

# The Nexus of Innovation: Electrochemically Synthesizing H<sub>2</sub>O<sub>2</sub> and Its Integration with Downstream Reactions

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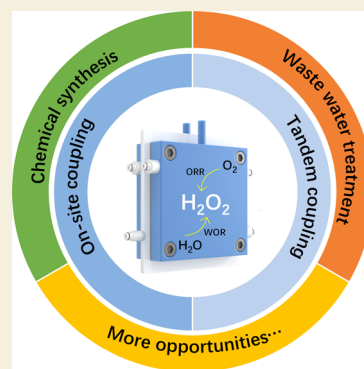
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**ABSTRACT:** Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) represents a chemically significant oxidant that is prized for its diverse applicability across various industrial domains. Recent innovations have shed light on the electrosynthesis of H<sub>2</sub>O<sub>2</sub> through two-electron oxygen reduction reactions (2e<sup>-</sup> ORR) or two-electron water oxidation reactions (2e<sup>-</sup> WOR), processes that underscore the attractive possibility for the on-site production of this indispensable oxidizing agent. However, the translation of these methods into practical utilization within chemical manufacturing industries remains an aspiration rather than a realized goal. This Perspective intends to furnish a comprehensive overview of the latest advancements in the domain of coupled chemical reactions with H<sub>2</sub>O<sub>2</sub>, critically examining emergent strategies that may pave the way for the development of new reaction pathways. These pathways could enable applications that hinge on the availability and reactivity of H<sub>2</sub>O<sub>2</sub>, including, but not limited to the chemical synthesis coupled with H<sub>2</sub>O<sub>2</sub> and waste water treatment by Fenton-like reactions. Concurrently, the Perspective acknowledges and elucidates some of the salient challenges and opportunities inherent in the coupling of electrochemically generated H<sub>2</sub>O<sub>2</sub>, thereby providing a scholarly analysis that might guide future research.

**KEYWORDS:** hydrogen peroxide, integration, chemical manufacturing, electrochemical synthesis, selectivity



## 1. INTRODUCTION

The electrification of chemical production represents a significant paradigm shift in the industry, with substantial implications for sustainability, efficiency, and economic development.<sup>1–3</sup> Leveraging electrical energy to drive chemical reactions enables the direct utilization of renewable energy sources, such as wind, solar, and hydroelectric power, thus reducing reliance on fossil fuels and mitigating the associated greenhouse gas emissions. This transformation also facilitates more precise control over the reaction conditions, leading to enhanced product selectivity and yield. Modular and decentralized production can be achieved through the electrification of chemical processes, allowing for localized manufacturing and reduced transportation needs. Furthermore, electrification offers the potential to unlock innovative synthetic pathways, enabling the production of novel materials and chemicals that were previously challenging or economically unviable to produce. The rapid development of new catalysts, reactors, and systems specifically designed for electrically driven conditions further augments the potential for electrified chemical production.

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a simple but intriguing inorganic chemical compound. Known for its strong oxidizing properties, H<sub>2</sub>O<sub>2</sub> is widely recognized as a green and efficient oxidant with versatile applications in areas such as textile

bleaching,<sup>4</sup> environmental remediation,<sup>5</sup> disinfection,<sup>6</sup> fuel cells,<sup>7,8</sup> and particularly as a nexus molecule for chemical synthesis.<sup>9–12</sup> Currently, the prevailing method for producing H<sub>2</sub>O<sub>2</sub> remains entrenched in the century-old anthraquinone process. This method's reliance on a complex sequence of hydrogenation, separation, oxidation, phase transfer, distillation, and recovery, culminating in an ~80% concentrated solution, challenges its compatibility with modern industrial and sustainability standards. The need to dilute these highly concentrated solutions at the site of use (normally <30%), coupled with the transportation risks stemming from explosion incidents, magnifies the process's inherent dangers. It thus calls into question whether the sustainability of the end product is being compromised by an outdated and potentially hazardous production method. The pursuit of technological innovations that could enable the synthesis of H<sub>2</sub>O<sub>2</sub> in safer, more controlled concentrations and the exploration of alternative

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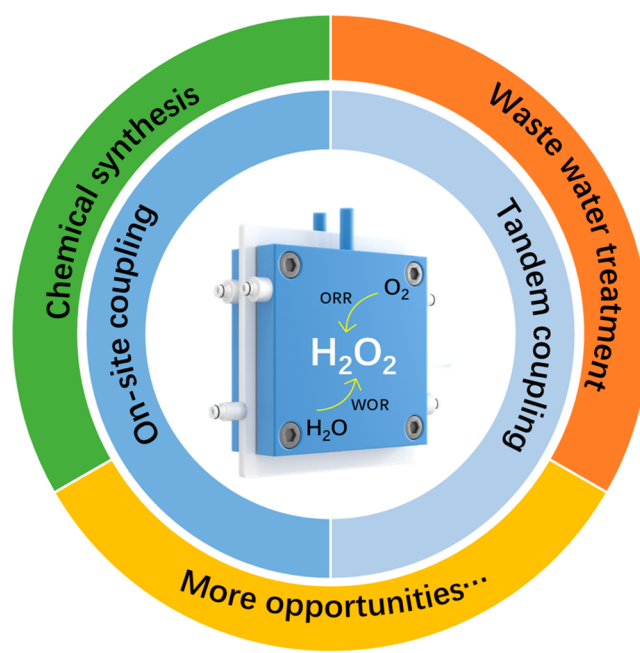


production pathways are not merely a response to the apparent contradictions but could represent an essential evolution in aligning chemical production with broader environmental and safety objectives.

Electrochemical synthesis of  $\text{H}_2\text{O}_2$  represents an alternative and promising pathway that aligns with modern sustainability goals. This method is based on the direct reduction of oxygen ( $\text{O}_2$ ) or the oxidation of water ( $\text{H}_2\text{O}$ ) at either the cathode or anode surface in an electrochemical cell. It offers several advantages, including the ability to control the concentration of  $\text{H}_2\text{O}_2$  by adjusting the electrochemical parameters and avoiding the complex multistep procedures associated with traditional anthraquinone process. Recent research indicates that the electrochemical method for  $\text{H}_2\text{O}_2$  production demonstrates a substantially lower energy consumption of less than 10 kWh/kg  $\text{H}_2\text{O}_2$ . This stands in contrast to the anthraquinone process, which requires an estimated 17.6 kWh/kg  $\text{H}_2\text{O}_2$ .<sup>13</sup> The key to this approach is the careful selection of electrode materials, catalysts, and electrolytes, which play vital roles in enhancing selectivity and efficiency toward  $\text{H}_2\text{O}_2$  formation. The exploration of electrocatalysts for oxygen reduction reactions (ORR) and water oxidation reactions (WOR) has led to significant advancements, particularly in achieving two-electron ORR, whose selectivity is reported to reach up to  $\sim 100\%$ . Several classes of catalysts have been identified as effective in this regard, such as heteroatom-containing carbons,<sup>14–16</sup> metal complexes with N-doped carbon matrices (M–N–C catalysts),<sup>17,18</sup> and various single-atom metals or alloys.<sup>19,20</sup> Meanwhile, efforts in the realm of partial water oxidation have yielded success with oxidized or oxygen-containing carbons and specific metal oxides, although these are often marked by poor selectivity toward the four-electron water oxidation pathway.

The coupling of  $\text{H}_2\text{O}_2$  with other chemical synthesis processes represents a dynamic area of chemistry that leverages the unique properties of  $\text{H}_2\text{O}_2$ . Its role as a mild oxidizing agent along with the ability to control selectivity and yield makes it a valuable tool in the synthesis of various products. Furthermore, the environmental benefits and potential cost-effectiveness of using  $\text{H}_2\text{O}_2$  contribute to its growing utilization in both research and industrial settings. However, its propensity to decompose into water and oxygen can lead to a loss of efficiency in the target reaction, and controlling this decomposition without hindering the desired synthesis process requires meticulous control of the reaction conditions. Moreover, achieving selectivity in the intended reaction while preventing side reactions is another major challenge. The handling of  $\text{H}_2\text{O}_2$ , especially the high interfacial concentration of the generated species, and the choice of compatible catalysts become critical aspects that necessitate careful scientific consideration in orchestrating successful direct coupling with other chemical syntheses.

This Perspective first delves into the intricacies of  $\text{H}_2\text{O}_2$  electrochemistry, elucidating the fundamental principles governing its electrochemical behavior. Subsequently, we broach the complex issue of  $\text{H}_2\text{O}_2$  coupling, positing challenges and potential avenues for investigation. Following this, the focus shifts to the design and operational aspects of reactor design. Finally, we commence with an exploration of the latest tandem and on-site interfacial coupling strategies that have been developed with electrosynthesized  $\text{H}_2\text{O}_2$  as the bridge nexus, evaluating their underlying mechanisms and effectiveness (Figure 1). It then delves into the integration of



**Figure 1.** Schematic representation of the coupling of the electrochemical synthesis of  $\text{H}_2\text{O}_2$  with chemical reactions.

these materials with reactor designs, critically assessing how they can be harnessed to achieve the maximum possible  $\text{H}_2\text{O}_2$  output. The paper further contemplates the significant challenges and key advances needed to propel  $\text{H}_2\text{O}_2$  electrosynthesis beyond the confines of laboratory-scale operations. By providing insights into the technological and practical barriers, we lay a foundation for understanding what is necessary to translate these scientific achievements into viable industrial-scale applications, reflecting on both the opportunities and the inherent complexities of this transition.

