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Selective Electrochemical H₂O₂ Production through Two-electron Oxygen Electrochemistry

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Direct electrochemical production of hydrogen peroxide (H₂O₂) through two-electron oxygen electrochemistry, the oxygen reduction in fuel cells or water oxidation in water electrolyzers, could provide an attractive alternative to locally produce such chemical on demand. The efficiency of these processes depends greatly on the availability of cost-effective catalysts with high selectivity, activity and stability. In recent years, various novel nanostructured materials have been reported to selectively produce H₂O₂. Through combined experimental and theoretical approaches, underlying mechanisms in the electrochemical synthesis of H₂O₂ via oxygen electrochemistry have been unveiled. Considering the remarkable progress in this area, we summarize recent development regarding the direct production of H₂O₂ through two-

electron electrochemical oxygen reactions. The fundamental aspects of electrochemical oxygen reactions are first introduced. We then present various types of catalysts that can effectively produce H_2O_2 via two-electron oxygen electrochemistry. In parallel, the unique structure-, component-, and composition-dependent electrochemical performances together with the underlying catalytic mechanisms are discussed. Finally, a brief conclusion about the recent progress achieved on electrochemical generation of H_2O_2 and an outlook on the future research challenges are given.

1. Introduction

Hydrogen peroxide is an important chemical with a wide range of applications in industry, medicine and environmental protection.¹⁻⁴ Due to its strong oxidative properties, H_2O_2 is considered a promising candidate for water treatment and represents a solution for improving access to clean drinking water, an issue that affects many parts of the world.⁴⁻⁸ Moreover, H_2O_2 can serve as a potential energy carrier.⁹ At present, H_2O_2 is manufactured indirectly via the hydrogenation of anthraquinone with H_2 and subsequent oxidation by O_2 in an organic solvent, which is a multistep process requiring significant energy input and generates substantial waste.¹ The anthraquinone process, despite being able to produce large quantities of H_2O_2 at high concentration, is not considered “green” as impurity separation is required and the obtained H_2O_2 has to be concentrated up to 70 wt% to reduce transportation costs. Such process is feasible mainly for applications in large industrial processes.¹⁰ In addition, the instability of H_2O_2 poses a safety issue for transportation.³ Therefore, there is increasing interest in the development of low-cost and decentralized H_2O_2 production methods that can greatly reduce the cost for H_2O_2 synthesis, storage and transportation. One alternative route is the direct synthesis from H_2 and O_2 .¹¹⁻¹⁴ This route can offer a continuous mode for H_2O_2 production and enable the decentralized production. However, the selectivity toward H_2O_2 production and production rate of H_2O_2 are usually very low. Moreover, safety issues related

to the explosive nature of H₂ and O₂ further hinders their practical use.³ Thus, in order to enable its widespread application, other direct, efficient and economic routes for production of H₂O₂ are highly desirable.

Recently, the electrochemical strategy through oxygen electrochemistry offers an attractive route for on-site production of H₂O₂ as it could effectively address the issues associated with the indirect anthraquinone process and direct synthesis ones.^{5, 15, 16} Moreover, the oxygen electrochemistry process can be coupled with renewable energy sources and thus can be used in remote regions.⁷ In the oxygen electrochemistry process, H₂O₂ can be directly produced via either the two-electron reduction of O₂ at the cathode side of a fuel cell or two-electron oxidation of water at the anode side of an electrolyser.

The research on electrochemical synthesis of H₂O₂ from two-electron oxygen electrochemistry is an emerging field and recent intensive studies have led to the development of various promising catalysts for these processes. Although extensive review articles regarding four-electron oxygen electrochemistry have been reported, as far as we know, none of them paid particular attention to the production of H₂O₂ via two-electron route.¹⁷⁻²¹ In this review, recent advances regarding the direct production of H₂O₂ through electrochemical oxygen reactions are discussed in details. A timeline illustrating the important finding are showed in **Figure 1**. Some major challenges and opportunities for the future development of electrochemical synthesis of H₂O₂ from the viewpoint of rational design of highly efficient electrocatalyst, reaction engineering, electrochemical reactor design, and their potential applications are also presented.

2. Fundamental aspects of electrochemical oxygen reactions

Electrochemical oxygen reactions, including oxygen reduction reaction (ORR) and water oxidation, can be expressed by using **Equation 1**:²²⁻²⁵

Generally, for ORR reaction, there are three possible reaction mechanisms (**Scheme 1**): the dissociation mechanism where the O-O bond of oxygen breaks directly upon adsorption to form O^{ads} , which is reduced successively to OH^{ads} and to H_2O^{ads} ; the association mechanism where the generated OOH^{ads} breaks into O^{ads} and OH^{ads} and the peroxo mechanism where two electron-transfer steps lead successively to OOH^{ads} and to $HOOH^{ads}$, and the $HOOH^{ads}$ then breaks into OH^{ads} . In contrast, the water oxidation mechanisms can be viewed as the reverse process of ORR.^{22,26,27}

Thus, as the intermediate product, H_2O_2 can be produced via either the ORR or the water oxidation process following the peroxo mechanism.

3. H_2O_2 production from electrochemical oxygen reduction reaction

The ORR involves a multi-electron transfer process in which O_2 can be reduced to produce H_2O in a four-electron process (**Equation 2 and 3**) or undergo a two-electron pathway to form H_2O_2 .²⁸⁻³¹ In the case of the two-electron process, the peroxide species (HO_2^- or H_2O_2) can be produced while it can be converted to H_2O by another two-electron process or back to O_2 via chemical disproportionation (**Equation 4-9**).

The four-electron pathway:

In alkaline medium

In acidic medium

The two-electron pathway:

In alkaline medium

followed by either the further two-electron reduction process

or the chemical decomposition reaction

In acidic medium

followed by either the two-electron reduction reaction

Or the chemical disproportionation

The electrochemical performance of oxygen reduction to H_2O_2 was usually investigated by the rotating ring-disk electrode (RRDE) technique in a three-electrode cell system.^{2, 32, 33} All the electrochemical experiments are normally performed in a single compartment or H-cell (**Scheme 2**) under N_2 or O_2 -saturated aqueous solution with different pH values. Typically, a glassy carbon (GC) disk - Pt ring electrode is employed as the working electrode. The measured potentials are quoted with respect to the reversible hydrogen electrode (RHE), and are corrected for ohmic losses. To quantify the amount of H_2O_2 generated, the ring is set at *ca.* 1.2 V *vs.* RHE, where the oxygen reduction current is negligible and the H_2O_2 oxidation on the ring electrode is mass transport limited. This gives rise to a positive current at the ring electrode as H_2O_2 is produced at the disk.

The selectivity for H_2O_2 formation can be obtained by measuring the currents of O_2 reduction at the disk and H_2O_2 oxidation at the Pt ring of RRDE electrode. Taking into account that the total disk current (i_D) is the sum of the O_2 reduction currents to water ($i_{\text{H}_2\text{O}}$), and to H_2O_2 ($i_{\text{H}_2\text{O}_2}$): $I_D = I_{\text{H}_2\text{O}} + I_{\text{H}_2\text{O}_2}$, and using the ring currents (I_R) and the collection efficiency N of the ring currents: $I_{\text{H}_2\text{O}_2} = I_R N^{-1}$, the selectivity for H_2O_2 formation ($\text{H}_2\text{O}_2\%$) could be calculated from the ratio between O_2 consumption rate towards H_2O_2 ($\dot{n}_{\text{O}_2(2e^-)} = I_{\text{H}_2\text{O}_2}/2F$) and total consumption rate ($\dot{n}_{\text{O}_2} = I_{\text{H}_2\text{O}_2}/2F + I_{\text{H}_2\text{O}}/4F$).³⁴

$$H_2O_2 \% = 200 \times \frac{I_R / N}{I_D + I_R / N}$$

Where the collection efficiency (N) can be determined from the measurement of hexacyanoferrate (III) reduction.

The number of electron transferred for ORR, n , can be calculated from:

$$n = 4 \times \frac{I_D}{I_D + I_R / N}$$

And the Faradaic efficiency ($\lambda\%$) can be defined as:^[2, 30]

$$\lambda \% = (i_R/N)/i_D \times 100$$

To extract information regarding the correlation between the kinetic activity and the mass transport of reactants, Koutecky-Levich (K-L) plot, which is obtained from the polarization curves at various rotation speeds, can be used. In the K-L equation (**Equation 10**), j is the measured current density, which is related to the kinetic current density (j_k) of disk current and the diffusion-limited current (j_d) of disk current, and ω is the angular velocity of the rotating disk electrode.³⁵

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{B \cdot \sqrt{\omega}} \quad (10)$$

In which the B factor and j_k are given by **Equation 11 and 12**:

$$B = 0.62 \cdot n \cdot F \cdot D_{O_2}^{2/3} \cdot \nu^{-1/6} \cdot C_{O_2} \quad (11)$$

$$j_k = n F k C_{O_2} \quad (12)$$

Where n is the number of transferred electrons, D_{O_2} and C_{O_2} are the diffusivity and solubility of oxygen, respectively, F is the Faraday constant, ν is the kinematic viscosity of the electrolyte, and k is the electron transfer rate constant.

