Voltammetric and electrochemical impedance spectroscopy characterization of a cathodic and anodic pre-treated boron doped diamond electrode

S. Carlos B. Oliveira, Ana Maria Oliveira-Brett

Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-535 Coimbra, Portugal

1. Introduction

BDD electrodes have been extensively studied in recent years, from the point of view of fundamental electrochemical properties as well as that of applications [1–13]. BDD electrodes are found to be attractive for electrochemical applications due to their physical, chemical, and electronic properties, e.g. high thermal conductivity; high hardness and chemical inertness; a wide electrochemical potential window in aqueous and non-aqueous media; a very low capacitance and a very high electrochemical stability [7,12,14].

A big advantage of the BDD electrode is also due to the facility of quickly changing its surface properties, which can be utilized for a large range of applications, e.g. in electroanalysis, electrosynthesis, and electrochemically based toxic waste remediation, but a disadvantage is the difficulty in standardization and understanding the various factors that influence the BDD electrode properties.

Although the properties mentioned make BDD electrodes very useful for a wide range of applications, they are also dependent on a large range of factors: dopant concentration; structural defects in the diamond film; non-diamond carbon impurity content (sp2 inclusions); crystallographic orientation and surface termination (H, O). Amongst all the factors that can influence the electrochemical response of the BDD electrode, possibly the most complex is the effect of the surface termination (H, O) due to its influence on the physical, chemical and electronic characteristics of the BDD surface, since the hydrogen terminated BDD surface is hydrophobic with a negative electron affinity and has high conductivity, whereas the oxygen terminated BDD surface is hydrophilic with positive electron affinity and has low conductivity [2–4,14–23]. Thus, a more extensive characterization of BDD surface termination is still needed to better understand the electrochemical response.

BDD thin film electrodes are prepared using chemical vapor deposition (CVD) techniques, grown using a feed-gas mixture of 0.3–1.0% CH4 in H2, which can be activated using either a hot filament or a microwave plasma source, and deposited on a suitable substrate, such as conducting silicon, at a substrate temperature of 700–900°C. The boron dopant is added to the source gas mixture, often in the form of diborane (B2H6), at concentrations ranging from 1,000 to 10,000 ppm. This results in the formation of a thin film of polycrystalline diamond with a thickness of 1–10 μm with hydrogen termination on the surface and a boron carrier concentration of 1 x 10^20 cm^-3 or greater [1,5,7,12].

The BDD surface termination is usually generated by electrochemical methods, hydrogen evolution by cathodic pre-treatment to produce H-termination, and oxygen evolution by anodic pre-treatment to produce O-termination, or plasma...
treatment to produce H- and O-terminations, among others [3,15,18,24,25].

Various methods with great sensitivity and specificity have helped to characterize the mechanism underlying the effect of the surface termination on the electrochemical properties of BDD interfaces, such as X-ray photoelectron spectroscopy (XPS) [14,15,19–22], Raman spectroscopy [21], atomic force microscopy (AFM) [1], electrochemistry [2–4,14–23] and electrochemical impedance spectroscopy (EIS) [2,4,15,16,18,19]. However, conflicting results have been reported [3,4,14,18,20,21,23,24].

This paper is aimed at giving a better understanding of the effect of cathodic and anodic pre-treatments on the electrochemical response of the BDD electrode in aqueous media and the influence of the pre-treatment in different supporting electrolytes on the final surface termination, using cyclic and differential pulse voltammetry and electrochemical impedance spectroscopy. EIS is well established as a powerful tool for investigating the mechanisms of electrochemical reactions, for measuring the dielectric and transport properties of materials, for exploring the properties of porous electrodes, and for investigating surface adsorption [26].

2. Experimental

2.1. Materials and reagents

K₃[Fe(CN)₆] was obtained from Sigma–Aldrich and used without further purification. Analytical-grade reagents and purified water from a Millipore Milli-Q system (conductivity <0.1 µS cm⁻¹) were used for the preparation of pH 4.5 0.1 M acetate buffer and pH 0.55 0.5 M sulphuric acid electrolyte solutions. A stock solution of K₃[Fe(CN)₆] 10 mM was made in pH 0.55 0.5 M sulphuric acid electrolyte solutions.

Microvolumes were measured using an EP-10 Plus and an EP-100 Plus motorized microliter pipette (Rainin Instrument, Woburn, MA, USA). The pH was measured with a Crison Model micropH 2001 pH meter with an Ingold combined-glass electrode. All experiments were done at room temperature (25 ± 1 °C).

