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An experimental comparison of a graphite electrode and a gas diffusion electrode for the cathodic production of hydrogen peroxide

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Abstract

This work studies the production of hydrogen peroxide through the cathodic reduction of oxygen in acidic medium, by comparing the results obtained using a commercial graphite and a gas diffusion electrode. A low pH was required to allow the application of hydrogen peroxide generation to an electro-Fenton process. The influence of applied potential and the gas flow composition were investigated. The gas diffusion electrode demonstrates a higher selectivity for hydrogen peroxide production, without significantly compromising the iron regeneration, thus making its successful application to a cathodic Fenton-like treatment, possible. Unlike the graphite cathode, the gas diffusion cathode also proved to be effective in the air flow.

1. Introduction

Hydrogen peroxide (H_2O_2) is a powerful and versatile oxidant used in several applications [1]. It is used to bleach textiles and paper products, to manufacture or process foods, minerals, petrochemicals, and consumer products such as detergents.

H_2O_2 is considered an environmentally friendly chemical since it has none of the problems of gaseous release or chemical residues associated with other chemical oxidants.

Its environmental applications include municipal odour control, BOD and COD removal from industrial waste water, control of bulking, toxicity reduction and biodegradability improvement of recalcitrant compounds [2–5].

Hydrogen peroxide is commercially prepared by the oxidation of alkylhydroanthraquinones and by the electrolysis of ammonium bisulphate.

The electrochemical reduction of molecular oxygen is a promising method of producing hydrogen peroxide. The overall process, which also involves the formation of numerous radical species such as superoxide radicals $O_2^{\bullet -}$ and hydroperoxide radicals $HOO^{\bullet}$, can be described by reaction 1 [6]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

The oxidising efficiency of hydrogen peroxide can be significantly increased by a combination with UV radiation or metal salts [7]. In particular the aqueous mixture of H_2O_2 and Fe^{2+}, named Fenton's reagent [8, 9], is one of the most interesting environmental treatments. Under acidic conditions, the reaction between H_2O_2 and Fe^{2+} generates the hydroxyl radical (reaction 2), which, with a standard potential of 2.8 V, is second only to fluorine, one of the most powerful oxidisers known. Its high reactivity allows it to oxidise most organic as well as many inorganic compounds [10–14].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^- \tag{2}$$

Fenton's reagent may be electrochemically produced in bulk solution, with the simultaneous generation of hydrogen peroxide by the cathodic reduction of dissolved molecular oxygen and the regeneration of ferrous ions consumed by Fenton's reaction, according to reactions 1 and 3 [15–25]

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3}$$

The two-electron reduction of oxygen to hydrogen peroxide in a strongly alkaline solution is a well-known reaction which gives high yields at carbon cathodes [26–28]. With a view to a Fenton treatment application, the optimisation of the hydrogen peroxide electrogeneration in acidic medium is needed.

The cathodic reduction of oxygen to produce hydrogen peroxide with various cathodic materials has been extensively studied. More recently, a new oxygen diffusion cathode has attracted great attention owing to its promising results [29–32]. The aim of this work was to compare a commercial graphite cathode with an oxygen diffusion cathode. Both cathodes were tested in a two-compartment membrane cell. In addition, the results obtained for the graphite cathode were also compared with those obtained in previous work using a salt bridge cell.

The effect of the gas composition on the reaction efficiency was also investigated by substituting the oxygen flow with an air flow with a view to a further saving.

2. Experimental details

2.1. *Materials*

All reagents were supplied by the Carlo Erba Company and used in their commercially available form with no further purification.

2.2. *Cell apparatus*

The apparatus, including a potentiostat (AMEL 2051) coupled with a programmable function generator (AMEL 568), was employed for controlled potential electrolyses, carried out in two different types of three-electrode cells. The electrochemical cell, P, (Figure 1), was a glass cylindrical cell with the anodic compartment constituted of a glass tube. An agar-H_2O–$NaClO_4$ plug sintered-glass disk was used to separate the two compartments. The electrochemical cell, M, (Figure 2) was an acrylic parallel-plate electrolyser where a cation exchange membrane (Nafion® 324) was used to separate cathodic and anodic compartments.

