ELECTROCHEMICAL OXIDATION OF Cu-EDTA ON BORON DOPED DIAMOND (BDD) ELECTRODE

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ABSTRACT

The electrochemical oxidation of Cu-EDTA was investigated on boron doped diamond. That electrode presents a wide potential window with the onset of the potential of oxygen evolution at ca. 2,5V. The BDD electrode presents a polycrystalline structure. XPS spectrum is dominated by C1s peak. The surface chemical bonds determined by the deconvolution of C1s leads to C-C, C-O, C=O, C-H and C-Si at 284,24eV, 284,73eV, 285,61eV, 283,45eV and 282,81eV respectively. Cyclic voltammetry investigations made in the supporting electrolyte ($NaClO_4$) at different pH leads to an oxidation peak at pH>10. That peak has been assigned to the oxidation of non-diamond (Csp^2) impurity that exists in the diamond grain boundaries in alkaline electrolyte.

Cu-EDTA oxidation led to the appearance of an irreversible oxidation peak at a potential more positive than that observed on free EDTA oxidation voltammogram in acidic electrolyte. The oxidation peak increases linearly with EDTA concentration and also with the square root of the potential sweeping rate. The electrochemical reaction before oxygen evolution potential domain is a diffusion controlled process. For EDTA concentration lower than that of copper ions in the $EDTA:Cu^{2+}$ mixture i.e. $EDTA:Cu^{2+}$ concentration ratio ($\leq1:1$), only one oxidation peak is observed but for EDTA concentration higher than that of copper ions i.e. $EDTA:Cu^{2+}$ concentration ratio (>1:1), two oxidation peaks appeared. Increasing only the concentration of copper ions in the $EDTA:Cu^{2+}$ mixture, no modification on the voltammogram is observed. During Cu-EDTA electrochemical oxidation process, dissociation of Cu-EDTA occurs and reduction of copper ions happens on the cathode (counter electrode) and EDTA oxidation occurs on the anode (working electrode) in the linear voltammetry method.

KEYWORDS: chelating agent, copper, EDTA, electrochemical oxidation, boron doped diamond

INTRODUCTION

EDTA (ethylenediaminetetraacetic acid) belongs to the organic pollutants which is released to natural waters in large amounts from industrial and domestic sources and cannot be removed easily either by conventional biological or by chemical wastewater treatment(Kari, et al., 1975, p: 1035,Siemion, et al., 2002, p: 247). Its chelated form with copper ions is widely used in the electroless copper process (Spearot, et al., 1984, p: 127). The main function of this complex is to stabilize the copper ions so that the electrolyte can remain stable within a wide pH range. However, this causes difficulty in the related effluent treatment.

Some works about the treatment of such effluent have been investigated where the authors tried to add ferrous ions to replace copper ions in the chelated molecules and then raised the pH to form $Cu(OH)_2$ precipitate. At the end, EDTA remained in the solution(Licsko, et al., 1986, p: 19). Thus, the complexing agents complicate the treatment of industrial effluents (Tunay, et al., 1994, p: 265). These problems lead to search for effective treatment processes. The treatment methods depend greatly on the particular complexing agent and metals and their concentrations(Martin, et al., 1996, p: 23,Mohamed, 1996, p: 741,Ruey, et al., 2000, p: 3179,Simonsson, 1997, p: 181). Some attempts have been made using electrochemical techniques in a divided and undivided electrochemical cell on platinum electrode(Johnson, et al., 1972, p: 574). Electrode surface oxide formation and oxygen evolution reaction during the investigation decreases its electrochemical activity and also the current efficiency.

To avoid such a problem, our interest was made on the use of a new electrode material such as boron doped diamond. In fact synthetic boron-doped diamond thin film electrodes (BDD) deposited on p-Si substrates are known to have a wide potential window for water discharge, low background of current density and a high anodic stability. It is therefore a promising material for the electrochemical oxidation of organic pollutant(Gandini, et al., 2000, p: 1,Gandini, et al., 1999, p: 303,Iniesta, et al., 2001, p:

3573,Iniesta, et al., 2001, p: 346,Michaud, et al., 2000, p: 77,Ouattara, et al., 2003, p: 97).

In this work, voltammetry investigation of the chelated form Cu-EDTA will be made on the boron doped diamond electrode.

Experimental procedure

Boron doped diamond (BDD) films were grown on conductive p-Si substrate (1-3 mΩ.cm, Siltronix) via the hot filament chemical vapour deposition technique (HF CVD). The temperature range of the filament was 2440-2560°C and that of the substrate was monitored at 830°C. The reactive gas used was 1% methane in hydrogen containing 1-3 ppm of trimethylboron. The gas mixture was supplied to the reaction chamber with a flow rate of 5 L min^{-1} giving a growth rate of 0,24 μm h^{-1} for the diamond layer.

The obtained diamond film thickness was about 1 μm with a resistivity of 20-30 mΩcm. This HF CVD process produces a columnar, random textured, polycrystalline films on conductive p-Si substrate.

BDD surface characterization has been performed physically using a (SEM, JEOL JMS 6300F) scanning electron microscope for SEM images and the surface bonds were analyzed by XPS using a Kratos Axis-Ultra spectrometer with a monochromatic Al K_α X-Ray source, operated at 15 kV and pass energy of 20 eV. Carbon C1s spectrum was deconvoluted using the CasaXPS computer program.

Linear and cyclic voltammetry measurements of the Cu-EDTA solution with different concentration were carried out in an undivided three electrodes electrochemical cell. The working electrode and the counter electrode were BDD and spiral platinum wire respectively. The reference electrode was a saturated mercuric sulphate electrode.
The voltammetric investigations were carried out using a potentiostat-galvanostat-Autolab PGStat-30 and the potential are all referred to normal hydrogen electrode (NHE).
Linear voltammetry was adopted to avoid the probable deposition of copper metal on the active sites of BDD in the reverse sweeping potential in the cyclic voltammetry method.

