# Electrochemical oxidation of water on synthetic boron-doped diamond thin film anodes

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## Abstract

Electrolysis in aqueous 1 M $HClO_4$ and 1 M $H_2SO_4$ solutions has been carried out under galvanostatic conditions using boron-doped diamond electrodes (BDD). Analyses of the oxidation products have shown that in 1 M $HClO_4$ the main reaction is oxygen evolution, while in $H_2SO_4$ the main reaction is the formation of $H_2S_2O_8$. In both electrolytes small amounts of $O_3$ and $H_2O_2$ are formed. Finally, a simplified mechanism involving hydroxyl radicals formed by water discharge has been proposed for water oxidation on boron-doped diamond anodes.

## 1. Introduction

One of the most important scientific and technological challenges faced by electrochemists is the design of stable electrocatalytic anode materials. This is especially illustrated by the case of the chlor-alkali industry. Precious metal-coated anodes were first developed to improve anode performance. But their lack of stability under high anodic polarization, as well as their price, lead to the development of so called dimensionally stable anodes (DSA) which consist of a thin active metal oxide or mixed metal oxide layer on an inert substrate, usually titanium [1–3]. Many different coating compositions have been developed for various applications including selective synthesis and oxidation of organics for the treatment of industrial effluents [4–9].

Diamond films as electrode materials exhibit very high overpotentials for both hydrogen and oxygen evolution in aqueous electrolytes, leading to a large potential range in which the background current is very low, as well as unique properties of high stability under strong oxidising conditions. Since the first publication concerning the electrochemistry of diamond [10], investigations have focused on the ability of well-controlled growth of polycrystalline diamond films on conductive substrates and on high concentrations of doping compound to increase the film conductivity without deterioration of the diamond structure. Most researches are related to boron-doped diamond films. Doping can change the electrical conductivity of diamond films from pure semiconducting to semimetal behaviour [11].

A few electrochemical studies have been made on synthetic boron-doped diamond films deposited on p-silicon substrate with the goal of developing applications in electroanalysis [12–16], reduction of nitrates in neutral or basic solutions [17], electrosynthesis [18, 19] and waste water treatment oxidations [20–22]. However, the main interest of diamond electrodes results from their anodic behaviour in corrosive media. Outer-sphere reactions have a kinetic behaviour which varies from reversible (ferrocene/ferricinium) to irreversible process ($Ce^{IV/III}$) [23, 24].

The aim of the present study is to elucidate the mechanism of water oxidation on boron-doped diamond electrodes. Cyclic-voltammetry and electrolyses were performed in acidic media and reaction products were analysed.

## 2. Experimental details

Boron-doped diamond (BDD) films were synthesised by the hot filament chemical vapor deposition technique (HF CVD) on single crystal p-type Si $\langle 1\,0\,0 \rangle$ wafers (1–3 mΩ cm, Siltronix). 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 methane in an excess of dihydrogen (1% $CH_4$ in $H_2$). The doping gas was trimethylboron of concentration 1–3 ppm [12]. The gas mixture was supplied to the reaction chamber at a flow rate of 5 l min$^{-1}$ giving a growth rate of 0.24 $\mu$m h$^{-1}$ for the diamond layer. The doping level

of boron in the diamond layer expressed as B/C ratio was about 3500 ppm. The obtained diamond film thickness was about 1 $\mu$m with a resistivity of 10–30 m$\Omega$ cm. This HF CVD process produces columnar, random textured, polycrystalline films terminated with hydrogen atoms which gave them a hydrophobic nature. In order to stabilize the electrode surface and to obtain reproducible results, the diamond electrode was pretreated by anodic polarization in 1 M HClO$_4$ at 10 mA cm$^{-2}$ for 30 min. This treatment made the surface hydrophilic. Electrochemical measurements were made in a conventional three-electrode cell using a computer controlled EG & G potentiostat (model M 273). Diamond was used as working electrode, Hg/Hg$_2$SO$_4$ · K$_2$SO$_4$ (sat) as reference and Pt as counter electrode. The exposed apparent area of the BDD was 1 cm$^2$.

Bulk electrolysis were performed in a two-compartment electrolytic flow cell separated by a Nafion® membrane. Diamond was used as anode, and zirconium as cathode. Both electrodes were discs (dia. 80 mm) with a geometric area of 50 cm$^2$ each. Anolyte and catholyte were stored in 500 ml thermoregulated glass tanks ($T$ = 25 °C) and circulated through the electrolytic cell by centrifugal pumps (Figure 1). Ozone and hydrogen peroxide concentrations were measured by iodometric titration and by potassium permanganate, respectively.