2.2. Voltammetric parameters and electrochemical cells

Voltammetric experiments were performed using a µAutolab running with GPES 4.9 software, Eco-Chemie, Utrecht, The Netherlands. The voltammetric conditions were: cyclic voltammetry (CV), scan rate ν = 50 mV s⁻¹; and differential pulse voltammetry (DPV), pulse amplitude 50 mV, pulse width 70 ms and scan rate v = 5 mV s⁻¹. The EIS measurements were carried out using FRA software version 4.9. A root-mean-square (r.m.s.) perturbation of 5 mV was applied over the frequency range 65–0.1 Hz with five frequency values per decade.

Measurements were carried out using a BDD working electrode, a Pt wire counter electrode, and an Ag/AgCl (3 M KCl) as reference, in a 2 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 CH₄, H₂ and trimethylboron (TMB). The boron dopant is introduced in the diamond film by in situ doping during the CVD process through a TMB gas source. This HF-CVD process gives a columnar, randomly textured polycrystalline BDD film with the surface dominated by facets. The final boron content was of the order of 8000 ppm, 5.7 × 6.1 mm² surface area, ∼1 µm thickness.

Two different procedures for BDD surface electrochemical pre-treatments were carried out before every electrochemical assay in different supporting electrolytes: pH 4.5 0.1 M acetate buffer and pH 0.55 0.5 M sulphuric acid electrolyte solution:

1. **Anodic pre-treatment:** a positive potential was applied for 30 min, Eₑₐₜ = +3.0 V, and the BDD surface was oxidized, Ox-BDD, together with long and intense oxygen evolution.

2. **Cathodic pre-treatment:** a negative potential was applied for 30 min, Eₐₖₐ = −3.0 V or Eₐₖₐ = −1.0 V, and the BDD surface was reduced, Red-BDD, together with long and intense hydrogen evolution.

3. Results and discussion

Before characterization by EIS, it was necessary to examine the electrochemical behavior of the BDD surface by CV and DPV after cathodic and anodic pre-treatments. This information was used to ascertain the potential window and which potentials should be chosen for the impedance measurements.

3.1. Voltammetric characterization

In order to evaluate the quality and the state of the BDD electrode surface after cathodic and anodic pre-treatments and the influence of the pre-treatment in different supporting electrolytes on the final surface termination, the voltammetric behavior of the redox couple [Fe(CN)₆]⁴⁻/³⁻ in pH 0.55 0.5 M sulphuric acid supporting electrolyte was investigated by CV at a Red-BDD and an Ox-BDD surface (Fig. 1).

CVs were obtained for the oxidation of 5 mM [Fe(CN)₆]⁴⁻ at a Red-BDD surface after pre-treatment in two different electrolytes, acetate buffer and sulphuric acid, as described in Section 2.2, Fig. 1A. In both cases, a reversible oxidation peak occurs at Eₚ₁ = +0.47 V, corresponding to the oxidation of the [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻, the reduction peak occurs at Eₚₑ₁ = +0.371 V. The difference between peak potential Eₚ₁ and the potential at half height of peak Eₚₑ₁ was Eₚₑ₁ = −Eₚₑ₁ = 0.139 mV, and this small difference suggests reversible transfer of one electron, on the Red-BDD surface in agreement with the literature [18,24].

CVs were also obtained for the oxidation of 5 mM [Fe(CN)₆]⁴⁻ at an Ox-BDD surface after pre-treatment in acetate buffer and sulphuric acid, as described in Section 2.2, Fig. 1B. In both cases, an oxidation peak occurs at Eₚ₁ = 1.0 V, corresponding to the oxidation of the [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻, the reduction peak occurs at Eₚₑ₁ = +0.2 V. The difference between peak potential Eₚ₁ and the potential at half height of peak Eₚₑ₁ was Eₚₑ₁ = −Eₚₑ₁ = 127 mV at Ox-BDD surface pre-treated in sulphuric acid and was Eₚₑ₁ = −Eₚₑ₁ = 137 mV at Ox-BDD surface pre-treated in acetate buffer. After either pre-treatment the Ox-BDD surface presented a quasi-reversible behavior for the redox couple, with a very large difference between the anodic and cathodic peak potentials, Eₚₑ₁ = −Eₚₑ₁ = 800 mV, due to the difficulty of electron transfer, in agreement with the literature [23,24].