The H_2O_2 concentration can be measured by a traditional cerium sulfate $\text{Ce}(\text{SO}_4)_2$ titration method based on that a yellow solution of Ce^{4+} will be reduced by H_2O_2 to colourless Ce^{3+} ($2\text{Ce}^{4+} + \text{H}_2\text{O}_2 \rightarrow 2\text{Ce}^{3+} + 2\text{H}^+ + \text{O}_2$). The concentration of Ce^{4+} before and after the reaction can be measured by ultraviolet-visible spectroscopy. The wavelength used for the measurement is usually 316 nm. Therefore, the concentration of H_2O_2 can be determined by $M(\text{H}_2\text{O}_2) = 2 \times M(\text{Ce}^{4+})$ (where $M(\text{Ce}^{4+})$ is the mole of consumed Ce^{4+}).³⁶

Generally, the as-synthesized H_2O_2 can decompose through either electrochemical peroxide reduction (PRR, **Equation 5** and **8**) or chemical peroxide disproportionation reaction (PDR, **Equation 6** and **9**), which represents a serious problem for H_2O_2 production via the two-electron ORR in a fuel cell. The chemical disproportionation experiment can be carried out by dispersing catalysts in a H_2O_2 solution and measuring the H_2O_2 concentration by titration method at specified time intervals. The PRR experiment can be carried out following the same method as ORR except for the use of an N_2 -saturated electrolyte containing 10 mM H_2O_2 .³²

3.1. Electrocatalysts for H_2O_2 production from ORR

Earlier studies on H_2O_2 production by cathodic reduction of oxygen are performed in an alkaline solution where the hydroperoxide ion HO_2^- is produced at the cathode side following **Equation 4**. Over the past years, intensive research has been carried out in alkaline medium and some progress have been achieved. However, as H_2O_2 degradation can be base-catalysed and thus the alkaline condition could greatly limit their widespread applications. As a result, electrochemical generation of H_2O_2 operated in acidic medium has been the subject of substantial studies recently. This is also echoed by extensive efforts on the investigation of oxygen reduction reaction in acidic solutions, due to the promising potential of proton exchange membrane fuel cells. Overall, from the practical application point of views, H_2O_2 generated in alkaline solution could be used for pulp and paper bleaching, and H_2O_2 produced in acidic medium can be usually used for oxidation purpose in organic synthesis. In contrast,

neutral aqueous H_2O_2 solution is thought to be the most useful and flexible form in their practical applications.

3.1.1 Noble metal-based electrocatalysts

Various prospective electrocatalysts for H_2O_2 production have been suggested recently, including noble metals and their alloys, single-atom catalysts, carbon-based materials and so on. Among these, the highest performance reported so far is achieved by using electrocatalysts that are made of noble metals such as gold, platinum and palladium. Generally, there are at least three different adsorbed intermediates for the four-electron reduction of O_2 to produce H_2O , i.e. HOO^* , O^* , and HO^* (**Equation 13-16**):^{23, 24, 37}

The two-electron reduction reaction, however, only involves one intermediate, OOH^* ($\text{O}_2 + * + \text{H}^+ + e^- \rightarrow \text{OOH}^*$). A further, single electron reduction of OOH^* could result in selective production of H_2O_2 ($\text{OOH}^* + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O}_2 + *$). Thus, H_2O_2 can be selectively formed if one can ensure that OOH^* is the only intermediate. Recent theoretical studies have pointed out the activity for H_2O_2 production was strongly related to the binding ability of OOH^* .^{2, 38} Specifically, for an ideal catalyst toward H_2O_2 production, the adsorption of OOH^* should be neither too strong nor too weak, where stronger binding will cause larger overpotential and weaker binding could lower their electrocatalytic activity. On the other hand, the selectivity of H_2O_2 production was determined by the ability of preserving the O-O bond during the oxygen reduction process.

Several metals interacting weakly with O_2 , such as Au, Ag, and Hg, were shown to be able to reduce O_2 selectively to H_2O_2 because the further reduction of H_2O_2 to H_2O was effectively

suppressed.³⁹⁻⁴¹ Adzic et al. first reported that two-electron oxygen reduction was observed on Au(111) and Au(110) surfaces.⁴² Various Au nanostructures were then demonstrated to be active catalysts.^{43,44} For example, it was reported that Au nanoclusters consisting of 25 Au atoms (Au_{25}) capped by thiol ligand could selectively produce H_2O_2 in alkaline medium with maximum H_2O_2 selectivity reaching 90% (**Figure 2**).⁴⁵ According to the previous theoretical and experimental studies,⁴⁶⁻⁴⁸ the excellent H_2O_2 selectivity of negatively charged Au_{25}^- nanoclusters was attributed to the efficient electron transfer between the cluster and O_2 molecules.

The selectivity of the Au-based materials was strongly related to the low Miller index faces of the crystallographic orientation. Au nanomaterials with high index faces, however, usually exhibited enhanced catalytic activity due to their higher surface energy.⁴⁹ To this end, by using Au nanorods with high-index facets as the substrate, Amal et al. demonstrated that both Au-Ni and Au-Ni-Pt core-shell nanorods could exhibit relatively high activity and selectivity for H_2O_2 production.⁵⁰ Notably, the selectivity and activity of Au-Pt-Ni nanorods could reach up to 95% and 1.01 mA cm^{-2} ($192.9 \text{ A g}^{-1}_{\text{noble metal}}$) at the overpotential of 150 mV.

Nevertheless, on these metals which interacted weakly with O_2 , the reaction rate was often low and high overpotentials were needed.³³ In contrast, metals that interacted strongly with oxygen, such as Pt and Pd, could directly reduce O_2 to H_2O in a four-electron process.⁵¹⁻⁵⁸ Thus, combining weakly and strongly interacting metals in homogeneous bimetallic catalysts are believed to be able to improve both selectivity and activity toward H_2O_2 production.¹³ For example, the Au-Pd alloy has been extensively studied.⁵⁹ In 2011, Jirkovsky et al. reported that a significant increase of H_2O_2 production selectivity, approaching 95%, was achieved on carbon-supported $\text{Au}_{1-x}\text{Pd}_x$ nanoparticles ($\text{Au}_{0.92}\text{Pd}_{0.08}/\text{C}$).³³ In another work, from the fundamental perspectives, Enrico et al. systematically investigated the electrocatalytic behavior of a series of Au-Pd nanoparticles with different compositions.³² It was demonstrated that the ORR performance was significantly affected by the composition of Au-

Pd nanoparticles (**Figure 3**). Based on the theoretical diffusion-limited currents obtained from the well-known Levich equation, the authors found that a mechanism change from a four- to a two-electron process was observed with increasing the Pd content in the Au-Pd system. Noted that the onset potential of H_2O_2 formation on the Au_9Pd and Au_3Pd was found to be close to the standard potential of the two-electron oxygen reduction to H_2O_2 , indicating their high activity toward H_2O_2 . However, different from Jirkovsky's work, the authors found that the Au_9Pd did not exhibit further improvement in terms of the H_2O_2 selectivity compared to pure Au sample, on which the H_2O_2 selectivity was already 95%. Actually, in Jirkovsky's work, the high H_2O_2 selectivity of $\text{Au}_{0.92}\text{Pd}_{0.08}/\text{C}$ catalyst was mainly caused by the presence of individual surface Pd atoms which are surrounded by Au. As is known, the product distribution of the ORR was greatly related to the ability of avoiding O-O bond breaking. To this end, Jirkovsky et al. introduced the idea of individual metal centers within an Au (111) surface. Then they used the DFT calculations to screen possible candidates for selective production of H_2O_2 . Finally, they studied the performance of $\text{Au}_{1-x}\text{Pd}_x$ nanoalloys with different Pd contents toward H_2O_2 production at the cathodic side of a fuel cell and found that individual surface Pd atoms surrounded by Au could significantly suppress O-O bond scission and thus exhibited the enhanced activity and selectivity toward H_2O_2 formation.

