Hydroxyl radicals electrochemically generated in situ on a boron-doped diamond electrode

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The hydroxyl radicals electrochemically generated in situ on a boron-doped diamond (BDD) electrode have been investigated for the first time in different electrolyte media, over the whole pH range between 1 and 11. A more extensive characterisation of BDD electrochemical properties is very important to understand the reactivity of organic compounds towards electrochemical oxidation on the BDD electrode, which is related to their interaction with adsorbed hydroxyl radicals due to water oxidation on the electrode surface. An oxidation peak corresponding to the transfer of one electron and one proton was observed in pH <9 electrolytes, associated with the water discharge process and electrochemical generation of hydroxyl radicals, which can interact and enhance the electro-oxidation of organic compounds. In pH >9 electrolytes the electrochemical generation of hydroxyl radicals was not observed; ammonia buffer electrolyte gave a pH-independent peak corresponding to the ammonia oxidation reaction. Additionally, for most pH values studied, a few small peaks associated with the electrochemical interaction between non-diamond carbon species on the doped diamond electrode surface and the electrolyte were also seen, which suggests that the doped diamond is relatively unreactive, but not completely inert, and the electrogenerated hydroxyl radicals play a role as mediator in the oxidation of organics.

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1. Introduction

Doped diamond electrodes have been used in electrochemical experiments since 1983 [1]. A more extensive characterisation of boron-doped diamond (BDD) electrochemical properties such as wide potential window, electrochemical stability in both aqueous and non-aqueous electrolyte solutions, negligible adsorption of organic molecules, low and stable voltammetric background current and low capacitance, resulting in a low detection limit, was only recently investigated [2–8]. Diamond is an extremely hard crystalline form of carbon, with each carbon atom being tetrahedrally bonded to four other sp3 hybridized carbons, and in natural diamond containing boron or synthetic boron-doped diamond, boron acts as an electron acceptor, due to an electron deficiency in its external shell which gives p-type semiconducting properties to the diamond electrodes [9,10]. Although BDD has an excellent electrochemical performance and electrochemically active species are not generally adsorbed on its surface, the BDD electrode behaviour is strongly related to the electrochemical generation (by water discharge) of hydroxyl radicals (HO·) and their subsequent reactions [11,12]. Hydroxyl radicals are extremely reactive and cause oxidative degradation, and a correct characterisation of the electrogenerated HO· in different electrolyte media is very important to explain and evaluate the mechanisms of interaction and electrochemical degradation of organic or inorganic compounds on the BDD electrode [13–15]. The reactivity of organic compounds towards electrochemical oxidation on the BDD electrode is related to their interaction with adsorbed hydroxyl radicals due to water oxidation on the electrode surface [16–18]. The direct oxidation of ammonia at BDD electrodes has been investigated and compared with the response obtained using different carbon electrodes [19].

In this work, the electrochemical characterisation of the electro-generated HO· on the BDD electrode has been investigated for the first time in different electrolyte media, over the whole pH range between 1 and 11, in order to establish the hydroxyl radical reactivity on the BDD surface and its role as mediator in the oxidation of organics.

2. Experimental

Atomic force microscopy (AFM) was performed with a PicoSPM interfaced with a PicoScan controller, a CS AFM S scanner (scan range 6 μm in x–y and 2 μm in z) and silicon nitride NanoProbes™...
V-shaped cantilevers (100 μm length and 0.58 N m⁻¹ spring constant), from Agilent Technologies, USA (formally Molecular Imaging). The images (256 samples line⁻¹ × 256 lines) were taken in air at room temperature and were processed by flattening. The root-mean-square (RMS) roughness (i.e. the standard deviation of the surface height) was calculated after a 1st order flattening using the PicoScan software version 5.3.3.

Voltammetric experiments were performed using a µAutolab running with GPES 4.9 software, Eco-Chemie, The Netherlands. Differential pulse (DP) voltammetry conditions were pulse amplitude 50 mV, pulse width 70 ms, scan rate 5 mV s⁻¹. Measurements were carried out using a boron-doped diamond (BDD) working electrode, a Pt foil counter electrode, and an Ag/AgCl (3 M KCl) as reference, in a 20 mL one-compartment electrochemical cell.

