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Electrochemical synthesis of peroxomonophosphate using boron-doped diamond anodes

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Abstract A new method for the synthesis of peroxomonophosphate, based on the use of boron-doped diamond electrodes, is described. The amount of oxidant electrogenerated depends on the characteristics of the supporting media (pH and solute concentration) and on the operating conditions (temperature and current density). Results show that the pH, between values of 1 and 5, does not influence either the electrosynthesis of peroxomonophosphate or the chemical stability of the oxidant generated. Conversely, low temperatures are required during the electrosynthesis process to minimize the thermal decomposition of peroxomonophosphate and to guarantee significant oxidant concentration. In addition, a marked influence of both the current density and the initial substrate is observed. This observation can be explained in terms of the contribution of hydroxyl radicals in the oxidation mechanisms that occur on diamond surfaces. In the assays carried out below the water oxidation potential, the generation of hydroxyl radicals did not take place. In these cases, peroxomonophosphate generation occurs through a direct electron transfer and, therefore, at these low current densities lower concentrations are obtained. On the other hand, at higher potentials both direct and hydroxyl radical-mediated mechanisms contribute to the oxidant generation and the process is more efficient. In the same way, the contribution of hydroxyl radicals may also help to explain the significant influence of the substrate concentration. Thus, the coexistence of both phosphate and hydroxyl radicals is required to ensure the generation of significant amounts of peroxomonophosphoric acid.

1 Introduction

Peroxophosphates have a wide variety of applications in areas such as oxidations in organic synthesis [1, 2], cosmetics [3, 4], agriculture [5], wastewater treatment [6], and also as bleaching agents in the detergent industry [7, 8]. Recently, the reaction mechanisms of these compounds have been studied and several synthesis routes have been proposed [9]—some of which are electrochemical. The synthesis of peroxodiphosphate ($H_2P_2O_8$) by electrochemical techniques using different electrode materials such as platinum [10–12] (in this case it is necessary to use reagents to block the sites of oxygen evolution at the anode) or boron doped-diamond electrodes has been reported [13]. Conversely, the synthesis of peroxomonophosphoric acid (H_3PO_5) is usually based on highly exothermal chemical reactions that lead to the rapid decomposition of the peroxo-compounds generated and this leads to a low efficiency [14]. Several improvements, such as the addition of inert diluents, have been proposed [15], but the poor reproducibility of the results limits their use. The hydrolysis of peroxodiphosphate salts in very acidic conditions appeared to be one of the best synthesis methods for peroxomonophosphoric acid [16]. However, the requirement of powerful reagents (peroxodiphosphate and perchloric acid or hydrogen peroxide)

and its high manufacture costs have limited its commercial application.

In recent years, electrochemical oxidation with conductive-diamond anodes has become one of the most promising technologies in the treatment of industrial wastes polluted with organics [17–32] and in the electrosynthesis of inorganic oxidants [13, 33–35]. Compared with other electrode materials, conductive-diamond has shown higher chemical and electrochemical stability as well as a higher current efficiency. In addition, the high overpotential for water electrolysis is the most important property of conductive-diamond in the processing of aqueous solutions; its electrochemical window is sufficiently large to produce hydroxyl radicals with high efficiency and this species seems to be directly involved in the oxidation mechanisms that occur on diamond surfaces. As a result, conductive-diamond electrooxidation of waste is presently considered as an advanced oxidation technology [36]. The advantageous properties described above have led to great improvements (in both efficiency and electrode stability) in the use of conductive diamond in the electrosynthesis of oxidants. A number of recent studies have been published in which the generation of peroxodisulphates [33], peroxodiphosphate [13], percarbonates [34], ferrates [35] and hypochlorite [37] by electrochemical techniques are described. Significant improvements are reported as compared to more commonly used synthesis methods.

With this background in mind, the goal of the work described here was to investigate the feasibility of generating monoperoxophosphoric acid, an oxidant that is very difficult to obtain by conventional techniques. In an effort to achieve this aim, voltammetric studies and bench-scale electrolysis assays of phosphate solutions on BDD anodes were carried out in order to characterize the mechanism of the process and to clarify the role of the most significant process parameters (temperature, concentration, pH and current density).

2 Experimental

2.1 Analytical procedures

I_2/I^- assays were carried out to measure electrogenerated oxidants. This technique involves potentiometric titrations with thiosulphate in an acidic medium of all the oxidants capable of oxidizing I^- to I_3^-. P-NMR spectroscopy was used to characterize the electrogenerated oxidant. Likewise, preliminary tests were carried out to detect the presence of hydrogen peroxide (according to the analytical procedure described by Eisenberg [38]) and percarbonates (using a Shimadzu TOC-5050 analyzer).

