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ABSTRACT
Hydrogen peroxide (H$_2$O$_2$), the simplest peroxide consisting of only hydrogen and oxygen, is globally used as a green oxidant. It is also a promising fuel source, and it can be produced on large scales in centralized containers. H$_2$O$_2$ is mainly produced by the anthraquinone process, but it involves energy-consuming reactions and generates organic waste. As the demand for H$_2$O$_2$ continues to grow, alternative technologies that overcome these drawbacks are sought for its generation. The generation of H$_2$O$_2$ through the redox reaction of water and oxygen can be a low-cost, sustainable, and efficient production method. However, this reaction requires active and stable catalysts. In general, H$_2$O$_2$ can be generated by the oxidation of H$_2$O at the anode of an electrochemical cell. Alternatively, H$_2$O$_2$ can also be formed by the reduction of O$_2$ at the cathode. Despite the progress in the development and advancement of materials that catalyze these reactions, further research is required to increase the electron transport rates and active sites of the catalyst. In this article, we review the available catalytic materials for the electrochemical production of H$_2$O$_2$ and provide a summary and outlook of this field.

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I. INTRODUCTION

Hydrogen peroxide (H$_2$O$_2$) was first artificially synthesized in 1818 by Baron Thenard, a French chemist. H$_2$O$_2$ is recognized as one of the 100 most historically significant chemicals, and it is produced industrially on a very large scale. It is used as a reagent in chemical, pulp industries, wastewater treatment, and fuel cell technologies. As it is completely soluble in water, which enables its easy transportation, it is regarded as an ideal energy carrier alternative to hydrogen (H$_2$) gas in the energy field. At present, H$_2$O$_2$ is predominantly produced by the anthraquinone process. However, this process is not eco-friendly because it involves multi-step reactions; it requires high energy input for the hydrogenation and further oxidation of alkylanthraquinone used as the precursor. In addition, alkylanthraquinone is not completely converted to anthraquinone because its chemical reactivity is moderate, which can lead to several undesired side reactions. Furthermore, anthraquinone should be continuously replenished to maintain a satisfactory rate of H$_2$O$_2$ production. Therefore, there is a demand for the development of alternative H$_2$O$_2$ production methods, for both environmental and economic reasons. Several articles have previously reviewed the established anthraquinone method and alternative methods of H$_2$O$_2$ production in detail. This mini-review provides a brief overview of this field and focuses on the most recent research progress in the development of catalysts for H$_2$O$_2$ synthesis.

The alternative approaches for H$_2$O$_2$ production can be divided into three major categories: direct H$_2$O$_2$ synthesis, photocatalyzed H$_2$O$_2$ synthesis, and electroreduction of O$_2$. Each of these methods has its advantages, and each has been developed gradually with the development of catalytic materials that boost the redox reactions of the H$_2$/O$_2$/water (H$_2$O) system. Among these approaches, the direct synthesis of H$_2$O$_2$ from H$_2$ and O$_2$ gases is efficient. Direct synthesis can be accomplished through noble metal catalysis, the fuel cell method, and plasma methods. However, this approach requires precisely controlled amounts of H$_2$ and O$_2$ gases because the H$_2$/O$_2$ mixture can explode over a wide range of H$_2$ or O$_2$ concentrations, which makes it difficult to implement
FIG. 1. Pathways for H$_2$O$_2$ production: direct synthesis, photocatalysis, and electroreduction of O$_2$.

FIG. 2. Theoretical volcano plot for two-electron (blue) and four-electron (red) redox reactions of O$_2$ or H$_2$O$_2$, including the potentials for various materials under ambient conditions. The solid and dashed lines represent reduction and oxidation reactions, respectively. The catalysts are categorized as pure metal (yellow), metal alloy (green), metal:nitrogen/carbon (black), and metal oxide (orange) catalysts. The equilibrium potentials for the two-electron reduction of O$_2$ and the two-electron oxidation of H$_2$O$_2$ are shown as dotted and dashed lines, respectively. $U_L$ represents the theoretical limiting potential, and SHE represents the standard hydrogen electrode. Adapted with permission from Yang et al., ACS Catal. 8, 4064 (2018) and Viswanathan et al., J. Phys. Chem. Lett. 6, 4224 (2015). Copyright 2018 and 2015 American Chemical Society.

Some inert gases, such as nitrogen, carbon dioxide (CO$_2$), and argon, can, however, be included into the H$_2$/O$_2$ mixture to mitigate the risk of explosion.

In comparison, the use of photocatalytic systems for H$_2$O$_2$ production has many merits, and it has been continuously studied to better understand the associated advantages. This approach is safer than the direct synthesis because H$_2$ gas is not used. Instead, abundantly available H$_2$O and O$_2$ are the only reagents required, and no toxic by-products are generated, which makes it a green method. The process starts from the photoexcitation of the catalyst to induce charge separation in its band structure. Light-induced electrons mediate the reduction of O$_2$ to H$_2$O$_2$, while the photoexcited holes oxidize H$_2$O to H$_2$O$_2$. Furthermore, H$_2$O$_2$ can also be generated by the two-electron oxidation of H$_2$O on catalytic anodes. However, this method suffers from low H$_2$O$_2$ selectivity because electrons and holes can also induce the decomposition of H$_2$O$_2$.

