Electrosynthesis of Ferrates with Diamond Anodes

Cristina Sáez, Manuel A. Rodrigo, and Pablo Cañizares
Dept. of Chemical Engineering, Universidad de Castilla-La Mancha, Campus Universitario s/n.,
13071 Ciudad Real, Spain

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This work is focused on the electrosynthesis of ferrates with boron-doped diamond (BDD) anodes. These compounds are oxo-anions of Fe(V) and Fe(VI) with a very high oxidant potential over a wide range of pHs, and with a great variety of industrial and environmental applications. It has been observed that the use of BDD electrodes can improve the results obtained by steel electrodes in the synthesis of ferrates. However, the results seem to be limited by the availability of oxidizable iron species in the reagent solution. The production yield is revealed to be strongly dependent on the iron raw material, hydroxyl anions concentration, temperature, and current density. The use of iron-powder bed as iron-raw material increases the availability of oxidizable-iron species and therefore allows improving the efficiency of the electrosynthesis with BDD. Likewise, current densities over 1000 A m^{-2} and temperatures around 25°C guaranty high current efficiencies and ferrates concentrations. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1600–1607, 2008
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Introduction

During the recent years, the appearance of diamond thin-film electrodes has allowed the development of highly efficient electrochemical processes. In addition to the good chemical and electrochemical properties,[1,2] its main remarkable characteristic is its high overpotential for water electrolysis[3] (large enough to allow the generation of large amounts of hydroxyl radicals). This radical is a very powerful oxidant (E^0: 2.80 V vs. SHE) and it seems to be directly involved in the oxidation mechanisms that occur on diamond surfaces. For this reason, conductive diamond electrooxidation of wastewaters is now considered as an advance oxidation technology (AOP).[3] In this context, in the recent years many works have been focused on the study of the electrochemical treatment with conductive diamond anodes of synthetic[4–22] and actual[23–26] wastewaters polluted with organics, and the results obtained have been compared to those attained with other commonly used AOP.[23,24,26,27] Likewise, it has also been characterized some aspects about the oxidation mechanisms involved in the conductive diamond electrooxidation, including direct electrooxidation, hydroxyl radical mediated oxidation, and oxidation mediated by oxidants generated during the treatment (from the salts contained in the waste[28]). The combination of these oxidation mechanism can be responsible for the better results (efficiencies and mineralization ratios) obtained by this technology. In this way and once established the availability of the generation of inorganic oxidants from the oxidation of supporting electrolyte during conductive diamond electrolysis, some works has also been focused on the electrochemical synthesis with diamond anodes of powerful oxidants such as persulphates,[29] perphosphates,[30] and percarbonates.[31] The results obtained showed that the use of conductive diamond anode allows achieving great process efficiencies in comparison to more known synthesis methods.

Ferrate ion is a very powerful oxidizing reagent with a great variety of environmental applications: "green" organic synthesis,[32,33] wastewater treatment (oxidation and coagulation),[34–36] and water treatment[37,38] (persistent disinfection,

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Correspondence concerning this article should be addressed to M. A. Rodrigo at manuel.rodrigo@uclm.es.

coagulation, and oxidation of nondesirable compounds). They have also been used in super-iron battery as cathode materials.[39–42] In the recent years, several techniques have been reported for the synthesis of these oxidant reagents including thermal,[43] chemical,[37,44] or electrochemical techniques.[45–51] However, in spite of the great scientific effort carried out, the results obtained are not very promising. Electrochemical synthesis of ferrate using iron-based electrodes in alkaline solutions has shown better yields, but, they also shown important problems such as the formation of passivation layers on the surface of the electrodes.

Recently, it has been demonstrated[52] the synthesis of these oxidants with diamond anodes. In this context, the goal of this work has been to study the influence of different parameters on the generation of ferrate by conductive diamond electrooxidation. To achieve this aim, voltammetric studies and bench-scale electrolysis essays of iron solutions on BDD anodes have been carried out to characterize the mechanisms of the process and to clarify the role of the more significant parameters (temperature, concentration, pH, and current density).

