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Electrochemical Behavior of Synthetic Diamond Thin Film Electrodes

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Abstract

Diamond's chemical inertness and unique electrochemical properties present great potential for a variety of applications in aggressive environments. Preliminary results have shown the widest known electrochemical window before water decomposition allowing new possibilities for both anodic and cathodic reactions. The study of the oxidation of organic compounds has been performed with alcohols like isopropanol, phenol, and organic acids. Cyclic voltammetry demonstrates no activity in the potential range where water is stable. In the potential region of oxygen evolution, the organic compounds are oxidized mainly to CO_2.

No deactivation or reduction in the thickness of the electrode has been observed. In addition, no fouling of the diamond surface has been detected. Furthermore, no hydrodynamic effects have been observed. Concentrated (1M) and diluted (3.10^{-4} M) cyanide solutions have been oxidized on diamond electrodes both in the presence and in the absence of chloride ions. The results show a direct oxidation with a current efficiency of about 40% for concentrated solutions. At low cyanide concentration, the current efficiency is strongly increased by the presence of Cl^-.

Electrochemical reduction of cadmium and copper has been carried out on diamond electrodes. Non adherent deposits have been obtained on diamond cathodes.

1. Introduction

For several years electrochemical properties of diamond have been studied. These are of particular interest as diamond displays the widest known electrochemical window allowing a variety of electrochemical reactions (1,2,3). The applications foreseen are both in analytical chemistry for cation and anion quantitative determination (2), for the dosage of electrolytic biocomponents by functionalising the diamond surface (4), as a preparative electrode for chemical synthesis and also for oxidizing organic residues in clear or waste water (5). Adding the structuration of the diamond layer with standard microelectronic processes, it is possible to manufacture more sophisticated electrodes for analytical applications. In order to compare with existing alpha carbon microelectrodes, similar microstructures have been developed (6). The diamond chemical inertness has been proved, especially in very oxidizing media which give an advantage against alpha carbon.

Standard hot filament deposition technique (HFCVD) has been used for conductive (0.1Ωcm) and non-conductive ($>10^9$Ωcm) 1 µm diamond coating.

Some adaptation of this technique has been developed to allow diamond deposition on titanium and zirconium plates (7).

2. Experimental

2.1 Diamond films preparation

Diamond films are conformally deposited on flat or structured low resistivity (1mΩcm) silicon wafers which are metallized on the backside with 1µm sputtered aluminum or directly on the titanium or zirconium plates. It is deposited by the hot filament technique at a deposition rate of 0.4 µm/h and in a temperature range 760-870 °C.

A boron dopant is introduced in the diamond film by in-situ doping during the CVD process through a tri-methyl boron gas source. This HFCVD process gives a columnar, random textured polycrystalline film with a surface dominated by {111} facets. The electrical resistivity is <0.1 Ωcm for the diamond layer. The diamond layer is conformal, pinhole free and has a thickness of 1µm.

2.2 Electrochemical measurements

Two electrochemical cells were used, a small laboratory cell without electrolyte circulation (Cell I) and a bench scale electrolytic cell with electrolyte circulation (Cell II).

Cell I: This was a one or two compartment cell; the anode was a p-Si plate coated with diamond and the cathode was Pt or Zr spiral enclosed in a porous porcelain pot, in the case of the tow compartment cell ; stirring was provided by a magnetic bar.

Cell II : This was a one-compartment cell with external circulation of the electrolyte. Diamond has been used as anode and zirconium as cathode, both electrodes are circular (80 mm diameter) with a geometric area of $50cm^2$ each and with an inter-electrode gap of 10 mm. The electrolyte was stored in a 500 ml thermoregulated glass tank and circulated through the electrolytic cell by a centrifugal pump.

Electrolysis was performed under galvanostatic conditions (I = const.) .

3. Results and Discussion

3.1 Oxidation of organic compounds

Oxidation of phenol (model aromatic organic compound for wastewater treatment) has been performed from a 2mM aqueous solution at pH 2 and 60 °C under galvanostatic conditions (30 mA/cm^2) using cell I with one compartment.

The fact that during electrolysis the rate of phenol elimination (giving a final phenol concentration < 3 ppm)is almost the same as those of TOC (Total Organic Carbon) and COD (Chemical Oxygen Demand) elimination indicates that phenol is directly oxidized at the anode to CO_2 (Fig.1).

$$C_6H_5OH + 11H_2O \rightarrow 6CO_2 + 28\ e^- + 28\ H^+$$

This has been confirmed by HPLC analysis of the intermediates formed during electrolysis. This technique shows that only very small amounts of intermediates are formed (hydroquinone, benzoquinone, maleic and formic acids).