## 2. $\text{H}_2\text{O}_2$ ELECTROCHEMISTRY

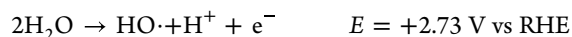
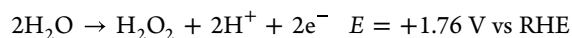
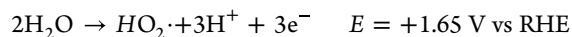
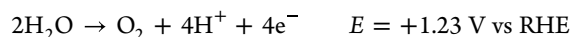
Understanding the electrochemistry of  $\text{H}_2\text{O}_2$  is a crucial prerequisite for effectively coupling its electrosynthesis with downstream reactions such as sharpless epoxidation,<sup>21</sup> the Wacker process,<sup>22</sup> Dakin reactions,<sup>23</sup> and sulfoxidation.<sup>24</sup> Actually,  $\text{H}_2\text{O}_2$  can be electrochemically synthesized either through the two-electron reduction of  $\text{O}_2$  ( $2e^-$  ORR) or through the two-electron oxidation of  $\text{H}_2\text{O}$  ( $2e^-$  WOR). The electrochemical pathway often depends on the specific catalyst and reaction conditions, including the potential, current density, and surrounding electrolyte environment. While the generation of  $\text{H}_2\text{O}_2$  has been extensively examined through the  $2e^-$  ORR,  $2e^-$  WOR offers an alternative method that does not rely on gas-phase reactants.

The  $2e^-$  ORR is recognized for its low overpotential and ability to achieve a Faradaic efficiency (FE) of 100% for  $\text{H}_2\text{O}_2$  production. However, it necessitates continuous  $\text{O}_2$  bubbling for the synthesis, a factor contributing to the limited current densities. On the other hand, the  $2e^-$  WOR is characterized by high productivity owing to its high current activity. Unlike  $2e^-$  ORR, it does not require  $\text{O}_2$  bubbling or specialized quantification tools, such as rotating ring-disk electrodes (RRDE). However, it faces challenges such as the potential formation of hydroxyl radicals, diminished FE due to competing four-electron oxygen evolution reactions (OER), an increased likelihood of further electrooxidation, and a

limited number of identified catalysts. Theoretically, coupling the cathodic ORR with anodic H<sub>2</sub>O<sub>2</sub> generation presents an opportunity for significant energy conservation. Such a combination could lead to enhanced H<sub>2</sub>O<sub>2</sub> yields and a theoretical FE of 100% for both the anode and cathode.<sup>25</sup>

### 2.1. Electrocatalytic Water Oxidation

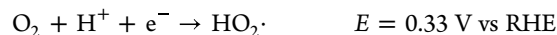
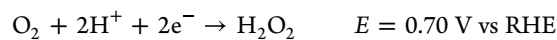
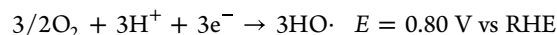
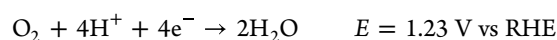
There are four possible pathways for electrochemical water oxidation reactions:<sup>26–29</sup>



As can be observed, the four-electron mechanism emerges as the thermodynamically favored path, possessing the lowest equilibrium potential of 1.23 V vs RHE. This pathway competes with the other three water oxidation reaction pathways that generate oxidative agents such as the hydroperoxyl radical, H<sub>2</sub>O<sub>2</sub>, and the hydroxyl radical. These reactive oxygen species exhibit varying oxidizing capabilities. Among them, the hydroxyl radical is known for its strongest oxidizing ability, followed closely by H<sub>2</sub>O<sub>2</sub>, with the hydroperoxyl radical and dioxygen showing relatively lower oxidizing strengths in practical terms. The successful formation of the hydroperoxyl radical through the three-electron water oxidation pathway has not been achieved previously, as the four-electron and three-electron paths are almost concurrent and indistinguishable. It is noteworthy that all three WORs initiate with the same primary step, that is, the formation of adsorbed hydroxide. Both H<sub>2</sub>O<sub>2</sub> and hydroxyl radicals (·OH) are of practical significance due to their potent oxidizing abilities, and they find applications in sanitization and water disinfection. The hydroxyl radical generally exhibits a short lifetime, making H<sub>2</sub>O<sub>2</sub> of greater practical interest. The initial foray into the realm of H<sub>2</sub>O<sub>2</sub> synthesis via 2e<sup>−</sup> WOR was made in 2004, utilizing a porous carbon-based catalyst.<sup>30</sup> Although carbon-based materials were an attractive initial choice, their lack of stability at anodic potentials has limited their broader application. This limitation has led to a pivot in research focus toward metal oxide catalysts,<sup>31–35</sup> which are generally more stable and offer high efficiencies. However, these efficiencies are commonly observed at lower current densities. Thus, the ongoing discovery of innovative catalyst designs remains crucial, which is especially pertinent as the field continues to evolve toward practical implementation.

### 2.2. Electrochemical Oxygen Reduction Reactions

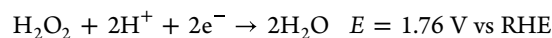
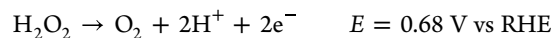
Initial studies of the 2e<sup>−</sup> ORR were primarily focused on the electrochemical reduction of oxygen in acidic aqueous solutions, but the techniques and materials used at that time yielded low H<sub>2</sub>O<sub>2</sub> Faradaic efficiencies and limited the commercial viability of the process. The latter half of the 20th century witnessed a surge in interest in electrochemical methods for H<sub>2</sub>O<sub>2</sub> production, catalyzed by growing environmental concerns and advancements in electrocatalyst materials that exhibited promising results in terms of selectivity and efficiency.<sup>36–41</sup> The introduction of gas diffusion electrodes further optimized the process by enhancing the mass transfer and reducing competing reactions. Some key reactions involved are summarized as follows:



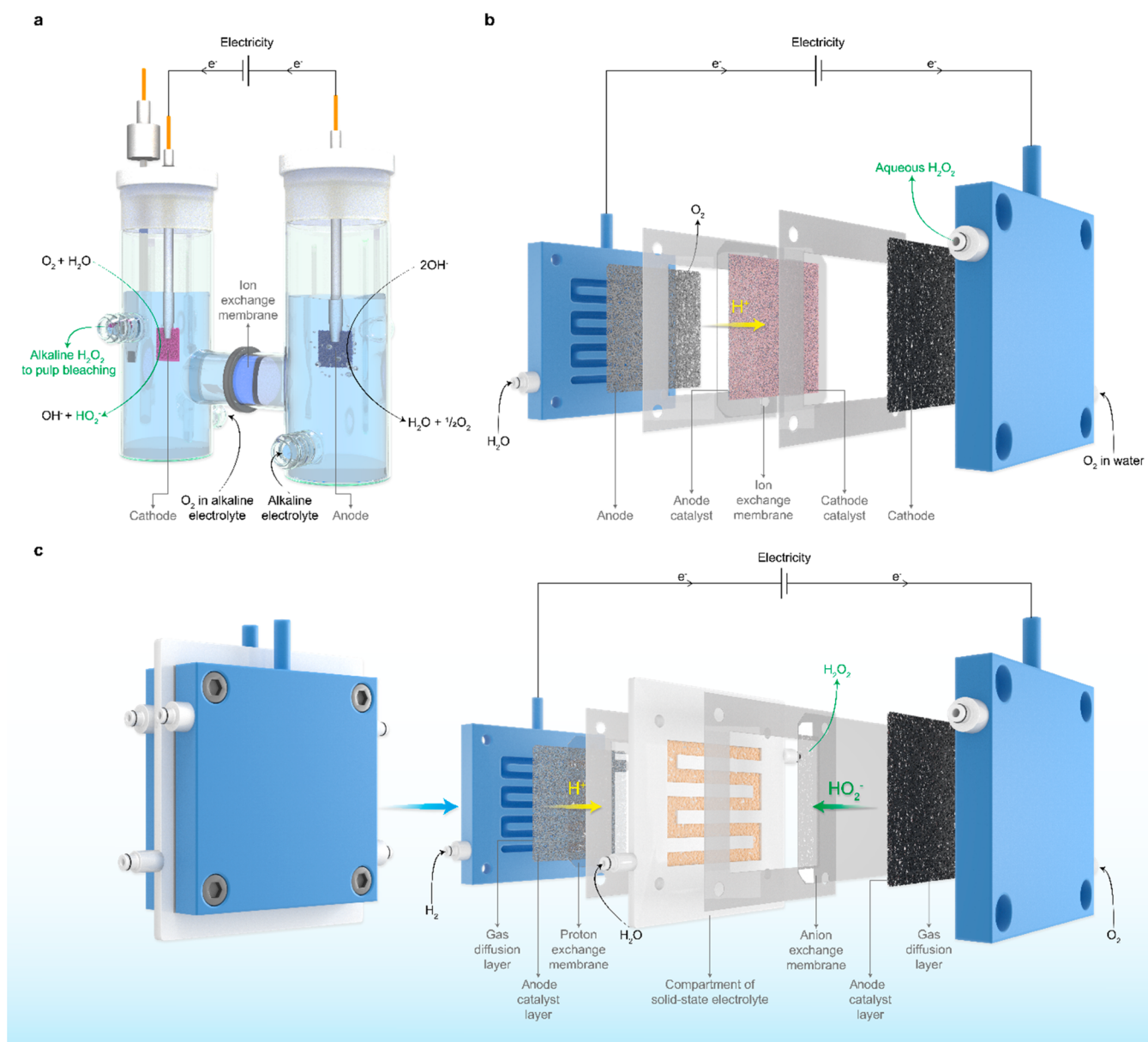
In the development of catalysts, meticulous attention to reaction kinetics and equilibrium potentials is imperative, particularly for managing intermediate species' absorption energy profiles. During electrocatalyst design, it is crucial to minimize the propensity for thermodynamically favored four-electron reactions at low overpotentials while constraining suboptimal single- and three-electron pathways at elevated overpotentials to ensure both high rate and selectivity. Theoretically, O<sub>2</sub> can engage with metal centers either through a side-on orientation (Griffith model)<sup>42</sup> or by bridging two metal centers.<sup>43</sup> Geometrical considerations of the active site for H<sub>2</sub>O<sub>2</sub> synthesis are essential for either promoting end-on O<sub>2</sub> binding or preserving the O–O bond during the ORR. The metal–oxygen interaction strength also plays a critical role in determining redox outcomes. Strong metal–oxygen bonds, arising from a significant electron density donation from the metal to adsorbed O<sub>2</sub>, facilitate low activation energies for the sequential reduction of O<sub>2</sub> to O<sub>2</sub><sup>·−</sup>, H<sub>2</sub>O<sub>2</sub>, and OH<sup>·</sup>. However, this strong binding paradigm increases the activation enthalpy for the final OH<sup>·</sup> reduction step, risking surface poisoning through stable metal–OH complexes, thereby slowing catalytic turnover and favoring H<sub>2</sub>O over H<sub>2</sub>O<sub>2</sub> as the end product. As a result, a variety of catalytic materials are employed. These include noble metals,<sup>44</sup> metal alloys,<sup>45,46</sup> and metal complexes embedded in carbon matrices with nitrogen-donor functionalities (known as M–N–C catalysts).<sup>47–49</sup> Additionally, single-atom catalysts, which minimize the likelihood of O–O bond cleavage,<sup>50</sup> and carbon-based materials, which engage in weak binding with H<sub>2</sub>O<sub>2</sub> after its initial two-electron reduction,<sup>51–55</sup> are also deployed. These catalytic materials, whether used individually or in composite forms, have been engineered to optimize the efficiency, selectivity, and stability during the 2e<sup>−</sup> electroreduction process.