Experimental

Analytical procedures

The concentration of ferrate was analyzed by the chromite method.[53] This method is based on the oxidation of chromite in strongly alkaline solutions with the ferrate (VI) ion according to Eq. 1. An aliquot of a solution containing the ferrate (VI) ion, is added to an excess of alkaline chromite solution. The chromate (VI) solution produced by the oxidation is acidified and the resulting dichromate is titrated with a standard solution of ferrous ions.

$$\mathrm{Cr(OH)_4^- + FeO_4^{2-} + 3H_2O \rightarrow Fe(OH)_2(H_2O)_4 + CrO_4^{2-} + OH^-} \quad (1)$$

Preliminary tests were carried out to detect the presence of hydrogen peroxide (according with Eisenberg (1943)[54]) and percarbonates (using a Shimadzu TOC-5050 analyzer). In addition, the stability of the oxidant discarded the presence of hydroxyl radicals, ozone, and other non-stable oxidants.

The soluble iron concentration was measured using an inductively coupled plasma LIBERTY SEQUENTIAL VARIAN according to a standard method[55] (plasma emission spectroscopy). The pH was monitored by means of the WTW-InoLab pHmeter.

Electrochemical cell

The electrosynthesis of ferrate was carried out in a double-compartment electrochemical flow cell.[30] A cationic exchange membrane (STEREOM L-105) was used to separate the compartments. Diamond-based material was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 $\mathrm{cm^2}$ 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. pH and temperature were monitored by means of LABWORLDSOFT 4.5. Temperature was also controlled by this device using a cooling fluid.

Preparation of the diamond electrode (BDD electrode)

Boron-doped diamond (BDD) films were provided by CSEM (Switzerland) and synthesised by the hot filament chemical vapour deposition technique (HF CVD) on single-crystal p-type Si ⟨100⟩ wafers (0.1 Ω cm, Siltronix). The temperature range of the filament was 2440–2560°C and that of the substrate was 830°C. The reactive gas was methane in excess dihydrogen (1% $\mathrm{CH_4}$ in $\mathrm{H_2}$). The dopant gas was trimethylboron with a concentration of 3 mg $\mathrm{dm^{-3}}$. The gas mixture was supplied to the reaction chamber at a flow rate of 5 $\mathrm{dm^3\ min^{-1}}$, giving a growth rate of 0.24 μm $\mathrm{h^{-1}}$ for the diamond layer. The resulting diamond film thickness was about 1 μm. This HF CVD process produces columnar, random texture, and polycrystalline films with an average resistivity of 0.01 Ω cm.

Preparation of the stainless steel electrode

Commercial AISI 304 stainless steel sheets were used in this work. These materials were degreased with acetone, polished with silicon carbide, and cleaned with deionized water in an ultrasonic bath. The electrodes used in the voltammetric studies were cathodically polarized at a potential of −0.5 V for 5 min, in a solution containing sodium sulphate (5000 mg $\mathrm{dm^{-3}}$) and sulphuric acid (pH 2), to remove surface oxides.

Experimental procedures

Bench scale electrolyses under galvanostatic conditions were carried out to determine the influence of the main parameters in the process. The anolyte and the catholyte consisted of NaOH or KOH solutions (concentration ranging from 5 to 14 M) with $\mathrm{Fe(OH)_3}$. Other iron salts or supporting electrolyte media were to avoid inhibit the synthesis of other oxidized species from the oxidation of the corresponding anions (such as phosphates, chlorides, or sulphates). The operation current densities ranged from 130 to 2300 A $\mathrm{m^{-2}}$, and the operation temperatures from 10 to 60°C.

Results and Discussion

Figure 1 shows the variation of the concentration of ferrate during the electrolysis of an alkaline solution (14 M NaOH) in a double compartment electrochemical flow-cell equipped with stainless steel or with boron-doped diamond anodes (in this latter case the solution was saturated with iron (III) hydroxide to provide raw iron reagent). As it can be observed, ferrates are generated in both electrolyses. However, the diamond anode achieves higher efficiencies (part b of Figure 1) and also higher concentration of ferrates. In addition, when the final solution obtained in the electrolysis with the iron anode was used as raw material for an electrolysis assay with BDD, an additional increase in the concentration of ferrate was achieved. This increase in the concentration of ferrates should be explained by the oxidation of iron species dissolved ($\mathrm{FeO_2^-}$) but not further oxidized during the iron-anode electrolyses[51] (Eqs. 2 and 3). This observation means

