). Secondly, target product generation pathway: $2\text{H}_2\text{O} - 2e^- \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+$ ($E = +1.76$ V vs. RHE). And oxygen evolution side reaction pathway: $2\text{H}_2\text{O} - 4e^- \rightarrow \text{O}_2 + 4\text{H}^+$ ($E = +1.23$ V vs. RHE)^[89,90].

All three pathways share a core initial step, the deprotonation of water molecules at the active sites of the catalyst to form $^*\text{OH}$ intermediates. This allows mechanistic regulation to focus on the subsequent conversion of $^*\text{OH}$, where the adsorption state and conversion direction of $^*\text{OH}$ on the catalyst surface directly determine the product distribution. Weak adsorption of $^*\text{OH}$ leads to its rapid desorption as $\cdot\text{OH}$ with an extremely short lifetime (only $10^{-7} \sim 10^{-8}$ s), which cannot be collected on a large scale^[91,92]. Therefore, the stable adsorption of $^*\text{OH}$ is the primary prerequisite for directing the reaction towards H_2O_2 generation. On the basis of stable $^*\text{OH}$ adsorption, the deprotonation capacity of the catalyst becomes the key variable for regulating the reaction pathway. The excessive deprotonation ability of the catalyst tends to take

hydrogen atoms from $^*\text{OH}$, thus accelerating its transformation into $^*\text{O}$ intermediates^[93]. These $^*\text{O}$ intermediates are prone to dissociation and eventually produce O_2 , resulting in a significant decrease in the selectivity of the target product. On the contrary, when the deprotonation ability of the catalyst is within the appropriate range, it can effectively inhibit the deep dehydrogenation of $^*\text{OH}$ and create conditions for the coupling reaction between $^*\text{OH}$ species. Two adsorbed $^*\text{OH}$ species form an O-O bond and combine with protons to generate H_2O_2 , thus completing the target reaction pathway of $2e^-$ WOR^[48]. To improve the selectivity of H_2O_2 , poor OER activity catalysts including BiVO_4 , TiO_2 , WO_3 , CaSnO_3 , ZnO , are used in anodic H_2O_2 production^[21,94-98]. Additionally, by regulating the electronic structure of the catalyst, the adsorption of $^*\text{OH}$ can be strengthened, and its deprotonation ability can be precisely adjusted, thus inhibiting the side-reaction pathway and promoting the directional coupling of $^*\text{OH}$ to generate H_2O_2 . Previous studies have employed strategies such as Gd doping^[52], d-band center modulation^[99], and oxygen vacancy engineering^[100] to optimize the adsorption free energy of key intermediates, including $^*\text{OH}$ and $^*\text{O}$, bringing ΔG_{OH} within the ideal range of 1.6-2.4 eV. Doping involves introducing heteroatoms into the catalyst lattice, leading to charge redistribution and thus optimizing the adsorption free energy of key intermediates. In a study by the team of Sotirios Mavrikis, they developed a $2e^-$ WOR electrode based on boron-doped diamond (BDD), a metal-free material, by finely tuning the crystal orientation, boron doping level, and catalyst loading thickness. This BDD electrode achieved excellent activity, selectivity, and stability without metal electrocatalysts, performing comparably to or even better than metal-based electrocatalysts. Specifically, it achieved a FE of 87%, a H_2O_2 production rate of $76.4 \mu\text{mol min}^{-1} \text{cm}^{-2}$, and maintained stable electrochemical performance for 10 h at a current density of 200 mA cm^{-2} in a carbonate solution^[83]. In contrast, oxygen vacancies are defects left by the departure of oxygen atoms from the lattice of metal oxides, representing a typical type of anion vacancy^[101]. The presence of oxygen vacancies creates electron-rich sites on adjacent metal cations, which facilitate the back-donation of electrons to adsorbed oxygen molecules, promoting the formation of $^*\text{OOH}$ and stabilizing reaction intermediates. Zhang *et al.* prepared an oxygen-vacancy-rich CaSnO_3 @carbon fiber membrane catalyst via electrospinning, achieving efficient anodic H_2O_2 production with an FE as high as 90% at 2.9 V *vs.* RHE, demonstrating the important role of oxygen vacancies in regulating the adsorption free energy of WOR intermediates^[44]. Furthermore, in Section "RECENT ADVANCES IN CONCERTED H_2O_2 PRODUCTION BY $2e^-$ ORR//WOR PAIRED ELECTROSYNTHESIS", we have specifically summarized the regulation of key intermediates by oxygen vacancies in the bifunctional catalysts currently studied. Apart from the catalyst, the reaction pathway mediated by $\text{CO}_3^{2-}/\text{HCO}_3^-$ is utilized, which can significantly reduce the onset potential of the anodic reaction, enabling efficient H_2O_2 generation at potentials below 2.0 V *vs.* RHE, thereby effectively circumventing direct potential competition with the OER^[88].

Despite these attractive strategies for lowering the onset potential and boosting FE, the anodic $2e^-$ WOR inherently occurs in a strongly oxidizing environment, which raises serious stability concerns that are independent of the improved thermodynamics, a challenge that calls for dedicated investigation. The anodic $2e^-$ WOR operates at strongly oxidizing potentials, posing stability challenges for catalysts during prolonged operation, including surface oxidation, structural reconstruction, and loss of active sites. For metal oxide catalysts (e.g., BiVO_4 , WO_3 , ZnO), metal ions such as V^{5+} and W^{6+} are prone to dissolution in the form of oxyanions at high potentials, particularly in bicarbonate electrolytes^[52,95,101]. Concurrently, irreversible phase transformations or passivation of active sites may occur on the surface. Strategies such as elemental doping^[52], construction of heterostructures^[102], or surface coating protection can effectively suppress dissolution, while crystal facet engineering can enhance thermodynamic stability. Although carbon-based catalysts (e.g., carbon fiber paper, oxidized carbon materials) exhibit high H_2O_2 yields, they are susceptible to electrochemical oxidation corrosion at strong anodic potentials, leading to structural collapse, reduced hydrophobicity, and disruption of the triple-phase interface, thereby diminishing selectivity^[103]. Modification with hydrophobic layers, increasing the degree of graphitization^[104], or heteroatom doping^[105] can enhance

their antioxidant capacity. Overall, future efforts should combine *in situ* characterization and theoretical calculations to gain deeper insights into the structural evolution of catalysts, and establish unified stability evaluation protocols to facilitate the development of highly efficient and stable 2e⁻ WOR catalysts.

2e⁻ ORR//WOR

Electrosynthetic coupling of 2e⁻ ORR and 2e⁻ WOR in pairs is an efficient green technology scheme for the production of H₂O₂ on site^[27]. However, how to improve efficiency remains a challenging proposition. Among the approaches to achieve concerted H₂O₂ production, it is crucial to steer the oxygen reduction at the cathode and the water oxidation at the anode toward the 2e⁻ pathways. Based on the preceding review, we can focus on two aspects: Firstly, for electrocatalytic 2e⁻ ORR, the oxygen intermediate *OOH on the catalyst surface is critical. Modifying the electronic structures of catalysts to regulate the formation energy and binding energy of *OOH within an appropriate range is essential. Secondly, in WOR, the binding energy of the oxygen intermediate *OH on catalysts should be optimized. If the binding is too strong, adsorbed *OH may be further oxidized to *O and *OOH, promoting the 4e⁻ WOR pathway toward O₂ evolution. Conversely, if the binding is too weak, H₂O molecules cannot be effectively activated to form *OH.

The electrosynthesis of H₂O₂ via coupled WOR and ORR is governed by the adsorption free energy of key intermediates. This aligns with the Sabatier principle, where the binding strength of intermediates serves as the critical parameter determining overall activity and performance. Among intermediates *O, *OH, and *OOH, ΔG_{*OH} has demonstrated exceptional effectiveness due to its linear correlations with other key intermediates (ΔG_{*OOH} = ΔG_{*OH} + 3.2 eV; ΔG_{*O} = 2ΔG_{*OH} + 0.28 eV). The thermodynamic limiting potentials for the 2e⁻ and 4e⁻ WOR pathways are defined as follows.

$$U_{L,H_2O_2}^{WOR} = \frac{\max(\Delta G_{*OH} - \Delta G_{H_2O}, \Delta G_{H_2O_2} - 2\Delta G_{*OH})}{e} \quad (1)$$

$$U_{L,O_2}^{WOR} = \frac{\max(\Delta G_{*O} - \Delta G_{*OH}, \Delta G_{*OOH} - 2\Delta G_{*O})}{e} \quad (2)$$

The 2e⁻ pathway is favored thermodynamically when U_i(H₂O₂) < U_i(O₂), with optimal H₂O₂ selectivity occurring at ΔG_{*OH} ≈ 1.76 eV, corresponding to intermediate *OH binding strength (1.6–2.4 eV)^[84]. Similarly, for ORR, the key parameter (descriptor) for controlling the catalyst activity is the *OOH binding energy (ΔG_{*OOH}). The reaction rate and the selectivity of the reaction pathway are closely related to *OOH, and the intermediates generated subsequently directly determine the final product. The thermodynamic limiting potential for 2e⁻ ORR is as follows.

$$U_{L,H_2O_2}^{ORR} = \frac{\max(\Delta G_{O_2} - \Delta G_{*OOH}, \Delta G_{*OOH} - \Delta G_{H_2O_2})}{e} \quad (3)$$

Combined with previous studies, making ΔG_{*OOH} infinitely approach the peak point of the Sabatier volcano plot (ΔG_{*OOH} = 4.2 ± 0.02 eV) can enhance the protonation of *OOH, thereby achieving efficient generation of H₂O₂^[84]. Kim *et al.* employed ΔG_{*OOH} and ΔG_{*OH} as thermodynamic descriptors for the activity of the 2e⁻ ORR and 2e⁻ WOR, respectively, and through Zn doping and the introduction of oxygen vacancies (O_v), tuned the optimal limiting potentials of D-PSFZ (Pr_{1.0}Sr_{1.0}Fe_{0.75}Zn_{0.25}O_{4-δ}) to 0.39 and 1.83 eV, respectively^[25]. Meanwhile, the selectivity is intrinsically governed by the thermodynamic instability of the competing *O intermediate, with ΔG_{*O} and ΔG_{*OOH} serving as the decisive selectivity-indicating parameters. Density

functional theory (DFT) calculations revealed that for the vast majority of surface sites on D-PSFZ, the energy state of $\ast\text{O}$ is significantly higher than that of the H_2O_2 formation pathway, thereby suppressing the competing 4e^- side reaction^[25]. Based on these insights, the designed oxygen-vacancy-rich D-PSFZ achieved > 99% FE for the 2e^- ORR over a wide potential and ionic strength range with stable operation for 500 h, a 2e^- WOR selectivity of 80% at 2.15 V, and a record FE of 163.0% in a membrane-free full electrolyzer.

While designing catalysts based on these mechanistic insights is highly important, the choice of electrolyte is equally critical. In alkaline environments, the 2e^- ORR tends to proceed via an outer-sphere electron transfer mechanism, generating stable HO_2^- ^[106], whereas carbonate media can stabilize the $\ast\text{OOH}$ intermediate in WOR^[107]. However, excessively high pH may steer the reaction toward the 4e^- pathway. Under acidic conditions, the high proton concentration favors an inner-sphere electron transfer mechanism for the 2e^- ORR, making the 4e^- reduction more likely while also rendering the produced H_2O_2 susceptible to further reduction or Fenton reactions, leading to catalyst corrosion and diminished selectivity^[108,109]. In neutral media, the reaction kinetics are sluggish, but catalyst stability is superior, and buffer systems can effectively maintain interfacial pH stability, facilitating H_2O_2 accumulation. In paired systems where both electrode reactions proceed simultaneously, weakly hydrated cations (such as K^+) can accumulate at the cathode to form a proton shielding layer, protecting H_2O_2 from over-reduction, while anions such as $\text{HCO}_3^-/\text{CO}_3^{2-}$ stabilize the $\ast\text{OOH}$ intermediate at the anode^[88]. Moreover, relevant studies emphasize that the electrolyte is not an inert solvent but rather an active interface that co-evolves with the catalyst. Its composition and pH collectively determine the reaction selectivity, intermediate adsorption energy, and interfacial mass transport behavior.