### 2.3. Challenges for the Coupling of Electrosynthesized H<sub>2</sub>O<sub>2</sub>

Several factors influence the overall efficiency for integrating the electrochemical production of H<sub>2</sub>O<sub>2</sub> with chemical reactions. First, on a chemical level, H<sub>2</sub>O<sub>2</sub> is inherently unstable and prone to decomposition, particularly in the presence of reactive oxygen species (ROS) and certain metal catalysts. The main decomposition mechanism can be summarized as follows:



The oxidation potential of H<sub>2</sub>O<sub>2</sub> is substantially lower than that needed for the electro-oxidation of water to form H<sub>2</sub>O<sub>2</sub>. Conversely, the reduction potential of H<sub>2</sub>O<sub>2</sub> is considerably higher than the potential for the reduction of molecular O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. These electrochemical disparities necessitate the immediate removal of synthesized H<sub>2</sub>O<sub>2</sub> from the vicinity of the electrode surface to prevent undesired reactions. Consequently, the electrocatalyst's selectivity for H<sub>2</sub>O<sub>2</sub> production is contingent not only upon its inherent catalytic



**Figure 2.** Schematic representation of the (a) H-cell configuration, (b) flow cell reactor, and (c) solid-state electrolyte reactor for  $\text{H}_2\text{O}_2$  synthesis.

activity but also on the efficacy with which the generated  $\text{H}_2\text{O}_2$  is transported away from the electrode–electrolyte interface. Therefore, it is highly desirable to design an integrated system that can efficiently consume  $\text{H}_2\text{O}_2$  in chemical reactions.

The rate of  $\text{H}_2\text{O}_2$  production and its reactivity in subsequent chemical processes must be carefully balanced. If  $\text{H}_2\text{O}_2$  is consumed faster than is generated, the overall efficiency of the coupled process could be compromised. Moreover, for efficient coupling, both the electrochemical synthesis of  $\text{H}_2\text{O}_2$  and the subsequent chemical reaction should ideally occur under similar conditions (e.g., pH, temperature, solvent). Matching these conditions can be challenging but is essential for process integration and optimization. Additionally, the redox potential at which  $\text{H}_2\text{O}_2$  is synthesized can have significant implications for its stability and reactivity. Electrochemical parameters must be optimized to avoid the generation of species that could facilitate the  $\text{H}_2\text{O}_2$  decomposition.

In cases where certain chemical reactions prove challenging to seamlessly integrate with an electrocatalytic cell—a topic we

will delve into in the subsequent section—special attention must be given to the self-disproportionate decomposition of  $\text{H}_2\text{O}_2$ . The challenge arises primarily during the transport phase as  $\text{H}_2\text{O}_2$  must be transferred to a separate reactor for further reactions, a process during which decomposition may occur. This issue can be mitigated by periodic dilution of the aqueous  $\text{H}_2\text{O}_2$  solution when its concentrations approach levels that would induce chemical decomposition. However, this strategy comes with its own set of limitations, particularly when dealing with reactions that necessitate high concentrations of  $\text{H}_2\text{O}_2$ .

### 3. TYPES OF CELLS FOR $\text{H}_2\text{O}_2$ ELECTROSYNTHESIS

The initial exploration into commercial electrochemical means of generating  $\text{H}_2\text{O}_2$  can be traced back to the 1980s, when Dow and Huron Technologies, Inc. capitalized on the electrochemical method to develop what would be known as the Huron-Dow process for the localized generation of alkaline  $\text{H}_2\text{O}_2$  solutions (Figure 2a). In this technique using H-cell

reactors, hydroxide ions undergo oxidation to form oxygen at the anode, while an introduced oxygen stream is reduced to hydroperoxyl ions at the cathode.<sup>12</sup> In the dilute alkaline solution, H<sub>2</sub>O<sub>2</sub> finds application in paper bleaching; the process negates the necessity for either neutralization or distillation, thereby enhancing its commercial feasibility. The process saw commercialization in 1991 and has been nearing competitiveness with the established anthraquinone method. Despite its merits, the Huron-Dow process is not without its shortcomings. The alkalinity of the resultant H<sub>2</sub>O<sub>2</sub> solution presents a challenge due to the compound's propensity to decompose under alkaline conditions. Consequently, immediate utilization is often needed. Moreover, the process is fraught with several other challenges that complicate its implementation. First, produced H<sub>2</sub>O<sub>2</sub> often demands a neutralization step depending on its designated application. Second, carbonate precipitates from ambient CO<sub>2</sub>, which can block the electrode's active areas. The corrosive nature of the highly alkaline milieu presents a third obstacle, putting additional strain on the system's longevity.<sup>56</sup>

To mitigate ohmic resistance and circumvent the challenges associated with alkaline conditions, proton-exchange membrane (PEM) flow cell reactors are employed for the uninterrupted synthesis of H<sub>2</sub>O<sub>2</sub>.<sup>57–62</sup> The reactor is an intricate assembly that includes flow field plates, gas diffusion electrodes (GDEs) equipped with catalytic layers, electrolyte chambers, circulating electrolytes, and ion-conductive membranes (Figure 2b). The use of GDEs, which comprise a hydrophobic gas diffusion layer loaded with catalysts, enables the direct delivery of O<sub>2</sub> to the active sites. In such a design, O<sub>2</sub> is channeled through the flow field plates to the cathode, thereby effectively eliminating diffusion barriers for the gas. This is demonstrated to increase the H<sub>2</sub>O<sub>2</sub> partial currents from 0.1 mA/cm<sup>2</sup> (three-electrode RRDE, O<sub>2</sub> bubbling) to ~300 mA/cm<sup>2</sup> when a carbon black catalyst was applied.<sup>63</sup> The design flexibility of GDEs makes them amenable to scaling from lab-scale experiments to industrial applications. Furthermore, the integration of advanced materials, such as nanostructured catalysts and high-conductivity backings, can drastically improve performance metrics such as the current density and FE. Nevertheless, the broader application of GDEs is not without challenges. Several critical considerations include long-term material stability under varied operational conditions, the need for pore structure optimization to ensure efficient mass transport, and economic aspects related to material and fabrication costs. Additionally, the large-scale manufacturing of GDEs for use in multistack electrolyzers introduces complexity, particularly given their sensitivity to pressure variations. On the anode side, water serves as the reactant and is separated by a membrane, typically Nafion, which allows for proton conduction. These protons migrate across the membrane to the cathode, thereby facilitating the 2e<sup>-</sup> ORR for H<sub>2</sub>O<sub>2</sub> production.

In a quest to surmount the challenge of ensuring high product purity in H<sub>2</sub>O<sub>2</sub> synthesis, our research group pioneered a reactor that incorporates a solid-state electrolyte (SSE). As depicted in Figure 2c,<sup>63,64</sup> this innovative reactor design features a central chamber sandwiched by cation and anion exchange membranes. The chamber serves the dual function of collecting synthesized H<sub>2</sub>O<sub>2</sub> and segregating it from ion conduits, thus maintaining a high degree of product purity. Independent streams of H<sub>2</sub> (or H<sub>2</sub>O) and O<sub>2</sub> are fed into the anode and cathode chambers, respectively. These membranes

mitigate the risk of electrode flooding, allowing electro-generated hydroperoxide ions (HO<sub>2</sub><sup>-</sup>) at the cathode and protons (H<sup>+</sup>) at the anode to traverse the membranes, driven by electrical and concentration gradients, and converge in the central chamber as pure H<sub>2</sub>O<sub>2</sub>. This novel configuration not only ensures a pure product but also augments electrochemical efficiency by inhibiting parasitic reactions that could otherwise degrade the synthesized H<sub>2</sub>O<sub>2</sub>. However, it is imperative to further investigate the material properties of the membranes and the SSE, as these factors could have subtle yet profound impacts on ion selectivity, transport kinetics, and ultimately the overall efficiency and purity of the product. On the other hand, the SSE cell incorporates an additional layer compared with the flow cell, which could introduce extra ohmic resistance. This could consequently diminish both the efficiency and current densities of the reactor compared to conventional flow cells.