CVs of each pre-treated BDD surface showed that the peak currents were linearly proportional to the square root of scan rate (ν1/2) in the range of 50–600 mV s⁻¹, indicating that the electrode processes were under diffusion control (results not shown).

A consequence of the cathodic pre-treatment is the increase of the adsorption layer compactness leading to a thicker monolayer of hydrogen terminations on the Red-BDD surface, reactions (a)–(c), in comparison with the absence of pre-treatment [18,21]. In fact, the cathodic pre-treatment only increases hydrogen termination, but does not change the original BDD surface physical and chemical characteristics, e.g. a hydrophobic surface, with negative electron affinity and high conductivity, all these characteristics being favorable to the reversible electrochemical behavior of the
Fig. 1. Cyclic voltammograms in 5 mM [Fe(CN)₆]⁴⁻, pH 0.55 0.5 M sulphuric acid solution, after surface pre-treatment in (−) sulphuric acid and (•••) acetate buffer solutions: (A) Red-BDD and (B) Ox-BDD. 

\[ \text{BDD} + \text{H}_2\text{O} \rightarrow \text{BDD}^{(*)\text{OH}} + \text{H}^+ + e^- \]  

On the other hand, during the anodic pre-treatment the BDD hydrogen terminations are converted to oxygen terminations during the discharge of water molecules to form hydroxyl radicals, reaction (d), and subsequent adsorption of its reaction products on the BDD surface [9,27]. Thus the Ox-BDD surface physical and chemical characteristics are changed to a hydrophilic surface, with positive electron affinity and low conductivity. The termination of the surface and presence of oxygen functionalities influence the kinetics of the reaction and explains the quasi-reversible electrochemical behavior of the redox couple [Fe(CN)₆]⁴⁻/³, observed in the CVs obtained using a Ox-BDD surface, Fig. 1B.

\[ \text{BDD} + \text{H}_2\text{O} \rightarrow \text{BDD}^{(*)\text{OH}} + \text{H}^+ + e^- \]  

A very important property of the hydroxyl radicals produced on the BDD surface during the anodic pre-treatment is their very high reactivity and hence it can be involved in parallel reactions on the BDD surface. An example is the oxidation of the supporting electrolyte and hydrogen peroxide formation [27–29], these reaction products being adsorbed on the BDD surface. As a consequence the Ox-BDD surface is not completely inert. The amount of hydroxyl radicals electrogenerated by BDD and its reaction products adsorbed on the BDD surface was strongly dependent on the electrolyte used in the anodic pre-treatment will be confirmed by the electrochemical impedance spectroscopy results.

The CVs presented indicate that the electrochemical behavior for the [Fe(CN)₆]⁴⁻/³ redox couple is very dependent on the state of the BDD surface and a reversible reaction was only observed after the cathodic pre-treatment. The interactions between the BDD surface termination and the supporting electrolyte have to be considered for the correct interpretation of the electrochemical results.

CVs were also recorded for the oxidation of 5 mM [Fe(CN)₆]⁴⁻ at a re-treated Red-BDD surface after anodic pre-treatment and at a re-treated Ox-BDD surface after cathodic pre-treatment (not shown); the electrochemical treatments were done in acetate buffer and in sulphuric acid, as described in Section 2.2. The CVs at re-treated Red- and Ox-BDD surfaces were equal to those obtained with pre-treated Red-BDD and Ox-BDD surfaces, respectively, indicating the facility of the BDD electrode to quickly change its surface properties when polarized under mild conditions. [21,30]. The BDD electrode surface, after different pre-treatments, cause changes in electrochemical behavior of H-terminated sites or the increase of oxygen content due to C–O functionalities, hydroxyl radicals or other groups produced in parallel reactions that occur on the BDD surface as a result of the very high reactivity of the hydroxyl radicals adsorbed on the BDD surface [27–29].

The Ox-BDD and Red-BDD electrode surfaces were pre-treated and characterized in acetate buffer as described in Section 2.2. The effect of each pre-treatment on the electrochemical response of a BDD electrode was studied in the high positive potential region using DPV, Fig. 2. The presence of electroactive surface groups due to the sp²-carbon incorporated into the diamond
structure is responsible for the higher surface activity, and provides the surface sites needed for adsorption of reaction intermediates, including those from hydrogen and oxygen evolution \([11,30]\). A bigger oxidation peak current, \(E_{pa} \sim +1.2\) V, at Red-BDD, and a smaller peak current, \(E_{pa} \sim +1.3\) V, at Ox-BDD, suggests a more difficult electron transfer reaction on the Ox-BDD surface since anodic pre-treatment led to the oxidation of the aromatic functional groups, eliminating the sp2-carbon from the surface \([30]\). These peaks disappeared quickly as the BDD electrode surface became deactivated. DP voltammograms, Fig. 2, showed that oxygen evolution started at Red-BDD at \(\sim +1.4\) V, and at Ox-BDD at \(\sim +1.6\) V vs. Ag/AgCl.