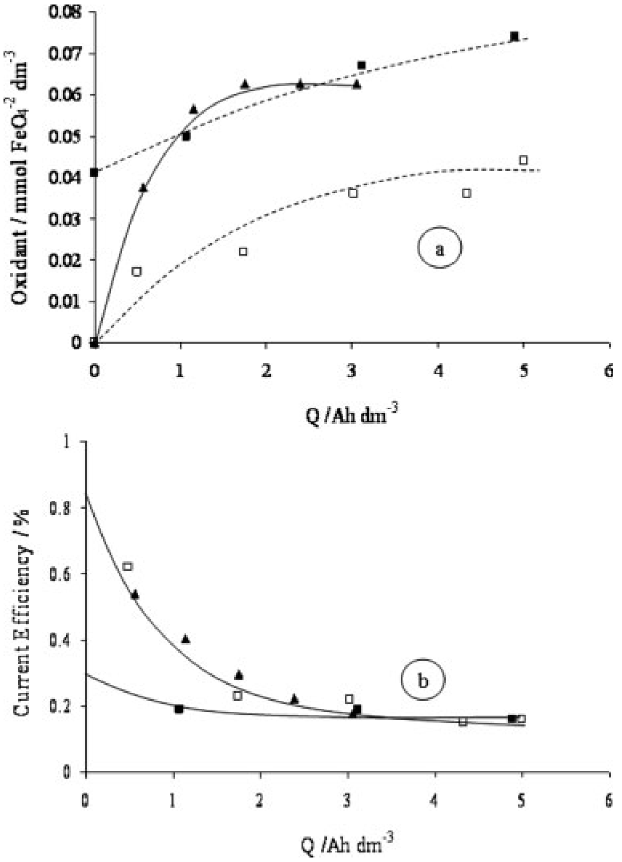

Figure 1. Variation of the ferrate concentration (a) and of the current efficiency (b) with the electrical charge passed during the electrolysis of alkaline solutions with stainless steel and boron-doped diamond electrodes (14 M NaOH; *j*: 130 A m^{-2}; *T*: 30°C).

that the use of diamond-based electrodes can improve the results obtained in the electrosynthesis of ferrates.

$$\mathrm{Fe} + 4\mathrm{OH}^- \rightarrow \mathrm{FeO}_2^- + 2\mathrm{H}_2\mathrm{O} + 3\mathrm{e}^- \quad (2)$$

$$\mathrm{FeO}_2^- + 4\mathrm{OH}^- \rightarrow \mathrm{FeO}_4^{2-} + 2\mathrm{H}_2\mathrm{O} + 3\mathrm{e}^- \quad (3)$$

Moreover, during the electrolyses an increase in the operating cell potential from 2.2 to 3.2 V was observed in the case of iron electrodes while the potentials was constant during the electrolyses with the diamond anode. According to literature,[46–48] this observation could be indicative of the passivation of the electrode surface.

Other important observation from Figure 1 is the rapid increase in the ferrates concentration during the first stages of the electrolyses. Then, the oxidation rate decreases markedly to a constant value, and the ferrate concentration starts to increase in a slower way. Consequently, the current efficiency of the electrosynthesis decreases during the electrolyses. This behavior was observed in all the experiments carried out in this work and it could be related to the available concentration of soluble iron (III) species. In this point, it is important to note that in literature[56] it is assumed that the generation of ferrate from the electrolysis of iron (III) hydroxide solutions is a complex process which consists of a sequence of three steps (chemical – electrochemical -chemical) as it is shown in Eqs. 4–6.

$$\text{Chemical reaction: } 2\mathrm{Fe(OH)}_3 + \mathrm{OH}^- \rightarrow 2\mathrm{FeO}_2^- + 4\mathrm{H}_2\mathrm{O} \quad (4)$$

$$\text{Electrochemical reaction: } \mathrm{FeO}_2^- + 4\mathrm{OH}^- - 2\mathrm{e}^- \rightarrow \mathrm{FeO}_4^{3-} + \mathrm{H}_2\mathrm{O} \quad (5)$$

$$\text{Disproportation: } \mathrm{FeO}_4^{3-} + 2\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{FeO}_4^{2-} + \mathrm{FeO}_2^- + 4\mathrm{OH}^- \quad (6)$$

Figure 2 shows the influence of the raw material concentration (obtained as a difference between the initial raw material concentration and the concentration of ferrates synthesized) on the current efficiency. In this context, the maximum concentration of soluble iron species was around 0.198 mM, which is very similar to the solubility data reported by other authors[33] for the same pH conditions. It can be observed a clear relation between both parameters. This clearly suggests that the small amounts of available iron can limit markedly the efficiency of the electrosynthesis.