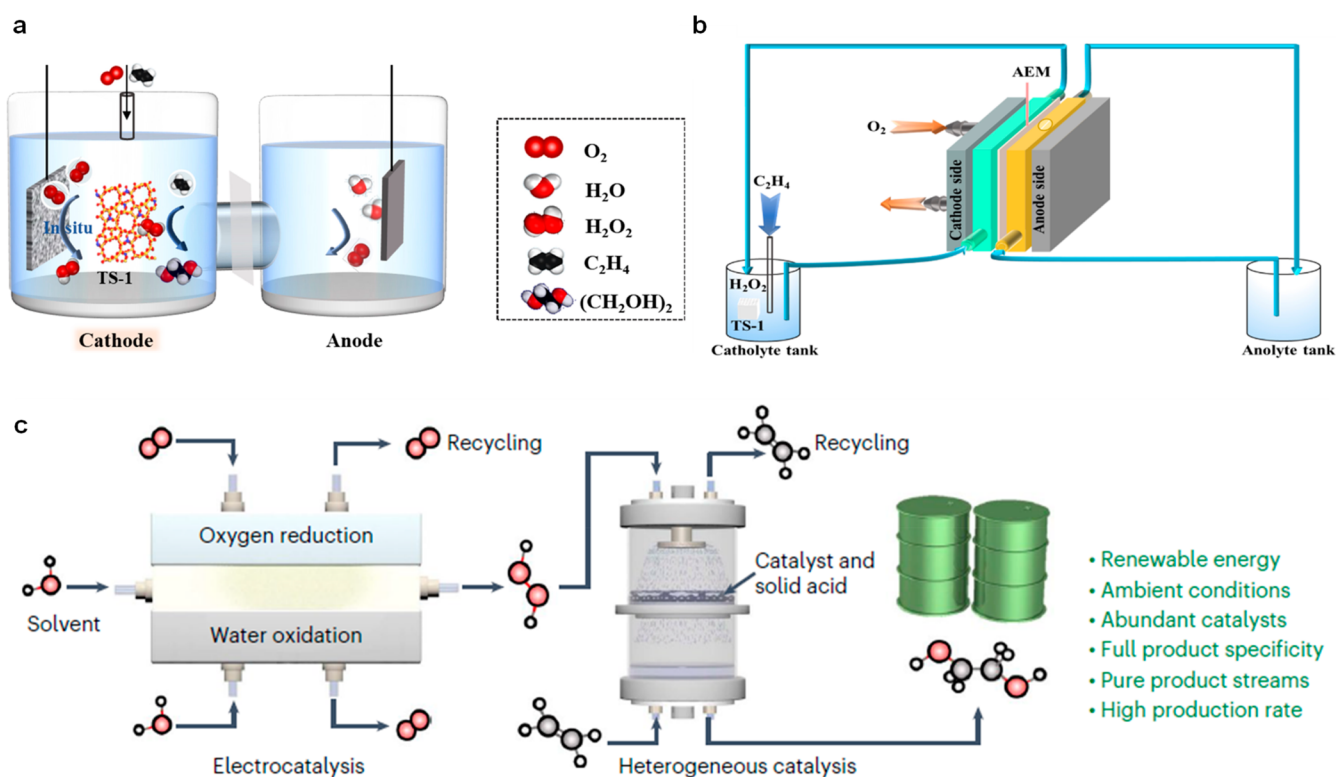
#### 4. TRENDS IN THE COUPLING OF H<sub>2</sub>O<sub>2</sub> ELECTROSYNTHESIS AND OTHER DOWNSTREAM REACTIONS

The integration of H<sub>2</sub>O<sub>2</sub> electrosynthesis with downstream reactions is increasingly gaining attention for its potential in enhancing the efficiency and sustainability of chemical processes. Particularly noteworthy are the trends in cascade reactions and in situ utilization of electrochemically generated H<sub>2</sub>O<sub>2</sub>. Cascade reactions offer an elegant approach to synthesizing more complex molecules by using hydrogen peroxide as an intermediate reactant, thereby extending the utility of the electrosynthesis process. On the other hand, in situ utilization presents an immediate application for the synthesized H<sub>2</sub>O<sub>2</sub>. By direct use of the generated hydrogen peroxide for oxidation reactions, in situ utilization maximizes the concentration gradients, thereby increasing the overall process efficiency. Both cascade reactions and in situ utilization are subjects of ongoing research aimed at process optimization and scalability. In this section, we summarize recent reports on the coupling of H<sub>2</sub>O<sub>2</sub> electrosynthesis with other downstream reactions, underscoring the advancements and potential in this burgeoning field.

##### 4.1. Chemical Synthesis

H<sub>2</sub>O<sub>2</sub> has emerged as a versatile and environmentally benign oxidant in the realm of organic oxidation, particularly in the formation of value-added compounds. Its application encompasses a variety of oxidation reactions, including but not limited to, the ammoxidation of cyclohexanone,<sup>65</sup> hydroxylation of phenol,<sup>66</sup> and the selective oxidation of alcohols.<sup>67</sup>

Olefin oxidation to alcohol is a critical reaction with broad implications in various industrial sectors.<sup>68</sup> The mechanism of olefin oxidation to alcohol typically begins with the activation of the olefin by coordination with a metal catalyst, such as palladium or ruthenium, which weakens the carbon-carbon double bond. An oxidizing agent, often H<sub>2</sub>O<sub>2</sub> or molecular oxygen, then coordinates to the metal center and undergoes oxidative addition. The direct use of H<sub>2</sub>O<sub>2</sub> in the absence of a suitable catalyst can lead to a lack of selectivity, resulting in overoxidation or side reactions. Additionally, the reaction may require harsh conditions, such as high temperatures or pressures, to proceed at a reasonable rate. The stability of H<sub>2</sub>O<sub>2</sub> can also be a concern as it can decompose into water and oxygen, particularly under acidic conditions or in the presence of metal impurities.



**Figure 3.** (a) Schematic illustration of ethylene glycol production over TS-1 using in situ generated  $\text{H}_2\text{O}_2$  from the electroreduction of  $\text{O}_2$ . (b) Schematic of ethylene glycol production using a flow cell. Reproduced with permission from ref 69. Copyright 2023, John Wiley and Sons. (c) Cascade ethylene oxidation process.  $\text{O}_2$  is initially converted into a pure stream of  $\text{H}_2\text{O}_2$  through electrochemical means. This stream of  $\text{H}_2\text{O}_2$  is then introduced into a second reactor, where it serves as the oxidizing agent to directly convert ethylene to pure ethylene glycol, with no other oxidation products observed. Reproduced with permission from ref 70. Copyright 2023, Springer Nature.

Ethylene glycol, a vital commodity chemical, mirrors the intricacies of olefin oxidation. Its global production exceeded 40 million tons in 2020, with an anticipated annual growth rate of 5–10%. Its applications span various industries, including its use as a precursor for polyester fibers, antifreeze, coolant, and energy carrier. The traditional method for producing ethylene glycol primarily involves the hydration of ethylene oxide. In this process, ethylene oxide reacts with water, and the reaction is typically catalyzed by acids or bases. The reaction can be carried out at elevated temperatures and pressures to enhance the rate of conversion. The resulting mixture contains ethylene glycol along with other oligomers and byproducts, which are then separated through a series of distillation and purification steps. This method, while effective, is energy intensive and can result in several hundred million tons of  $\text{CO}_2$  emissions.