Based on the concept of isolated active site, Jan Rossmeisl and co-workers have screened for new alloy catalysts by DFT calculations and discovered that an optimal $^*\text{OOH}$ binding value could be obtained by alloying Pt nanoparticles with Hg.² The electrochemical experiments results showed that both extended surfaces and nanoparticles of Pt-Hg were highly active and selective for oxygen reduction to H_2O_2 , which further confirmed their theoretical predictions. For polycrystalline Pt-Hg catalyst, the efficiency of H_2O_2 production could achieve 96% in the potential region of 0.2 and 0.4 V vs RHE. Surprisingly, the current density of H_2O_2 production on the polycrystalline Pt-Hg reached 3 mA cm^{-2} , which was close to the theoretical mass transport limit of the two-electron process. Subsequently, they studied the

electrochemical performance of carbon supported Hg-modified Pt nanoparticles. As can be seen from **Figure 4B**, over 90% H_2O_2 yield was achieved in the potential range of 0.3 and 0.5 V. More importantly, the catalyst could exhibit highly stable activity under the reaction conditions, with no measurable losses in H_2O_2 production activity even after 8,000 potential cycles in O_2 -saturated HClO_4 solutions. After correcting the electrochemical data for mass transport losses, the catalytic performance toward H_2O_2 production of various types of catalysts reported in the literatures were summarized by them and shown in **Figure 5**. It was found that the specific activity of the nanoparticulate Pt-Hg/C was 4-5 times higher than that of polycrystalline Pt-Hg. Notably, the Pt-Hg/C catalyst presented the highest selectivity and its mass activity was more than one order of magnitude higher than that of the Pd-Au/C or Au/C reported by Jirkovsky's group.

Following this exciting finding, Ifan and co-workers systematically studied the trends for H_2O_2 production on different metal surfaces modified with Hg.³⁸ **Figure 6B** presented the partial current densities of H_2O_2 production on polycrystalline electrodes as a function of the applied potential. One can see that all the Hg-modified catalysts exhibited higher activity than Au-based catalysts, with the Pd-Hg electrode exhibiting the highest activity. It was found that the activity of Pd-Hg was two orders of magnitude higher than that of Au. From the electron microscopy characterization, the Pd-Hg/C catalysts can be viewed as core-shell structure with Pd as the core and Hg-rich Pd_2Hg_5 as the shell.⁶⁰ Oxygen reduction results showed that the H_2O_2 selectivity on Pd-Hg/C nanoparticles was higher than 95% in the potential range between 0.35 and 0.55 V. More interestingly, at 50 mV overpotential, the mass activity of Pd-Hg/C was five times higher than Pt-Hg/C catalyst. In addition, Pd-Hg/C catalyst showed high stability with negligible losses even after 8,000 potential cycles. These studies further confirmed that the single active sites surrounded by inert atoms could be used as the potential electrocatalyst toward the H_2O_2 production from oxygen reduction. The concept of individual

atomic sites presented above represents a new approach in the electrochemical reduction of oxygen to preferential H_2O_2 production. All these results indicated that the individual atomic sites are unable to break the O-O bond, thus endow them highly selective to generate H_2O_2 via the two-electron oxygen reduction process.

Previous studies have shown that there are two types of oxygen adsorption: bidentate adsorption (two O atoms coordinated with the catalyst, also known as “side-on” adsorption) and “end-on” adsorption configuration (one O atom coordinated perpendicularly to the catalyst).^{33, 61, 62} The “side-on” adsorption of O_2 , which weakens O-O bonding and thus contributes mainly to the direct four-electron pathway on Pt surface (**Scheme 3A**). In contrast, the “end-on” adsorption configuration could result in a two-electron pathway to selective production of H_2O_2 . Inspired by this, Choi et al. found that Pt nanoparticles coated with amorphous carbon layers could induce predominately “end-on” adsorption of O_2 on the their surface to eliminate Pt ensemble sites and thus enhance their H_2O_2 selectivity (Scheme 3B).⁶³ Electrochemical studies showed that the amorphous carbon-coated Pt could exhibit an onset potential of ~ 0.7 V and a remarkably enhanced H_2O_2 selectivity up to 41%. More importantly, no significant H_2O_2 decomposition via chemical disproportionation/further reduction process were observed due to the steric hindrance of the coated amorphous carbon layers on the Pt catalysts surface.

3.2.2 Single-atom catalyst

Although isolated active sites with high selectivity for H_2O_2 production could be obtained by covering/surrounding the catalysts with inert metals, such as Hg and Au, or amorphous carbon layers, the mass activity was greatly limited due to the large amount of occluded active atoms on these catalysts.

Single-atom catalyst (SAC), in which catalytically active metal is exclusively atomically dispersed as single atoms, are emerging as a new area in the catalysis community.⁶⁴⁻⁷² Firstly,

the construction of SAC could provide a simple and ideal model for understanding the catalytic mechanism and pathways of a specific reaction at the atomic level.⁷³⁻⁷⁶ Secondly, the application of SAC as catalysts could afford an opportunity for obtaining maximum atom utilization efficiency and thus increase the mass activity toward the specific reaction.^{77, 78} Over the past several years, various types of SAC have been successfully applied to tune the selectivity of some electrocatalytic reactions, such as formic acid oxidation⁷⁸⁻⁸¹, methanol/ethanol oxidation^{82, 83}, carbon dioxide electrochemical reduction^{84, 85}, hydrogen evolution^{74, 86, 87}, and oxygen reduction^{88, 89}. As far as oxygen reduction reaction is concerned, Anderson's group systematically studied the ORR performance of Pt_n clusters which were deposited on indium oxide.⁹⁰ They found that the H₂O₂ selectivity increased with decreasing the cluster size and a maximum H₂O₂ selectivity was observed on the smallest Pt₁ cluster. By using the incipient wetness impregnation strategy, Lee's group successfully prepared a Pt single-atom catalyst supported on titanium nitride nanoparticles (Pt/TiN).⁸⁸ The DFT calculations predicted that the N-vacancy sites on the TiN support are essential to stabilize single Pt atoms. Both the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and extended X-ray absorption fine structure (EXAFS) analysis confirmed the presence of isolated Pt atoms. The RRDE results showed that the single-atom Pt catalyst with 0.35 wt% of Pt on TiN support (0.35 wt% Pt/TiN) exhibited the highest H₂O₂ selectivity (**Figure 7C**). The mass activity of 0.35 wt% Pt/TiN was nearly one order of magnitude higher than Pt nanoparticles. Notably, the highest mass activity for electrochemical H₂O₂ production recorded in previous literatures was 26 A g⁻¹_{Pt} at a 50 mV overpotential; while the 0.35 wt% Pt/TiN achieved a record-breaking value of 78 A g⁻¹_{Pt}. In spite of its thermodynamic instability, the 0.35 wt% Pt/TiN catalyst exhibited high durability for H₂O₂ production. All these results clearly demonstrated that single-atom catalyst can not only effectively tune the selectivity of oxygen reduction reaction but also maximize the utilization efficiency of noble metals, which was essential to the commercial applications.

Usually, single atom catalysts possess much higher surface energy than their corresponding nanoparticles and clusters, which could induce severe agglomeration during the preparation and catalytic reaction process.⁹¹ One efficient strategy was to directly anchor the single-atom on the support through strong metal-support interaction. This strong metal-support interaction could protect single atom catalysts against aggregation and significantly influence the catalytic properties of the supported metal via the geometric and/or electronic modification by the support.⁹²⁻⁹⁵ In a recent work, Lee' group investigated the support effect on single-atom Pt catalysts toward H_2O_2 production.⁹⁶ Electrochemical studies indicated that single-atom Pt supported on titanium carbide (Pt_1/TiC) showed higher activity, selectivity, and stability for electrochemical H_2O_2 production than that of single-atom Pt supported on titanium nitride (Pt_1/TiN) catalysts. By using DFT calculations, they attributed the enhanced H_2O_2 activity to the weak affinity of oxygen species on Pt_1/TiC . This work clearly showed that supports play an important role in single-atom Pt catalyst toward H_2O_2 production.