2.2 Electrochemical cell

The electrosynthesis of peroxomonophosphate was carried out in a double-compartment electrochemical flow cell, which has been described elsewhere [13]. A cationic exchange membrane (STEREOM L-105) was used to separate the compartments. During the experiments it was observed that the properties of the membrane have a significant influence on the performance of the generated oxidants. The membrane was therefore carefully cleaned after each experiment and changed periodically. A diamond-based material was used as the anode and stainless steel (AISI 304) as the cathode. Both electrodes were circular with a geometric area of 78 cm^2 each and an electrode gap of 15 mm. The anolyte and the catholyte were stored in dark glass tanks (500 ml) and circulated through the electrolytic cell by means of a centrifugal pump. A heat exchanger was used to maintain the temperature at the desired set point. The pH was monitored using a WTW-InoLab pH meter.

2.3 Conductive diamond electrochemical oxidation

Bench-scale electrolyses under galvanostatic conditions were carried out to determine the influence of the main process parameters. The anolyte and the catholyte consisted of solutions of phosphoric acid (range of concentrations from 0.5 to 2.00 M) in the pH range 1 to 5. The pH was kept constant at the desired set point ($\pm$ 0.1 units) by the continuous addition of potassium hydroxide. The range of current densities employed was 200 to 1300 A m^{-2} and the range of temperatures studied was 10 to 40 °C. The cell potential was constant during each electrolysis, indicating that appreciable deterioration of the electrode or passivation phenomena did not take place.

Boron-doped diamond films were provided by CSEM (Neuchâtel, Switzerland) and synthesized by the Hot Filament Chemical Vapor Deposition Technique (HF CVD) on single-crystal p-type Si(100) wafers (0.1 Ωcm Siltronix).
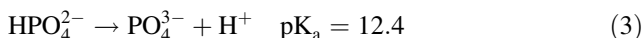
2.4 Voltammetry experiments

Electrochemical measurements were made using a conventional three-electrode cell in conjunction with a computer-controlled potentiostat/galvanostat (Autolab model PGSTAT 30, Ecochemie B.V., Utrecht, The Netherlands). Diamond was used as the working electrode (1 cm^2), Hg/Hg$_2$Cl$_2$.KCl (saturated) as a reference electrode and stainless steel (AISI 304) as a counter electrode.

Voltammetric experiments were performed in unstirred solutions (200 ml). The anode was anodically polarized for 10 min with a 1 M H_2SO_4 solution at 0.1 A prior to each experiment.

3 Results and discussion

3.1 Voltammetric study

Cyclic voltammograms on conductive-diamond anodes of sodium phosphate solutions (pH values in the range 2.5 to 12.5) are shown in Fig. 1. It can be seen that the presence of phosphate ions (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$) leads to the appearance of an oxidation peak very close to oxygen evolution and this seems to be strongly influenced (in both peak size and peak potential) by the pH of the medium. Lower pH values lead to a shift of the peak towards higher potential. The speciation of phosphate depends on the pH of the solutions according to Eqs. 1–3.

$$H_3PO_4 \rightarrow H_2PO_4^- + H^+ \quad pK_a = 2.14 \tag{1}$$

$$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+ \quad pK_a = 6.86 \tag{2}$$

$$HPO_4^{2-} \rightarrow PO_4^{3-} + H^+ \quad pK_a = 12.4 \tag{3}$$

In this context, the oxidation peak observed in these voltammograms can be explained in terms of the oxidation of the primary phosphate species to its respective phosphate radical (Eqs. 4–6).
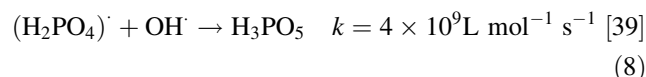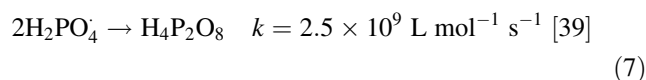
$$PO_4^{3-} \rightarrow (PO_4^{2-})^\cdot + e^- \tag{4}$$
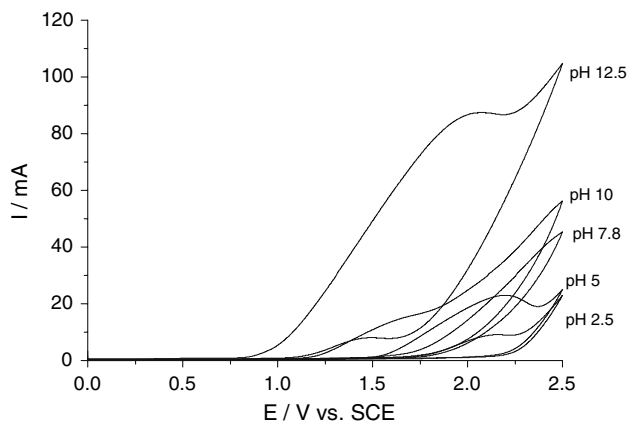
Fig. 1 Cyclic voltammograms on BDD anodes of phosphate solutions (0.2 mol dm^{-3}). Auxiliary electrode: Stainless steel AISI 304. Reference electrode: SCE. Scan rate: 100 mV s^{-1}