Once verified the capability of generating highlyoxidized iron species from the electrolysis of alkaline iron solutions with boron-doped diamond electrodes, the influence of several operation parameters (concentration of hydroxyl ions, iron raw material, temperature, and current density) was studied.

According to literature, the stability of ferrate is very influenced by the pH of the system,[47,49,50] and ferrate salts seem to be more stable in strongly alkaline conditions. In this context, hydroxide anion concentration was found to be a key parameter in the electrosynthesis of ferrates with iron electrodes.[50] To test its influence on the electrosynthesis with BDD some electrolyses were carried out. Thus, Figure 3a shows

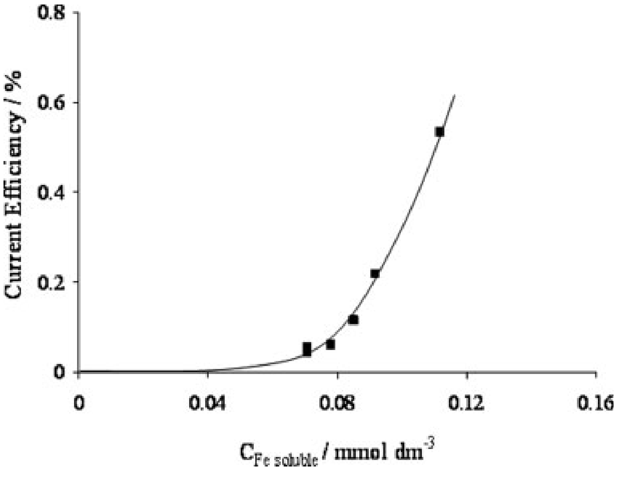

Figure 2. Variation of the current efficiency with the concentration of soluble iron to be oxidized, in the electrolysis of Fe(OH)$_3$ solutions with boron doped diamond electrodes (10 M KOH; *T*: 10°C; *j*: 1000 A m^{-2}).

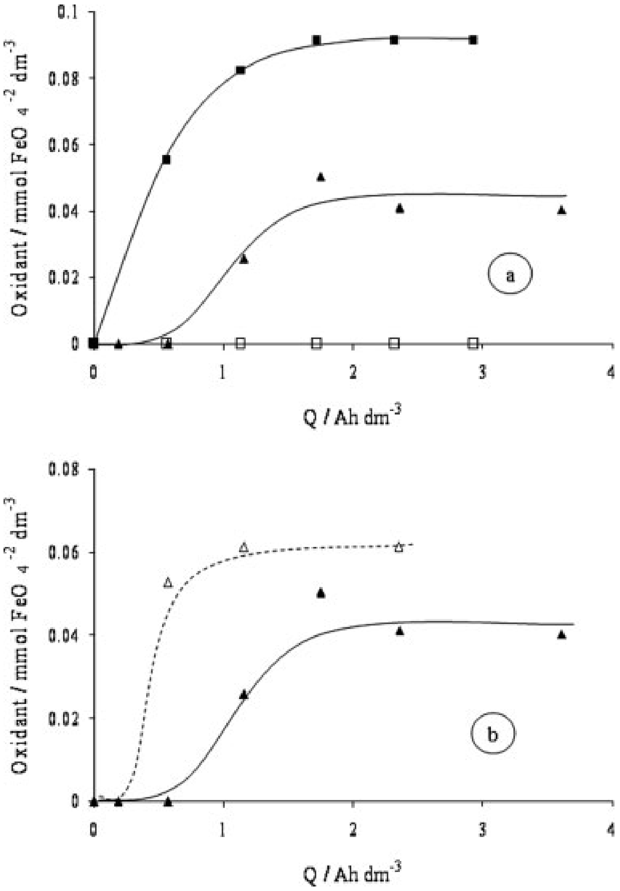

Figure 3. Variation of the ferrate concentration with the electrical charge passed, in the electrolysis of $Fe(OH)_3$ solutions with boron doped diamond electrodes (*T*: 30°C; *j*: 130 A m^{-2}).

(a) □ 5 M NaOH; ▲ 10 M NaOH and ■ 14 M NaOH. (b) ▲ 10 M NaOH and Δ 10 M KOH.

the variation of the concentration of ferrate during electrolyses carried out at different concentrations of hydroxide anions. As it is shown, the concentration of ferrate obtained strongly depends on this parameter. For low hydroxide concentrations (below 5 M) the amount of ferrate electrogenerated is negligible, but it increases markedly working at higher values. This fact seems to indicate that hydroxyl anions can have an important role in the electrolysis of alkaline iron solutions with BDD anodes. In addition, it can be observed (Figure 3b) that, at the operation conditions used, the use of KOH leads to higher ferrate concentration. As it is reported in literature[47,50] this can be related to the stability of the salt of ferrate generated (K_2FeO_4 or Na_2FeO_4) that also seems to be directly related to the hydroxide concentration of the reaction system.