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All the chemicals used in this work were reagent grade and they were supplied from Fluka GmBH.

The pH of the electrolyte was adjusted using droplets of concentrated $HClO_4$ and NaOH.

RESULT AND DISCUSSION

Physical characterization of the BDD surface

Figure 1 presents SEM (scanning electron microscopy) images of the surface morphology of the BDD electrode. The electrode consists of a polycrystalline diamond film of randomly oriented crystallites with well-developed triangular (111) facets. The arrangement of the crystallites sizes makes the electrode surface to be rough.

X-ray photoelectron spectra of the diamond film to determine the elemental composition of the surface is presented on figure 2. The survey spectrum of the BDD reveals in addition to the presence of a large peak of C1s located at 285eV only a very small peak due to O 1s core level at 532,5 eV.
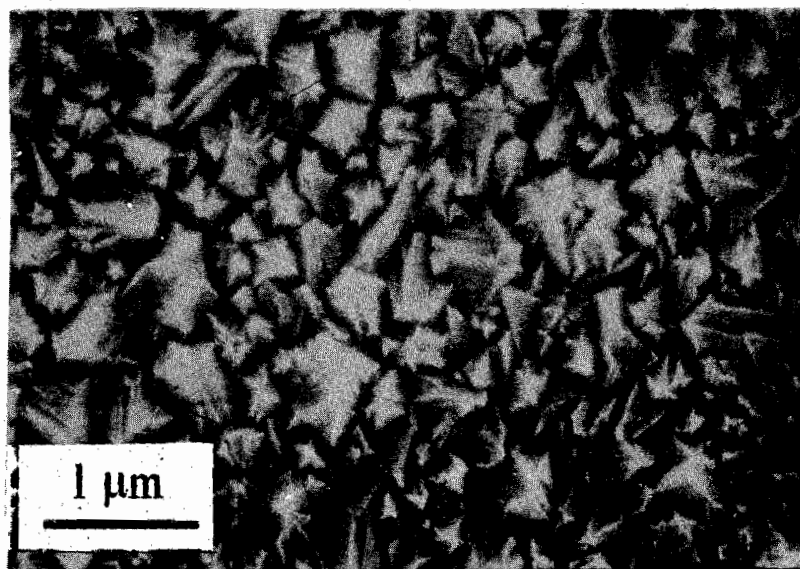

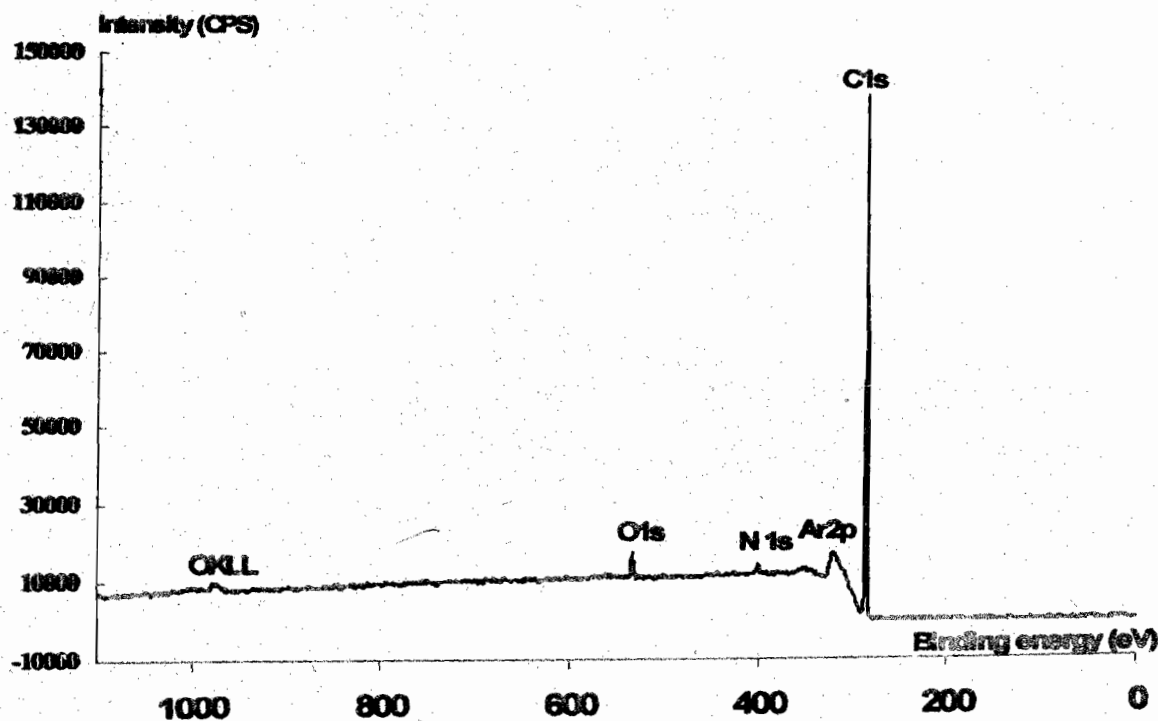Figure 1 : SEM micrograph of BDD electrode

Figure 2: XPS spectrum of BDD surface

The surface chemical bonds were investigated by the deconvolution of C1s spectra (figure 3). On that figure, the deconvolution leads to five peaks at 284,24eV, 284,73eV, 285,61eV, 283,45eV and 282,81eV. They are assigned to C-C, C-O, C=O, C-H and C-Si bonds respectively.