$$HPO_4^{2-} \rightarrow (HPO_4^-)^\cdot + e^- \tag{5}$$

$$H_2PO_4^- \rightarrow (H_2PO_4)^\cdot + e^- \tag{6}$$

According to the literature [39, 40], the reduction potentials of these phosphate radicals can differ significantly and it has been reported that $(PO_4^{2-})^\cdot$ oxidizes I^- rapidly, $(HPO_4^-)^\cdot$ can also oxidize Br^- and $(H_2PO_4)^\cdot$ can even oxidize Cl^-. This indicates an increase in the oxidant potential upon protonation and this is consistent with the results observed in the voltammetric study. However, accurate values could not be found in the literature (rather some estimations of the values that confirm these observations [39]).

The phosphate radicals, once formed, can oxidize other compounds in the region close to the anode surface (for instance water peroxide to oxygen) or they can couple with other phosphate radicals to form peroxodiphosphate (Eq. 7) or react with hydroxyl radicals generated by water oxidation to form peroxomonophosphoric acid (Eq. 8) [2, 39, 41, 42].

$$2H_2PO_4^\cdot \rightarrow H_4P_2O_8 \quad k = 2.5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \text{ [39]} \tag{7}$$

$$(H_2PO_4)^\cdot + OH^\cdot \rightarrow H_3PO_5 \quad k = 4 \times 10^9 \text{L mol}^{-1} \text{ s}^{-1} \text{ [39]} \tag{8}$$

These species are well-known oxidants that can be easily measured in solution by titration and can also be isolated by precipitation.

3.2 Electrolysis study

The concentration of oxidants generated during the electrolyses (in a double-compartment electrochemical flow cell) of solutions containing 1 M H_3PO_4 (pH 1.2, T: 25 °C, j: 640 A m^{-2}) are shown in Fig. 2. The concentration of oxidants increases progressively until a constant value is achieved when an electrical charge above 60 Ah dm^{-3} is passed. This behaviour was observed in all the electrolysis experiments carried out in this work and was also reported [13] for the electrolysis of alkaline phosphate solutions.
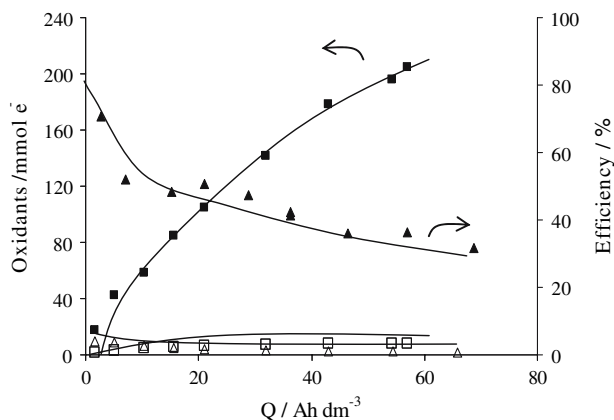
The oxidant concentrations and the current efficiencies obtained in electrolyses of solutions at pH 1.2 and pH 12.5 are compared in Fig. 3. The amount of oxidant generated (expressed in terms of mmol of electrons) is significantly lower at acidic pH values. In addition, current efficiencies below 10% are obtained in the former case, while in the electrolyses in alkaline media the current efficiency is over 50%. This finding is in agreement with the results obtained in the voltammetric study and seems to confirm the
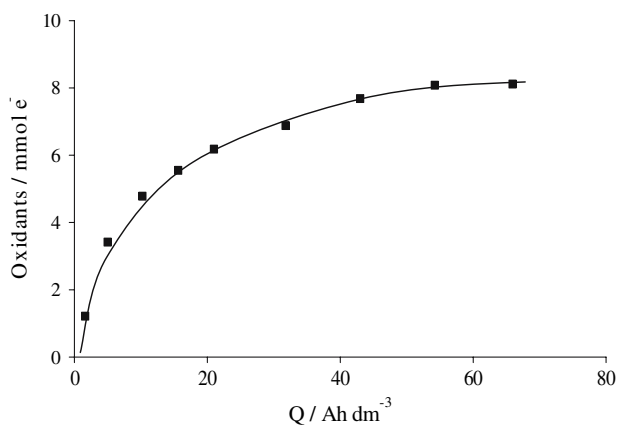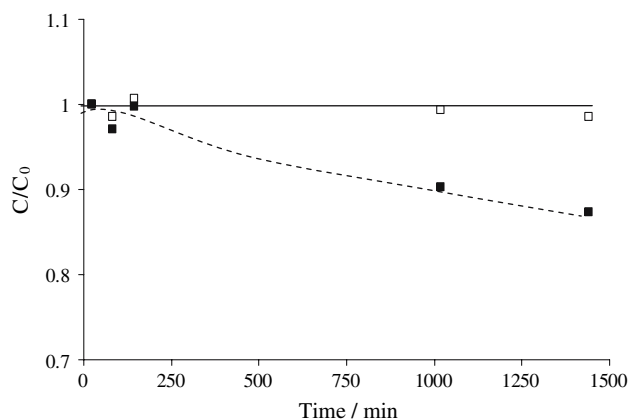
Fig. 2 Variation of the oxidant concentration with electrical charge passed in the electrochemical oxidation of 1 M H_3PO_4 (pH 1.2; T: 10 °C; j: 640 A m^{-2})

