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**Recent advances in electrocatalytic oxygen reduction for on-site hydrogen peroxide synthesis in acidic media**

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ABSTRACT
Electrocatalytic oxygen reduction reaction (ORR) via two-electron pathway is a promising approach to decentralized and on-site hydrogen peroxide (H₂O₂) production beyond the traditional anthraquinone process. In recent years, electrochemical H₂O₂ production in acidic media has attracted increasing attention owing to its stronger oxidizing capacity, superior stability, and higher compatibility with various applications. Here, recent advances of H₂O₂ electrosynthesis in acidic media are summarized. Specifically, fundamental aspects of two-electron ORR mechanism are firstly presented with an emphasis on the pH effect on catalytic performance. Major categories of promising electrocatalysts are then reviewed, including noble-metal-based materials, non-noble-metal single-atom catalysts, non-noble-metal compounds, and metal-free carbon-based materials. The innovative development of electrochemical devices and in situ/on-site application of electrogenerated H₂O₂ are also highlighted to bridge the gap between laboratory-scale fundamental research and practically relevant H₂O₂ electrosynthesis. Finally, critical perspectives on present challenges and promising opportunities for future research are provided.

Keywords: Hydrogen peroxide; Oxygen reduction reaction; Acidic media; Selectivity; Electrosynthesis
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1. Introduction

Hydrogen peroxide (H$_2$O$_2$) is recognized as one of the 100 most important chemicals in the world with its annual production reaching 5.5 million tons in 2015 [1,2]. As a versatile and green oxidant, H$_2$O$_2$ is widely used in pulp and textile bleaching, chemical synthesis, disinfection and wastewater treatment [3–7]. Remarkably, U.S. Environmental Protection Agency listed H$_2$O$_2$ as one important disinfectant for COVID-19 [8], which has also been proposed to play a pivotal role in reducing the hospitalization rate and complications with the use of 0.5–3 wt% H$_2$O$_2$ [9]. Currently, more than 95% of H$_2$O$_2$ are synthesized by the multi-step anthraquinone process [10]. However, this process requires huge and centralized infrastructure, which makes it unsuitable for on-site and on-demand H$_2$O$_2$ production in remote areas. To lower the transportation and storage costs, additional distillation processes are performed to generate up to 70 wt% H$_2$O$_2$, leading to significant safety hazards. Other drawbacks of anthraquinone process include the substantial volume of waste generated from organic solvents, and extra costs incurred by the removal of unwanted stabilizers. To achieve decentralized H$_2$O$_2$ production, a more straightforward route is the direct synthesis of H$_2$O$_2$ from hydrogen (H$_2$) and oxygen (O$_2$) over Pd-based catalysts [11–14]. However, the mixture of H$_2$ and O$_2$ is explosive and thus requires dilution to keep away from the flammable range, which significantly limits the efficiency of this process. In addition, similar to anthraquinone process, direct synthesis also involves undesired removal of toxic additives such as acid promoters and halide ions. Consequently, there has been increasing interest in finding alternative methods that can overcome the issues related to anthraquinone and direct synthesis processes.

Compared with above-mentioned methods, electrocatalytic oxygen reduction
reaction (ORR) under ambient conditions offers a safe and environmentally friendly solution to decentralized \( \text{H}_2\text{O}_2 \) synthesis [15–19]. In ORR, oxygen molecules can be reduced to \( \text{H}_2\text{O} \) via four-electron (4e\(^-\)) reaction pathway or \( \text{H}_2\text{O}_2 \) via two-electron (2e\(^-\)) pathway [20]. Traditionally, 4e\(^-\) ORR is the cathode reaction in fuel cells, but if the selectivity is steered toward 2e\(^-\) process, \textit{in situ} \( \text{H}_2\text{O}_2 \) production can be achieved in fuel cell configurations while generating electric energy, and the danger of explosion is avoided by separating \( \text{H}_2 \) and \( \text{O}_2 \) [21]. \( \text{H}_2\text{O}_2 \) can also be formed in electrolysis cells powered by renewable electricity, which is an intrinsically green process and could be easily controlled by the applied potential. For electrochemical \( \text{H}_2\text{O}_2 \) production, the pH value of electrolyte is a critical parameter. While 2e\(^-\) ORR could occur in acidic, neutral or basic electrolytes, producing \( \text{H}_2\text{O}_2 \) in acidic environment is particularly attractive for a number of reasons. Firstly, given the acid dissociation constant of \( \text{H}_2\text{O}_2 \) (p\( \text{K}_a \) = 11.7), its main form in acidic media would be \( \text{H}_2\text{O}_2 \) instead of \( \text{HO}_2^- \). The stronger oxidation capacity of acidic \( \text{H}_2\text{O}_2 \) enables its efficient utilization in various industrial processes [22]. Secondly, \( \text{H}_2\text{O}_2 \) is more stable in acidic than in alkaline environment, as higher pH would facilitate its decomposition [23]. Thirdly, acidic \( \text{H}_2\text{O}_2 \) production is attainable in proton exchange membrane (PEM)-type devices, and PEM is a mature technology with good stability and ionic conductivity. Since \( \text{H}_2\text{O}_2 \) is the thermodynamically unfavorable product of ORR [24], rational design of electrocatalysts with high activity, selectivity and stability toward 2e\(^-\) ORR pathway is a precondition for acidic \( \text{H}_2\text{O}_2 \) generation.

To date, numerous materials have been identified as promising 2e\(^-\) ORR electrocatalysts in acidic electrolyte [6], such as noble metals and their alloys, non-noble transition metal compounds, single-atom catalysts (SACs), and metal-free carbon-based materials. Noble metal-based materials are currently the state-of-the-art
catalysts in acidic media with outstanding ORR activity and H₂O₂ selectivity. However, their scarcity and high cost largely hinder the practical application and trigger research in non-noble metal catalysts as promising alternatives. The performance of non-noble metal catalysts is generally inferior in acidic media to that in alkaline media. Catalyst engineering and a thorough understanding of pH effect are thus imperative to improve their catalytic performance [25]. Furthermore, beyond the development of electrocatalysts, innovations in electrochemical devices that scale up laboratory tests to practical applications are also necessary. In the 1930s, Berl pioneered the development of electrocatalytic ORR for H₂O₂ production [26]. This process was later commercialized to produce dilute H₂O₂ solution in alkaline media and used for pulp and paper bleaching, known as Huron-Dow process [14]. However, compared with catalyst design, relatively fewer efforts have been devoted to reactor design beyond such traditional processes for a long time. Recent progress in electrocatalysts has inspired a variety of novel device configurations to produce bulk or even pure H₂O₂ solution, such as flow cell, phase-transfer devices, and solid electrolyte cell [27,28]. The electrogenerated H₂O₂ in devices has shown promise for \textit{in situ} applications in degradation of organic pollutants, disinfection and chemical synthesis [29–31]. Ultimately, the combined progress of mechanistic insights, catalyst design, and electrochemical cell design will help realize practical H₂O₂ electrosynthesis and utilization.

Considering these facts, this review aims to sum up recent advances of H₂O₂ production from ORR in acidic environment. Firstly, fundamental aspects of acidic 2e⁻ ORR will be provided, with special emphasis placed on the reaction mechanism and the influence of electrolyte pH on catalytic performance over metal and non-metal catalysts. Based on this mechanistic understanding, major categories of state-of-the-
art electrocatalysts and their design strategies toward acidic H$_2$O$_2$ production will be summarized, including noble-metal based nanoparticles and SACs, non-noble-metal SACs, non-noble-metal compounds and metal-free carbon-based materials. Furthermore, the practical electrochemical devices for H$_2$O$_2$ generation and the *in situ* applications of electrogenerated H$_2$O$_2$ will be discussed in detail. In the final section, the critical challenges, future opportunities and research directions in the field of acidic 2e$^-$ ORR will be presented.

2. Fundamental aspects of acidic H$_2$O$_2$ production from ORR

2.1. Reaction mechanism

In general, electrocatalytic oxygen reduction is a multi-step reaction that can proceed through the competing 4e$^-$ and 2e$^-$ reaction pathways (Fig. 1a) [20]. In acidic media, the 4e$^-$ pathway generates water (H$_2$O) as the final product (O$_2$ + 4H$^+$ + 4e$^-$ → 2H$_2$O, $E^o = 1.23$ V vs reversible hydrogen electrode (RHE)) and involves three intermediates (*OOH, *O and *OH), which is extensively studied for fuel cell and metal–air battery applications [32,33]. On the other hand, the 2e$^-$ pathway leads to H$_2$O$_2$ generation (O$_2$ + 2H$^+$ + 2e$^-$ → H$_2$O$_2$, $E^o = 0.70$ V vs RHE). The 2e$^-$ pathway is comprised of two proton-coupled electron transfer (PCET) steps with only *OOH intermediate, as shown in Equation (1) and (2):

\[
O_2 + * + (H^+ + e^-) \rightarrow * \text{OOH} \quad (1)
\]

\[
* \text{OOH} + (H^+ + e^-) \rightarrow \text{H}_2\text{O}_2 + *
\] (2)

For selective 2e$^-$ ORR to happen, the cleavage of O–O bond should be avoided in order to suppress the undesirable formation of water. Both pathways share the common *OOH intermediate. The binding free energy of *OOH intermediate on the electrocatalyst ($\Delta G_{*\text{OOH}}$) should be appropriate, such that the O–O bond is preserved during catalysis [20]. Ideally, the binding strength of oxygen molecules on catalyst
surface should be strong enough to facilitate the production of *OOH, meanwhile the *OOH adsorption should be weak enough to allow H₂O₂ desorption. Therefore, an optimal catalyst needs to overcome the kinetic barriers of O₂ activation and *OOH protonation (desorption) for high activity, while maximize the kinetic barrier of *OOH dissociation (reduction) for high selectivity [34,35].

Fig. 1. Reaction mechanism of 2e⁻ ORR in acidic media. (a) Schematic illustration of 4e⁻ and 2e⁻ ORR pathways. Reprinted from Ref. [20] with permission from the American Chemical Society. (b) Schematic illustration of three adsorption modes of molecular oxygen on catalytic active sites. Reprinted from Ref. [36] with permission from the Royal Society of Chemistry. (c) Sabatier volcano plot of 2e⁻ ORR. (d) Free energy diagram of 4e⁻ and 2e⁻ ORR pathways on Au (111) surface. (c and d) are reprinted from Ref. [24] with permission from the American Chemical Society.

During ORR process, the adsorption of oxygen molecule is the first step and can provide unique insights into selectivity. The oxygen molecule can adsorb on the metal surface by three different modes: Pauling-type (end-on adsorption on one surface
atom), Griffith-type (side-on adsorption on one surface atom) and Yeager-type (side-on adsorption on two surface atoms) (Fig. 1b) [3,22,36,37]. The adsorption mode of oxygen is an important determinant of ORR selectivity. On bulk metal surfaces, side-on adsorption can elongate and weaken the O–O bond while the resulting *O and *OH intermediates can adsorb onto adjacent atoms, leading to significant H₂O production. In contrast, SACs with isolated active centers would favor end-on adsorption, which lowers the possibility of O–O bond cleavage with inherent advantage for H₂O₂ production [21,38,39]. Thus, optimizing the adsorption strength of reaction intermediates by tuning adsorption configurations represents a general strategy to design high-performance 2e⁻ ORR catalysts.

