

Review Article

Indirect Oxidations Using Electrogenerated Hydrogen Peroxide

Derek Pletcher

The Department of Chemistry, The University, Southampton SO17 1BJ, UK

Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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Hydrogen peroxide is a unique redox reagent in that it may be produced from air and after use in synthesis, manufacturing technology or effluent treatment, it leaves no residual chemicals. New concepts in cell technology for *in situ* generation of hydrogen peroxide, as well as recent developments in its chemistry, have made more attractive the use of hydrogen peroxide as a mediator in indirect electrolysis. This review discusses some of the factors contributing to these developments.

For many years, there has been considerable interest in mediated or indirect electrolytic oxidation for both the synthesis of organic compounds, the treatment of effluents and the destruction of organic wastes. This has led to an extensive literature^{1,2} and several industrial processes employing, for example, Cr(VI)^{3,4} Mn(III)⁵ and Ce(IV)^{6–9} for indirect electrosynthesis, Ag(II) for the destruction of wastes^{10,11} and hypohalites for water and effluent treatment.¹²

Hydrogen peroxide as a redox mediator in indirect electrolysis has several unique characteristics. Firstly, it is a strong oxidising agent produced at the *cathode* under rather mild conditions by the reduction of oxygen. The source of the oxygen may be air or oxygen enriched air, i.e. the reactant is cheap. The on site electrogeneration of the hydrogen peroxide and its use as a dilute solution in or close to the electrolysis cell greatly reduce the safety hazards associated with the chemistry of hydrogen peroxide. In general, its reactions lead to water and hence its reactions also leave no stoichiometric residuals in the reaction environment or effluent stream. Finally, by control of the reaction conditions, it is possible to carry out rather selective oxidation, e.g. the conversion of sulfoxides into sulfones, or the complete oxidation of rather complex molecules, e.g. azodyes to carbon dioxide. The main factors influencing the type of oxidation observed are the ratio of the concentrations, $[H_2O_2]/[substrate]$, and the choice of catalyst for the hydrogen peroxide oxidation. Hydrogen peroxide is already recognised as an environmentally friendly chemical for organic

oxidations, bleaching paper pulp, within fabrication technology as well as for water and effluent treatment.^{13–15} Indeed, it has been predicted that demand will grow by 10% per annum for the next few years.¹⁶ Hydrogen peroxide certainly reacts with a wide variety of organic compounds although the chemistry possible in dilute solutions such as those present close to the cathode surface should be differentiated from that employing very concentrated solutions, e.g. peracid chemistry.

The electrogeneration of hydrogen peroxide

Electrolysis has an extensive history in the chemistry 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. This technology became recognised as too energy inefficient for large-scale production and it was displaced by the reduction of oxygen by hydrogen catalysed by anthraquinone.¹⁷ On the other hand, the anthraquinone route requires the availability of hydrogen and the large scale use of non-aqueous solvents. Hence, it is unsuited to small-scale or on-site production of hydrogen peroxide. Such processes are, however, of increasing interest because of the hazards associated with the transport and handling of concentrated hydrogen peroxide. For this reason, interest has recently focused on the manufacture of hydrogen peroxide by the cathodic reduction of oxygen, eqn. (1),



a reaction which occurs in high yield at certain cathodes including mercury, gold and carbon. At most other cathodes, the overall reaction (2)



predominates although hydrogen peroxide may be an unstable intermediate. Practical utility of reaction (1) for the production of hydrogen peroxide demands the choice of carbon as the cathode. In addition, commercial exploitation has required the development of technology to overcome the problems of low oxygen solubility in aqueous solutions; the maximum possible current density (i.e. rate of production of H_2O_2) at a plate electrode is $\ll 1 \text{ mA cm}^{-2}$ (equivalent to $\ll 20 \mu\text{mol cm}^{-2} \text{ h}^{-1}$) because of mass transport limitations. As a result processes have been developed based on both various types of three-dimensional electrode such as beds of carbon particles or reticulated vitreous carbon¹⁸⁻²³ and gas diffusion cathodes fabricated from carbon powders without metal catalysts.^{19,24} Both types of electrode permit an increase by a factor of 100-1000 in the rate of hydrogen peroxide production. These pilot and production scale developments are, however, limited to the manufacture of hydrogen peroxide in concentrated alkaline solutions, media not of great interest in the context of this review. More recently, however, it has been demonstrated in the laboratory that both three-dimensional electrodes²⁵ and gas diffusion electrodes²⁶ 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 which will transform these concepts into useful laboratory procedures and candidates for industrial exploitation.

