Future Perspectives for the Advancement of Electrochemical Hydrogen Peroxide Production

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Abstract

H_2O_2 is an important chemical with multiple uses across domestic and industrial settings. A global need for wider adoption of green synthetic methods, there has been a growing interest in the electrochemical synthesis of H_2O_2 from oxygen reduction or water oxidation. State of the art catalyst and reactor developments are beginning to advance to a stage where electrochemical synthesis is discussed as a viable alternative to current industrial methods. In this review, we highlight some of the most promising candidates for H_2O_2 electrosynthesis technologies, and what further advancements are needed before the electrochemical route could challenge the ubiquitous anthraquinone process.

Introduction

Anthraquinone autooxidation: H_2O_2 is a strong, green oxidant with a broad scope of applications ranging from domestic use to industrial bleaching, chemical synthesis and wastewater treatment.[1] Present production is ~5.5 million tonnes per year, with an expected market value of ~$6 billion over the next few years.[2] The majority of H_2O_2 is produced via the anthraquinone autooxidation (AO) process. Here, a 2-alkylanthraquinone (AQ) is hydrogenated in organic solvent over a Pd catalyst, then oxidised by O_2 to release H_2O_2 and recover the AQ (Fig 1A).[3] Despite large yields and ~99% selectivity, crucial drawbacks exist, including waste from organic contamination and over-hydrogenation of AQ,[4] high labour costs and risks from storing and transporting concentrated H_2O_2.[5] Operating costs extend beyond the initial synthesis, since H_2O_2 must be extracted so the AQ can be returned to the reactor and reused.[6]

The AO process is often presented as energy intensive, particularly when considering the full synthesis, extraction, concentration and purification.[7] Recent reports estimate the energy consumption at 17.6 kWh $kg_{H_2O_2}^{-1}$ corresponding to ~8.6 GWyr in 2015.[8] It is worth noting that this energy consumption is not prohibitive; logically it cannot be given the widespread adoption of the AO process. Estimates from 2009 rate operating costs at \$700 $t^{-1}{}_{H_2O_2}$, including materials, maintenance and capital costs, with sales ranging from \$700 to \$1200 t^{-1}.[6]

Direct synthesis: Direct synthesis produces H_2O_2 from H_2 and O_2 under high pressure with metallic catalysts like Pd and Pt. O_2/H_2 mixtures are highly flammable within a concentration range of 5:1-20:1 (O_2:H_2), which unfortunately is the ratio where H_2O_2 selectivity is optimal.[9] Reactors must dilute the gas stream with an inert carrier, lowering the overall yield.[10] The commonly employed noble metal catalysts, aside from their cost and scarcity, catalyse a series of undesirable and thermodynamically favourable competing reactions (Fig 1B), making selectivity a key challenge.[11]

A shared limitation for both processes is the necessity for gaseous H_2. As well as safety, it is important to consider the financial, energy and carbon costs. H_2 sourced from steam reformation of methane produces 13 tons of CO_2 per million SCF of H_2, which increasing to 21.9 tons when considering combustion for energy inputs, steam production and thermal inefficiencies.[12] Carbon costs could be lowered using water electrolysis as the H_2 source, although present electrolysis technologies cannot compete at the industrial scale.[13]

