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Short Report

Ultramicroelectrode Array Behavior of Electrochemically Partially Blocked Boron-Doped Diamond Surface

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Demonstra-se, pela primeira vez usando experimentos simples de voltametria cíclica, que a pré-polarização anódica de eletrodos de diamante dopado com boro (DDB) conduz a superfícies parcialmente bloqueadas. Eletrodos de DDB anodicamente pré-polarizados, com diferentes níveis de dopagem de boro, apresentaram respostas de voltametria cíclica sigmoidais para o par redox ferro/ferricianeto a baixas velocidades de varredura (0,5 mV s^{-1}). Por outro lado, quando os mesmos eletrodos são pré-polarizados catodicamente, observaram-se respostas quase-reversíveis e reversíveis na mesma velocidade de varredura, correspondendo a superfícies eletroquimicamente heterogêneas. Assim, as superfícies de DDB podem atuar parcialmente bloqueadas ou com eletroatividade heterogênea, dependendo da polarização, anódica ou catódica, respectivamente.

It is demonstrated, for the first time using simple cyclic voltammetry experiments, that the anodic pre-polarization of boron-doped diamond electrodes (BDD) leads to partially blocked surfaces. Anodically pre-polarized BDD electrodes, with different boron-doping levels, presented sigmoidal cyclic voltammetry profiles to the ferro/ferri-cyanide redox couple under low scan rate (0.5 mV s^{-1}). On the other hand, when the same electrodes are cathodically pre-polarized, quasi-reversible and reversible responses were observed under the same scan rate, corresponding to surfaces with heterogeneous electroactivity. Thus, BDD surfaces can act as partially blocked or with heterogeneous electroactivity, depending on the polarization, anodic or cathodic, respectively.

Keywords: surface termination, anodic polarization, cathodic polarization, spherical diffusion, cyclic voltammetry

Introduction

The understanding of boron-doped diamond (BDD) surface termination features and behavior is of particular interest mainly due to their potential applications in electroanalysis, biosensing, molecular electrochemistry, organic electrochemistry, among other applications.

Our group revealed that the width of the electrochemical potential window in acid media depends inversely on the boron-doping level of diamond electrodes.[1] Since the hydrogen (HER) and oxygen (OER) evolution reactions are catalytic, they require available active sites on the electrode surface for the initial adsorption of the species involved in these reactions. Hence, the increment in the number of active sites on the electrode surface, due to the increase in the doping level, can yield a reduction of the potential window, probably related to the superficial boron content. Thus, when the doping level is high, the higher electrocatalytic activity of the electrode is associated with a large amount of boron sites, which act as the catalyst for these reactions, as concluded by Cai *et al.*[2,3] In contrast, a lower concentration of boron-rich sites on the electrode

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surface could make difficult both the hydrogen and the oxygen adsorption step needed for gas evolution reactions.

Alternatively, this increment in the electrode surface activity when the boron content is higher was not previously reported for commonly used redox couples like $Fe(CN)_6^{4-/3-}$, $Ru(NH_3)_6^{3+/2+}$, among others, which are traditionally known as outer-sphere and diffusion-controlled reactions.[4-7] The question to be solved is: why is the electrochemical activity for HER and OER obtained at differently doped hydrogen-terminated diamond electrodes so different from the one obtained for the $Fe(CN)_6^{4-/3-}$ redox couple?

Holt *et al.*,[8] using conductive probe atomic force microscopy (CP-AFM) and scanning electrochemical microscopy (SECM), reported that hydrogen-terminated BDD surfaces with different boron-doping levels are predominantly insulating, with discrete conducting areas randomly distributed on the surface. The higher the boron doping level, the higher is the active area of these electrodes.

In the case of highly-doped polycrystalline BDD with oxygen-termination,[9] while CP-AFM and cathodoluminescence (CL) imaging techniques demonstrated that boron uptake is non-uniform across the BDD surface, SECM depicted local currents of the magnitude expected for metal-like behavior in some regions, suggesting degenerative doping of the grains. The other regions displayed slower electron transfer.