Over the past years, density functional theory (DFT) calculation has provided powerful tools for describing adsorption energies of intermediates on catalyst surface, and the results can be well-correlated with experiments in acidic media [21,40,41]. Nørskov et al. developed a computational hydrogen electrode (CHE) model to calculate the adsorption free energy of intermediates in which the chemical potential of a proton-electron pair is equivalent to that of 1/2 H₂ in gas phase at an electrode potential of \( U = 0 \) V [42]. The influence of electrode potential on free energies of intermediates is considered by defining the free energy of a proton-electron pair as \(-eU\), where \( e\) is elementary charge and \( U \) is electrode potential vs RHE. The scaling relation implies that there is only one degree of freedom in ORR [43], as the free energies of intermediates on metal surfaces are correlated by the equations: \( \Delta G^\circ_{\text{OOH}} = \Delta G^\circ_{\text{OH}} + 3.2 \pm 0.2 \) eV and \( \Delta G^\circ_{\text{O}} = 2\Delta G^\circ_{\text{OH}} \). \( \Delta G^\circ_{\text{OH}} \) can be used as a descriptor to construct a volcano-type relationship, where the limiting potentials are plotted as a function of \( \Delta G^\circ_{\text{OH}} \) (Fig. 1c) [24,35]. The lower limiting potential lines (solid lines) comprise the limiting potential for the overall reaction, and their intersection at the
peak of volcano plot corresponds to the equilibrium limiting potential of 2e\(^-\) ORR (0.70 V vs RHE). For catalysts at the left segment of the volcano, the strong binding of *OOH leads to easier formation of *O and *OH, causing the domination of 4e\(^-\) pathway. For catalysts lying on the right segment of the volcano, the weak binding of *OOH increases H\(_2\)O\(_2\) selectivity but decreases ORR activity [44]. Based on the classic Sabatier principle, an ideal catalyst should be situated near the volcano peak to have moderate binding strength of \(\Delta G_{*OH}\) and thus optimal H\(_2\)O\(_2\) production. Besides, kinetic parameters are also important to complement thermodynamic analysis and rationalize experimentally observed selectivity (Fig. 1d) [24]. For example, in the case of Au (111) surface, the free energy diagram indicates that the step of *OOH to H\(_2\)O\(_2\) is thermodynamically unfavorable as compared with O–O bond cleavage, but Au (111) is experimentally selective for H\(_2\)O\(_2\) formation due to the lower kinetic barrier of H\(_2\)O\(_2\) formation step [24,40]. This finding highlights the crucial roles of kinetic aspects on determining ORR selectivity. The combination of thermodynamic and kinetic insights will help guide rational design of electrocatalysts that are selective for H\(_2\)O\(_2\) production with low overpotentials [34].

2.2. The pH effect

Since the activity and selectivity of 2e\(^-\) ORR catalysts strongly depend on the pH values of electrolyte, it is critical to understand the effects of pH for rational catalyst design in acidic media. For example, the pH dependence for H\(_2\)O\(_2\) production on extended surfaces of polycrystalline (pc) Pt, Pt-Hg, Ag, Ag-Hg and glassy carbon was studied in 0.1 M HClO\(_4\) and 0.1 M KOH [14]. Ag(pc), Pt-Hg(pc) and Ag-Hg(pc) exhibited much higher selectivity toward H\(_2\)O\(_2\) production but slightly lower ORR activity in acidic media relative to alkaline media (Fig. 2a) [14]. In contrast, glassy carbon exhibited similar selectivity regardless of electrolyte pH, but its ORR current
density in 0.1 M HClO₄ was smaller than that in 0.1 M KOH. They reasoned that all catalysts studied bind *OOH weakly and their ORR activity would be limited by *OOH formation in acidic media. For metal-based catalysts, the kinetic barrier for O–O bond dissociation is higher in acidic media than that in alkaline media, indicating a less favored 4e⁻ ORR pathway and more selective H₂O₂ electrosynthesis in acidic media [14]. Compared to metal-based catalysts, the ORR activity of carbon-based catalysts is lower due to the intrinsically weaker *OOH binding, but their selectivity is less influenced by electrolyte pH.

The difference in electron transfer mechanisms under different pH conditions can also influence catalytic ORR performance. By varying electrolyte pH from 0 to 14, different species are present in the inner-Helmholtz plane (IHP) and outer-Helmholtz plane (OHP) of the double-layer structure at electrode-electrolyte interface (Fig. 2b) [45]. In acidic media, IHP consists of chemisorbed molecular O₂, adsorbed hydroxyl species (OH_ads) and solvent water dipoles, whereas OHP is populated by solvated molecular O₂ and electrolyte anions. As protons are abundant and highly mobile in acidic electrolyte, superoxide radical anion (·O₂⁻)_ads species formed by the first electron transfer to the adsorbed O₂ would soon be protonated with 4H⁺ and 4e⁻ to form H₂O as the final product. Under this circumstance, 4e⁻ ORR is promoted by the predominant inner-sphere electron transfer mechanism, with directly adsorbed molecular O₂ onto pristine Pt surfaces and stabilization of peroxide intermediate [45]. On the other hand, in a highly alkaline environment, water is both the proton source and the solvent, and the low rate of proton transfer is conducive to (·O₂⁻)_ads stabilization. In this case, outer-sphere electron transfer can occur by the non-covalent interaction (hydrogen bond) between *OH and the solvated O₂·(H₂O)ₙ cluster, which allows the desorption of *OOH intermediate and formation of HO₂⁻. However, it is
noticeable that the above explanation may not be applicable to some well-performed noble-metal catalysts in acidic media [7] and therefore more elaborate models are required to fully understand the pH-dependent $2e^-$ ORR behaviors.

**Fig. 2.** The effect of pH on $2e^-$ ORR process. (a) RRDE measurements and Faradaic efficiencies of polycrystalline Pt-Hg in 0.1 M HClO$_4$ and 0.1 M KOH. Reprinted from Ref. [14] with permission from the American Chemical Society. (b) Schematic illustration of inner- and outer-sphere electron transfer ORR mechanisms in acidic (left) and alkaline (right) electrolytes, respectively. Red: oxygen; Blue: hydrogen; Green: Alkali metal cation; Orange: Supporting electrolyte anion. Reprinted from Ref. [45] with permission from the American Chemical Society. (c) Surface chemistry and RRDE measurements of Fe-N-C catalysts in electrolytes with pH $>$ 10.5. Reprinted from Ref. [46] with permission from the American Chemical Society. (d) OOH$^-$ ion mechanism of $2e^-$ ORR on carbon catalysts. Reprinted from Ref. [60] with permission from the American Chemical Society.

The pH dependence of non-noble metal-nitrogen-carbon (M-N-C) catalysts in
ORR have also been reported [46,47]. Researchers studied the surface chemistry of Fe-N-C catalyst over a wide pH range (1.1–13.5) using X-ray photoelectron spectroscopy (XPS) in order to unveil the relationship between electrolyte pH and ORR activity/selectivity (Fig. 2c) [46]. It was shown that the number of accessible Fe–N$_x$ sites decreases with hydroxyl concentration. When the electrolyte pH is below 10.5, ORR is limited by PCET, and the protons on the surface of Fe-N-C catalyst neutralize adsorbed OH$^-$ toward 4e$^-$ ORR on Fe–N$_x$ active sites. When pH value is higher than 10.5, the excess OH$^-$ ions adsorbed at Fe–N$_x$ centers make ORR occur via the OHP mechanism, which is favorable for H$_2$O$_2$ production via 2e$^-$ ORR. Moreover, protonation of pyridinic nitrogen is critical to H$_2$O$_2$ production as it can provide protons for ORR and neutralize the adsorbed OH$^-$ at Fe–N$_x$ centers. Besides Fe-N-C, Co-N-C catalyst manifests pH-related ORR activity, selectivity and mechanism as well [47]. H$_2$O$_2$ selectivity of Co-N-C depends on both pH and potential; in acidic media, H$_2$O$_2$ selectivity increases with more negative potential, whereas in neutral and alkaline media, H$_2$O$_2$ selectivity remains nearly unchanged over the entire potential range.

The 2e$^-$ ORR performance of carbon-based metal-free catalysts under varying pH conditions is remarkably different from metal-based catalysts. In general, many functionalized carbon materials, such as defective carbon [48–50], oxidized carbon materials [51,52], nitrogen-doped carbons [53–55], boron-doped carbons [56], and boron-nitrogen co-doped carbon [57], can perfectly catalyze 2e$^-$ ORR in alkaline media with a low overpotential and outstanding H$_2$O$_2$ selectivity (> 90%). In neutral and acidic media, some carbon catalysts still maintain high selectivity, but their overpotentials are usually high due to the intrinsically weak *OOH adsorption [14]. In one study of N-doped carbon materials, the best H$_2$O$_2$ selectivity and durability were
achieved in neutral solution, where independent Rotating ring disk electrode (RRDE) and photometric UV-Vis techniques showed that H$_2$O$_2$ selectivity and formation rates are strongly dependent of pH in the order of neutral (KClO$_4$) > acid (HClO$_4$) > alkaline (KOH) on mesoporous N-doped carbons [58]. However, the reaction mechanism for neutral H$_2$O$_2$ synthesis is unclear and highly efficient catalysts are rather rare. Noffke et al. proposed an interface solvation model to understand acidic and alkaline ORR selectivity of a graphene nanostructure N-doped graphitic carbons [59]. As in enzyme-catalyzed reactions, the hydrophobic microenvironment around carbon electrocatalysts decreases the accessibility of water and destabilizes H$_2$O$_2$ molecule. In acidic electrolytes, this model implies that both 2e$^-$ and 4e$^-$ ORR are thermodynamically feasible, but the 2e$^-$ pathway is kinetically favored; whereas in alkaline electrolyte, the 4e$^-$ ORR pathway is both thermodynamically and kinetically favored. This model can be generalized to understand the pH-dependent selectivity of N-doped graphitized carbon materials.

Given that the adsorption barrier of oxygen molecules is high on the surfaces of carbon materials, alternative mechanisms that consider the interaction between O$_2$ molecules and hydrogen (H) site on carbon materials have been developed [60]. Different from metal-catalyzed ORR where H$_2$O$_2$ is formed by O$_2$ adsorption and subsequent reduction (ad-O$_2$ mechanism), on carbon materials, the O$_2$ molecule could abstract a catalyst H site to form OOH radical (or OOH$^-$) and undergo reduction reaction by decoupled proton-electron transfer process (Fig. 2d). The OOH$^-$ ion mechanism is probably dominant in acidic media, as it is thermodynamically more favorable than OOH radical mechanism and kinetically more favorable than ad-O$_2$ mechanism by around 0.3 eV [60]. The maximum limiting potential of OOH$^-$ ion mechanism under standard condition (0.36 V) agrees well with experimental values
(0.40 V) of metal-free carbons in acidic media [60]. For non-standard conditions, the limiting potential is estimated to be 0.44 V and can be altered by the ratio between sp² and sp³ hybridization. However, hydrogenation to O₂ by the surface H sites is less preferred with the increase in pH, and the ad-O mechanism that promotes H₂O₂ production dominates in alkaline media. On the other hand, the interaction between *OOH and hydrogen (proton) in the electrolyte was also proposed to rationalize the pH dependence of ORR selectivity on metal-free carbons [61]. Carbon catalysts prefer proton adsorption to the latter O atom in *OOH, resulting in immediate stabilization of OH⁻ and the breaking of O–OH bond. The energy barrier of O–OH bond breaking is lowered by 0.14 eV in the presence of protons (acidic condition) compared with systems without proton (neutral or alkaline condition), thus explaining the low H₂O₂ selectivity of carbon materials in acidic condition. In short, the diverse conclusions drawn from pH-effect models imply that more factors need to be considered for a thorough understanding of ORR mechanism on carbon materials in different electrolytes.