3.2. Electrochemical impedance spectroscopy characterization

Electrochemical impedance spectroscopy (EIS) is an efficient method to probe and model the interfacial characterization of electrodes \([31,32]\), and \([\text{Fe(CN)}_6]^{4-}\), of different concentrations, was used as the redox probe in the impedance measurements performed in sulphuric acid media at BDD electrode surface immediately after cathodic and anodic pre-treatments.

The Nyquist plots of the electrochemical impedance spectra were obtained at \(E_{ap} = +1.0\) V using the Ox-BDD surface pre-treated in sulphuric acid, Fig. 3A, and acetate buffer, Fig. 3B, for different concentrations of \([\text{Fe(CN)}_6]^{4-}\), as described in Section 2.2. It was found that the cell resistance varied according to the electrolyte used in the pre-treatment.

The Nyquist plots for the Ox-BDD surface pre-treated in acetate buffer, Fig. 3B, can be described as a semicircle near the origin, at high frequencies, followed by a linear tail with a unit slope, fits adequately the Randles circuit \([31,32]\) of Fig. 5, and the fitted values for charge transfer resistance, \(R_{ct}\), and constant phase element, CPE, are given in Table 1. The diameter of the semicircle is a measure of the charge transfer resistance, \(R_{ct}\), and for these experiments was observed that \(R_{ct}\) decreased with increasing redox couple concentration.

The Nyquist plots for the Ox-BDD surface pre-treated in sulphuric acid, Fig. 3A, showed greater values for \(R_{ct}\) when compared with those for Ox-BDD pre-treated in acetate buffer, Table 1, and the Nyquist plots are composed of two depressed semicircles. The high frequency semicircle has no correlation with the \([\text{Fe(CN)}_6]^{4-}\) concentration, showed by results of the \(R_{ct}\) and the low frequency semicircle very flattened for all \([\text{Fe(CN)}_6]^{4-}\) concentrations suggesting a slow diffusion process through the compact oxygen terminated adsorbed monolayer.

![Fig. 3. Complex plane impedance spectra for various concentrations of \([\text{Fe(CN)}_6]^{4-}\) in sulphuric acid solution at +1.0 V, after Ox-BDD surface pre-treatment in: (A) sulphuric acid and (B) acetate buffer solutions.](image)

![Fig. 4. Complex plane impedance spectra for various concentrations of \([\text{Fe(CN)}_6]^{4-}\) in sulphuric acid solution at +0.45 V, after Red-BDD surface pre-treatment in: (A) and (C) sulphuric acid and (B) acetate buffer solutions.](image)
Concerning Ox-BDD surface modifications, the present study clearly shows that an increase of oxygen termination on BDD surface was obtained for BDD electrodes after the anodic treatment in sulphuric acid solution. This effect was observed by EIS, Fig. 3A, and confirmed by the CPE values obtained for the Ox-BDD surface pre-treated in sulphuric when compared with the Ox-BDD surface pre-treated in acetate buffer, Table 1. A compact oxygen terminated adsorbed monolayer is formed during the anodic pre-treatment in sulphuric acid solution due to the higher amount of OH⁻ produced, reaction (d), and subsequent adsorption of its reaction products.

The Nyquist plots of the electrochemical impedance spectra were obtained at +0.45 V using the Red-BDD surface pre-treated in sulphuric acid, Fig. 4A and C, and acetate buffer, Fig. 4B, for different concentrations of [Fe(CN)₆]⁴⁻, as described in Section 2.2.

For all Red-BDD surfaces a typical shape of a Faradaic impedance spectrum for a solution of a redox species, and an excellent fit to the Randles circuit. Fig. 5, was obtained and the fitted values for $R_{ct}$ and CPE are given in Table 2. Comparing the results for the fitting, Table 2, it is confirmed that the $R_{ct}$ and CPE varied according to the electrolyte used in the cathodic pre-treatment. In all experiments was observed that the $R_{ct}$ decreased as the redox couple concentration was increased and that the $R_{ct}$ and CPE were lower at Red-BDD surface pre-treated in acetate buffer, Fig. 4B, than at Red-BDD surface pre-treated in sulphuric acid, Fig. 4A.