Different crystal faces of polycrystalline BDD incorporate boron to different extents during growth by chemical vapor deposition.[10] This heterogeneity in the local concentration of charge carriers led to speculation in the literature as to whether the entire surface of polycrystalline BDD is active or whether there are "hot spots" of activity.[8,9] In this sense, Patten *et al.*[11] studied, at high spatial resolution, the local rate of heterogeneous electron transfer for various aqueous electrochemical reactions (inner-sphere, outer-sphere and complex process) at oxygen-terminated BDD electrodes using scanning electrochemical cell microscopy (SECCM). They concluded that the entire BDD surface is electrochemically active, but apparent heterogeneous electron transfer rates are highly correlated with facet-dependent boron concentration. Facets with higher boron content have higher heterogeneous electron transfer activity.

Some reports recently showed that partially blocked electrodes behave as microelectrode arrays.[12,13] Depending on the microelectrode sizes, the center-to-center distance separations between them, and the scan rate used in the voltammetric experiments, they observed sigmoidal (spherical diffusion) cyclic voltammetric responses. Moreover, these authors also predicted the voltammetric behavior of electrochemically heterogeneous electrodes. Therefore, the heterogeneous conductivity of BDD surfaces or the existence of partially blocked electrode surfaces could be verified by cyclic voltammetry at low scan rates. In this sense, low scan rate (long experiment duration) is needed to avoid linear diffusion since the center-to-center separations between the "hot spots" of activity working as ultramicroelectrodes could be very small.

The verification of the electrochemical character of BDD surfaces is crucial for their application, mainly for electroanalysis. Thus, here, a straightforward electrochemical approach was used to study the electrochemical characteristics of BDD surfaces with different doping levels as a function of the surface termination. Cyclic voltammetry data demonstrated that the surface electroactivity of BDD is highly dependent on the surface termination.

Experimental

All electrochemical measurements were carried out in a three-electrode single compartment Pyrex® glass cell (50 mL) equipped with degassing facilities for bubbling N_2. The counter and reference electrodes were a 2 cm^2 platinum foil and a hydrogen electrode in the same solution (HESS) connected by a Luggin capillary, respectively. All the polycrystalline BDD electrodes were prepared at the Centre Suisse d'Electronique et de Microtechnique SA (CSEM), Neuchâtel, Switzerland on silicon wafers. The final boron content of the electrodes was of the order of 300, 800, 2000 and 8000 ppm. In this sense, the order of magnitude of the concentration of boron in the solid phase varies roughly with the square of the B/C ratio in the gas phase from about 8.0×10^{17} cm^{-3} at 200 ppm up to 1.5×10^{22} cm^{-3} at 14000 ppm.[14] Thus, the final boron content of the electrodes with 300, 800, 2000 and 8000 ppm of boron corresponds to approximately 9.0×10^{18}, 2.0×10^{19}, 1.0×10^{20} and 5.0×10^{21} cm^{-3}, respectively.

Working electrodes were clamped in firm contact with the side of the cell by means of a rubber O-ring, leaving an exposed area of the BDD plate of 0.65 cm^2. In this way, the electrical contact was made through a copper plate at the gold plated bottom of the silicon wafers.

All the experiments were carried out at room temperature in a 0.5 mol L^{-1} H_2SO_4 (Merck, supra-pure grade) aqueous solution as a supporting electrolyte also containing 1.0 mmol L^{-1} potassium ferrocyanide (Merck, 99.0%) or 1.0 mmol L^{-1} hydroquinone (Sigma-Aldrich, 99.0%) solutions. The solutions were prepared using water supplied by a Milli-Q system from Millipore® Inc. Solutions were also N_2-saturated prior to the measurements. The electrochemical experiments were carried out in duplicate using an Autolab Model PGSTAT 30 potentiostat/galvanostat coupled to an IBM-PC compatible microcomputer.

Fresh samples of the BDD electrodes with different doping levels were subjected to galvanostatic anodic polarization, by applying +10 C cm^{-2} using +1 A cm^{-2}, or galvanostatic cathodic polarization, by applying –10 C cm^{-2} using –1 A cm^{-2}, for electrodes previously anodically pre-treated to clean the electrode surfaces, as already pointed out.[1] These treatments were carried out in 0.5 mol L^{-1} H_2SO_4 aqueous solutions, for the evaluation of the influence of the electrochemical pre-treatments tested on the electrochemical activity of the BDD electrodes at different scan rates (from 0.1 to 1000 mV s^{-1}).

Results and Discussion

The potential window width of polycrystalline BDD is inversely dependent on the increase in the doping level, with differences as high as 1.3 V in the potential windows taken between 8000 ppm and 300 ppm BDD electrodes.[1] Since HER and OER are catalytic reactions, this diminution in the potential window could be due to an increment in the number of active sites of the electrode surface associated with the higher superficial boron content.