Two types of cathode, having a surface area of about 5 cm^2, were tested as working electrodes: the first was a traditional graphite electrode supplied by Amel, while the second was a gas diffusion electrode [38–41] supplied by De Nora Tecnologie Elettrochimiche.

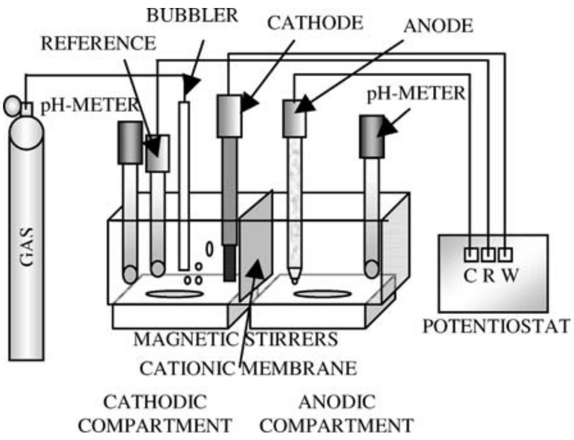

Fig. 2. Detail of the M electrochemical cell.

The gas diffusion electrode (Figure 3) was constituted by a carbon-PTFE layer in contact with a metal mesh as current collector. The gas flow passed over the inner face of the cathode through a tube inside the holder, the top of which was connected to a drechsel to maintain the right pressure in the Plexiglas holder. No bubbles were observed on the cathode surface thus excluding any passage of gas into the solution.

During the electrolyses conducted with the graphite electrode a continuous gas flow of 130 ml min^{-1} was supplied inside the cathodic solution.

The gas employed was always oxygen unless otherwise indicated.

A platinum anode and a SCE (saturated calomel electrode) reference electrode were used.

2.3. *Procedure*

The electrogeneration of hydrogen peroxide was carried out in 100 ml of aqueous solutions under conditions of constant agitation (1000 rpm) and ambient temperature. As indicated previously, the optimal pH value for the production of hydrogen peroxide is [33], and this is the value adopted in this research by means of a Na_2SO_4/$NaHSO_4$ ($[Na_2SO_4] = 0.04$ M, $[NaHSO_4] = 0.05$ M) buffer solution. No supporting electrolyte was added to the catholyte, since conductivity was guaranteed by the buffer solution.

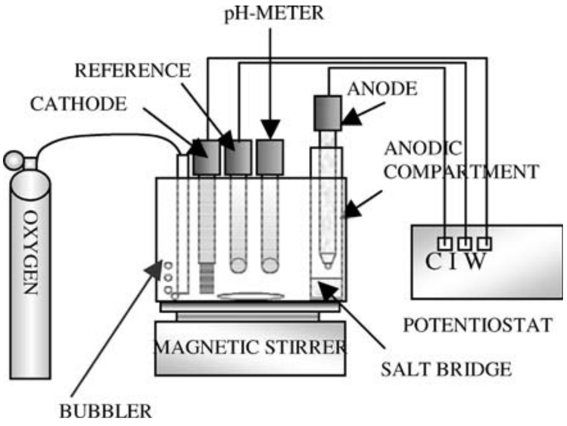

Fig. 1. Detail of the P electrochemical cell.

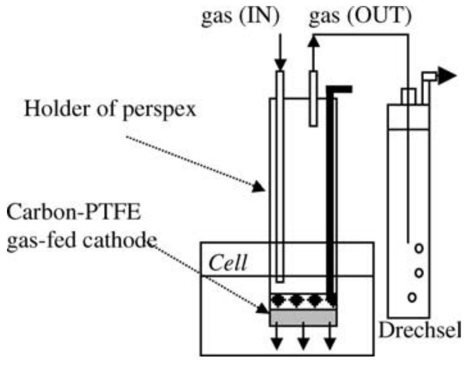

Fig. 3. Schematic representation of the gas diffusion electrode (GDE).