**Electrochemical measurements in the supporting electrolyte (NaClO₄)**

Figure 4 indicates that water decomposition leading to oxygen evolution occurs at higher potential around 2,5V in low acidic media (pH=5,3). The inset of figure 4 shows the whole potential domain between hydrogen and oxygen evolution on BDD. Decreasing the pH to ca. 1, the voltammograms do not change. But increasing the pH to 10, one observes the appearance of a shoulder on the voltammogram. That phenomenon became more important when the pH attained ca. 11 where a peak is observed.
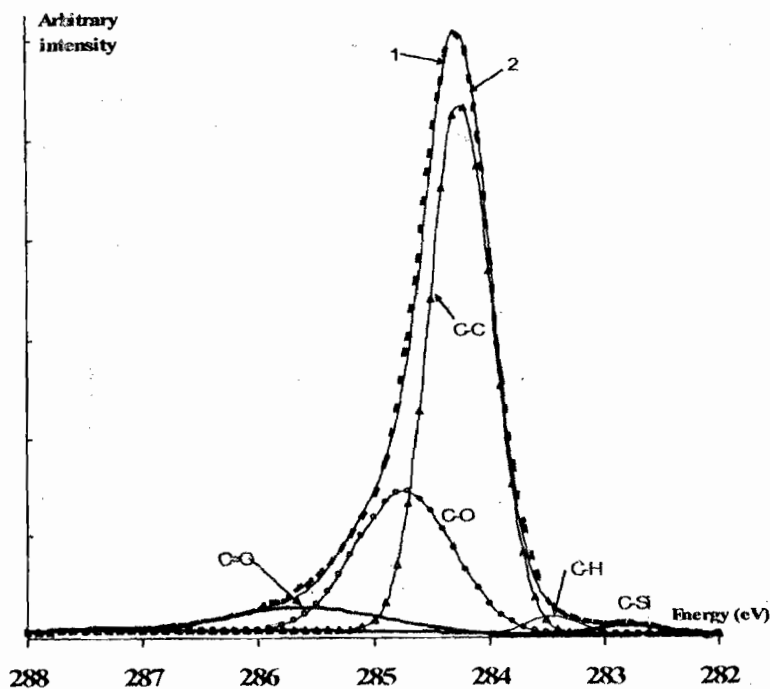
Figure 3: Result of the C1s deconvolution by Casa XPS

1: dashed line corresponds to the envelope of C1s spectrum

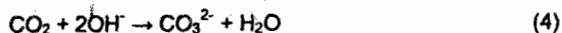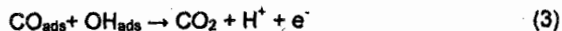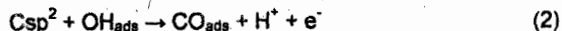2: solid line corresponds to the sum of all the curves resulted from C1s deconvolution
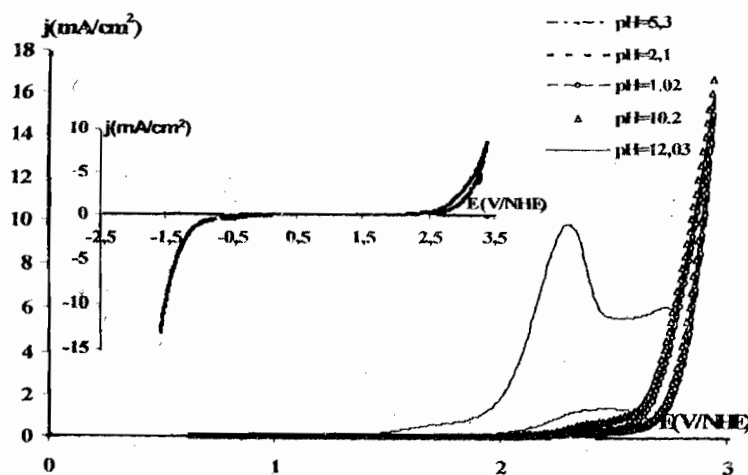
Figure 4: Cyclic voltammetry of BDD in NaClO₄ 1M at different pH, 100mV/s, 25°C

The inset: Cyclic voltammetry of BDD in NaClO₄ (pH5) between oxygen and hydrogen evolution reaction, 100mV/s, 25°C

In fact, in the acidic media, the obtained results could be explained by the fact that there's no change on the BDD surface. These results are in agreement to that obtained in perchloric acid and in sulphuric acid(Duo, et al., 2003, p: 183,Ouattara, et al., 2003, p: 97,Panizza, et al., 2003, p: D17,Rodrigo, et al., 2001, p: D60). It could indicate the stability of BDD in that medium. But, the observation made on the voltammograms in alkaline media could be explained by the oxidation of adsorbed species. In fact, Duo and al. have already pointed out the existence of few amount of Csp^2 in the grain boundary of BDD surface contributing in the electrode activity enhancement(Duo, et al., 2003, p: 695).

The mechanism detail that can explain the modification on the voltammogram at higher pH is assumed to be given as followed:

$$OH^- \rightarrow OH_{ads} + e^- \tag{1}$$

$$Csp^2 + OH_{ads} \rightarrow CO_{ads} + H^+ + e^- \tag{2}$$

$$CO_{ads} + OH_{ads} \rightarrow CO_2 + H^+ + e^- \tag{3}$$

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \tag{4}$$

Indeed, hydroxide ions adsorbed on the BDD surface in the form of OH_{ads} (1). These adsorbed species react with Csp^2 leading to adsorbed CO (2) and then reaction

between adsorbed species, CO_{ads} and OH_{ads}, occurs leading to CO_2 (3). Diffusing in the bulk of the alkaline electrolyte, CO_2 is transformed to CO_3^{2-} according to equation (4).