Reactor configurations

H-type cell

As a classic two-compartment reactor in electrochemical research, the H-type cell [Figure 3] is characterized by membrane-separated independent chambers and compartmentalized reactions at dual electrodes^[38]. Its advantages include a simple structure, ease of operation, and straightforward product detection, making it suitable for preliminary catalyst screening and mechanistic studies. In recent work on electrochemical ORR for H_2O_2 production, Sun *et al.* used an H-cell to systematically screen and characterize their Ni-SAC electrode, obtaining its key initial performance data. The Ni-SAC electrode achieved a high FE of 89.02% and a H_2O_2 yield rate of $0.73 \text{ mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$, outperforming most reported catalysts^[42]. It has become an important basic device for the paired electrosynthesis of H_2O_2 , with the cathode performing 2e^- ORR and the anode for 2e^- WOR. This configuration can accommodate electrolytes with different pH requirements and effectively address issues such as reactant competition and product cross-contamination in single-chamber systems^[35]. Despite these advantages, the H-type cell suffers from inherent limitations that hinder its practical application: poor oxygen solubility, which leads to slow, inefficient, and highly resistive transport of oxygen from the gas phase to the catalyst active sites, further severely limiting the reaction rate. Additionally, the H-type cell typically operates at low current densities, which restricts reaction kinetics and overall production efficiency^[110,111].

Flow cell

The H-type cell offers the advantages of ease of operation and a clear distinction during preliminary screening of catalysts at the laboratory stage. However, its reliance on dissolved oxygen for the ORR imposes an inherent limitation due to the low solubility and slow diffusion rate of O_2 in the electrolyte. This fundamental constraint makes it difficult to sustain high current densities, which are essential for practical production rates. In contrast, the flow cell combined with a gas diffusion electrode (GDE) can directly supply oxygen at the three-phase interface and significantly reduce the thickness of the mass transfer boundary layer

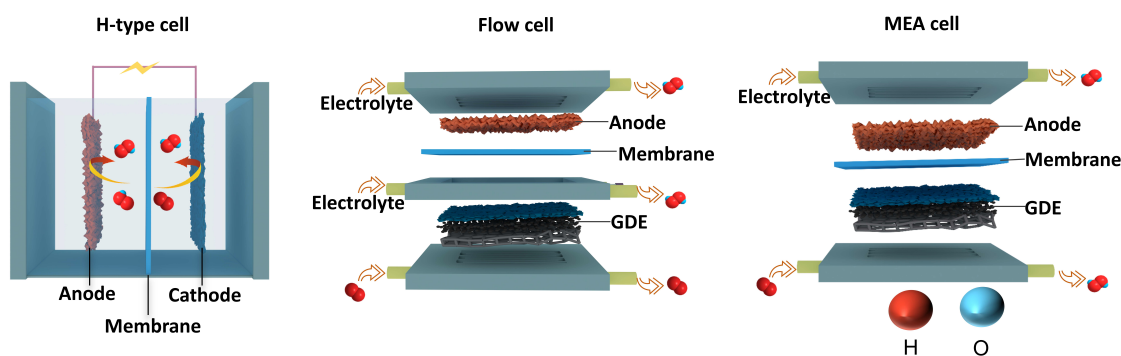


Figure 3. H-type cell, flow cell and membrane electrode assembly (MEA) cell configurations for H_2O_2 electrosynthesis.

through forced convection [Figure 3], thus effectively overcoming the bottleneck of insufficient dissolved oxygen supply, significantly improving the O_2 mass transfer efficiency and promoting electrosynthesis at higher current density. For example, Wang coupled 2e^- WOR and 2e^- ORR in a flow cell, achieving a current density of 240 mA cm^{-2} and an overall FE of 146%^[16]. Compared to the H-type cell, the flow cell is inherently a system whose performance is critically dependent on precise fluidic management^[112]. For the H-cell, efforts will target mitigating O_2 mass transfer limits and optimizing cell geometry. Flow-cell designs require precise fluid dynamics control and advanced gas diffusion electrode engineering, focusing on wettability and pore structure. For MEA, key challenges include improving material stability and reducing internal resistance. Beyond catalysts, fluid simulation of gases and liquids is indeed a mainstream research direction. It is explicitly highlighted as a key tool for advanced reactor design. Studies demonstrate that simulation-assisted flow-field engineering can enhance reaction uniformity and mass transfer. This approach is central to optimizing the gas-liquid-solid interface and improving overall reactor performance. Thus, fluid simulation is integral to the next generation of electrolyzer development. This performance leap starkly illustrates the advantage of overcoming dissolved oxygen limitations. Its performance optimization can usually be carried out from three aspects: (i) Liquid flow channel and flow field design, which improves the uniformity of electrolyte distribution by optimizing the flow field mode, reduces the local concentration difference and pH gradients, and integrates the monitoring and regulation strategy of pH; (ii) Diaphragm selection, combined with the reaction mechanism and ion conduction needs, gives priority to ion conduction membrane materials with appropriate ion conduction characteristics and matching with relevant reactions to maintain circuit closure and inhibit the side reactions caused by cross-osmosis; and (iii) Pressure difference management: precise control of the pressure difference between O_2 and electrolyte is the key to maintaining the stable operation of GDE and avoiding electrode submersion or gas leakage^[35].

Scaling up for continuous H_2O_2 production shifts the priority towards long-term operational robustness and system intelligence. The device design and methodology of the flow tank for H_2O_2 preparation should give priority to the durability of GDE (anti-submersion/anti-inactivation), the selectivity of membrane materials and long-term chemical stability, and combine online analysis and process control to realize the intelligent operation of the system, such as pH, solution real-time monitoring of key parameters such as deoxygenation, H_2O_2 concentration and gas-hydraulic pressure difference to improve data comparability and reproducibility of working conditions^[35].

Membrane electrode assembly

Membrane electrode assembly (MEA) [Figure 3] serves as the core component of fuel cells and electrolyzers, undertaking the interconversion of chemical energy and electrical energy. In comparison with H-type and flow cells, the MEA represents the most commercially advanced design to date, featuring extremely low

internal resistance and higher energy efficiency^[108,113]. The GDEs utilize porous carbon substrates to separate the gaseous oxygen feed from the liquid electrolyte, thereby enhancing mass transport of the gaseous reactant to the catalyst surface. This configuration effectively circumvents the low solubility limitation of O₂ in aqueous media and reduces the diffusion distance for O₂ to reach the catalytic sites. However, in a conventional GDE-based flow cell, the produced H₂O₂ mixes with the electrolyte, necessitating energy-intensive downstream separation to obtain high-purity H₂O₂ suitable for downstream applications. In contrast, a dual-MEA solid-electrolyte electrolyzer integrates the mass-transport advantages of GDEs with a porous solid electrolyte sandwiched between two ion-exchange membranes. This design enables the direct generation of nearly ion-free, pure aqueous H₂O₂ solution, which can be readily utilized in subsequent processes without further purification. Zhang *et al.* performed H₂O₂ electrosynthesis from O₂ and H₂O in MEA with a solid-state electrolyte (SSE), utilizing 0.1 M HClO₄ as the sole electrolyte supplied to the anode chamber (denoted as the O₂//SSE//HClO₄ cell). Using this structure, a pure H₂O₂ solution with a concentration of 3.5 wt% was continuously produced at a low cell voltage of 2 V and a current of 3,300 mA, without the need for subsequent distillation or purification^[114]. However, the slow diffusion rate of the H₂O₂ produced and its degradation due to the accumulation on the electrode surface can significantly impair the overall electrosynthesis performance in MEA cells. Researchers can explore the impacts of mass transport by tuning the electrode components (e.g., catalyst and hydrophobic particle loading) and reactor operating conditions (e.g., reactant/ flow rate), address the degradation of H₂O₂ caused by its accumulation on the electrode surface, and thereby enhance the electrocatalytic synthesis efficiency of H₂O₂.

Performance metrics and benchmarking

The advancement of electrochemical H₂O₂ synthesis technology is fundamentally dependent on a robust and standardized evaluation framework [Figure 4]. Such a framework is indispensable for elucidating reaction mechanisms, screening efficient catalysts, and optimizing electrolyzer performance. More importantly, it serves as a critical bridge connecting fundamental laboratory research to industrial-scale applications. The current mainstream evaluation methodology comprises two complementary approaches that form a complete performance assessment chain: the rotary electrode test and the electrolytic cell test combined with H₂O₂ quantification. The two approaches complement each other and form a complete performance evaluation chain. The rotary electrode test can accurately characterize the inherent electrochemical properties of the catalysts by constructing a controllable mass transfer environment, while the electrolytic cell test combines the efficient H₂O₂ quantitative method to comprehensively evaluate the application potential of the system under actual reaction conditions^[115]. This section will systematically elucidate the core principles, operational protocols, data analysis methods, and application boundaries of these two approaches. The aim is to provide a comprehensive theoretical and practical reference for standardized research in H₂O₂ electrosynthesis. As a classic tool for quantifying the performance of catalysts in the laboratory, the rotary electrode relies on the forced convection generated by high-speed rotation, which can effectively eliminate the interference of mass transfer restrictions, so as to accurately obtain the intrinsic activity, selectivity, and kinetic parameters of the catalysts^[116]. The two primary configurations are: rotating disc electrodes (RDE) and rotating ring disc electrodes (RRDE). RDE adopts a three-electrode system, and the working electrode surface has a uniform catalytic layer. When conducting the ORR test, the electrolyte should be kept in an oxygen-saturated state, while the WOR test directly uses water as the reactant. After obtaining the current density-potential curves by linear scanning voltammetry (LSV), key indicators such as the number of transferred electrons, the reaction rate constant, the starting potential and the half-wave potential can be calculated by fitting data at different rotation speeds with the Koutecky-Levich (K-L) equation^[84]:

$$\frac{1}{j_D} = \frac{1}{j_K} + \frac{1}{j_{\text{Diff}}} = \frac{1}{1000nFKC_{\text{O}_2}} + \frac{1}{1000B\sqrt{\omega}} \quad (4)$$

