Hydrogen peroxide (H$_2$O$_2$) is a valuable chemical with a wide range of applications. A recent trend in H$_2$O$_2$ production focuses on electrochemical reduction of oxygen, which represents an environmentally friendly method for on-site H$_2$O$_2$ generation. To realize highly efficient practical-scale electrosynthesis of H$_2$O$_2$, catalytic materials design and electrochemical reactor engineering play equally important roles and must be carefully investigated. A highly active catalyst with superior selectivity and stability is the foundation for efficient H$_2$O$_2$ production, and well-configured reactors are important to realize practical deployment of on-site H$_2$O$_2$ production in large scales. In this review, an overview of the recent progress (over the past 3 years) in electrochemical production of H$_2$O$_2$ is presented, with an emphasis on the development of selective catalysts, especially the atomic tuning of carbon-based catalysts and single-atom catalysts, as well as electrode engineering and electrochemical cell design.

Catalyst Design and Reactor Engineering for H$_2$O$_2$ Production

H$_2$O$_2$ is one of the most valuable chemicals that is attractive for both civil and industrial applications, such as surgical disinfection, water purification, industrial pulp bleaching, chemical synthesis, and fuel cell technology [1–7]. The varied applications give H$_2$O$_2$ a high annual demand of approximately 4 million tonnes globally and the value is continuously increasing. The industrial process for producing H$_2$O$_2$ is primarily based on the energy-intensive anthraquinone process via the hydrogenation of 2-alkyl-9,10-anthraquinone, followed by subsequent oxidation [8]. High energy and material costs, as well as transportation difficulties, severely limit the economical and sustainability prospects of this indirect process. As one of the alternatives, the direct synthesis of H$_2$O$_2$ from gas phase H$_2$ and O$_2$ in a liquid medium enables decentralized H$_2$O$_2$ production and avoids long-distance transportation, which has attracted significant attention over the past few decades [2,9–11]. However, the mixture of H$_2$ and O$_2$ gases during the process poses safety issues and thus hinders the practical use of this method. Hence, recent focus has gradually shifted to safer and more efficient approaches.

The 2e$^-$ electrochemical oxygen reduction reaction (ORR) (see Glossary), which transforms oxygen to H$_2$O$_2$ through electrocatalysis, is emerging as an environmentally friendly alternative for the on-site production of H$_2$O$_2$ [3,12–15]. Compared with the previous two processes, this electrochemical method shows advantages of: (i) using green and natural sources without fossil fuel consumption; (ii) being environmentally clean without organic waste; (iii) requiring mild reaction conditions with ambient temperature and pressure; (iv) avoiding an explosive gas environment, circumvented by separating the anode and cathode; and (v) delivering on-site generation. In the past, the focal point of the ORR has been more on its 4e$^-$ pathway (i.e., the formation of H$_2$O) to enhance the fuel-cell energy efficiency. It was not until recently, with the sustainable development of electrocatalysts, electrochemical cells, and membranes, that electrochemical H$_2$O$_2$ production returned to stage and gained increased interest in both fundamental research and industrial applications [3,13,16–19]. As two of the most essential parts in the electrocatalytic process, catalyst design and reactor engineering play equally important roles and must be carefully investigated.
process, the electrocatalysts and electrochemical cells have been undergoing extensive innovations, which, to a large extent, contribute to recent achievements in \( \text{H}_2\text{O}_2 \) electrosynthesis.