In summary, the pH effects for noble metal materials, transition metal SACs and carbon-based materials are different. Briefly, noble metals are the most active ORR catalysts and tend to be more selective for 2e⁻ pathway in acidic media than in alkaline media. The pH effect for SACs is complex, which depends on the metal center, coordination structure and chemical states of substrate. Carbon-based materials can exhibit similarly high H₂O₂ selectivity in both acidic and alkaline electrolytes, but are limited by poor activity in acids and thus suitable to produce H₂O₂ in alkaline media. The different pH-related behaviors among catalysts are explained by their difference in ORR mechanisms. Metal catalysts typically perform ORR through two PCET steps with *OOH intermediate [24], whereas alternative
mechanisms, such as OOH$^-$ ion mechanism [60], have been proposed for carbon materials. However, as there are several exceptions to the above-mentioned pH effects, the relationship between electrolyte pH and catalytic performance still needs further development.

3. Electrocatalysts for acidic H$_2$O$_2$ production from ORR

Electrochemical H$_2$O$_2$ production from 2e$^-$ ORR requires catalysts that meet several criteria, including high ORR activity, high H$_2$O$_2$ selectivity, high electrical conductivity, long-term durability, fast mass transport and low cost. Early studies of 2e$^-$ ORR catalysts were mainly performed in alkaline media; however, the base-catalyzed H$_2$O$_2$ decomposition largely hinders its practical application. As such, searching for suitable 2e$^-$ ORR catalysts in acidic media has attracted much attention recently. The most studied heterogeneous electrocatalysts toward acidic H$_2$O$_2$ production can be categorized as noble-metal based catalysts, non-noble-metal SACs, non-noble-metal compounds and metal-free carbon materials. This section provides a comprehensive overview of electrocatalysts that have achieved decent catalytic performance in acidic media, and some of the most representative findings is highlighted in Fig. 3 as a timeline.

**Fig. 3.** Timeline of some significant findings of 2e$^-$ ORR electrocatalysts in acidic media. The corresponding values of the highest H$_2$O$_2$ selectivity are provided for each

3.1. Noble-metal based catalysts

Noble-metal materials are the state-of-the-art catalysts for electrochemical $\text{H}_2\text{O}_2$ production in acidic media in terms of their small ORR overpotentials, high $\text{H}_2\text{O}_2$ selectivity and good stability under operating conditions [17]. Strategies to regulate the geometric structure in aspects of active site isolation, particle size, mass loading and inter-particle distance prove effective to tune the selectivity of pure metals [62–64]. Moreover, as monometallic nanoparticles are often inefficient in $\text{H}_2\text{O}_2$ electrocatalysis, electronic structure modulation by alloying with a secondary metal is effective to tune the binding energy of $^\ast\text{OOH}$ and prevent O–O bond dissociation for desired $2e^-$ selectivity [35].

3.1.1. Noble-metal based nanoparticles

*Regulating the geometric structure.* Pure noble-metal nanoparticles of Au, Pt and Pd have been widely investigated for $2e^-$ and $4e^-$ oxygen reduction. Among them, Au
is most suitable for $\text{H}_2\text{O}_2$ formation since it resides the right leg of the volcano-type activity plot and binds $^\ast\text{OOH}$ weakly [35]. Au-based catalysts such as Au/Vulcan XC-72R [65] and $\text{Au}_{25}(\text{SC}_{12}\text{H}_{25})_{18}$ nanoclusters [66] have been found to catalyze $2\text{e}^\text{-}$ ORR experimentally. However, the weak binding of $^\ast\text{OOH}$ on Au means low ORR activity and large overpotential. For pure Pt and Pd nanoparticles with strong binding of $^\ast\text{OOH}$ and high activity, their selectivity toward $2\text{e}^\text{-}$ ORR can be improved by regulating the surface geometry and accessibility of active sites. It is shown that by controlled carbon coating on Pt surface, the surface Pt sites are partially blocked and ORR selectivity is changed to $2\text{e}^\text{-}$ pathway (Fig. 4a) [62]. Due to steric hindrance effect, carbon coating decreases the availability of adjacent Pt sites and suppresses side-on adsorption mode of $\text{O}_2$. Instead, the thermodynamically unfavored end-on $\text{O}_2$ adsorption is forced on isolated sites, which facilitates selective $\text{H}_2\text{O}_2$ formation. Owing to the isolated sites, the carbon-coated Pt exhibited an onset potential of $\sim0.7$ V vs RHE and enhanced $2\text{e}^\text{-}$ selectivity of 41% [62].

The size of nanoparticle is another critical parameter in electrocatalytic $2\text{e}^\text{-}$ ORR. Smaller nanoparticles have larger surface to volume ratio and exposure of active sites, which would entail better electrocatalytic activity. For example, electrodeposited sub-5 nm amorphous Pd nanoparticles have shown $>95\%$ $\text{H}_2\text{O}_2$ selectivity across 0–0.6 V vs RHE with high partial kinetic current densities [63]. The lack of crystalline order also plays an important role in accelerating $\text{H}_2\text{O}_2$ synthesis. This versatile in situ synthesis can be used to derive ultra-small Pt particles with high tunability toward $2\text{e}^\text{-}$ ORR [63]. Besides, the mass loading of nanoparticles and inter-particle distance have great influence on the accessibility of active sites and thus $\text{H}_2\text{O}_2$ performance. It is discovered that ORR selectivity shifts from $2\text{e}^\text{-}$ to $4\text{e}^\text{-}$ pathway with the increase in Pd nanoparticles loading and decrease in inter-particle distance [64]. The degree of
particle dispersion clearly impacts product selectivity with more \( \text{H}_2\text{O}_2 \) formed on highly isolated sites, owing to the favored end-on adsorption configuration and enhanced release of \( \text{H}_2\text{O}_2 \) product [62].

**Fig. 4.** Noble-metal nanoparticles for electrochemical \( \text{H}_2\text{O}_2 \) production in acidic media. (a) End-on adsorption of \( \text{O}_2 \) molecule and \( \text{H}_2\text{O}_2/\text{H}_2\text{O} \) formation on carbon-coated Pt nanoparticles. Reprinted from Ref. [62] with permission from the American Chemical Society. (b) Schematic illustration and (c) free energy diagram of \( \text{PtHg}_4 \) (110) surface for selective oxygen reduction to \( \text{H}_2\text{O}_2 \). Reprinted from Ref. [35] with permission from Springer Nature. (d) Pd-Hg alloy for electrocatalytic \( \text{H}_2\text{O}_2 \) production. Reprinted from Ref. [21] with permission from the American Chemical Society. (e) Polarization curves of \( \text{PtP}_2 \) nanocrystals in \( \text{O}_2 \)-saturated 0.1 M \( \text{HClO}_4 \) at 1600 rpm. (f) Enhanced \( 2\text{e}^- \) ORR selectivity on \( \text{PtP}_2 \) nanocrystals by geometric and electronic effects. (e and f) are reprinted from Ref. [72] with permission from Springer Nature.

**Optimizing the electronic structure.** The interaction between \( \text{O}_2 \) molecule and mono-metal surfaces is not ideal. This has stimulated interest in alloying a host noble-metal with a secondary metal to induce electronic effects and tune the binding energy of ORR intermediates toward optimal level [35]. According to Sabatier’s principle,
this level corresponds to the peak of 2e\textsuperscript{−} ORR volcano plot where the binding of *OOH (or *OH) is neither too strong nor too weak, such that O\textsubscript{2} can be actively and selectively reduced to H\textsubscript{2}O\textsubscript{2}. As Pt and Pd bind *OOH too strongly, alloying with a catalytically inactive weak-binding metal is a possible way to improve their H\textsubscript{2}O\textsubscript{2} selectivity. In 2013, Siahrostami et al. identified that PtHg\textsubscript{4} is a promising candidate for H\textsubscript{2}O\textsubscript{2} electrosynthesis by DFT calculations with a thermodynamic overpotential lower than 0.1 V (Fig. 4b and 4c) [35]. Electrochemical measurements confirmed that in 0.1 M HClO\textsubscript{4}, Pt-Hg alloy shows a H\textsubscript{2}O\textsubscript{2} selectivity of up to 96% and a mass activity of 26 ± 4 A g\textsuperscript{−1} noble metal at an overpotential of 50 mV. Following this, the same group also screened other metals with Hg-modified surface and discovered that Pd-Hg and Ag-Hg outperform Pt-Hg for H\textsubscript{2}O\textsubscript{2} production [21]. Notably, Pd-Hg is situated closer to the peak of the volcano plot than previously reported Pt-Hg with five times higher activity per mass of precious metal, making it the state-of-the-art noble-metal catalyst for H\textsubscript{2}O\textsubscript{2} production in acidic media (Fig. 4d). Due to the toxicity of Hg, this alloying approach has also been extended to other Hg-free systems, including Au-Pd nanoparticles [67,68], PdAu nanoframes [69], and atomically dispersed Pt@AuCu [70]. Because Au binds *OOH relatively weakly, alloying Au with the strong-binding Pd is promising to achieve better electrocatalytic performance. For example, PdAu nanoframes prepared by controlled solution growth and etching exhibited much enhanced onset potential (~0.56 V vs RHE) and H\textsubscript{2}O\textsubscript{2} selectivity (> 90%) in acid superior to pure Au and other Au alloys [69]. The introduction of dilute Pd atoms to PdAu nanoframes could stabilize the adsorption of *OOH through direct Pd–O bonding, which was identified as the origin of enhanced 2e\textsuperscript{−} ORR performance.

Furthermore, the interplay between electronic effect and geometric site isolation effect is more advantageous to boost H\textsubscript{2}O\textsubscript{2} activity and selectivity. For example, the
partially oxidized Pd clusters with an average size of 0.61 nm loaded on oxidized carbon nanotube (Pd\textsuperscript{δ+}-OCNT) was reported to manifest 95–98% selectivity for H\textsubscript{2}O\textsubscript{2} production and unprecedented mass activity of 1.946 A mg\textsuperscript{−1} in acidic media [71]. It has been revealed that the exceptional 2e\textsuperscript{−} ORR performance originates from the interaction between small Pd clusters (Pd\textsubscript{3} and Pd\textsubscript{4}) and epoxy functional groups of carbon, which moves the catalyst toward the apex of thermodynamic volcano plot. In another work, platinum diphosphide (PtP\textsubscript{2}) nanocrystals synthesized by hot-injection method displayed 98.5% H\textsubscript{2}O\textsubscript{2} selectivity at 0.27 V vs RHE with negligible overpotential (Fig. 4e) [72]. DFT calculations implied that P is responsible for lowering the end-on adsorption energy of O\textsubscript{2} molecule and weakening the binding strength of Pt–OOH\*, rendering PtP\textsubscript{2} highly selective for 2e\textsuperscript{−} ORR (Fig. 4f). Very recently, it has been reported that alloying Pd with semi-metal Se could derive Pd\textsubscript{4}Se\textsubscript{4} nanoparticles for pH-universal H\textsubscript{2}O\textsubscript{2} electrosynthesis [73]. PdSe\textsubscript{4} outcompeted commercial Pd/C and Pd-based nanoparticles in terms of better H\textsubscript{2}O\textsubscript{2} selectivity (93.5%) in 0.1 M HClO\textsubscript{4} and durability after 5000 cycles. The incorporation of Se atoms leads to both geometric effect and electronic effect for the remarkable performance. The isolated Pd atoms by Se would favor end-on adsorption of oxygen, and the strong p-d repulsion promotes mismatch of O-2p band to stabilize *OOH, both of which are favorable factors for 2e\textsuperscript{−} ORR process.