The hydroxylation and oxidation of aromatic hydrocarbons

There is a substantial literature²⁷⁻⁴² on the oxidation of aromatic hydrocarbons using 'electrogenerated Fenton's reagent'. An aqueous acidic solution containing both Fe(III) and O_2 is reduced at a cathode to give the active $\text{H}_2\text{O}_2/\text{Fe(II)}$ composition; often it has been found that the Fe(III) concentration should be selected so that there is an equal flux of H_2O_2 and Fe(II) away from the cathode surface. In an early paper, Tomat and Vecchi²⁷ describe the electrolysis at a temperature of 323 K of a suspension of benzene in aqueous sulfuric acid saturated with oxygen and also containing Fe(III) in a cell with a Hg pool cathode. The product was phenol with a yield of 70%. The same group extended this study to other liquid aromatic hydrocarbons. In similar conditions,

however, the oxidation of toluene occurred in the side-chain and gave benzaldehyde as the major product, yield $> 60\%$, with only a small amount of nuclear substitution to a mixture of 2-, 3- and 4-cresols.²⁸ Polymethylated benzenes also largely underwent side-chain oxidation with, for example, 4-xylene being converted into 4-methylbenzaldehyde in an almost quantitative yield.³¹ In cases where there was some nuclear substitution, the ratio of side-chain to nuclear substitution could be enhanced by the addition of chloride ion and a mechanism involving the initial formation of Cl^\cdot radicals was proposed. The beneficial effect of chloride ion was even more marked in attempts to oxidise cyclohexane to cyclohexanone when its addition led to an increase in yield by a factor of five.³² Moreover, comparison of the catalysts Fe(II) , Cu(I) and V(IV) for the oxidation of toluene gave higher yields of benzaldehyde with V(IV) ; indeed, the yield approached quantitative levels.³⁵

These results appear impressive but the reactions are far from practical. Overoxidation could be avoided only by stopping the reactions at very low conversions. Moreover, the current densities were very low, limited by the solubility of oxygen and hence the rates of conversion were also extremely slow. Finally, the use of a mercury cathode is now unlikely to be acceptable. These problems were recognised early. Steckhan and Wellman^{29,30} sought to remove the limitation associated with oxygen solubility by continuous addition of hydrogen peroxide and using the cathode only to control the concentration of Fe(II) . They also introduced continuous extraction and separation of the product. In these ways, they were therefore able to achieve higher conversions of benzene into phenol and extended the chemistry to some other substituted benzenes. Particularly successful was the oxidation of fluorobenzene to fluorophenol with a yield of 80% of two isomers; the ratio of 2- to 4-fluorophenol was 85:15. Osa and coworkers³³ reverted to the reduction of $\text{O}_2 + \text{Fe(III)}$ but used a graphite plate cathode. They studied the oxidation of toluene, ethylbenzene and isopropylbenzene as an emulsion in aqueous sulfuric acid. In contrast with the Italian group, they found that the oxidation of toluene gave a mixture of cresols as the major product and report a yield of 82% with a ratio of 2-, 3-, 4-isomers of 41:53:6. The conditions were, however, significantly different; they used a lower temperature (273 K) and a higher concentration of Fe(III) . The ethylbenzene and isopropylbenzene both underwent side-chain oxidation with acetophenone as the major product. Tzedakis *et al.*³⁶ later confirmed that continuous extraction was also effective when the hydrogen peroxide was electrogenerated *in situ*. Otherwise while the more recent papers confirm these results, they have not improved the performance of these systems significantly.