$$B = 0.62nFC_{\text{O}_2}D^{\frac{2}{3}}\nu^{\frac{1}{6}} \quad (5)$$

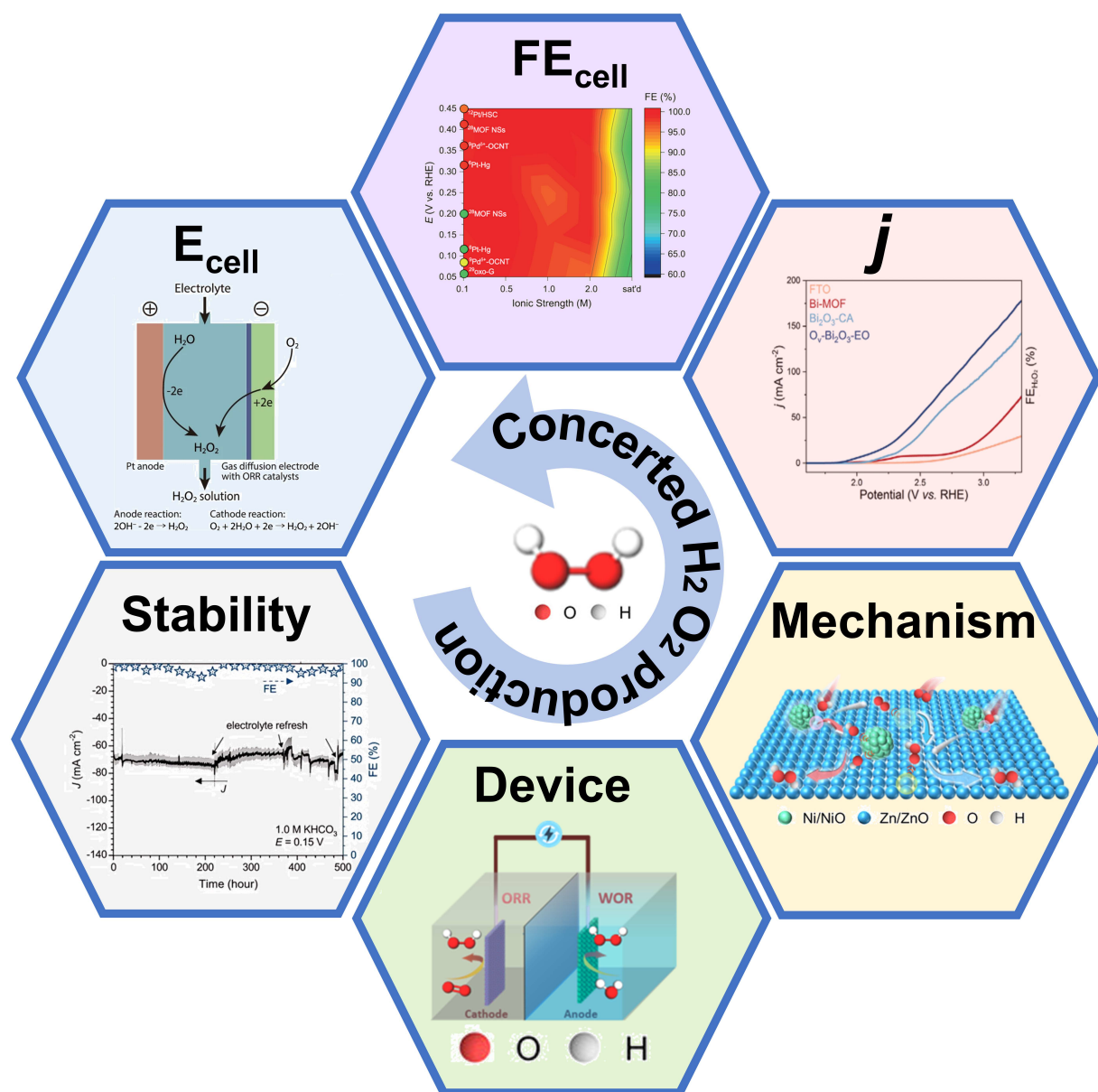


Figure 4. Performance metrics and benchmarking of coupled 2e⁻ ORR//WOR for concerted H₂O₂ production: the figures for FE_{cell} and stability are adapted with permission from^[25]. Copyright © 2023 Springer Nature. The figure for *j* is adapted with permission from^[28]. Copyright © 2024 Wiley-VCH GmbH; The figure for the mechanism is adapted with permission from^[102]. Copyright © 2025 Wiley VCH-GmbH; The figure for E_{cell} is adapted with permission from^[19]. Copyright © 2024 Springer Nature.

Through linear fitting of $1/j_a$ and $1/\omega$ (electrode rotation angular velocity), the number of transferred electrons and the reaction rate constant can be accurately derived. Based on RDE, RRDE adds coaxial annular electrodes to form a disc-ring dual-working electrode structure: The plate electrode reacts to produce H₂O₂, and the ring electrode applies a constant potential to completely oxidize the H₂O₂ diffused to its surface. By synchronously collecting the disk current (i_d) and ring current (i_r), precise quantification of H₂O₂ selectivity and the number of transferred electrons is achievable, making it the gold standard for evaluating catalyst selectivity^[84]. Its core calculation formulas are the H₂O₂ selectivity:

$$S_{\text{H}_2\text{O}_2} = \frac{2i_R}{N_C} \frac{1}{|i_D| + \frac{i_R}{N_C}} \quad (6)$$

and the number of transferred electrons:

$$n = \frac{4|i_D|}{|i_D| + \frac{i_R}{N_C}} \quad (7)$$

Where N_C is the collection efficiency of the ring electrode. In order to ensure the accuracy of the test, it is necessary to control the catalyst loading, select suitable electrode materials such as gold rings, and calibrate N_C (ring current collection efficiency). This method can also be expanded to evaluate the $2e^-$ WOR catalysts, without oxygen supply, expand the potential window of the disk electrode, and directly follow the selective calculation logic of ORR.

It should be noted that the rotary electrode test depends on idealized conditions and forced convection, which is significantly different from the actual operation of electrolytic cells involving natural mass transfer and restricted electrode structure, and often overestimates the H_2O_2 selectivity of catalysts. In contrast, the electrolytic cell test is closer to the actual application scenario, because it comprehensively considers the electrode structure, mass transfer efficiency, electrolyte properties, and other engineering factors. Combined with accurate H_2O_2 quantitative analysis, this test can comprehensively evaluate the H_2O_2 production capacity of the electrode under actual working conditions^[117]. Its core evaluation index is FE, which directly reflects the charge utilization efficiency in reactions^[31]. The calculation formula is:

$$FE = \frac{nFM_{H_2O_2}}{\int_0^t I(t)dt} \times 100\% \quad (8)$$

where $n = 2$ (corresponding to the two-electron reaction), $M_{(H_2O_2)}$ is the molar amount of generated H_2O_2 , and $I(t)$ is the current as a function of time. H_2O_2 quantification methods should be selected on demand: indirect spectrophotometry is simple to operate and highly anti-interferent, suitable for quantifying low to medium concentration H_2O_2 in complex electrolyte systems; titration has high accuracy and low detection limit, mostly used for offline precise quantification; chemiluminescence and fluorescence methods exhibit excellent sensitivity for trace H_2O_2 analysis, only limited by reagent costs or external light interference; colorimetric test strip and refractometry methods are fast to operate, suitable for on-site rapid screening or preliminary evaluation with low accuracy requirements, but have relatively large errors. In practical research, a synergistic strategy of rotating electrode screening and electrolytic cell verification is usually adopted: high activity and high selectivity catalyst candidates are quickly identified via rotating electrode testing, then fabricated into practical electrodes. Their actual performance is evaluated through electrolytic cell testing combined with appropriate quantification methods, and finally, catalyst structures or electrolytic cell parameters are optimized based on test results, forming a closed-loop research and development process of screening-verification-optimization to facilitate the efficient iteration of H_2O_2 electrosynthesis technology.

The H_2O_2 yield rate is another important performance metric, which is a comprehensive embodiment of FE, current density, and stability. Based on the amount of H_2O_2 produced per unit catalyst or electrode area within a unit time, the performance of the catalysts can be directly compared. Recently, the Zhang team reported that they applied a flow cell to evaluate BBL-PcNi as a $2e^-$ ORR catalyst for H_2O_2 production, which achieved the yield rate of $9.7 \text{ mol g}^{-1} \text{ h}^{-1}$ at 135 mA cm^{-2} ^[114]. Subsequently, they employed a membrane

electrode assembly-solid-state electrolyte (MEA-SSE) electrolyzer to verify its capability for continuous production of pure medical-grade H_2O_2 under practical conditions. In the MEA-SSE configuration, BBL-PcNi achieved continuous operation for over 6 h with a low cell voltage of 2 V. Furthermore, the accumulated concentration of H_2O_2 in the electrolyte, its decomposition rate, and the long-term stability of the system ultimately determine the practical productivity. Therefore, the H_2O_2 yield rate of catalysts needs to be further evaluated and compared, as it is a prerequisite for practical applications.

Current literature predominantly emphasizes FE and productivity, but it lacks systematic accounting for actual production costs. According to the economic estimation in Siahrostami's study, which is based on the International Renewable Energy Agency (IRENA) green electricity price (0.05 USD/kWh) and an experimental productivity of 15 $\mu\text{mol}/\text{min}$, the base costs of electrochemically producing high-concentration H_2O_2 are lower, respectively, than those of the conventional anthraquinone process^[7]. This indicates that the electrochemical route is already cost-competitive at the fundamental level. However, this estimation is based on the following conservative assumptions: First of all, the long-term stability cost of the 2e^- WOR catalyst under high potential was not included. Then, the energy consumption for membrane separation required to concentrate the dilute solution (< 5%) to the commercially relevant concentration of 35% was not accounted for. The differences in catalyst preparation costs arising from the possible use of different anode and cathode catalysts in a 2e^- system were not considered. We have therefore given this further thought. IRENA predicts that the green electricity price could drop to 0.02-0.03 USD/kWh by 2030, and the share of electricity cost in the total H_2O_2 production cost will decrease further from the current 30%-50%. Against this background, catalyst lifetime, membrane cost, and separation cost will become the dominant factors governing economic viability. Consequently, future economic assessments should establish a full life-cycle cost model that incorporates catalyst replacement intervals (target: > 8,000 h), membrane lifetime (target: > 5,000 h), and energy consumption for concentration (target: < 0.5 kWh/kg H_2O_2). In particular, our analysis reveals that if a single bifunctional catalyst can be used in a 2e^- system to simultaneously drive both the anodic and cathodic reactions, the costs for catalyst preparation and replacement can be substantially reduced, making this the most economically promising technical pathway for the future.

RECENT ADVANCES IN CONCERTED H_2O_2 PRODUCTION BY 2e^- ORR//WOR PAIRED ELECTROSYNTHESIS

Coupling the 2e^- ORR with 2e^- WOR enables concerted H_2O_2 production with improved electronic efficiency and better overall energy utilization^[84], as both electrodes can be productively engaged rather than dissipating energy through parasitic half reactions. To date, however, most efforts have focused on catalyst design and mechanistic understanding of H_2O_2 generation via a single half reaction, typically emphasizing activity and selectivity on either the cathode or the anode. In contrast, paired-electrosynthesis strategies that integrate anodic and cathodic processes for concerted H_2O_2 production remain at an early stage and are still significantly underexplored. Against this background, the following section systematically categorizes the reported paired-electrosynthesis strategies for concerted H_2O_2 production and critically compares their performance using key metrics, including catalytic electrode design, electrolyte, FE_{cell} , and production rate [Table 1].

Asymmetric catalytic electrode pairs

The development of concerted H_2O_2 production by a sustainable paired-electrosynthesis strategy commonly hinges on the design of advanced asymmetric catalytic electrode pairs. This strategy involves engineering the anode catalysts to tackle the more challenging 2e^- WOR. In a pioneering study, Xia *et al.*^[103] employed a surface modification approach by coating carbon fiber paper (CFP) with a hydrophobic PTFE polymer to locally confine generated O_2 gas near active sites. This confinement alters interactions with oxygen

Table 1. The various parameters of the concerted H_2O_2 production by paired-electrosynthesis