The catalyst is key to determining the activity and selectivity of the ORR process. The first groundbreaking catalyst of electrochemical \( \text{H}_2\text{O}_2 \) generation from \( \text{O}_2 \) was the Hg-Au electrode \([20]\). Since then, noble metal catalysts with diverse structures, including Pd-Hg \([14,21]\), Ag-Hg \([21]\), Pt-Hg \([14,21]\), Pd-Au \([22,23]\), Pt-Au \([24]\), Au-Ni \([25]\), Au-Ni-Pt \([25]\), Pt-Ni \([26]\), and Cu-Hg \([21]\), as well as their core–shell structures, have been developed, showing higher \( \text{H}_2\text{O}_2 \) selectivity than their corresponding pure metals. Currently, noble metals and their alloys are the most efficient and stable electrocatalysts for \( \text{H}_2\text{O}_2 \) production, offering lower overpotentials and high \( \text{H}_2\text{O}_2 \) selectivity (up to \(~98\%\)) \([27]\). However, the large-scale \( \text{H}_2\text{O}_2 \) production using noble metal catalysts has clear drawbacks related to the high price and scarcity of noble metals. Hence, most of the current efforts are devoted to developing efficient catalysts by reducing noble metal consumption. Based on this direction, carbon-based materials and recently developed single-atom catalysts (SACs) are emerging as alternative candidates for producing \( \text{H}_2\text{O}_2 \) from the ORR on both laboratory and practical pilot scales. Pristine carbon materials, such as carbon black and graphite, have been demonstrated for reducing oxygen decades ago \([13,28,29]\). It was not until 2012 that a seminal work demonstrated that N-doped carbon derived from an ionic liquid is efficient to produce \( \text{H}_2\text{O}_2 \) with good selectivity (\(~80\%) \([30]\), revealing the local atomic structure that dominates the 2e\(^-\) pathway of \( \text{H}_2\text{O}_2 \) production. With further development of synthetic and characterization techniques, the local atomic engineering of carbon-based catalysts is being extensively investigated as an efficient tool to tune the \( \text{H}_2\text{O}_2 \) production efficiency within a broad pH range. However, SACs with a more unique local atomic environment greatly reduce metal usage by atomically isolating metal active centers on well-defined substrates, while exhibiting enhanced ORR performance for \( \text{H}_2\text{O}_2 \) production. Their unique structures provide different catalytic performance compared with metal particles and clusters, presenting a new frontier in electrocatalysis.

Along with achievements in electrocatalyst development, developing electrocatalytic devices with well-designed configurations to enable practical-scale \( \text{H}_2\text{O}_2 \) production is especially important for the future of this field. Prior research on laboratory-scale electrosynthesis of \( \text{H}_2\text{O}_2 \) primarily focuses on catalyst performance evaluation, with relatively less emphasis on device development and optimization. Over the past several decades, reactors used for electrochemical \( \text{H}_2\text{O}_2 \) laboratory-scale research were primarily based on traditional cell designs with few modifications, for example, the Huron-Dow process \([7]\) and proton-exchange membrane (PEM) fuel cell technology \([31–34]\). Reactor design development has been relatively slow, with limited well-designed configurations. It was not until recent years that more innovative electrocatalysis techniques with novel reactor configurations \(\text{e.g.}, \text{the introduction of gas diffusion electrode (GDE) into flow cells, solid-electrolyte cells, and membrane-free electrolyzers}\) have been developed to make large-scale electrochemical \( \text{H}_2\text{O}_2 \) production with a desired concentration and purity more realistic, providing new impetus to this field.

The objective of this short review is to provide an update on state-of-the-art progress in electrochemical \( \text{H}_2\text{O}_2 \) synthesis through electrochemical reduction of \( \text{O}_2 \). An overview of the historical development is introduced (Figure 1), followed by a discussion of contemporary electrocatalysts, with an emphasis on the relations between their unique structural features and their \( \text{H}_2\text{O}_2 \) production performance. Since noble metal catalysts have been well summarized in several previous reviews \([3,12,13]\), this review focuses on the most recently developed carbon-based catalysts and SACs. Going beyond the scope of electrocatalysts, the most recent innovations in electrochemical cells that incorporate these catalysts into real devices for electrocatalysis of \( \text{H}_2\text{O}_2 \) are introduced, with
a focus on cell configurations. Both the advances in catalyst design and cell development in recent years have made future practical-scale H$_2$O$_2$ production more realistic.