However to avoid that influence on the oxidation of EDTA and its related metal complex, all our investigations will be made in acidic electrolyte.

Linear voltammetry of EDTA in the domain of oxygen evolution

Linear voltammetry measurements have been undertaken in EDTA containing electrolyte and in electrolyte free of EDTA and the result is presented on figure 5. One observer that the current starts to increase at ca. 1,6V and an oxidation peak appears at ca. 1,8V. On the inset of that figure, cyclic voltammetry measurement indicates only an irreversible peak on the whole potential domain investigated. Comparing the voltammograms on figure 5 (a and b), one observes that in the presence of EDTA the overpotential of oxygen evolution decreases.

Indeed, these observations can be explained by the fact that EDTA oxidation proceeds by a simple electron transfer process at the electrolde/electrolyte interface and also by the hydroxyl radicals produced via electrochemical water decomposition (Gandini, et al., 2000, p: 1,Gandini, et al., 1999, p: 303).
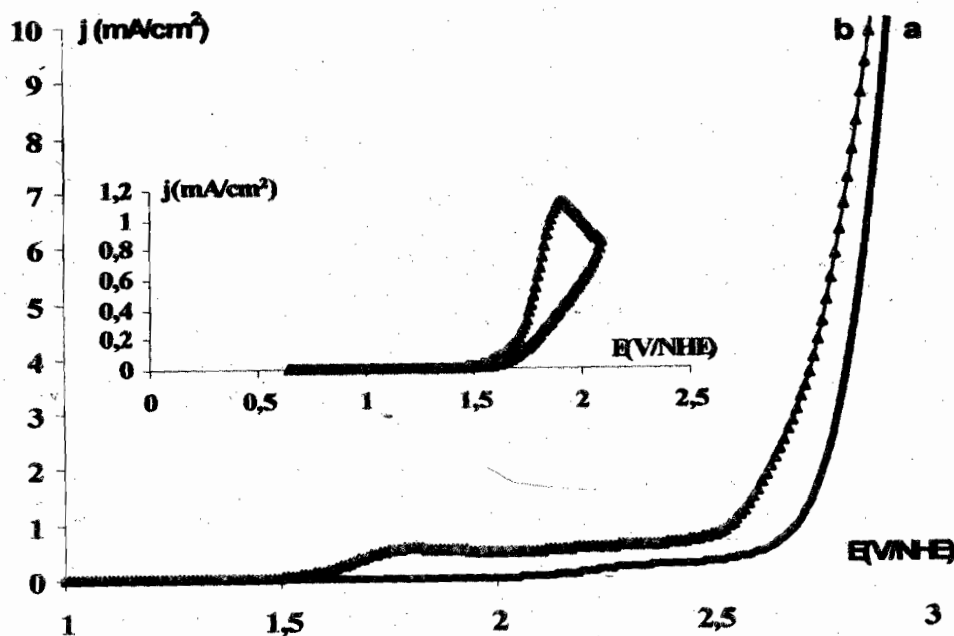
Figure 5: Linear voltammetry of EDTA oxidation on BDD, 100mV/s, 25°C, pH4

(a): $NaClO_4$ 1M

(b): $NaClO_4$ 1M + EDTA 1mM

The inset: Cyclic voltammetry of EDTA oxidation on BDD electrode, 100mV/s, $NaClO_4$ 1M + EDTA 1mM, pH4

Linear voltammetry study in Cu-EDTA solution before the domain of oxygen evolution

In the case of the chelated form of EDTA with copper in the equimolar concentration ratio of $EDTA:Cu^{2+}$ (1:1), one oxidation peak is observed in the sweeping potential domain of 0 to 2,5V before oxygen evolution reaction. The oxidation process is therefore irreversible. In the electrolyte containing the complexed form of EDTA, the peak oxidation potential is shifted to more positive value almost equal to 2,2V(figure 6).