Otsuka and coworkers^{37,38,41} have tested the interesting concept of carrying out the chemistry in a fuel cell configuration. Hydrogen is fed to a standard fuel cell anode and a mixture of hydrocarbon and oxygen to the back of a porous cathode fabricated from carbon fibres and PTFE

with phosphoric acid absorbed into glass wool as the electrolyte. The cell is shorted and the requirement is to find conditions where oxygen is reduced to hydrogen peroxide at the cathode and hopefully power is also generated. In the earlier papers,^{37,38} the oxygen and hydrocarbon (benzene or toluene) was fed to the back of the cathode as an aqueous solution and, although some phenol and benzaldehyde was formed, this approach cannot remove the limitations associated with oxygen solubility or over-oxidation. The final paper,⁴¹ however, describes experiments where benzene and oxygen are fed to the back of the cathode in the gas phase at 353 K. The rate of formation of phenol is enhanced by additions of palladium and ferric oxide to the cathode composition but the rate of benzene oxidation remains low and accounts for only $\approx 2\%$ of the charge passed through the cell; while power is generated, it probably results from the simple combination of H_2 and O_2 as in a normal O_2/H_2 fuel cell. Bringing to fruition the concept of combining power generation and synthesis in a fuel cell requires substantial improvements in the cathode design to ensure that the current efficiency for hydrogen peroxide is high. There are, however, real opportunities and, for example, Dow⁴³ have developed O_2/H_2 fuel cells which make hydrogen peroxide with reasonable efficiency and are active in the design of improved cathode catalysts.

Overall, it can be seen that many of the problems associated with the oxidation of benzene and toluenes via electrogenerated hydrogen peroxide have now been solved. In particular, over-oxidation can be prevented by efficient continuous extraction. The remaining factor is to achieve efficient and high rate production of hydrogen peroxide and there is now good evidence from other studies that this can be achieved with either three-dimensional electrodes or oxygen gas diffusion electrodes (see later).

The formation of the same product at both anode and cathode

All electrolysis cells have two electrodes and it is inevitable that (in terms of electrons) the same amount of chemistry occurs at both electrodes. In many electrolytic processes, only one electrode reaction is used productively and some 'minimum interference' chemistry, commonly O_2 or H_2 evolution, is selected for the counter electrode. The formation of the same product at both anode and cathode offers the opportunity to (a) double the rate of chemical conversion, (b) halve the number of cells for the wanted annual tonnage, as well as (c) halve the energy consumption per ton of product. The formation of an oxidising agent, hydrogen peroxide, at the cathode offers one approach to forming the same product at both electrodes.

A group in Taiwan have demonstrated the success of this approach.⁴⁴⁻⁴⁷ The earliest example^{44,45} was the oxidation of toluene to benzaldehyde. A divided cell was used and the anode was used to oxidise Mn(II) to Mn(III) in sulfuric acid while the cathode was graphite and 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.⁴⁶ 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 system⁴⁷ 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. A further example from Nonaka *et al.*⁴⁸ is presented in the selection on selective oxidation.

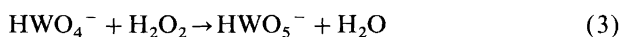
Essentially the same concept has been proposed for effluent treatment. Do and Yeh⁴⁹ showed that the destruction of phenol (as measured by COD, chemical oxygen demand) could be achieved more efficiently in a cell where hypochlorite is made at the anode and hydrogen peroxide at the cathode. Again the decomposition of the phenol occurs at both electrodes.

As described, in all these systems, the current densities were low and even then it was necessary to use a much larger cathode area than anode surface area. These characteristics again result from the limitation of the current density at a plate electrode due to the low solubility of oxygen in aqueous solution. The introduction of three-dimensional cathodes or oxygen diffusion cathodes would again make these systems much more attractive.

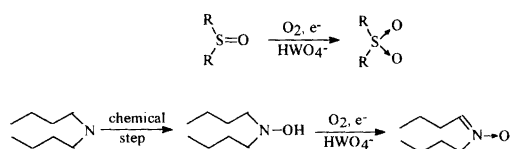
More selective oxidations

While at least at low conversions, it is possible to obtain reasonable yields from oxidations by hydrogen peroxide in the presence of Fe(II), Cu(I) or V(IV), there is little possibility of truly selective oxidation when the mechanism involves reactive intermediates such as OH^\cdot radicals. More selective oxidation can, however, be achieved by using a suitable mediator for the hydrogen peroxide/organic compound reaction.