3.1.2. Noble-metal single-atom catalysts

Recently, single-atom catalysts have attracted great attention for their unique structure and outstanding performance in electrocatalytic H\textsubscript{2}O\textsubscript{2} production [22]. Unlike their bulk nanoparticle counterparts, SACs usually contain atomically dispersed metal atoms over metal compounds or carbon-based substrates, and the utilization efficiency of metal is thus maximized (∼100%) [74]. Their well-defined
active centers allow clear characterization of structure-property relationships, while the electronic structure of SACs can be modified by tuning metal atoms and their coordination environment \[22,75\]. More importantly, SACs are intrinsically suitable for selective \(2e^-\) ORR in terms of the adsorption configuration of oxygen molecules. As discussed in Section 2, the isolated metal sites in SACs would favor end-on (Pauling-type) adsorption of \(O_2\) instead of side-on adsorption. For end-on adsorption, the axis of \(O-O\) bond is vertical to the material surface, which lowers the possibility of \(O-O\) bond dissociation and is beneficial for the desorption and release of \(H_2O_2\).

**Fig. 5.** Noble-metal single-atom catalysts for electrochemical \(H_2O_2\) production in acidic media. (a) Atomically dispersed Pt catalysts in sulfur-doped zeolite-templated carbon. Reprinted from Ref. [77] with permission from Springer Nature. (b) Schematic illustration of the support effect in Pt SACs with high \(H_2O_2\) selectivity for Pt/TiC. Reprinted from Ref. [80] with permission from the American Chemical Society. (c) Schematic illustration of highly concentrated Pt single atoms embedded in amorphous CuS\(_x\) support. Purple: Pt; Blue: Cu; White: S. Reprinted from Ref. [81] with permission from Elsevier. (d) Pd single atom hotspots at Au\(_{1-x}\)Pd\(_x\) nanoalloys for selective \(H_2O_2\) production. Reprinted from Ref. [5] with permission from Springer
In acidic solution, Pt is a well-known $4e^-\text{ORR}$ catalyst; however, similar to active site isolation of nanoparticles, the selectivity can be shifted to $2e^-\text{pathway}$ when Pt is dispersed on atomic scale [76–78]. For example, Choi et al. synthesized atomically dispersed Pt catalysts (5 wt%) embedded in sulfur-doped zeolite-templated carbon (ZTC) using a facile wet-impregnation method. The sample achieved selective $\text{H}_2\text{O}_2$ production in 0.1 M HClO$_4$ with an electron transfer number of 2.1 and $\text{H}_2\text{O}_2$ production rate of 97.5 μmol h$^{-1}$ cm$^{-2}$ in an electrochemical H-cell reactor [77]. This performance is ascribed to the unique structure of Pt SACs compared with bulk Pt nanoparticles, as polycrystalline Pt surface would favor further reduction of $\text{H}_2\text{O}_2$ [79]. The substrate also plays a crucial role in affecting the ORR selectivity of Pt SACs. Pt single atoms supported on titanium carbide (Pt$_1$/TiC) showed higher activity, selectivity and stability for electrocatalytic $\text{H}_2\text{O}_2$ production than those on titanium nitride (Pt$_1$/TiN) (Fig. 5b) [80]. DFT analysis explained that Pt$_1$/TiC prevents the O–O bond from dissociation, whereas Pt$_1$/TiN affords strong affinity of oxygen species and poisons the catalyst surface. Therefore, it is important to carefully select the substrate when designing SACs, as it not only provides anchoring sites for metal atoms but also directly tunes the electrocatalytic ORR pathway. In addition, SACs are often plagued by limitations in metal loading and thus low activities. If the amount of isolated active sites is increased, the resulting catalysts can achieve desired selectivity without compromising their electrochemical activity. For example, Shen et al. designed a novel ion exchange method to prepare single atomic Pt supported on amorphous CuS$_x$ with an exceptional concentration of Pt (24.8 at%) (Fig. 5c) [81]. The obtained sample achieved a high $\text{H}_2\text{O}_2$ selectivity of 92–96% over a wide potential range of 0.05–0.7 V vs RHE and a great kinetic $\text{H}_2\text{O}_2$ generation mass.
activity of 35 A mg\textsubscript{cat}^{-1} at 0.4 V vs RHE in 0.1 M HClO\textsubscript{4} electrolyte.

Apart from Pt, noble metals such as Au and Pd SACs also exhibit great potential toward 2e\textsuperscript{-} ORR pathway in acidic media. By combining DFT calculations and experiments, Sahoo et al. investigated transition metal M-SACs (M = Cu, Ag, Au, Ni, Pd or Pt) supported on TiC substrates and demonstrated that Au and Pd SACs are more promising for acidic H\textsubscript{2}O\textsubscript{2} production than Pt SACs [82]. At applied potential of 0.2 V vs RHE, the H\textsubscript{2}O\textsubscript{2} selectivity of Au and Pd SACs are 87\% and 80\%, respectively, compared to 71\% of Pt SACs. The promoting effect of Pd single atoms for H\textsubscript{2}O\textsubscript{2} production was also shown in a report by Jirkovský et al., where the increase of atomically dispersed Pd content to 8 wt\% in Au nanoparticles results in corresponding increase in H\textsubscript{2}O\textsubscript{2} selectivity (up to 95\%) [83]. The selectivity improvement is attributed to the isolated surface Pd atoms present in Au\textsubscript{1-x}Pd\textsubscript{x} nanoalloys that favor side-on adsorption of oxygen and thus selective 2e\textsuperscript{-} ORR process (Fig. 5d) [83]. Pd supported on C@C\textsubscript{3}N\textsubscript{4} [84], Pd bound with defect graphene [85] and PdCl\textsubscript{x}/C [86] are also among the Pd SACs with high H\textsubscript{2}O\textsubscript{2} selectivity. In another work, Kim et al. designed a general strategy to synthesize noble metal (Os, Ru, Rh, Ir and Pt) SACs by immobilizing metal precursors in carbonaceous coating and SiO\textsubscript{2} layer [87]. It was discovered that the binding energy difference between *OOH and *O governs the H\textsubscript{2}O\textsubscript{2} selectivity, with the Rh SACs possessing the best ORR activity and Pt SACs showing the highest selectivity. In summary, compared to noble-metal nanoparticles, noble-metal SACs with isolated active sites favor end-on O\textsubscript{2} adsorption and H\textsubscript{2}O\textsubscript{2} formation due to the lack of neighboring sites. The selectivity toward 2e\textsuperscript{-} ORR can be further tailored by the type and content of metal center, coordination structure, and support matrix.

3.2. Non-noble-metal single-atom catalysts
Non-noble-metal SACs are emerging as alternatives to replace noble-metal based catalysts in a wide range of electrocatalytic reactions [74,88–90]. In ORR, while the most explored metal-nitrogen-carbon (M-N-C) type SACs have offered excellent performance comparable to that of noble-metal based catalysts toward 4e\textsuperscript{–} process, fewer studies have focused on tuning the selectivity to produce H\textsubscript{2}O\textsubscript{2} [91–93]. The structure-property relationship of SACs is dependent on metal centers, local coordination environments and host matrix, which makes the rational design of selective catalysts more elusive than previously thought [94]. Without a clear identification of real active sites and catalytic mechanism, the reported performances of SACs are sometimes contradictory even for the same catalyst. For example, Co-N-C SACs have been reported as promising candidates for fuel cell applications due to their outstanding 4e\textsuperscript{–} ORR performance [95–98], yet a few studies also show their ability to selectively catalyze 2e\textsuperscript{–} ORR [99,100]. For this reason, it is necessary to acquire atomic-level insights into SACs design for H\textsubscript{2}O\textsubscript{2} electrocatalysis.

At the atomic level, transition-metal based SACs usually consist of atomically dispersed metal centers coordinated in a carbon-based matrix. This chemical feature combines the advantages of both homogeneous catalysts and heterogeneous catalysts, exhibiting high electrochemical activity without compromising durability. The structure of SACs has been compared with naturally occurring metalloenzyme systems, which offers unique and comprehensive understanding of active sites in electrocatalytic reactions [34,100–102]. Metalloenzymes are comprised of metal centers, the immediately surrounding organic ligands (first coordination sphere) and ligands bonding to the first coordination sphere (second coordination sphere) [103]. Analogously, the catalytic performance of SACs can be collectively influenced by metal center, atoms in the first coordination sphere and functionalization in the second
coordination sphere (Fig. 6a) [34]. Thus, regulation of these components is expected to derive SACs with desired acidic ORR activity and selectivity [104,105].

3.2.1. Regulation of metal center and first coordination sphere

The ORR selectivity of SACs largely depends on the central metal atom. In most cases, metal center is the active site that does the catalysis, and its careful selection is able to achieve appropriate binding of ORR intermediates for desired 2e⁻ selectivity.
Sun et al. investigated the effect of 3d metal on the 2e\(^{-}\) ORR activity and selectivity of M-N-C (M = Mn, Fe, Co, Ni, Cu) SACs [47]. Co-N-C was found to be the optimal catalyst due to its highest ring current for ORR (0.18 mA at 0.1 V vs RHE), highest selectivity for acidic H\(_2\)O\(_2\) production (80% at 0.1 V vs RHE) and lowest activity for H\(_2\)O\(_2\) reduction (Fig. 6b). In another study, the Co-N-C anchored in N-doped graphene was also identified as ideal 2e\(^{-}\) ORR catalyst exceeding the performance of state-of-the-art noble-metal based catalysts [99]. In 0.1 M HClO\(_4\), the kinetic current of Co SACs reached 1 mA cm\(^{-2}\) at 0.6 V vs RHE with H\(_2\)O\(_2\) Faradaic efficiency > 90%, as well as stability for a period of 10 h. DFT calculations revealed that the binding energies of ORR intermediates over transition metals increase with the number of valence electron, and Co SACs has the optimized binding energy of *OOH, rendering Co–N\(_4\) motif as the active site for H\(_2\)O\(_2\) production (Fig. 6c) [99].

To confirm the crucial role of metal centers, Liu et al. adjusted the metal centers in SACs while controlled the coordination environment by the same porphyrin moieties using well-defined covalent organic framework models [106]. They drew similar conclusion that Co is the most intrinsically active, and showed that difference in binding energy of *O\(_2\) and *HOOH could serve as a new descriptor to evaluate the activity of SACs.

Introducing metals into carbon skeleton inevitably induces changes in the electronic structure of neighboring atoms. Therefore, beyond controlling metal centers, regulating first coordination sphere is deemed important for H\(_2\)O\(_2\) production as well. By varying center atoms (Fe, Pd, Co, Mn) and adjacent coordination atoms (N, O, C), researchers established a trend in ORR pathway and elucidated the effect of metal centers and first coordination sphere in alkaline media [30]. Fe-C-O motif displays the best performance for H\(_2\)O\(_2\) generation with the highest H\(_2\)O\(_2\) selectivity >
95%; in contrast, when the coordinating atom is changed to N, Fe-C-N motif becomes selective for $4e^{-}$ ORR. Similarly, Mo SACs with sulfur and oxygen dual-coordination could tune the adsorption behavior toward $2e^{-}$ ORR in alkaline electrolytes [75]. Single-atom Mo complex is the active origin of $2e^{-}$ ORR, whereas atoms in the first coordination sphere (Mo–S$_4$–C and Mo–O$_3$S–C) greatly affect the reaction pathway. It is noticeable that the resultant Mo SACs have a high metal loading of > 10 wt% without agglomeration, which represents a promising strategy for large-scale synthesis of high-loading SACs toward high activity and selectivity. The above studies were mainly conducted in alkaline media, but it is expected that strategies to engineer first coordination sphere are also applicable for acidic $\text{H}_2\text{O}_2$ production.

