

# Electrochemical characterisation and oxygen evolution at a heavily boron doped diamond electrode

Mário H.P. Santana<sup>a</sup>, Luiz A. De Faria<sup>b</sup>, Julien F.C. Boodts<sup>a,b,\*,1</sup>

<sup>a</sup> Departamento de Química, FFCLRP/USP, Av. Bandeirantes 3900, 14040-901 Ribeirão Preto, SP, Brazil

<sup>b</sup> Instituto de Química, Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2160 Uberlândia, MG 38400-902, Brazil

Received 8 June 2004; accepted 14 August 2004

Available online 27 October 2004

## Abstract

Characterisation of a commercial heavily doped BDD electrode demonstrated it contains a small  $sp^2$  content, which on anodic potential scanning, is oxidised to CO/CO<sub>2</sub>. This surface modification alters the electrode activity, increasing the overpotential for the hydrogen and oxygen evolution reactions (HER and OER). Ex situ and in situ investigations indicate film morphology is mainly composed of “chain of hills”, presenting relatively high differential capacitance values and morphology factor, which is attributed to the effect of surface states and high surface roughness of the BDD film. The voltammetric behaviour depends on the applied potential; the heavily doped BDD electrode behaving as a metallic electrode at more anodic potentials. Polarisation curves (potentiostatic ( $1 \text{ mV s}^{-1}$ ) or galvanostatic (point-by-point)), recorded at different temperatures and H<sub>2</sub>SO<sub>4</sub> concentrations, lead to the same conclusions. The high Tafel coefficients and low apparent electronic transfer coefficient ( $\alpha_A$ ) are independent of overpotential and temperature but show a dependence on H<sub>2</sub>SO<sub>4</sub> concentration. The linear relationship observed between the apparent electrochemical enthalpy of activation ( $\Delta H^\ddagger_\eta$ ) and overpotential supports  $\alpha_A$  is constant. An OER mechanism was proposed taking into account the absence of adsorption sites at the BDD surface. The OER is inhibited, explaining the high overpotentials and elevated  $\Delta H^\ddagger_\eta$  values.

© 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Boron doped diamond; Oxygen; Activation energy; Electrode mechanism; Electrochemical characterisation

## 1. Introduction

Technological development of preparing thin diamond films of low resistivity has stimulated the investigation of the surface and electrochemical properties of this material. Fundamental electrochemical properties investigated include the working potential window, the capacitive current, charge transfer kinetics for some redox couples, characterisation by electrochemical impedance spectroscopy, etc [1–10]. However, the relationship between the physical, chemical and electronic properties of BDD electrodes and their electrochemical behaviour are not yet completely understood [2].

BDD thin films deposited on self-passivating metals (e.g. Nb) or silicon present the highest overvoltage for O<sub>2</sub> evolution [11–14] and exhibit high chemical and mechanical stability. All these properties have stimulated the application of this material in electroanalysis [1,7,15], preparation of powerful oxidants [11,13,16], electrochemical oxidation of organic pollutants for wastewater treatment [14,17,18] and electrosynthesis [19]. In all these electrochemical processes the OER is the most important side reaction to be considered.

An important consequence of the BDD technology employed is the possible different behaviour between well-defined BDD thin films and commercial electrodes. Whereas the former tend to be fairly pure CVD diamond, commercial electrodes may contain a large amount of inhomogeneities (amorphous,  $sp^2$  carbon). The BDD electrode used in this work was gently furnished by M. Fryda from Condiás GmbH

\* Corresponding author. Tel.: +55 34 3239 4143; fax: +55 34 3239 4208.

<sup>1</sup> ISE member.

(Germany) [20] and is commercially available. According to the manufacturers [12], Raman spectra of these films exhibit a sharp peak at  $1334\text{ cm}^{-1}$ , which is characteristic of crystalline diamond [21]. In addition a broad peak centred at  $1200\text{ cm}^{-1}$  is observed, often found with heavily doped samples, which is ascribed either to amorphous diamond or, more usually, to very small diamond crystallites [21,22]. According to the manufacturer [20], the boron doping and impurity levels are homogeneously distributed over the whole film.

The aim of this study is to characterise this commercial heavily boron doped diamond electrode and investigate the OER.

## 2. Experimental

### 2.1. Electrodes and cell

The electrodes employed in this work were produced by the hot filament chemical vapour deposition (HFCVD) technology. The heavily doped BDD thin film (thickness:  $5\text{ }\mu\text{m}$ ; doping level: B/C = 3000–4000 ppm, corresponding to a concentration of  $10^{20}$  to  $10^{21}$  boron atoms  $\text{cm}^{-3}$  [2]) was deposited on a niobium support, Nb. The sand blasting treatment applied to the support led to a rough surface with an average hill to valley distance of  $5\text{ }\mu\text{m}$ . A copper wire was soldered to the Nb substrate using stain solder and the back of the electrode covered with epoxy resin. The geometric active electrode area was  $1\text{ cm}^2$ . Prior to its use, the as-grown BDD electrode was washed with isopropanol followed by rinsing with Milli-Q (Millipore) quality water.