The hydrogen evolution reaction (HER) in acid media is established at a BDD surface [33] considering the mechanisms in reactions: (a) the reaction step of proton discharge with electrosorption, Volmer reaction, (b) electrochemical desorption, Heyrovsky reaction, and (c) H recombination, Tafel reaction. Also the rate of reaction (b) becomes limited by the rate of reaction (a) and this reaction has the equilibrium constant and the rate influenced by proton concentration. So when sulphuric acid is utilized the in the cathodic pre-treatment the rate of both reactions (a) and (b) increased favouring the H₂ production. However, when acetate buffer was utilized in the cathodic pre-treatment the rate of both reactions (a) and (b) decreased, but a higher amount of boron–hydrogen complex due the lower H₂ production was obtained increasing the Red-BDD surface conductivity.

The effect of the applied potential in the cathodic pre-treatment on a Red-BDD surface conductivity is also observed in Fig. 4A and C. The fitted values for $R_{ct}$ and CPE after applying −3.0 or −1.0 V during the cathodic pre-treatment are also reported in Table 2. For different concentrations of [Fe(CN)₆]⁴⁻ the $R_{ct}$ was lower at Red-BDD surface when applied −3.0 V and reduced by a factor of about 20. However, comparing the values for $R_{ct}$ in different concentrations of [Fe(CN)₆]⁴⁻ at Ox-BDD surface, Table 1, and at Red-BDD surface when the cathodic pre-treatment applied −1.0 V, Table 2, a progressive decrease of $R_{ct}$ at Red-BDD surface occurs and consequently the Red-BDD surface conductivity is lower than that of the Ox-BDD surface.

EIS in acetate buffer electrolyte at Red-BDD and Ox-BDD surfaces also pre-treated in acetate buffer, in the absence of the [Fe(CN)₆]⁴⁻ redox probe, was recorded, Fig. 6. The EIS behavior at Red-BDD surface when the potentials of +0.45 V and +1.0 V were applied was essentially capacitive, modified by surface roughness effects, leading to a straight line, Fig. 6A. However, the lowest $R_{ct}$ values at +1.5 V are related with the fact that the oxygen evolution are commencing and some electrode reaction is occurring, also demonstrated by the semi-circular form of the spectra. The EIS behavior at Ox-BDD surface when were applied the potentials of +0.45 V and +1.0 V was also essentially capacitive leading to a straight line, but for applied potentials higher than +2.0 V the oxygen evolution begins to have an influence on the shape of the spectra, Fig. 6B. All these results are in agreement with the DP voltammograms in Fig. 2.

Some redox couples, such as [Fe(CN)₆]⁴⁻/³⁻, which are traditionally treated as outer sphere behave anomalously at carbon electrodes and may change to an inner-sphere electron transfer mechanism at diamond electrodes, where some degree of interaction occurs between the redox species and the electrode surface [1]. Based on the results obtained here, factors such as the termination of the surface can influence the kinetics of the reaction. An important factor that leads to uncertainty is that in many cases, the value of the apparent heterogeneous rate constant has been extracted from CV experiments without any consideration of the resistance of the electrodes.

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**Table 1**

<table>
<thead>
<tr>
<th>Anodic pre-treatment</th>
<th>[Fe(CN)₆]⁴⁻/mM</th>
<th>$R_{ct}$/$Ωcm²$</th>
<th>CPE/µF cm⁻² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox-BDD pre-treated in acetate buffer (+3.0 V/30 min)</td>
<td>2.5</td>
<td>4.46</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>2.70</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1.75</td>
<td>3.5</td>
</tr>
<tr>
<td>Ox-BDD pre-treated in sulphuric acid (+3.0 V/30 min)</td>
<td>2.5</td>
<td>4.3</td>
<td>3.98</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>3.1</td>
<td>3.98</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>2.5</td>
<td>3.98</td>
</tr>
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**Table 2**