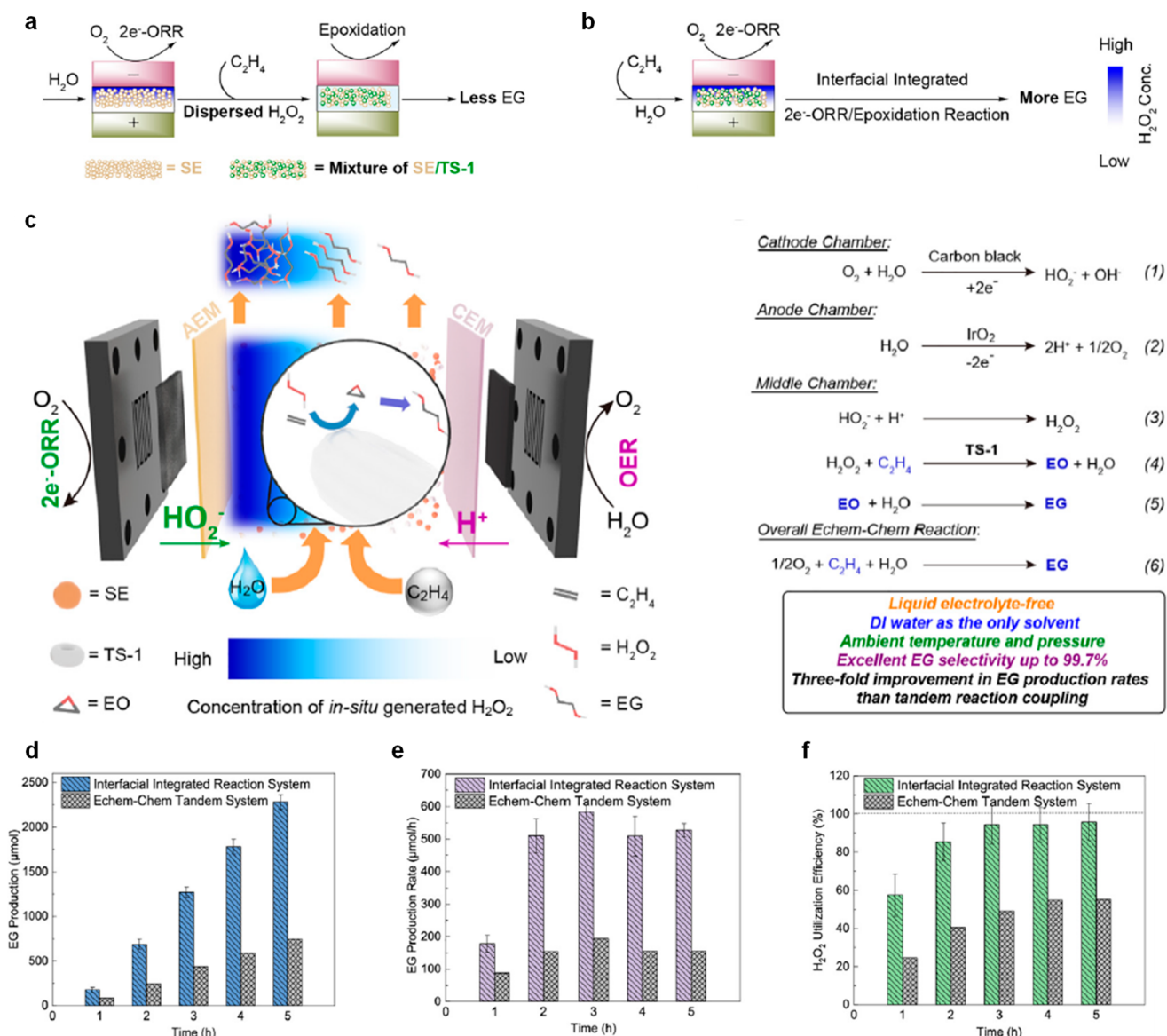
An integrated and efficient  $\text{H}_2\text{O}_2$  pathway has been established for the oxidation of ethylene into ethylene glycol. This pathway involves a two-step tandem route that leverages the unique properties of two distinct catalysts (Figure 3a).<sup>69</sup> In the first step, a mesoporous carbon catalyst is employed to produce  $\text{H}_2\text{O}_2$ , and then a titanium silicalite-1 (TS-1) catalyst is utilized to oxidize ethylene into ethylene glycol using the in situ generated  $\text{H}_2\text{O}_2$ . The synergy between these two catalysts in the tandem route results in remarkable activity. Specifically, the process achieves an 86% conversion of  $\text{H}_2\text{O}_2$ , coupled with an impressive 99% selectivity toward ethylene glycol. The overall yield, measured as  $51.48 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ , underscores the efficiency of this innovative pathway. The integration of mesoporous carbon and titanium silicalite-1 catalysts in a tandem route not only enhances the reaction efficiency but

also provides insights into the potential development of other catalytic systems for similar oxidation processes.

In addition to the aforementioned process, they also implemented a continuous system using a flow cell. (Figure 3b). In this system, consecutively produced  $\text{H}_2\text{O}_2$  is used to directly oxidize ethylene. This setup enables a stable production rate of  $0.5 \text{ mol g}_{\text{cat}}^{-1}$  of ethylene glycol, demonstrating the efficiency and consistency of the continuous process. The utilization of a flow cell in this manner represents a significant advancement in the field, allowing for the continuous and controlled oxidation of ethylene, thereby enhancing the overall productivity of the reaction.

Electrogenated  $\text{H}_2\text{O}_2$  can also be coupled to thermodynamic reactions. For example, in the pursuit of an efficient method for the oxidation of propylene to propylene glycol, Sun et al. have engineered a tandem system within a flow cell.<sup>71</sup> This system uniquely combines the electro-synthesis of  $\text{H}_2\text{O}_2$  through a  $2e^-$  ORR on oxygen-doped XC-72R carbon with the thermocatalysis of propylene oxidation over  $\text{H}_2\text{O}_2/\text{TS-1}$ . The innovation in this approach lies in the meticulous optimization of the C-O/TS-1 catalyst composition, culminating in peak values of 79.7% selectivity for propylene glycol and 47.6% utilization efficiency of  $\text{H}_2\text{O}_2$ , with a yield of  $4.28 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$  at  $-53 \text{ mA/cm}^2$ .

The tandem oxidation process, encompassing both electrocatalysis and thermocatalysis, presents a complex interplay between electron transfer and mass transport. In this system,  $\text{O}_2$  is reduced through the acquisition of electrons and protons to form  $\text{H}_2\text{O}_2$  in the electrocatalytic stage. Subsequently,  $\text{H}_2\text{O}_2$  is conveyed to the active sites of TS-1, where it acts as an

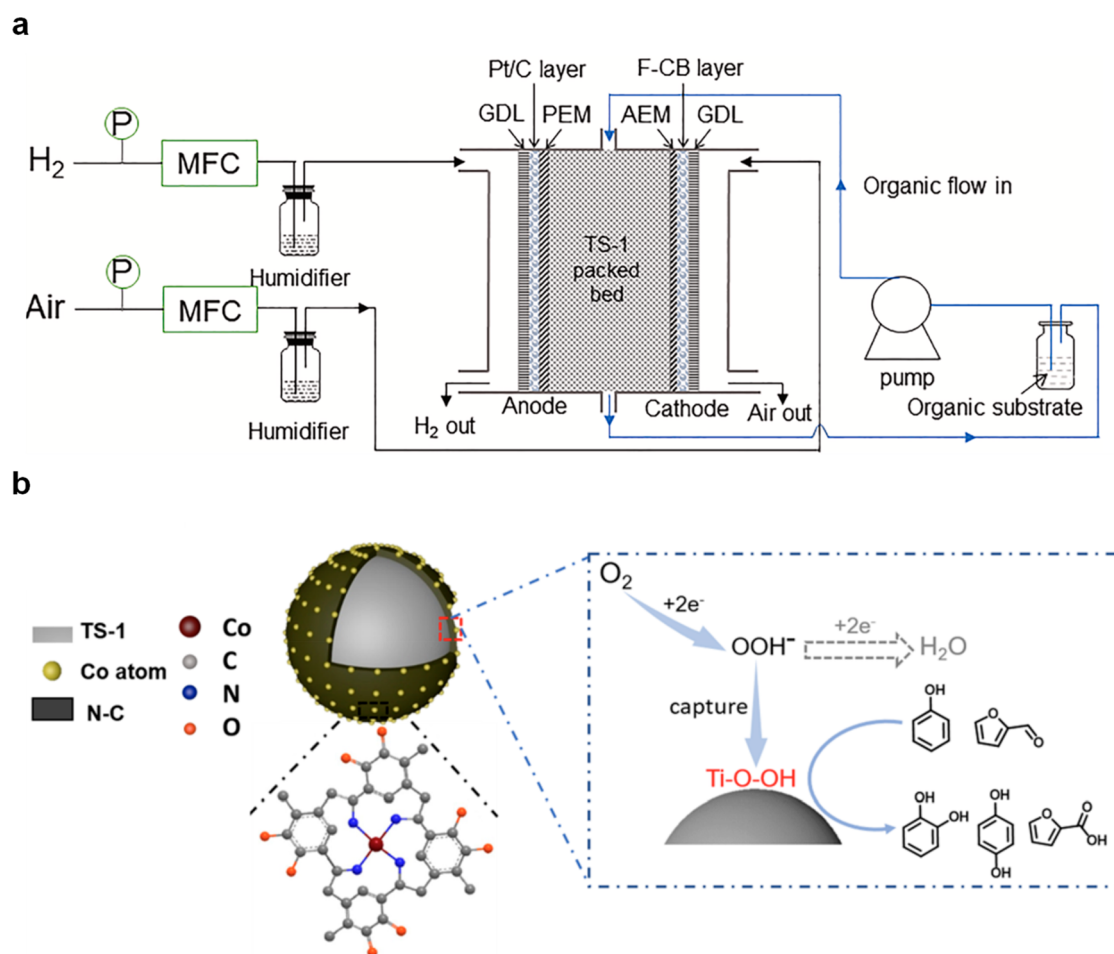


**Figure 4.** (a, b). Reaction diagram illustrating the conventional tandem reaction system alongside the interfacial electrochemical-chemical reaction coupling system. (c) Schematic of an integrated three-chamber solid electrolyte reactor designed for the coupling of interfacial  $\text{H}_2\text{O}_2$  generation and  $\text{C}_2\text{H}_4$  oxidation. Comparison of ethylene glycol production utilizing the interfacial integrated solid electrolyte reactor versus the traditional tandem reactor at the same ORR current densities. Reproduced with permission from ref 72. Copyright 2023, Elsevier.

oxidizing agent for propylene in the thermocatalytic phase. The critical analysis, including TOF-SIMS and EIS, unveils the underlying mechanism that makes this system effective. The optimal mass ratio of 1:3 between C–O and TS-1 creates a delicate balance between electron transfer and mass transport, both vital for the tandem oxidation process that involves both electrocatalysis and thermocatalysis. This balance is not merely a technical achievement but represents a deeper understanding of the interplay among different catalytic processes.