## 3. Results and discussion

### 3.1. Electrochemical measurements

Figure 2 shows linear polarisation curves and the corresponding Tafel plots of a p-Si/BDD electrode obtained in 1 M HClO$_4$ and 1 M H$_2$SO$_4$ at a scan rate of 100 mV s$^{-1}$. Current–potential curves are almost identical although the reactions that take place in perchloric acid and sulfuric acid media are different. In fact, in
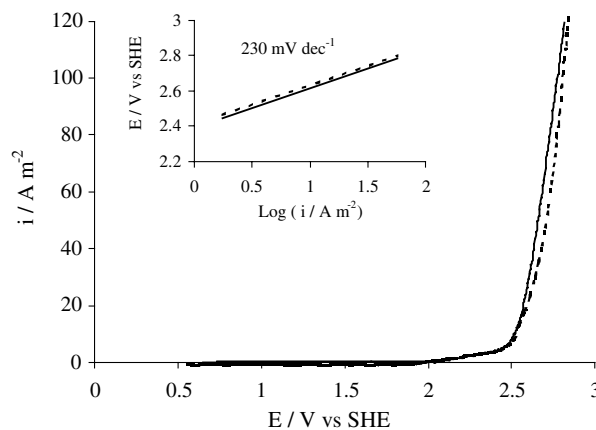
Fig. 2. Linear polarisation curves and Tafel plots of BDD recorded in 1 M H$_2$SO$_4$ (dotted line) and 1 M HClO$_4$ (continuous line) at 25 °C. Scan rate 100 mV s$^{-1}$.

H$_2$SO$_4$ the main reaction is the formation of peroxodisulfuric acid due to oxidation of the sulfuric acid supporting electrolyte (Equation 1) [19] in contrast to HClO$_4$ where the main reaction is oxygen evolution due to water oxidation (Equation 2):

$$2\,H_2SO_4 \rightarrow H_2S_2O_8 + 2\,e^- + 2\,H^+ \tag{1}$$

$$2\,H_2O \rightarrow O_2 + 4\,e^- + 4\,H^+ \tag{2}$$
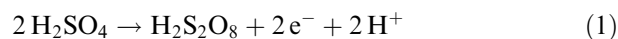
Also the value of Tafel slope is almost the same for both media (0.23 V decade$^{-1}$) and is about twice as high as on other classical electrodes (Pt, SnO$_2$–Sb$_2$O$_5$) [25]. Such a value of Tafel slope is in agreement with those reported in the literature [26] and is probably due to the semimetal/semiconductor nature of the diamond film.

Bulk electrolysis using 1 M HClO$_4$ and 1 M H$_2$SO$_4$ have shown that O$_3$ and H$_2$O$_2$ have been formed in both electrolytes. To evaluate the amount of O$_3$ and H$_2$O$_2$ formed during water oxidation in 1 M HClO$_4$ several electrolyses at different current density were performed. Both the concentration of O$_3$ in the gas leaving the anodic compartment and the concentration of H$_2$O$_2$ in the anolyte were determined during electrolysis. Figure 3 shows the influence of current density on the gas phase O$_3$ concentration produced by water oxidation (Equation 3):

$$3\,H_2O \rightarrow O_3 + 6\,e^- + 6\,H^+ \tag{3}$$

Ozone concentration in the gas increases almost linearly from 110 to 800 ppm with applied current density in the range 230–1500 A m$^{-2}$. Higher O$_3$ concentration was obtained by Katsuki et al. [27] during electrolysis in sulfuric acid with much higher current density (Figure 3) but, in this case, the current efficiency decreased.