Cathode	Anode	Electrolyte	E or j	FE_{cell} (%)	H_2O_2 yield rate	Ref.
O-CNT	PTFE-CFP	1.0 M Na_2CO_3	1.7 V	153	$23.4 \mu\text{mol cm}^{-2} \text{min}^{-1}$	[103]
NADE	S-CFP	2 M KHCO_3	2.8 V	152.9	$38 \mu\text{mol cm}^{-2} \text{min}^{-1}$	[118]
GDE	Pt	2 M KHCO_3	150 mA cm^{-2}	150	N/A	[119]
CB/PTFE	CuWO_4/Sn	2 M KHCO_3	140 mA cm^{-2}	161	$66 \mu\text{mol cm}^{-2} \text{min}^{-1}$	[120]
O-CNT	$\text{Ni}_x\text{Ti}_{1-x}\text{O}_{2-y}$	0.5 M $\text{KOH}/0.5 \text{ M KHCO}_3 + 3.5 \text{ M KCO}_3$	240 mA cm^{-2}	146	$109.12 \mu\text{mol cm}^{-2} \text{min}^{-1}$	[16]
O-ND	Cu-OND	0.1 M $\text{KOH} + 2 \text{ M KHCO}_3$	1.8 V	161.1	$28.5 \mu\text{mol cm}^{-2} \text{min}^{-1}$	[121]
$\text{O}_x\text{-Bi}_2\text{O}_3\text{-EO}$	$\text{O}_x\text{-Bi}_2\text{O}_3\text{-EO}$	0.1 M KOH	100 mA cm^{-2}	154.8	$4.3 \text{ mmol cm}^{-2} \text{h}^{-1}$	[28]
C-doped BN	C-doped BN	2 M KHCO_3	50 mA cm^{-2}	171.5	$2,750 \text{ mmol g}^{-1} \text{h}^{-1}$	[126]
$\text{NiZnO}_x\text{-C}$	$\text{NiZnO}_x\text{-C}$	2 M KHCO_3	1,000 mA cm^{-2}	150.9	N/A	[102]
NiSn-HITP	NiSn-HITP	0.1 M KOH	50 mA cm^{-2}	171.5	$9.1 \text{ mol g}^{-1} \text{h}^{-1}$	[127]
$\text{CeO}_2\text{ NCs}$	$\text{CeO}_2\text{ NCs}$	1 M KOH	30 mA cm^{-2}	> 85	$4.6 \text{ mol g}^{-1} \text{h}^{-1}$	[124]
TiO_{2-x}	TiO_{2-x}	0.1 M KOH	10 mA cm^{-2}	134	$20 \text{ mmol L}^{-1} \text{h}^{-1}$	[122]
D-PSFZ	D-PSFZ	2.0 M KHCO_3	50 mA cm^{-2}	163.0	N/A	[25]
$\text{TiO}_x\text{@MCHS}$	$\text{TiO}_x\text{@MCHS}$	2.0 M $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$	100 mA cm^{-2}	145	$108.3 \mu\text{mol cm}^{-2} \text{min}^{-1}$	[123]

intermediates, boosting the selectivity and activity of the $2e^-$ WOR pathway. When coupled with an oxidized carbon nanotube (O-CNT) cathode as the $2e^-$ ORR catalyst, this system achieved an exceptional H_2O_2 FE_{cell} of 153% [103]. The mechanism study shows that the direct $2e^-$ WOR pathway occurs on the carbon-based electrode rather than the indirect over-carbonate-mediated pathway. This conclusion is supported by evidence such as ^{18}O isotope markers. The universality of this local gas-limit concept has been further verified after applying it to a typical OER catalyst, i.e., foam nickel, enabling the generation of H_2O_2 . It is worth noting that in a sodium carbonate electrolyte, the generated H_2O_2 can form solid sodium percarbonate, which is convenient for storage and transportation, and highlights its application potential in organic synthesis.

In a parallel approach, Ling *et al.* functionalized a CFP anode with a self-assembled monolayer (SAM) of (3-Mercaptopropyl) triethoxysilane (MPTES) [118]. The modification constructs a highly ordered interface and optimizes the microenvironment around the active sites, which is conducive to generating the $2e^-$ WOR pathway. The resulting SAM-modified anode (S-CFP) achieved a H_2O_2 selectivity of 62.1% in sodium carbonate electrolyte. In order to build a practical system, the anode was coupled with the natural air diffusion cathode (NADE) based on carbon cloth. The cathode can passively use oxygen in the atmosphere without forcing aeration with intense energy consumption. In a membrane-separated electrolyzer, this paired system delivered a total H_2O_2 FE of 152.9% and a production rate of $38 \mu\text{mol cm}^{-2} \text{min}^{-1}$, demonstrating the viability of decentralized H_2O_2 production. This strategy highlights the potential of metal-free catalysts for decentralized H_2O_2 generation with low energy consumption. A common strategy highlighted in these works involves boosting the $2e^-$ WOR on the anode through precise interfacial microenvironment engineering. This is combined with leveraging established, high-performance $2e^-$ ORR catalysts on the cathode to assemble an effective asymmetric electrode pair for concurrent H_2O_2 generation.

Supplementary to carbon materials, investigations confirm that the metal-based electrocatalysts are equally effective for the $2e^-$ WOR. Zhu *et al.* investigated H_2O_2 production on a Pt electrode in carbonate solutions using *in-situ* Raman spectroscopy [Figure 5A] and ^{18}O isotope labeling, revealing that carbonate coupling is the dominant pathway [Figure 5B] [119]. These researchers also suggest that during electrochemical H_2O_2 production from water oxidation in carbonate electrolyte, the vast majority of H_2O_2 is generated via the

coupling of two adsorbed CO_3^{2-} species to form a peroxodicarbonate intermediate ($\text{C}_2\text{O}_6^{2-}$), which subsequently dissociates to yield H_2O_2 . In contrast, the conventionally presumed $^*\text{OH}$ - $^*\text{OH}$ coupling pathway contributes negligibly, while the CO_3^{2-} - $^*\text{OH}$ cross-coupling pathway accounts for approximately 7% of the total contribution^[119]. This mechanism highlights the critical role of carbonate adsorption on the Pt surface in suppressing competing reactions and enhancing the selectivity of the $2e^-$ WOR. Their study showed that 93% of H_2O_2 originates from CO_3^{2-} coupling via a $\text{C}_2\text{O}_6^{2-}$ intermediate, with minimal contribution from OH-mediated routes. The Pt electrode achieved high selectivity, exceeding 90% FE in 2 M K_2CO_3 under optimized potentials [Figure 5C]. This work highlights the key role of carbonate adsorption in inhibiting competitive reactions and achieving selective H_2O_2 electrosynthesis. By coupling the commercial ORR cathode with the matching anode in the flow cell configuration [Figure 5D], the synchronous generation of H_2O_2 by paired electrosynthesis was realized. When the flow cell operated at a current density of 1 A cm^{-2} , it showed an FE_{cell} of up to 150% for H_2O_2 , and the required cell voltage was only 2.3 V [Figure 5E].

In addition, Li *et al.* pioneered the development of a Sn-doped CuWO_4/Sn anode catalyst prepared by pyrolysis^[120]. The X-ray diffraction (XRD) spectroscopy [Figure 5F] and high-resolution transmission electron microscopy (HRTEM) [Figure 5G] analysis confirmed that the catalyst has a pure wolframite CuWO_4 structure with uniform element distribution [Figure 5H]. The hydrophobic CC/ CuWO_4/Sn electrode achieved 72% H_2O_2 FE at 2.5 V vs. RHE [Figure 5I], and the yield rate reached $11.6 \mu\text{mol cm}^{-2} \text{ min}^{-1}$. In the full-cell system coupled with a nitrogen-doped carbon nanotube air self-respiration cathode, the total FE under 100 mA cm^{-2} reached 161%, showing efficient paired-electrosynthesis performance [Figure 5J]. DFT calculations indicate that atomic-level doping of Sn modulates the adsorption energies of key intermediates (especially $^*\text{OH}$) on the CuWO_4 surface, thereby facilitating the formation and coupling of $^*\text{OH}$ toward H_2O_2 production. Concurrently, the high-energy-barrier $4e^-$ WOR pathway is suppressed, thereby enhancing selectivity for the $2e^-$ WOR [Figure 5K]. Moreover, Wang *et al.* synthesized a single atomic Ni-doped TiO_2 ($\text{Ni}_x\text{Ti}_{1-x}\text{O}_{2-y}$) anode through a solvothermal method, which displays a rutile structure with Ni atoms substituting Ti sites^[16]. The anode delivered a FE of 70% for H_2O_2 at 300 mA cm^{-2} in weakly alkaline media, and when paired with an O-CNT cathode, the full-cell reached 146% FE at 240 mA cm^{-2} . Specifically, DFT calculations suggest that the incorporation of Ni atoms into the TiO_2 lattice weakens the excessively strong adsorption of $^*\text{OH}$, while simultaneously enhancing the kinetic favorability of the $^*\text{OH}$ - $^*\text{OH}$ coupling pathway, thereby improving the selectivity of the $2e^-$ WOR. Jia *et al.* synthesized an oxygen-doped nanodiamond (O-ND) cathode through acid washing and heat treatment, which removes the surface graphite layer and increases the sp^3 carbon content^[121]. The cathode delivered an FE of 87.1% for H_2O_2 via $2e^-$ ORR in 0.1 M KOH electrolyte, demonstrating excellent stability over 24 h. The full-cell reached a combined FE of 161.1% at a voltage of 1.8 V. DFT calculations revealed that the oxygen doping modulates the local charge distribution of sp^3 carbon, optimizing the $^*\text{OOH}$ adsorption energy for $2e^-$ ORR, while the Cu_2O component in Cu-OND exhibits an optimal d -band center that balances $^*\text{OH}$ adsorption, thereby enhancing the selectivity of the $2e^-$ WOR pathway. Overall, these studies have advanced this field by demonstrating the efficient and on-site production of H_2O_2 using rich resources.

Assembling asymmetric catalytic electrode pairs usually includes two steps, namely optimizing the WOR catalyst and then coupling it with the standard carbon-based anode catalyst. Through strategic methods such as local oxygen limitation, atomic doping, and interface engineering, the WOR performance can be effectively optimized, so as to improve its selectivity and activity. These modifications can regulate the adsorption behavior of key intermediates (such as $^*\text{OH}$), making them more inclined to the $2e^-$ pathway rather than the competitive response^[16]. In the end, this kind of electrode pair can achieve synergy, which verifies the feasibility of high-yield and distributed H_2O_2 production.