Moving forward, Fan et al introduce a cascade strategy for the efficient and selective production of pure ethylene glycol solution under ambient conditions without detectable by-product formation.<sup>70</sup> Specifically, ethylene is converted to ethylene glycol on a catalyst/solid-acid composite using electrochemically generated  $\text{H}_2\text{O}_2$  as the oxidant. (Figure 3c) The reaction is facilitated by a composite of heterogeneous catalysts and solid acid. Remarkably, the entire process can be conducted at ambient temperature and pressure, consuming

only  $\text{O}_2$ , water, and renewable electricity, thus presenting an efficient and environmentally friendly approach. The introduction of a solid-acid electrolyte into the system was a key innovation as it allowed for continuous production of a pure ethylene glycol stream at practical relevant current densities, overcoming challenges such as unsatisfactory current density and costly downstream separation. The researchers achieved a high electron utilization efficiency of 60–70% at industrially relevant current densities ( $500 \text{ mA/cm}^2$ ) for ethylene glycol production with full product selectivity ( $\sim 100\%$ ). The integration of a solid-acid electrolyte into the system allowed for continuous production of a pure ethylene glycol stream at practical relevant current densities, overcoming challenges such as unsatisfactory current density and costly downstream separation. The techno-economic analysis of the cascade ethylene glycol production from  $\text{CO}_2$  further highlights the potential of this method in reducing  $\text{CO}_2$  emissions compared to traditional pathways. This finding represents a significant



**Figure 5.** (a) The design of the flow cell was for the coupling of  $2e^-$  reduction of  $O_2$  and the selective oxidation of organic compounds. Reproduced with permission from ref 73. Copyright 2022, Elsevier. (b) Schematic representation of the integrated interface strategy for the concurrent electro-synthesis of  $H_2O_2$  and hydroxylation of phenol. Reproduced with permission from ref 74. Copyright 2022, Royal Society of Chemistry.

step toward sustainable chemical manufacturing, potentially transforming the ethylene glycol production industry by reducing energy consumption, emissions, and costs.

In the realm of those reactions, considerable advancements have been achieved in the formulation of coupling reactions. Nevertheless, the prevailing methodologies in design and engineering have been confined to the optimization of singular reactions, neglecting a salient feature intrinsic to electrocatalysis: the pronounced concentration gradient from the accumulation of generated products or intermediates at the juncture of the catalyst and electrolyte. Pertaining to the synthesis of liquid products, the acute delineation between the catalyst/electrolyte interface and the bulk electrolyte results in an interfacial concentration that may exceed the mean concentration by several orders of magnitude when molecules are equitably dispersed within the electrolyte. However, within conventional electrochemical-chemical tandem reaction systems, this concentration gradient is dissipated before the product stream is conveyed into the downstream reactor, thereby forfeiting the opportunity to exploit the augmented interfacial concentrations to expedite the subsequent reaction. The strategies to utilize this distinctive property of electrocatalysis, along with the implications of these elevated interfacial concentrations on the activity of the ensuing reaction, remain facets that warrant further exploration and elucidation.

To demonstrate this concept, Wang et al.<sup>72</sup> proposed a novel approach that transcends the limitations of traditional tandem systems by introducing a fully integrated system, demonstrating a marked enhancement in the catalytic performance (Figure 4a,b). This system's innovation lies in the strategic utilization of the electro-synthesis of  $H_2O_2$ , followed by the olefin oxidation reaction. By confining the chemical reaction precisely at the electrode–electrolyte interface within a solid electrolyte reactor, the system capitalizes on the interfacial high concentration of  $H_2O_2$ , a product of electrocatalysis. This concentration is leveraged to augment the subsequent ethylene oxidation reaction, resulting in a 3-fold improvement in electrolyte-free ethylene glycol generation compared to conventional tandem reactor systems.

The reactor comprises several integral parts that function in unison. (Figure 4c) At the core of this system lies the main chamber (middle layer) of the solid electrolyte (SE) cell, filled with a blend of SE and TS-1 particles. This chamber is flanked by an anion exchange membrane (AEM) and a cation exchange membrane (CEM), which segregate it from the cathode and anode, respectively. In the cathode, the ORR is facilitated by a  $2e^-$  ORR catalyst (carbon black), selectively yielding  $HO_2^-$  species. These anions are then channeled through the AEM into the middle layer, where they merge with a proton flux transported from the anode chamber via the CEM and SE particles. What sets this design apart is the



strategic positioning of the AEM/SE interface, where the highest concentration of  $\text{H}_2\text{O}_2$  is achieved during electrolysis. This concentration is not an incidental occurrence but a carefully engineered outcome. By cofeeding ethylene and deionized water into the middle chamber during ORR electrolysis, ethylene is efficiently oxidized by the interfacial  $\text{H}_2\text{O}_2$ . This leads to the formation of ethylene oxide, which subsequently undergoes hydrolysis on the surface of the SE to yield ethylene glycol (EG) as the final product.

The integration of  $2e^-$  ORR electrolysis with olefin epoxidation within the integrated reactor led to a remarkable enhancement in both the EG formation and  $\text{H}_2\text{O}_2$  utilization efficiency. This integrated approach has yielded an increase of over 300% in EG formation and a 175% improvement in  $\text{H}_2\text{O}_2$  utilization compared to conventional tandem reactors (Figure 4d–f).

The critical innovation in this design is the SE reactor's ability to operate without any liquid electrolyte, achieving a 200 h operation to produce pure EG with an exceptional selectivity of 99.7% and an  $\text{H}_2\text{O}_2$  utilization efficiency of 93%. This not only underscores the system's efficiency but also eliminates the need for further salt purification, thus reducing additional expenses.

The insight here is the recognition of the potential to harness the interfacial concentration as a driving force to enhance the reaction efficiency. This approach not only demonstrates the feasibility of improving a specific reaction but also opens up new avenues for rethinking the design of electrochemical-chemical coupling reactions. Particularly in cases where the coupled reaction is sensitive to reactant concentrations, this integration strategy could circumvent the need for energy-intensive separation or concentration steps typically needed between electrochemical and chemical reactions.

In a quest to elevate reactor efficiency, the coupling of gas–liquid–solid electrochemical reduction and liquid–solid thermocatalytic oxidation warrants meticulous structural and operational optimization. In this context, the work of Wei et al. emerges as pioneering,<sup>73</sup> establishing an integrated framework that adroitly amalgamates electrochemically generated  $\text{H}_2\text{O}_2$  with the ensuing oxidation of various organic substrates, thereby yielding high-value products. As elucidated in Figure 5a, humidified hydrogen and ambient air are directed toward the hydrogen oxidation reaction and  $2e^-$  ORR catalyst-coated gas diffusion layer electrodes. These electrodes are judiciously partitioned via an ion-exchange membrane. Within this assembly, an intricate internal catalytic bed, composed of anion-exchange resin and TS-1, orchestrates the seamless union of protons and hydroperoxyl ions from the cathode and anode, engendering the in situ formation of  $\text{H}_2\text{O}_2$ . This subsequently prompts the activation of TS-1, paving the way for selective interactions with organic substrates. In the domain of phenol hydroxylation, under optimized conditions, the methodology demonstrated an impressive 94.68% selectivity toward the desired end products—catechol and hydroquinone—coupled with an overall FE of 30.25% at a conversion rate of 10.61%.

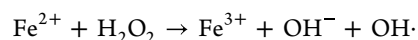
Extending this paradigm, researchers have explored the coupled oxidation of benzyl alcohol, furfuryl alcohol, styrene, and cyclohexanone. The results illuminated that high selectivity was observed for the target products, thereby underscoring the versatility and industrial viability of this approach. Most strikingly, when applied to the paired synthesis

of furoic acid from furfural oxidation, the dual-membrane reactor achieved an FE of an astonishing 132.79%, outperforming the theoretical 100% benchmark for nonpaired oxidation processes.

In the aforementioned design, the spatial separation of the  $2e^-$  ORR and the organic oxidation reactions poses intrinsic challenges, particularly concerning mass-transfer resistance and escalated reactor complexity. To circumvent these limitations, the same research group further innovatively devised a bifunctional catalyst, termed TS-1@Co–N–C.<sup>74</sup> This unique catalyst amalgamates two distinct functionalities within a single material architecture: a cobalt–nitrogen–carbon (Co–N–C) shell that serves as a proficient catalyst for the electrochemical reduction of oxygen to  $\text{H}_2\text{O}_2$  and a titanium silicalite-1 (TS-1) core that is tailored for the catalytic oxidation of organic substrates. Figure 5b illustrates this design paradigm. Remarkably, this catalyst achieved a high selectivity of >95% for  $\text{H}_2\text{O}_2$  production; when integrated with phenol oxidation, an impressive bisphenol selectivity of 99.45% was attained. Moreover, they explored the versatility of this catalyst by coupling the cathode reactions with the anodic oxidation of furfural to synthesize furoic acid. This device yielded an overall FE of 141.09%, notably exceeding that of traditional designs. The bifunctional catalyst not only simplifies the reactor design but also markedly enhances mass transfer and reaction efficiencies, thereby offering a robust solution to long-standing challenges in coupled electrochemical systems.