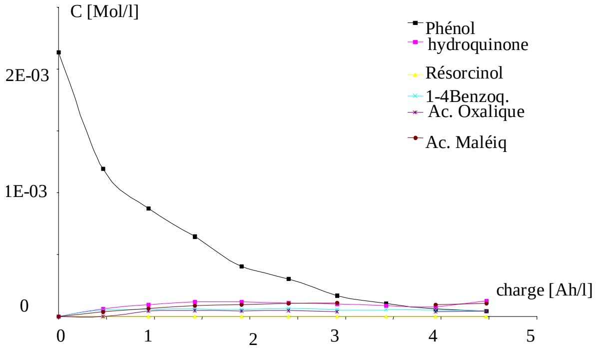

Figure 1. Oxidation of phenol

Isopropanol oxidation (model aliphatic organic compound for wastewater treatment) in concentrated aqueous solution (170 mM isopropanol) at $30mA/cm^2$ using cell II follows another mechanism. This compound is firstly oxidized to acetone which is further oxidized into formic and acetic acids and finally to CO_2 (Fig 2).

High current efficiencies (>95%) can be obtained for isopropanol conversions <90% .The current efficiency decrease for higher conversions due to limitation by mass transfer.

Over 350 working hours and more than 65 experiment cycles have not affected the properties of the diamond and no poisoning of the surface has been detected.

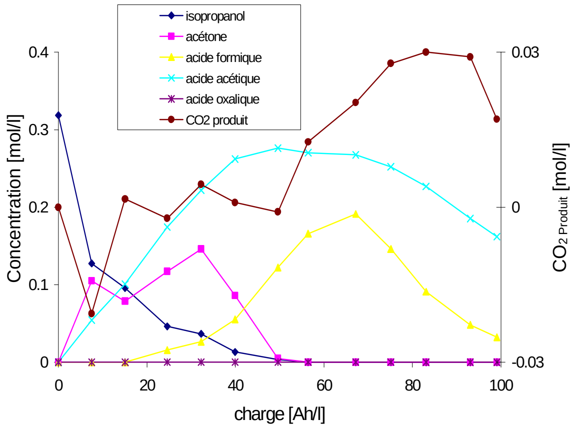

Figure 2 . Oxidation of isopropanol, concentration of the intermediates and CO_2 in real time, in function of charge

3.2 Cyanide oxidation

Two main electrochemical techniques for the treatment of aqueous cyanide solutions are commonly used: the direct and the indirect electrochemical oxidation (8,9,10).

In the direct electrochemical oxidation the cyanide ion is directly oxidized at the anode giving firstly cyanate (Eq 1) which is further oxidized to urea, oxalate, carbonate and nitrogen (Eq 2).

$$CN^- + 2\ OH^- \rightarrow CNO^- + 2\ e^- \qquad (1)$$

$$CNO^- \rightarrow CO_3^{2-} + NH_2CONH_2 + (COOH)_2 + N_2 + ze^- \quad (2)$$

In the indirect electrochemical process, chloride ions act as an oxygen carrier (forming ClO^-) in the oxidation of cyanide to cyanate (Eq 3).

$$CN^- + ClO^- \rightarrow CNO^- + Cl^- \qquad (3)$$
$$\uparrow\underline{\qquad\qquad\qquad}\downarrow$$

Up to now these electrochemical treatments were unsatisfactory because of the poor stability of the traditional anodes (Pb, IrO_2 , RuO_2 ,...) and the low current efficiency.

Diamond electrodes have shown a perfect chemical and electrochemical stability during both direct and indirect oxidation of cyanide.

The direct electrochemical oxidation of cyanide on diamond anodes has been studied under galvanostatic conditions (36 mA/cm^2) using cell I with one compartment and 1M KCN + 1M KOH as electrolyte.

Figure 3 shows the evolution of the KCN concentration during electrolysis. The concentration decreases exponentially with the electrical charge passed. After the passage of 220 Ah/l (283 h), 95 % of CN^- has been eliminated. The specific energy consumption for the elimination of 1 M KCN can be estimated to be 60 kWh/kg CN^- (95 % elimination of cyanide), value that can be reduced by optimization of the electrolysis conditions. Nevertheless a current efficiency of 41 % has been already reached.