**3.2.2. Regulation of second coordination sphere**

Although second coordination sphere does not directly interact with metal center, recent studies have shown its importance in fine-tuning the adsorption configurations and affecting catalytic behaviors. Jung et al. found that the *OOH binding on Co-N-C SACs could be tuned by the surrounding atomic configuration of Co [100]. Specifically, introducing electron-deficient *H or electron-rich *O has different effects on the charge state and ORR intermediate binding energy of Co-N$_4$/graphene moieties. When oxygen groups are attached near Co–N$_4$ to form Co–N$_4$(O), $\Delta G_{\text{OOH}}$ increases from 3.9 eV to 4.1 eV, becoming closer to the peak of volcano where $\Delta G_{\text{OOH}} = 4.2$ eV. When the electron-poor hydrogen groups are adsorbed, $\Delta G_{\text{OOH}}$ decreases from 3.9 eV to 3.8 eV. As such, it is possible to fine-tune the electronic structure of Co–N$_4$ in the second coordination sphere. Guided by insights from theoretical prediction, the researchers synthesized Co$_2$G(O) with electron-rich oxygen species (such as C–O–C) surrounding Co centers, resulting in selective $\text{H}_2\text{O}_2$ production in 0.1 M $\text{HClO}_4$. Furthermore, the role
of surface epoxy groups in the second coordination sphere was also confirmed by another research group (Fig. 6d) [107]. In acidic electrolytes, Co SACs on N-doped carbon nanotubes showed previously unachieved near-zero overpotential and ~100% selectivity for 2e\textsuperscript{-} ORR. To rationalize this exceptional performance, spectroscopic analyses proved that the presence of epoxy groups near Co–N\textsubscript{4} centers significantly modifies the electronic structure of Co atoms, uncovering the synergy between Co–N\textsubscript{4} and second coordination sphere (epoxy O).

Very recently, the synergetic modification of first coordination sphere and second coordination sphere has been reported to optimize electrocatalytic 2e\textsuperscript{-} ORR of SACs in acidic media (Fig. 6e) [34]. Theoretically, similar to metalloenzymes, changes in the first and second coordination spheres of SACs affect the electronic structures and intermediate adsorption behavior. In Co SACs, Co atoms coordinated with N and O (CoNOC) exhibited H\textsubscript{2}O\textsubscript{2} selectivity of > 95%, in sharp contrast to the low selectivity < 30% over pure N-coordinated catalyst (CoNC) [34]. The combined calculations and \textit{in situ} infrared absorption spectroscopy confirmed that both first and second coordination spheres are critical to the performance of SACs. In the first coordination sphere, different coordinating atoms (N, O, etc.) could modulate the binding energy of *OOH on Co centers, as witnessed by the selectivity difference of CoNC and CoNOC. Introducing O atom into first coordination sphere (Co–N\textsubscript{x}) weakens the adsorption of *OOH, and shifts the active sites from Co center to the nearby O-adjacent carbon. In the second coordination sphere, Bader charge analysis revealed a negative relationship between ΔG\textsubscript{*OOH} and charge state of catalytic active carbon atoms. The CoO\textsubscript{4}(O) is an exception, where the out-of-plane epoxy group exerts steric hindrance to stabilize *OOH binding as confirmed by charge difference analysis. This work highlights the molecular-level design principles of SACs for
efficient electrocatalysis.

3.3. Non-noble-metal compounds

Apart from non-noble-metal SACs, a number of non-noble-metal compounds have also been investigated for acidic 2e\(^{-}\) ORR process, such as metal chalcogenides [108–113], metal oxides [114–116], metal-organic framework [117], and hybrids [118]. The activity, selectivity and stability toward H\(_2\)O\(_2\) production are highly dependent on their nanostructure, morphology, composition and exposed facets. Furthermore, these compounds are often supported on carbon materials to enhance conductivity and better isolate active sites, which can optimize adsorbate binding and thus improve their catalytic performance. For example, Sheng et al. reported a combined experimental and computational study to demonstrate that cobalt pyrite (CoS\(_2\)) is an active and selective 2e\(^{-}\) ORR electrocatalyst in acidic and neutral solutions [109]. In 0.05 M H\(_2\)SO\(_4\), CoS\(_2\) drop-casted on RRDE showed its intrinsic H\(_2\)O\(_2\) selectivity peaking at 70\%–80\%, while CoS\(_2\) nanowires supported on carbon fibers paper showed a selectivity of \(~70\%\) at 0.5 V vs RHE in bulk ORR electrolysis. Computation modelling revealed that this performance is attributed to the modest binding of *OOH on the isolated Co site of CoS\(_2\) (100) facet and the suppressed O–O bond cleavage in kinetics. In a more recent work, the same group discovered that two structural polymorphs of cobalt diselenide (CoSe\(_2\)), i.e. the cubic pyrite-type (c-CoSe\(_2\)) and the orthorhombic marcasite-type (o-CoSe\(_2\)), are selective for H\(_2\)O\(_2\) electrosynthesis and stable against catalyst leaching [110]. Surface Pourbaix diagrams confirmed the weak binding of *O to Se sites and better stability of Co atoms than those in CoS\(_2\). In electrochemical H-cell setup, o-CoSe\(_2\) nanowires grown on carbon paper electrodes achieved an accumulated H\(_2\)O\(_2\) concentration of 547 ppm in 0.05 M H\(_2\)SO\(_4\) and enabled electro-Fenton process for rhodamine B degradation. Besides
metal chalcogenides, other metal compounds can also be endowed with high activity and selectivity toward acidic H₂O₂ production. For example, Gao et al. engineered the crystal facets and oxygen vacancies to activate the inert hematite (α-Fe₂O₃) for selective H₂O₂ production [115]. DFT calculations found that the oxygen-defective (001) facet of α-Fe₂O₃ is promising for H₂O₂ production by preventing O–O bond cracking. The rich oxygen vacancies favor end-on adsorption of oxygen and subsequent protonation to produce H₂O₂. Electrochemical experiments verified that single-crystal with exposed (001) facets exhibited > 90% selectivity in weakly acidic solution (5 mM H₂SO₄), providing a feasible catalyst with earth-abundant elements in electrosynthesis.

Remarkably, Co-based nanomaterials are a class of unique candidates for acidic H₂O₂ production. Co nanoparticles encapsulated within N-doped graphitic carbon were reported to trigger H₂O₂ synthesis in acidic media with almost 100% Faradaic efficiency and production rate of 49 mmol g⁻¹ h⁻¹ [119]. The ability to synthesis H₂O₂ in acidic media is related to a combination of materials properties, including pH values, applied potential, porosity and distribution of N moieties. In another study, it was found that cobalt-triethylenetetraamine complex pyrolyzed at different temperatures (Co/TETA/C) exhibits a rise in H₂O₂ yield from 60% to nearly 100% in 0.1 M HClO₄ when the pyrolysis temperature is below 500 °C [120]. Temperature exceeding 500 °C is detrimental to H₂O₂ yield because of the formation of metallic cobalt particles. A detailed kinetic analysis confirmed that the reaction mechanism of obtained cobalt-containing catalysts is unchanged whether Co is in metallic or Co(II)-like form after heat treatment. Cobalt phthalocyanine (CoPe) compounds can also act as modifier of carbon materials for enhanced H₂O₂ production in acidic media, leading to a maximum H₂O₂ Faradaic efficiency of 92.3% with 1 wt% CoPe
modification and a positive overpotential shift of 340 mV with 10 wt% CoPc modification [121]. Despite these advances in non-noble-metal compounds for acidic H₂O₂ electrosynthesis, further efforts to regulate their active centers, refine the mechanism understanding, and improve long-term stability are urgently needed.

3.4. Metal-free carbon-based catalysts

Fig. 7. Metal-free carbon-based materials for electrochemical H₂O₂ production in acidic media. (a) H₂O₂ production rates and I_D/I_G ratio of hierarchically porous carbon. (b) H₂O₂ selectivity of HPC-24 at pH value of 1, 4 and 7 and applied potential of −0.1 V, −0.3 V and −0.5 V vs SCE. (a and b) are reprinted from Ref. [124] with permission from Wiley VCH. (c) Transmission electron microscopy (TEM) image of mesoporous nitrogen-doped carbon synthesized from 100% (1-methyl-1H-pyrrole-2-yl)methanol precursor. (d) Schematic illustration of ORR pathways on mesoporous nitrogen-doped carbon and micropore-dominant activated nitrogen-doped carbon. (c and d) are reprinted from Ref. [125] with permission from the American Chemical
Society. (e) Koutecky-Levich plot of meso-BMP-800 in 0.1 M HClO$_4$. Reprinted from Ref. [132] with permission from the American Chemical Society. (f) Synthetic diagram of g-N-CNHs and related TEM images at intermediate stages during synthesis. (g) H$_2$O$_2$ Faradaic efficiency of g-N-CNHs electrode at pH of 1 and different potentials. (f and g) are reprinted from Ref. [53] with permission from Elsevier.

In contrast to metal-based catalysts, metal-free carbon-based materials are regarded as highly promising electrocatalysts due to their earth abundance, low cost, high surface area, good electrochemical stability and electrical conductivity [122,123]. In acids, the ORR activity of pristine carbon materials is low because of the intrinsically weak adsorption of *OOH intermediate. Therefore, it is imperative to create active sites in carbon frameworks by means of morphology control and heteroatom functionalization.

3.4.1. Morphology control

Morphology control strategies by defect and pore engineering have been reported to boost electrochemical acidic H$_2$O$_2$ production of carbon catalysts [124,125]. Topological defective sites naturally exist and can be facilely introduced to sp$^2$ carbon planes during physical and chemical synthesis [126]. These defects, including disorders, in-plane vacancies and edge sites, can effectively alter the electronic structure of carbons [127]. For example, Liu et al. performed carbonization of MOF-5 precursor under H$_2$ atmosphere to introduce sp$^3$ type defects into hierarchically porous carbon (HPC) [124]. The rich sp$^3$-C bonds and defects can serve as active sites for adsorption and reaction of oxygen. More importantly, the H$_2$O$_2$ production rates were found to increase with the intensity ratio of D and G bands in Raman spectra ($I_D/I_G$), indicating that defect may facilitate H$_2$O$_2$ production (Fig. 7a). For the optimized
HPC-H24 catalyst (hydrothermal treatment for 24 h and pyrolysis under H₂ atmosphere), the H₂O₂ selectivity is 80.9%–95.0% in acidic media at potential range of –0.1 V to –0.5 V vs saturated calomel electrode (SCE) (Fig. 7b), and the current efficiencies for H₂O₂ production are 85.2%–91.2% at pH of 1 and 73.0%–82.4% at pH of 4, respectively. Similar relation between defects (represented by I_D/I_G ratio) and H₂O₂ selectivity was also unveiled for nitrogen-doped mesoporous carbon to prove that defect sites are favorable for H₂O₂ production [128]. The aliphatic-like defect sites on several commercially available carbons were revealed to increase surface hydrogen content, contributing to better 2e⁻ selectivity and Faradaic efficiency in 0.1 M HClO₄ [129].