#### 4.2. Fenton-like Oxidation

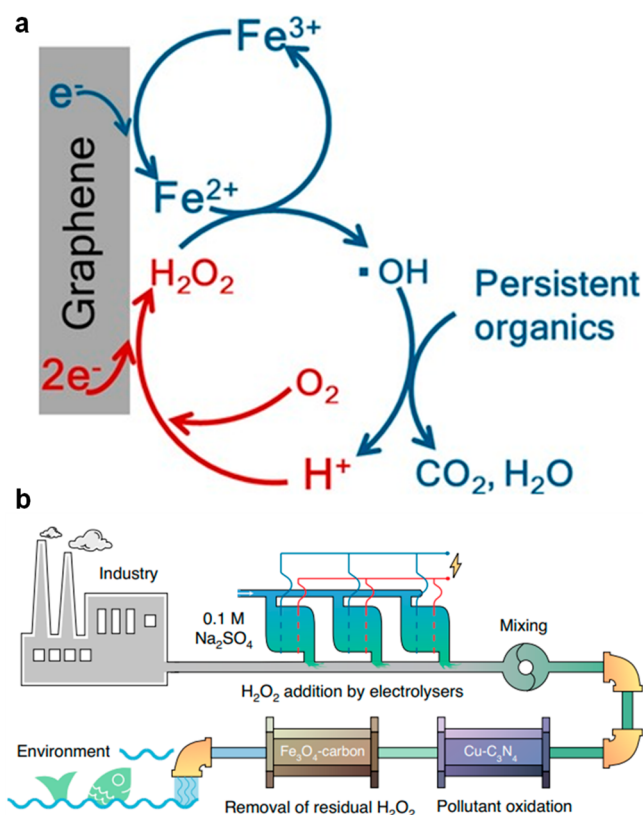
The Fenton process serves as a seminal method for the treatment of wastewater, relying on advanced oxidation techniques that utilize  $\text{H}_2\text{O}_2$  and ferrous ions ( $\text{Fe}^{2+}$ ) as reactants. The underlying mechanism involves the generation of hydroxyl radicals ( $\text{OH}\bullet$ ), potent oxidizing agents, through the catalytic reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  ions according to the following reaction:



These hydroxyl radicals nonselectively oxidize organic pollutants, effectively breaking down complex, recalcitrant compounds into simpler, biodegradable molecules or even completely mineralizing them to carbon dioxide and water. The cutting-edge electro-Fenton process predominantly operates under acidic conditions, given that the optimal pH for Fenton reactions falls within an acidic range.

In the conventional methodologies of Fenton and Fenton-analogous reactions, the incorporation of  $\text{H}_2\text{O}_2$  is often executed via bulk feeding, a technique that has been empirically shown to yield suboptimal  $\text{H}_2\text{O}_2$  utilization efficiencies. This inefficient utilization becomes even more salient when viewed in the context of the logistical and economic complexities associated with the process. Specifically, the need for handling, transporting, and storing  $\text{H}_2\text{O}_2$  at high concentrations not only escalates operational risks but also imposes a significant financial burden, thereby challenging the economic viability and safety of these conventional approaches. The application of in situ production of  $\text{H}_2\text{O}_2$  represents a promising alternative to Fenton/Fenton-like processes with the bulk feeding of  $\text{H}_2\text{O}_2$ <sup>75</sup> (Figure 6a).

The Fenton reaction and its coupled variants have been widely explored for the efficient degradation of an array of pollutants including organic dyes, pesticides, and pharmaceutical compounds. Extensive literature reviews have elucidated



**Figure 6.** (a) Electrochemical production of hydroxyl radicals was used for the degradation of organics. Reproduced with permission from ref 75. Copyright 2016, John Wiley and Sons. (b) Wastewater treatment system, including the  $H_2O_2$  electrolyzer, the Fenton filter, and the  $Fe_3O_4$ -carbon filter. Reproduced with permission from ref 78. Copyright 2021, Springer Nature.

the efficacy of these ideas;<sup>76,77</sup> however, practical implementation remains limited. Homogeneous systems such as Fenton's reagent have long been employed, albeit with inherent limitations. These include the necessity for acidic conditions, the problematic recyclability of  $Fe^{2+}$ , and the undesirable iron-based sludge. Heterogeneous Fenton reactions offer a more elegant alternative, especially when one considers the advent of single-atom catalysts stabilized within judiciously chosen host matrices. An innovative work was reported by Yi Cui et al. (Figure 6b),<sup>78</sup> who proposed a system involving a series of interconnected processes: electrolyzers generate  $H_2O_2$  from a  $0.1\text{ M Na}_2\text{SO}_4$  solution using electricity and ambient air. This synthesized  $H_2O_2$  solution is then mixed thoroughly with wastewater. The mixed solution passes through the Fenton filter, where organic contaminants undergo oxidation. Subsequently, the solution was flowed through an  $Fe_3O_4$ -carbon filter to quench any residual  $H_2O_2$  before the treated effluent is safely discharged into the environment. The Fenton filter and hydrogen peroxide electrolyzer are central to this system, collectively addressing both the activation and production of  $H_2O_2$  and thus offering a comprehensive and efficient solution for wastewater treatment.

To date, the majority of studies have been preoccupied with the development of innovative catalysts optimized for Fenton reactions, sometimes at the expense of considering reactor design or scale-up feasibility. Notably, advances in reactor technologies are emerging, as evidenced by recent reports on solid-state electrolyte reactors that represent a significant step

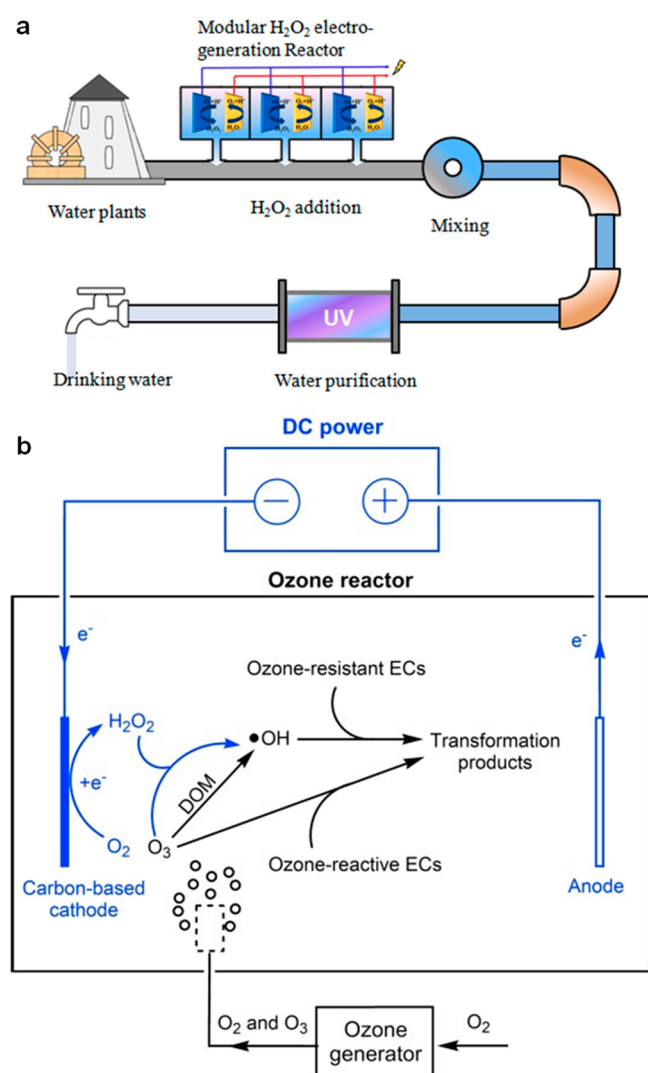
toward operational viability. However, these technological advancements have not fully bridged the gap between experimental promise and real-world application, highlighting the need for continued research focused on scalable and economically viable solutions.

### 4.3. Other Coupling Strategies

The conversion of vegetable oils and their associated unsaturated fatty acids into epoxides holds significant promise due to the myriad applications of these resultant epoxides, including their use as ecofriendly lubricants, plasticizers, polymer stabilizers, and components in paints and coatings. Liang et al. presented an innovative electrochemical approach for epoxide synthesis via paired electrosynthesis.<sup>79</sup> The study explores the electrochemical epoxidation of unsaturated fatty acids, facilitated by formate ( $HCOOH$ ), generated in situ through the reduction of  $H_2O_2$  and formic acid in the catholyte as well as by hypochlorous acid ( $HOCl$ ), also produced in situ in the anolyte through the oxidation of chloride ions. Under optimal conditions, a relative epoxy yield approaching 40% was achieved.

The direct partial oxidation of methane into liquid oxygenates offers a promising avenue for methane valorization. In research conducted by Hwang et al., an electro-assisted technique was deployed for this partial oxidation under ambient conditions.<sup>80</sup> The process utilized metal-free acid-treated carbon as a catalyst to generate  $H_2O_2$  through the  $2e^-$  ORR. Liquid oxygenates such as  $CH_3OH$ ,  $CH_3OOH$ , and  $HCOOH$  were generated with a total production rate of  $18.9\ \mu\text{mol/h}$  under ambient temperature and pressure. Notably, the unstable  $CH_3OOH$  could be further converted into  $CH_3OH$  at the electrochemical potential used for the electro-assisted methane partial oxidation, thereby enhancing the product selectivity to 80.7% toward the more stable liquid fuel,  $HCOOH$ . The team also showcased the versatility of this electro-assisted method by applying it to activate the C–H bond in  $C_2H_6$ .