Finally, the synthesis of H$_2$O$_2$ by the electrochemical reduction of O$_2$ is also a promising alternative. In this process, noble metals, metal alloys, and carbon-based materials are used as catalytic materials either individually or in combination. These electrocatalysts have been developed to achieve high efficiency, selectivity, and even stable properties in the two-electron reduction process. Since the discovery of the Electro-Fenton (EF) reactions, O$_2$ reduction has been developed further, leading to improved H$_2$O$_2$ production.$^{26}$ H$_2$O$_2$ can be produced by the in situ reduction of the OH$^-$ radical on the surface of a catalyst-loaded cathode in a treated solution fed with O$_2$ or air.$^{26}$ However, as O$_2$ might be reduced via the direct four-electron or two-electron pathways, there is a need to develop efficient electrocatalysts with high selectivity for the reduction of O$_2$ to H$_2$O$_2$.

In general, H$_2$O$_2$ can be generated by electron- and proton-associated reactions of O$_2$ and H$_2$O, which can be categorized as follows: (i) direct synthesis from H$_2$ and O$_2$; (ii) 2e$^-$/2H$^+$ oxidation of H$_2$O$_2$; (iii) 2e$^-$/2H$^+$ reduction of O$_2$; and (iv) the combination of the 4e$^-$/4H$^+$ oxidation of H$_2$O and the 2e$^-$/2H$^+$ reduction of O$_2$. The electrochemical synthesis of H$_2$O$_2$ involves competitive H$_2$O$_2$ generation and decomposition reactions. The development of catalysts for H$_2$O$_2$ synthesis is not simple because catalysts generally promote both of these competing reactions. An ideal catalyst should promote the completion of redox reactions to H$_2$O$_2$ and also facilitate the rapid release of H$_2$O$_2$ from the reaction site before further
oxidation or reduction to H\textsubscript{2}O or O\textsubscript{2}, respectively. Therefore, many studies have focused on developing catalysts that show high selectivity in the oxidation of H\textsubscript{2}O and the reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2}. Figure 2 shows the calculated limiting potential (U\textsubscript{L}) as a function of free energy change (AG) for the two- or four-electron reactions on various materials. Density functional theory (DFT) calculations aid the design and application of catalysts suitable for H\textsubscript{2}O\textsubscript{2} synthesis. Such catalysts are mainly metals, carbon-based materials, and transition metal oxides, and these materials exhibit both small overpotentials and high H\textsubscript{2}O\textsubscript{2} selectivities.\textsuperscript{10–14} In addition, studies on the scale-up of the reaction for industrialization are also being actively pursued and reviewed.\textsuperscript{15–18} This manuscript briefly and broadly surveys the catalytic materials used in H\textsubscript{2}O\textsubscript{2} synthesis, and in particular, their modification for achieving efficient electrochemical H\textsubscript{2}O\textsubscript{2} generation.

II. CATALYTIC MATERIALS FOR ELECTROCHEMICAL H\textsubscript{2}O\textsubscript{2} GENERATION

Various materials can act as catalysts with high selectivity in H\textsubscript{2}O\textsubscript{2} synthesis. Carbon-based materials have been widely developed and used because of their high performance, durability, and economic benefit. Meanwhile, metal, alloy, and their oxide forms also have superior catalytic abilities, and their syntheses and surface modification have been studied well. To achieve high efficiency, the electrode and catalytic materials can be developed as nanostructures. Small particles or structures provide a higher specific surface area and hence more active sites. In addition, small particles or pores induce high O\textsubscript{2} bubble binding affinity, which can enhance the H\textsubscript{2}O\textsubscript{2} selectivity. For instance, decreasing the size of platinum nanoparticles increases the efficiency of the generation of H\textsubscript{2}O\textsubscript{2} from O\textsubscript{2}.\textsuperscript{19} In the following subsections, we provide an account of the catalytic materials available for the efficient electrochemical production of H\textsubscript{2}O\textsubscript{2}.

A. Carbon-based materials

Carbon materials can be easily prepared and used in industrial applications that require chemical and mechanical stability.\textsuperscript{20} Therefore, they have been widely studied, and their activities have been shown to be comparable to or even better than those of other H\textsubscript{2}O\textsubscript{2} catalysts.\textsuperscript{21–23} Hitherto, carbon materials, such as graphite,\textsuperscript{24–26} graphene,\textsuperscript{27–29} and carbon nanotubes (CNTs),\textsuperscript{30–32} have been adopted in various forms, for example, as powders and thin films, to promote O\textsubscript{2}-reduction and H\textsubscript{2}O-oxidation reactions in order to produce H\textsubscript{2}O\textsubscript{2}. To further promote the catalytic activities and electron transfer rates, pores and/or sufficient defects can be deliberately introduced into these catalysts. However, a catalyst with high porosity can decrease the H\textsubscript{2}O\textsubscript{2} output by impeding O\textsubscript{2} release from the reaction sites.\textsuperscript{33} Therefore, the degree of porosity and structural defects should be optimized precisely.