Current efficiency for ozone production on BDD anode was found to be lower than that obtained with PbO$_2$ under the same conditions, although BDD has a higher oxygen evolution overpotential. Similar results
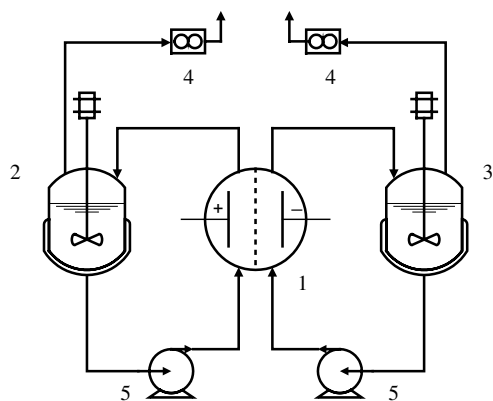
Fig. 1. Experimental set-up for preparative electrolysis Legend: (1) electrochemical cell with BDD anode and Zr cathode; (2) thermoregulated anolyte reservoir; (3) thermoregulated catholyte reservoir; (4) gas analysers; (5) pumps.
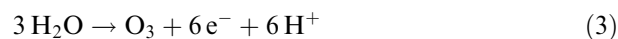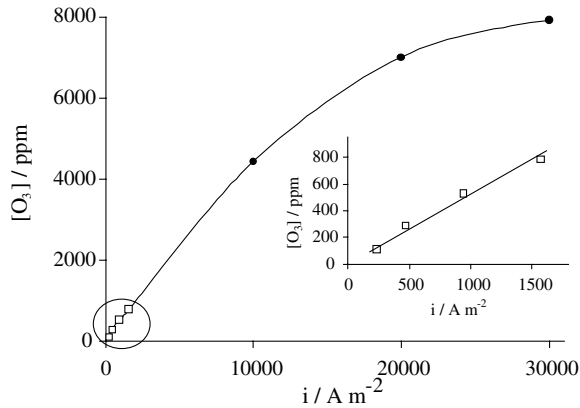
Fig. 3. Influence of current density on ozone concentration in the anodic gas during electrolysis with BDD at 25 °C. Comparison of our results in HClO$_4$ 1 M ($\square$) with the experimental data obtained by Katsuki et al. [27] during electrolysis in 1 M H$_2$SO$_4$ ($\bullet$).

were also obtained by other authors [28] using a Nafion® membrane as electrolyte.

Figure 4 shows the trend of H$_2$O$_2$ concentration in the anolyte during electrolysis in 1 M HClO$_4$ at different current densities. The concentration of H$_2$O$_2$ due to water oxidation (Equation 4) increases with time until reaching a limiting value after about two hours (Figure 4):

$$2\,H_2O \rightarrow H_2O_2 + 2\,e^- + 2\,H^+ \qquad (4)$$
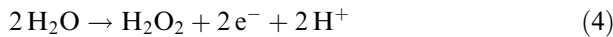
The limiting concentration increases almost linearly with applied current and is higher than that obtained with other electrode materials such as Pt or PbO$_2$ [28].

## 3.2. Discussion

The results of voltammetric measurements and bulk electrolysis with BDD in 1 M HClO$_4$ and in 1 M H$_2$SO$_4$ have shown that even if the main reaction products are different (O$_2$ in HClO$_4$ and peroxodisulfuric acid in H$_2$SO$_4$), similar current–potential curves are obtained in both electrolytes. In order to explain this behaviour a simplified model is proposed for water oxidation on BDD (Figure 5).

According to this model, the first step is water discharge on BDD with the formation of hydroxyl radicals (Equation 5):

$$H_2O \rightarrow OH^\bullet + H^+ + e^- \qquad (5)$$

The electrogenerated hydroxyl radicals can be involved in four parallel reactions:

(i) Oxidation of supporting electrolyte: In the case of H$_2$SO$_4$ supporting electrolyte, electrogenerated hydroxyl radicals react with sulfuric acid giving peroxodisulfuric acid (Equation 6):

$$2\,H_2SO_4 + 2\,OH^\bullet \rightarrow H_2S_2O_8 + 2\,H_2O \qquad (6)$$
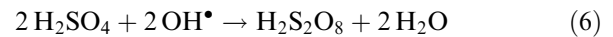
(ii) H$_2$O$_2$ formation: as HClO$_4$ supporting electrolyte is stable towards OH$^\bullet$ oxidation, the main reaction is O$_2$ evolution probably via H$_2$O$_2$ formation. In fact, electrogenerated hydroxyl radicals may react with each other forming hydrogen peroxide near the electrode (Equation 7); this then diffuses into the bulk of the electrolyte (Equation 8) or is oxidised to oxygen (Equation 9).

$$2\,OH^\bullet \rightarrow H_2O_2 \qquad (7)$$

$$(H_2O_2)_{\text{electrode}} \rightarrow (H_2O_2)_{\text{solution}} \qquad (8)$$

$$H_2O_2 \rightarrow O_2 + 2\,H^+ + 2\,e^- \qquad (9)$$

These reactions explain both the presence of hydrogen peroxide in the electrolyte and the trend of its concentration towards a limiting value (Figure 4). Furthermore, from the mass balance of hydrogen peroxide in the diffusion layer, it is possible to obtain the equation describing its concentration as a function of time (Equation 10):