Electrochemically generated  $H_2O_2$  also offers promising avenues when integrated with physical processes for pragmatic applications, such as improving drinking water quality. One significant issue in drinking water is the presence of taste and odor (T&O) compounds, as they strongly influence public perception regarding water safety and quality. To address this, Huang et al. designed an electrochemical reactor for the on-site generation of pure  $H_2O_2$ ,<sup>81</sup> which was subsequently employed in tandem with ultraviolet (UV) irradiation to degrade trace T&O compounds (Figure 7a). Within a solid-state electrolyte reactor, protons and oxygen were sourced from the anodic chamber through OER and air pumping, respectively. The  $H_2O_2$  production rate and concentration were finely tuned by manipulating the applied current efficiency and the flow rate of deionized water in the cathodic chamber. Remarkably, this system exhibited long-term stability in  $H_2O_2$  production rates, maintaining outputs of  $4.3$  and  $13.3\ \text{mg/cm}^2\ \text{h}^{-1}$  under applied current densities of  $10$  and  $30\ \text{mA/cm}^2$  over  $100\ \text{h}$ . Furthermore, the degradation rates for T&O compounds exceeded 95% in a static setup and were also effective in a dynamic flow system when combined with a UV reactor. These findings underscore the potential of electrochemically produced  $H_2O_2$  as a robust component in advanced oxidation processes, laying the groundwork for small-scale drinking water purification systems.



**Figure 7.** (a) Schematic illustration of the drinking water treatment system comprising an electrochemical hydrogen peroxide generation reactor, a water mixing chamber, and an ultraviolet reactor. Reproduced with permission from ref 81. Copyright 2022, Elsevier. (b) Schematic illustration of the electro-peroxone process. Reproduced with permission from ref 82. Copyright 2018, Elsevier.

The electro-peroxone method has gained recognition as a novel and efficient form of electrochemical advanced oxidation for water treatment<sup>82,83</sup> (Figure 7b). This process operates by combining in situ generated  $\text{H}_2\text{O}_2$  with ozonation. The electrogenerated  $\text{H}_2\text{O}_2$  enhances the conversion of ozone into hydroxyl radicals, thereby significantly improving treatment outcomes such as total organic carbon mineralization and the removal of ozone-resistant pollutants compared to traditional advanced oxidation processes such as UV/ $\text{H}_2\text{O}_2$ . Additionally, the electro-peroxone method offers superior kinetics in contaminant breakdown, thereby serving as a more reliable, time-saving, energy-efficient, and efficacious approach for reducing pollutants.<sup>82</sup> However, it is worth noting that the majority of studies on electro-peroxone have been confined to laboratory settings, employing either batch or semibatch reactors. Comprehensive pilot-scale studies under realistic water and wastewater treatment conditions are still needed to conclusively evaluate its long-term efficiency and economic viability.<sup>84</sup>

## 5. OUTLOOK

The electrochemical synthesis of  $\text{H}_2\text{O}_2$  and its integration into downstream reactions for various industrial and environmental applications represent an emerging interdisciplinary frontier in electrochemistry and chemical engineering. The present Perspective outlines methodologies for some of the key reported reactions that have been integrated (Table 1). While a majority of the studies covered herein showcase electrochemical reactions at the laboratory level, the transition to industrial-scale production remains an unresolved issue. Ensuring the long-term stability of these reactions under conditions of high current density, selectivity, and energy efficiency will be crucial for scaling up the innovations in electrochemical catalysis and reaction engineering discussed here. A multifaceted approach involving various research strategies will be essential to meet these performance criteria.

Several challenges must be addressed for the wide-scale adoption of electrochemical  $\text{H}_2\text{O}_2$  production. Electrode material stability, selectivity toward  $\text{H}_2\text{O}_2$  over other intermediates, and the overall energy efficiency of the process are ongoing research areas. An additional layer of complexity arises when one considers the integration of this  $\text{H}_2\text{O}_2$  into downstream reactions as reaction kinetics, mass transfer issues, and competing side reactions can impact overall process

**Table 1. Summary of the Typical Examples of Coupling Electrolytic  $\text{H}_2\text{O}_2$  Production with Downstream Reactions**

application	$\text{H}_2\text{O}_2$ Faradaic efficiency	electrolyte	performance	stability (h)
ethylene conversion to ethylene glycol <sup>70</sup>	~90% @ 50 mA/cm <sup>2</sup>	0.1 M $\text{H}_2\text{SO}_4$	electron-to-ethylene-glycol efficiency of 60–70% at 100–500 mA/cm <sup>2</sup>	100
methane oxidation to formic acid <sup>80</sup>	>90% at 0–0.3 V vs RHE	0.05 M $\text{H}_2\text{SO}_4$	80.7% $\text{HCOOH}$ selectivity	6
organic wastewater treatment <sup>78</sup>		0.1 M $\text{Na}_2\text{SO}_4$	100% dye removal efficiency	100
ethylene oxidation to ethylene glycol	83%–86% @ 10–50 mA/cm <sup>2</sup> <sup>372</sup>	Solid electrolyte	99.7% ethylene glycol selectivity	200
	86% @ 4 mA/cm <sup>2</sup> <sup>269</sup>	0.1 M KOH	99% ethylene glycol selectivity	56
phenol oxidation to bisphenol <sup>74</sup>	95%	0.1 M $\text{H}_2\text{SO}_4$	99.45% bisphenol selectivity, 30.05% FE	
propylene to propylene glycol <sup>71</sup>	30%–50%	0.1 M $\text{H}_2\text{SO}_4$	79.7% selectivity	
phenol oxidation to catechol and hydroquinone <sup>73</sup>	>80%	0.1 M $\text{K}_2\text{SO}_4$	94.68% selectivity toward catechol and hydroquinone, 30.25% FE	18
benzyl alcohol oxidation <sup>85</sup>		2	conversion = 94%, selectivity = 99%	
epoxidation of fatty acids <sup>79</sup>		0.1 M HCl (pH = 6.5)	castor oil yield of 40%	

efficiency. Recent advances in membrane technology and reactor design, including the use of solid-state electrolyte reactors and bifunctional catalysts, have shown promise in overcoming some of these limitations. Moreover, advances in in situ monitoring techniques are beginning to provide real-time insights into reaction dynamics, thus offering opportunities for process optimization.

The electrosynthesis of  $\text{H}_2\text{O}_2$  is sensitive to various factors, such as pH and electrolyte composition, each of which directly impacts its downstream applications. In the realm of pH, there exists a trade-off; an increase in pH decreases the number of electrons accepted by each  $\text{O}_2$  molecule, favoring the formation of  $\text{H}_2\text{O}_2$  at the expense of its stability. However, basic solutions increase the risk of electrode poisoning, and a high  $\text{OH}^-$  concentration can also accelerate the decomposition of  $\text{H}_2\text{O}_2$ .<sup>86</sup> Therefore, a balanced pH level is crucial for optimizing both the synthesis and the reactivity of  $\text{H}_2\text{O}_2$  for practical applications. Electrolyte composition presents another set of complexities. For instance, modifying platinum electrodes with solutions containing halides such as  $\text{Br}^-$ ,  $\text{I}^-$ , or  $\text{Cl}^-$  can significantly alter  $\text{H}_2\text{O}_2$  selectivity.<sup>87</sup> The addition of  $\text{N}(\text{alkyl})_4^+$  halide salts has also been demonstrated to effectively modulate localized  $\text{H}_2\text{O}_2$  production by affecting the electrical double layer and local pH.<sup>88</sup> However, these electrolytes may also introduce contaminants, limiting the utility of  $\text{H}_2\text{O}_2$  in industries requiring high purity such as pharmaceuticals. Additionally, the compatibility of the electrolyte with the electrocatalyst used can influence the long-term economic viability of the  $\text{H}_2\text{O}_2$  production process. Given these considerations, both pH and electrolyte composition must be judiciously managed to customize  $\text{H}_2\text{O}_2$  characteristics for specific industrial or research needs.

In applications where  $\text{H}_2\text{O}_2$  functions as a critical reactant for concentration-sensitive chemical transformations, the meticulous regulation of  $\text{H}_2\text{O}_2$  concentrations becomes paramount in dictating the reaction kinetics, selectivity, and overall yield. For example, in organic oxidation reactions or advanced oxidation processes, either an excess or a lack of  $\text{H}_2\text{O}_2$  can precipitate undesirable side reactions or incomplete conversions. One promising avenue for precise concentration control lies in the in situ utilization of  $\text{H}_2\text{O}_2$  at the electrochemical interface, achievable via the strategic development of electrocatalysts, the nuanced manipulation of electrocatalyst-electrolyte interfaces, and device architecture optimization. Optimized designs not only accelerate reaction kinetics but also enhance reaction specificity, thereby mitigating energetically costly side reactions. Additionally, minimizing ohmic losses through the deployment of highly conductive electrolytes—be they liquid or solid—holds considerable merit. Advanced electrolyte materials, including ionic liquids and solid-state matrices, can be engineered to exhibit elevated ionic conductivities, thus attenuating resistive losses within the electrolyte framework. Finally, modulation of the transport dynamics is indispensable for averting reaction inefficiencies, a goal achievable through the deliberate geometric arrangement of electrodes and fluidic channels to guarantee homogeneous ion dispersal and leverage concentration gradients.

In conclusion, the electrochemical production of  $\text{H}_2\text{O}_2$  presents an exciting avenue not only for compound synthesis but also for its immediate utilization in a variety of chemical processes. Integrated systems that can “close the loop”, turning reactants into products and even waste into resources, could

pave the way for more sustainable and economically viable chemical processes in the future.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have approved the final version of the manuscript. CRediT: **Qiu Jiang** writing-original draft, writing-review & editing; **Yuan Ji** visualization; **Tingting Zheng** writing-review & editing; **Xu Li** writing-review & editing; **Chuan Xia** conceptualization, visualization, writing-original draft, writing-review & editing.

### Notes

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