Graphite has been used as a basic carbon support to enhance the efficiency of H\textsubscript{2}O\textsubscript{2} production. For example, Yang et al. fabricated a gas diffusion electrode (GDE), in which carbon black was deposited on graphite gas diffusion layers to catalyze the production of H\textsubscript{2}O\textsubscript{2} through O\textsubscript{2} reduction. Owing to the porous structure of the electrode, which has hydrophobic surfaces, the interfacial areas between the gas, electrolyte, and electrode were considerably higher, which is beneficial to the catalytic efficiency. Furthermore, Yu et al. deposited composites of carbon black and polytetrafluoroethylene (PTFE) emulsion on graphite to improve H\textsubscript{2}O\textsubscript{2} production.\textsuperscript{34} They optimized the performance of the catalyst layer in the GDE to achieve an accumulation of H\textsubscript{2}O\textsubscript{2} of 1855 mg l\textsuperscript{−1} in 180 min at a flow rate of 0.05 (O\textsubscript{2}) l min\textsuperscript{−1}. Furthermore, annealing of the graphite enhanced the H\textsubscript{2}O\textsubscript{2} selectivity, owing to the enlargement of the hydrophobic areas where the diffusion of O\textsubscript{2} to the electrode could be accelerated. Perez et al. fabricated carbon cathodes with different PTFE loadings to determine the optimal permeability of the catalytic surface.\textsuperscript{35} Upon the calculation of the electrode, the accumulation of H\textsubscript{2}O\textsubscript{2} increased by more than one order of magnitude. They demonstrated that structural modification was responsible for the observed rapid reactions at the diffusion electrodes.

Furthermore, graphene, a single layer of graphite with a two-dimensional (2D) honeycomb-like structure, has also been applied in H\textsubscript{2}O\textsubscript{2} production owing to its excellent optical, mechanical, electrical, thermal, and physicochemical properties, as well as a high specific surface area.\textsuperscript{36} Yang et al. developed a hybrid electrode with carbon black and electrochemically exfoliated graphene.\textsuperscript{37} The O\textsubscript{2}-reduction reactions (ORRs) were promoted owing to higher rates of electron transfer in the exfoliated graphene electrode without a change in the mechanism of the ORR. Furthermore, the introduced graphene increased the number of active sites and the hydrophilicity of the cathode surface, thus leading to enhanced O\textsubscript{2} diffusion. The efficiency of the catalytic electrode in H\textsubscript{2}O\textsubscript{2} production was found to be 7.7 mg cm\textsuperscript{−2} h\textsuperscript{−1}, with a relatively low energy consumption of 9.7 kW h kg\textsuperscript{−1}. Reduced graphene oxide (rGO), which has unique properties, can also be used as a co-catalyst and electron mediator. As its Fermi level can be adjusted, rGO can be used along with other semiconductors with a suitable band structure to serve as an electron transfer medium. Kim et al. synthesized highly selective and efficient rGO-based electrocatalysts through the mild thermal reduction of GO (mrGO) for generating H\textsubscript{2}O\textsubscript{2} from O\textsubscript{2}.\textsuperscript{38} Through spectroscopic and in situ Raman spectroelectrochemical analyses, they confirmed that the sp\textsuperscript{2}-hybridized carbons near the ring ether defects along the mrGO sheet edges are the most active sites for peroxide production. Furthermore, they reported that the annealing of the catalyst further improved the electrocatalytic O\textsubscript{2} reduction. The derivatives of the mrGO electrocatalysts exhibited highly selective and stable activity in peroxide synthesis at low overpotentials under basic conditions, which was unprecedented when the study was reported.\textsuperscript{39}

Carbon nanotubes (CNTs), which exhibit π–π stacking interactions, can be utilized in redox reactions because they can accept, transport, and store electrons.\textsuperscript{40} They have been prepared in both pure and modified forms. Khataee et al. tested three carbon-based materials (bare graphite, activated carbon/graphite, and CNT/graphite) to increase the catalytic activity.\textsuperscript{41} CNT/graphite was found to be the most efficient catalyst; the H\textsubscript{2}O\textsubscript{2} productivity under the catalysis of this composite was nearly three or seven times higher than that of activated carbon/graphite or bare graphite, respectively. Zhang et al. fabricated a modified electrode using N-functionalized CNTs to enhance the H\textsubscript{2}O\textsubscript{2} generation efficiency in the EF system.\textsuperscript{42} This electrode provided a higher H\textsubscript{2}O\textsubscript{2} formation rate than both graphite and bare CNT electrodes at a potential of ~0.85 V. The concentrations of H\textsubscript{2}O\textsubscript{2} produced by the graphite, CNT, and...
N-functionalized CNT electrodes were 92.59 mg l$^{-1}$, 103.97 mg l$^{-1}$, and 145.62 mg l$^{-1}$, respectively. Furthermore, metal-decorated CNTs exhibit high electron transfer and generation rates owing to their modified bandgap structures and high reducing activities. Recently, Jiang et al. synthesized M-CNTs (M: metal atom) and discovered that M–C–O is an efficient catalytic motif for H$_2$O$_2$ generation. It showed high selectivity (above 95%) in both alkaline and neutral conditions (Fig. 3). Specifically, Fe–C–O was identified as a highly active and selective motif for reducing O$_2$ to H$_2$O$_2$. Through DFT calculations, considering all the possible sites of metal atom binding, the ORR activity and selectivity of different motifs were examined for a structure with a single Fe atom coordinated to a 2D carbon sheet, with and without O species. The calculations indicated that the C atoms of the Fe–C–O motifs could be selective for the two-electron-mediated production of H$_2$O$_2$, over the 4e$^-$ product to H$_2$O.