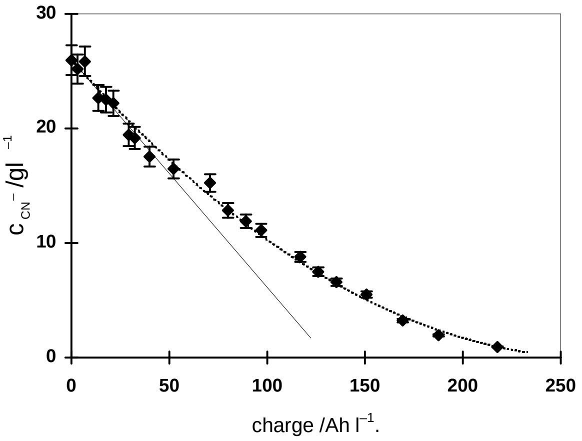

Figure 3. Direct oxidation of CN^- on diamond electrodes. Evolution of CN^- concentration during electrolysis.

In the indirect electrochemical oxidation of cyanide using Cl^- as mediator (treatment of dilute CN^- effluents) has been studied using 0.1 M KOH + 8.1 mg /l CN^- as electrolyte in the presence of different amounts of KCl (1, 10, 50, 100 mM).

Figure 4 shows the influence of the Cl^- concentration on the rate of cyanide elimination. Even a small amount of Cl^- increase strongly the efficiency of the reaction .

In this process the chloride ion is firstly oxidized to ClO^- (with a current efficiency of about 60%). Then reacts with CN^- forming CNO- and regenerating the Cl^- (Eq 3).

The specific energy consumption for a solution containing 8 mg/l CN^- in 0.1M KOH with 90 % elimination of cyanide is given in Table 1 for different Cl^- concentrations. Increasing the chloride concentration results in a decrease in the specific energy consumption.

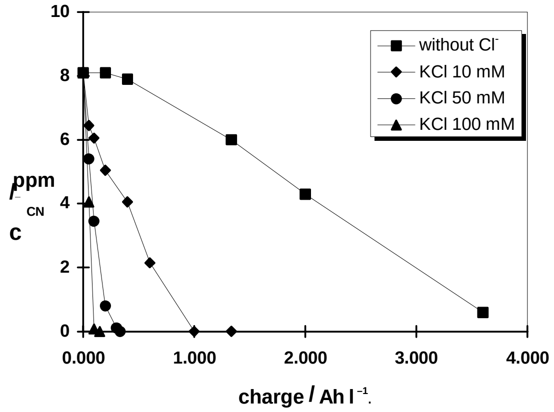

Figure 4. Indirect electrochemical oxidation of CN^- in presence of KCl.

Conc Cl^- (mM)	0	10	50	100
kWh/m^3	16.5	4.5	1.1	0.5

Table 1 : Specific energy consumption for the electrochemical treatment of dilute CN^- solution in presence of Cl^-.

3.3 *Electrochemical reduction of heavy metals*

Cadmium reduction (a model heavy metal) from a dilute aqueous solution has been carried out at pH 1.5 at 4 different overpotentials (-880, -920, -960, -1020 mV) to evaluate the deposition morphology on diamond cathodes in comparison to the deposition on metallic cadmium . The results have show that fine non adherent deposits have been obtained on diamond cathodes (Fig 5). Same results have been obtained with copper deposition. The main advantage of the diamond is that, on completion of the electrolysis, the metal desorbs leaving a clean surface. This simplifies the recuperation of the metal after the electrochemical reduction.

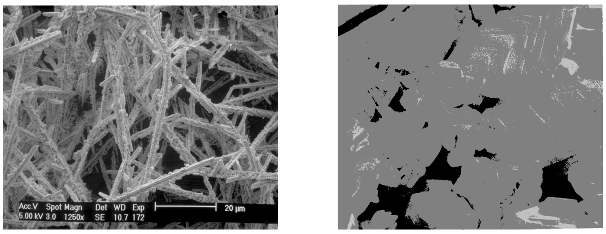

Figure 5. SEM pictures of the deposition of cadmium on cadmium (left) and diamond (right) electrodes.

4. Conclusions

Diamond coating has shown outstanding electrochemical properties in the oxidation of organic and inorganic compounds. The chemical inertness of the diamond layer has been clearly demonstrated. Substances like isopropanol and phenol can be oxidized into CO_2 following different oxidation steps. Cyanide ions in high and low concentrations can also be totally oxidized with or without the help of chloride anions. Non adherent deposited cadmium and copper films have been obtained on diamond cathodes.

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