Nonaka *et al.*^{48,50} have proposed the use of the tungstate/pertungstate couple for this purpose. Hydrogen peroxide was formed at a graphite plate electrode in a phosphate buffer, pH 5, at 333 K and reacts with tungstate in the catholyte, eqn. (3),



and the two papers describe the *in situ* use of the pertungstate for the oxidation of sulfoxides to sulfones



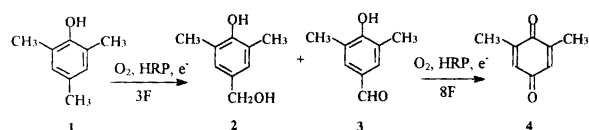
Scheme 1.

and of dibutylamine to *N*-butylidenebutylamine *N*-oxide (Scheme 1).

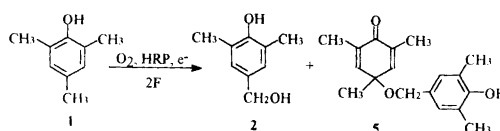
Both reactions give good selectivity at an acceptable current efficiency and neither occurs in the absence of tungstate in solution. The latter reaction⁴⁸ was also carried out in an undivided cell where bromine was formed at the anode. The bromine also carried out the oxidation of the N–OH group so that the total current efficiency for the formation of *N*-butylidenebutylamine *N*-oxide was >180%, a very successful example of a simple electrolysis cell forming the same product at both anode and cathode.

While the tungstate/pertungstate couple is an interesting example of a selective catalyst for oxidations by electrogenerated hydrogen peroxide, the chemical literature provides many pointers to other suitable catalysts which could be tested. These would include molybdate,⁵¹ polyoxometalates containing transition metals such as Ru, Mn and Cr,⁵² selenium dioxide,⁵³ RuO₂,⁵⁴ CH₃ReO₃,⁵⁵ and Sharpless Os(VI) reagents.⁵⁶

Another type of catalyst for reactions between hydrogen peroxide and organic compounds is the peroxidase enzymes. Enzymes offer many opportunities for selective and unusual chemistry usually in a neutral buffer at close to room temperature. A recent paper has described the oxidation of 2,4,6-trimethylphenol by electrogenerated hydrogen peroxide catalysed by horseradish peroxidase⁵⁷ in a phosphate buffer at pH 7. In the chemical reactions of hydrogen peroxide and 2,4,6-trimethylphenol in the presence of horseradish peroxidase, the products are a function of the concentration of H₂O₂ and the way in which it is added. In an electrolysis cell where the hydrogen peroxide is formed by reduction of oxygen at a reticulated vitreous carbon cathode, these are controlled through the current and charge passed. The major products from the electrolysis can be, as in the classical chemical procedure, formed via the pathway in Scheme 2, with either **2**, yield 83% after 3 F of charge or **4**, yield >70%, after 8 F of charge as the major products. These yields are significantly higher than those reported for chemical oxidations and also higher than could be achieved by Bartlett *et al.* using several rates and methods of addition of hydrogen peroxide solutions in homogeneous reactors. In a cell with a very high cathode area to



Scheme 2.



Scheme 3.

catholyte volume a further product was identified, Scheme 3.

The yield of the interesting coupled product **5** 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. Therefore, electrolysis introduces the possibility of new reaction pathways into these biosynthetic reactions as well as providing a convenient and controlled way to carry out the enzyme-catalysed reactions of hydrogen peroxide. Moreover, the choice of enzyme is, of course, not limited to horseradish peroxidase. Peroxidases in the presence of hydrogen peroxide are known to allow the selective and often chiral conversions of, for example, sulfides into sulfoxides, of anilines into hydroxylamines or nitrosobenzenes, olefins into olefin oxides, alkyl benzenes into alcohols or aldehydes and indoles into oxindoles.^{58,59} In all such systems the hydrogen peroxide could be electrogenerated and the use of a reticulated vitreous carbon electrode allows an acceptable rate of conversion.

The use of three-dimensional electrodes and oxygen diffusion electrodes for the generation of hydrogen peroxide in the presence of selective catalysts would certainly seem a fruitful field for further research.