Figure 4 shows the variation of the ferrates concentration with the electrical charge passed in the electrolysis of iron hydroxide solutions at different values of operation temperature (monitored at the anolyte reservoir). The concentration of ferrates obtained is strongly dependent on the temperature of the electrosynthesis, and the generation process seems to be favored at temperatures around 25°C. The observed maximum may be explained in terms of two opposite processes: the solubility of iron (III) (raw material) and the stability of ferrates. Thus, low temperature can lead to lower concentration of iron species available to be oxidized and thus to a more significant mass-transfer control. This explains the lower efficiency obtained at this operation condition. On the other hand, higher temperatures can disfavor the stability of the electrogenerated oxidant and lead to higher decomposition rates.

Figure 5 compares the concentration of ferrates electrogenerated at different current densities. It can be seen that the higher the current density, the better the results obtained. For current densities below 1000 A m^{-2}, maximum concentrations do not exceed 0.1mM, while for higher current densities concentration around 0.2 mM are obtained. This behavior has been observed previously in the electrosynthesis of other oxidants such as peroxodiphosphate[30] and it has been explained in terms[28] of the hydroxyl radical contribution. In this context, the generation of hydroxyl radicals during the oxidation of water on conductive-diamond anodes has been recently demonstrated.[3] However, there is almost no information about the particular role of this radical in the ferrates

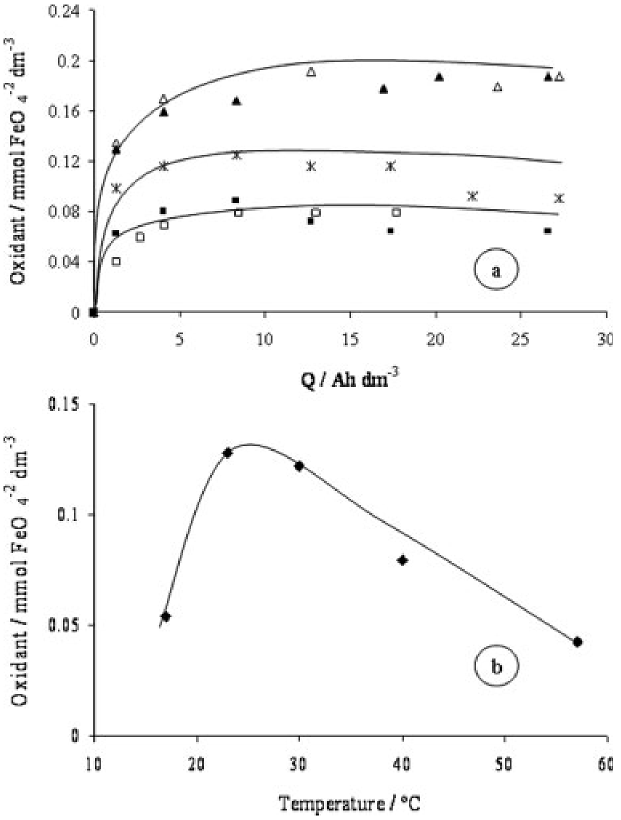

Figure 4. Variation of the ferrate concentration with the electrical charge passed and temperature, in the electrolysis of $Fe(OH)_3$ solutions with boron doped diamond electrodes (10 M KOH; *j*: 1000A m^{-2}).

(a) □ T = 17°C; Δ T = 23°C; ▲ T = 30°C; *T = 40°C; ■ T = 57°C. (b) Ferrates concentration obtained at an electrical charge passed of 1.5 Ah dm^{-3}.