**Electrocatalyst Design for H$_2$O$_2$ Production via Oxygen Reduction**

**General Principles for Electrocatalyst Design**

The electrocatalyst is a vital component that largely determines the overall activity and selectivity of H$_2$O$_2$ through the ORR [35,36]. A qualified electrocatalyst for H$_2$O$_2$ production should show typical characteristics of: (i) high activity, operating at low overpotential with high current density; (ii) high selectivity, inhibiting the 4e$^-$ process (i.e., the formation of H$_2$O) and ensuring high H$_2$O$_2$ production yields through the 2e$^-$ process; and (iii) high stability, enabling long-lasting performance and long-term durability. Typically, the ORR over a catalyst undergoes a possible tandem reaction pathway, in which an oxygen molecule is first adsorbed on the catalyst surface to form the intermediate *OOH, which consequently transforms into H$_2$O$_2$ (desorption of *OOH through 2e$^-$ process), or to form intermediate *O (dissociation of O–O bonding through 4e$^-$ process) [3,12]. Generally, the activity is described by the ability of the catalyst to bind with the reaction intermediate, *OOH, and the selectivity toward H$_2$O$_2$ is determined by the ability of the catalyst to split the O–O bond (the easier it splits the O–O bond, the less favored it proceeds through the 2e$^-$ process). An ideal electrocatalyst toward H$_2$O$_2$ should bind O$_2$ neither too strong nor too weak to ensure that the reduction reaction occurs on the catalyst (high activity), while disabling the cleavage of the O–O bond so that the reaction is dominated by the 2e$^-$ pathway (high selectivity).

In the ORR process, activation of O$_2$ molecules typically occurs as the first step and whether O$_2$ adsorption proceeds via an *end-on* or *side-on* pathway (Figure 2A) during the ORR process is mechanistically critical in determining the selectivity of the 2e$^-$ process. The geometric structure of the active site needs to be carefully controlled such that it prefers to bind O$_2$ with an end-on pathway or properly bind O$_2$ to maintain the O–O bond in the ORR process. Early works on noble metal catalysts have shown that reducing accessible active metal sites by modifying the adjacent metal atoms and separating binding sites for the oxygen atoms can weaken the dissociative adsorption of O$_2$ and induce the adsorption of O$_2$ through the end-on pathway, thus increasing the H$_2$O$_2$ production selectivity while maintaining high activity [37–39]. This design concept has been applied afterwards to design SACs for selective production of H$_2$O$_2$ [40]. To date, numerous catalysts, including noble metals [37,38,41,42], transition metals [43], metal alloys [22], carbonate materials [17,19,30,44,45], and their corresponding composites [41,46–49], have been developed for producing H$_2$O$_2$ through the 2e$^-$ ORR. Although noble metal catalysts show good activity for the ORR toward H$_2$O$_2$, their large-

![Figure 1. Several Major Milestones in Catalyst and Reactor Development for the Electrochemical Synthesis of H$_2$O$_2$ from O$_2$. Abbreviation: CNT, carbon nanotube.](image-url)
scale application is still limited by high cost and scarcity. Therefore, atomically tuned earth-abundant carbon materials and SACs are emerging as the next-generation catalysts for cost-effective production of H2O2 through ORR.

**Atomic Tuning of Carbon Catalysts for the ORR toward H2O2**

Carbon is well-known for its low cost, diversified allotropes, and electrochemical stability under ORR conditions [30,44,45,50–52]. Pristine carbon materials (e.g., carbon black and graphite) have been previously demonstrated for selective H2O2 production, but most of these materials typically exhibit poor activity and selectivity [29]. Recent advances in synthetic and characterization techniques brought new vitality to boost H2O2 production by tuning the local atomic structure of carbon materials (e.g., surface functionalization and foreign atom doping). Meanwhile, structure–property relationships that determine the 2e– process are being intensively investigated.