Among various support materials for single-atom catalysts, carbon-based materials, which could provide large surface area and high conductivity, have been considered as promising candidates. However, carbon materials often show weak metal-support interactions. To this end, surface modifications are extensively explored to enhance the interaction and thus stabilize the single-atom catalyst. Recently, Choi et al. found that zeolite-templated carbon (ZTC) modified with abundant sulfur (up to 17%) could effectively stabilize atomically dispersed Pt atoms with a loading of up to 5 wt%.⁸⁹ It was found that the single-atom Pt supported on high S-content carbon (Pt/HSC) catalyst could selectively produce H_2O_2 without H_2O_2 decomposition and further conversion under an acidic environment. As can be seen from **Figure 8B**, the H_2O_2 selectivity on the Pt/HSC could achieve 96%, while Pt nanoparticles and clusters exhibited only 28 and 60%, respectively. Since H_2O_2 could further react through either PRR or PDR, a catalyst suitable for selective electrochemical production of H_2O_2 should be efficient at producing H_2O_2 and at the same time inactive towards further

reduction to water and chemical disproportionation to oxygen. The PDR (**Figure 7C**), PRR (**Figure 8D**) and CN^- poisoning experiments indicated that the high yield of H_2O_2 on Pt/HSC was due to the presence of single-atom Pt catalyst. Furthermore, the authors fabricated an electrochemical reactor to validate the concept of selective H_2O_2 production via a fuel cell setup (**Figure 8E**). It was found that the Pt/HSC showed a high H_2O_2 production rate by using the reactor, and the concentration of H_2O_2 generated could reach up to 160 mM. More importantly, the Pt/HSC showed excellent stability without significant aggregation of Pt atoms after 2 h operation cycles (**Figure 8F**).

3.1.3 Carbon-based electrocatalysts

Compared to noble metal-based catalysts, carbon-based materials are inexpensive and earth abundant, and have unique surface and structural properties that can be finely tuned. Thus, carbon-based materials are thought to be interesting alternative to precious metals for H_2O_2 electrochemical synthesis. Actually, carbon-based materials were first studied as alternative electrocatalysts for ORR in fuel cells. It has been widely reported that their activities in alkaline medium can be comparable to or even better than commercial Pt catalysts.⁹⁷⁻¹⁰⁰ However, their activities in acidic medium were usually low. One of the reasons for the low activity was believed to be due to the generation of H_2O_2 through the two-electron process on these carbon-based materials. Since then, much attention has been paid to focus on their selective production of H_2O_2 through ORR under different pH values.

Using carbon catalysts, Brillas and co-workers proposed a Alkaline Fuel Cell (AFC) setup for on-site generation of HO_2^- , which contained a H_2 -diffusion anode and O_2 -diffusion cathode in a KOH electrolyte.¹⁰¹ In such alkaline medium, H_2 was oxidized to water via the two-electron oxidation reaction in the anode: $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2e^-$. Therefore, the overall two-electron process in the AFC setup could then be expressed as follows:

Subsequently, they successfully built up a small-scale flow AFC and found that this setup was able to produce HO_2^- with current efficiency close to 100% and the current densities achieved 100 mA cm^{-2} under optimum conditions. More importantly, this setup could potentially be used for industrial applications of H_2O_2 . Yamanaka et al. demonstrated that neutral H_2O_2 could be obtained effectively by using a solid polymer electrolyte (SPE) setup fed with deionized water, which consisted of a Pt/carbon black anode, a mixed-carbon cathode, and membrane.^{10, 102} Surprisingly, when decreasing the amount of deionized water to expose half of the cathode to an O_2 atmosphere, neutral H_2O_2 aqueous solution at a concentration of 8.06 wt% was obtained with a current efficiency of 26.5%. This neutral H_2O_2 solution produced could then be directly used as disinfectant for daily life purpose.

3.1.3.1 Porous carbon-based materials

Due to the competitive reduction of H_2O_2 to H_2O via another two-electron process, the concentration of H_2O_2 generated using traditional carbon-based materials was normally low. While researchers found the H_2O_2 concentration generated was usually far higher than that of O_2 , which was mainly caused by the low concentration of O_2 on the surface of these carbon-based materials. By using porous graphitic carbon powder as catalyst, Yamanaka et al. found a concentration of 7 wt% H_2O_2 could be produced continuously at a relatively high rate.³ Since then, porous carbon-based materials have been extensively studied as promising candidates for H_2O_2 production.^{7, 103, 104}

The large surface area, tunable pore structure, uniform and adjustable pore size as well as their good conductivity making such material highly suitable for electrochemical H_2O_2 production. Very recently, Bao et al. investigated two different porous carbon-based electrocatalysts for the two-electron oxygen reduction reaction under alkaline conditions.¹⁰⁴ The electrochemical results showed that both porous carbon materials exhibit high activity with a positive onset potential, which is close to the thermodynamic equilibrium potential, and a high H_2O_2 selectivity of $> 70\%$. By using the spectroscopic characterizations and DFT

calculations, the authors found that the sp^2 -type defects are the active sites for the H_2O_2 selection. A practical application of electrochemical production of H_2O_2 from oxygen reduction was recently carried out by Jaramillo's group. They first studied the electrochemical performance of a highly defective carbon with ordered mesoporous structure (CMK-3) in KOH solution and found that a high selectivity of over 90% for H_2O_2 production was achieved.⁷ Apart from the excellent activity and selectivity, the authors found that there was no significant activity loss even after 1000 cycles, suggesting its good stability. Considering the intrinsic stability of defect sites on carbon materials, the authors attributed the observed high stability to their strong resistance to oxidation from the highly active radicals created by the chemical disproportionation of H_2O_2 . Then they fabricated a small-scale membrane-free electrochemical reactor by using CMK-3 as the cathode catalyst and $NiFeO_x$ materials as the anode water oxidation catalyst (**Figure 9**). This reactor demonstrated a continuous production of ca. 0.3 wt% H_2O_2 at a cell voltage of 1.6 V. Notably, such a product solution containing H_2O_2 could be directly used in many commercial applications (**Figure 9C**). In another study, Liu et al. found that the dominant products on hierarchically porous carbon (HPC) for oxygen reduction was H_2O_2 .¹⁰³ The H_2O_2 selectivity of HPC-H24 (hydrothermal treatment for 24h) was 80.9-95.0% in acidic solution, which was comparable to those of noble metal-based catalysts under similar conditions. By using the X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy characterization, the authors found that the excellent performance of HPC was due to their high extent of sp^3 -C bonds and defects.

3.1.3.2 Doped carbon-based materials

Chemical doping has been widely utilized to tune the electronic properties of carbon-based materials. Extensive studies have showed that the electrochemical production of H_2O_2 was strongly correlated to the type and content of the heteroatom. In 2012, Feller et al. reported that the number of transferred electrons during the oxygen reduction on the N-doped

mesoporous carbon was found to be in good agreement with the theoretical one of the two-electron process, demonstrating its highly selective formation of H_2O_2 (**Figure 10B**).³⁵ Based on the structure characterization, the authors pointed out that the favored two-electron process arose from their increased nitrogen content, the radical character of nitrogen-bound carbon as well as the pyrrolic nitrogen sites within the mesoporous N-doped carbon materials. Very recently, the same group found that the peroxide formation of N-doped carbon was twice than that of pure carbon catalysts in 0.1 M HClO_4 .¹⁰⁵ However, the exact correlation between the reactivity and the structure of N-doped carbon materials remains unclear and needs further study. To this end, Nabae and co-workers compared the performance of nitrogen-doped mesopore-dominant carbon and a nitrogen-doped micropore-dominant carbon toward H_2O_2 .¹⁰⁶ They proposed that the mesoporous structure could facilitate the mass transport and the H_2O_2 produced on mesoporous carbon could be released within a relatively short contact time and thus exhibited higher selectivity toward H_2O_2 (**Figure 10C**).

Zhang et al. also found that N-doped carbon can serve as a highly selective H_2O_2 production electrocatalyst.¹⁰⁷ Pescarmona and co-workers reported that N-doped ordered mesoporous carbons prepared by a two-step nanocasting strategy showed not only high selectivity toward the H_2O_2 production but also excellent long-term stability.¹⁰⁸ Recently, Durante and co-workers studied the electrocatalytic activity of N and S doped or N, S co-doped mesoporous carbon toward selective production of H_2O_2 via the two-electron oxygen reduction.¹⁰⁹ In their work, they found that the high selectivity of N-doped mesoporous carbon materials toward H_2O_2 was due to their favorable mass transport ability inside their pores, where a relatively short contact time occurred and it could thus greatly avoid subsequent H_2O_2 reduction to generate H_2O . This phenomenon was also supported by Laura's work in which they found that mesoporous carbon doped with nitrogen content of 4wt% and around 80% of pore volume present the best performance with nearly complete production of H_2O_2 in the alkaline medium.¹¹⁰

Very recently, Fornasiero's group reported an outstanding metal-free electrocatalyst for the unexpectedly selective production of H_2O_2 from oxygen reduction.¹¹¹ The metal-free catalyst consisting of graphitized N-doped single-wall carbon nanohorns (CNHs) was obtained through a multi-step protocol (**Figure 11, top**). It was found that the highly N-doped graphitized carbon layer on the graphitized single-wall carbon nanohorns (g-N-CNHs) played a key role in their enhanced H_2O_2 production performance. This metal-free carbon catalyst could selectively produce H_2O_2 in a wide pH range (1-13). **Figure 12** presented the variation of faradic efficiency in relation to pH and applied potential and the evaluation of the stability over long-term electrolysis. The catalyst can operate at acidic pH to reach a faradic efficiency as high as 98%, outperforming the latest precious metal- and other carbon-based catalysts. Moreover, it also shows excellent performance at either physiological or alkaline pH. The stability test demonstrated that the catalyst sustains a very stable current after 24 hr for the full range of pH values tested. The authors attributed the outstanding activity to a combination of their CNH-dependent facilitation of electron delivery, suitable porosity, and a favorable distribution of the types of N atoms.