Considering the progress made so far, there is significant room for improving the performance of catalysts for efficient H$_2$O$_2$ production. This could be achieved by modifying the carbon materials through strategies, such as metal nanoparticle loading, morphology tuning, or elemental doping. H$_2$O$_2$ production is known to depend on the surface area and band structure of the catalyst, which can be adjusted by controlling the ratio of the metal nanoparticles to the carbon structures. Figure 4 summarizes the catalytic performance of various types of catalysts in H$_2$O$_2$ production. It is clear from Fig. 4 that the specific activity of Pt–Hg/C (metal on carbon) is 4–5 times higher than that of polycrystalline Pt–Hg (without carbon). The Pd–Au/C catalyst also showed higher selectivity and higher mass activity than those of the Pd–Au nanoparticles (NPs). Furthermore, Choi et al. reported that Pt NPs coated with amorphous carbon layers could induce single O atom adsorption of O$_2$ on their surface.

FIG. 3. Scanning transmission electron microscopy (STEM) images of [(a) and (e)] Fe-, [(b) and (f)] Pd-, [(c) and (g)] Co-, and [(d) and (h)] Mn-CNT. Bright dots in the high-angle annular dark-field STEM images (marked by red arrows) show single metal atoms. Scale bars are 5 nm. [(i) and (j)] ORR performances of M-CNT catalysts cast onto rotation ring disk electrodes in 0.1M KOH. (i) Linear sweep voltammetry of the CNT background and Fe-, Pd-, Co-, and Mn-CNT catalysts recorded at 1600 rpm and a scan rate of 5 mV s$^{-1}$, together with the detected H$_2$O$_2$ currents on the ring electrode (upper panel) at a fixed potential of 1.2 V vs reversible hydrogen electrode. (j) Calculated H$_2$O$_2$ selectivity and electron transfer number during the potential sweep. [(k) and (l)] DFT calculations of the ORR activity and selectivity on different motifs. (k) All configurations for a single Fe atom coordinated with C atoms, with and without O species. Green, red, and gray colors denote Fe, O (or N), and C atoms, respectively. (l) The calculated ORR activity volcano plot for two-electron-mediated pathway to H$_2$O$_2$. Red and blue symbols indicate $^\ast$OOH adsorption at C and Fe, respectively. The equilibrium potential of O$_2$/H$_2$O$_2$ is shown as a black dashed line. Some of the points are not shown in the volcano plot as their binding energies are out of range. Reprinted with permission from Jiang et al., Nat. Commun. 10, 3997 (2019). Copyright 2019 Nature Publishing Group.

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The tuning of the morphology of a catalyst not only allows us to increase the active sites, but also to modify the bandgap structure. Recently, Sa et al. fabricated an ordered graphitic mesoporous carbon (GOMC) material for H\textsubscript{2}O\textsubscript{2} production via the ORR in 0.1M KOH.\textsuperscript{32} They showed that additional oxidative treatment of the graphitic carbon could preferentially generate active oxygenated species at the carbon edge. The experimental data suggested that a faster heterogeneous electron transfer was responsible for the higher ORR activity of the oxidized and edge-rich carbon catalysts. GOMC could stably catalyze the production of H\textsubscript{2}O\textsubscript{2} for 16 h with the Faradaic efficiency reaching 99%, and the accumulated H\textsubscript{2}O\textsubscript{2} concentration was 24 mM.

It has been shown that doped carbon materials can have significant catalytic effects when additional elements are introduced into carbon frameworks, and this aspect has been actively studied recently. Various elements including boron (B),\textsuperscript{27} nitrogen (N),\textsuperscript{26} phosphorus (P),\textsuperscript{28} sulfur (S),\textsuperscript{29} and transition metals\textsuperscript{30} have been investigated as dopants of carbon materials. Chen et al. designed B–carbon–N (BCN) materials by varying the ratio of B and N precursors to increase the 2e\textsuperscript{-} ORR selectivity.\textsuperscript{31} They demonstrated that the BN domains embedded in the co-doped graphitic structures facilitated higher activity and selectivity in the 2e\textsuperscript{-} ORR to H\textsubscript{2}O\textsubscript{2} than the corresponding singly doped materials (B-doped or N-doped carbon). However, in some cases, the H\textsubscript{2}O\textsubscript{2} selectivity of doped carbon materials was found to decrease owing to the increase in the electron transfer rates of dopants.\textsuperscript{32} Therefore, it is not easy to determine the exact redox mechanisms, potentials, and reactivity according to the identities of the dopants. However, in general, dopants partially reorganize the localized electronic density on carbon lattices and generate polar regions; therefore, their influence on the electron transfer rate of carbon materials is not significant.\textsuperscript{32,33} Recently, Jung et al. incorporated a Co–N\textsubscript{4} moiety in nitrogen-doped graphene for electrochemical H\textsubscript{2}O\textsubscript{2} production.\textsuperscript{34} This catalyst showed a high H\textsubscript{2}O\textsubscript{2} productivity of 418 ± 19 mmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} at a catalyst loading of ∼1 mg cm\textsuperscript{-2}. The fine-tuning of the interaction between a given metal atom and the surrounding atomic configuration of a catalyst is required for achieving high catalytic activity in H\textsubscript{2}O\textsubscript{2} production. The changes in the activity of a catalyst upon doping thus originate mainly from the chemical effects of dopants.