Additionally, the pore structures of carbon materials greatly influence electrocatalytic selectivity by regulating active site exposure and mass transport of reactants and products. Micropores with a diameter less than 2 nm provide large surface area but are limited by low accessibility of active sites, whereas macropores (> 50 nm) display the opposite trend. Mesopores (2–50 nm) with decent surface area and mass transfer properties are most beneficial. For example, mesoporous nitrogen-doped carbon prepared by SiO₂-templated carbonization of (1-methyl-1H-pyrrole-2-yl) methanol was found to deliver H₂O₂ selectivity of over 90% in 0.5 M H₂SO₄ (Fig. 7c) [125]. By contrast, an activated nitrogen-doped carbon with microporous structure exhibited significantly lower H₂O₂ selectivity of 56–70%. The enhanced selectivity of mesoporous carbons was attributed to the ease of mass transport in the catalyst layer and reduced residence time of H₂O₂ to prevent its further reduction (Fig. 7d). A comparison between microporous and mesoporous carbons with similar physical and chemical properties except the difference in pore size, albeit in alkaline conditions, showed that mesoporous carbon demonstrated better electrochemical accessibility,
activity, selectivity and stability toward H\textsubscript{2}O\textsubscript{2} production [50]. It is notable that they investigated the role of carbon defects by spectroscopic characterizations and DFT calculations and revealed that most sp\textsuperscript{2}-type defect configurations are inherently selective for 2e\textsuperscript{-} ORR, highlighting the interplay between pore size and defect in affecting electrochemical ORR performance of carbon materials. To gain a better understanding of the structure-performance relation and guide further optimization, well-defined mesoporous carbon-based model materials and advanced simulation by finite-element method is highly anticipated [130].

3.4.2. Heteroatom functionalization

Functionalization of carbon materials with heteroatoms has become a simple yet powerful approach to tune the electronic structure of carbon for ORR application. The difference in electronegativity, atom size and chemical states of non-metal heteroatoms could induce spin and charge redistribution within sp\textsuperscript{2} carbon and modulate the binding energies of ORR intermediates [127]. Also, the heteroatom-induced defective structure in carbon materials and the increase in surface area may contribute to enhanced 2e\textsuperscript{-} ORR activity and selectivity.

Nitrogen doping is the most widely reported strategy to optimize the binding strength of *OOH. From the kinetic perspective, nitrogen-doped carbon catalysts have higher kinetic rate constant of 2e\textsuperscript{-} ORR than 4e\textsuperscript{-} ORR and H\textsubscript{2}O\textsubscript{2} reduction processes, indicating their high selectivity toward 2e\textsuperscript{-} pathway [131]. In 2012, Fellinger et al. synthesized mesoporous nitrogen-doped carbon from ionic liquid N-butyl-3-methylpyridinium dicyanamide as a highly efficient and selective catalyst for electrochemical H\textsubscript{2}O\textsubscript{2} synthesis [132]. In 0.1 M HClO\textsubscript{4}, meso-BMP-800 (mesoporous N-doped carbon heat-treated at 800 °C) showed an approximate 2e\textsuperscript{-} process by Koutecky-Levich analysis (Fig. 7e). The researchers discovered that the reactivity
toward H$_2$O$_2$ depends on the nitrogen content and configuration of N-doped carbon. An increased amount of nitrogen and the “radical” character of nitrogen-bound carbon were believed to favor 2e$^-$ ORR process. They found that pyrrolic nitrogen sites were responsible for 2e$^-$ ORR, but higher synthesis temperature would decrease the amount of pyrrolic nitrogen and is therefore detrimental to H$_2$O$_2$ production. Iglesias et al. prepared N-doped graphitized carbon nanohorns (g-N-CNHs) through facile coating and controlled annealing of polydopamine (Fig. 7f) [53]. The catalyst could work under pH of 1.0 with a H$_2$O$_2$ Faradaic efficiency as high as 98% at 0.30 V vs RHE (Fig. 7g) and very positive onset potential of 0.40 V vs RHE. The long-term durability was confirmed by the stable H$_2$O$_2$ production rate of 33 mmol g$^{-1}$ h$^{-1}$ cm$^{-2}$ over 24 h. The researchers correlated the high selectivity under acidic conditions to the microporosity for decreased residence time of H$_2$O$_2$ and the protonated pyridinic N atoms for preferentially maintained O–O bond.

The electrocatalytic performance of N-doped carbon materials can be further tuned by the nitrogen content and configurations. For example, Sun et al. unveiled a volcano-type relationship between H$_2$O$_2$ selectivity and the amount of N functionalities, suggesting that there is an optimal level of nitrogen dopant density for maximized H$_2$O$_2$ production [128]. A balanced distance of individual N dopant from each other is beneficial for 2e$^-$ ORR pathway, as the excessive doping may facilitate O–O bond cleavage and H$_2$O$_2$ decomposition. Furthermore, the same research group investigated the structure-activity relationship and individual role of chemically distinct N functionalities in different electrolytes by XPS [133]. They prepared nitrogen-doped porous carbons by direct pyrolysis of ordered mesoporous carbon CMK-3 and polyethylenimine mixture, achieving a high H$_2$O$_2$ selectivity of 95.3% in acidic electrolyte. However, the H$_2$O$_2$ production rate by bulk electrolysis in acid
(34.1 mmol g h\(^{-1}\)) is lower than that in neutral electrolyte (570.1 mmol g h\(^{-1}\)), which may be ascribed to the gradual chemical disproportionation and further electrochemical reduction. In acidic solution, the amount of pyridinic N decreased and the amount of graphitic N increased after electrocatalysis, whereas the opposite trend was observed in neutral and alkaline solutions; meanwhile, the pyrrolic N content increased irrespective of the pH values of electrolyte. Such dynamic changes in specific type of N functionality during catalysis were ascribed to the adsorbed oxygenated groups (*O and *OH). Specifically, a covalently attached OH group to a carbon atom can transform the adjacent pyridinic N into pyridonic N, while a similar OH attachment to an adjacent carbon atom of graphitic N can downshift its binding energy to that of pyrrolic N. These phenomena suggested that pyridinic N has a deterministic role in controlling acidic H\(_2\)O\(_2\) production, while graphitic N is the catalytic active site in neutral and alkaline solutions. It should be noted that the real active sites and reaction mechanism of N-doped carbons in 2e\(^{-}\) ORR are still under debate. Despite the above evidence of pyridinic N sites for selective 2e\(^{-}\) ORR, they have also been reported to actively catalyze 4e\(^{-}\) ORR in 0.1 M H\(_2\)SO\(_4\) [134]. Thus, determining the individual role of N configuration in acidic H\(_2\)O\(_2\) production is an ongoing challenge. The ORR selectivity debate of N-doped carbons largely originates from the uncontrolled synthesis methods and lack of direct evidence of active sites. Existing synthesis methods typically generate multiple N configurations in one catalyst and cannot precisely control other factors that affect ORR selectivity, such as defects and porosity. In order to identify the active site and construct structure-property relationship, further work is needed to prepare well-defined platforms of N-doped carbon with single N configuration, and develop advanced *in situ* characterization techniques to probe the chemical states of N-doped carbons under
operating conditions.

In addition to nitrogen dopants, doping with other heteroatoms (O, S, F, etc.) and dual-doping can also tailor the electronic structure of carbon catalysts toward acidic H₂O₂ production [51,135–140]. For example, oxidized carbon materials can incorporate various active and selective oxygen-containing functional groups to achieve outstanding 2e⁻ ORR performance. Lu et al. demonstrated that surface oxidation of carbon nanotubes by nitric acid can significantly boost their performance for electrochemical H₂O₂ production [51]. The activity and selectivity of 2e⁻ ORR are positively correlated with oxygen content. Through DFT calculation and a series of control experiments, the researchers found that oxygen species modulate adjacent carbon atoms for optimized adsorption of *OOH, and the active sites for 2e⁻ ORR are the carbon atoms adjacent to –COOH and –C–O–C groups. To directly identify the real active sites, Han et al. studied a series of activated carbon materials with dangling edge sites and decorated with targeted functional groups, including quinone, carbonyl and etheric ring [136]. In acidic media, the quinone-enriched carbon exhibited higher selectivity (up to 97.8 % at 0.75 V vs RHE) and activity than other two counterparts, and the most active motif was determined to be the quinone functional group in the edge and basal plane of carbon. However, it is noticeable that while the oxidation of carbon materials enhances 2e⁻ ORR, their performance in acidic media is not as good as that in alkaline media as with the general trend of carbon materials. Fluorine, the element with the highest electronegativity, is powerful to alter the polarization and electronic structure of carbon for boosted H₂O₂ synthesis [135]. At pH of 1, F-doped hierarchically porous carbon with a fluorine content of 3.41 at% achieved the best H₂O₂ selectivity of 97.5% and production rate of 792.6 mmol h⁻¹ g⁻¹. The CF₂ and CF₃ motifs are critical to 2e⁻ ORR by promoting O₂ activation and *OOH desorption.
4. Electrochemical device design and in situ/on-site utilization

4.1. Electrochemical device design

Alongside electrocatalyst design, developing well-configured electrochemical devices and reactors to perform bulk electrosynthesis of H$_2$O$_2$ is another important factor to achieve practical-scale application in this field. The design of real electrochemical devices should consider the mass transport of reactants and H$_2$O$_2$ disproportionation/decomposition during long-term electrolysis. In laboratory research, RRDE setup is typically used to quickly and quantitatively examine the H$_2$O$_2$ production on electrocatalysts (Fig. 8a) [14,28,141,142]. The Pt ring electrode should be electrochemically cleaned and refreshed before each use to make the H$_2$O$_2$ detection accurate [34,75]. However, because RRDE-based measurements are conducted under forced convection conditions in relatively short periods, it often fails to reflect the impact of mass transport limitation and long-term stability. In addition, the reported H$_2$O$_2$ selectivity by RRDE (molar fraction selectivity) is in most cases higher than the value reported at device level (Faradaic selectivity), which causes overestimation of catalyst performance [143]. The H-type cell is another widely used laboratory-scale cell configuration to accumulate H$_2$O$_2$ (Fig. 8b). In acidic electrolyte, the anode and cathode compartments are separated by a proton-exchange membrane to only allow H$^+$ transfer and avoid product crossover. Yamanaka et al. reported a series of H-type cell configurations to produce H$_2$O$_2$ in H$_2$/O$_2$ fuel cell and electrolyzer setups [144–147]. Using activated carbon and vapor-grown carbon fiber as cathode materials and a solid polymer electrolyte, the researchers synthesized neutral H$_2$O$_2$ solution of up to 8 wt% by electrolysis of water and oxygen [146]. Although H-type cells can simulate bulk electrosynthesis of H$_2$O$_2$, it is difficult to reach industrial-level current densities (e.g., > 100 mA cm$^{-2}$) and overcome the issue
of mass transport limitation.

Fig. 8. Electrochemical device configurations for H$_2$O$_2$ synthesis. (a) RRDE setup and (b) H-type cell. (a and b) are reprinted from Ref. [14] with permission from the American Chemical Society. (c) Continuous flow cell by adopting a GDE. Reprinted from Ref. [148] with permission from the American Chemical Society. (d) Solid-electrolyte fuel cell. Reprinted from Ref. [154] with permission from AAAS. (e) Phase-transfer device. Reprinted from Ref. [155] with permission from Elsevier. (f) Membrane-free electrochemical H$_2$O$_2$ generator. Reprinted from Ref. [160] with permission from Royal Society of Chemistry.