The H_2O_2 selectivity of the N-doped carbon was mainly due to the electronic structure change induced by the incorporation of N atoms. Typically, the nitrogen atoms with a higher electronegativity could activate π electrons and induce charge redistribution, which changes the adsorption properties of carbon materials toward OOH intermediate and thus favors H_2O_2 generation. Therefore, one can expect that fluorine, with the highest electronegativity, could also be able to tune the electronic structure of carbon to create the catalytic active sites when doped into carbon materials. Along this direction, using aluminum-based MOF as precursor, Quan's group demonstrated that F-doped hierarchically porous carbon catalysts can be used for improving the activities for electrochemical oxygen reduction to generate H_2O_2 .¹¹² The yield of H_2O_2 generation was found to depend on the F content and the catalyst with F content of 3.41 at.% exhibited H_2O_2 selectivity of 97.5-83.0% in acidic media. Both the DFT

calculations and experimental measurements revealed that the enhanced selectivity toward H_2O_2 production originated from the activation of O_2 molecule and favorable desorption of OOH intermediate by F doping.

3.1.3.3 Surface oxygen functionalized carbon-based materials

Surface oxygen functional groups on carbon-based materials can also be used to tune their electrocatalytic properties. Very recently, Cui's group developed an effective and general approach to improve the H_2O_2 performance of various carbon materials by means of surface oxidation treatment.³⁶ Notably, compared with standard carbon nanotubes (CNTs), a significant decrease in overpotential (~ 130 mV at 0.2 mA) and an enhanced selectivity up to $\sim 90\%$ in both basic and neutral media were observed for oxidized carbon nanotubes (O-CNTs) (**Figure 13**). Various characterization revealed that the existence of C-O and C=O functional groups play the key role in their enhanced performance towards H_2O_2 production. The authors also found that the activity and selectivity for H_2O_2 production were positively correlated with the oxygen content, further indicating the importance of oxygen functional groups. This surface oxidation approach established by Cui's group was also effective for enhancing the H_2O_2 performance of other types of carbon materials with a much lower cost. A similarly enhanced H_2O_2 production performance on other oxidized carbon materials was also observed. Based on the DFT calculations, the authors assigned the origin of the high activity on oxidized carbon materials to the $-\text{COOH}$ functional group in the armchair edge and the C-O-C functional group in the basal plane of the graphene.

Graphene oxide-based materials, which contain various oxygen functional groups both on its basal planes and plane edges, are also expected to show good performance towards H_2O_2 production. Recently, Bryan D. McCloskey et al. found that annealed few-layered mild reduction of graphene oxide at 600°C ($F\text{-mrGO}(600)$) could exhibit outstanding electrochemical HO_2^- production in terms of activity (< 10 mV overpotential), selectivity ($\sim 100\%$) and stability (over 15 h at 0.45V) in alkaline media.²⁸ Structural characterization,

such as XPS, FTIR and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy in combination with in situ Raman spectroelectrochemistry indicated that epoxy or ring ether groups located either on their basal planes or at plane edges are active sites for HO_2^- production (**Figure 14**).

The supporting electrolyte could strongly influence the H_2O_2 selectivity and production rates.¹⁰⁵ Hasché et al. demonstrated that the selectivity and formation rates of metal-free mesoporous nitrogen-doped carbon catalysts was found to increase in the order of neutral (KClO_4) > acidic (HClO_4) > alkaline (KOH) at low potential range (**Figure 15A and B**). Notably, at 0.1 V potential, the peroxide selectivity in neutral media was 1.4 and 6 times higher than that in acidic and alkaline media, respectively. The authors also examined the activity-selectivity-stability relations of the catalysts and found that the catalysts showed a high electrochemical stability toward peroxide in neutral solution (**Figure 15C**). Fornasiero's group found that graphitized single-wall carbon nanohorns with a high degree of N doping (g-N-CNHs) could achieve a 90% faradic efficiency for H_2O_2 production at +0.45 V in PBS solution (pH = 7.4).¹¹¹ Cui's group found that the selectivity of H_2O_2 on oxidized CNTs (O-CNTs) in PBS solution (pH ~ 7) could achieve ~85%.³⁶

3.1.4 Metal complexes

Metal complexes, composed of earth-abundant metals (mainly first-row transition metals such as Fe, Co, Ni, Cu and Mn), have also been extensively used for the two-electron reduction of oxygen to H_2O_2 .^{113, 114} Previously, several Co-porphyrins-based materials have been suggested to serve as highly active and selective electrocatalyst towards H_2O_2 production in fuel cell system.³⁷ Using DFT calculation, Sun et al. found that O_2 can be completely reduced to H_2O_2 without further reduction to H_2O on the Co-porphyrin and Co-phthalocyanine surfaces.¹¹⁵ In another work, Yamanaka et al. found that by using Co-porphyrin derivative as cathode electrocatalyst, 13.5 wt% H_2O_2 solution was obtained with 42% current efficiency at room

temperature.¹¹⁶ The X-ray absorption near-edge structure (XANES) results indicated that Co on a bidentate *N*-coordination site was the active site for H₂O₂ formation.¹¹⁷ More details about this part can be found in a recent focus review by Wonwoo Nam et al. who systematically summarized the two-electron oxygen reduction to form H₂O₂ catalyzed by metal complexes from the viewpoint of catalytic mechanism.¹¹⁸

3.1.5 Metal oxides

Some types of metal oxides have also been shown to exhibit excellent performance on electrochemical H₂O₂ production in alkaline media. For instance, Sun et al. found that when Fe₃O₄ nanoparticles were supported on graphene and/or Printex 6L carbon, the Fe₃O₄/graphene and Fe₃O₄/Printex 6L carbon composites could effectively produce H₂O₂ with selectivity up to 60% through the oxygen reduction under alkaline conditions.¹¹⁹ Accordingly, the authors attributed the enhanced performance of these composites to the synergetic effect between the Fe₃O₄ and carbon supports. Very recently, Yumauchi and co-workers showed that nanoporous Mn-Ru oxides prepared from the thermal treatment of cyano-bridged coordination polymers in air could also serve as a kind of promising catalyst for the direct electrochemical production of H₂O₂ in 0.1 M KOH solution.¹²⁰ The Mn-Ru oxide electrocatalyst in this study could also exhibited a good long-term stability in comparison with previously reported materials.

4. H₂O₂ production from electrochemical water oxidation

4.1 Fundamental aspects of electrochemical water oxidation

Water oxidation has been recognized as one of the most promising technologies for H₂ production in large scale.¹²¹ It normally involves hydrogen evolution at the cathode and O₂ evolution through the four-electron pathway at the anode, as shown in **Equation 18-20**.^{122, 123}

H_2O_2 could also be obtained via the two-electron process, as shown in **Equation 21**.

Thus, the overall water splitting reactions to produce H_2O_2 via the two-electron oxidation of water could be expressed as follows:

However, the production of H_2O_2 by the two-electron oxidation of water usually exhibit relatively low faradaic efficiency, due to competitive O_2 evolution which is thermodynamically more favorable than H_2O_2 formation. On the anode, the as-generated H_2O_2 could be oxidized to O_2 (**Equation 23**) and/or undergo chemical disproportionation to water and oxygen (**Equation 9**).

Besides, water can also be oxidized electrochemically to form OH radicals ($\cdot\text{OH}$) via the one electron process (**Equation 24**) on the anode.¹²⁴

The water oxidation activity of the catalyst can be characterized by using cyclic voltammetry in a three electrode electrochemical cell. The working electrode can be carbon paper, carbon cloth, Ni foam, and so on. A carbon rod was usually used as the counter electrode, while Ag/AgCl or SCE were normally used as the reference electrode. All the potentials were preferentially *iR*-compensated and reported vs RHE for easy comparison.