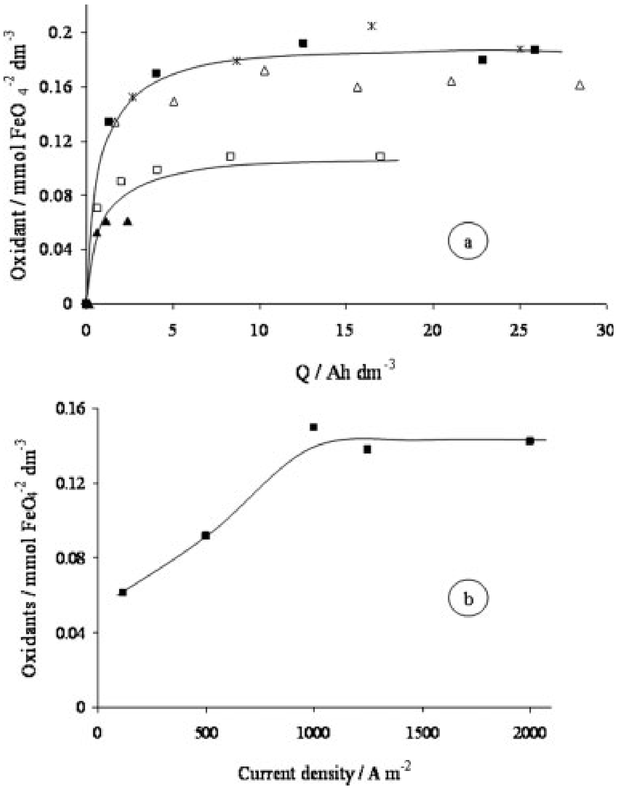

Figure 5. Variation of the ferrate concentration with the electrical charged passed and current density, in the electrolysis of $Fe(OH)_3$ solutions with boron doped diamond electrodes (10 M KOH; T: 30°C).

(a) ▲ j = 130 A m^{-2}; □ j = 500 A m^{-2}; ■ j = 1000 A m^{-2}; Δ j = 1250 A m^{-2}; *j = 2000 A m^{-2}. (b) Ferrates concentration obtained at an electrical charge passed of 1.5 Ah dm^{-3}.

formation, because works related to Fenton technology are not usually focused on this topic. In spite of this, some of these works suggest that ferrates can be even the main oxidants in the Fenton process and in some cases[57–60] the role of oxoiron (V) species produced by the interaction of hydroxyl ions with iron species has been discussed. In this point, it is important to remark that these oxoiron (V) species can be the precursors of ferrate as it is shown in Eq. 5.

In this context, and to try to obtain more information about the mechanisms involved in the generation of ferrates, Figure 6a compares the voltammetric behaviour of diamond with solutions containing sodium hydroxide in the presence and absence of iron species (dosed as iron (III) hydroxide). In both cases no peaks are observed and the small shift of the oxygen evolution does not depend on the presence of iron species, because other studies carried out in this work shows the opposite trend (as it will be shown in Figure 7). On the contrary, the concentration of hydroxide ions seems to have a significant effect (part b of Figure 6). Thus, Figure 7a shows the current density monitored for a particular anodic potential of 3.0 V vs SCE (in the same range to that used in bulk electrolytic processes). A maximum for a concentration of hydroxide ions close to 0.2 M is clearly observed. This maximum may be explained in terms of the effect of oxygen bubbles which increase significantly the resistance of the cell and hence diminish the efficiency of the hydroxyl ions oxidation. Small differences observed between the presence or absence of iron can be explained by the decrease in the concentration of hydroxyl ions caused by the dose of iron (Figure 7b). Consequently, it can be assumed that no direct oxidation of iron develops on the surface of the diamond and that hydroxyl radicals should be completely responsible of the formation of the ferrates into the system. However, more work has to be done to clarify the mechanisms that describe the role of the hydroxyl radicals on the formation of ferrates.

Hydroxyl radicals exert their action only in the thin film near the anode surface. Hence, from the mass transfer point of view there is no differences between a direct or an OH·-mediated electrochemical process, and mass transfer should be a key point to explain the results as it was pointed out in Figure 2. In this point it is important to note that the high