In summary, carbon materials are excellent catalysts for H\textsubscript{2}O\textsubscript{2} synthesis. However, they are relatively unstable in the presence of H\textsubscript{2}O\textsubscript{2} in comparison with other catalysts, such as metals and metal oxides.\textsuperscript{35} As the catalytic stability is indispensable for practical application, further studies are required to enhance the catalytic stabilities of carbon-based materials in H\textsubscript{2}O\textsubscript{2} synthesis.

B. Pure metals and alloys

For efficient H\textsubscript{2}O\textsubscript{2} generation, it is very important to investigate and calculate the associated enthalpy changes as well as activation energies, for both forward and reverse reactions of H\textsubscript{2}O and O\textsubscript{2}.\textsuperscript{36} On this basis, noble metals, such as palladium, platinum, silver, and gold, have been applied in various ways to promote the 2-electron pathway of H\textsubscript{2}O\textsubscript{2} synthesis. Among the noble metals, Pd is preferred as an electrochemical catalyst because of its activity in the ORR and O\textsubscript{2} evolution reaction.\textsuperscript{37} Kim et al. investigated the changes in the activity of Pd catalysts in H\textsubscript{2}O\textsubscript{2} synthesis according to the exposed crystal plane and particle size. They found that a larger particle size and the (111) crystal plane are favorable for this reaction.\textsuperscript{38} Iwamoto et al. also reported that saturated active sites located on the (111) crystal plane of Pd particles are beneficial for the generation of H\textsubscript{2}O\textsubscript{2} through a DFT study. They also determined that unsaturated active sites located at the crystal angles and crystal edges of Pd particles easily lead to the formation of H\textsubscript{2}O as a by-product.\textsuperscript{39} Au has been considered a potentially reactive metal among...
precious metals for \( \text{H}_2\text{O}_2 \) formation for some time, based on theoretical calculations that predicted the stable formation of \( \text{H}_2\text{O}_2 \) molecules on its surfaces.

Such characteristics of Au have been practically demonstrated by various groups. Furthermore, with respect to the catalyst size, small Au nanoclusters (~2 nm) have been shown to have active sites suitable for the synthesis of \( \text{H}_2\text{O}_2 \). The rate of \( \text{H}_2\text{O}_2 \) formation was found to decrease with the increasing size of the Au nanoparticles. This tendency has also been experimentally proven with an Au/silica \((\text{SiO}_2)\) catalyst; a catalyst consisting of Au nanoparticles with a mean diameter of 30 nm could produce \( \text{H}_2\text{O} \) but not \( \text{H}_2\text{O}_2 \). Therefore, when using materials based on precious metals as catalysts, it is important to consider the choice of element and their structure. According to DFT calculations, for catalytic metals as catalysts, it is important to consider the choice of active metals and relatively inert metals, activation potentials can also be an important factor in controlling a series of reduction and re-oxidation.

Bimetallic alloys have been studied as catalysts for achieving high catalytic performances in \( \text{H}_2\text{O}_2 \) synthesis. By alloying active metals and relatively inert metals, activation potentials can be enhanced by discrete reactive sites embedded in a relatively inert material (Fig. 2). As Pd alloys exhibit better performance than pure metals, the activities of Pd, Au, and Ru-based bimetallic catalysts in \( \text{H}_2\text{O}_2 \) synthesis have been studied. Among them, Pd–Au has attracted significant attention, while only a few studies on the Pd–Pt, Ru–Pd, or Pt–CuS systems have been reported. Various Pd-based bimetallic nanoparticles have been shown to perform better than single metal catalysts.

Interestingly, metal alloy catalysts have exhibited enhanced H atom selectivity toward \( \text{H}_2\text{O}_2 \) compared to pure Pd catalysts. Studies on Pd-based catalysts have been reviewed previously.

Typically, for \( \text{H}_2\text{O}_2 \) generation, two electrons should be transferred from a catalyst to \( \text{O}_2 \). The attachment of \( \text{O}_2 \) to Au is too weak for efficient electron transfer. However, \( \text{O}_2 \) binds strongly to Pd; therefore, the O–O bond can be cleaved easily, which is not beneficial for \( \text{H}_2\text{O}_2 \) generation (Fig. 5). Thus, alloying with Au can lead to appropriate \( \text{O}_2 \)−metal binding strength for two-electron transfer, resulting in high \( \text{H}_2\text{O}_2 \) generation efficiency.