Effluent treatment

It was noted above that Fenton's reagent is not a specific oxidant and selectivity in oxidation usually only results when the reaction is limited to very low conversion. By the same argument, introduction of hydrogen peroxide into effluents containing relatively low amounts of organics so that the ratio of [H₂O₂]:[organic] is high, should be an effective method of effluent treatment. The hydrogen peroxide in the presence of Fe(II) should be capable of converting many molecules into carbon dioxide. A number of papers^{60–71} have reported preliminary studies of the complete oxidation of organic molecules to CO₂. Such processes have been followed by measuring chemical oxygen demand (COD), CO₂ evolution and/or the organic intermediates formed as a function of charge passed. The emphasis in such studies is on the treatment of solutions containing <1000 ppm COD. 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 into CO₂; commonly, the oxidation of an organic molecule may involve 20–150 e⁻ and for higher concentrations, the

energy consumption becomes prohibitive. Many chemical effluent streams, however, contain relatively low COD.

Two of the earliest papers,^{60,61} 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 oxidised and largely converted into CO₂; final COD were <40 ppm.⁶⁰ 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 oxidised.⁶¹ 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 favourable for complete oxidation. The current densities were, however, typically 0.4 mA cm⁻² and clearly with the cells employed this is not sufficient for practical effluent treatment technology.

Hsiao and Nobe⁶² introduced the concept that a reticulated vitreous carbon cathode could be used to enhance the rate of oxidation using chlorobenzene and phenol as the substrates. This approach has been followed up more extensively by Pletcher *et al.*^{64,71} using a reticulated vitreous carbon cathode 50 mm × 50 mm × 12 mm thick. The first substrate to be investigated was formaldehyde⁶⁴ 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,⁷¹ the study has been extended to the sulfate media, pH 2, containing phenol, cresol, catechol, quinone, hydroquinone, aniline, oxalic acid or the azodye, amaranth; with each compound, chemical oxygen demand (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 decolourise a dye effluent stream, this could be achieved rapidly and with only a low energy consumption (the removal of colour requires only a relatively small change in chemical structure).

Brillas and coworkers^{65–69} were the first to introduce gas diffusion electrodes into these effluent treatment processes. In the initial study,⁶⁵ they looked at 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. In a gas diffusion cathode, the oxygen is fed to the back of the electrode and reduction to hydrogen peroxide occurs at a three-phase interface between the gas, solution and carbon electrode structure fabricated from a high surface area carbon powder and PTFE, e.g. by screen printing a slurry onto a fine, inert metal mesh or carbon fibre paper support, followed by firing. The following paper⁶⁶ considers 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. Later papers of the series^{67–69} confirmed that the Fe(II) could 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. Indeed, it was shown⁷⁰ that the destruction of organics possible in an Fe/O₂ cell could be operated as a battery and that significant power could be drawn from such a battery.

Harrington and Pletcher²⁶ 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. Certainly, the conductivity of 50 mM Na₂SO₄ at pH 2 is very significantly lower than of 1 M H₂SO₄ or 1 M NaOH. 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 azodyes (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 consumptions.

It is apparent that electrogenerated hydrogen peroxide has considerable generality as a chemical for effluent treatment and that both three-dimensional electrodes and oxygen diffusion cathodes should be capable of pushing this chemistry into industrial technology.

Conclusions

Electrogenerated hydrogen peroxide has been shown to have a role in both electrosynthesis and effluent and waste water treatment. In effluent treatment, the chemistry coupled to three-dimensional electrodes and/or oxygen diffusion cathodes is already approaching a performance where it is practical technology. In electrosynthesis, the future must lie in finding selective catalysts for the reaction of hydrogen peroxide with the organic and also introducing and optimising the three-dimensional electrodes and/or oxygen diffusion cathodes which will permit the chemical change to take place at a meaningful rate for laboratory and larger scale synthesis.