Sodium perchlorate 0.01 M was used as supporting electrolyte in the anodic compartments. The applied cathodic potential range investigated varied from −0.6 to −1.1 V vs SCE.

A final series of experimental tests were carried out to compare the efficiency of the two cathodes tested on the removal of an inorganic substrate. An hypophosphite/phosphite/phosphate system was adopted as a reference reducing agent due to its extremely linear oxidative pathway and quick analytical determination. These experiments were carried out on a 100 ml solution at phosphorus concentrations of 100 mg l^{-1} in terms of hypophosphites (added as NaH_2PO_2 H_2O at 98% by weight). About 100 mg l^{-1} of iron were then added (as heptahydrate iron sulphate $FeSO_4 \cdot 7H_2O$) at the start of the electrolysis. The experiments were stopped when an oxidation efficiency of 95% was achieved, where the oxidation efficiency was defined as the percentage ratio between phosphorus as phosphates $[P]_{\text{phosphate}}$ and the initial phosphorus concentration $[P]$, Equation (4).

$$\text{oxidation efficiency} = \frac{[P]_{\text{phosphate}}}{[P]} \times 100 \tag{4}$$

All the experiments were conducted in triplicate.

2.4. *Analysis*

Dissolved oxygen concentration was measured with a Hanna Instruments D.O. metre. The pH was monitored by using a continuous Crison 421 m. The concentrations of hydrogen peroxide, ferrous iron and total iron (determined as ferrous iron after reduction with ascorbic acid) were determined reflectometrically by means of Merck analytical tests.

Hypophospites, phosphites and phosphates were determined by means of a Dionex DX 120 ionic chromatograph, equipped with an IONPAC AS12A anionic column. The concentration of total phosphorus was determined by an UV–VIS spectrophotometer in accordance with Standard Methods [34].

3. Results and discussion

3.1. *Hydrogen peroxide production*

A preliminary series of tests was performed to evaluate the hydrogen peroxide production at a constant potential of −0.9 V vs SCE, since previous research found this value as optimal for oxygen cathodic reduction [33]. Experiments employing the gas diffusion cathode were conducted in the membrane cell, while those employing the graphite electrode were performed in the salt bridge cell.

Hydrogen peroxide production as a function of the charge is shown in Figure 4, where the experimental data are compared with the ideal production curve, calculated according to the following equation

$$[H_2O_2] = \frac{Q \times 34 \times 10000}{n \times F} \tag{5}$$

where $[H_2O_2]$ is the hydrogen peroxide concentration, as mg l^{-1}, reached in a 100 ml solution, Q is the required charge, expressed in Coulomb, 34 is the molar weight of hydrogen peroxide, n is the number of electrons involved in the reaction (1), F is the Faraday constant, 96 490 C, and 10 000 is a conversion factor.

The results indicate that, in the investigated range, the gas diffusion cathode gives remarkably higher production of hydrogen peroxide with respect to the graphite cathode, showing a linear trend similar to the ideal curve. As regards the graphite electrode, the runs conducted in the P cell showed a linear trend. Those conducted in the M cell, where, due to the geometry less effective stirring was supplied, gave a plateau and a hydrogen peroxide concentration never exceeding 100 mg l^{-1}.

The two cathode performances were due to the different mechanism through which oxygen reached the electrodic surface. As to the graphite cathode the process was controlled by the solubilisation of the molecular oxygen into the solution and then diffusion from the bulk to the electrode surface. The use of a gas