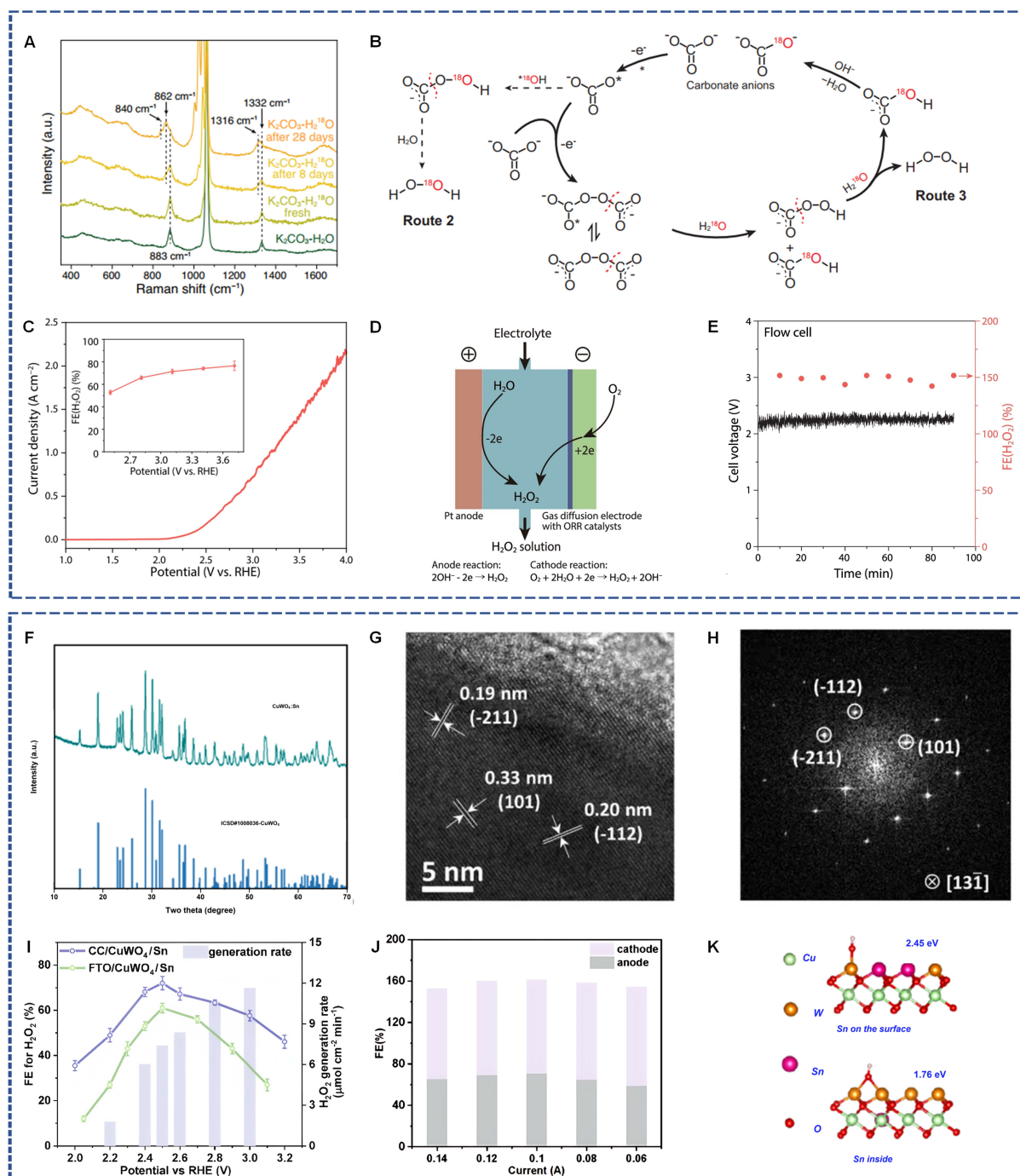


Figure 5. Asymmetric catalytic electrode pairs for the concerted H_2O_2 production: (A) Comparison of *in-situ* Raman spectra recorded at a roughened Pt electrode in 2 M $\text{K}_2\text{C}^{16}\text{O}_3\text{-H}_2^{16}\text{O}$ and 2 M $\text{K}_2\text{C}^{16}\text{O}_3\text{-H}_2^{18}\text{O}$ electrolyte; (B) Main reaction pathway for two-electron water oxidation to H_2O_2 in a high-concentration K_2CO_3 solution; (C) LSV plots for Pt electrode in 2 M K_2CO_3 electrolyte (pH = 12.1 ± 0.2). Inset is the corresponding FE of H_2O_2 ; (D) Schematic design of the flow cell coupling 2e^- WOR and 2e^- ORR for H_2O_2 production; (E) Cell voltage and H_2O_2 FE in the flow cell at a constant cell current of 150 mA; (A-E) are adapted with permission from^[119]. Copyright © 2024 Springer Nature; (F) XRD pattern of the CuWO_4/Sn catalyst; (G) HRTEM image of CuWO_4/Sn . (H) Selected area electron diffraction of CuWO_4/Sn ; (I) FE of H_2O_2 for CC/ CuWO_4/Sn and FTO/ CuWO_4/Sn and H_2O_2 generation rate of CC/ CuWO_4/Sn ; (J) FE_{cell} of H_2O_2 generated from the cathode and anode operated at different current densities; (K) Structures of OH^* absorbed on Sn-doped CuWO_4 with Sn inside (upper) and on the surface (lower); (F-K) are adapted with permission from^[120]. Copyright © 2022 American Chemical Society.

Symmetric catalytic electrode pairs

A symmetric catalytic electrode pair employs the same material at both the cathode and anode to couple the $2e^-$ ORR and the $2e^-$ WOR for concerted H_2O_2 electrosynthesis. This configuration not only simplifies the device structures but also has unique operational advantages. When the activity of the catalysts decreases due to overreduction or peroxidation, the polarity of the switching electrodes can regenerate the active structures *in situ*, so as to achieve continuous operation without replacing the electrodes. However, the central material challenge is non-negligible, since one catalyst must remain selective and stable across strongly different interfacial environments (cathodic reductive vs. anodic oxidative potentials), while concurrently suppressing the competing four-electron pathways ($4e^-$ ORR to H_2O and $4e^-$ WOR to O_2). Building on this concept, this subsection highlights that the bifunctional catalysts are used on both electrodes to drive the two half-reactions in a concerted manner. The following representative studies illustrate how tuning the adsorption behaviors of $*OOH$ and $*OH$ intermediates via defect, facet, and interfacial regulation, which can simultaneously promote the $2e^-$ ORR and the $2e^-$ WOR while suppressing competing $4e^-$ pathways, thereby enabling efficient coupled H_2O_2 production.

Defect engineering becomes an effective route to bifunctionality in symmetric electrode pairs, such as oxygen vacancies (O_v), which provide a direct lever to reshape local electronic structures of the electrocatalysts and thus the binding strengths of $*OOH$ and $*OH$. The first example is TiO_{2-x} nanocrystals obtained by hydrogen plasma etching, where “defects with spatial roles” were explicitly demonstrated^[122]. The inner oxygen vacancies stabilize $*OOH$ during $2e^-$ ORR and inhibit its dissociation, whereas surface lattice distortion promotes $*OH$ coupling during $2e^-$ WOR. *In-situ* Raman spectroscopy demonstrated that the characteristic peaks of the TiO_{2-x} surface remained nearly unchanged within the ORR potential window. The post-reaction decrease in oxygen vacancy concentration indicated that the residual oxygen vacancies are located in the inner layer rather than on the surface. During the WOR process, the Raman signals gradually attenuated above 2.2 V, revealing that a slight surface distortion of TiO_{2-x} is the origin of the high selectivity. DFT calculations further confirmed that surface and subsurface oxygen vacancies are readily healed by reaction intermediates, while only the near-surface oxygen vacancies can stably persist and optimize $*OOH$ adsorption. Experimental tuning of the oxygen vacancy concentration additionally showed that the ORR performance correlates positively with the oxygen vacancy concentration, whereas the WOR performance is independent of it. This bifunctional partitioning translated to a $2e^-$ ORR H_2O_2 selectivity of 94.5% in 0.1 M KOH and a $2e^-$ WOR selectivity up to 55% at 2.1 V vs. RHE. In a $2e^-$ electrolyzer, TiO_{2-x} delivered 20 mmol $L^{-1} h^{-1}$ of H_2O_2 at 2.0 V with a FE_{cell} of 134%. Importantly, *in situ* Raman spectroscopy evidenced that the anatase (101) plane remains stable under operation to improve defect-site durability under anodic bias. Subsequent studies pushed defect chemistry from qualitative toward quantitatively controlled and stability-validated. In the oxygen-deficient D-PSFZ perovskite oxides [Figure 6A], Zn^{2+} doping induces $\delta \approx 0.14$ –0.15 oxygen vacancies that regulate Fe/Zn electronic structures, strengthening $*OOH$ binding while increasing the adsorption energy of $*O$ intermediates to thermodynamically inhibit $4e^-$ ORR/OER. D-PSFZ achieved > 99% FE for $2e^-$ ORR over 0.05–0.45 V vs. RHE (0.1–2.0 M $KHCO_3$), retained 98% FE after 500 h, and reached 80% FE for $2e^-$ WOR at 2.15 V vs. RHE [Figure 6B]^[25]. In a membrane-free electrolyzer, the FE_{cell} reached 163% at 2.1 V and 50 mA cm^{-2} (remaining 150% after 100 h) [Figure 6C]. This study elegantly unifies the selectivity for the two key intermediates, $*OOH$ and $*OH$, into a thermodynamic suppression of their common decomposition intermediate, $*O$, by engineering an oxygen-deficient perovskite oxide rich in oxygen vacancies. DFT calculations reveal that Zn-doping-induced oxygen vacancies modulate the electronic structure of adjacent B-site cations, simultaneously optimizing the binding energies of both $*OOH$ and $*OH$ to promote the $2e^-$ ORR and $2e^-$ WOR, respectively. The crucial insight lies in introducing ΔG_{*O} as a more accurate selectivity descriptor, which unveils that $*O$ binding is energetically highly unfavorable on the vast majority of surface active sites. This fundamentally prohibits O–O bond scission, robustly steering the reaction towards H_2O_2 . Leveraging this intrinsic mechanism and the synergistic carbonate effect, the

bifunctional catalyst achieves up to 99% ORR selectivity and 80% WOR selectivity in a membrane-free symmetric electrolyzer. In another work, amorphous TiO_x embedded in mesoporous carbon hollow spheres ($\text{TiO}_x\text{@MCHS}$) combined abundant O_v with low-coordinated Ti^{3+} (average coordination number 5.1) [Figure 6D–F], enabling 55.5% FE for $2e^-$ WOR at 2.6 V vs. RHE [Figure 6G], alongside 99.3% FE for $2e^-$ ORR at 0.2 V vs. RHE with 104 mA cm^{-2} [Figure 6H]^[123]. When deployed in a membrane-free flow cell coupling synthesis system, the H_2O_2 yield rate reached $108.3 \mu\text{mol cm}^{-2} \text{ min}^{-1}$ at a constant current of 240 mA, and the total FE was 145% at a cell voltage of 2.5 V [Figure 6I]. Additionally, the FE only slightly decreased from 114% to 107% after 7 test cycles, indicating excellent stability in both structure and catalytic performance [Figure 6J].

Our group synthesized porous bismuth oxide nanorods enriched with oxygen vacancies ($\text{O}_v\text{-Bi}_2\text{O}_3\text{-EO}$) via *in situ* electrochemical oxidation of a bismuth-based metal-organic framework (MOF) precursor [Figure 7A–C]^[28]. The introduction of oxygen vacancies modulates the electronic structure of bismuth atoms, DFT calculations reveal that the introduction of oxygen vacancies significantly reduces the ΔG_{OOH} adsorption from 0.456 to 0.296 eV, thermodynamically promoting the $2e^-$ ORR, while the ΔG_{OH} is much higher than $\Delta G_{\text{H}_2\text{O}_2}$, rendering the dissociation of $^*\text{OOH}$ to $^*\text{O}$ energetically highly unfavorable and thus effectively suppressing the $4e^-$ ORR pathway^[28]. Concurrently, $\text{O}_v\text{-Bi}_2\text{O}_3$ lowers the energy barrier for $^*\text{OH}$ oxidation to H_2O_2 from 1.519 to 1.380 eV, whereas the barrier for the competing $4e^-$ WOR is as high as 1.801 eV, granting a thermodynamic preference to the $2e^-$ WOR. *In situ* Raman spectroscopy further confirms the preferential emergence of $^*\text{OH}$ intermediate signals at elevated potentials. The origin of this performance lies in the oxygen-vacancy-induced optimization of the Bi p-band center from -2.36 to -2.04 eV, which endows the catalyst with an optimal intermediate adsorption strength.

Under alkaline conditions, $\text{O}_v\text{-Bi}_2\text{O}_3\text{-EO}$ delivered an H_2O_2 selectivity as high as 90% for the $2e^-$ ORR at 0.4 V vs. RHE [Figure 7D], with a production rate of $0.465 \text{ mmol cm}^{-2} \text{ h}^{-1}$ in a flow cell configuration^[28]. In a 2 M KHCO_3 electrolyte, the same catalyst achieved an FE of 78.8% for the $2e^-$ WOR at 2.9 V vs. RHE, corresponding to a yield rate of $2.01 \text{ mmol cm}^{-2} \text{ h}^{-1}$ [Figure 7E]. Notably, when implemented in a flow cell configured for paired electrosynthesis, the integrated system exhibits an overall FE of 154.8% and a total H_2O_2 output of $4.3 \text{ mmol cm}^{-2} \text{ h}^{-1}$ [Figure 7F]. After 12 h of continuous operation, the accumulated H_2O_2 concentration remained at 159.1 mM, indicating good operational stability [Figure 7G]. These results collectively affirm the strong practical potential of $\text{O}_v\text{-Bi}_2\text{O}_3\text{-EO}$ for efficient and scalable electrochemical H_2O_2 production.