Increasing the concentration of copper ions from the equimolar concentration ratio (1:1) to (1:8), no significant change is observed on the voltammogram (figure 7). But, the variation of EDTA concentration modifies significantly the current intensity on the voltammograms. The current intensity increases as the concentration of EDTA increases (figure 8). When the EDTA concentration is lower than that of copper ions, i.e. concentration ratio ($\leq$1:1), one oxidation peak is observed but for concentration of EDTA higher than
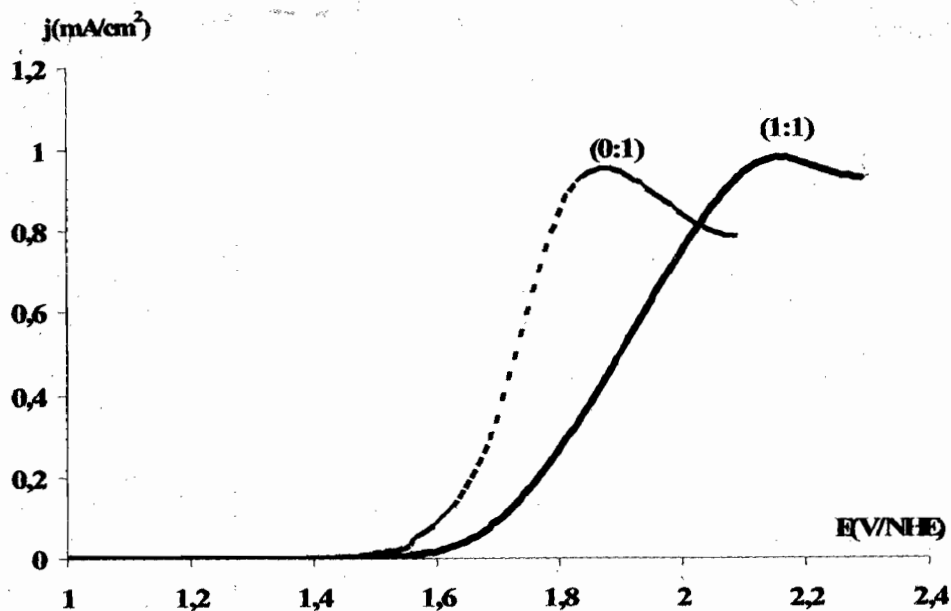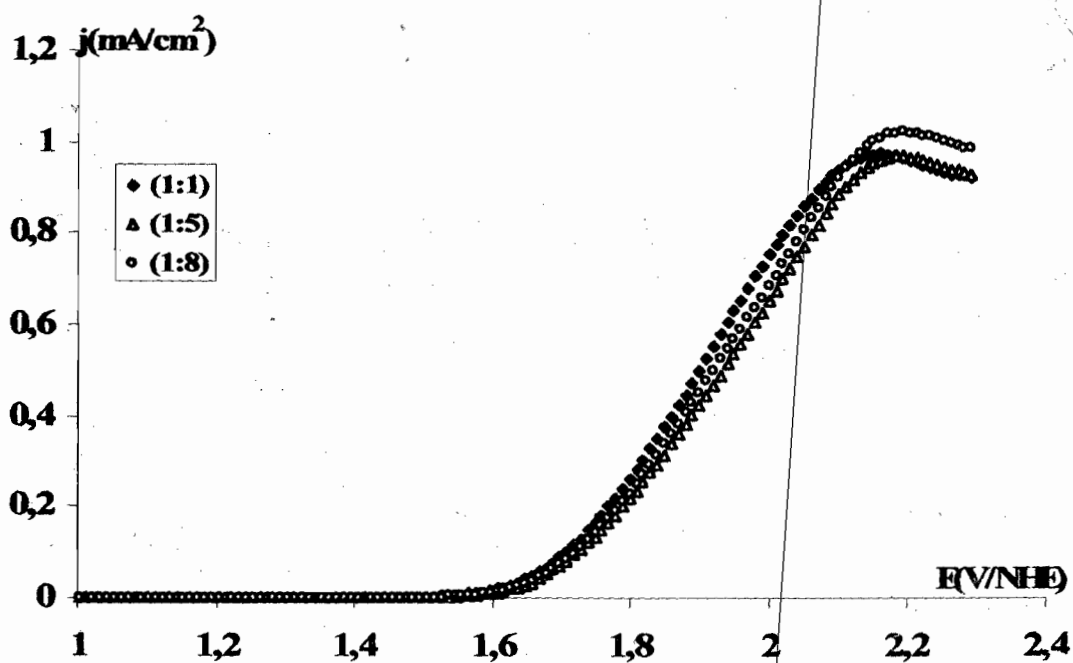
Figure 6: Linear voltammetry of Cu-EDTA and EDTA oxidation on BDD electrode, pH4

(0:1): corresponding to 1mM of free EDTA

(1:1): corresponding to equimolar concentration ratio (1mM:1mM)

100mV/s, 25°C

Figure 7: Influence of the concentration of copper ions on the chelated Cu-EDTA oxidation, 100mV/s, 25°C
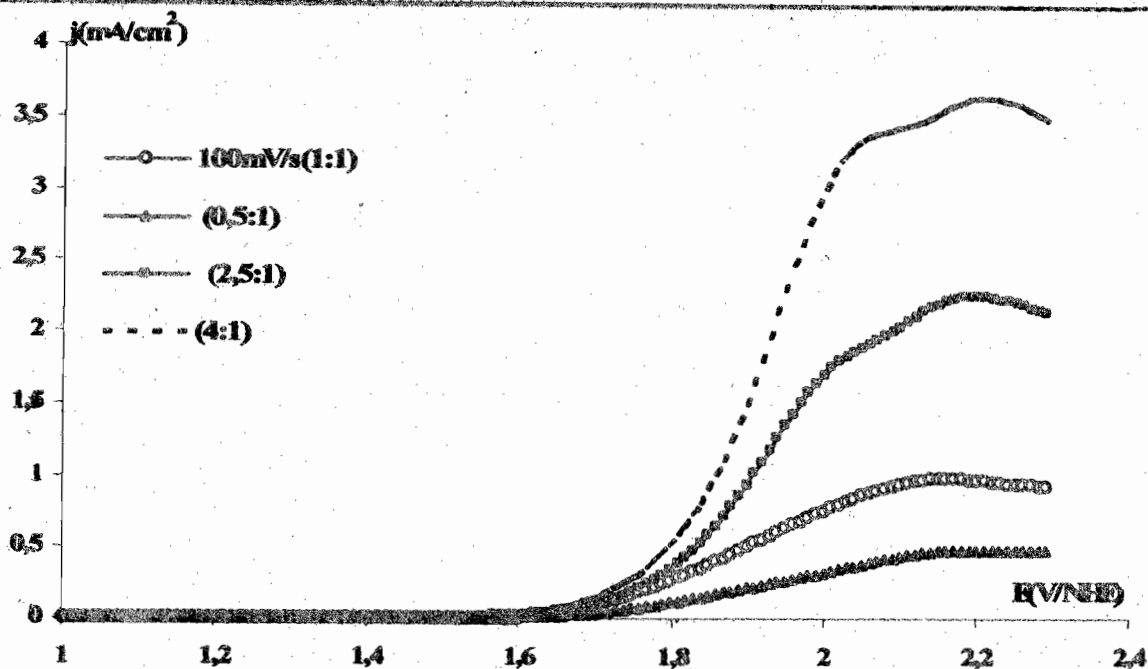
Figure 8: Influence of EDTA concentration on the chelated Cu-EDTA oxidation, 100mV/s, 25°C, pH4

that of copper ions, i.e. concentration ratio (>1:1), two peaks are observed. One peak appeared at the potential ca. 1,9V and the second peak at around 2,2V.