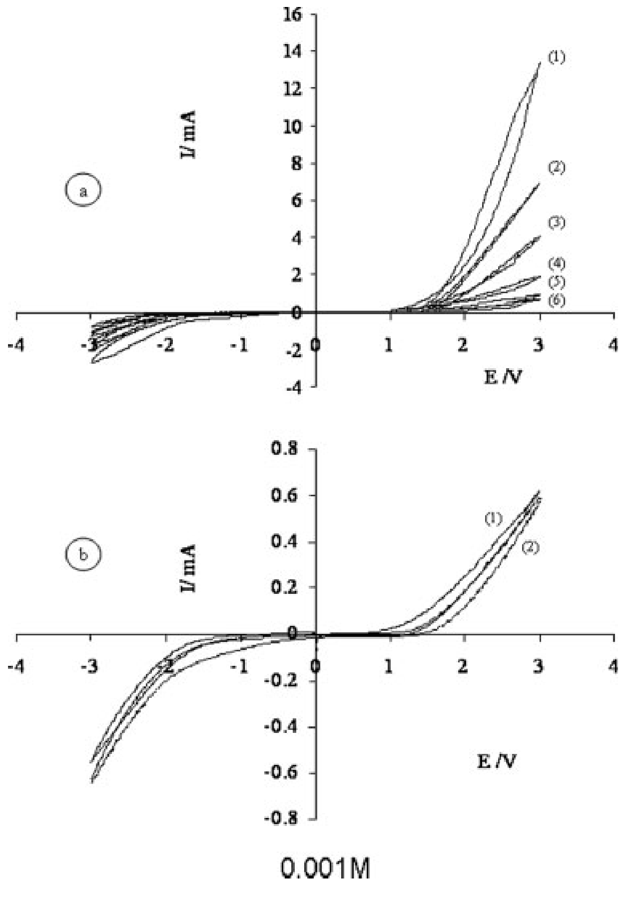

Figure 6. (a) Cyclic voltammograms on BDD anodes of hydroxide solutions (NaOH): (1) 0.2 M; (2) 0.4 M; (3) 0.1 M; (4) 0.6 M; (5) 0.8 M; (6) 0.01 M; (b) cyclic voltammograms on BDD anodes of hydroxide solution (0.001 M NaOH): (1) saturated with $Fe(OH)_3$; (2) without $Fe(OH)_3$.

Auxiliary electrode: Stainless steel AISI 304. Reference electrode: SCE. Scan rate: 100 mV s^{-1}.

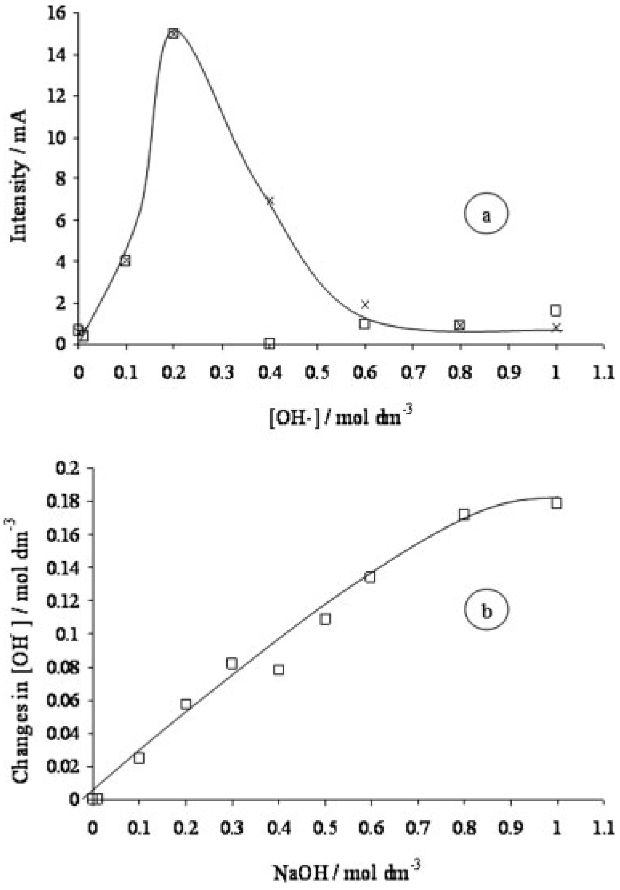

Figure 7. (a) Variation of the intensity (at an anodic potential of 3 V vs, SCE) with the hydroxide concentration; (b) changes in the pH due to the presence of iron vs. the sodium hydroxide concentration.