However, cyclic voltammograms taken for the $Fe(CN)_6^{4-/3-}$ redox couple at 50 mV s^{-1} (Figure 1) show very similar shapes (reversibility) and similar current density values for both anodic and cathodic peaks for cathodically pre-treated BDD electrodes with different doping levels. The anodic current peaks observed for 8000 and 300 ppm BDD electrodes present a small difference of ca. 6%, with lower differences for the responses obtained at the 2000 and 800 ppm electrodes. The subject under consideration is: why is the electrochemical activity of cathodically pre-polarized BDD electrodes with different doping levels for HER and OER so different from that observed for the $Fe(CN)_6^{4-/3-}$ redox couple?

These discrepancies suggest that the electrochemical responses for the $Fe(CN)_6^{4-/3-}$ redox couple obtained with differently doped BDD are not influenced by the amount of active sites available on the electrode surface. Thus, two hypotheses are that (*i*) the diamond electrode surfaces have heterogeneous conductivity[12,13] or (*ii*) they act as ultramicroelectrode arrays,[15] as will be discussed hereafter.

On the other hand, Figure 2 shows cyclic voltammograms carried out at several scan rates (including 50 mV s^{-1}) for anodically pre-polarized BDD electrodes with different doping levels. These electrode surfaces are very different depending on the doping level. For the less doped BDD electrode, there are irreversible responses at low scan rates, suggesting a blocked surface. In contrast, a quasi-reversible behavior is observed for the other, highly doped, electrodes,

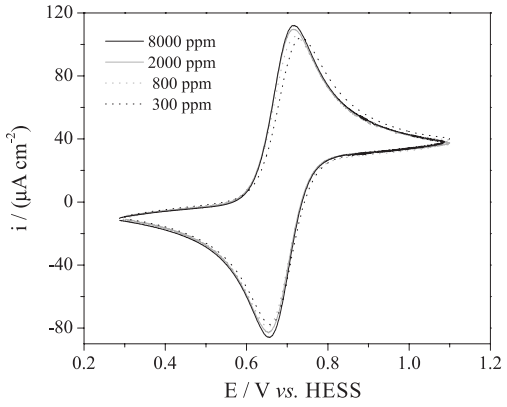

Figure 1. Cyclic voltammograms recorded in 1×10^{-3} mol L^{-1} $K_4[Fe(CN)_6]$ + 0.5 mol L^{-1} H_2SO_4 at BDD electrodes cathodically pre-polarized at –10 C cm^{-2} using –1 A cm^{-2}, ν = 50 mV s^{-1}.

particularly the 8000 ppm BDD electrode. In this case, two well defined peaks are observed for the ferro/ferri-cyanide redox couple. However, the magnitude of the anodic peaks for all the studied electrodes is similar to those observed for the cathodically pre-polarized electrodes in Figure 1.

Cyclic voltammetry studies were carried out at low scan rates to address the heterogeneous electroactivity of BDD surfaces. Figure 3a shows the cyclic voltammetry curves taken at anodically pre-polarized 300 and 8000 ppm BDD electrodes. At a low scan rate (0.5 mV s^{-1}), the $Fe(CN)_6^{4-/3-}$ redox couple shows sigmoidal cyclic voltammetric responses. This sigmoidal shape is commonly observed for ultramicroelectrodes in which the mass transfer of species to the electrode surface follows spherical diffusion. Similar voltammograms were obtained for BDD ultramicroelectrodes,[16-19] ultramicroelectrode arrays[20-22] and nanoelectrode arrays.[23] Moreover, 800 and 2000 ppm BDD electrodes also showed comparable behaviors.

Conversely, at the same scan rate, quasi-reversible and reversible responses are observed at the same electrodes when they are cathodically pre-polarized (Figure 3b), presumably corresponding to a heterogeneous surface with boron-rich sites (high conductivity) and H-terminated sites (with moderate conductivity).[24,25]

The most important point is that at anodically pre-polarized BDD electrodes (8000 ppm, for instance) the quasi-reversible profile observed in Figure 2, at different scan rates, changes to sigmoidal when the scan rate decreases to 1 mV s^{-1} (Figure S1), but at cathodically pre-polarized BDD electrodes, the reversible behavior is still observed at scan rates as low as 0.5 mV s^{-1}, as can be observed in Figure 3b. This different behavior of the same electrode, but with different electrochemical pre-polarization, demonstrates the existence of two very different surfaces.