The peak current density (at ca. 2,2V) increases linearly with EDTA concentration (figure 9). That led to a diffusion coefficient of the electroactive species of $2,2 \times 10^{-8} m^2/s$ calculated using the slope of the straight line and equation (5)(Bard, et al., 1983).

$$i_p = 2.99 \times 10^5 \alpha^{\frac{1}{2}} A C_0 D^{\frac{1}{2}} v^{\frac{1}{2}} \qquad (5)$$

where i_p : peak current intensity, α =0,5: charge transfer coefficient, A: electrode area, C_0: electroactive species concentration, D: electroactive species diffusion coefficient, v : potential sweeping rate.
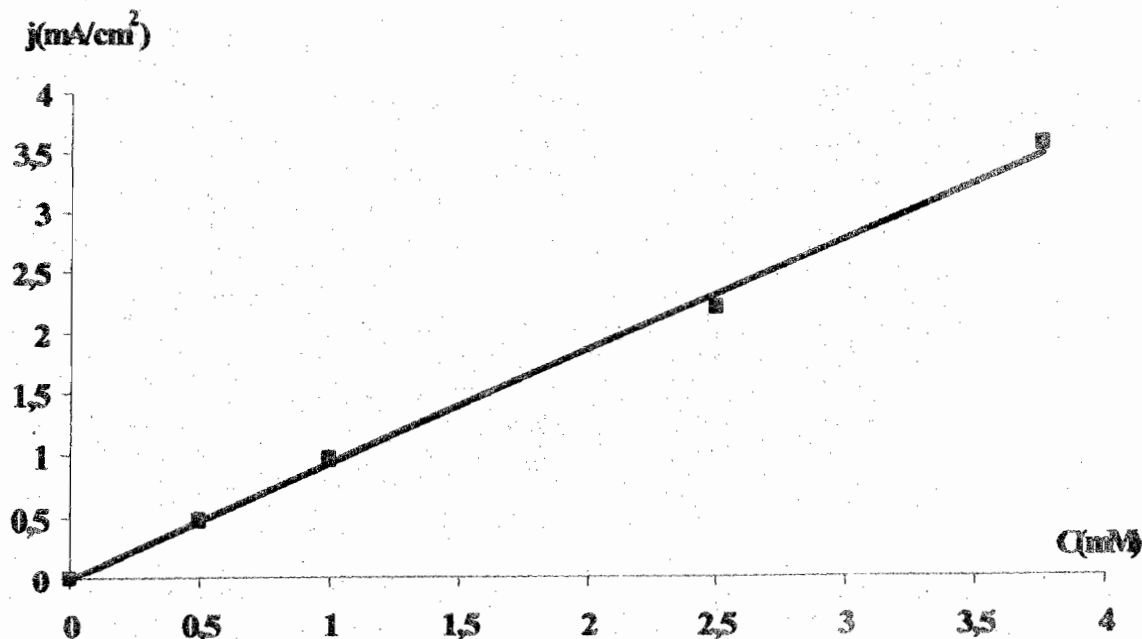

Figure 9: Evolution of the Cu-EDTA oxidation peak current density at ca. 2.2V versus EDTA concentration, 100mV/s, 25°C, pH4

Increasing the potential sweeping rates for the EDTA: Cu^{2+}, concentration ratio (1:1), the peak current density increases (figure 10). Plotting the current density against the square root of the potential sweeping rate, a linear straight line is obtained (figure 11). That led to a diffusion coefficient of the electroactive species of $2,07 \times 10^{-8} m^2/s$ calculated with equation (5). This value is almost the same as that obtained when the concentration of EDTA was increased.

In fact, in aqueous electrolyte the dissociation state of EDTA influences its electrochemical oxidation. Therefore for the mixture that contains an excess of EDTA, a superimposed phenomenon is observed such as the oxidation of uncoordinated ligand (free EDTA) and coordinated ligand (Cu-EDTA). Cu-EDTA oxidation reaction is a diffusion controlled process according to the obtained result. A simple electron transfer reaction occurs either the oxidation concerns EDTA or its chelated form. The
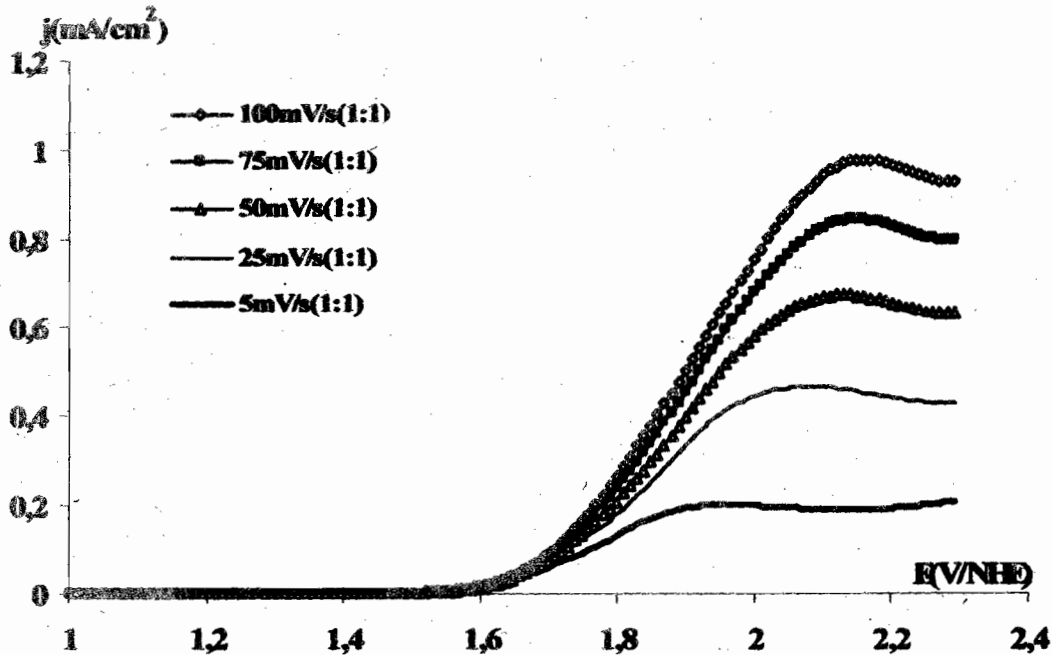