current densities used in the electrolyses promote the generation of large amounts of oxygen bubbles on the anodic compartment and this increases the turbulence and enhances significantly mass transfer. In fact, some preliminary essays with a ferro/ferrricyanide test shows that the influence of the flowrate on the mass transfer is very limited within the conditions used. This means that only the increase in the concentration of reactant can help to increase mass transfer. Thus, to increase the availability of oxidizable-iron species and therefore to improve the efficiency of the electrosynthesis with BDD, several electrolyses using a modified cell were carried out. To do this, an iron-powder bed was used as iron reagent and placed near to the anode surface (separated of the anode surface by means of a very thin plastic mesh). During the electrolysis of aqueous solutions, the oxygen evolution that takes place on the anodic surface consumes large amounts of hydroxyl anions. This fact leads to changes in the pH in a region very close to the anode surface that can favor the chemical dissolution of the iron particles.[61] This would increase the amount of iron ionic species in the reaction system (coming from the dissolution of iron particles) and consequently, the efficiencies of the electrosynthesis of ferrate. Figure 8a shows the variation of the ferrate concentration with the electrical charge passed during the electrolysis of a hydroxide solution (10 M KOH) using iron-powder as raw iron. As it can be observed, high ferrates concentrations are obtained (one fold higher than those obtained with $Fe(OH)_3$) although the initial generation rate seems to be lower than in the other case. Likewise, as it is shown in Figure 8b, the operation current density and operation temperature influence the efficiency of the electrosynthesis process in the same way than those previously explained.

At the light of the good results obtained it can be affirmed that the electrochemical oxidation with BDD anodes of hydroxide solutions containing soluble iron species can be successfully used to generated ferrate. Likewise, these results help to confirm that the process is only limited by the availability of iron reagents. However, it is very important to advice against the stability of the diamond surfaces at very alkaline pHs. In some cases, the appearance of small corrosion circles on the diamond surface after the treatment has been observed. This fact can become an important drawback for this technology, and consequently a great effort in the

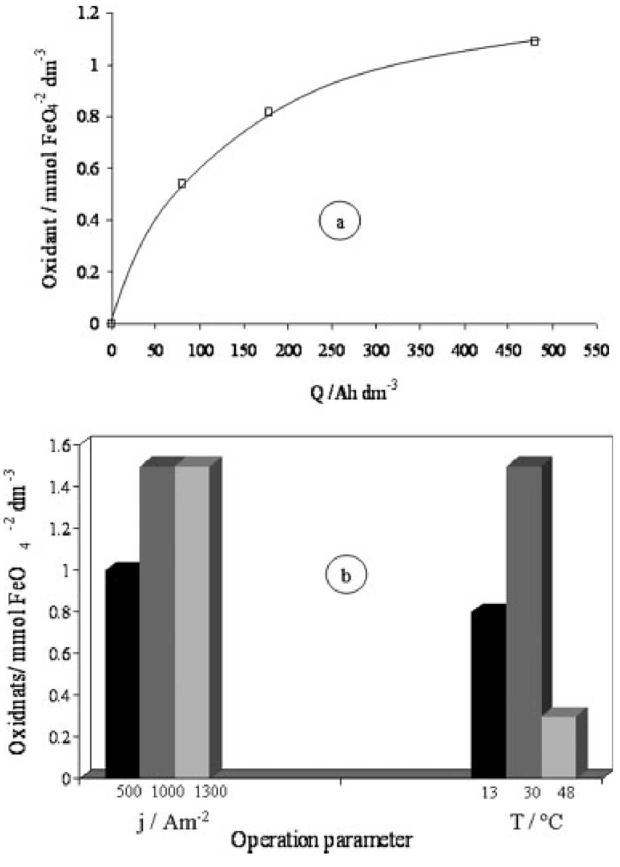

Figure 8. (a) Variation of the ferrate concentration with the electrical charged passed during the electrolysis of hydroxide solutions using iron-powder as raw material. (10 M KOH, *T*: 30°C; *j*: 1000 A m^{-2}); (b) concentration of ferrate electrogenerated at a given electrical charge passed as a function of the current density and temperature.

synthesis of conductive diamond stable in strongly alkaline conditions should be made.

Conclusions

From this work the following conclusion can be drawn:

– The electrolysis with boron-doped diamond anodes of hydroxide solutions saturated with iron (III) hydroxide leads to the generation of significant amounts of ferrates.

– The use of diamond-based electrodes can improve the results obtained by electrolyses of steel electrodes, but the results of the process in the former case seem to be limited by the availability of oxidizable iron species in the reagent solution.

– The concentration of hydroxide anion was found to be key parameters in the results obtained during the electrosynthesis of ferrates with diamond electrodes. Low hydroxide concentrations leads to the electrogeneration of negligible ferrates concentrations.

– The use of iron-powder bed as iron raw material increases the availability of oxidizable-iron species, and therefore allows improving the efficiency of the electrosynthesis with BDD. Likewise, current densities over 1000 A m^{-2} and temperatures around 25°C guaranty high current efficiencies and ferrates concentrations.

Acknowledgments

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