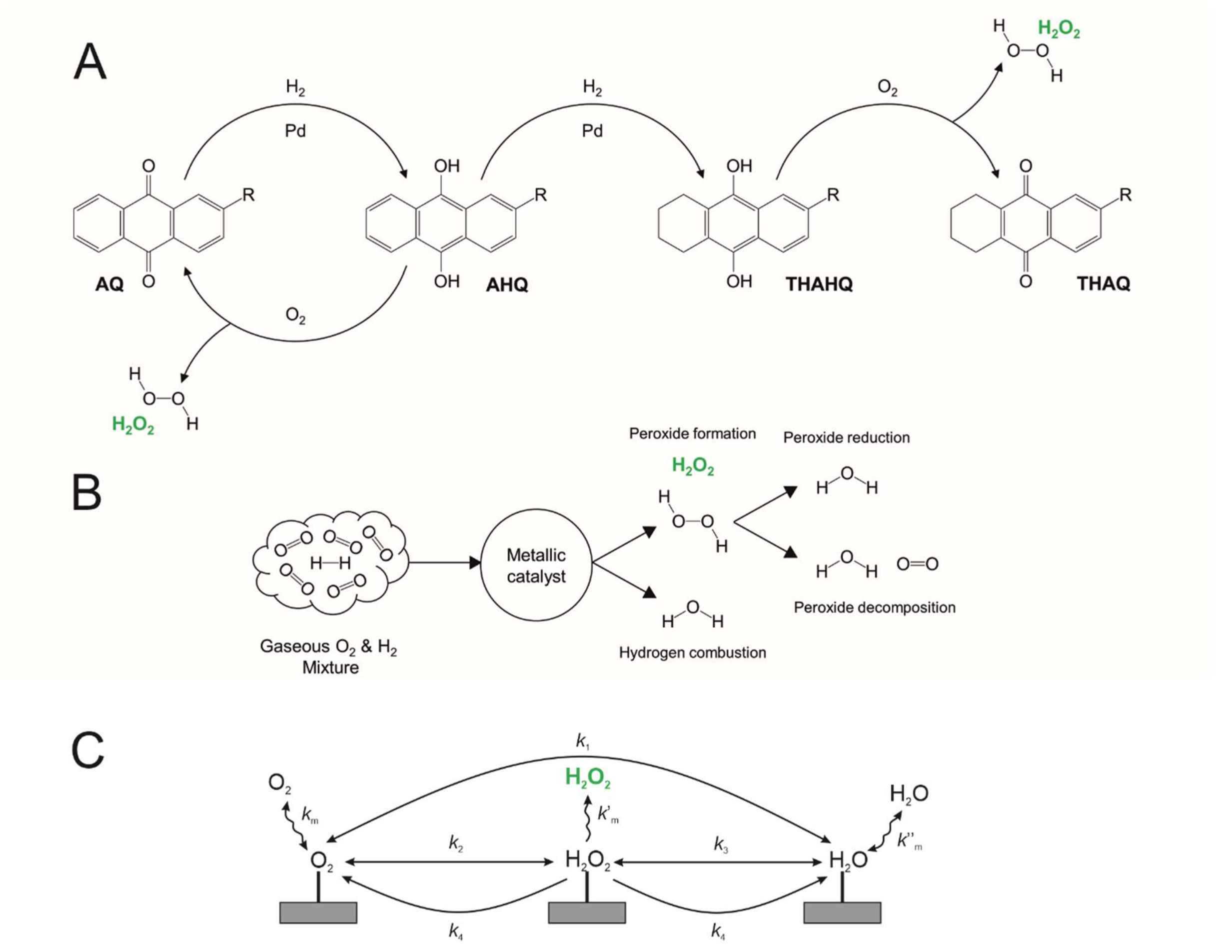

Figure 1A. A simplified schematic mechanism for the AO process, including a non-reversible process that consumes the AQ. **B.** The direct synthesis of H_2O_2 from H_2 and O_2, including potential competing reactions. Mechanisms taken from references [2, 14]. **C.** Electrochemical synthesis of H_2O_2 via the two-electron reduction of O_2 (k_2) and two-electron oxidation of H_2O (k_3). Poorly performing catalysts drive the four-electron redox process (k_1) or may catalyse the decomposition of H_2O_2 into O_2 and H_2O (k_4). Parts A and B adapted with permission from reference [2]. Copyright (2021) American Chemical Society.

Electrochemistry: Electrochemical synthesis of H_2O_2 is unusual because H_2O_2 sits as an intermediate in the middle of the O_2/H_2O redox system (Figure 1C, Eq. 1).

$$O_2 + 4H^+ + 4e^- \rightleftharpoons H_2O_2 \qquad E^0 = 1.23\ \mathrm{V}\ vs.\ \mathrm{RHE} \tag{1}$$

This results in two mechanistic routes: the two-electron water oxidation reaction (WOR, Eq. 2) or the two-electron oxygen reduction reaction (ORR, Eq. 3).

$$2H_2O \rightleftharpoons H_2O_2 + 2H^+ + 2e^- \qquad E^0 = 1.76\ \mathrm{V}\ vs.\ \mathrm{RHE} \tag{2}$$

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad E^0 = 0.68\ \mathrm{V}\ vs.\ \mathrm{RHE} \tag{3}$$

The electrochemical production of H_2O_2 is inherently attractive thanks to the cheap and abundant starting materials (O_2 or H_2O) and the desirable safety and cost from operations at low temperature and pressure. Additionally, poor selectivity during the WOR and ORR routes results in the production of only O_2 and H_2O respectively, practically negating separation costs.