Figure 10: Influence of the sweeping potential rate on Cu-EDTA oxidation, 100mV/s, 25°C, pH4
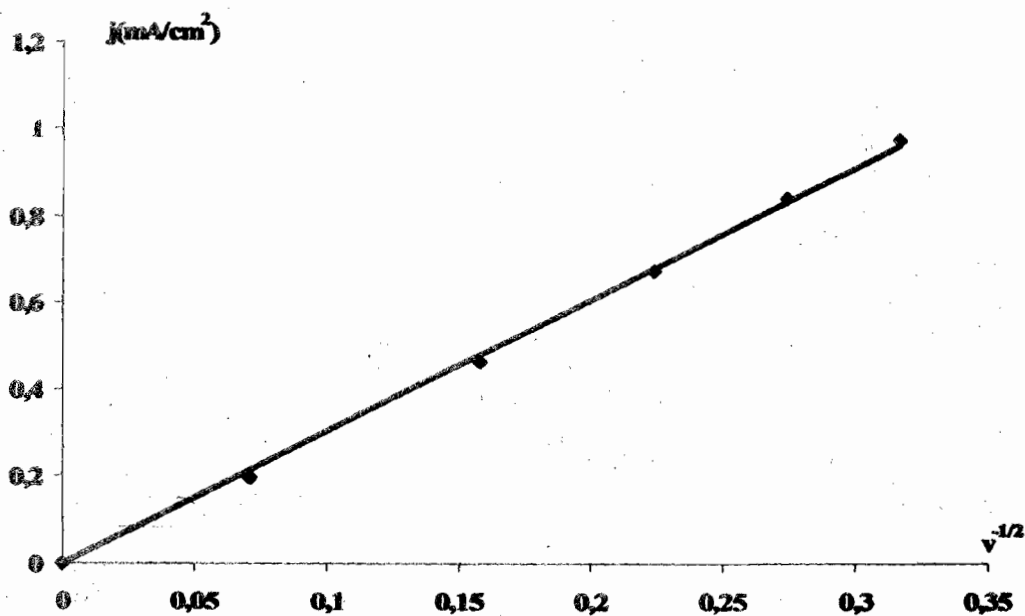

Figure 11: Evolution of the Cu-EDTA oxidation peak current density versus the square root of the sweeping potential rate, Cu-EDTA equimolar concentration ratio (1:1), 25°C, pH4

calculated diffusion coefficient of the electroactive species is in agreement to the obtained value of the literature(Ouattara, et al., 2003, p: 97).

Based on the findings of Duo et al., charge transfer reaction at BDD electrode occurs mostly via the non diamond impurities (Csp^2) that exist on the diamond grain boundaries. The surface chemical bonds investigated led to the existence of C=O (quinonic form), C-O (phenolic form) which are characteristic of the presence of Csp^2. Their presence in the diamond grain boundaries facilitates the simple electron transfer reaction between EDTA, Cu-EDTA and the electrode.

In the presence of copper ions, the chelated form of EDTA is obtained as below:

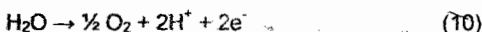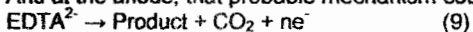$$Cu^{2+} + EDTA^{2-} \rightarrow Cu\text{-}EDTA \tag{6}$$

In the electrochemical process, the working electrode acts as an anode and the counter electrode acts as a cathode since the linear voltammetry method is employed.

So that at the cathode, the following equation could happen:

$$Cu\text{-}EDTA + 2e^- \rightarrow Cu + EDTA^{2-} \tag{7}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{8}$$
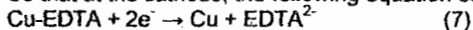
And at the anode, that probable mechanism could occur

$$EDTA^{2-} \rightarrow Product + CO_2 + ne^- \tag{9}$$

$$H_2O \rightarrow \tfrac{1}{2} O_2 + 2H^+ + 2e^- \tag{10}$$

According to (Oldham, et al., 1994, p: chap. 9), step (7) could be divided in two steps as followed:

$$Cu\text{-}EDTA \rightarrow Cu^{2+} + EDTA^{2-} \tag{11}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \tag{12}$$

That result implies that in step (11) the chelated forms of EDTA are destroyed, possibly on the outside of the electric double layer of the cathode before the metals are deposited onto the cathode. Then after, the ligands (EDTA) diffuse to the anode to be oxidized. Steps (8) and (10) are the side reactions that occur on the cathode and on the anode respectively.

CONCLUSION

Boron doped diamond electrode presents a polycrystalline structure and its XPS spectrum is dominated by C1s peak. The surface chemical bonds determined by the deconvolution of C1s leads to C-C, C-O, C=O, C-H and C-Si at 284,24eV, 284,73eV, 285,61eV, 283,45eV and 282,81eV respectively. Its electrochemical characterization in $NaClO_4$ indicated a wide potential window with the onset of the potential of oxygen evolution at ca. 2,5V.