Despite these successes, defect strategies face some inherent questions, such as defect groups may be heterogeneous, dynamically variable, and difficult to clearly attribute to a single active site, especially under oxidative potentials. This limitation has prompted research to turn to more structurally certain regulatory methods, the most prominent of which is crystal surface engineering. In this strategy, the adsorption geometry is dominated by a clear crystalline surface, not a set of defects in the statistical sense. For example, CeO_2 nanocubes (NCs) that predominantly expose (100) facets have been reported as an efficient bifunctional electrocatalyst for H_2O_2 production via both the $2e^-$ ORR and the $2e^-$ WOR^[124]. Electrochemical measurements showed that the CeO_2 NCs achieved an H_2O_2 FE of 95.3% and a production rate of $632 \text{ mmol g}^{-1} \text{ h}^{-1}$ for the $2e^-$ ORR, significantly outperforming facet-unspecified CeO_2 nanodots (NDs)^[124]. Mechanistic studies combining spectroscopy tests indicated that the enhanced activity and selectivity were mainly governed by the crystal facet effect rather than oxygen vacancies^[124]. When deployed in a flow cell reactor for paired H_2O_2 electrosynthesis, the CeO_2 NCs attained a total H_2O_2 yield rate of $4.6 \text{ mol g}^{-1} \text{ h}^{-1}$, underscoring their practical potential for sustainable oxidant production.

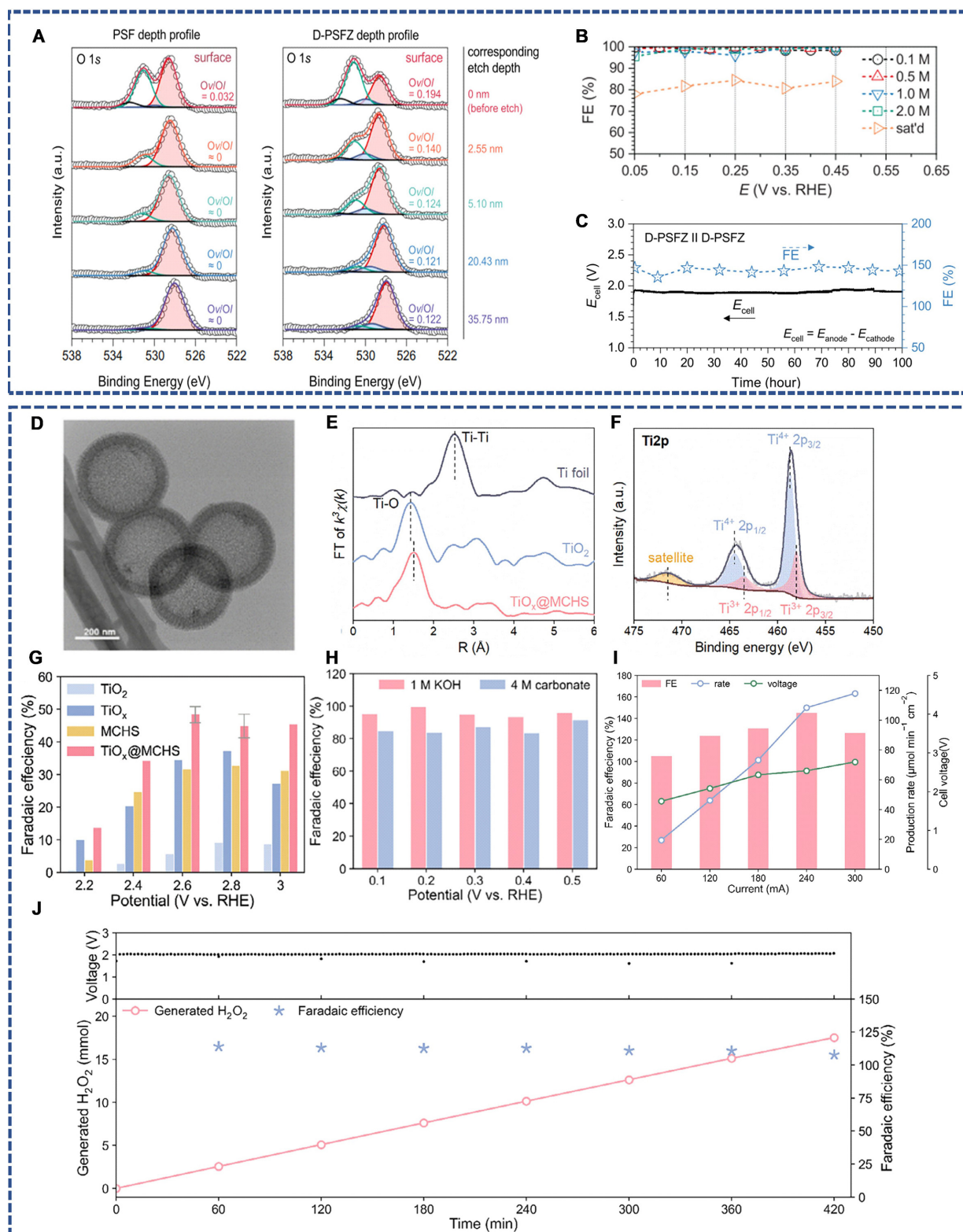


Figure 6. Symmetric catalytic electrode pairs for the concerted H₂O₂ production: (A) XPS depth profile analysis in the O 1s region for PSF and D-PSFZ and the corresponding O_v/O_i ratio upon the depth as the footnote; (B) 2e⁻ ORR FE of D-PSFZ at the various solution concentrations of 0.1 to 2.0 M and saturated KHCO₃ solution; (C) The stability profile for D-PSFZ || D-PSFZ E_{cell} measured in O₂ saturated 2.0 M KHCO₃/K₂CO₃ at 50 mA cm⁻²; (A-C) are adapted with permission from^[25]. Copyright © 2023 Springer Nature. (D) The TEM image of TiO_x@MCHS; (E) Fourier transform Ti K-edge EXAFS profiles of TiO_x@MCHS, Ti foil, and TiO₂; (F) The XPS Ti 2p spectra of TiO_x@MCHS; (G) The FE of H₂O₂ for 2e⁻ WOR over different catalysts as a function of potential tested in 1 M Na₂CO₃; (H) The FE of 2e⁻ ORR for H₂O₂ on TiO_x@MCHS at different potentials performed in a 1 M KOH or 3.5 M K₂CO₃ + 0.5 M KHCO₃ solution; (I) The H₂O₂ FE, generation rates and the total voltages of the 2e⁻ WOR//2e⁻ ORR cell at constant currents; (J) The FE, generation amounts of H₂O₂ and the cell voltages during long-term stability test at 120 mA (anode current density: 120 mA cm⁻²); (D-J) are adapted with permission from^[123]. Copyright © 2025 Wiley-VCH GmbH.

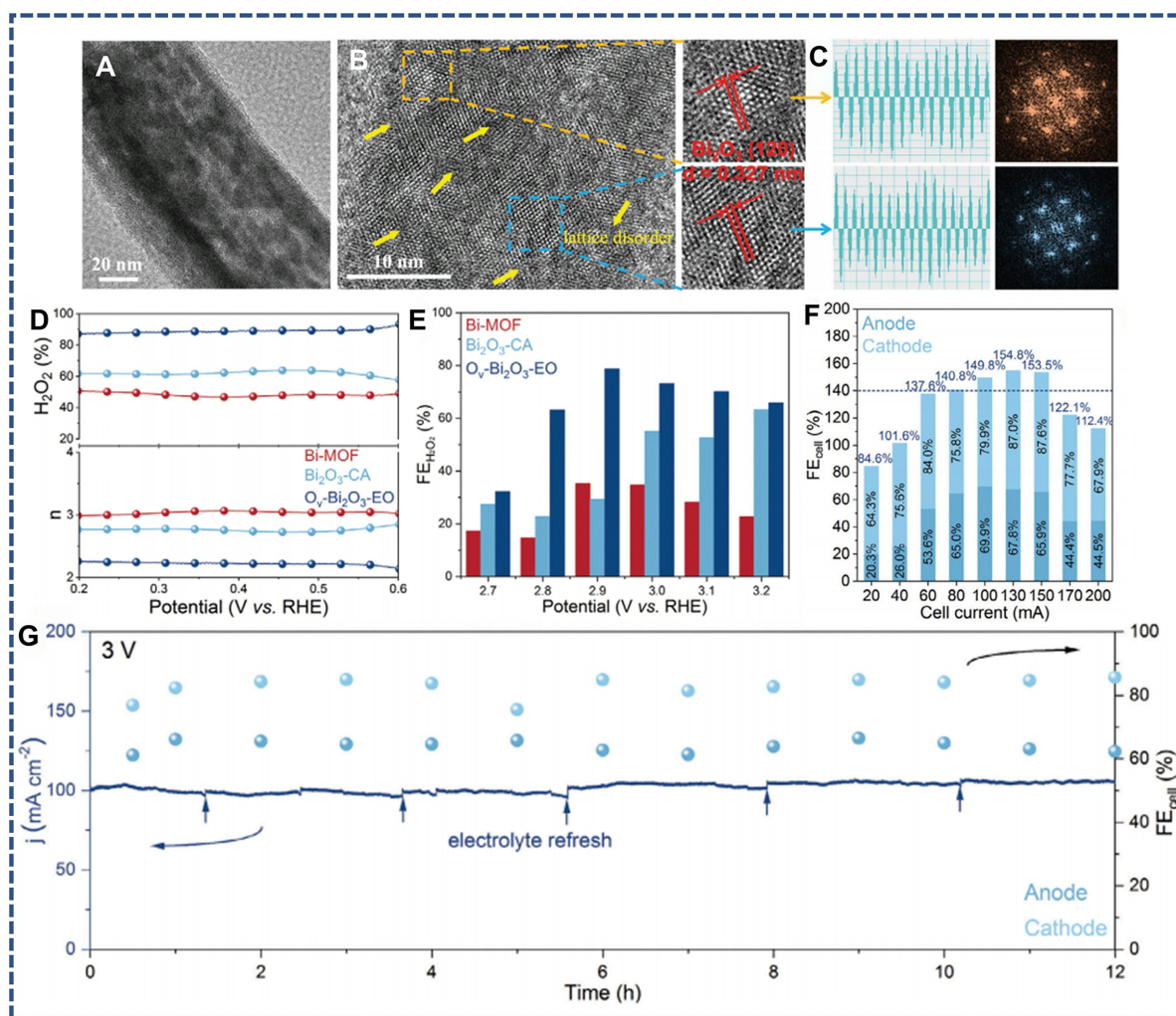


Figure 7. Symmetric catalytic electrode pair for the concerted H_2O_2 production: (A) TEM image of $\text{O}_v\text{-Bi}_2\text{O}_3\text{-EO}$; (B) and (C) HRTEM images of $\text{O}_v\text{-Bi}_2\text{O}_3\text{-EO}$; (D) Calculated H_2O_2 selectivity and electron transfer numbers based on LSV curves; (E) FE for $2e^-$ WOR; (F) FE_{cell} for H_2O_2 electrosynthesis at the cathode and anode under different current densities; (G) Long-term stability test of $\text{O}_v\text{-Bi}_2\text{O}_3\text{-EO}$ at the applied potential of 2.9 V; (A–G) are adapted with permission from [28]. Copyright © 2024 Wiley-VCH GmbH.