existence of different species and, therefore, of different oxidation mechanisms in the two cases studied (pH 1.2 and pH 12). At this point it was decided to test the stability of the oxidants formed under both pH conditions and several samples that contained the final product of the electrolysis assays were stored at room temperature. The variation with time of the oxidant concentration during one day at room temperature is represented in Fig. 4. It can be seen that the oxidants formed in acidic media can suffer significant chemical decomposition within this period, which is opposite to the behaviour observed with the product obtained at pH 12.5.

In order to verify the nature of the oxidant generated in both cases, several analytical assays were carried out. The stability of the oxidant ruled out the presence of hydroxyl or phosphate radicals, ozone and other non-stable oxidants. Likewise, a preliminary test showed that the oxidant

Fig. 3 Variation of oxidant concentrations (square symbols) and current efficiencies (triangular symbols) with electrical charge passed in the electrolysis of acidic (pH = 1.2; 1 M H_3PO_4; T: 13 °C; j: 640 A m^{-2}) (empty symbols) and alkaline (pH = 12.5; 1 M K_3PO_4; T: 25 °C; j: 1250 A m^{-2}) phosphate salts (solid symbols)


Fig. 4 Variation of the oxidant concentration in the final product obtained with time at room temperature in the electrolysis of 1 M H_3PO_4 (T: 10 °C, j: 640 A m^{-2}). ■ pH 1.2; □ pH 12.5

formed was not hydrogen peroxide or percarbonates. The P-NMR spectra of final aqueous solutions containing the electrogenerated reagents are shown in Fig. 5. It can be seen that the chemical shift of the singlet differs: $\delta = 7.8$ and 0.8 ppm in alkaline and acidic solutions, respectively. This seems to confirm that the nature of the electrogenerated oxidant depends on the alkalinity or acidity of the electrolyte. The spectra were compared with those of standard compounds $H_4P_2O_8$ and H_3PO_5. This established that the peroxodiphosphate ion ($P_2O_8^{4-}$) and peroxomonophosphoric acid (H_3PO_5) are the compounds generated at alkaline and acidic pH values, respectively.

Having verified the generation of stable oxidants from the electrochemical oxidation of acidic phosphate solutions, the influence of the most important operational parameters (concentration of the substrate, pH, temperature and current density) on the efficiency of this process was studied. As the product formed at alkaline pH (around pH 12) has been exhaustively described [13], the focus of this work only concerns the product formed under acidic conditions.