The quantities of H_2 and O_2 can be measured by gas chromatography analysis. The generated H_2O_2 concentration can be measured by the traditional cerium sulfate $\text{Ce}(\text{SO}_4)_2$ titration method or the potassium permanganate titration one, where the dark purple color of permanganate ion disappears during titration when the MnO_4^- is totally consumed based on the **Equation 25**:⁶

The FE for H_2O_2 production ($\text{H}_2\text{O}_2\%$) is then calculated by

$$\text{FE} = \frac{\text{Generated H2O2 (mol)}}{\text{Theoretical generated H2O2}} \times 100$$

4.2 Electrocatalysts for H_2O_2 production from water oxidation

4.2.1 Carbon-based Materials

Over the past years, the research on water oxidation was mainly focused on the O_2 generation and less attention has been paid to the selective two-electron oxidation to generate H_2O_2 .^{125, 126} A main challenge is to find a material that can selectively produce H_2O_2 instead of O_2 and at the same time inhibit H_2O_2 reduction and conversion. In 2004, Ando and co-workers demonstrated a system that could effectively produce two products: hydrogen and hydrogen peroxide simultaneously via the water oxidation.¹²⁷ The system was composed of a platinum mesh cathode, a carbon material anode and a Nafion polymer electrolyte. In their work, five kinds of carbon material were examined. The remarkable difference among the five kinds of carbon materials were found to originate from the difference of surface condition of these carbon materials. However, despite the potential application of these carbon materials for the electrochemical water oxidation to produce H_2O_2 , the low stability of these carbon materials under high potential, the low current efficiencies and low current densities greatly limit their practical use.

4.2.2 Metal Oxides

In contrast to the oxygen reduction reaction, the oxygen evolution activity was extensively studied on the oxidized surfaces.^{126, 128-133} Currently, the highest catalytic activities were reported on RuO_2 and IrO_2 .²² These catalysts, however, were unstable at high operation potentials and their high cost and scarcity make them unsuitable for large scale applications. Moreover, from the perspective of energy storage, water oxidation to form hydrogen peroxide/hydrogen could be another option with a more favorable value than that for

molecular oxygen/hydrogen, as well as the desirable advantage of producing a more useful oxidizing agent than oxygen.

Recently, for the first time, MacFarlane's group reported that a MnO_x electrocatalyst can effectively catalyze water oxidation to generate H₂O₂ at low overpotentials.¹⁵ The H₂O₂ production yield was determined to be 77% by permanganate oxidation experiment. The authors attributed the efficiency loss of MnO_x to the competing process of four-electron pathway to oxygen, the H₂O₂ chemical disproportionation, and further oxidation to water especially in alkaline medium and the presence of ammonia. In another work, the same group systematically investigated the effect of various parameters (pH, potential and electrolyte ions) on the electrochemical oxidation of water to produce H₂O₂.¹³⁴ It was found that H₂O₂ production occurred at pH > 9.5. And a nearly 100% Faradaic efficiency of H₂O₂ formation was observed in the pH range of 10-10.5 in the presence of 1M butylammonium sulphate.

H₂O₂ production that is from water and utilizes sustainable electricity from renewable power sources would offer unique opportunities for sanitization and purification of drinking water to people having limited access to clean water. Recently, Jens K. Nørskov's group fabricated a novel decentralized device that could directly utilize sunlight to split water into H₂O₂ and H₂ simultaneously.⁵ The generated H₂O₂ could be directly used to oxidize the organics in water while the hydrogen gas bubbles out. In enabling this device, an electrocatalyst that can oxidize water to generate H₂O₂ while suppressing the thermodynamically favored four-electron pathway to oxygen are needed. By using the thermodynamic analysis based on density functional theory calculation, they showed that the free energy of adsorbed OH* could be used as a descriptor for determining trends in two-electron oxidation of H₂O to produce H₂O₂. Based on that, they found that SnO₂ and TiO₂ are good candidate materials for H₂O₂ generation (**Figure 16A**). This work provides a quantitative foundation for the identification of efficient and selective electrocatalyst materials.

As aforementioned, water can be oxidized electrochemically to form OH radicals ($\cdot\text{OH}$), H_2O_2 and O_2 via the one, two, and four electron processes, respectively. However, there is lack of criteria characterizing catalysts with a tendency for selectivity toward the different products. To this end, Jens K. Nørskov's group developed a two-dimensional selectivity diagram of the catalyst toward the one, two, and four electron pathways during the water oxidation process.¹²⁴ After rationalizing the experimental observations, the two-dimensional selectivity diagram for $\cdot\text{OH}$, H_2O_2 , and O_2 evolution were presented in **Figure 15B**. It was found that WO_3 , BiVO_4 , MnO_2 , and SnO_2 , which are known to produce H_2O_2 , are well located in the green region.¹⁵ TiO_2 , which is known to form both $\cdot\text{OH}$ and H_2O_2 , is close to the border of weak OH adsorption (red region). And catalysts such as IrO_2 , RhO_2 , and PtO_2 , which are known to evolve O_2 as the major product, are located in the selectivity region for O_2 evolution. Therefore, the selectivity diagram developed by Jens K. Nørskov's group could be used to guide the development of new catalysts for H_2O_2 production.

Both theoretical and experimental studies of how the H_2O_2 generation efficiency on metal oxides vary with applied biases was critical for understanding the competition among one-, two- and four-electron processes of water oxidation. In a recent work, by using the DFT calculations and experimental studies, Jens K. Nørskov's group investigated the activity trends of several different metal oxides towards water oxidation for H_2O_2 production.⁶ It was found that all the metal oxide investigated were able to generate H_2O_2 with the onset potentials for H_2O_2 production increased in the order of $\text{TiO}_2 > \text{SnO}_2 > \text{BiVO}_4 > \text{WO}_3$ (**Figure 17 A and B**). The faraday efficiency and the amount of H_2O_2 generated as a function of the applied bias were presented in **Figure 17C and D**, respectively, for each metal oxide. Note that due to the competition with one, and four-electron oxidation reactions, there was an optimal potential window for H_2O_2 production on these metal oxides. Surprisingly, the BiVO_4 exhibited the highest FE (70%) and H_2O_2 production rate albeit at low current densities. All

these works has demonstrated the potential of H_2O_2 production over metal oxides, especially BiVO_4 , which was thought to be best electrocatalysts for the two-electron water oxidation reaction to generate H_2O_2 .

5. Conclusions and future outlook

Oxygen electrochemistry represents an attractive alternative for the selective production of H_2O_2 via the two-electron pathway of oxygen reduction in fuel cells and water oxidation in electrolyser. Typically, the electrochemical production of H_2O_2 in a fuel cell via the two-electron oxygen reduction reaction allows for eventual H_2O_2 production and co-generation of electrical current on a large scale; while the H_2O_2 generation from the two-electron water oxidation can produce two valuable products in a single electrochemical device by using water as the only raw materials. Both processes are efficient for small-scale application in water cleaning and disinfection, for which typical concentration requirements are in the range of 2-8%. Moreover, they can be coupled with renewable power sources and thus can be suitable for applications in remote regions.

Intensive researches have been carried out over the past years in this field. However, due to the lack of efficient electrocatalysts, the electrochemical production of H_2O_2 through oxygen electrochemistry often shows low efficiency. In addition, the issue of instability caused by the chemical decomposition and further conversion of the as-generated H_2O_2 also inhibit their practical applications. As a result, there is a need to develop good catalysts which are not only active but also selective, favoring the two-electron pathway over the four-electron one and at the same time being able to inhibit the H_2O_2 decomposition and further conversion.

In this review, for the first time, recent research progress on direct electrochemical production of H_2O_2 through the two-electron oxygen reduction and water oxidation has been summarized. Specifically, for the electrochemical production of H_2O_2 from oxygen reduction, recent theoretical and experiments studies have showed that the activity for the H_2O_2 production is a function of the binding energy of the OOH^* intermediate. An ideal catalyst

means that the adsorption of OOH^* should be neither too strong nor too weak so that the overpotential for the two-electron oxygen reduction reaction to produce H_2O_2 can be minimized. And the selectivity is related to the ability of the catalyst to split the O-O bond. Several kinds of materials (**Table 1**): metallo-porphyrins (M-porphyrins), graphitic porous carbon materials, a gold surface modified with isolated Pd guest atoms, a Hg surface with isolated Pt, Pd, and Cu, single Pt atoms, metal oxides, were found to favor OOH^* formation and disfavor O-O bond breaking during the oxygen reduction. Among these, the concept of single active sites is interesting and may represent the most efficient electrocatalyst towards the H_2O_2 production with the highest activity and selectivity as well as the good stability. Accordingly, the single active sites will potentially open the door to find suitable electrocatalyst toward the electrochemical production of H_2O_2 .