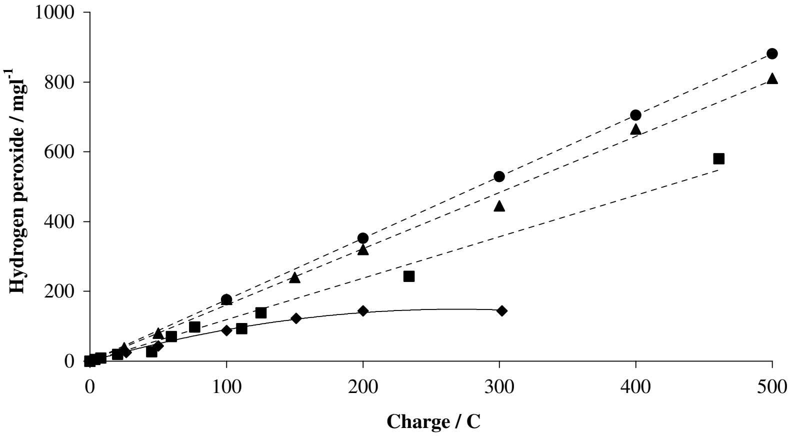

Fig. 4. H_2O_2 electro-generation vs charge at $E = -0.9$ V vs SCE: ideal production (●), GDE in M cell (▲), graphite electrode in P cell (■), graphite electrode in M cell (♦).

diffusion cathode, where oxygen is directly supplied to the electrodic surface, overcame these limiting steps thus enhancing the process yield.

Though the oxygen diffusion cathode proved to be very effective for hydrogen peroxide production, a considerably faster drop in efficiency during its life was noted if compared to the graphite electrode, as shown in Figure 5. Ageing phenomena are induced by coating degradation with a significant and rapid loss of dispersed graphite.

3.2. *Influence of the gas*

A series of tests was performed to evaluate the influence of the supplied gas on the hydrogen peroxide production yield comparing oxygen and air feed. Results, for both the cathodes, are reported in Figures 6 and 7, as a function of charge and time respectively.

As for the graphite electrode a negative effect was expected for air given that the concentration of dissolved oxygen in this case dropped to about 9 mg l^{-1} from 40 mg l^{-1} obtainable with oxygen flow. Data confirmed that the inflow gas composition notably affected both the yield and the reaction rate, as shown in Figures 6 and 7.

In the case of the gas diffusion electrode a notable effect was observed, even though the amount of hydrogen peroxide produced was high and comparable with the graphite runs conducted in oxygen flow.

The graphite electrode showed a very low current density with unacceptable reaction time when air was supplied leading at most to the production of less than 100 mg l^{-1} of hydrogen peroxide after a 800 min treatment. Under the same conditions the gas diffusion cathode led to considerable production (450 mg l^{-1} of hydrogen peroxide after a 400-min treatment) with clear economic benefits.

3.3. *Influence of potential*

To determine the influence of the working potential on hydrogen peroxide production, a further series of electrolyses was carried out, in the M cell, at selected potentials in a range between −0.6 and −1.1 V vs SCE.

Data were reported as faradic efficiency and current (Figures 8 and 9) as a function of the charge. The

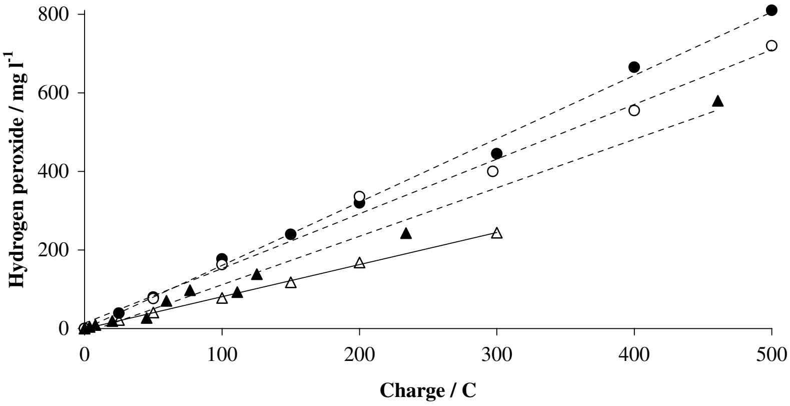

Fig. 5. Influence of cathode ageing on the H_2O_2 electro-generation vs charge: GDE (●), GDE after two months (○), graphite electrode (▲), graphite electrode after two years (△).