The changes in the amount of oxidant electrogenerated during the electrolysis of different solutions of phosphoric acid (initial concentration from 0.2 to 2 mol dm^{-3}) are shown in Fig. 6. The pH, current density and temperature were maintained during these electrolysis assays at values close to pH 5, 13 °C and 200 A m^{-2}, respectively. As can be observed, the concentration of oxidant obtained is largely influenced by the concentration of the solute. The amount of peroxomonophosphate increases significantly with the amount of $H_2PO_4^-$ ions available for oxidation until a given value is achieved (around 1 M H_3PO_4) and a decrease in the amount of peroxomonophosphate generated is subsequently observed. As a result, it can be suggested that 1 M H_3PO_4 is the optimum concentration for the peroxomonophosphate synthesis with BDD anodes under
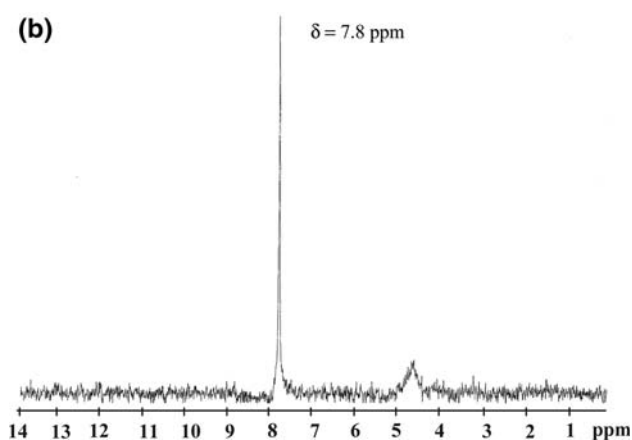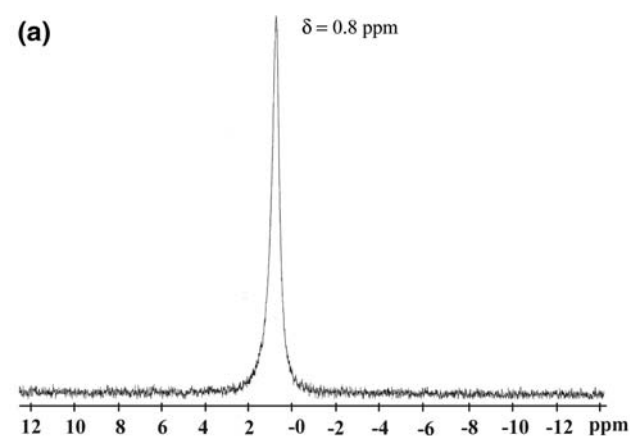
Fig. 5 Nuclear magnetic resonance (P-NMR) spectra of aqueous solutions of peroxomonophosphate (**a**) and peroxodiphosphate (**b**)
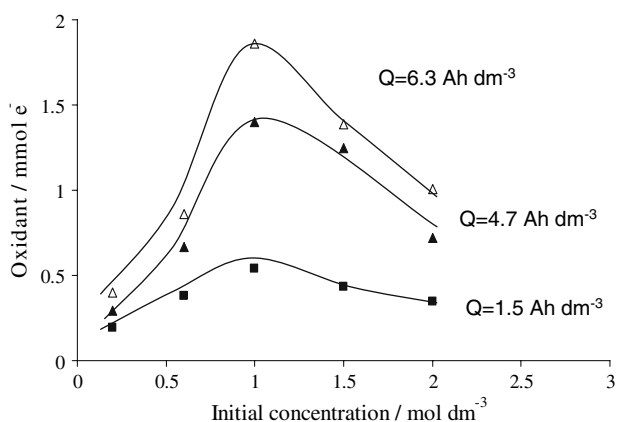
Fig. 6 Amount of oxidant generated in the electrosynthesis of peroxomonophosphate as a function of the initial concentration of H_3PO_4 (pH 5; T: 13 °C; j: 200 A m^{-2}). ■ 1.5 Ah dm^{-3}; ▲ 4.7 Ah dm^{-3}; △ 6.3 Ah dm^{-3}

the operating conditions used in this work. For this reason, the subsequent assays were carried out with this value kept constant.
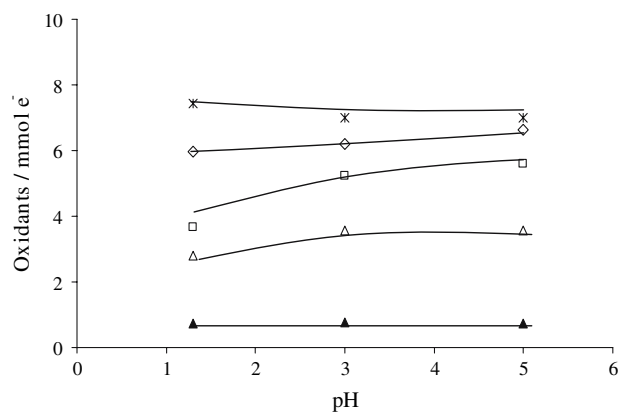

Fig. 7 Amount of oxidant generated in the electrosynthesis of peroxomonophosphate as a function of the pH of the solutions (1 M H_3PO_4; T: 13 °C; j: 640 A m^{-2}). ▲ 1.7 Ah dm^{-3}; △ 5 Ah dm^{-3}; □ 10 Ah dm^{-3}; ◇ 15 Ah dm^{-3}; ✳ 20 Ah dm^{-3}

The amount of oxidant electrogenerated during the electrolysis of phosphate solutions as a function of the anolyte-pH (acidic pH) and of the charge passed through during the electrolyses are shown in Fig. 7. In all the electrolysis assays, the pH was kept constant at the initial value by the continuous addition of KOH (to compensate for the protons generated from the side water oxidation process) to the anolyte reservoir. It can be seen that in the pH range studied and under the experimental conditions used, the performance of the process does not depend on pH. It is important to bear in mind that in this pH range, H_3PO_4 and $H_2PO_4^-$ are the major species present.