The BDD films were prepared at the Centre Suisse de Electronique et de Microtechnique SA (CSEM), Neuchatel, Switzerland, on silicon wafers using the hot filament chemical vapour deposition (HF-CVD) technique with a filament temperature in the range 2440–2560 °C and a gaseous mixture containing methane, H₂ and trimethylboron. This HF-CVD process gives a columnar, randomly textured polycrystalline BDD film with the surface dominated by (1 1 1) facets. The final boron content was of the order of 8000 ppm, 5.7 × 6.1 nm² surface area, ~1 μm thickness [10].

The electrolyte solutions of 0.1 M ionic strength were, pH 1.0 sulphuric acid, pH 2.0 KCl/HCl, pH 3.5–5.5 acetate buffer, pH 6.0–8.0 phosphate buffer, pH 9.0–11.0 NaHCO₃/Na₂CO₃, pH 8.9–10.5 NH₃/NH₄Cl, and pH 11.5 NaOH, prepared with analytical grade reagents and purified water from a Millipore Milli-Q system (conductivity <0.1 μS cm⁻¹). The pH measurements were carried out with a Crison micropH 2001 pH-meter using an Ingold combined glass electrode.

### 3. Results and discussion

The morphology of the BDD electrode was characterized by and AFM, Fig. 1A, showing a continuous and rough surface consisting of sharp grains of 200 nm–1 μm size. The polycrystalline BDD film presented a RMS roughness of 35.7 nm, calculated in the 4000 × 4000 nm² size AFM image from Fig. 1A. Higher magnification AFM demonstrated that the grains are randomly oriented diamond crystallites with well defined facets, Fig. 1B, presenting a high degree of triangular facets due to the {1 1 1} planes exposed. Additionally, non-faceted, rounded, small aggregates were observed sporadically at the crystallite boundaries.

Prior to the voltammetric study, a physical and electrochemical pretreatment was applied to the BDD electrode, in order to obtain qualitatively reproducible results. The electrode was washed with ethanol and Milli-Q water, and several different electrochemical procedures were investigated for the “activation” of the BDD surface. The best results were obtained by cycling the potential in each supporting electrolyte solution, between the potential limits of E₁ = 0.0 V and E₂ = ± 2.50 V, until a stable signal was recorded (15–20 cycles at a scan rate of 0.15 V s⁻¹). This pretreatment procedure was chosen for all electrochemical experiments described below.

The electrochemical generation of hydroxyl radicals in situ at the BDD electrode was studied using DP voltammetry in different electrolyte solutions, pH range between 1 and 11, Fig. 2. All the DP voltammograms presented were recorded between the potential limits of E₁ = 0.0 V and E₂ = ± 2.50 V. For most of the pH values, a few very small shoulders were observed in the region of potential from +0.10 to +1.20 V (not shown).

DP voltammograms in the pH range between 1 and 9 are presented in Fig. 2A. The first voltammogram was recorded in pH 1.0 sulphuric acid and showed two oxidation peaks, P₁ at Eₚ₁ = +1.55 V, Iₚ₁ = 3 μA, and P₂ at Eₚ₂ = +2.10 V, Iₚ₂ = 1.9 μA. The oxidation potential of peak P₂ is associated with the electrochemical generation of hydroxyl radicals at the BDD electrode, and shifted to less positive values with increasing pH and the peak current decreased until it disappeared at pH 9.0, Fig. 2A and C.

The Eₚ₂ peak dependence of pH was linear, and followed the relationship Eₚ₂(V) = 2.15 – 0.059 pH, Fig. 2B. The slope of the dotted line in Fig. 2B is 59 mV per pH unit, showing that the oxidation involves the same number of electrons and protons. Also the width at half height of the oxidation peak P₂ is W₁/₂ ~110 mV, close to the theoretical value of 90 mV corresponding to an electrochemical reaction involving the transfer of one electron [11]. Thus it can be concluded that the oxidation reaction corresponding to P₂ occurred with the transfer of one electron and one proton.