On the other hand, carbon materials and metal oxides have been examined as electrocatalysts towards the H_2O_2 production from two-electron oxygen evolution reaction, although low efficiency on carbon-based materials was reported. Theoretical studies have demonstrated that the free energy of adsorbed OH^* could be used as the descriptor for predicting activity trends towards H_2O_2 production through the two-electron water oxidation reaction. By using the DFT calculations and experimental measurements, Jens K. Nørskov's group identify that WO_3 , SnO_2 , TiO_2 , and BiVO_4 could be used as excellent electrocatalyst for the H_2O_2 evolution from two-electron oxygen evolution reaction, with the BiVO_4 exhibiting the best activity.⁶

Despite all the significant achievements have been made in the past years in the field of direct electrochemical production of H_2O_2 through oxygen electrochemistry, there are still some challenges in this fascinating field.

(1) Noble metals are currently thought to be the most efficient catalysts toward the two-electron oxygen reduction to generate H_2O_2 . However, the high cost and scarcity of noble metals greatly hinder their large-scale application. Thus, in order to enable the industrial

application of the electrochemical production of H_2O_2 , low-cost, earth-abundant and highly stable electrocatalysts are needed.

(2) Catalysts usually need to be deposited on supports to prevent them from aggregation and at the same time to increase their utilization efficiency during the catalytic reactions. Previous studies have demonstrated that supports played an important role in the catalytic process. Therefore, more efforts should be devoted to find good catalytic supports and investigate their effect on the electrocatalytic properties.

(3) Single-atom catalysts are a new frontier in selective H_2O_2 production through two-electron oxygen reduction. Single-atom catalysts can not only effectively tune the selectivity of a specific reaction but also maximize their utilization efficiency.⁷⁷ Because of their well-defined composition, it could be used as an ideal model to understand the correlation between structure and their catalytic mechanism. However, although many different synthesis techniques have been developed, there is still lack of an efficient route for obtaining single-atom catalyst with high yield and high stability, which hinders the viability of them in practical applications. As a result, developing general and simple strategies to prepare single-atom catalysts is highly needed and will be challenging.

(4) Although extensive studies have demonstrated the capability of carbon-based materials for the electrochemical production of H_2O_2 , it remains difficult to establish the activity trends for H_2O_2 production of these materials. Thus, more efforts should be paid to better understand the activity trends of carbon-based materials.

(5) Metal oxides are predicted to be good electrocatalysts for H_2O_2 production from two-electron water oxidation reaction. However, only several metal oxides were reported so far. Therefore, research efforts should be extended to more metal oxides including their composites.

(6) Only a few setups at device level have been successfully fabricated over the past years for the production of H_2O_2 and direct application in water treatment,⁸ while the efficiency was

still very low and the devices are complicated. More engineering efforts are needed to develop better electrode/reactor configuration in the future.

(7) Production of H_2O_2 from two-electron oxygen electrochemistry using renewable energy is promising from the viewpoint of practical applications.^{137, 138} Recent studies have demonstrated the optimal potential range of BiVO_4 for H_2O_2 production via two-electron oxygen evolution under sun illumination could decrease significantly compared to that in dark and the Faraday efficiency of H_2O_2 production could achieve up to 98% under sun illumination.⁶ Thus, future study on electrochemical production of H_2O_2 should be linked to the use of renewable energy sources.

Overall, the deployment of electrocatalyst for oxygen electrochemistry has brought about significant improvements to the efficiency and selectivity. More challenges in the design of efficient catalysts, understanding the correlations between catalysts' structure and their activities, as well as the practical applications of these processes have to be faced in future work.

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Conflict of Interest

The authors declare no conflict of interest.

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ORR

Water oxidation

Figure 1. A brief summary of some important finding of H_2O_2 production through two-electron oxygen electrochemistry. Images reproduced with permission as follows: “ $\text{Au}_{92}\text{Pd}_8/\text{C}$ ”: reproduced with permission.^[33] Copyright 2011, American Chemical Society.

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Scheme 1. Proposed oxygen reduction and oxygen evolution reaction mechanisms.

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Scheme 2. (A) Schematic of a single compartment cell. Reproduced with Permission.^[30]

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Figure 2. (A) CVs of ORR on different charged Au₂₅ nanoclusters in O₂ and N₂-saturated 0.1 M KOH. (B) RRDE voltammograms recorded on Au₂₅ nanoclusters with different charges in O₂-saturated 0.1 M KOH solution at 1600 rpm and the ring potential was constant at 0.5 V vs saturated calomel electrode (SCE). (C) H₂O₂ selectivity and (D) the electron transfer number (n) of Au₂₅ nanoclusters as a function of the applied potentials, based on the RRDE data in B. (E) Schematic illustration of selective electrochemical production of H₂O₂ on Au₂₅⁻ nanoclusters. Reproduced with permission.^[45] Copyright 2014, The Royal Society of Chemistry.

Figure 3. RRDE results obtained for ORR on different Au-Pd catalyst in O_2 saturated 0.1 M $HClO_4$. Rotation speed: 900 rpm. Scan rate: 50 mV s^{-1} . Ring potential: 1.28 V. The colors (green for I_d , violet for I_r , brown for $S_{H_2O_2}$) are graded with the change in composition. (a) Disk anodic polarization current (I_D) (b) Ring current (I_R) profiles during one potential cycle. (c) Calculated values of $S_{H_2O_2}$. (d) $S_{H_2O_2}$ and I_R maxima vs disk potential. Reproduced with permission.^[32] Copyright 2017, Elsevier B.V.

Figure 4. Experimental characterization of Pt-Hg/C nanoparticles. (A) H₂O₂ selectivity as a function of the applied potential. (B) RRDE voltammograms at 1,600 rpm in O₂-saturated electrolyte with the disk current, ring current and current corresponding to hydrogen peroxide obtained from the ring current (only the anodic cycle is shown). All electrochemical measurements were taken in 0.1 M HClO₄ and at 50 mVs⁻¹ at room temperature. The disk current is normalized to the electrochemical surface area of Pt nanoparticles before deposition of Hg. (C) TEM image of Pt-Hg/C nanoparticles. (D) Schematic representation of a Pt-Hg/C nanoparticle. (Mercury - blue, Platinum - grey). (E) HRTEM image of a single Pt-Hg nanoparticle, with the corresponding EDS spectrum of the particle superimposed on top, with peaks corresponding to Pt and Hg from the nanoparticle, and Cu, from the TEM grid. Reproduced with permission.^[2] Copyright 2013, Nature Publishing Group.

Figure 5. Overview of different electrocatalysts for H₂O₂ production. (A) Mass-transport corrected Tafel plots of kinetic current densities in acidic media based on RDE or RRDE measurements. (B) Faradaic efficiency for each electrocatalyst. Reproduced with permission.^[30] Copyright 2018, American Chemical Society.

Figure 6. Trends in activity and selectivity for H_2O_2 production. (A) Schematic representation of oxygen reduction to H_2O_2 on a model Pd_2Hg_5 (001) surface. Palladium atoms are represented in green, mercury in blue, oxygen in red, and hydrogen in yellow. (B) Partial kinetic current density to H_2O_2 as a function of the applied potential, corrected for mass transport losses. (C) Potential required to reach 1 mA cm^{-2} of kinetic current density to H_2O_2 on polycrystalline catalysts as a function of the calculated HOO^* binding energy. The solid lines represent the theoretical Sabatier volcano plot. The dotted line represents the thermodynamic potential for oxygen reduction to H_2O_2 . (D) H_2O_2 selectivity for different catalysts at 2.5 mA cm^{-2} of total current density. All electrochemical experiments were performed at 50 mV s^{-1} and 1600 rpm in O_2 -saturated 0.1 M HClO_4 at room temperature with corrections for Ohmic drop. Geometrical surface area was used. Reproduced with permission.^[38] Copyright 2014, American Chemical Society.

Scheme 3. The proposed ORR pathways on Pt surface of (A) Pristine Pt/C and (B) Amorphorous carbon layer-coated Pt. (C-F) HRTEM images of the catalysts: (C) Pt/C, (D-F) Pt nanoparticles coated with amorphorous carbon layers at different times. Reproduced with permission.^[63] Copyright 2014, American Chemical Society.

Figure 7. (A) Ring currents concurrently obtained during the ORR with a potential maintained at 1.2 V for various samples. (B) ORR polarization curves in O_2 -saturated 0.1 M HClO_4 . (C) H_2O_2 selectivity calculated from the oxygen reduction current and the H_2O_2 oxidation current. (D) Mass activity and (E) Surface area specific activity of various Pt catalysts at overpotential of 0.25 V. Reproduced with permission.^[88] Copyright 2015, Wiley-VCH.