The influence of temperature on the process is represented in Fig. 8. The conversion of $H_2PO_4^-$ to the peroxomonophosphate ion shows a marked dependence on this parameter. The higher the temperature, the lower the oxidant concentrations obtained at the steady state (plateau value of the concentration of oxidant). This plateau value results from a balance between the rate of formation of
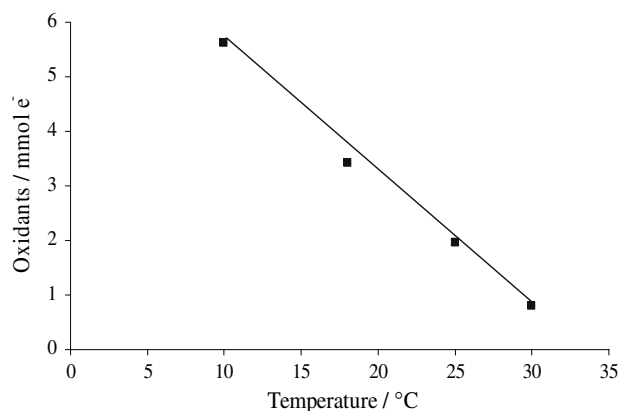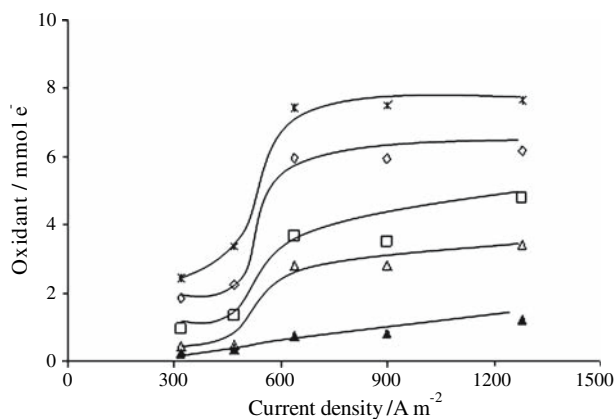

Fig. 8 Amount of oxidant generated in the electrosynthesis of peroxomonophosphate as a function of the temperature at an electrical charge passed of 10 Ah dm^{-3} (1 M H_3PO_4; pH 5; j: 640 A m^{-2})
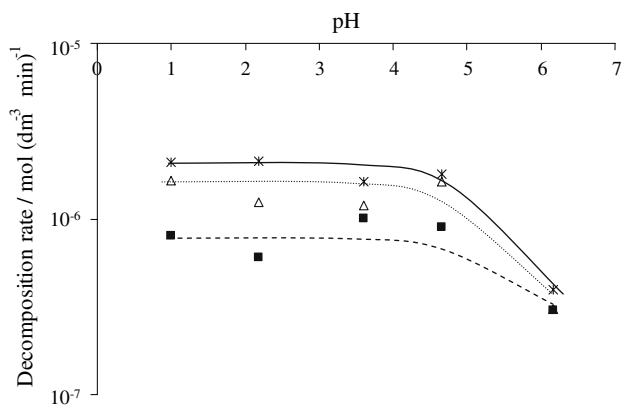
Fig. 9 Decomposition rates of the peroxomonophosphate generated in the electrolysis of peroxomonophosphate (1 M H_3PO_4; j: 640 A m^{-2}). ■ 10 °C; △ 22 °C; ✱ 35 °C

oxidant and its decomposition rate. The same phenomenon was observed during the electrosynthesis of peroxodisulphates [33] and possibly peroxodiphosphate [13]. Thus, to study the chemical decomposition of the peroxomonophosphoric acids generated as a function of the temperature and also pH, the solutions obtained in the electrolyses carried out at different pH values were stored at different temperatures and the oxidant concentrations were monitored. The decomposition rate as a function of temperature and pH is represented in Fig. 9. As expected, the chemical decomposition rate strongly depends on the temperature but no marked influence of pH was observed for values lower than pH 5. The decomposition rate of the oxidant electrogenerated at 35 °C is around double that observed at 10 °C. Moreover, at pH 6 the decomposition rate converges towards a single value regardless of temperature. Taking into account that pKa_2 of H_3PO_5 is 5.38 [43], the major species present at pH6 is HPO_5^{2-}.


Fig. 10 Amount of oxidant generated in the electrosynthesis of peroxomonophosphate as a function of the current density (1 M H_3PO_4; pH 1.3; T: 13 °C). ▲ 1.7 Ah dm^{-3}; △ 5 Ah dm^{-3}; □ 10 Ah dm^{-3}; ◇ 15 Ah dm^{-3}; ✱ 20 Ah dm^{-3}

The influence of current density in the electrosynthesis of peroxomonophosphate on BDD anodes is shown in Fig. 10. The concentration of oxidants generated strongly depends on the operating conditions and two significantly different types of behaviour can be discerned. Similar behaviour was also observed in the electrolysis assays carried out at different pH values (pH 3 and 5). It can be suggested that at low current densities the direct mechanism is mainly responsible for peroxomonophosphate generation. At higher current densities, however, the mechanism may also involve hydroxyl radicals, as explained previously for the generation of peroxodiphosphate [13, 44].