**Carbon Surface Oxidation**

Oxidized carbon blacks have been reported with H2O2 activity over the past several decades [13]. Recently, novel carbon substrates, such as carbon nanotubes (CNTs) and graphene oxides...
(GOs), sparked a large wave of development of carbon-based materials in the ORR for \( \text{H}_2\text{O}_2 \) electrosynthesis and provided a more thorough platform to investigate how efficient the surface oxygen groups can be in regulating the reaction pathways of the ORR \[16,18\]. Mildly oxidized CNTs can reduce the overpotential and enhance \( \text{H}_2\text{O}_2 \) selectivity up to \( \sim 90\% \) in basic and neutral electrolytes \[16\]. Similar phenomena were observed on mildly reduced GO nanosheets, showing up to \( \sim 90\% \) \( \text{H}_2\text{O}_2 \) selectivity \[18,53\]. With such performance, the surface oxygen functional group acting as the active site for producing \( \text{H}_2\text{O}_2 \) is still under debate \[54,55\]. Typically, there are several types of functional groups on the carbon surface after oxidation (e.g., ether and carboxyl groups). The groups of \( \text{–COO}^- \) and \( \text{–C–O–C} \) on mildly oxidized CNTs were demonstrated to be responsible for \( 2e^- \) ORR with low computed overpotentials, while the \( \text{–OH} \) group, in contrast, showed negligible contribution to \( 2e^- \) ORR \[16\]. With a similar conclusion, Guo and colleagues further pointed out that the \( \text{–COO}^- \) group, which allows peroxide formation and easier desorption, is critical to enhanced \( \text{H}_2\text{O}_2 \) selectivity \[56\]. The surface carbonyl group (\( \text{–C–O} \)) also participates in peroxide synthesis, but it has stronger binding with peroxide, thus prohibiting peroxide desorption at higher overpotentials \[56\]. With a more straightforward protocol, Baek and colleagues functionalized the activated dangling edge sites with targeted functional groups and demonstrated specifically that the quinone group dominates the selectivity and activity of the ORR toward \( \text{H}_2\text{O}_2 \) \[55\]. With the quinone-enriched sample, a high selectivity of 97.8\% under 0.75 V versus reversible hydrogen electrode (RHE) was achieved. Of note is that with an optimized oxidized surface, nearly all oxidized carbon materials, regardless of the carbon species, show high efficiency for \( \text{H}_2\text{O}_2 \) production in alkaline electrolytes. However, suitable stability and selectivity at high current densities remain challenging. Moreover, carbon catalysts with high selectivity in acidic solution still need to be developed further.

**Heteroatom-Doped Carbon**

In addition to surface oxidation, heteroatom doping is an effective way to tune the local atomic structure of carbon-based electrocatalysts. To date, a variety of doped carbonates such as B-, \[57\], N-, \[45,51,58–60\], P-, \[61\], F-, \[62\], B and N co-doped- \[63\], and S and N co-doped-carbon \[64\] catalysts have been developed for cathodic \( \text{H}_2\text{O}_2 \) production. Different from oxidized carbon for \( \text{H}_2\text{O}_2 \) production in alkaline solutions, several of the heteroatom-doped carbon materials realized high \( \text{H}_2\text{O}_2 \) production rates and selectivities in acidic solutions. For example, nitrogen-doped mesoporous carbon has been reported to exhibit high \( \text{H}_2\text{O}_2 \) selectivities of \( \sim 95–98\% \) in acidic solution in the potential range from 0.1 to 0.3 V versus RHE \[59\]. The heteroatom dopants (especially N and S) can act further as ligands to bind with isolated metal atoms or clusters on the carbon material surface to further improve the catalytic performance. Following this concept, SACs are now trending as electrocatalysts for producing \( \text{H}_2\text{O}_2 \).