References

1. Steckhan, E. *Angew. Chem., Int. Ed. Engl.* 25 (1986) 683.
2. Simonet, J. In: Baizer, M. M. and Lund, H., Eds., *Organic Electrochemistry*, 3rd edn., Marcel Dekker, New York 1991, Chap. 29.
3. Käppel, M. *Chem.-Ing.-Techn.* 35 (1963) 366.
4. Clarke, R. In: Genders, J. D. and Pletcher, D., Eds., *Electrosynthesis - from Laboratory, to Pilot, to Production*, The Electroynthesis Co., Lancaster, NY 1990, Chap. 4.
5. Vaudano, P., Plattner, E. and Comminellis, C. *Chimia* 49 (1995) 12.
6. Kreh, R. P., Spotnitz, R. M. and Lundquist, J. T. *J. Org. Chem.* 54 (1989) 1526.
7. Spotnitz, R. M., Kreh, R. P., Lundquist, J. T. and Press, P. J. *J. Appl. Electrochem.* 20 (1990) 209.
8. Kreh, R. P., Spotnitz, R. M. and Lundquist, J. T. In: Genders, J. D. and Pletcher, D., Eds., *Electrosynthesis from Laboratory, to Pilot, to Production*, The Electroynthesis Co., Lancaster, NY 1990, Chap. 10.
9. Théorêt, A. *The Ninth International Forum on Electrolysis in the Chemical Industry*, Clearwater Beach, Florida, November 1995.
10. Steele, D. F. *Atom July* (1989) 10.
11. Steele, D. F. *Platinum Metals Rev.* 34 (1990) 10.
12. Ibl, N. and Vogt, H. In: Bockris, J. O'M., Conway, B. E., Yeager, E. and White, R. E., Eds., *Comprehensive Treatise on Electrochemistry*, Plenum Press, New York 1981, Vol. 2, p. 169.
13. Dodson, M. *TAPPI J.* 73 (1990) 82.
14. Shearman, J. *Chem. Eng.* 99 (1992) 55.
15. Wilson, S. *Chem. Ind.* (1994) 255.
16. Reisch, M. S. *Chem. Eng. News* (1995) 15.
17. Kirk-Othmer, *Encyclopedia of Chemical Technologies*, 3rd ed., Wiley Interscience, New York 1981, Vol. 13, p.12.
18. Pletcher, D. and Walsh, F. C. *Industrial Electrochemistry*, Chapman and Hall, London 1990.
19. Foller, P. C. and Bombard, R. T. *J. Appl. Electrochem.* 25 (1995) 613.
20. Oloman, C. and Watkinson, A. P. *J. Appl. Electrochem.* 9 (1979) 1885.
21. Oloman, C. *J. Electrochem. Soc.* 126 (1979) 1885.
22. McIntyre, J. A. *Interface* 4 (1995) 29.
23. Oloman, C. *Electrochemical Processing for the Pulp and Paper Industry*, The Electrochemical Consultancy, Romsey, UK 1996.
24. Alcaide, F., Brillas, E., Cabot, P.-L. and Casado, J. *J. Electrochem. Soc.* 145 (1998) 3444.
25. Alvarez-Gallegos, A. and Pletcher, D., *Electrochim. Acta* 44 (1998) 853.
26. Harrington, T. and Pletcher, D. *J. Electrochem. Soc.* Submitted.
27. Tomat, R. and Vecchi, A. *J. Appl. Electrochem.* 1 (1971) 185.
28. Tomat, R. and Rigo, A. *J. Appl. Electrochem.* 6 (1976) 257.
29. Steckhan, E. and Wellman, J. *Angew. Chem., Int. Ed. Engl.* 15 (1976) 294.
30. Wellman, J. and Steckhan, E. *Chem. Ber.* 110 (1977) 3561.
31. Tomat, R. and Rigo, A. *J. Appl. Electrochem.* 9 (1979) 301.
32. Tomat, R. and Rigo, A. *J. Appl. Electrochem.* 10 (1980) 549.
33. Matsue, T., Fujihira, M. and Osa, T. *J. Electrochem. Soc.* 128 (1981) 2565.
34. Fleszar, B. and Sobkwiak, A. *Electrochim. Acta* 28 (1983) 1315.
35. Tomat, R. and Rigo, A. *J. Appl. Electrochem.* 14 (1984) 1.
36. Tzedakis, T., Savall, A. and Clifton, M. J. *J. Appl. Electrochem.* 19 (1989) 911.