Relatively speaking, the ORR is further ahead on the development pathway, with carbonaceous materials achieving high rates and faradaic efficiencies (*FE*), where *FE* is the percentage of charge passed used for H_2O_2 production.[15] Remaining challenges focus on material costs, cell potential and durability.[16] Developments in the WOR suffer from a compromise between selectivity and production rate; many materials show excellent selectivity provided the current density is low and vice versa.[17] Although water is cheap as a starting material, the relatively low market price of H_2O_2 and the large overpotential make the WOR prohibitively costly with presently available technologies.[18]

Reported energy costs associated with the electrochemical route vary depending on the catalyst and the operating current density, with values ranging between 3.1 and 60 kWh $\mathrm{kg}_{H_2O_2}^{-1}$.[19] The viability of the electrochemical route must consider energy costs in the context of turnover rate, material costs and component longevity.

Latest Developments for H_2O_2 Electrosynthesis

ORR materials: Modifying four-electron ORR materials through catalyst poisoning[20] or particle dispersion favours H_2O_2,[21] although lessening catalytic sites inherently decreases the turnover rates. Noble metals also increase costs, although the high dispersion somewhat offsets this. Similarly, single atom catalysts decrease the likelihood of O-O bond splitting, leading to higher H_2O_2 selectivity vs. the equivalent bulk material.[22, 23] Alternatively, weakly binding materials release H_2O_2 after the initial two-electron reduction before further reduction to water occurs. This is dominated by carbonaceous materials, with hydrophobic modifications[24, 25], functionalisation,[26, 27] doping[28, 29] and diamond-like carbons[30] improving selectivity, activity and stability (Fig 2A,B). Although carbon is cheap and abundant, leading materials often involve nanostructured carbons such as graphene oxide[31, 32] or nanotubes[21, 28], increasing complexity and cost.

WOR materials: Commonly employed carbon materials are unstable at anodic potentials, so high current densities are only feasible on diamond-like carbons. Some of these show high production rates,[33] but poor selectivity makes them energetically wasteful. Optimising factors such as doping level and electrolyte composition can address this to give a sizeable increase in faradaic efficiency and production rate.[34] A popular alternative are metal oxides, which give high efficiencies,[35, 36] but are usually reported at low current densities (Fig 2C,D). It is worth noting that it is difficult to compare the activity of many metal oxides to carbon catalysts due to the different surface areas: carbon catalysts tend to be porous whereas metal oxides are often thin films with much lower active areas.[37]