Interfacial engineering aims to create interfacial regions with distinct electronic structures by constructing heterojunctions^[125]. A representative example is the $\text{NiZnO}_x\text{-C}$ dual-site catalyst fabricated via the Kirkendall effect [Figure 8A], which simultaneously regulates (100) plane exposure and heterointerface density^[102]. Here, NiO_x clusters are dispersed within a ZnO_x matrix to generate an abundant $\text{NiO}_x/\text{ZnO}_x$ heterointerface. Oxygen vacancies and built-in electric fields at these interfaces facilitate water dissociation, producing reactive $^*\text{H}/^*\text{OH}$ species and improving interfacial charge transfer, features that directly benefit anodic kinetics and suppress parasitic O_2 evolution. Crucially, the catalyst implements an explicit site assignment, where the Zn sites dominate $2e^-$ ORR, while the Ni sites dominate $2e^-$ WOR [Figure 8B], thereby easing the conflicting adsorption requirements for $^*\text{OOH}$ versus $^*\text{OH}$. *In situ* ATR-FTIR and EPR spectroscopies confirmed the preferential adsorption of $^*\text{OOH}$ and $^*\text{OH}$ at the respective active sites, while DFT calculations revealed that interfacial charge transfer upshifts the d-band centers of both Zn and Ni, optimizing the adsorption energies of the key intermediates. This interface-driven water activation and dual-site spatial separation strategy enables a single catalyst to rapidly synthesize H_2O_2 at both electrodes simultaneously, achieving selectivity exceeding 90% for both $2e^-$ ORR and $2e^-$ WOR. The FE for H_2O_2 production increased with current from 400 to 1,200 mA, peaking at 148.5% at 1,000 mA [Figure 8C]. At 1 A,

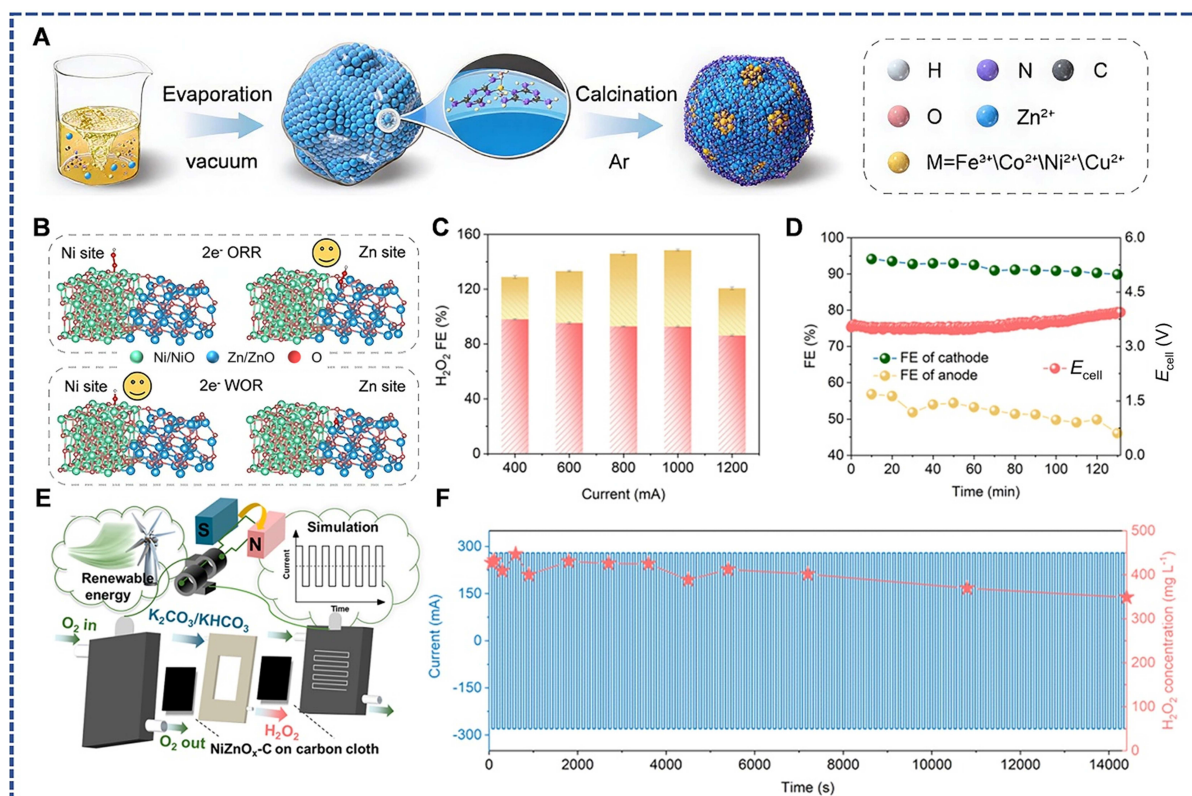


Figure 8. Symmetric catalytic electrode pairs for the concerted H_2O_2 production: (A). Schematic diagram of material synthesis; (B) Key intermediates adsorption schematic diagram of 2e^- ORR and 2e^- WOR; (C) FE_{cell} at current of 400–1200 mA; (D) The stability profile for H_2O_2 electrosynthesis coupling of 2e^- ORR and 2e^- WOR; (E) Simulated AC system for electrocatalytic H_2O_2 synthesis under intermittent renewable energy conditions; (F) Stability test of H_2O_2 production under AC; (A–F) are adapted with permission from^[102]. Copyright © 2025 Wiley-VCH GmbH.

the cell voltage remained stable near 3.5 V, while the FE_{cell} reached 150.9% before stabilizing at $\sim 140\%$ [Figure 8D]. In 0.1 M Na_2SO_4 , this design reached 96.7% H_2O_2 selectivity for 2e^- ORR and 93.6% for 2e^- WOR. In flow-cell tests, the FE_{cell} reached 145.8% under simulated alternating current (AC) operation with sustained H_2O_2 accumulation ($33,987 \text{ mg L}^{-1}$) after 4 h [Figure 8E and F]. This work is strategically important because it demonstrates how symmetry-specific operational modes (e.g., AC-like switching or polarity reversal) can synergize with interface-rich catalysts to maintain activity and mitigate degradation.

Except for oxides, Yang *et al.* prepared mesoporous carbon-doped boron nitride (C-doped BN) by high-temperature annealing of organic resin and silica composites in $\text{NaBH}_4/\text{NaNH}_2$ molten salts^[126]. Carbon substitution at B/N sites generates CB and CN defect interfaces, which narrows the BN band gap from 3.97 to 1.67 eV and improves electronic conductivity, while also providing active sites for both the 2e^- ORR and the 2e^- WOR^[126]. The defect active sites introduced by carbon doping respectively optimize the adsorption of $^*\text{OOH}$ and the conversion of $^*\text{OH}$. In 2 M KHCO_3 , the H_2O_2 FE for the 2e^- ORR reached 93%–98% with a yield rate of $1,650 \text{ mmol g}^{-1} \text{ h}^{-1}$, and the 2e^- WOR yield rate was $551 \text{ mmol g}^{-1} \text{ h}^{-1}$. When applied to an H-type cell in a coupling mode, the cathodic H_2O_2 yield rate reached $2,750 \text{ mmol g}^{-1} \text{ h}^{-1}$, achieving efficient coupling generation of H_2O . This system serves as a conceptual bridge, retaining a defect-interface logic while moving toward more chemically describable motifs than oxygen-vacancy ensembles in metal oxides.

An even more explicit approach is provided by a conductive MOF, Wang *et al.* prepared a nitrogen-bridged dual-atom Ni–Sn catalyst (NiSn–HITP) via a post-synthetic metallization strategy using the conductive MOF Ni–HITP as the support^[127]. In NiSn–HITP, the atomically dispersed Ni and Sn sites are precisely engineered

such that Sn predominantly serves as the active center for $2e^-$ ORR, while Ni facilitates $2e^-$ WOR^[127]. Crucially, the Ni-N-Sn coordination motif induces orbital coupling that upshifts the Ni d-band center and enhances the density of electronic states near the Fermi level, thereby simultaneously optimizing the adsorption energies of *OOH at Sn sites and *OH at Ni sites. The incorporation of Sn precisely regulates the electronic structure of Ni sites through orbital coupling among the Ni 3d orbitals, ligand N 2p orbitals, and Sn 5p orbitals, shifting the d-band center of Ni upward from -1.560 to -1.513 eV. Meanwhile, the adsorption energies of key intermediates are optimized. The adsorption energy of *OOH on Sn sites is reduced to 0.80 eV, suggesting thermodynamic stability, and the desorption barrier of *OH on Ni sites decreases from 1.72 to 1.41 eV, thereby suppressing the side reactions of $4e^-$ ORR to H_2O and $4e^-$ WOR to O_2 ^[127]. DFT calculations reveal that the formation of *OOH at Sn sites is exergonic (-0.80 eV), while the desorption barrier for *OH coupling to H_2O_2 at Ni sites is markedly reduced to 1.41 eV. *In situ* ATR-FTIR spectroscopy confirms the accumulation of *OOH and *OH intermediates during the ORR and WOR processes, respectively, validating the dual-pathway mechanism. This complementary dual-site catalysis enables breakthroughs in both FE and production rate in a single electrolytic cell. In 0.1 M KOH, NiSn-HITP reached an H_2O_2 selectivity up to 98.8% for the $2e^-$ ORR at 0.2 V vs. RHE, with a yield rate of $17.9 \text{ mol g}^{-1} \text{ h}^{-1}$ in the GDE system. Notably, the FE remained nearly 100% after a 15-h stability test^[127]. In 2 M $KHCO_3$, the H_2O_2 FE for $2e^-$ WOR reached 66.9% at 2.1 V vs. RHE, with an overpotential of 0.69 V at 10 mA cm^{-2} and a yield rate of $1.3 \text{ mol g}^{-1} \text{ h}^{-1}$. When applied in a membrane-free flow cell for coupled synthesis, the total FE reached 171.5% at a cell voltage of 3.0 V, and the total H_2O_2 yield rate was $9.1 \text{ mol g}^{-1} \text{ h}^{-1}$. After 15 h of stable operation at 50 mA cm^{-2} , the H_2O_2 concentration reached 0.61 wt%, demonstrating excellent practical application potential. Although the FE promoted by bifunctional catalysts has now exceeded 170%, practical large-scale H_2O_2 production via $2e^-$ ORR//WOR still requires a catalyst that can operate at the lowest possible potential, or deliver a current density of at least 200 mA cm^{-2} , while simultaneously achieving near-perfect selectivity and high FE, and maintaining its performance for a long duration (> 100 h). However, as shown in Figure 9, existing catalysts struggle to simultaneously meet these requirements. For instance, Ni-HTIP exhibits an exceptionally high H_2O_2 FE (> 170%), yet the corresponding potential is 3 V vs. the counter electrode and the current density under catalytic conditions is only 50 mA cm^{-2} , such performance falls far short of practical production demands. This is not an isolated case; this deficiency is common among the bifunctional catalysts we have investigated. Increasing the operating potential is indeed a strategy to raise the current density, thereby enhancing the rate of H_2O_2 generation. However, this approach often introduces significant competitive reactions, such as $1e^-$ and/or $4e^-$ pathways, and can even promote the decomposition of H_2O_2 ^[128]. Under highly oxidative conditions, the durability of the anode may also be compromised. Therefore, future research directions should take this practical issue into account to promote the industrial-scale mass production of electrocatalytic H_2O_2 .

For symmetric catalytic electrode pairs that need to simultaneously catalyze both the WOR and ORR, and to selectively regulate the conversion of the key intermediates *OH and *OOH , the existing literature has primarily developed strategies such as bifunctional active sites, precise regulation of oxygen vacancies, and interfacial micro-environment engineering. Based on these strategies, the design of symmetric catalytic electrode pairs can address the challenges of bifunctional catalysis while fully leveraging their unique advantages in structural simplicity and operational stability. Viewed through the strategy evolution, the symmetric catalytic electrode pairs advanced along a clear development route. The next-step designs are hybrids that fuse determinism across length scales: In the first place, facet-constrained defect construction places oxygen vacancies or low-coordination sites at crystallographically defined locations. Second, interface engineering combined with single-/dual-atom motifs, interfaces for water activation and charge mediation, and atomic motifs for precise $^*OOH/^*OH$ tuning. Methodologically, operando characterization that resolves how $^*OOH/^*OH$ energetics evolve under alternating redox polarization will be essential to transform these concepts into design rules, ensuring that half-reaction selectivity reliably translates to high-rate, long-life symmetric devices.