3.3 Role of hydroxyl radicals in the synthesis of peroxomonophosphates

As reported in the literature [2, 13, 40–42, 44, 45] and according to the voltammetric study, the oxidation of phosphates follows a direct oxidation mechanism (Eqs. 4–6). However, the prevalence of this oxidation mechanism cannot explain the changes observed in the electrosynthesis assays carried out under different operating conditions (current density and initial concentration).

In this context, it has recently been demonstrated that the electrolysis of aqueous solutions on BDD anodes leads to the generation of large amounts of hydroxyl radicals from the water oxidation process [36]. These radicals are very reactive and can play an important role in the electrolytic process. In the literature [2, 40–42, 44, 45] it has been proposed that the dihydrogenophosphate radical can also be formed through the oxidation of phosphate ions by hydroxyl radicals, according to Eq. 9. Hence, the contributions of both processes (direct and hydroxyl radical-mediated oxidations) must be considered to explain the significant influence of the operating conditions.

$$H_2PO_4^- + OH^. \rightarrow (H_2PO_4)^. + OH^- \qquad (9)$$
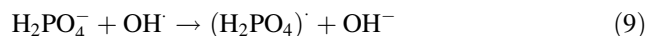
In the first mechanism, the resulting phosphate radicals are formed by direct heterogeneous charge transfer. However, in the second mechanism they are also generated directly in solution in a zone very close to the anode surface due to the reaction of $H_2PO_4^-$ with the hydroxyl radicals [40–42, 44, 45]. The possibilities for interaction between two radicals are higher in the second case, as the decay of the phosphate radical can be very rapid [39–42, 44, 45]. This factor may explain the higher concentrations observed in the latter case and the abrupt change between the results obtained on working at higher or lower current densities (potentials). In this way, it can be suggested that working over a given current density

(640 A m^{-2}) (which in our experimental device corresponds to a cell potential of 3.5 V) should cause the formation of large amounts of hydroxyl radicals at the anodic surface. This species can then promote the changes observed in the bulk oxidation.

In the same way, the contribution of OH$^-$-mediated oxidation processes could also help to explain the significant (and unexpected) influence of the solute concentration. As mentioned previously, hydroxyl radicals can contribute to the generation of the $H_2PO_4^-$ radical (see Eq. 9) and its presence is also needed to promote the generation of peroxomonophosphoric acid (see Eq. 8). As a result, an increase in the initial concentration of phosphate is not sufficient to ensure the generation of a higher amount of generated oxidant, but the coexistence of both radical reagents is required. This finding may explain the maximum observed in Fig. 6, where the concentration of peroxomonophosphate generated is plotted as a function of the initial concentration of the phosphate solution for different specific current charges passed.

4 Conclusions

From this work the following conclusions can be drawn:

– The electrolysis of phosphate solutions at acidic pH values leads to the generation of peroxomonophosphate. The process is less efficient than the generation of peroxodiphosphate (from the electrolysis of phosphate solutions at alkaline pHs) and this seems to be due to the lower chemical stability of the peroxomonocompound.
– The amount of oxidant electrogenerated depends on the substrate concentration and on the operating conditions (temperature and current density). In order to obtain high efficiencies it is recommended to work at low temperature, high current densities and to check the effect of the concentration (for the experimental conditions used in this work a maximum was found on operating at around 1 M of phosphoric acid solution).
– The effect of the current density and of the initial solute can be explained in terms of the contribution of hydroxyl radicals to the oxidation mechanism that occurs on diamond surfaces. In the assays carried out below the water oxidation potential, the generation of hydroxyl radicals does not take place. In these cases, the direct mechanism is the only one responsible for the generation of peroxomonophosphate and, therefore, lower concentrations are obtained. On the other hand, at higher potentials, both direct and hydroxyl radical-mediated mechanisms contribute to the oxidant

generation and the process is more efficient. In the same way, the contribution of hydroxyl radicals may also help to explain the significant influence of the substrate concentration.