The homogeneous alloy nanoparticles were prepared by the simultaneous addition and reduction of metal salts, whereas the core−shell structure was formed by the reduction of Pd followed by the reduction of Au (Fig. 6). They claimed that the incorporation of a small amount of Au into the Pd lattice affected the electronic structure of Pd, which could lead to significant enhancement in catalytic activity in \( \text{H}_2\text{O}_2 \) generation. Although high \( \text{H}_2\text{O}_2 \) production was observed for Au/Pd at a 1:2M ratio, side hydrogenation reactions of \( \text{H}_2\text{O}_2 \) were also promoted [Fig. 6(g)]. Edwards et al. demonstrated that nanocomposites with 2.5 wt. % Au–2.5 wt. % Pd exhibited significantly enhanced activity in \( \text{H}_2\text{O}_2 \) synthesis. Furthermore, the rate of \( \text{H}_2\text{O}_2 \) production under their catalysis was much higher than that under pure Pd and pure Au catalysts.

Moreover, the authors claimed that the Pd/Pt ratio may also be an important factor in controlling a series of reduction and re-oxidation.

Xu et al. observed that Pd catalysts alloyed with Pt could show improved activity in \( \text{H}_2\text{O}_2 \) synthesis. The Pd–Pt alloy achieved a \( \text{H}_2\text{O}_2 \) production rate of 1.77 mol h\(^{-1}\) g\(^{-1}\) and selectivity of 60%, while pure Pd showed a rate of 0.99 mol h\(^{-1}\) g\(^{-1}\) and selectivity of 12%. However, the Pd–Pt alloys showed enrichment of Pt on their surfaces. The authors claimed that tuning the electronic structure of Pd with a small amount of Pt might help stabilize \( \text{O}_2 \) molecules on the Pd sites. After their formation from adsorbed

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**FIG. 5.** Effect of the presence or absence of gold metal in \( \text{O}_2 \) and \( \text{H}_2\text{O}_2 \) chemisorption leading to hydrogen peroxide or water formation selectivity, respectively. The high activity of Pd and the high selectivity of Au play roles in the enhancement of \( \text{H}_2\text{O}_2 \) synthesis. This scheme is Reproduced with permission from J. Li and K. Yoshizawa, Catal. Today 248, 142 (2015) and Pengfei et al., Chin. J. Catal. 34, 1002 (2013). Copyright 2015 and 2013 Elsevier B.V.
FIG. 6. Hydrogen peroxide synthesis using Pd–Au catalysts prepared by sol-immobilization with varying Pd and Au compositions. Transmission electron microscopy images of [(a)–(c)] homogeneous random alloys and [(d)–(f)] heterogeneous alloys of Pd and Au. The particles progressively become more Pd-rich and less Au-rich from (d) to (f). The smaller particles were Au-rich, whereas the larger ones tended to be Pd-rich. (g) Comparison of the specific activity of 1 wt. % Au–Pd/C with a Pd/Au molar ratio of 1.85 prepared by sol-immobilization in H$_2$O$_2$ synthesis and H$_2$O$_2$ hydrogenation. The H$_2$O$_2$ productivity was calculated after 30 min (solid black rhombuses), and the rates of H$_2$O$_2$ hydrogenation were calculated after 30 min (open red squares). Adapted with permission from Pritchard et al., Langmuir 26, 16568 (2010). Copyright 2010 American Chemical Society.

O$_2$, the OOH$^*$ radicals can produce H$_2$O$_2$. Thus, excess Pt on the shell layer deteriorated the catalytic performance by destabilizing the OOH$^*$ radicals.

When combining different kinds of metals for H$_2$O$_2$ synthesis, multiple characteristics of the resultant alloys and composites should be considered simultaneously. For example, as mentioned earlier, the loading of Au into Pd can enhance the H$_2$O$_2$ selectivity of Pd; however, the loading of Au can decrease the overall catalytic activity of the Pd–Au alloy. Some combinations of metals can have a high catalytic activity but poor performance retention. Therefore, a deeper understanding of the catalytic mechanisms of these metallic materials is required to meet the industrial demands of catalytic activity, selectivity, stability, and durability.

Noble metals are currently considered as one of the most efficient catalysts to generate H$_2$O$_2$. However, the high cost and scarcity of noble metals greatly hinder their large-scale application. Thus, to enable the industrial application of the catalysts for electrochemical production of H$_2$O$_2$, low-cost, earth-abundant, and highly stable electrocatalysts are required. Therefore, it is necessary to develop noble metal catalysts with high H$_2$O$_2$ catalytic efficiency with very low noble metal content.