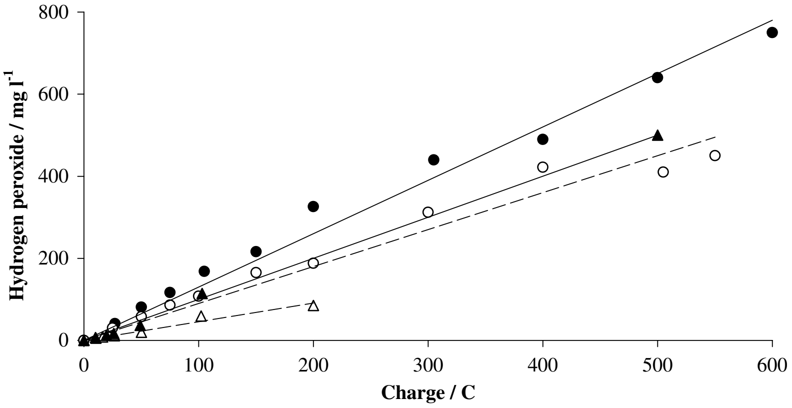

Fig. 6. Influence of the gas flow composition on the H_2O_2 electro-generation vs charge at $E = -0.9$ V vs SCE, M cell: GDE in O_2 (●), GDE in air (○); graphite electrode in O_2 (▲), graphite electrode in air (△).

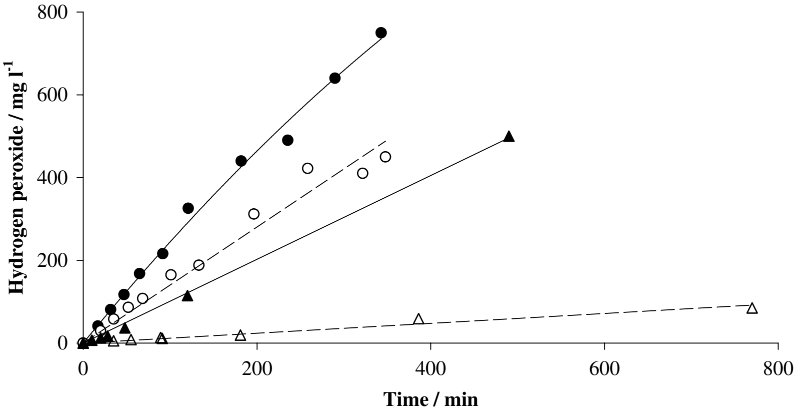

Fig. 7. Influence of the gas flow composition on the H_2O_2 electro-generation vs time at $E = -0.9$ V vs SCE in M cell: GDE in O_2 (●) GDE in air (○), graphite electrode in O_2 (▲) graphite electrode in air (△).

faradic efficiency of hydrogen peroxide production is expressed as:

$$\text{Current efficiency} = \frac{nFC_{H_2O_2}V}{\int_0^t I\mathrm{d}t} \times 100\% \tag{6}$$

where n is the stoichiometric number of transferred electrons (2), F is the Faraday constant (96 490 C mol^{-1}), $C_{H_2O_2}$ represents the H_2O_2 concentration in bulk solution (M) and V is the catholyte volume (L).

The oxygen diffusion cathode showed very high faradic efficiencies at any potential with a maximum at −0.9 V vs SCE when values always higher than 85% were observed.

The curves indicate that the efficiency remained almost constant in the whole range of charge except for $E = -1.0$ and $E = -1.1$ V vs SCE. At these potentials, after a charge of 200 C, there was a reduction in the efficiency of production due to the higher rate of side reactions: the 4-electron reduction of oxygen to water (7) and the decomposition of hydrogen peroxide (8).

$$O_2 + 4H^+ + 4e^- \rightarrow 6H_2O \tag{7}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^0 = 1.534\,\text{V vs SCE} \tag{8}$$

In this case the occurrence of the main side reaction, that is hydrogen gas evolution, (9) was excluded given that no bubbles were observed on the cathode surface during the run.