**SACs**

SACs, in which the metal atoms are atomically bonded to supports, are particularly effective for electrocatalytic reactions with enhanced mass activity \[65–75\]. By maximizing the atom utilization efficiency and minimizing size effects, atomically dispersed SACs exhibit drastically different catalytic performance compared with metal particles and clusters, presenting a new frontier in electrocatalysis. Mechanistically speaking, the isolated single atoms can only adsorb \( \text{O}_2 \) with the end-on configuration, which is different from metal particles that have dominant side-on adsorption of \( \text{O}_2 \) on the metal surface (as schematically shown in Figure 2A) \[22\]. The end-on adsorption of \( \text{O}_2 \) can reduce \( \text{O}_2 \) through competitive \( 2e^- \) and \( 4e^- \) pathways, while the side-on configuration more easily dissociates the O–O bond and over-reduces the \( \text{O}_2 \) through the \( 4e^- \) pathway \[22,71,72\]. Therefore, well-defined SACs are more desirable to produce \( \text{H}_2\text{O}_2 \) through the ORR.
For SACs, the cathodic activity and selectivity are sensitive to the reactive metal atom coordination, ligand structure, and metal loading [73–76]. Recently, with the benefit of characterization techniques (e.g., transmission electron microscopy and X-ray absorption spectroscopy), the local environment of SACs and active sites for catalysis have been better understood and numerous SACs have been rationally designed to produce H₂O₂ (Table 1). Recently, Wang and colleagues demonstrated that single atoms guide the ORR pathways with a full range control from the 2e⁻ pathway to H₂O₂ toward the 4e⁻ pathway to H₂O [73]. A series of single atoms, including Pd, Fe, Mn, and Co, were decorated onto CNTs with neighboring C, O, or N coordination (Figure 2B–D). Among those catalysts, Fe-decorated-CNT (Fe-CNT) performs the best toward H₂O₂ generation in terms of activity and selectivity. An early onset potential of 0.822V versus RHE and more than 95% H₂O₂ selectivity were achieved in alkaline conditions. In addition, the 2e⁻ ORR pathway can be shifted toward the 4e⁻ pathway by replacing the neighboring O with N coordination. With optimized Co-N₄ moieties in N-doped graphene, Co–N–C catalysts showed not only high selectivity, but also a high kinetic current of 2.8mA cm⁻² and a mass activity of 155Ag⁻¹ [at 0.65V versus RHE] for H₂O₂ production with negligible activity decay over 110 hours in basic electrolyte [75]. The metal centers of SACs are not only limited to the traditional transitional metals (e.g., Fe, Co, and Ni), but other metal sites (e.g., Mo SACs with sulfur and oxygen dual coordination, Mo–S₄–C and Mo–O₃S–C) also show highly selective 2e⁻ ORR [76]. The atomic Mo sites are defined as the activity origin for the 2e⁻ pathway and the local atomic environment contributes to the high activity and selectivity.