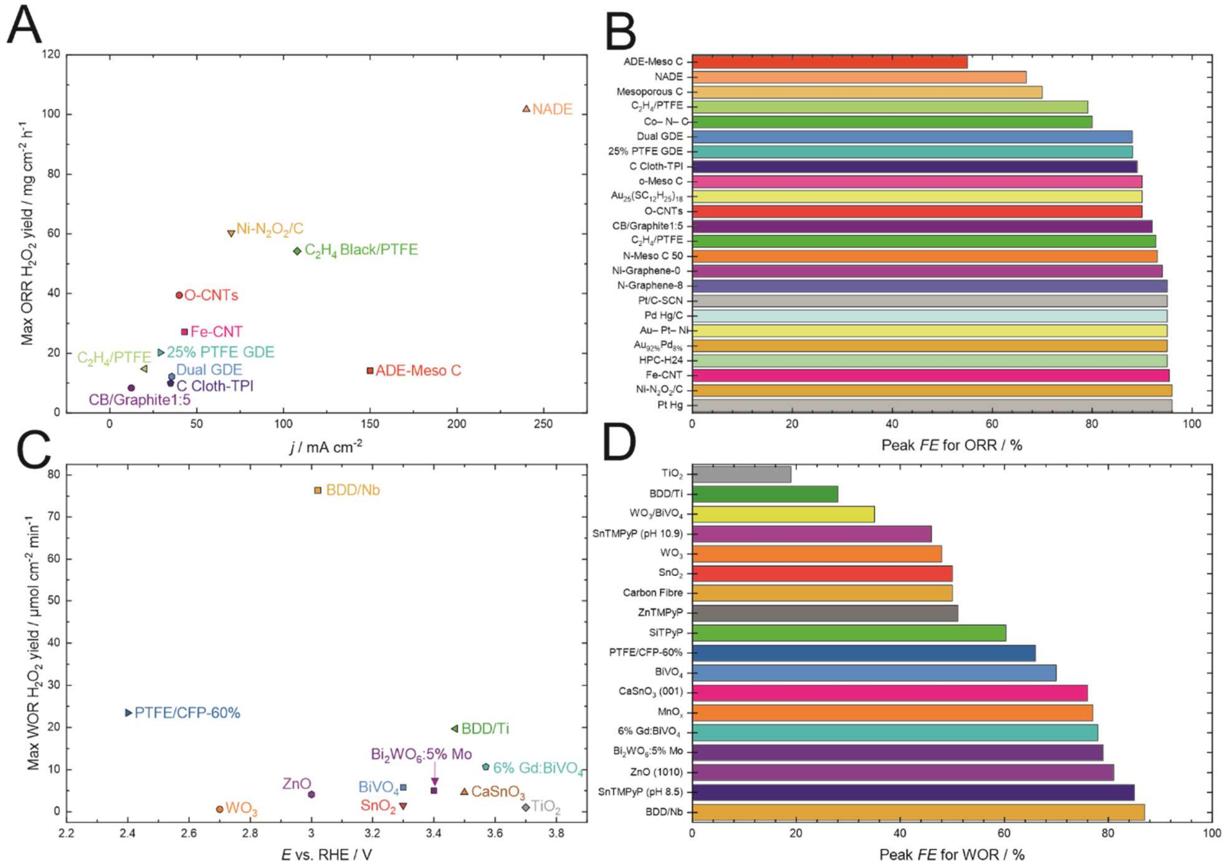

Figure 2. Key parameters for some of the leading recent catalyst materials for the electrocatalytic production of H_2O_2 via the ORR (**A** and **B**) and WOR (**C** and **D**), showing their maximum production rates (**A** and **C**) and faradaic efficiencies (**B** and **D**). Acronyms used in material descriptions are taken from the original works. Data taken from references [15, 25, 34, 38-41]

Figure 2 highlights that the scope of possible materials is incredibly broad and outside the scope of this discussion. A number of excellent reviews are available for more detailed insights specifically into materials development.[1, 2, 15, 38, 42]

Reactor design: H-cells separate anode and cathode via an ion-conductive membrane (Fig 3A).[43] This is useful for catalyst screening, but fixed volumes and liquid-phase diffusion limit the maximum turnover rate and yield. Flow cells are more promising for high throughput H_2O_2 production (Fig 3B,C), which can be used in a separated configuration, as seen in H-cells, or an unseparated configuration with a single flow chamber between anode and cathode. Rapid flow rates improve selectivity by carrying H_2O_2 away from the catalyst before further reduction. The ORR is further accelerated with gas diffusion electrodes (GDEs), which give rapid, gas-phase O_2 transport to the catalyst.[44] Designs tend to strive for a high single-pass efficiency, as circulating systems have been shown to preferentially consume H_2O_2 in place of the desired ORR or WOR.[27]

Zero-gap cells based on membrane electrode assemblies (MEAs) lower the cell potential by reducing the inter-electrode distance. The cathode and anode are compressed either side of an ion-conductive membrane, often within proton exchange membrane (PEM) electrolysers (Fig 3D).[45] Where a liquid electrolyte is desirable, a narrow channel between the electrode and membrane can introduce electrolyte while minimising the distance.[46] MEAs offer a straightforward route to upscaling through stacked electrolysers.

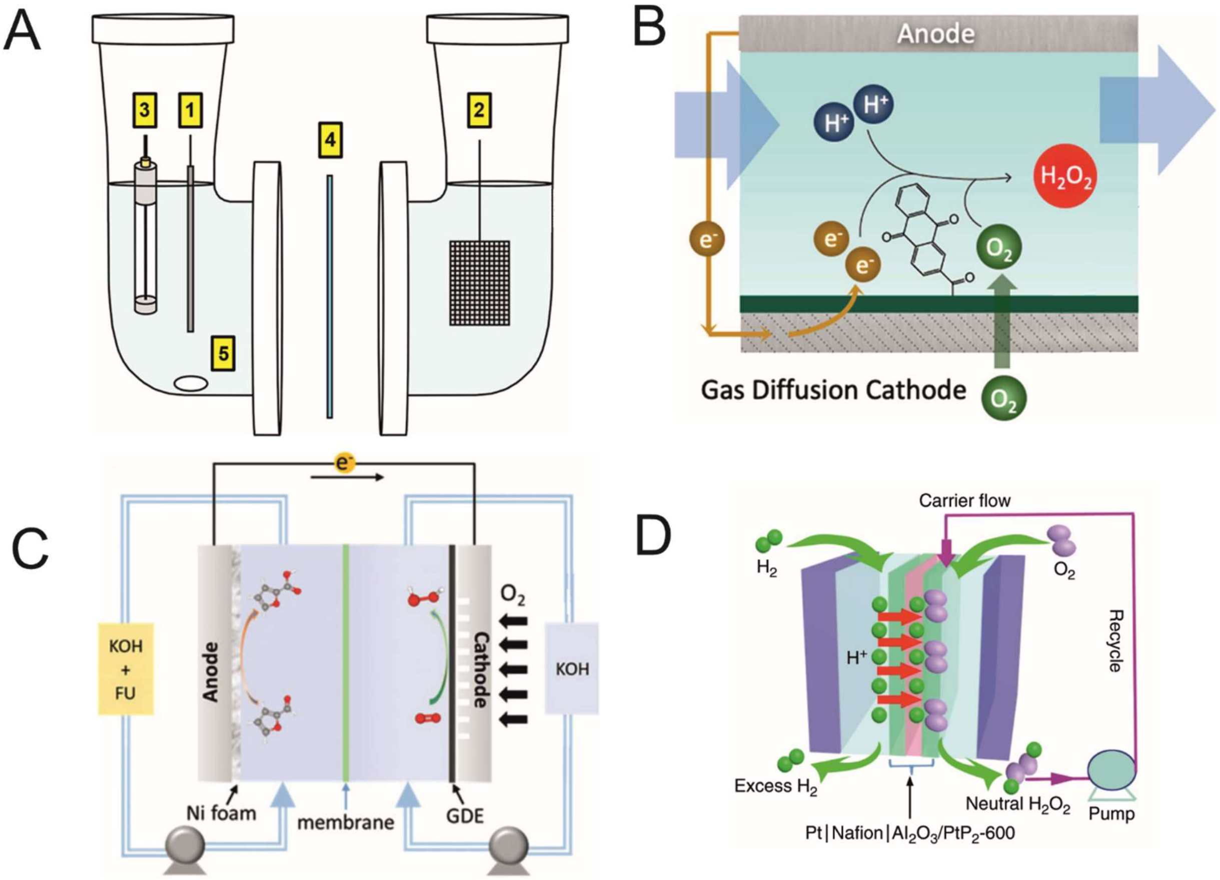

Figure 3 Schematic designs for some commonly employed electrochemical cells for H_2O_2 electrochemical synthesis. **A.** Low volume H-cell for rapid catalyst analysis where the working (1) and reference (3) electrodes separated from the counter (2) by an ion exchange membrane (4). Stirring is possible via a magnetic stirrer bar (5). Figure adapted with permission from reference [33], Copyright (2020) American Chemical Society. **B.** Undivided flow cell with an organic-modified GDE. Figure adapted with permission from reference [46], Copyright (2020) American Chemical Society. **C.** Divided flow cell with a cathode electrode separated from an anode by an ion exchange membrane. The GDE cathode separates the liquid and gas phases. Figure adapted with permission from reference [40], Copyright (2020) John Wiley and Sons. **D.** PEM fuel cell with O_2 and H_2 fed to the cathode and anode respectively, separated by a cation exchange membrane. The pump recycles the catholyte to increase the H_2O_2 concentration. Figure adapted with permission from reference [45], Copyright (2020) Hui Li et al.

Considering the anode: Half-cell studies negate how enhanced anodic materials can benefit cathodic H_2O_2 production, and vice versa, by lowering the cell voltage thereby reducing energy costs. A PEM cell from Xia et al. gave similar H_2O_2 production rates at 0.61 V with H_2 oxidation at the anode as at 2.13 V with water oxidation.[26] The decision on H_2 *vs.* H_2O oxidation must weigh the lower potential against the costs of H_2 sequestration, storage and usage. Similarly at the cathode, air is a cheaper feed gas than O_2, but decreased O_2 availability increases the cell potential.[46] A desirable cell would simultaneously produce H_2O_2 at the cathode and anode. However, this design must address the high cell potential associated with two-electron WOR. Xia et al. achieved this with carbon catalysts in a membrane-free flow cell, giving 153% *FE* for H_2O_2 (~60% WOR, ~90% ORR) at 120 mA cm^{-2}, 1.7 V.[24]

Future Perspectives

Future materials development: With ORR catalysts showing promising selectivity at high current density, the next developments will work towards consistent H_2O_2 production over thousands of hours. Next generation cathode material may increase hydrophobicity to hinder GDE flooding or make modifications to hinder catalyst poisoning or passivation. For the WOR, a materials approach is still needed to provide high selectivity at high current density. It is worth mentioning that the by-products of the electrosynthesis are only water and oxygen, so low selectivity does not increase separation costs. The desire to increase selectivity is due to faster H_2O_2 production coming with a steeper energy cost; Zhang et al. reported energy costs of 4.6 kWh $\mathrm{kg_{H_2O_2}}^{-1}$ at 20 mA cm^{-2} compared to 19.4 kWh $\mathrm{kg_{H_2O_2}}^{-1}$ at 240 mA cm^{-2} due to a ~20% decrease in current efficiency.[25]

Table 1: Summary of some of the leading examples of electrolytic H_2O_2 production from different types of electrochemical cells. Balancing protons and electrons are omitted from the anodic and cathodic reactions for clarity. ^{a} indicates the value was either not explicitly given or was not provided in these units, so was calculated from available parameters. ^{b} indicates the value was read off a graph in the original work.

Design	**Anodic reaction**	**Cathodic rection**	**Anode**	**Cathode**	**Electrolyte**	**$\|j\|$ / mA cm^{-2}**	**E_{cell} / V**	***FE* / %**	**v_{H2O2} / mmol cm^{-2} h^{-1}**	**Ref.**
Solid electrolyte MEA	$H_2 \rightarrow 2H^+$	$O_2 \rightarrow H_2O_2$	Pt/C	Oxidised carbon black	DI water (pH ~ 7)	200	0.61	~90	3.4	[26]
	$H_2O \rightarrow O_2$	$O_2 \rightarrow H_2O_2$				200	2.13	~90	3.3	
PEM electrolyser	$H_2O \rightarrow O_2$	$O_2 \rightarrow H_2O_2$	Pt/C	AQ/C	DI water (pH ~ 7)	245	~2.7	~12.5	0.58	[27]
PEM electrolyser	$H_2 \rightarrow 2H^+$	$O_2 \rightarrow H_2O_2$	Pt/C	PtP_2 / Al_2O_3	DI water (pH ~ 7)	150	0.4	78.8	2.26	[45]
Membrane free batch electrolyser	$H_2O \rightarrow O_2$	$O_2 \rightarrow H_2O_2$	$NiFeO_x$	Mesoporous carbon	0.1 M KOH (pH ~ 13.5)	46	1.6	~90	0.07^a	[47]
Membrane free flow cell	$H_2O \rightarrow H_2O_2$	$O_2 \rightarrow H_2O_2$	PTFE/ carbon fibre paper	Oxidised carbon nanotubes	1 M Na_2CO_3 (pH ~ 12)	120	1.7	153 (WOR + ORR)	3.4^a	[24]
Flow through cell	$H_2O \rightarrow O_2$	$O_2 \rightarrow H_2O_2$	IrO_2/ Ta_2O_5 / Ti	Carbon foam	50 mM Na_2SO_4 (pH ~ 7)	5.9	-	4.9	0.005	[48]

GDE narrow gap flow cell	H_2O → O_2	O_2 → H_2O_2	IrO_2/Ti	AQ/ polyaniline/ carbon nanotubes	0.1 M phosphate buffer (pH ~ 8.8)	25	~1.7	96	0.45[a]	[46]
GDE narrow gap flow cell	Furfural → 2-furoic acid	O_2 → H_2O_2	Ni foam	N-doped graphene	0.1 M KOH (pH ~ 13.5)	108	1.8	95	2.3[a]	[40]
GDE micro-flow cell	H_2O → O_2	O_2 → H_2O_2	IrO_2/ RuO_2 / Ti	Co-N/C	0.1 M KOH (pH ~ 13.5)	50	~2[b]	~45[b]	0.433[a]	[49]

Developing the anode: The lowest cell potentials use H_2 oxidation. Continued advancements in WOR catalysts must lower the overpotential and likely move away from costly Ru and Ir materials to compete with H_2. Materials that increase selectivity or lower the WOR overpotential, along with zero-gap reactors, will make simultaneous H_2O_2 production at the anode and cathode more feasible. An alternative concept took advantage of the photocatalytic properties of mixed metal oxides to give H_2O_2 at both electrodes with no external potential, although this has only been demonstrated at low photocurrents.[36]

Alternatively, a different anodic process could generate a second product in a paired electrochemical process, as in chlor-alkali technology that produces Cl_2 and NaOH from brine.[50] Multiple oxidation candidates are available, including biomass,[40, 51] various amines,[52] or the production of high value oxidants e.g. HClO and $S_2O_8^{2-}$.[53] Anodic targets could be chosen based on the end use of cathodically produced H_2O_2, such as urea oxidation for wastewater treatment in two compartments.[54] Catalysts for the anode will need to be tailored to the specific oxidation reaction, and costs will have to consider sourcing and storing raw materials and market value of products.

Long-term costing: Strategic decisions must weigh up-front costs with overall operating costs. Cheaper earth-abundant materials tend to give lower efficiencies or greater cell voltages compared to costlier noble metals.[1, 42] More expensive materials may lower long-term costs, particularly if they can combine activity with stability and operate without replacement for thousands of hours. Similarly, H_2 and O_2 may prove cheaper than H_2O and air if the cell potential is low enough. Although current technologies still have H_2O and air as the cheaper options,[26] future electrolysis technologies for H_2 production may change this.

Pumping costs: Energy requirements to circulate gas and electrolyte around flow cells can exceed the energy required for the electrocatalytic reaction.[55] Both costs significantly increase when components are up-scaled; Salmerón et al. reported 54 kWh $kg_{H_2O_2}^{-1}$ at a 100 cm^2 carbon cathode at 65 mA cm^{-2}, compared to 1077 kWh $kg_{H_2O_2}^{-1}$ aeration costs.[56] Natural air diffusion cathodes have been proposed as a pump-free alternative,[25] though these rely on cathode exposure to ambient air, so an innovative approach to up-scaling is needed when stack manufacture does not seem feasible.

Stability: As with many areas of electrosynthesis, investigations into the long term (>1,000 hours) stability of catalyst, electrode or reactor designs are few and far between. One of the most promising ORR cathodes, hydrophobic carbon GDEs, show promising selectivity and reaction rates, but are prone to failure due to flooding of the porous GDE structure.[43] Li et al. showed ~85% efficiency over ~1,000 hours before decreasing to ~70% over the following days.[19] Based on the need to replace the GDE every 46 days, the authors estimated H_2O_2 production costs at ~\$880 $t^{-1}_{H_2O_2}$, moderately more expensive than the AO process.[6] Clearly movement away from carbon materials to more expensive catalysts would have to come with a sizeable increase in performance in order to challenge this level of financial viability.

Investigations into stability must consider practically relevant conditions, especially current density (>100 mA cm^{-2}) and electrode geometry, in order to assess failure modes such as electrowetting, catalyst dissolution, delamination or passivation and membrane failure. Since many failure modes are indicated by increased cell potential and decreased *FE*, component deconstruction is often necessary to identify the cause. Post-mortem analysis through SEM imaging, contact angle and resistance measurements can aid analysis, though many failure modes can be seen by eye, particularly through colour changes to ion conductive membranes or catalyst surfaces. An interesting line of research is into the recovery of failed components, particularly electrowetted GDEs, which can be restored through by washing with DI water.[57] Costs associated with reactor downtime would need to be considered here, and options to refresh components without reactor disassembly would be preferable.

Decentralised H_2O_2: Decentralised production of working concentrations of H_2O_2 with a small, on-site reactor negates the need to produce, store or transport concentrated H_2O_2, and materials and operation costs.[5, 19] This concept is behind the recently spun-out hpnow project, producing up to 5 kg H_2O_2 a day.[58] The same is true at the anode; biomass oxidation hyphenated with cathodic H_2O_2 production is more feasible if the reactor is built on-site at a bio-refinery, particularly if the H_2O_2 is used for further oxidations downstream.[59] Many applications of H_2O_2 do not require concentrated solutions, so cheaper systems that produce working concentrations of H_2O_2 may be viable on this scale, despite not being able to compete with the AO process in a centralised system.

Sequential flow reactors: Delocalised production allows construction of hybrid systems, where H_2O_2 at the correct concentration is directly supplied to a second process. The simplest example uses in situ H_2O_2 production alongside a species to be oxidised in the same solution. This is a common design for wastewater treatment, particularly with catalytic iron to increase oxidation via the Fenton reaction.[60, 61] More complex designs could feed H_2O_2 into a secondary reactor, where oxidation to value-added products would take place.[62] This would be suitable for systems where the oxidation target would interfere with H_2O_2 electrosynthesis.

Alternatively, microfluidic reactors could use laminar flow profiles to separate H_2O_2 produced at one electrode from a second reaction at the other.[43] Oxidation by H_2O_2 could occur either at the interface between flow profiles or in a downstream mixer chamber. Introducing reaction components in immiscible solvents is a facile means to remove separation costs. This has been used in an alternative H_2O_2 synthesis route mediated by an organic-phase precursor and could also be applied to the oxidation of key organics that are not water soluble.[8]

Tailored concentrations: The viability of in situ reactors relies on the H_2O_2 concentration matching the needs of the reaction. Propylene oxidation requires a continuous supply of 8-12 wt.% H_2O_2. This is well within the scope electrochemical synthesis, with one reactor producing 18.7 wt.% H_2O_2 at 55% efficiency.[63] One report predicted a 24% reduction in total costs if in situ H_2O_2 were implemented, although this value was based on the direct rather than electrochemical route.[64] Cyclohexanone ammoximation requires 30 wt.% H_2O_2,[65] and so would require the reactor to increase up to 90% efficiency. This is a distinct advantage of the electrochemical route in that outflow concentration can be decreased by lowering the overpotential or increasing flow rate to give a fair degree of control. The opposite alterations could increase the concentrations, so long as this is within the scope of the catalyst, else higher concentrations are feasible through engineering solutions such as recirculating flow systems.

Alternative oxidants: With many H_2O_2 applications focusing on oxidations, it is worth mentioning that the oxidising $HO^•$ radical is a product of both the ORR and WOR.[1] When discussing H_2O_2, $HO^•$ is only shown as a selectivity loss. However, if the goal is in situ oxidation, materials that produce large amounts of $HO^•$ alongside H_2O_2 may be more energy efficient than more H_2O_2-selective alternatives.

Conclusions

The readiness of H_2O_2 electrosynthesis appears to depend on the end application. Current technologies for delocalised H_2O_2 production via the ORR are approaching viability. Cathodic developments focus on stability, as treated carbon cathodes look to exceed the 1000-hour threshold. Energy efficiency is tied into related technologies depending on applications. A key example is the choice of water or H_2 oxidation at the anode; H_2 gives a low cell potential but comes with additional financial, carbon and energy costs for its sequestration, storage, and transport. Electrosynthesis of H_2O_2 is therefore made more viable by advancements in water electrolysis technologies. Similarly, coupling cathodic H_2O_2 production to value-added oxidations will make reactors more cost effective. This could be done with the WOR to give H_2O_2 at both electrodes, although significant improvements to the WOR selectivity at large current densities are needed to compensate for the increased cell potential. The niche of the electrochemical route is the delocalised H_2O_2 production with direct feed into a secondary reactor, reducing costs and hazards associated with concentrated H_2O_2 synthesis, transport, storage, and application.

Acknowledgements

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