C. Metal oxides

Metal oxides have been used in various applications owing to their earth-abundance, low cost of production, and chemical inertness. Metal oxides can also be used as catalysts for electrochemical or photocatalyzed generation of H$_2$O$_2$. Iridium or ruthenium oxides can induce anodic reactions at the lowest overpotentials, but they tend to favor O$_2$ formation and are expensive for large-scale application. Thus, less expensive metal oxides, such as titanium dioxide (TiO$_2$), manganese oxide (MnO$_x$), bismuth vanadate (BiVO$_4$), and tin dioxide (SnO$_2$), have been actively investigated for H$_2$O$_2$ generation. Some metal oxides have been studied as photocatalysts as well as electrocatalysts. Electrons ($e^-$) and holes

FIG. 7. (a) Oxidative H$_2$O$_2$ generation on a bare FTO electrode at the applied electric charge of 1.8 C at 0 V under CO$_2$ or Ar gas bubbling into various 0.5M aqueous solutions (35 ml) maintained in an ice bath (below 5 °C). (b) Comparison of H$_2$O$_2$ generation using anodes with various metal oxides loaded on FTO electrodes in an ice bath (below 5 °C) in a 0.5M KHCO$_3$ aqueous solution (35 ml) under CO$_2$ gas bubbling at an electric charge of 1.8 C and applied voltage of 3.0 V. Reprinted with permission from Fuku et al., ChemistrySelect 1, 5721 (2016). Copyright 2016 Wiley-VCH.
(h⁺) generated through photocatalysis or electrocatalysis cause O₂ reduction and H₂O oxidation, respectively, in H₂O₂ redox reactions. Fuku et al. tested the electrocatalytic activities of a fluorine-doped SnO₂ (FTO) substrate and FTO with various metal oxides in salt solutions for H₂O₂ production. On bare FTO, H₂O₂ can be generated as expected from Fig. 2, and the H₂O₂-production efficiency increased significantly in the cases of an aqueous potassium bicarbonate (KHCO₃) electrolyte and a phosphate buffer [Fig. 7(a)]. Furthermore, this group applied various metal oxides on the FTO substrate to compare their electrocatalytic activities in H₂O₂ synthesis in a KHCO₃ aqueous solution. The data were consistent with the results of thermodynamic analysis, which suggested that WO₃, SnO₂, BiVO₄, and TiO₂ can catalyze the production of H₂O₂ (Fig. 2). The enhanced activities of FTO substrates supported by Al₂O₃, TiO₂, and BiVO₄ may be attributed to the favorable adsorption of HCO₃⁻ on acidic oxide surfaces [Fig. 7(b)].

TiO₂ has been widely studied as a catalyst for various reactions because of its high stability, biocompatibility, and useful physical, optical, and electrical properties. The potential of the lowest unoccupied molecular orbital (LUMO) of TiO₂ (−0.19 V vs normal hydrogen electrode, pH 0) is lower than the potential for the two-electron reduction of O₂ (0.68 V). Therefore, the excited electrons of TiO₂ can promote the ORR for H₂O₂ generation. However, TiO₂ can hardly facilitate electron and hole transfers because of its relatively large bandgap; therefore, its onset potential is high for H₂O₂ generation. Furthermore, after the H₂O₂ binds to the surface of TiO₂, the intermediates (Ti–OOH complexes) can decompose to

FIG. 8. (a) Energy diagram of the electrode system for the production and recovery of H₂O₂ and H₂ using a WO₃/BiVO₄ electrode. (b) Scanning electron microscopy images of (i) FTO, (ii) FTO with WO₃ underlayer, and (iii) FTO with WO₃ underlayer and WO₃/BiVO₄. (c) (i) Time courses of oxidative H₂O₂ generation in 0.1M (yellow rhombuses), 0.5M (green rhombuses), 1.0M (red circles), and 2.0M (blue squares) KHCO₃ electrolyte (35 ml) and (ii) oxidative H₂O₂ generation in a 2.0M KHCO₃ electrolyte under CO₂ gas bubbling in an ice bath (below 5°C) at an applied voltage of 1.5 V, using a WO₃/BiVO₄ electrode. Reproduced with permission from K. Fuku and K. Sayama, Chem. Commun. 52, 5406 (2016). Copyright 2016 The Royal Society of Chemistry.
Ti–OH and OH\(^+\) radicals through reduction because TiO\(_2\) has a high OH\(^+\)-free energy.