Table 1. Selected Electrode Materials for the Cathodic Electrosynthesis of H₂O₂

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Electrolyte</th>
<th>Selectivity (H₂O₂ %) @mA cm⁻²</th>
<th>pH</th>
<th>Onset potential versus RHE</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon catalysts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-doped carbon nanohorns</td>
<td>0.1 M H₂SO₄</td>
<td>~98 @ 0.7</td>
<td>1</td>
<td>0.4 V</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>0.1 M PBS</td>
<td>~90 @ 1.25</td>
<td>7.4</td>
<td>0.53 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 M NaOH</td>
<td>~63 @ 0.7</td>
<td>13</td>
<td>0.71 V</td>
<td></td>
</tr>
<tr>
<td>Mild reduced GO</td>
<td>0.1 M KOH</td>
<td>~100</td>
<td>13</td>
<td>0.78 V</td>
<td>[18]</td>
</tr>
<tr>
<td>B, N-doped C</td>
<td>0.1 M KOH</td>
<td>~90 @ 2⁸</td>
<td>13</td>
<td>0.79 V</td>
<td>[63]</td>
</tr>
<tr>
<td>F-doped porous carbon</td>
<td>0.05 M H₂SO₄</td>
<td>~97.5–83.0 @ 1–2.5⁰</td>
<td>1</td>
<td>0.425 V</td>
<td>[62]</td>
</tr>
<tr>
<td>N-doped mesoporous carbon</td>
<td>0.5 M H₂SO₄</td>
<td>~95–98% @ 0.3–1⁰⁸</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 M K₂SO₄</td>
<td>~75</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 M KOH</td>
<td>~82</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidized CNTs</td>
<td>0.1 M KOH</td>
<td>~95 @ 40</td>
<td>13</td>
<td>~0.8 V</td>
<td>[16]</td>
</tr>
<tr>
<td>KOH-treated rGO</td>
<td>0.1 M KOH</td>
<td>~100 @ 3⁰</td>
<td>13</td>
<td></td>
<td>[53]</td>
</tr>
<tr>
<td>Oxidized carbon black</td>
<td>0.1 M Na₂SO₄</td>
<td>~98 @ 1⁰</td>
<td>7</td>
<td>~0.438 V</td>
<td>[17]</td>
</tr>
<tr>
<td>CTAB modified oxidized carbon</td>
<td>0.1 M KOH</td>
<td>~96 @ 2.5⁰</td>
<td>13</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td><strong>Single atom catalysts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-N-C</td>
<td>0.1 M KOH</td>
<td>~82 @ 2.8⁰</td>
<td>13</td>
<td>0.75 V</td>
<td>[75]</td>
</tr>
<tr>
<td>Single atomic Pt-CuSₓ</td>
<td>0.1 M HClO₄</td>
<td>~92–96 @ 0.1–2.8⁰</td>
<td>1</td>
<td>0.05–0.7 V</td>
<td>[46]</td>
</tr>
<tr>
<td>Ptₓ/Coₓ</td>
<td>0.1 M HClO₄</td>
<td>~90 @ &lt;0.05⁰</td>
<td>1</td>
<td>~0.5 V</td>
<td>[41]</td>
</tr>
<tr>
<td>Mo-S₄-C/Mo-O₃S-C</td>
<td>0.1 M KOH</td>
<td>~95 @ 0.5–2.8⁰</td>
<td>13</td>
<td>~0.78 V</td>
<td>[76]</td>
</tr>
<tr>
<td>Co-N-C</td>
<td>0.1 M HClO₄</td>
<td>&gt;90% @ 1⁰</td>
<td>13</td>
<td>~0.7 V</td>
<td>[76]</td>
</tr>
<tr>
<td>Fe–C–O</td>
<td>0.1 M KOH</td>
<td>~95.4 @ 43</td>
<td>13</td>
<td>0.822 V</td>
<td>[76]</td>
</tr>
</tbody>
</table>

*¹⁰ in selectivity indicates that the test was performed in an RRDE. Current densities (mA cm⁻²) in RRDEs typically represent the disk current densities, which are eyeballed estimates from the current-potential curves.
SACs are particularly attractive for the \(2e^-\) ORR process under acidic conditions. Recently, a high loading single-atom Pt (up to 5 wt.\%) supported on sulfur-modified carbon produced \(\text{H}_2\text{O}_2\) with selectivity up to 96\% in an acidic medium [77]. A further increase in Pt loading in amorphous CuS\(_x\) support can reduce \(\text{O}_2\) to \(\text{H}_2\text{O}_2\) with selectivities of 92–96\% over a broad potential range of 0.05–0.7 V versus RHE in acidic electrolytes [46]. Moreover, by anchoring the cobalt single atom on nitrogen-doped graphene, the current density could reach 1 mA cm\(^{-2}\) at 0.6 V versus RHE and \(\text{H}_2\text{O}_2\) selectivity >90\% in 0.1 M HClO\(_4\) [78].

Still, whether the number of active sites of SACs is large enough to reach the requirement of high current and long-term stability for \(\text{H}_2\text{O}_2\) production is a major concern during the catalytic process. It is anticipated that SACs can be further developed in two directions: (i) increasing the number of active sites to enhance the catalyst activity, and (ii) improving the stability of SACs in the \(2e^-\) ORR, especially by increasing the corrosion resistance of the underlying carbon materials.