References

1. Rosso JA, Rodríguez FJ, González MC, Martire DO (1998) J Photochem Photobiol A: Chem 116:21
2. Rosso JA, Caregnato P, Mora VC, González MC, Martire DO (2003) Helvetica Chim Acta 86(7):2509
3. Cohen B (1969) FMC Corp, DE patent 1 926 434
4. Cohen B, Mucenieks PR (1971) FMC Corp, US Patent 3 555 147
5. Puetzer B, Finn AV, Mackles L (1967) Tintex Corp, US Patent 3 337 466
6. Gaffar A, Calvin DB (1983) DE Patent 3 246 946 A1
7. Gaffar A, Edwards CJ (1983) DE Patent 3 627 759 A1
8. Moreno EC, Kresak M, Gaffar A (1994) J Colloid Interf Sci 168(1):173
9. Griffith WP, Powell RD, Skapski AC (1988) Polyhedron 7(14):1305
10. Tyurikava OC, Kasatkin EV, Miller NB, Tishakina AE, Kantor ZhN (1987) Electrokhim 23:199
11. Battaglia CJ, Edwards JO (1965) Inorg Chem 4:552
12. Kasatkin EV, Lubnin EN (1987) Electrokhim 23:679
13. Cañizares P, Larrondo F, Lobato J, Rodrigo MA, Sáez C (2005) J Electrochem Soc 152(11):D191
14. Schmidlinm J, Massini O (1910) Ber 43:1162
15. Toennies G (1937) J Am Che Soc 59:555
16. Shu T, Chang H, Kadla JF (2003) Can J Chem 81:156
17. Boye B, Michaud PA, Marselli B, Dieng M, Brillas E, Comninellis Ch (2002) New Diamond Front Carbon Technol 12:63
18. Brillas E, Boye B, Sirés I, Garrido JA, Rodríguez RM, Arias C, Cabot PL, Comninellis Ch (2004) Electrochim Acta 49:4487
19. Cañizares P, Martínez L, Paz R, Sáez C, Lobato J, Rodrigo MA (2006) J Chem Technol Biotechnol 81:1661
20. Cañizares P, Paz R, Lobato J, Sáez C, Rodrigo MA (2006) J Haz Mater B138:173
21. Cañizares P, Sáez C, Lobato J, Paz R, Rodrigo MA (2007) Chemosphere 67:832
22. Gandini D, Mahe E, Michaud PA, Haenni W, Perret A, Comninellis Ch (2000) J Appl Electrochem 30:1345
23. Iniesta J, Michaud PA, Panizza M, Cerisola G, Aldaz A, Comninellis Ch (2001) Electrochim Acta 46:3573
24. Iniesta J, Michaud PA, Panizza M, Comninellis Ch (2001) Electrochem Commun 3:346
25. Montilla F, Michaud PA, Morallon E, Vazquez JL, Comninellis Ch (2002) Electrochim Acta 47:3509
26. Panizza M, Michaud PA, Cerisola G, Comninellis Ch (2001) J Electroanal Chem 507:206
27. Panizza M, Cerisola G (2004) Electrochim Acta 49:3221
28. Polcaro AM, Vacca A, Palmas S, Mascia M (2003) J Appl Electrochem 33:885
29. Polcaro AM, Mascia M, Palmas S, Vacca A (2004) Electrochim Acta 49:649
30. Rodrigo MA, Michaud PA, Duo I, Panizza M, Cerisola G, Comninellis Ch (2001) J Electrochem Soc 148(5):D60

31. Weiss E, Groenen-Serrano K, Savall A (2006) J New Mat Electrochem Systems 7(3):249
32. Weiss E, Groenen-Serrano K, Savall A, Comninellis Ch (2007) J Appl Electrochem 9(3):41
33. Serrano K, Michaud PA, Comninellis Ch, Savall A (2002) Electrochim Acta 48:431
34. Saha MS, Furuta T, Nishiki Y (2003) Electrochem Solid-State Lett 6:5
35. Cañizares P, Arcís M, Sáez C, Rodrigo MA (2007) Electrochem Commun 9:2286
36. Marselli B, García-Gómez J, Michaud PA, Rodrigo MA, Comninellis Ch (2003) J Electrochem Soc 150(3):D79
37. Panizza M, Cerisola G (2006) Int J Environ Pollution 27:64
38. Eisenberg GM (1943) Ind Eng Chem 15:327
39. Jiang PY, Katsumura Y, Domae M, Ishikawa K, Nagaishi R, Ishigure K (1992) J Chem Soc Faraday Trans 88(22):3319
40. Neta P, Huie RE, Ross AB (1988) J Phys Chem 17:1027
41. Mártire DO, González MC (2001) Progress Reac Kin Mechanism 26:201
42. El Ghazali A, Beldaci S, Rameua JJ, Dalard F (1998) J Appl Electrochem 28:725
43. Panigrahi GP, Jagannath Panda (2000) Proc Indian Acad Sci (Chem Sci) 112(6):615
44. Cañizares P, Sáez C, Lobato J, Paz R, Rodrigo MA (2007) J Electrochem Soc 154(3):E37
45. Buxton GV, Greenstock CL, Helman WP, Ross AB (1988) J Phys Chem Ref Data 17(2):513