<table>
<thead>
<tr>
<th>Cathodic pre-treatment</th>
<th>[Fe(CN)₆]⁴⁻/mM</th>
<th>$R_{ct}$/$Ωcm²$</th>
<th>CPE/µF cm⁻² s⁻¹</th>
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<tbody>
<tr>
<td>Red-BDD pre-treated in acetate buffer (−3.0 V/30 min)</td>
<td>1.0</td>
<td>33.30</td>
<td>7.76</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>12.57</td>
<td>10.1</td>
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<tr>
<td></td>
<td>5.0</td>
<td>6.59</td>
<td>10.3</td>
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<tr>
<td></td>
<td>10.0</td>
<td>3.44</td>
<td>21.1</td>
</tr>
<tr>
<td>Red-BDD pre-treated in sulphuric acid (−3.0 V/30 min)</td>
<td>1.0</td>
<td>51.70</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>20.16</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>10.53</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>5.17</td>
<td>17.6</td>
</tr>
<tr>
<td>Red-BDD pre-treated in sulphuric acid (−1.0 V/30 min)</td>
<td>1.0</td>
<td>639</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>327</td>
<td>13.4</td>
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<tr>
<td></td>
<td>10.0</td>
<td>104</td>
<td>13.8</td>
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Comparison between the EIS results obtained for the anodic and cathodic pre-treatments shows that the Red-BDD surface presents much smaller $R_{ct}$ values than the Ox-BDD surface. The EIS data, agrees very well with the voltammetric results, and is consistent with a model proposed to describe the charge transfer at BDD surface. The difference between $R_{ct}$ values for both Ox-BDD and Red-BDD surfaces, when the sulphuric acid solution was used in the pre-treatment, tends to increase with increasing the oxygen and decreasing of the boron–hydrogen complex at BDD surface. The relationship between resistance and rate of electron transfer is complex, because the formation of a conductive adsorption layer on BDD after the anodic and cathodic pre-treatment occurs, which mediates the exchange of the electrons between the valence band of the diamond and the redox system. If the electron transfer involves tunnelling then the rate of electron transfer is expected to decrease exponentially with surface layer thickness [1,34]. Nevertheless, the resistance is inversely proportional to the rate of electron transfer so that the effects, due to oxygen and hydrogen terminations, of the adsorption monolayer compactness at BDD surface will provide some insight into the mechanism of electron transfer.

On the basis of EIS results using different supporting electrolytes in the anodic and cathodic pre-treatments the kinetics of the $H^+$/H and $H_2O/OH^*$ redox couples has been discussed in order to elucidate their influence on the evolution of oxygen and hydrogen BDD surface termination and the origin of the reactivity of the Red-BDD and Ox-BDD surfaces. The kinetics of the $H^+$/H and $H_2O/OH^*$ redox couples at Red-BDD and Ox-BDD surfaces is pH-dependent. The oxidation of the BDD surface by anodic pre-treatment was more intense when utilized sulphuric acid electrolyte solution and a compact adsorption monolayer was formed due to the higher concentration of OH* produced and subsequent adsorption of its reaction products on the BDD surface decreasing the Ox-BDD surface conductivity. The reduction of BDD surface by cathodic pre-treatment was also more intense when utilized the sulphuric acid electrolyte however when the acetate buffer was utilized in the cathodic pre-treatment a higher amount of boron–hydrogen complex, due to the lower H$_2$ production, was obtained which increases the Red-BDD conductivity. It has been shown that the acetate buffer is a better electrolyte than the sulphuric acid for either electrochemical treatment and in general that the electrolyte chosen for the electrochemical pre-treatment is very important influencing the evolution of the final surface termination, the BDD conductivity, the electrochemical response and the reproducibility of experimental results.

4. Conclusions

The BDD electrodes are very attractive due to their unique chemical, physical and electronic properties when compared with other electrode materials but their properties are dependent on a large range of factors such as the electrochemical pre-treatment. The results in this study showed that the electrochemical properties of BDD electrodes are very dependent on the state of the surface termination, due to oxygen and hydrogen terminations, and also on the electrolyte used in the pre-treatment.

All CV, DPV and EIS results demonstrated that a better response was obtained when the BDD surface was pre-treated cathodically in comparison with the anodic pre-treatment. The interaction and adsorption of the electrochemical species with the BDD surface pre-treated cathodically was facilitated due to a higher conductivity of the BDD electrode. The hydroxyl radicals adsorbed on BDD surface during the anodic pre-treatment are highly reactive and consequently the Ox-BDD surface has a less good response because it is not completely inert.

Acknowledgements

Financial support from Fundação para a Ciência e Tecnologia (FCT), Ph.D. Grant SFRH/BD/27322/2006 (S.C.B. Oliveira), projects PTDC/QUI/65255/2006, PTDC/QUI/65732/2006, and PTDC/QUI/098562/2008, POCI (co-financed by the European Community Fund FEDER), and CEMUC-R (Research Unit 285), is gratefully acknowledged.

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