**Rector Configuration Design and Development**

The electrochemical cell is another critical component for \(\text{H}_2\text{O}_2\) electrocatalysis. Although laboratory-scale electrochemical cells, such as the rotating ring-disk electrode (RRDE), H-type cells, and flow cells, have been widely used in laboratory settings, these cell designs

### Box 1. Laboratory-Scale Electrochemical Cells for \(\text{H}_2\text{O}_2\) Synthesis

RRDE cells, H-type cells, and flow cells (Figure I) are three main types of cells used in laboratory-scale research for \(\text{H}_2\text{O}_2\) production performance evaluation. The RRDE electrode is normally used for evaluating the intrinsic activity and selectivity of a catalyst. The performance tested by RRDE is normally the upper limit of a catalyst, which is far different from that observed in real devices. The H-type cell is one of the most widely used cells in laboratory research. The anode chamber and the cathode chamber are separated by a proton-exchange membrane (e.g., Nafion), which transfers \(\text{H}^+\) and simultaneously prevents the permeation of \(\text{H}_2\text{O}_2\) to the anode side. The flow cell, in which the \(\text{O}_2\) continuously feeds to cathode, forms the \(\text{H}_2\text{O}_2\) at cathode and removes products away from the continuously flowing liquid electrolyte. The gas diffusion layer (GDL), typically consisting of a hydrophobic layer mounted with a carbon substrate, is used as cathode catalyst support to enhance the \(\text{O}_2\) diffusion. In this way, \(\text{O}_2\) is concentrated effectively near the electrode so that faster mass transfer, a higher reaction rate, and a higher current density can be achieved simultaneously.

![Figure I. Laboratory-Scale Electrochemical Cells for \(\text{H}_2\text{O}_2\) Synthesis. Abbreviations: GDL, gas diffusion layer; ORR, oxygen reduction reaction; RRDE, rotating ring-disc electrode.](image-url)
1. The device should operate under mild conditions to reduce manufacturing costs and energy consumption and to make the process safer.  
2. The main body of the cell should be capable of minimizing the decomposition of as-produced H₂O₂ while minimizing material costs.  
3. The device should be able to achieve a meaningfully high current for a sufficiently long time with high current efficiency to afford future scale-up with high production rates.  
4. There should be very little (or more preferably no) product crossover to the anode.  
5. The device should be able to minimize downstream separation costs (i.e., produce pure H₂O₂ solution without impurities).

To realize these goals, electrochemical reactors that enable stable and cost-effective electrochemical H₂O₂ production are required. In contrast to catalyst design, the development of electrochemical reactors for producing H₂O₂ has occurred at a relatively slow pace, with most innovations stemming from modifications of old reactor configurations and following the trend of enhancing H₂O₂ production yield, maximizing energy efficiency, and minimizing cost. The first H₂O₂ electroreactor was based on the Huron-Dow process (Figure 3A), during which OH⁻ is oxidized to O₂ at the anode, while an externally fed O₂ stream is reduced to HO₂⁻ at the cathode [7]. However, this process inevitably faces issues such as decomposition of the as-produced H₂O₂ and corrosion from alkaline conditions and suffers from a large ohmic resistance. As another typical example of a traditional cell configuration, the PEM fuel cell was used for the first time in the 1990s for electrochemical H₂O₂ synthesis [31]. The anode and...
cathode were separated by a Naﬁon membrane and the protons generated at anode were transferred through Naﬁon to drive the ORR at the cathode during catalysis (Figure 3B). In contrast to older reactors that only consume energy for H2O2 production, this cell provides the opportunity of harvesting energy simultaneously while producing H2O2.

Recently, several novel reactor designs have emerged targeting several different but important technical hurdles. To solve the challenge of high product purity, Wang and colleagues recently developed a solid-electrolyte fuel cell to produce pure H2O2 solutions (Figure 3C-E) [17]. Independent H2 (H2O) and O2 streams were delivered to the anode and cathode, respectively. A cation exchange membrane and an anion exchange membrane (AEM) were used between the middle chamber and electrodes to avoid flooding in the case of direct contact of electrodes with water. Specifically, HO2– generated at the cathode and H+ generated at the anode were transported to the middle chamber and recombined to form pure H2O2 facilitated by the solid-electrolyte layer and collected by pure deionized (DI) water flow. In this way, H2O2 solutions with a wide range of concentrations were achieved by tuning the DI water flow rate with no introduction of ionic impurities. By using this device, over 90% Faradaic efﬁciency and 20 wt.% H2O2 were achieved, with an operation of 100 hours without catalytic degradation.