To facilitate O$_2$ diffusion at the cathode, many studies have turned to the gas diffusion electrode (GDE) comprising a porous and hydrophobic gas diffusion layer
(GDL) and a catalyst layer (Fig. 8c) [148]. The electrocatalyst is deposited onto the catalyst layer to create a solid-liquid-gas triple-phase boundary. Mass transport of oxygen is significantly enhanced as its solubility in gas phase is greater than that in solution. Oxygen is continuously supplied to the cathode and the electrolyte containing $\text{H}_2\text{O}_2$ products is continuously drained away to regenerate catalytic active sites, thereby achieving large current density, high production rate and high $\text{H}_2\text{O}_2$ concentration simultaneously [149–151]. Since the produced $\text{H}_2\text{O}_2$ molecules need to transport through the GDL and catalyst layer to be collected in the electrolyte, the local $\text{H}_2\text{O}_2$ concentration near electrode surface can reach an excessive level for further reduction to water. Therefore, it is critical to control the continuous reactant and product circulation, which enables sufficient mass transport and prevents $\text{H}_2\text{O}_2$ accumulation. Li et al. developed a GDE-based $\text{H}_2\text{O}_2$ production system with a continuous flow of carrier water to remove the product, leading to a high $\text{H}_2\text{O}_2$ production rate of 200 $\mu\text{mol h}^{-1} \text{cm}^{-2}$ without significant degradation of cobalt-carbon composite catalyst [152]. Considering that the as-produced $\text{H}_2\text{O}_2$ needs to be separated from the liquid electrolyte to obtain pure solutions, it is highly desirable to perform electrolyte-free $\text{H}_2\text{O}_2$ production to avoid further purification process [153]. Remarkably, Xia et al. achieved direct production of pure $\text{H}_2\text{O}_2$ solution in a solid-electrolyte $\text{H}_2/\text{O}_2$ fuel cell [154]. As shown in Fig. 8d, the electrogenerated $\text{H}^+$ and $\text{HO}_2^-$ ions could transfer to the middle chamber and recombine to form $\text{H}_2\text{O}_2$ molecule in the porous solid electrolyte, which is then collected by pure deionized water. No ion contaminants are involved in this process, and a wide range of $\text{H}_2\text{O}_2$ concentration (up to 20 wt%) can be facilely and controllably acquired by tuning the water flow rate. This device achieved a high $\text{H}_2\text{O}_2$ selectivity $> 90\%$ and could retain performance after 100 hours.
Other types of reactors such as phase-transfer devices [155], jet reactors [156] and pressurized reactors [157–159] are also proposed for electrochemical \( \text{H}_2\text{O}_2 \) production. Murray et al. discovered that 2,7-disulfonyl anthraquinone (AQDS\(^{2-}\)) can catalyze \( 2e^- \) ORR and shuttle between aqueous and organic phases, which guides the design of phase-transfer \( \text{H}_2\text{O}_2 \) production devices (Fig. 8e) [155]. AQDS\(^{2-}\) was first reduced to AQDSH\(^{2-}\) by gaining two electrons, which subsequently performed phase-transfer between the aqueous electrolyte and organic phase, and finally was extracted from organic phase to form pure aqueous \( \text{H}_2\text{O}_2 \) solution. Continuous production of \( \text{H}_2\text{O}_2 \) at 2–3 \( \mu \text{mol min}^{-1} \text{ cm}^{-2} \) with a concentration of 33 mM was achieved, highlighting the simultaneous generation and separation synthesis method. Generally, a permselective membrane is used between two electrode compartments, which however increases the ohmic resistance loss of the whole system and may become a limiting factor of stability. To this end, Chen et al. developed a membrane-free reactor with carbon catalysts, demonstrating a high \( \text{H}_2\text{O}_2 \) selectivity > 90% and an accumulated \( \text{H}_2\text{O}_2 \) concentration of 0.3 wt% (Fig. 8f) [160]. In the cathode compartment, oxygen is reduced to \( \text{H}_2\text{O}_2 \) and the GDE coated with hydrophobic polymer blocks the diffusion of \( \text{H}_2\text{O}_2 \), which enables the collection of concentrated \( \text{H}_2\text{O}_2 \) solution. Xia et al. also reported \( \text{H}_2\text{O}_2 \) production at both cathode and anode sides of a membrane-free cell with a high production rate of 24 \( \mu \text{mol min}^{-1} \text{ cm}^{-2} \) [151]. Because \( \text{H}_2\text{O}_2 \) can be generated by \( 2e^- \) oxygen reduction at the cathode and \( 2e^- \) water oxidation at the anode, the cell delivered an actual efficiency of 153%.

4.2. In situ and on-site application of electrosynthesized \( \text{H}_2\text{O}_2 \)

Using intermittent and renewable electricity as an input, electrochemical \( 2e^- \) ORR enables the production of \( \text{H}_2\text{O}_2 \) in small amounts and flexible mode at the place and time of need. This method is especially suitable for decentralized and on-demand
H$_2$O$_2$ production in remote areas, and avoids the cost and hazard associated with the handling of concentrated H$_2$O$_2$ solution. Along with electrocatalyst design and device engineering, the *in situ* application of electrosynthesized H$_2$O$_2$ from ORR is also an important determinant of scalability. Recent studies have shown the potential applications of electrosynthesized H$_2$O$_2$ in a diverse range of fields, involving degradation of organic contaminants, disinfection and synthesis of value-added chemicals.

**Fig. 9.** Applications of electrosynthesized H$_2$O$_2$ from 2e$^-$ ORR. (a) Organic wastewater treatment by *in situ* generated H$_2$O$_2$. Reprinted from Ref. [29] with permission from Springer Nature. (b) Bacteria killing and water disinfection by H$_2$O$_2$ produced on Fe-C-O SACs. Reprinted from Ref. [30] with permission from Springer Nature. (c) Synthesis of peroxyacetic acid by oxidation of acetic acid and *in situ* electrogenerated H$_2$O$_2$. Reprinted from Ref. [31] with permission from Elsevier.

Large amounts of organic pollutants are released to wastewater and natural water...
bodies, which presents significant threats to human health and the environment [4]. The well-known electro-Fenton process is utilized as advanced oxidation process to convert organic contaminants into minerals, CO$_2$ and water. It features continuous electrocatalytic generation of Fenton reagents (Fe$^{2+}$ and H$_2$O$_2$) and subsequent reaction to produce the strong oxidant hydroxyl radicals (·OH) [161–163]. Operating at the optimal pH range of 2.8–3.0, electro-Fenton system is able to treat organic dyes, pesticides, pharmaceuticals and other refractory compounds [4]. Dyes are present in wastewater from textile and printing industries, which would cause adverse effect on human health and present undesirable color. Electrocatalytic H$_2$O$_2$ generation on WO$_3$-modified Vulcan XC72 carbons showed 77% efficiency for Orange II decolorization as a result of $\textit{in situ}$ generated hydroxyl radicals [164]. Methylene blue [165], methyl orange [166], rhodamine B [110], acid red 14 [167] and acid orange [168] can also be degraded in a similar way. Electro-Fenton is also a powerful process to remove pesticides and pharmaceutical compounds. For example, Fe$_3$O$_4@$Fe$_2$O$_3$/activated carbon aerogel electrode exhibited 90% removal of imidaclorpid within 30 min [169]. The outstanding activity was facilitated by the high surface area (2410 m$^2$ g$^{-1}$) of activated carbon aerogel, whereas the dissolved Fe ions and surface Fe sites were responsible for the conversion of H$_2$O$_2$. Considering the fact that electro-Fenton system requires significant chemical and energy inputs, Xu et al. recently reported a combined H$_2$O$_2$ electrolyzer and Cu single-atom catalytic Fenton filter for organic wastewater treatment (Fig. 9a) [29]. Cu single atoms embedded in graphitic carbon nitride (C$_3$N$_4$) can activate H$_2$O$_2$ at pH of 7.0 to oxidize 50 µM rhodamine B within ~20 min and mineralize 95% of total organic carbon within 1 h. The use of Cu-C$_3$N$_4$ prevents catalyst leaching and does not affect effluent water quality. The designed organic wastewater treatment system can continuously produce
10 g L\(^{-1}\) H\(_2\)O\(_2\) and completely oxidize triclosan, 17\(\alpha\)-ethinyl oestradiol and cefazolin sodium to CO\(_2\), thus demonstrating the significant potential of the whole system for organic removal.

The strong oxidation capacity of H\(_2\)O\(_2\) makes it applicable for on-site and de-localized water disinfection. Wang group conducted a prototype experiment to examine the effectiveness of iron SACs with Fe-C-O motifs in neutral conditions (Fig. 9b) [30]. The achieved H\(_2\)O\(_2\) selectivity maintained > 90% from 0.5 to 0.3 V vs RHE and the concentration reached 1613 ppm within 210 min electrolysis, corresponding to an average H\(_2\)O\(_2\) Faradaic efficiency of 90.8%. The catalysts enabled > 99.9999% bacteria removal in 120 min at an electrode processing rate of 125 L h\(^{-1}\) m\(^{-2}\). In addition, on-site generation of H\(_2\)O\(_2\) from ORR for disinfection has been commercialized with some small-scale technological products available. For example, Lynntech, Inc. devised an electrochemical generator for H\(_2\)O\(_2\) production under acidic conditions [170]. Using a GDE as cathode and platinized titanium as anode, the electrochemical cell can generate high-purity H\(_2\)O\(_2\) solution of 6–7 wt% for use in disinfection directly or after proper dilution. HPNow, a Denmark-based technology and market leader of on-site electrochemical H\(_2\)O\(_2\) generation, uses only air, water and electricity as inputs for safe, high-efficiency and scalable H\(_2\)O\(_2\) synthesis [171]. A series of products based on the company’s HPGen technology provide pure H\(_2\)O\(_2\) solution of 1 to 5 kg per day, solving issues in agricultural, industrial and residential water treatment as well as sterilizing pathogens including COVID-19. Therefore, in situ and on-site H\(_2\)O\(_2\) electrosynthesis is of great industrial interest as an environmentally friendly route for water disinfection.

Additionally, the as-generated H\(_2\)O\(_2\) can be in situ integrated with subsequent oxidation reactions for synthesis of value-added chemicals [172,173]. In these
reactions, the active species derived from H₂O₂ may include intermediates such as ·HO₂, ·HO and HO₂⁻, but their activities differ by 5–6 orders of magnitude [174]. As such, it is possible to perform selective organic oxidation to different extents and yield target products by regulating conditions. For example, electrogenerated H₂O₂ from 2e⁻ ORR is able to oxidize acetic acid to peroxyacetic acid of concentration up to 0.02 M on GDEs (Fig. 9c) [31,175]. Mechanistic study revealed that both H₂O₂ and *O species can react with acetic acid to form peroxyacetic acid, and H₂O₂ formation is the rate-limiting step. Such indirect electrochemical synthesis method is also applicable to the oxidation of n-butanol to n-butyric acid [176] and oxidation of olefinic compounds to corresponding epoxides [177]. More work remains to be done to uncover the reaction mechanism, especially the oxidation mechanism for the subsequent reaction, and the role of electrocatalysts in these tandem reactions [173].