The high overpotentials observed for oxygen evolution in different electrolytes over the whole pH range studied suggest that the BDD surface undergoes little interaction with the electrolyte, in agreement with the fact that the BDD surface is expected to be inert. However, BDD is synthesized under conditions where graphite synthesis is competitive, and non-diamond components may be also incorporated in its structure. The small aggregates observed in the AFM images, Fig. 1, can be associated with these amorphous regions of sp² graphite domains [9]. The BDD background current and the working potential window are influenced by the electroactivity of these non-diamond carbon impurities. The small peaks observed in the potential range from +0.10 to +1.20 V, as well as peak P₁, depend on the sp² carbon incorporated into the diamond
structure which plays the role of electrocatalytic centres and places functional groups on the electrode surface. Using a single-crystal BDD electrode, peak P1 does not appear, while for low quality polycrystalline BDD the oxidation is so extensive that it cannot be distinguished from the oxygen evolution peak [2–7].

The electrochemical generation of hydroxyl radicals in situ at the BDD electrode corresponds to peak P2 and involves water oxidation with the transfer of one electron and one proton:

$$\text{H}_2\text{O} \rightarrow \text{HO}^- + \text{H}^+ + \text{e}^-$$  \hspace{1cm} (1)

The hydroxyl radicals electrogenerated in situ, peak P2, at the BDD electrode interact with organic compounds [13–15]. The oxidation of organic compounds at BDD can be divided into two types of mechanism, depending on the applied potential: direct electrochemical oxidation, in the region of water stability before oxygen evolution, where only reactions involving simple electron transfer can occur, and indirect electrochemical oxidation caused by a sequence of reactions that is initiated by HO' radicals formed at the BDD surface in the potential region of oxygen evolution (water discharge) [15–18]. Moreover, because of the high reactivity of HO' radicals, these reactions are confined to an adsorbed thin film adjacent to the electrode surface [11,12].

In the DP voltammograms obtained in solutions in pH 9.0–11.0 NaHCO₃/Na₂CO₃ and pH 11.5 NaOH, Fig. 2C, peak P2 was not observed. This may also be due to the properties of both carbonate and bicarbonate as hydroxyl radical scavengers [20].

However, pH 8.9–10.5 NH₃/NH₄⁺ solutions as expected peak P2 was not observed but another oxidation peak P3 at $E_{\text{pa}} = +1.25 \text{ V}$ occurred, Fig. 2D. Peak P3 was only observed in ammonia electrolyte solutions, and its potential is independent of the electrolyte pH. Therefore peak P3 is attributed to ammonia oxidation at the BDD electrode [19].

Concerning electroanalytical applications, the peaks related with the electrochemical activity at the BDD sp² carbon are usually hindered by the large oxidation peak currents from concentrated solutions of electroactive organic compounds [13–15].

However, for electrochemical applications that involve a very low concentration of analyte the BDD cannot be regarded as inert. Since the hydroxyl radicals electrogenerated in situ, peak P2, at the BDD electrode react with organic compounds, the interactions between the functional sp² regions and the electrolyte have to be considered for the correct interpretation of the electrochemical results.

4. Conclusion

The electrochemical generation of hydroxyl radicals in situ at the BDD electrode was investigated by DP voltammetry in different supporting electrolyte solutions, over a wide range of pH. An
oxidation peak in the oxygen evolution region, which occurs with the transfer of one electron and one proton, was observed in all electrolytes, associated with the water discharge process and electrochemical generation of hydroxyl radicals, which can interact and enhance the electro-oxidation of organic compounds. Additionally, different oxidation processes were observed and associated with the interaction between the electrolyte and sp² hybridized carbon domains incorporated in the BDD structure.

The results obtained show the importance of the characterisation of BDD electrochemical behaviour in different pH electrolyte solutions, prior to an electrochemical study of organic compounds in order to clarify and correctly evaluate all factors influencing the interaction mechanism and the role of the hydroxyl radicals electrochemically generated in situ on a BDD electrode as mediators in the oxidation of organics.

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