The use of AEMs still poses several challenges, however, such as low stability and high local pH around the membrane surface. To mitigate and potentially eliminate these issues, a membrane-free electrolyzer was developed (Figure 3F) [79]. This device utilized GDE electrodes to allow gas diffusion while preventing signiﬁcant water diffusion. On the cathode side, supplied oxygen contacted the ORR catalyst, where it was reduced to H2O2, which later dissolved in the liquid electrolyte (middle chamber). On the anode side, water was oxidized in contact to the anode catalyst. The hydrophobic polymer layer prevented H2O2 crossover, making the as-produced H2O2 highly concentrated and collectable.

In addition, to improve the O2 supply to the cathode, PTFE-treated hydrophobic cathodes [80,81] and pressurized reactors [82], jet reactors [83], and reactors equipped with rotating cathodes [84] were developed to enhance the H2O2 production efﬁciency. In a jet reactor (Figure 4A), the atmospheric oxygen and water were supplied to a three-dimensional flow-through carbon felt cathode...
Air was entrained by the suction created by the jet aerator and water became supersaturated by air. In this way, no compressor is required for pumping in oxygen, which reduces the equipment and energy costs. Compared with the flow cell using a typical GDE, the jet cell demonstrates more efficient H$_2$O$_2$ accumulation. Moreover, to reduce energy consumption and enhance the H$_2$O$_2$ production rate, stacked electrosynthesis reactors composed of different electrode pairs with varying spacing distances as gas diffusion cathodes were developed [85].

Despite these recent advances, compared with the design of electrocatalysts, there is relatively less attention paid to improving electrochemical reactor configurations. As electrochemical H$_2$O$_2$ synthesis becomes more important in the near future, more effort should be devoted to reactor development for practical large-scale H$_2$O$_2$ production.

**Concluding Remarks**

Electrogenation of H$_2$O$_2$ through oxygen reduction is a relatively green and safe strategy that represents a promising alternative route to the traditional anthraquinone process. In recent years, considerable progress has been made in this area, including enhancements in activity and selectivity stemming largely from advances in electrocatalyst and electrochemical cell design and configuration.

Despite all the significant recent progress, several critical challenges still remain (see Outstanding Questions) regarding long-term stability, selectivity under high current densities, and large-scale electrochemical production of H$_2$O$_2$. So far, there are relatively few reports that meet the requirement for practical-scale operations [i.e., high current densities (e.g., >200 mA cm$^{-2}$), high selectivity (e.g., >90%), and long-term stability (e.g., >100 hours)]. This is due in part to limitations of the electrocatalysts, cell designs, gas diffusion layer techniques, and membrane stability (especially so for AEMs). The acidic ORR can operate without an AEM yielding high stability. However, currently reported catalysts still suffer from low activity and selectivity, especially under high current conditions. These aspects will require more attention in the future. Moreover, for H$_2$O$_2$ production at high concentrations, high energy is consumed at practical scales. Theoretically, significant amounts of energy can be saved if one can couple the cathodic ORR and anodic H$_2$O$_2$ generation together (Figure 4B,C), with enhanced H$_2$O$_2$ yield and a maximal theoretical Faradaic efficiency of 200%.

The final target of electrochemical H$_2$O$_2$ synthesis is to realize continuous production in a practically large scale with high energy efficiency and long-term durability. The accomplishment of electrochemical H$_2$O$_2$ generation will eventually be assessed by the feasibility of economically producing H$_2$O$_2$ at industrial scales and how much improvement it shows compared with current processes. We reiterate that reports focusing solely on the activity and selectivity of model electrodes at small scales with only short-term stability are still far from satisfying the above requirements. Therefore, to push forward the fundamental production method into practical scales, increased collaboration between industrial and research laboratories is needed as well as focus in areas such as catalyst dispersibility, electrolyte and reactor design, volumetric area, long-term durability, system assembly, and suitability for practical scale-up and industrial processing.

**Disclaimer Statement**

The authors declare no conflict of interest.
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