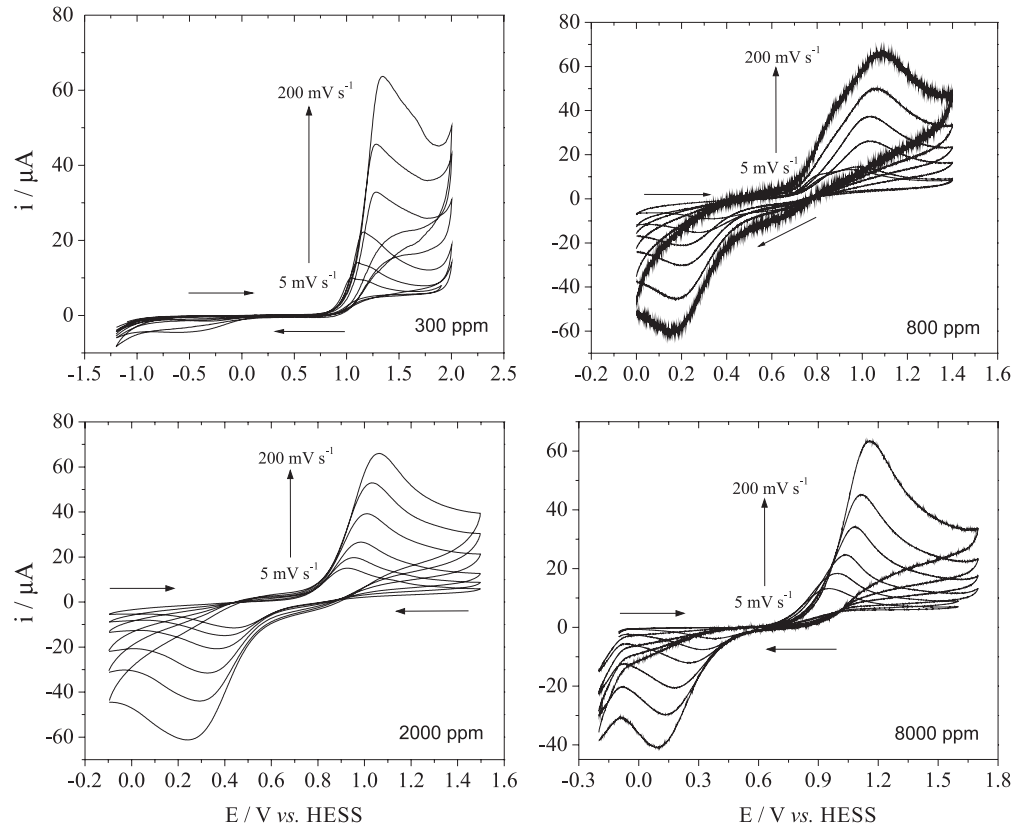

Figure 2. Cyclic voltammograms recorded in 1×10^{-3} mol L^{-1} $K_4[Fe(CN)_6]$ + 0.5 mol L^{-1} H_2SO_4 at BDD electrodes anodically pre-polarized at 10 C cm^{-2} using 1 A cm^{-2}. Doping levels and scan rates are indicated in each figure.