BiVO\(_4\) has a bandgap of 2.4 eV and is commonly used as a visible-light photosensitizer or electrocatalyst.\(^2\) Specifically, it has been intensively investigated for splitting H\(_2\)O.\(^5\) As the LUMO level of BiVO\(_4\) is more negative compared with the two-electron O\(_2\)-reduction potential, it is also active in H\(_2\)O production. BiVO\(_4\) can also be used as a constituent of composites. Fukui \textit{et al.} used a tungsten trioxide (WO\(_3\))/BiVO\(_4\) composite as a photoelectrocatalyst on a FTO anode for oxidative H\(_2\)O\(_2\) production from H\(_2\)O along with the simultaneous production of H\(_2\) gas on a Pt cathode (Fig. 8).\(^6\) The WO\(_3\)/BiVO\(_4\) oxide layer on FTO was confirmed through scanning electron microscopy, and the bicarbonate (HCO\(_3^-\)) electrolyte was found to permit stable oxidative H\(_2\)O\(_2\) production and accumulation on the BiVO\(_4\) surface, even at a lower voltage than the theoretical electrolysis voltage. Furthermore, the suppression of oxidative degradation could be accomplished by increasing the HCO\(_3^-\) concentration significantly at a low temperature. In addition, the same group also reported the oxidative and reductive H\(_2\)O production from H\(_2\)O and O\(_2\), respectively, by using a BiVO\(_4\) anode and Au cathode without external bias.\(^6\) By introducing the Au cathode, the two-electron reduction of O\(_2\) was selectively catalyzed. In their follow-up study, to enhance the generation of H\(_2\)O\(_2\), a mesoporous and amorphous aluminum oxide (Al\(_2\)O\(_3\)) layer was applied as an additional layer to inhibit the oxidative degradation of the generated H\(_2\)O\(_2\) on the electrode. The modified electrode provided high H\(_2\)O\(_2\) selectivity (~80%) and catalytic stability.\(^7\) Other metal oxide-coated electrodes were also tested for H\(_2\)O\(_2\) generation. Their selectivity can be ranked as follows: Al\(_2\)O\(_3\) > (zirconium dioxide) ZrO\(_2\) > TiO\(_2\) > SiO\(_2\) > cobalt oxide (CoO\(_x\)). The authors attributed the excellent selectivity on the WO\(_3\)/BiVO\(_4\)/Al\(_2\)O\(_3\) photoanode to the blocking effect of the mesoporous Al\(_2\)O\(_3\) layer, which inhibits oxidative H\(_2\)O\(_2\) degradation into O\(_2\) on the BiVO\(_4\) electrode. They also reported an enhancement effect resulting from the increased HCO\(_3^-\) concentration around the electrode owing to the adsorption of HCO\(_3^-\) (a weak base) to the weakly acidic surface of Al\(_2\)O\(_3\). Recently, the surface reactivity of the BiVO\(_4\) anode has been investigated through a combination of experimental and computational studies.\(^8\) The authors claimed that the adsorption of anion species can be promoted to inhibit H\(_2\)O\(_2\) dissociation on the high index (~121) surface of the catalyst, compared with that on the low index (010) surface.

Various other oxides, such as WO\(_3\), CoO\(_2\), cerium oxide (CeO\(_2\)), NbO\(_2\), tantalum pentoxide (Ta\(_2\)O\(_5\)), and vanadium oxide (V\(_2\)O\(_5\)), have also been used as anodic electrode materials to provide electrons. They can be used along with carbon-based materials in the form of nanoparticles to greatly increase their O\(_2\)-reduction activities. Carneiro \textit{et al.} fabricated NbO\(_2\)-based nanocomposites decorated with rGO to generate H\(_2\)O\(_2\). The NbO\(_2\)-rGO electrode provided a higher H\(_2\)O\(_2\) output than the bare rGO electrode in both acidic and alkali conditions.\(^9\) Ta\(_2\)O\(_3\) nanoparticles mixed with carbon black were also investigated as catalytic materials for H\(_2\)O\(_2\) synthesis.\(^10\) Ta\(_2\)O\(_3\) mixed with rGO exhibited a higher H\(_2\)O\(_2\) output and selectivity than those of pure metal oxide or rGO. Metal oxides can also have activities for 4e\(^-\) O\(_2\) reduction to H\(_2\)O. Therefore, synthesis methods and surface modification should be further developed to tune the physical or chemical properties for suppressing 4e\(^-\) O\(_2\) reduction on metal oxides to achieve higher selectivities in H\(_2\)O\(_2\) synthesis.

Metal oxides are considered as highly promising materials for the efficient catalysis of H\(_2\)O\(_2\) generation from two-electron-mediated reactions. Compared with other materials, however, the number of reports on metal oxides as catalysts for H\(_2\)O\(_2\) production is relatively small. Therefore, further studies should be conducted for enhancing the H\(_2\)O\(_2\) catalytic activities of metal oxides because they are readily available and also incur low cost.

III. CONCLUSION AND OUTLOOK

This article outlined the catalytic materials that have been studied in the electrochemical generation of H\(_2\)O\(_2\). Recent studies on carbon-based materials, metals, metal oxides, and their composites have shown that they have promising catalytic activities to enable the replacement of the anthraquinone process with other H\(_2\)O\(_2\) synthesis routes. However, further challenges should be overcome before they can be applied in large-scale H\(_2\)O\(_2\) production. The chemical decomposition of the as-generated H\(_2\)O\(_2\) on the catalyst inhibits their practical application. Therefore, rational theoretical calculations and experiments should be conducted for the design of H\(_2\)O\(_2\) catalysts. Such studies can assist the design of better catalysts to minimize overpotentials in order to produce H\(_2\)O\(_2\) through the 2e\(^-\) oxygen reduction for high stability. The smart tailoring of materials for the optimal conversion of H\(_2\)O or O\(_2\) to H\(_2\)O\(_2\) through methods, such as size reduction, surface modification, doping, delib- erate generation of defects, and heterostructuring, can lead to further improvement in electrochemical H\(_2\)O\(_2\) generation. Therefore, active research is required to address the issues of catalytic instability and material costs toward overall process optimization and scale-up of the reaction.

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