A glass wall surrounding the cell permitted control of the temperature by means of a refrigerant fluid. All potentials were read against the reversible hydrogen electrode (RHE) containing the basic supporting electrolyte. The RHE was located in a separate compartment, maintained at constant temperature, and connected to the main body of the cell via a Luggin capillary. The counter electrode was a heavily platinumized platinum wire.

### 2.2. Electrolyte

Different electrolyte concentrations (3.0; 2.0; 1.0; 0.5 and  $0.1\text{ mol dm}^{-3}$ ) were prepared volumetrically from Milli-Q quality water and concentrated  $\text{H}_2\text{SO}_4$  (Merck). Solutions, before and during each experiment, were deaerated and heavily stirred using ultra pure nitrogen (purity: 99.995%).

### 2.3. Techniques and equipments

The BDD electrode was characterised by SEM analysis using a ZEISS DSM 940A equipment. Raman spectrum was recorded with a Renishaw Microscope System 2000. Cyclic voltammetry (CV), morphology factor determination [23], steady state polarisation curves using two different approaches (potentiostatic and galvanostatic perturbations), at

different temperatures and  $\text{H}_2\text{SO}_4$  concentrations, were all carried out with an AUTOLAB<sup>®</sup> model PGSTAT20 potentiostat/galvanostat (Eco Chemie, The Netherlands). Temperature control was done with a model FC55A01-FTS ( $\pm 0.1\text{ }^\circ\text{C}$ ) cooling system.

## 3. Results and discussions

### 3.1. Surface characterisation

Fig. 1 shows a representative SEM micrograph. The surface is composed of randomly oriented crystallites, with plane faces and nominal crystal size between 1 and  $3\text{ }\mu\text{m}$ . The exposed polycrystalline surfaces are mainly formed of triangular facets, with well-faceted  $\{111\}$  planes, as commonly reported in literature [3,8,9]. At several locations smaller grains can be observed among the well-faceted diamond crystallites. These grains may be associated with  $\text{sp}^2$  micro domains; a common impurity of CVD diamond films [2,3]. Several authors demonstrated that, due to secondary nucleation promoted by boron incorporation [12,10], the average crystallite size decreases at high B/C ratios [10,24,25], even for films presenting a thickness of several  $\mu\text{m}$ . A second consequence of the high boron doping level is that, with smaller crystallites, higher surface roughness is achieved [10,24]. The surface roughness of the sample is further increased by the Nb support pre-treatment, whose roughness is superimposed on the diamond film roughness [12,21]. Some authors [3,26], based on average crystalline size determined from SEM micrographs, have estimated a roughness factor of the order of 10 or greater. The results of a detailed investigation of the roughness of this heavily boron doped film, based on

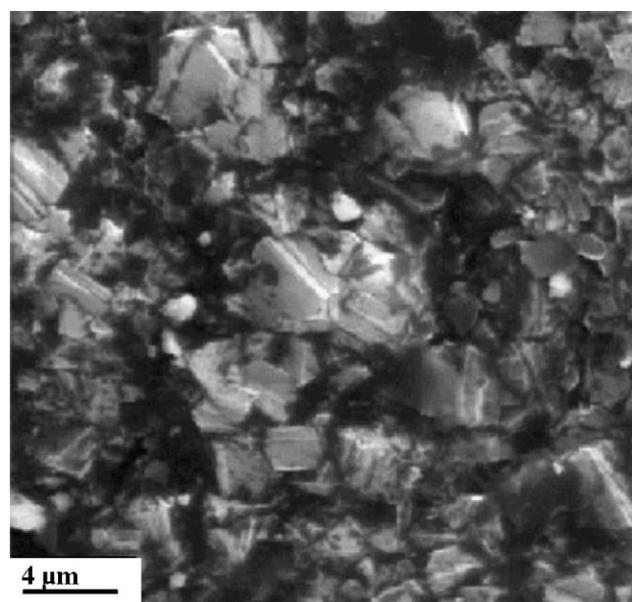


Fig. 1. SEM micrograph of BDD thin film deposited on Nb substrate. Magnification:  $5000\times$ .

Download English Version:

<https://daneshyari.com/en/article/197433>

Download Persian Version:

<https://daneshyari.com/article/197433>

[Daneshyari.com](https://daneshyari.com)