Figure 8. (A) ORR activities of the catalysts measured in O₂-saturated 0.1 M HClO₄ electrolyte with 900 rpm rotation. (B) H₂O₂ production selectivity estimated by RRDE experiments. (C) PDR activities derived from the decline in H₂O₂ concentration in a 10 mM H₂O₂ starting solution (50 ml) containing 10 mg catalysts. For comparison, the PDR of a blank solution without catalyst was also investigated. (D) PRR activities measured in a 10 mM H₂O₂/0.1 M HClO₄ electrolyte with 900 rpm rotation. (E) Accumulated H₂O₂ concentrations in an H-cell with a 1 M HClO₄ electrolyte and a Nafion 115 membrane. The H-cell was operated in short-circuit condition ($V = 0$) at 278 K. (F) Concentrations of H₂O₂ produced on the Pt/HSC in an electrochemical H-cell during repeated 2 h operation cycles. Concentrations of H₂O₂ are evaluated by iodometry. Reproduced with permission.^[89] Copyright 2016, Nature Publishing Group.

Figure 9. (A) Schematic diagram of the H₂O₂ generation device in an electrolyzer mode. (B) Electrochemical performance by chronoamperometry and chronopotentiometry. (C) Schematic illustration of an on-site electrochemical H₂O₂ production device for water purification. Reproduced with permission.^[7] Copyright 2017, The Royal Society of Chemistry.

Figure 10. (A) Schematic illustration of H_2O_2 production of meso-BMP-800; (B) Koutecky–Levich plot. Reproduced with permission.^[35] Copyright 2012, American Chemical Society. (C) Schematic illustration of the oxygen reduction reaction over mesoporous carbon catalysts (left) and microporous carbon catalysts (right). Reproduced with permission.^[106] Copyright 2014, American Chemical Society.

Figure 11. Scheme of the synthetic protocol to obtain g-N-CNHS (Top) and relevant TEM images of the nanostructured material at each stage of the synthesis (Bottom). Reproduced with permission.^[111] Copyright 2018, Elsevier B.V.

Figure 12. (A–C) FE% of H₂O₂ produced after 1 hr of electrolysis at three different fixed potentials (for each pH value) using a g-N-CNH modified electrode at pH 1.0 (A), pH 7.4 (B), pH 13.0 (C) at three different potential values for each medium. (D) Plots of FE percentage versus time. (E) A stability test at pH 1.0, 7.4, and 13.0 over 24 hr. Reproduced with permission.^[111] Copyright 2018, Elsevier B.V.

Figure 13. Oxygen reduction performance of CNTs and O-CNTs. Polarization curves at 1600 rpm (solid lines) and simultaneous H_2O_2 detection currents at the ring electrode (dashed lines) in 0.1 M KOH (A) or 0.1 M phosphate buffered saline (PBS) (B). Calculated selectivity of these two catalysts at various potentials in 0.1 M KOH (C) and 0.1 M PBS (D). Stability measurements of O-CNTs in 0.1 M KOH (E) and 0.1 M PBS (F). Reproduced with permission.^[36] Copyright 2018, Nature Publishing Group.

Figure 14. Structural characterization and electrocatalytic activity of thermally annealed *F*-mrGO electrodes. A), Atomic ratio of the as-prepared, unannealed mrGO and annealed (300 and 600 °C) mrGO powders measured by C1s XPS. B), ORR behaviour of the catalysts measured by cathodic linear sweep voltammetry (LSV, 2.0 mV S⁻¹) in O₂-saturated (~800 torr O₂) in 0.1 M KOH solution. C), FTIR spectra of various mrGO powder samples. D), High-resolution oxygen K-edge near-edge X-ray absorption fine structure (NEXAFs) spectra of unannealed and annealed mrGO powder samples. E), Idealized schemes of proposed low-overpotential active sites on *F*-mrGO and *F*-mrGO (600). Reproduced with permission.^[28]

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Figure 15. (A) RRDE measurements of the mesoporous N-doped carbon with 1600 rpm in dependence of the nature of electrolyte and pH values. The ring current was detected on the pure Pt ring at 1.2 V and the disk current density was normalized to the geometric area of glassy carbon disk (0.196 cm^2). Roman I to IV and the dashed lines indicated the different observed regimes for the H_2O_2 formation and its lifetime in each electrolyte; (B) Percentage peroxide formation detected on the Pt ring electrode in various 0.1 M electrolyte solutions at different pH values in a potential range from 0.06 to 0.20 V, obtained from RRDE measurements shown in (A); (C) Long-term RRDE measurements for the meso-BMP catalyst in 0.1 M KClO_4 electrolyte at room temperature. Reproduced with permission.^[105] Copyright 2016, Elsevier B.V.

Figure 16. (A) Activity volcano for the 2e⁻ and 4e⁻ oxidation of water. The scaling relations used to construct the volcano are $\Delta G_{OOH} = \Delta G_{OH} + 3.2$ (eV) and $\Delta G_O = 2\Delta G_{OH} + 0.28$ (eV). Reproduced with permission.^[5] Copyright 2015, American Chemical Society. (B) Phase diagram in terms of the binding energies of O* versus OH*. The black solid line displays the scaling line between O* and OH* on different oxides adapted from refs^{5, 37, 133} and ¹³⁵. The corresponding adsorption energies for IrO₂, RhO₂, and PtO₂ are adapted from ref ¹³³. For MnO₂, the energies are from ref ¹³⁶ with selected Hubbard U value of 2 as recommended by Wang et al.¹³⁷ BiVO₄ adsorption energies are calculated in this work. Blue, green, and red highlighted colors indicate regions in which O₂, H₂O₂, or OH radical are expected to be the major product, respectively, in terms of purely thermodynamic constraints. Reproduced with permission.^[124] Copyright 2017, American Chemical Society.

Figure 17. (A) The J–V curves of four metal oxides without illumination, in which the current onset suggests the onset of H₂O₂ production. (B) Theoretical predicted onset potentials vs experimental measured onset potentials for H₂O₂ production. (C) The Faraday efficiency (FE). (D) The mole amount of H₂O₂ generated (n) vs potential (V) without illumination. Both show that BiVO₄ has the highest FE and n for H₂O₂ production over other metal oxides. Reproduced with permission.^[6] Copyright 2017, Nature Publishing Group.

Table 1. A comparative summary of H₂O₂ production performance from ORR.

Electrocatalysts	Electrolytes	H ₂ O ₂ yield (%)	Mass Activity (A g ⁻¹)	Onset potential vs. RHE	References
PtHg ₄ /C	0.1 M HClO ₄	96	26±4	0.6 V	[2]
Pd ₂ Hg ₅ /C	0.1 M HClO ₄	95	~133	~0.7 V	[38]
<i>F</i> -mrGO(600)	0.1 M KOH	~100	~150	0.78 V	[28]
Pt ₁ /TiN	0.1 M HClO ₄	90	78	~0.50 V	[88]
Pt ₁ /HSC	0.1 M HClO ₄	96	None	0.71 V	[89]
	0.1 M H ₂ SO ₄	98	None	0.40 V	
g-N-CNHS	0.1 M PBS	90	None	0.53 V	[111]
	0.1 M NaOH	63	None	0.71 V	
Au ₉₂ Pd ₉ /C	0.1 M HClO ₄	95	~14	~0.60 V	[33]
CMK-3	0.1 M KOH	90	None	~0.80 V	[7]
Meso N-doped carbon	0.1 M HClO ₄	65.2	None	~0.60 V	[35]
	0.5 M H ₂ SO ₄ + 0.05 M Na ₂ SO ₄	95	None	~0.70 V	
Hirarchically Porous Carbon	0.1 M Na ₂ SO ₄ + 0.5 M H ₂ SO ₄	82.4	None	~0.60 V	[103]
	0.1 M Na ₂ SO ₄	70.8	None	~0.60 V	
Oxidized CNTs	0.1 M KOH	~90	None	~0.80 V	[36]
	0.1 M PBS	~85	None	~0.60 V	
Au ₂₅ ⁻ nanoclusters	0.1 M KOH	90	None	~0.80 V	[45]
Au-Pt-Ni nanorods	0.1 M KOH	95	192.9	~0.70 V	[50]
AuPd nanoparticles	0.1 M HClO ₄	95	None	~0.70 V	[32]
Carbon-coated Pt nanoparticles	0.1 M HClO ₄	41	None	~0.70 V	[63]

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Direct electrochemical production of hydrogen peroxide (H_2O_2) through two-electron oxygen reduction and water oxidation is summarized. The structure, component and composition of the electrocatalysts strongly correlate with their selectivity, activity and durability. This review also provides some guidelines for rational design of highly efficient electrocatalysts towards electrochemical H_2O_2 generation on demand.

Keyword: H_2O_2 production, selective, electrochemical, oxygen electrochemistry, two-electron

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Selective Electrochemical H_2O_2 Production through Two-electron Oxygen Electrochemistry