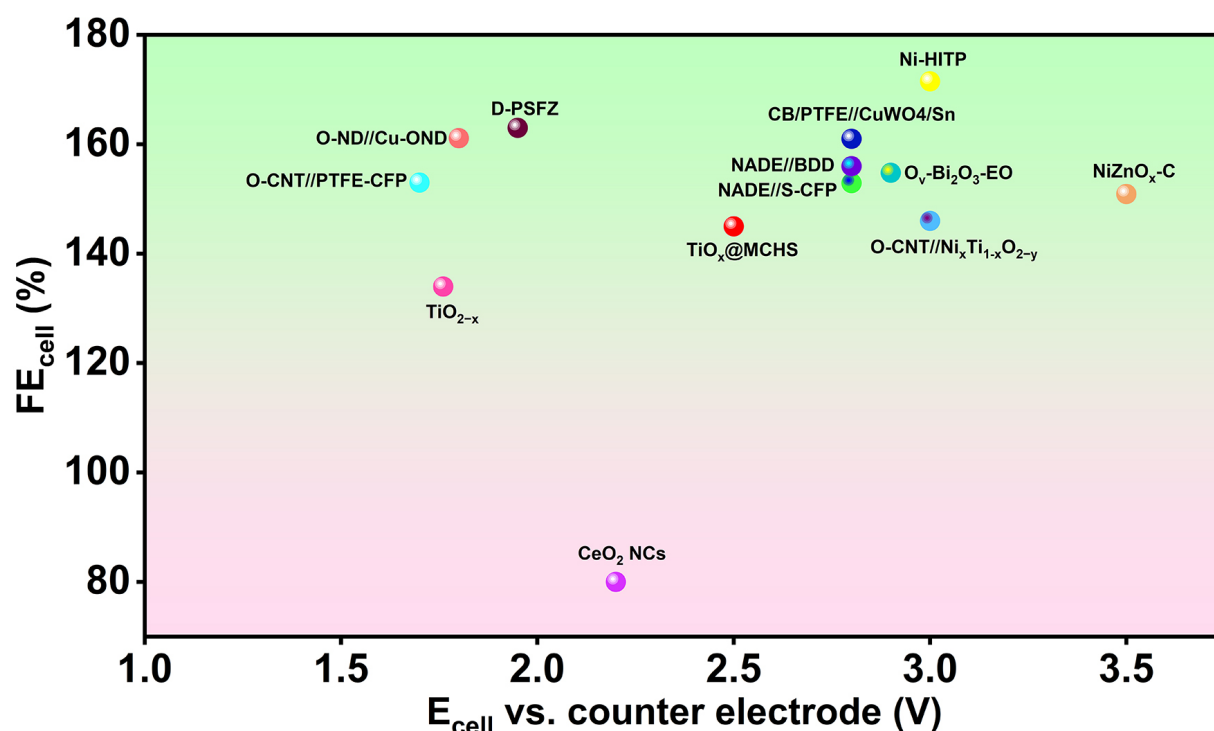


Figure 9. Faradaic efficiency (FE_{cell}) and cell voltage (E_{cell}) of the relevant catalysts for paired H_2O_2 electrosynthesis.

CONCLUSION AND OUTLOOK

Coupling the cathodic $2e^-$ ORR with the anodic $2e^-$ WOR to realize concerted H_2O_2 generation via paired electrosynthesis represents a sustainable electrochemical route that simultaneously improves electronic utilization and energy efficiency. Using O_2 and H_2O as feedstocks, H_2O_2 can be produced concurrently at both electrodes, which in principle drives the cell-level FE toward the $\sim 200\%$ upper limit and avoids the energy waste associated with employing the low-value OER as a sacrificial anodic process. In recent years, systematic progress has been achieved across both bifunctional electrode catalysts and electrolyzer configurations. Nevertheless, there is a broad consensus that $2e^-$ ORR//WOR concerted H_2O_2 production remains largely at the laboratory proof-of-concept stage, and several critical gaps must still be closed before engineering-scale implementation.

Firstly, prioritizing the $2e^-$ WOR pathway as the key breakthrough involves enhancing its selectivity, activity, and high-current compatibility. Relative to $2e^-$ ORR, the efficiency and selectivity of $2e^-$ WOR are more likely to constitute the bottleneck at the full-cell level, and deficiencies on the anodic side can directly cap the overall performance of paired systems. Future efforts should therefore advance in parallel along (i) suppression of competing reaction pathways; and (ii) regulation of key intermediate adsorption/turnover, with particular emphasis on maintaining $2e^-$ WOR selectivity at high current densities through material design and scalable electrode engineering. Additionally, a critical future direction lies in resolving the incompatibility of disparate electrolytes. This can be achieved through the rational design of membranes and robust solid-state electrolytes, which are pivotal for minimizing cross-contamination and enabling the continuous production of high-purity H_2O_2 . Prior studies have underscored the need for ion-transport membranes, while also noting that electrocatalytically produced H_2O_2 is frequently contaminated with electrolytes, which limits downstream utilization. Consequently, solid-state electrolytes and pure-water

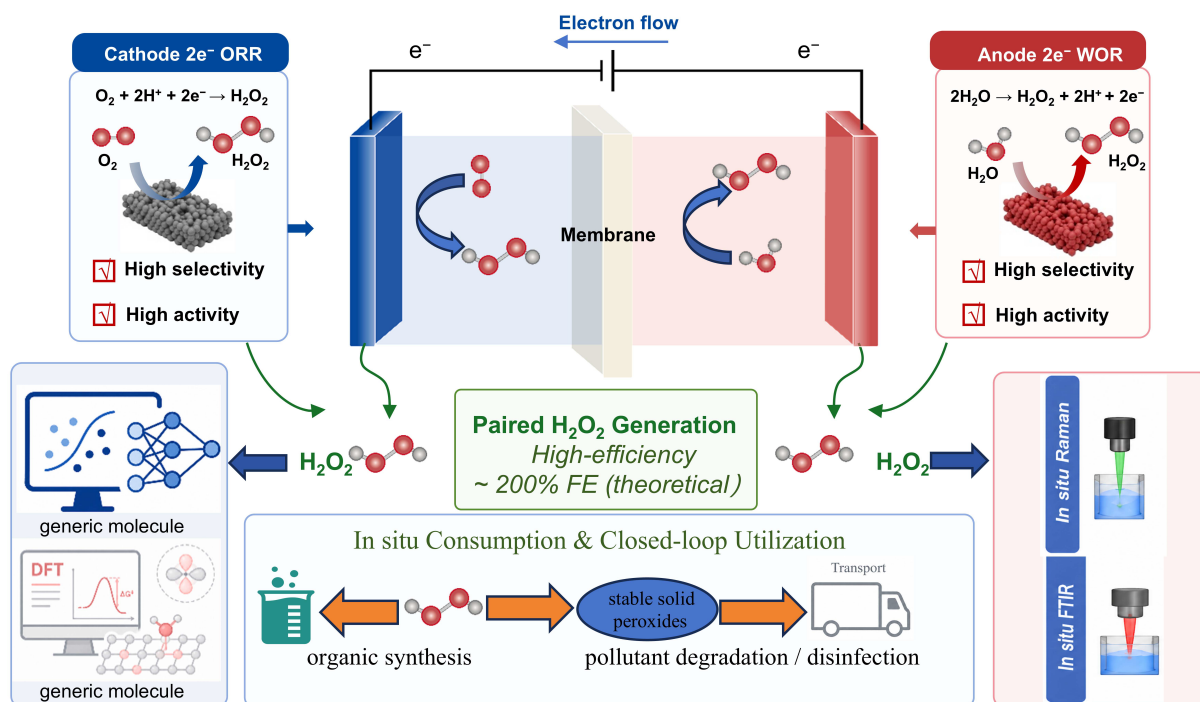


Figure 10. Paired electrosynthesis of H_2O_2 : from lab to application

operation are promising directions. In light of progress in polymer solid electrolytes and MEA concepts for H_2O_2 electrosynthesis, it is plausible that new electrolyzer paradigms will emerge for distributed production, featuring low electrolyte carryover or even electrolyte-free operation. And, the interplay between mechanism and characterization provides operando evidence, establishing a direct link between the 2e^- ORR//WOR synergy and the mitigation of side reactions. On the WOR side, bicarbonate/carbonate electrolytes may involve mediator pathways such as carbonate radicals and percarbonate species. However, a clearer picture is still required regarding how the true reaction network evolves with potential, electrolyte composition, and interfacial structure. Greater deployment of spatially and temporally resolved *in situ* and operando techniques (e.g., local pH mapping and liquid-cell TEM) is recommended to resolve interfacial dynamics and deactivation processes, thereby shifting the field from empirical screening to mechanism-guided design.

Second, when transitioning from laboratory-scale production to industrial implementation, the core advantage of H_2O_2 electrosynthesis over the anthraquinone process lies in its capability for on-site generation and immediate utilization within an integrated system. However, future application scenarios (e.g., photovoltaic- or wind-driven systems) are inherently intermittent and fluctuating, whereas most current laboratory studies operate under constant current or constant voltage modes, without considering the impact of fluctuating power input on catalyst performance and selectivity. This is critical because, for weakly adsorbing catalysts, the electric field can markedly alter the adsorption energy of $^*\text{OOH}$; for carbon-based catalysts, the electron transfer step is the rate-determining step under alkaline conditions. Given that different catalysts exhibit fundamentally distinct response behaviors to fluctuating power sources, future 2e^- systems must be specifically designed for compatibility with such power inputs. Specifically, this involves: first, developing catalysts capable of maintaining stable selectivity over a wide pH range (4–10) and a broad current density window ($10\text{--}300\text{ mA cm}^{-2}$), for instance through defect engineering or hydrophobic interface modification; second, establishing accelerated start-stop testing protocols that simulate real photovoltaic/wind power output profiles to evaluate the catalyst resistance to deactivation under fluctuating conditions; and finally, designing self-breathing or pumpless micro-reactors that reduce reliance on auxiliary equipment, thereby enabling instant-on, instant-off outdoor applications (e.g., disinfection in remote areas, field rescue operations). Our blueprint for future development, which addresses the existing problems, is

presented in Figure 10.

Next is the construction of a closed-loop production-utilization integration system. At present, most studies stop at collecting dilute H_2O_2 solutions (typically < 5 wt%) in electrolytes. However, because H_2O_2 is thermodynamically unstable and prone to decomposition, and its transportation and storage pose safety risks, the costs of concentration, storage, and transport often exceed the production cost itself. The future emphasis should therefore be on high-value utilization and *in situ* consumption of the product. Promising application directions that can be accelerated include: first, reactions where H_2O_2 serves as the oxidant, such as the Baeyer-Villiger reaction, aliphatic oxidation, aromatic hydroxylation; second, metal- H_2O_2 batteries, which employ H_2O_2 in place of O_2 as the cathodic oxidant, thereby bypassing the overpotential bottleneck of ORR/OER in conventional metal-air batteries (a theoretical loss of at least 0.4 V) and achieving higher energy density and power output. The core concept is that the electro-synthesized H_2O_2 , without undergoing concentration and storage, is fed directly into a downstream reactor or battery module. Accordingly, we propose that future 2e^- systems can be designed as integrated reaction-separation-conversion modules. Specific pathways include: (i) directly coupling the electrosynthesis system with advanced oxidation processes, where the produced dilute H_2O_2 solution is fed straight into a catalytic oxidation bed for the degradation of organic pollutants (e.g., antibiotics, dyes) or for disinfection, thus eliminating the need for separation and purification steps; (ii) *in situ* conversion of H_2O_2 into high-value solid peroxides, such as sodium percarbonate and sodium perborate, through simple reactions, these solid forms are more stable, easier to store and transport, and can be directly marketed as commercial bleaching and disinfecting agents; and (iii) coupling the 2e^- system with a metal- H_2O_2 battery, whereby H_2O_2 is electro-synthesized during off-peak or low-electricity-price periods and stored, and then discharged to release energy during peak periods, thereby achieving energy time-shifting from electrical to chemical and back to electrical energy.

DECLARATIONS

Acknowledgements

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Authors' contributions

Data curation, writing - original draft: Lu, X.

Data curation, figure design: Ma, D. D.; Wei, W.

Conceptualization, data curation, writing - editing, supervision: Han, S. G.

Writing - review and editing, funding acquisition, supervision: Zhu, Q. L.

Availability of data and materials

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AI and AI-assisted tools statement

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Conflicts of interest

Dr. Zhu, Q. L. is the guest editor of the special issue “Advanced Catalysts for Green Electrocatalysis and

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Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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