5. Conclusions and perspectives

H₂O₂ plays a critical role in chemical industries and environmental remediation. Electrochemical H₂O₂ synthesis by 2e⁻ ORR offers a sustainable solution to on-site H₂O₂ production beyond traditional anthraquinone and direct synthesis approaches. The ability to produce H₂O₂ in acidic environment is of great importance, since acidic solutions of H₂O₂ is versatile in its most stable form and can fit in proton exchange membrane devices. In this Review, we presented recent advances in electrochemical H₂O₂ production from 2e⁻ ORR in acid electrolytes, in terms of the pH effect on ORR mechanism, major types of electrocatalysts (Table 1), electrochemical devices, and potential applications. Despite significant advances, there are several aspects that need to be emphasized for further development of efficient H₂O₂ electrosynthesis in acidic solutions.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>$j_{0.1V}$ (mA cm$^{-2}$)</th>
<th>Selectivity (%@V)</th>
<th>Stability</th>
<th>Production rate (mmol g$_{cat}^{-1}$ h$^{-1}@V$)</th>
<th>Reference</th>
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<tr>
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<tr>
<td>Pt-Hg</td>
<td>0.1 M HClO$_4$</td>
<td>3.6</td>
<td>~96 @ (0.2–0.4)</td>
<td>N/A</td>
<td>N/A</td>
<td>[35]</td>
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<tr>
<td>Pd-Hg/C</td>
<td>0.1 M HClO$_4$</td>
<td>N/A</td>
<td>&gt;95 @ (0.35–0.55)</td>
<td>8,000 cycles</td>
<td>N/A</td>
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<td>2.0</td>
<td>95–98 @ (0.3–0.6)</td>
<td>&gt;8 h</td>
<td>1701@0.1 (H-cell)</td>
<td>[71]</td>
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<tr>
<td>PtP$_2$</td>
<td>0.1 M HClO$_4$</td>
<td>3.0</td>
<td>95–98.5 @ (0.1–0.4)</td>
<td>120 h</td>
<td>2825@0.4 (PEMFC)</td>
<td>[72]</td>
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<tr>
<td>Pt/HSC</td>
<td>0.1 M HClO$_4$</td>
<td>1.6@900 rpm</td>
<td>@ (0.1–0.7)</td>
<td>2 h</td>
<td>546@0.05 (H-cell, 0.5 M HClO$_4$)</td>
<td>[77]</td>
</tr>
<tr>
<td>h-Pt$_1$-CuS$_x$</td>
<td>0.1 M HClO$_4$</td>
<td>2.7</td>
<td>92–96 @ (0.05–0.7)</td>
<td>10 h</td>
<td>546@0.05 (H-cell, 0.5 M HClO$_4$)</td>
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<td>Co-NC</td>
<td>0.1 M HClO$_4$</td>
<td>3.0</td>
<td>90–94 @ (0.3–0.6)</td>
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<td>275@0.4 (H-cell)</td>
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<td>Co-N-C</td>
<td>0.5 M H$_2$SO$_4$</td>
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<td>75–80 @ (0.1–0.3)</td>
<td>4 h</td>
<td>90.9@0.1 (H-cell)</td>
<td>[47]</td>
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</table>

Table 1. Performance of 2$e^-$ ORR electrocatalysts in acidic media. $j_{0.1V}$ is disk current density at 0.1 V vs RHE estimated from LSV measurements with rotation speed of 1600 rpm unless otherwise specified. All potentials shown are versus RHE. PEMFC is Proton Exchange Membrane Fuel Cell.
<table>
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<th>Catalyst</th>
<th>Acid</th>
<th>pH</th>
<th>Conversion</th>
<th>Overpotential</th>
<th>Time</th>
<th>Temperature</th>
<th>Source</th>
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<td>3.0</td>
<td>&gt;95</td>
<td>@ (0.3–0.6)</td>
<td>12 h</td>
<td>N/A</td>
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<td>Co₁–NG(O)</td>
<td>0.1 M HClO₄</td>
<td>N/A</td>
<td>40–50</td>
<td>@ (0.2–0.7)</td>
<td>10 h</td>
<td>N/A</td>
<td>[100]</td>
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<td>CoNOC</td>
<td>0.1 M HClO₄</td>
<td>2.8</td>
<td>&gt;95</td>
<td>@ (0.1–0.6)</td>
<td>11 h</td>
<td>590@0.1 (H-cell)</td>
<td>[34]</td>
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Non-noble-metal compounds

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<th>pH</th>
<th>Conversion</th>
<th>Overpotential</th>
<th>Time</th>
<th>Temperature</th>
<th>Source</th>
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<tr>
<td>CoS₂</td>
<td>0.05 M H₂SO₄</td>
<td>2.0</td>
<td>70–80</td>
<td>@ (0.2–0.7)</td>
<td>1 h</td>
<td>~24.5@0.5 (H-cell)</td>
<td>[109]</td>
</tr>
<tr>
<td>o-CoSe₂</td>
<td>0.05 M H₂SO₄</td>
<td>4.4</td>
<td>~80</td>
<td>@ (0.5–0.7)</td>
<td>6 h</td>
<td>~15.2@0.5 (H-cell)</td>
<td>[110]</td>
</tr>
<tr>
<td>{001}-Fe₃O₃-x</td>
<td>5 mM H₂SO₄</td>
<td>1.2</td>
<td>90–100</td>
<td>@ (0.1–0.4)</td>
<td>~28 h</td>
<td>N/A</td>
<td>[115]</td>
</tr>
</tbody>
</table>

Metal-free catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acid</th>
<th>pH</th>
<th>Conversion</th>
<th>Overpotential</th>
<th>Time</th>
<th>Temperature</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNC-50</td>
<td>0.5 M H₂SO₄</td>
<td>2.5</td>
<td>93–95</td>
<td>@ (0.1–0.3)</td>
<td>N/A</td>
<td>N/A</td>
<td>[125]</td>
</tr>
<tr>
<td>HPC-H24</td>
<td>0.05 M H₂SO₄</td>
<td>2.7</td>
<td>80–95</td>
<td>@ (–0.2–0.2)</td>
<td>2.5 h</td>
<td>294.0@0 (H-cell)</td>
<td>[124]</td>
</tr>
<tr>
<td>NCMK3IL50–800T</td>
<td>0.5 M H₂SO₄</td>
<td>1.7</td>
<td>95–98</td>
<td>@ (0.1–0.3)</td>
<td>6 h</td>
<td>159.9@0.1 (H-cell)</td>
<td>[128]</td>
</tr>
<tr>
<td>g-N-CNHS</td>
<td>0.1 M H₂SO₄</td>
<td>N/A</td>
<td>~80</td>
<td>@ 0.2</td>
<td>24 h</td>
<td>N/A</td>
<td>[53]</td>
</tr>
</tbody>
</table>
Firstly, elucidating the mechanism of 2e⁻ ORR and pH effect using advanced technologies is highly desired for catalyst development. Current CHE model-based DFT calculation works well in delineating the adsorption free energies of reaction intermediates, protons and electrons on the surface at constant potential [42]; however, it often oversimplifies a number of complex factors and has limitations in modelling the structure of electrode-electrolyte interface, the applied potential at operating conditions, surface charge effect and pH effect [178]. Therefore, it is urgent to develop more accurate models that consider these implicit factors, such as post-Hartree-Fock cluster calculations, embedding schemes, hybrid functionals and operando computations [61,179–181]. Moreover, with the advances in computer technologies and interdisciplinary research, machine learning has been applied in electrocatalysis for high-throughput catalyst screening that accelerates the discovery of new catalysts [182–184]. It is expected that future progress of machine learning algorithm will also help identify active catalysts and catalytic mechanisms of 2e⁻ ORR. In addition, for acidic H₂O₂ generation, a thorough understanding of pH effect is important but challenging. Most studies explore the pH dependency of 2e⁻ ORR by analyzing a specific material platform under different pH conditions, while the fundamental reasons behind the pH-dependent catalytic performance require further investigation.

Secondly, developing high-performance 2e⁻ ORR catalysts in acidic solutions is still an ongoing challenge. Practical application of electrochemical H₂O₂ production necessitates electrocatalysts with high ORR activity, high H₂O₂ selectivity, excellent stability, good electrical conductivity, facile mass transport and low cost. Unfortunately, no known materials satisfy all these criteria. Noble metals and their alloys exhibit the best activity and selectivity, but their scarcity and high cost largely
hinder practical application. Synthesizing SACs is an effective way to maximize their atomic utilization efficiency, and their selectivity can be tuned to 2e\textsuperscript{-} route with favorable end-on adsorption of oxygen molecules. However, further explorations are needed to achieve high mass loading of metal atoms for maximized current density and resolve the complex structure-property relationship of SACs involving metal centers, first and second coordination spheres [34]. For metal-free materials, their ORR activity in acids is intrinsically lower than that in alkaline solutions. Thus, defect engineering, pore engineering and heteroatom doping are necessary to overcome the obstacles associated with the weak activation of O\textsubscript{2}. Besides, present catalyst synthesis approaches inevitably generate carbon materials with heterogeneous surface features, leading to controversy over identifying the active sites. One possible remedy is to probe the surface chemistry under operating conditions by advanced in situ or operando characterizations to pinpoint the exact active motif. In all, there remains large room for improvement of H\textsubscript{2}O\textsubscript{2} production performance in acidic media.

Lastly, research into electrochemical reactor design and in situ/on-site applications of H\textsubscript{2}O\textsubscript{2} is as important as electrocatalyst design toward practical operation. The reported ORR performances are commonly based on half-cell test using RRDE setup, but relatively fewer reports test the catalysts in prototype or pilot-scale systems and achieve the standard of commercial viability. Efforts need to be devoted to the design of advanced electrochemical reactors, membranes and gas diffusion layers to obtain representative data under working conditions. Benchmarks of parameters, e.g., production rate, long-term durability, Faradaic efficiency and cost-effectiveness, also need to be established to allow meaningful performance comparison among different groups. Additionally, most applications of electrogenerated H\textsubscript{2}O\textsubscript{2} are now based on the mature electro-Fenton process and take
advantage of the strong oxidation capacity of ·OH, but the attack by reactive ·OH causes chemical degradation of proton-exchange membranes and hinders the application in acidic media [185]. Hence, alternative technologies should be exploited to reach a diverse range of industrially relevant applications in chemical, energy and environmental fields. Moreover, the issue of energy input cannot be overlooked in practical application under large current densities. Ways to increase the energy conversion efficiency may be further explored for energy-saving decentralized H₂O₂ synthesis, for example by novel electricity and H₂O₂ co-generation systems [36] or pairing the anode side with 2e⁻ water oxidation to yield H₂O₂ with a theoretical Faradaic efficiency of 200%.

In short, we believe that the combined achievements of reaction mechanism, catalyst development, reactor engineering and on-site applications are necessary to accelerate the advancement of H₂O₂ electrosynthesis in acidic media. Overcoming the above-mentioned challenges will contribute to industrially relevant on-site H₂O₂ electrosynthesis performance, and laboratory-level research needs to be integrated closely with industries for promising commercialization. It is expected that the insights provided in this Review can also inspire developments of other electrocatalytic reactions for sustainable production of commodity chemicals, i.e. electrocatalytic refinery [173], eventually realizing a sustainable energy economy.

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1461.
2058-2062.


1606459.
Graphical Abstract

This article reviewed the recent progress in the mechanism, electrocatalysts, electrochemical devices and applications of \( \text{H}_2\text{O}_2 \) electrosynthesis in acidic environment from electrocatalytic two-electron oxygen reduction reaction.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: