

Electrogenerated Hydrogen Peroxide - From History to New Opportunities

by Derek Pletcher

Hydrogen peroxide is probably a unique chemical, ideally suited to the present age where environmental considerations are always to the fore.

Why unique? Firstly, it is capable of very diverse chemistry. Hydrogen peroxide may act as either an oxidizing agent or a reducing agent. As an oxidizing agent, its application ranges from highly selective oxidation chemistries applicable to the manufacture of many organic compounds, through the bleaching of pulp, to the total oxidation of large organic compounds to carbon dioxide. Its reactivity as an oxidizing agent is determined largely by the ratio of the concentrations of H_2O_2 to substrate and the reaction conditions, particularly the choice of catalyst and factors such as UV irradiation. Secondly, it is a strong oxidizing agent that may be formed by cathodic reduction under mild and varied conditions, opening up the possibility of producing the same product at both anode and cathode. Thirdly, the feedstock for electrogenerated hydrogen peroxide may be air (an unusually cheap and available feedstock!) while its reactions lead only to oxygen and/or water.

Why environmentally friendly? Again, because its reactions leave no residuals in the reaction stream and it may be manufactured with only air and electricity as feedstocks. In addition, when used in dilute solutions such as those produced in electrolysis cells, its reactions are non-hazardous and carried out in very moderate conditions. In this respect, the chemistry of electrogenerated hydrogen peroxide should be distinguished from that employing very concentrated hydrogen peroxide and peracids which can indeed be hazardous.

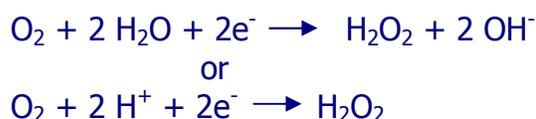
The markets for hydrogen peroxide are well established and include organic oxidations, bleaching in the pulp and paper industry, applications in fabrication technology, and water and effluent treatment [1-4]. Indeed, it has been predicted that demand will grow by 10% per annum for the next few years [5]. The opportunities for electrogenerated hydrogen peroxide arise now because of (i) interest in on-site manufacture of hydrogen peroxide (ii) the recent availability of technology, namely gas diffusion electrodes and three dimensional electrodes, which allow the reduction of oxygen to hydrogen peroxide at a practical current density (iii) the recognition that the yield of hydrogen peroxide may be high in acidic and neutral solutions as well

as strongly alkaline media (iv) the identification of new catalysts which expand the chemistry of hydrogen peroxide. All of these factors will be illustrated below.

History and Background

Electrolysis has an extensive history in the manufacture of hydrogen peroxide. For many years, all hydrogen peroxide was manufactured by electrolysis using a route where persulfate is formed at the anode and then hydrolysed [1]. Although there have been recent proposals to reinstate this technology [6], it has generally been considered to have an excessive energy requirement for large-scale production. Hence, at the present time almost all hydrogen peroxide is manufactured by a route involving the reduction of oxygen by hydrogen with anthraquinone as the catalyst [1]. On the other hand, the anthraquinone route requires the availability of hydrogen feedstock and the large-scale use of non-aqueous solvents for catalyst recycle. Hence, it is unsuited to small-scale manufacture or to on-site production of hydrogen peroxide.

Small scale, on-site processes are, however, of increasing interest because of the cost and hazards associated with the transport and handling of concentrated hydrogen peroxide. Particular attention has been focused on processes for the pulp and paper industry which require ~2 % HO₂⁻ in 1.5 M NaOH). Interest has concentrated on the manufacture of hydrogen peroxide by the cathodic reduction of oxygen:



These reactions occur in high yield at certain cathodes including mercury, gold and carbon. Practical utility of these reactions demands the choice of a carbon cathode. In addition, commercial exploitation has required the development of technology to overcome the problems resulting from the low solubility of oxygen in aqueous solutions; at a plate electrode, the mass transport limited current density is $\ll 1 \text{ mA cm}^{-2}$ (equivalent to $\ll 20 \mu \text{ moles cm}^{-2} \text{ hour}^{-1}$). As a result, processes have been developed based on both various types of three dimensional electrodes such as beds of carbon particles or reticulated vitreous carbon and gas diffusion cathodes fabricated from carbon powders without metal catalysts [7-13]. Both types of electrode permit an increase by a factor of 30 - 1000 in the rate of hydrogen peroxide production. Dow [11] and Huron Chemicals [6] have described processes

which employ cathodes fabricated from a bed of carbon chips, 0.5 - 2 mm in size and coated with a high surface area carbon powder/PTFE composite through which an oxygen saturated NaOH solution is allowed to trickle so as to give a film of catholyte over the surface of the cathode within an oxygen atmosphere. Such cells give a current efficiency 60-70 % at 15 mA cm⁻². E-Tek [12,13] have pioneered the use of gas diffusion electrodes and demonstrated that HO₂⁻ in NaOH solutions can be produced at a current efficiency of > 90 % at current densities > 100 mA cm⁻². McIntyre [14] has also reported the development of cathode catalysts for an O₂/H₂ fuel cell so that the reaction of O₂ and H₂ leads to hydrogen peroxide with an output of electrical energy from the cell.

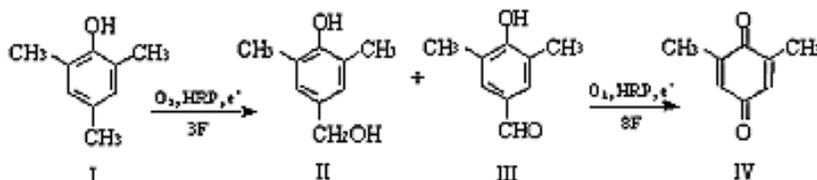


Figure 1: Reaction of 2,4,6 trimethylphenol with electrogenerated H₂O₂ Catalyzed by HRP

While these technologies appear to be moving towards commercial success, published data on pilot and production scale developments are, however, limited to the manufacture of hydrogen peroxide in concentrated alkaline solutions. Such media are not of great interest in synthesis or effluent treatment. On the other hand, they demonstrate the way forward and recent papers have confirmed that both three dimensional electrodes made from reticulated vitreous carbon [15,16] and gas diffusion electrodes [16-20] may also be used to reduce oxygen to hydrogen peroxide in both neutral and acid solutions at rates which are appropriate to the needs of synthesis and effluent treatment. Some examples of the use of electrogenerated hydrogen peroxide discussed below already use such electrodes although most authors have chosen to demonstrate the concept of using electrogenerated hydrogen peroxide using plate electrodes and accepting the very low current density. It is, however, the introduction of three-dimensional electrodes and gas diffusion cathodes that will transform these concepts into useful laboratory procedures and candidates for industrial exploitation.

Applications in Electrosynthesis

Much of the early work emphasized the conversion of aromatic hydrocarbons to phenols and/or aldehydes using an acidic catholyte containing Fe(III) and O₂ [21-24]. The cathode was used to produce both constituents of Fenton's reagent, Fe(II) and H₂O₂, and typical reactions were the oxidation of benzene to phenol and of toluene to benzaldehyde. The reactions gave good yields (60 - 100 %) provided over-oxidation was avoided by stopping the reactions at very low conversions or continuously extracting the products from the catholyte (often using a suspension of the hydrocarbon substrate in the aqueous catholyte). Some studies employed mercury cathodes but the more practical procedures used graphite plate cathodes; in consequence, an acceptable current efficiency could only be achieved at very low current densities. It would be timely to re-investigate these oxidations with three-dimensional and/or gas diffusion cathodes. Otsuka [25,26] has described preliminary but unconvincing attempts to carry out such oxidations at the cathode of an O₂/H₂ fuel cell with an energy output.

More interesting, however, are studies which use more selective catalysts than Fe(II) since Fenton's reagent is known to lead to the formation of hydroxyl radicals. The most selective catalysts for the reactions of hydrogen peroxide are the peroxidase enzymes; these enzymes have a diverse chemistry, which often leads selectively to unusual products as well as the introduction of chirality [27,28]. Examples of reported reactions include the conversion of sulfides to sulfoxides, of anilines to hydroxylamines or nitrosobenzenes, olefins to olefin oxides, alkyl benzenes to alcohols or aldehydes and indoles to oxindoles. The Southampton Group [16] have demonstrated the use of horseradish peroxidase as a catalyst for the reaction of electrogenerated hydrogen peroxide and 2,4,6-trimethylphenol in a phosphate buffer. Electrolysis is shown to be a convenient and controlled way to carry out such enzyme catalyzed reactions. In addition, it appears to introduce the possibility of new reaction pathways and products from these biosynthetic reactions. The major products from the electrolysis can be, as in the classical chemical procedure, formed via the pathway shown in Figure 1, with either II, yield 68% after 3F of charge or IV, yield > 70%, after 8F of charge as the major products. These yields are significantly higher than those reported for classical chemical procedures for this reaction. In a cell with a very high cathode area to catholyte volume (e.g. a cell where the reticulated vitreous carbon cathode fills the catholyte compartment), a further product was identified as shown in Figure 2.

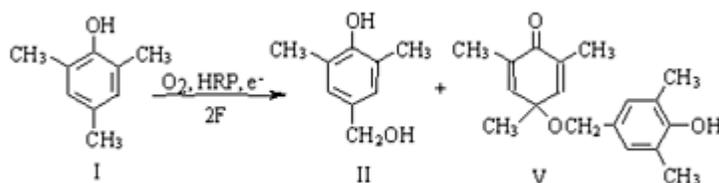


Figure 2: HRP-catalyzed reaction of electrogenerated H_2O_2 with trimethylphenol in a cell with high area to volume ratio.

The yield of the interesting coupled product V could be > 50 % and its formation has not been reported for chemical reactions. This implies that its formation results from the cathodic reduction of an intermediate in the enzyme reaction cycle. The use of a reticulated vitreous carbon electrode also allows the reactions to be carried out at a significant current density.

Another recently reported example of a selective catalyst for electrogenerated hydrogen peroxide is tungstate [29,30]. Nonaka et al have shown that when hydrogen peroxide is formed at a graphite plate electrode in a phosphate buffer, pH 5, at 333 K, it reacts with tungstate



and describe the in situ use of the pertungstate for the oxidation of sulfoxides to sulfones and of di-butylamine to N-butylidene-butylamine N-oxide as in Figure 3.

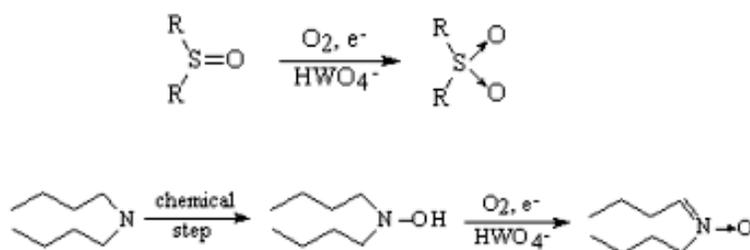


Figure 3: Tungstate - catalyzed reactions of electrogenerated H_2O_2 .

Both reactions give good selectivity and an acceptable current efficiency and neither occurs in the absence of tungstate in solution. In addition, the literature provides many pointers to other suitable catalysts for reactions of electrogenerated hydrogen peroxide. These would include MoO_4^- , polyoxometalates containing transition metals such as Ru, Mn and Cr, SeO_2 , RuO_2 , CH_3ReO_3 and Sharpless Os(VI) reagents.

As noted in the introduction, the formation of an oxidizing agent, hydrogen peroxide, at the cathode introduces the possibility of carrying out oxidations at both electrodes and, indeed, carrying out the same reaction at both electrodes, thereby (a) doubling the rate of chemical conversion (b) halving the number of cells required for the wanted annual tonnage as well as (c) halving the process energy consumption. A group in Taiwan has demonstrated this approach. [31-33]. The earliest example was the oxidation of toluene to benzaldehyde. A divided cell was used and the anode was used to oxidize Mn(II) to Mn(III) in sulfuric acid while the graphite cathode was used to reduce oxygen to hydrogen peroxide. The oxidation of toluene was carried out *in situ* in the catholyte in the presence of V(IV) as a catalyst while the Mn(III) was reacted with toluene external to the cell after the electrolysis. The overall current efficiency is reported as 171% (84% at the anode and 87% at the cathode) and the selectivity is also excellent.

It was also possible to employ a similar approach to the oxidation of anthracene to anthraquinone and this could even be carried out in an undivided cell using a concentrated sulfuric acid electrolyte. Here, the mediator at the anode was the V(IV)/V(V) couple and the V(IV) also acted as the catalyst for the reaction of hydrogen peroxide formed at the graphite plate cathode. The current efficiency for anthraquinone was 151% and the selectivity 98%.

The third system was the oxidation of n-butanol to n-butyric acid in basic solution and again it was possible to use an undivided cell. Here, the anodic oxidation was a direct process at a nickel anode and the hydrogen peroxide formed at the cathode reacted with the alcohol without an added catalyst. The current efficiency was > 170 % and no by-products were identified. Nonaka et al [29] have also used this concept in the oxidation of a N-OH group to a N → O group; the oxidation was carried out in an undivided cell where bromine was formed at the anode and hydrogen peroxide at the cathode (in an electrolyte containing tungstate). The total current efficiency for the formation of N-butyldiene-butylamine N-oxide was > 180 %.

Effluent Treatment

In effluent treatment technology, the objective may be the complete oxidation of all organics in the stream to carbon dioxide, the removal of particular toxic compounds or just decolorization of the stream. Fenton's reagent is not a specific oxidant. It reacts with many molecules and in situations where the ratio of [H₂O₂]:[organic] is high, complete oxidation of

organics to CO₂ would be expected. Hence the electrogeneration of hydrogen peroxide in the presence of Fe(II) should be an effective method of effluent treatment. In commercial application it must be envisaged that the source of oxygen is air and the Fe catalyst as well as any proton requirement results from the anode chemistry in the cell (i.e. the anode has a component of iron capable of dissolution). Several papers have demonstrated that electrogenerated H₂O₂ may be used successfully for effluent treatment. The emphasis in such studies is on the treatment of solutions containing < 1000 ppm COD (chemical oxygen demand). The reason is associated with energy consumption. The energy consumption for an effluent treatment process (usually quoted as kWh m⁻³) is proportional to the concentration of organic in solution and the number of electrons involved in the conversion of the organics to CO₂; commonly, the oxidation of an organic molecule may involve 20 - 150e⁻ and for higher concentrations, the energy consumption becomes prohibitive. Many chemical effluent streams, however, contain relatively low COD.

Two of the earliest papers [34,35], using hydrogen peroxide generated at a graphite plate, examined the destruction of phenol and formaldehyde as a function of pH. At pH 1 - 4, it was shown that in the presence of Fe(II), phenol (COD 260 - 2600 ppm) could be effectively oxidized and largely converted to CO₂; final COD was < 40 ppm. The authors also followed the intermediates formed during the oxidation and were able to identify at least six compounds; it is clear that the oxidation pathway is complex but also that the H₂O₂/Fe(II) combination is able to decompose a wide range of organic structures. Formaldehyde was also readily oxidized. At pH 13, the oxidation of formaldehyde is efficient but the product of oxidation was formic acid. In acidic solutions where it was possible to add Fe(II), complete oxidation to CO₂ took place. These papers confirmed that hydrogen peroxide could be formed at a graphite cathode in conditions appropriate for effluent treatment and also that the chemistry could be favorable for complete oxidation. The current densities were, however, typically 0.4 mA cm⁻² and clearly this is not sufficient for practical effluent treatment technology.

To overcome this difficulty, Pletcher et al [15,16] used a reticulated vitreous carbon cathode. The first substrate to be investigated was formaldehyde and it was confirmed that the three dimensional electrode greatly accelerated the rate of formaldehyde removal; with oxygen saturated solutions, current densities could reach > 20 mA cm⁻² (higher values could also be reached using a thicker cathode). Formaldehyde (5 - 200 ppm) oxidation could be achieved in alkaline, neutral and acidic media but Fe(II) as a catalyst was essential to achieve complete oxidation to CO₂; in its absence, the reaction stopped at formic acid. More recently [16], the study has been extended to

sulfate media, pH 2, containing phenol, cresol, catechol, quinone, hydroquinone, aniline, oxalic acid or the azo-dye, amaranth. With each compound, COD could be reduced from 50 - 500 ppm to below 10 ppm, generally with a current efficiency > 50% and using a current density of ~ 20 mA cm⁻². Much of the carbon in the solutions could be identified as carbon dioxide after the electrolyses. If the objective were to decolorize a dye effluent stream, this could be achieved rapidly and with only a low energy consumption (the removal of color requires only a relatively small change in chemical structure).

Brillas and co-workers [17-20] were the first to introduce gas diffusion electrodes into these effluent treatment processes. They have described the oxidation of aniline and 4-chloroaniline in aqueous solutions with a pH 10.1 - 12.7 and they were able to reduce the COD of such solutions from 100 ppm to < 5 ppm with a current density as high as 200 mA cm⁻². They also consider sulfate solutions with pH ~ 3 where complete oxidation of the aniline was again observed provided Fe(II) was present. It was also found that UV irradiation accelerated oxidation. In the acid solutions, the current densities for the reduction of oxygen to hydrogen peroxide were lower, ~ 30 mA cm⁻². The final paper of the series confirmed that the Fe(II) could, indeed, be formed in situ in an undivided cell by using an iron anode and the Fe(II) was sufficiently active to allow the rapid degradation of both 100 ppm and 1000 ppm aniline solutions.

Harrington and Pletcher [16] have also used an oxygen diffusion cathode at pH 2 - 3. They investigated the voltammetry of the solutions and concluded that the limitation on the oxygen reduction current densities to 50 - 100 mA cm⁻² (cf. 200 - 500 mA cm⁻² in strongly acidic or alkaline solutions) resulted from IR drop within the pores of the electrode structure. Even so these current densities are of a practical level and it was shown that the gas diffusion electrode could be used to remove phenol, aniline, acetic acid, formaldehyde and three azo-dyes (amaranth, fat brown RR and methyl orange) provided Fe(II) were present in the solution; the COD of solutions containing such organics may be reduced by > 90 % with a current efficiency > 50 %, leading to acceptable energy consumption.

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Professor Derek Pletcher is a Professor of Electrochemistry at the University of Southampton. He also acts as a consultant for industry through the Electrochemical Consultancy and gives short courses on electrochemical technology throughout the world. In his spare time, Derek likes to play golf.