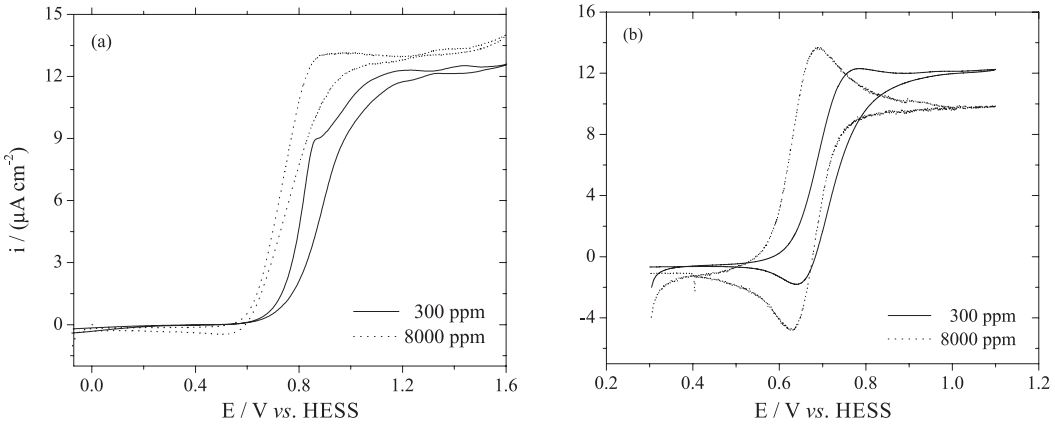

Figure 3. Cyclic voltammograms recorded in 1×10^{-3} mol L^{-1} $K_4[Fe(CN)_6]$ + 0.5 mol L^{-1} H_2SO_4 at BDD electrodes (a) anodically and (b) cathodically pre-polarized at ± 10 C cm^{-2} using ± 1 A cm^{-2}, ν = 0.5 mV s^{-1}.

Thus, it is demonstrated for the first time using cyclic voltammetry experiments that anodically pre-polarized electrodes have partially blocked BDD surfaces. It is also established that cathodically pre-treated BDD surfaces have surfaces with heterogeneous electroactivity.

A broad study of the influence of the voltammetric scan rate on the limiting current observed at an 800 ppm anodically pre-treated diamond electrode is depicted in Figure 4 for the $Fe(CN)_6^{4-/3-}$ redox couple. The limiting current is almost constant in the scan rate range from 0.1 to 1 mV s^{-1} due to the spherical diffusion, which is characteristic of ultramicroelectrode arrays.[16-22] After the transitory behavior observed between 1 and 20 mV s^{-1}, the limiting current increases linearly with increases in the scan rate. This is typical of macroelectrodes or conventionally sized electrodes due to the diminution of the diffusion layer thickness when compared with the dimensions of the microelectrodes, which, in turn, depends on the time

scale of the experiment, that is, the scan rate in cyclic voltammetry experiments.[20]

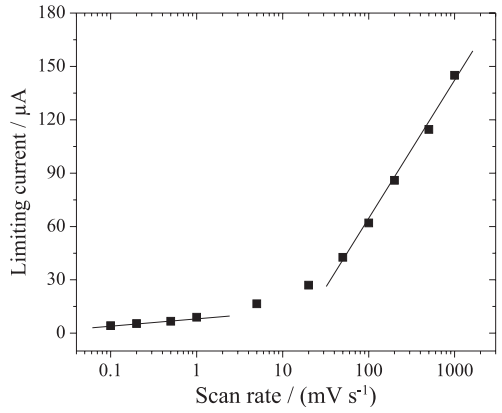

Figure 4. Dependency of current on the scan rate for the oxidation of 1×10^{-3} mol L^{-1} $K_4[Fe(CN)_6]$ without supporting electrolyte recorded at 800 ppm BDD electrodes pre-polarized at 10 C cm^{-2} using 1 A cm^{-2}.

The different electrochemical behavior of cathodically and anodically pre-treated BDD electrodes for the $Fe(CN)_6^{4-/3-}$ redox couple is also seen when the quinone/hydroquinone redox couple is used in voltammetric studies performed at very low scan rates (Figure 5). The sigmoidal shape of the anodically pre-treated BDD electrode corroborates with both the observations made using the $Fe(CN)_6^{4-/3-}$ couple and the statement that a partially blocked BDD surface is obtained when an anodic pre-treatment is applied to the electrode.

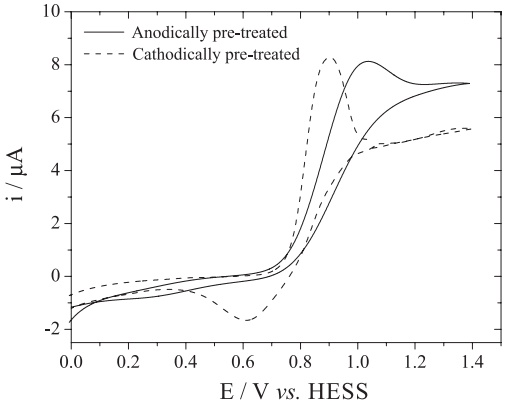

Figure 5. Cyclic voltammograms recorded in 1×10^{-3} mol L^{-1} hydroquinone + 0.5 mol L^{-1} H_2SO_4 on 800 ppm BDD electrodes anodically (solid curve) and cathodically (dashed curve) pre-polarized at ± 10 C cm^{-2} using ± 1 A cm^{-2}, ν = 0.5 mV s^{-1}.