$$C = C^{\text{s}} \left[ 1 - \exp\left( -\frac{Ak_{\text{d}}}{V} t \right) \right] \qquad (10)$$
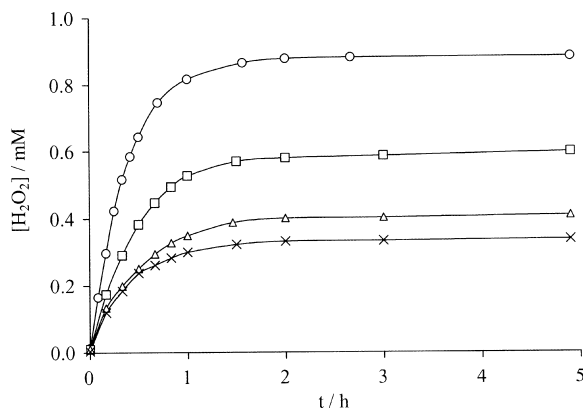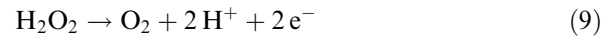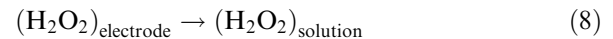


Fig. 4. Trend of hydrogen peroxide concentration in the anolyte during electrolyses on BDD at different current densities in 1 M HClO$_4$ at 25 °C. Current density: ($\times$) 230, ($\triangle$) 470, ($\square$) 950 and ($\bigcirc$) 1600 A m$^{-2}$.
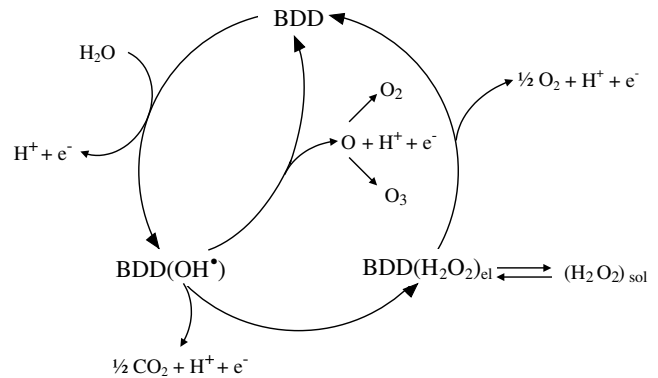


Fig. 5. Scheme of the proposed mechanism for water oxidation on BDD electrode in acidic solution containing a non electroactive supporting electrolyte (HClO$_4$).

where $C^S$ is the bulk limiting concentration (mmol m$^{-3}$), $A$ is the electrode area (m$^2$), $V$ the volume of electrolyte (m$^3$) and $k_d$ the mass-transfer coefficient (m s$^{-1}$).

(iii) $O_3$ production: A further possible reaction of $OH^{\bullet}$ is oxidation to atomic oxygen (Equation 11) followed by formation of ozone (Equation 12) or evolution of oxygen (Equation 13):

$$OH^{\bullet} \rightarrow O^{\bullet} + H^+ + e^- \tag{11}$$

$$O^{\bullet} + O_2 \rightarrow O_3 \tag{12}$$

$$2\,O^{\bullet} \rightarrow O_2 \tag{13}$$

A similar mechanism involving adsorbed hydroxyl radicals was proposed by Babak et al. [29] for ozone evolution on $PbO_2$ electrode. The fact that boron-doped diamond gives a current efficiency for ozone evolution lower than $PbO_2$ can be explained by the different adsorption properties of BDD and $PbO_2$ electrode surfaces. In fact, ozone evolution is favoured by the adsorption of hydroxyl radicals on the anode surface, as occurs on the hydrated surface of lead dioxide, while on boron-doped diamond, which is well known to have an inert surface, $OH^{\bullet}$ radicals are very weakly adsorbed.

(iv) BDD corrosion: Another possible reaction pathway for the electrogenerated hydroxyl radicals is the combustion of BDD to $CO_2$ (Equation 14) during the anodic polarisation at high current density [27].

$$C_{BDD} + 2\,OH^{\bullet} + \rightarrow CO_2 + 2\,H^+ + 2\,e^- \tag{14}$$
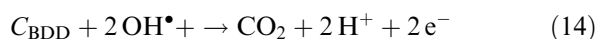
## 4. Conclusion

It has been shown that during electrolysis in 1 M $HClO_4$, the main anodic reaction is oxygen evolution, however, other oxidants such as $O_3$ and $H_2O_2$ are formed. In particular, both the ozone and hydrogen peroxide concentrations increases almost linearly with applied current in the range 230–1500 A m$^{-2}$.

On the basis of these experiments, a simplified mechanism for water oxidation is presented. According to this mechanism, the first oxidation step is water discharge with concomitant formation of hydroxyl radicals on the BDD (Equation 5) surface which further produce oxygen, ozone, hydrogen peroxide or participate in the corrosion of the BDD anode.

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