37. Otsuka, K., Kunieda, M. and Yamagata, H. *J. Electrochem. Soc.* 139 (1992) 2381.
38. Otsuka, K., Ishizuka, K. and Yamagata, H. *Chem. Lett.* (1992) 773.
39. Hsiao, Y.-L. and Nobe, K. *Chem. Eng. Commun.* 126 (1993) 97.
40. Tomat, R., Salmasso, R. and Zecchin, S. *Electrochim. Acta* 39 (1994) 2475.
41. Yamanaka, I., Akimoto, T. and Otsuka, K. *Electrochim. Acta* 39 (1994) 2545.
42. Oturan, M. A. and Pinson, J. *J. Phys. Chem.* 99 (1995) 13948.
43. McIntyre, J. A. at *The 10th International Forum on Electrolysis in the Chemical Industry*, Clearwater Beach, Florida, November 1996.
44. Jow, J.-J., Lee, A.-C. and Chou, T.-C. *J. Appl. Electrochem.* 17 (1987) 753.
45. Chou, T.-C. In: Torii, S., Ed., *Recent Advances in Electroorganic Synthesis*, Kodansha/Elsevier, Amsterdam 1987, p. 149.
46. Lee, A.-C. and Chou, T.-C. *J. Appl. Electrochem.* 23 (1993) 1259.
47. Chen, Y. L. and Chou, T.-C. *J. Appl. Electrochem.* 26 (1996) 543.
48. Li, W. and Nonaka, T. *Chem. Lett.* (1997) 1271.
49. Do, J. S. and Yeh, W.-C. *J. Appl. Electrochem.* 26 (1996) 673.
50. Li, W. and Nonaka, T. *Chem. Lett.* (1997) 387.
51. Bortolini, O., Conte, V., Di Furia, F. and Modena, G. *J. Org. Chem.* 51 (1986) 2661.
52. Sadakane, M. and Steckhan, E. *Chem. Rev.* 98 (1998) 219.
53. Murahashi, S. I. and Shiota, T. *Tetrahedron Lett.* 21 (1987) 2383.
54. Torii, S., Inokuchi, T. and Sugiura, T. *J. Org. Chem.* 51 (1986) 155.
55. Rudolph, J., Reddy, K. L., Chiang, J. P. and Sharpless, K. B. *J. Am. Chem. Soc.* 119 (1997) 6189.
56. Kolb, H. C., van Nieuwenhze, M. S. and Sharpless, K. B. *Chem. Rev.* 94 (1994) 2483.
57. Bartlett, P. N., Pletcher, D. and Zeng, J. *J. Electrochem. Soc.* In press.
58. Everse, J., Everse, K. E. and Grisham, M. B., Eds., *Peroxidases in Chemistry and Biology*, CRC Press, Boca Raton 1991, Vols. 1 and 2.
59. van Deurzen, M. P. J., van Rantwijk, F. and Sheldon, R. A. *Tetrahedron* 53 (1997) 13183.
60. Sudoh, M., Kodera, T., Sakai, K., Zhang, J. Q. and Koide, K. *J. Chem. Eng. Jpn.* 19 (1986) 513.
61. Do, J.-S. and Chen, C.-P. *J. Electrochem. Soc.* 140 (1993) 1632.
62. Hsiao, Y.-L. and Nobe, K. *J. Appl. Electrochem.* 23 (1993) 943.
63. Do, J.-S. and Chen, C.-P. *J. Appl. Electrochem.* 24 (1994) 936.
64. Ponce de Leon, C. and Pletcher, D. *J. Appl. Electrochem.* 25 (1995) 307.
65. Brillas, E., Bastida, R. M., Llosa, E. and Casado, J. *J. Electrochem. Soc.* 142 (1995) 1733.
66. Brillas, E., Mur, E. and Casado, J. *J. Electrochem. Soc.* 143 (1996) L49.
67. Brillas, E., Sauleda, R. and Casado, J. *J. Electrochem. Soc.* 144 (1997) 2374.
68. Brillas, E., Mur, E., Sauleda, R., Sánchez, L., Peral, J., Domevech, Z. and Casado, J. *J. Appl. Catal. B* 16 (1998) 31.
69. Brillas, E., Sauleda, R. and Casado, J. *J. Electrochem. Soc.* 145 (1998) 759.
70. Brillas, E., Sauleda, R. and Casado, J. *Electrochem. Solid-State Lett.* 1 (1998) 168.
71. Alvarez-Gallegos, A. and Pletcher, D. *Electrochim. Acta* 44 (1999) 2483.

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