Cyclic voltammetryic investigations made in the supporting electrolyte ($NaClO_4$) at different pH leads to an oxidation peak at pH>10. That peak has been assigned to the oxidation of non-diamond (Csp^2) impurities that exist in the diamond grain boundaries.

The obtained results indicated that it is possible to oxidize electrochemically Cu-EDTA on boron doped diamond. EDTA oxidation process is a simple electron transfer reaction in the potential domain of water stability and is oxidized by hydroxyl radicals in the potential domain of water decomposition.

Cu-EDTA oxidation led to the appearance of an irreversible oxidation peak at a potential more positive than that observed on free EDTA oxidation voltammogram. The oxidation peak increases linearly with EDTA concentration and also with the square root of the potential sweeping rate. The electrochemical reaction before oxygen evolution potential domain is a diffusion limited process. For EDTA:Cu^{2+} concentration ratio about (≤1:1), only one oxidation peak is observed but for a mixture ratio about (>1:1), two oxidation peaks appeared indicating that a

superimposed phenomenon such as the oxidation of uncoordinated ligand (free EDTA) and coordinated ligand (Cu-EDTA) occurs. During the electrochemical process, using linear voltammetry method, copper reduction occurs on the cathode (counter electrode) and EDTA oxidation occurs at the anode (working electrode) Increasing the concentration of the copper ions do not modify the voltammograms.

REFERENCES

Bard, A. J. and Faulkner, L. R.,1983. electrochimie: principes, méthodes et applications. Paris New York barcelone, mexico Sao Paulo, Masson.

Duo, I. and Comninellis, C., 2003. control of electron transfer kinetics at boron-doped diamond electrodes by specific surface modification. chemical et electrochemical engeneering. Lausanne, EPFL: 183.

Duo, I., Fujishima, A. and Comninellis, C.,2003. "Electron transfer kinetics on composite diamond (sp3)-graphite (sp2) electrodes." Electrochemistry Communications 5(8): 695.

Gandini, D., Mahé, E., Michaud, P.-A., Haenni, W., Perret, A. and Comninellis, C.,2000. "Oxidation of carboxylic acids at boron-doped diamond electrodes for waste water treatement." J. Appl. Electrochem. 30: 1.

Gandini, D., Michaud, P.-A., Duo, I., Mahé, E., Haenni, W., Perret, A. and Comninellis, C.,1999. "Electrochemical behavior of synthetic boron-doped diamond thin film anodes."New Diamond Front. Carbon Technol. 9(5): 303.

Iniesta, J., Michaud, P. A., Panizza, M., Cerisola, G., Aldaz, A. and Comninellis, C.,2001. "Electrochemical oxidation of phenol at boron-doped diamond electrode." Electrochimica Acta 46(23): 3573.

Iniesta, J., Michaud, P. A., Panizza, M. and Comninellis, C.,2001. "Electrochemical oxidation of 3-methylpyridine at a boron-doped diamond electrode: application to electroorganic synthesis and wastewater treatment." Electrochemistry Communications 3(7): 346.

Johnson, J. W., Jiang, H. W., Hanna, S. B. and James, W. J.,1972. "Anodic oxidation of ethylenediaminetetraacetic acid on Pt in acid sulfate solutions." J Electrochem. Soc. 119: 574.

Kari, F. G., Hilger, S. and Canonica, S.,1975. Environ. Sci. Technol. 9: 1035.

Licsko, I. and Takacs, I.,1986. "Heavy metal removal in the presence of colloid-stabilizing organic material and complexing agent." Wat. Sci. Technol. 8: 19.

Martin, S. B. and Allen, A. E.,1996."Recycling EDTA after heavy metals extraction." chemtech. 26(4): 23.

Michaud, P. A., Mahé, E., Haenni, W., Perret, A. and Comninellis, C.,2000. "Preparation of perxodisulfuric acid using Boron-doped Diamond thin film electrodes."electrochemical and solid state letters 3(2): 77.

Mohamed, A. M. O.,1996. "Remediation of heavy metal contaminated soils via integrated electrochemical processes." Waste Manage 16: 741.

Oldham, K. B. and Myland, J. C., 1994. Fundamentals of Electrochemical Science. Academic Press. San Diego C. A.: chap. 9.

Ouattara, L., Duo, I., Diaco, T., Ivandini, A., Honda, K., Fujishima, A. and Comninellis, C., 2003. "Electrochemical oxidation of ethylendiaminetetraacetic acid (EDTA) on BDD electrodes: Application to waste water treatment."New Diamond and Front. Carbon Technol. 13(2): 97.

Panizza, M., siné, G., Duo, I., Ouattara, L. and Comninellis, C., 2003. "Electrochemical polishing of boron-doped diamond in organic media."Electrochemical and Solid State Letters 6(12): D17.

Rodrigo, M. A., Michaud, P. A., Duo, I., Panizza, M., Cerisola, G. and Comninellis, C., 2001. "Oxidation of 4-Chlorophenol at Boron-Doped Diamond Electrode for Wastewater Treatment." J. Electrochem. Soc. 148: D60.

Ruey, S. J. and Shiow, W. W., 2000. Wat. Res. 34(12): 3179.

Siemion, U., Bahnemann, D., Testa, J. J., Rodriguez, D. and Bruno, N., 2002. J. Photochem. Photobiol. 148(A): 247.

Simonsson, D., 1997. "Electrochemistry for a cleaner environment." Chem. Soc. Rev. 26: 181.

Spearot, R. M. and Peck, J. V., 1984. "Recovery process for complexed copper-bearing rinse waters." Envir. Progr. 3: 127.

Tunay, O., Kabdashi, I. and Tasli, R., 1994. "Pretreatment of complexed metal wastewater." Wat. Sci. Technol. 29(9): 265.