In this sense, the fractional hydrogen/oxygen surface termination of diamond on the nanometer scale, after anodic electrochemical oxidation, was recently demonstrated using the selective attachment of nitrophenyl diazonium on H-terminated BDD surfaces.[26] Electrodes polarized at 3.5 V for 10 s in acid media showed that the fraction of the area which was oxidized was ca. 79% and this value increased to 93% when voltages as high as 6 V were used. Thus, it is clear that the electrochemical anodic polarization of H-terminated BDD electrodes leads to a high degree of O-terminated sites and a portion of nanometric hydrophobic H-terminated "islands". These more conductive islands could act as nanoelectrode arrays, correlating with the sigmoidal voltammetric shapes displayed in Figures 3a and 5 for the $Fe(CN)_6^{4-/3-}$ and quinone/hydroquinone couples, respectively.

Similarly to what was observed for the $Fe(CN)_6^{4-/3-}$ redox couple displayed in Figure 3b, the cathodically pre-treated BDD electrode shows anodic and cathodic peaks for the quinone/hydroquinone redox couple (Figure 5), proving the assertion that a heterogeneous electrochemical surface is working in this case. The heterogeneous electrochemical surface could be due to the presence of sites with different activities probably due to the high electroactivity/conductivity of boron-rich sites[8,9] and the moderate electroactivity of H-terminated diamond sites.[24,25]

The straightforward electrochemical approach used here proves, in a simple way, that the electrical properties of H-terminated BDD surfaces are heterogeneous and that the boron uptake is non-uniform across the surface of BDD. These statements have been previously demonstrated using complicated and sophisticated techniques like CL, CP-AFM, SECM and SECCM.[8-11] In addition, anodically treated surfaces behave as a sea of H-terminated zones which act as the electrodes, whilst the oxygen-terminated surrounding areas remain insulating, well correlating with the observations of Nebel and co-workers[26] using nitrophenyl diazonium molecules attached to H-terminated BDD sites and further oxidized.

Conclusions

In this report, the electrochemical characteristics of BDD electrode surfaces with different doping levels were studied as a function of surface termination by cyclic voltammetry. H- or O-terminated BDD electrodes show very different electrochemical behaviors for both the $Fe(CN)_6^{4-/3-}$ and the quinone/hydroquinone redox couples at low scan rates. The sigmoidal shape of the cyclic voltammograms taken at the O-terminated BDD electrodes indicated the formation of ultramicroelectrode arrays (or nanoelectrode arrays) on these surfaces, while the typical voltammograms seen at the H-terminated BDD electrodes suggest non-homogeneous surfaces with sites with different activities. Thus, it was demonstrated using a simple electrochemical approach that BDD surfaces can be partially blocked or can exhibit heterogeneous

electroactivity, depending on the polarization, that is, anodic or cathodic, respectively.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as a PDF file.

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Supplementary Information

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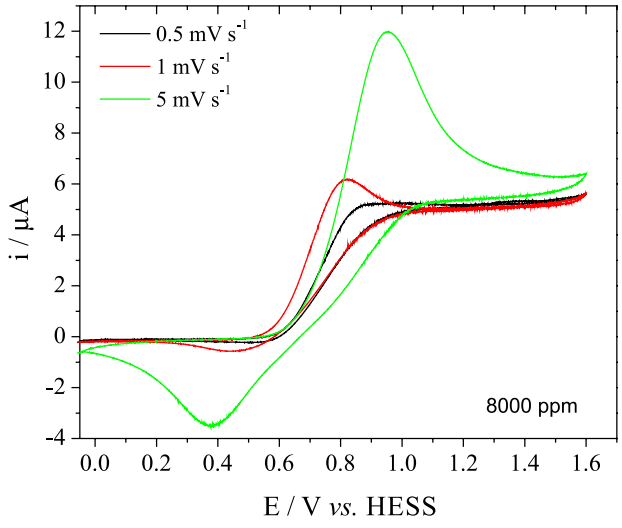

Figure S1. Cyclic voltammograms recorded in 1×10^{-3} mol L^{-1} $K_4[Fe(CN)_6]$ + 0.5 mol L^{-1} H_2SO_4 at 800 ppm BDD electrodes anodically pre-polarized at 10 C cm^{-2} using 1 A cm^{-2}.

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