$$2H^+ + 2e^- \rightarrow H_2 \quad E^0 = -0.242\,\text{V vs SCE} \tag{9}$$

With regard to the graphite cathode, it can be seen that potential notably affected the faradic efficiency which was comparable only at −0.6 V vs SCE with that observed using the diffusion cathode. At more negative potentials (−0.7 and −0.9 V vs SCE) the current efficiencies dropped significantly (63 and 53% respectively after the passage of 25 C), and furthermore, decreased with the charge passed (43 and 27%, respec-

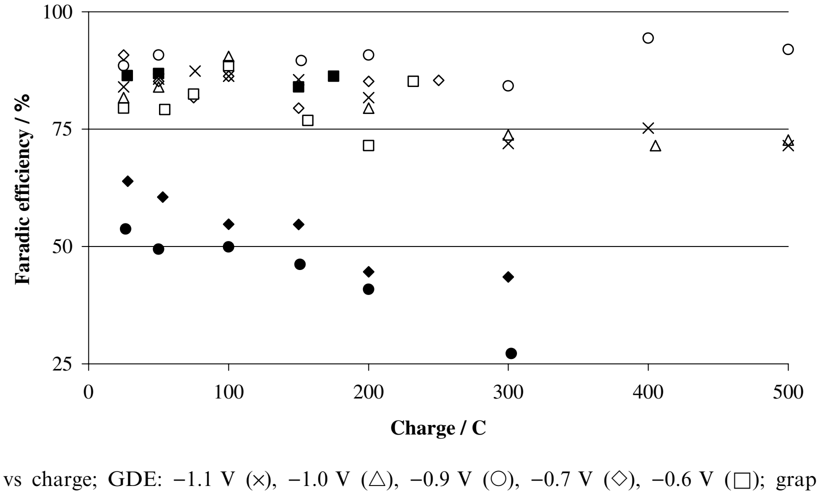

Fig. 8. Current efficiency vs charge; GDE: −1.1 V (×), −1.0 V (△), −0.9 V (○), −0.7 V (◇), −0.6 V (□); graphite electrode: −0.9 V (♦), −0.7 V (●), −0.6 V (■).

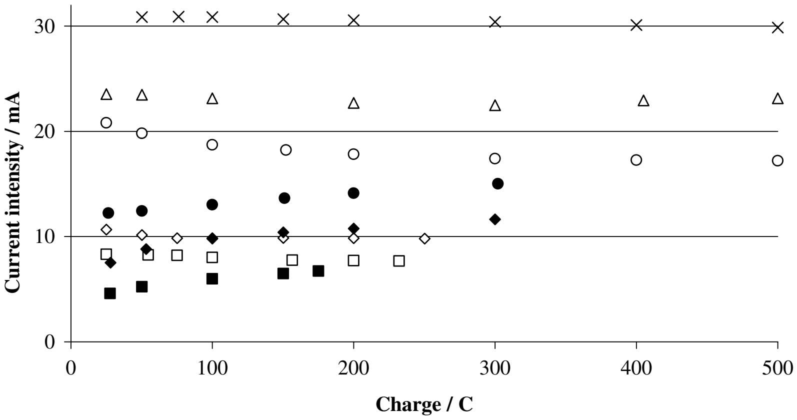

Fig. 9. Current intensity vs charge; GDE: −1.1 V (×), −1.0 V (△), −0.9 V (○), −0.7 V (◇), −0.6 V (□); graphite electrode: −0.9 V (♦), −0.7 V (●), −0.6 V (■).

tively after 300 C). Unlike the diffusion cathode, where the high selectivity for hydrogen peroxide production led to a minimisation of side reactions, in the case of the graphite cathode a strong competition of all the side reactions and especially hydrogen evolution, in accordance with Equation (9), was noted.

Considering Figure 9, it is evident that a more negative working potential produced a significant increase in the current intensity for both cathodes.

As for the graphite cathode, the potential with the best faradic efficiency led to currents, which were too low, with a subsequently unacceptable reaction time; in the case of the diffusion cathode, a potential of −0.9 V combined the maximum efficiency with notably high currents, thus representing the best compromise.

3.4. *Application to a Fenton's reaction*

The great selectivity in oxygen reduction shown by the gas diffusion cathode could compromise the iron regeneration which simultaneously occurs in a Fenton-like treatment, according to Equation (3). To investigate this problem, two identical oxidation experiments were carried out using a solution containing 100 mg l^{-1} of phosphorus as ipophosphites. In these experiments, conducted at −0.9 V hydrogen peroxide was electrogenerated while 100 mg l^{-1} of ferrous ions were added at the start of the electrolysis. The concentrations of hydrogen peroxide, ferrous ions and total iron were monitored during the electrolyses. As shown in Figure 10 both cathodes led to a quantitative oxidation of the examined ipophosphite thus confirming that the gas diffusion electrode could cathodically reduce iron ions.

Nonetheless a different trend was shown by the two curves. In particular the oxygen diffusion electrode gave an initial better oxidation efficiency which decreased with increasing charge. This behaviour can be explained by the fact that in this phase the hydrogen peroxide concentration was the limiting factor, since the run started with no initial amount of this reagent. Therefore, the gas diffusion electrode appears to be favoured having a higher rate of hydrogen peroxide production.

When the concentration of bivalent iron in the solution dropped because of the occurrence of Fenton's reaction, the regeneration of ferrous ions became the limiting step: the graphite cathode showed a better oxidation efficiency which led to complete transformation of the substrate after the passage of a lower amount of charge.

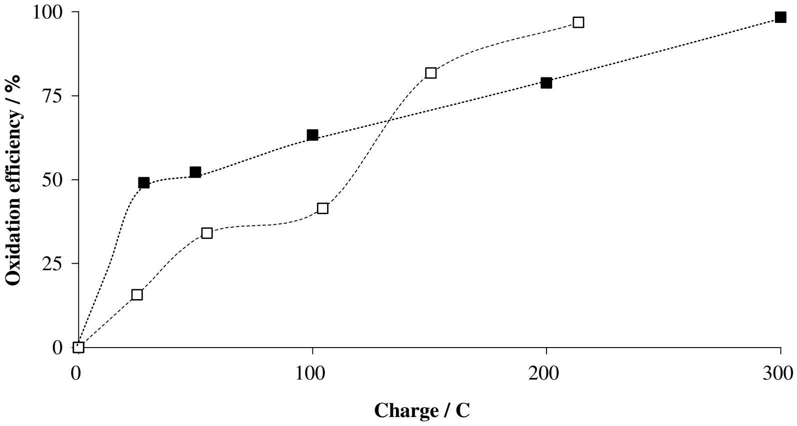

Fig. 10. Phosphorus oxidation efficiency vs charge: GDE (■), graphite cathode (□).

Monitoring of the species in solution indicated that the total iron concentration remained constant during the electrolyses and was equal to the initial added concentration. This demonstrates that the subtraction of iron by means of adsorption phenomena on the electrode surface, as well as by the formation of iron complex can be excluded, thus indicating a higher capacity of the graphite cathode to iron reduction.

4. Conclusions

The gas diffusion cathode showed a higher current efficiency in the cathodic reduction of oxygen with a high selectivity for hydrogen peroxide production, which is explained by the fact that in this electrode the diffusion of the involved species does not represent a limiting step thus minimising the occurrence of side reactions with comparable performances in a wide range of potentials.

Conversely, the graphite cathode, due to the simultaneous occurrence of several side reactions, was significantly affected by the working potential, so that the optimal value appeared to be a compromise between current efficiency and reaction time.

With a view to electro-Fenton application, the gas diffusion cathode was shown to be less effective in the reduction of ferric ions to ferrous ions but the possibility of working at a lower potential value makes it possible to test working conditions more suitable for the regeneration of iron, which is essential for the continuous production of hydroxyl radicals. A further advantage of the gas diffusion cathode is the possibility of also maintaining a high yield in air flow.

The main drawback is its short lifetime, induced by the loss of dispersed graphite from the cloth. Improvement in the characteristics of the electrode material is thus required to reduce the ageing phenomena and to enhance its application in an electro-Fenton treatment.

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