# Sonoelectrochemical production of hydrogen peroxide at polished boron-doped diamond electrodes

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**Power ultrasound applied to erosion resistant and mechanically stable free standing highly boron-doped diamond electrodes allows the electrochemical reduction of dioxygen to hydrogen peroxide under conditions of extremely high rates of mass transport and in the presence of cavitation.**

The ability to manufacture boron-doped CVD (chemical vapour deposited) diamond routinely is opening the way to the use of this material for technically demanding applications such as a novel electrode material.[1] Advantages of CVD diamond in this new application include its extreme hardness, chemical inertness, and dimensional stability.[2] The electrode material used in this study is in the form of a 5 × 5 × 0.6 mm diamond square with a typical boron-doping level of $10^{20}$ $cm^{-3}$ corresponding to a B/C atom ratio of 1/1000 which allows a resistivity of $3 \times 10^{-4}$ Ω m to be achieved. The use of the free standing diamond plate allows problems with substrate interference and adhesion[3] to be overcome. Further, polishing of the electrode surface produces an essentially flat (surface roughness 20–30 nm $R_A$) and therefore, in the electrochemical sense, ideal electrode surface with properties which are likely to be different to those reported for 'as grown' diamond electrodes.

In sonoelectrochemistry[4] electrode materials are exposed to extreme conditions with mechanical strain induced by pressure waves of some 10 bar amplitude and cavitation induced liquid jets[5] strong enough to cause severe erosion.[6] As an extremely hard material diamond has been extensively characterised *e.g.* for its resistance to water jet erosion.[7] In this test a diamond surface withstands a 0.8 mm diameter water jet with a velocity in excess of 500 m $s^{-1}$. This compares to a value of 150 m $s^{-1}$ for the erosion of soda lime glass and to jets caused by cavitation in aqueous media with a velocity in the order of 200 m $s^{-1}$. Therefore diamond appears to be a promising alternative replacing especially the commonly employed carbon based materials graphite and glassy carbon.

An AFM image of the surface of a highly boron-doped and polished diamond plate electrode is shown in Fig. 1. Owing to the polishing the surface is flat down to the nanometer scale and the characteristic faceting typically observed on a 10–100 µm scale for the polycrystalline material has been removed. Raman spectroscopy (excitation wavelength 632.8 nm) reveals this material to be high quality diamond with a strong and sharp signal at 1331 $cm^{-1}$ (FWHM 4.4 $cm^{-1}$) characteristic for diamond $sp^3$-carbon.

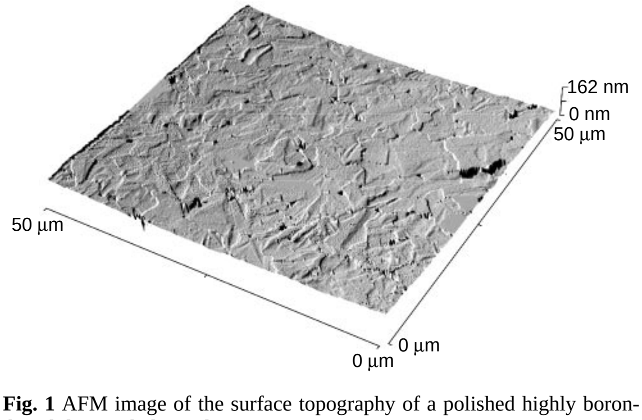

**Fig. 1** AFM image of the surface topography of a polished highly boron-doped diamond electrode.

In Fig. 2(a) a cyclic voltammogram† for the one electron reduction of 1 mM $Ru(NH_3)_6^{3+}$ in aqueous 0.1 M KCl is shown [eqn.(1)].

$$Ru(NH_3)_6^{3+} + e^- \leftrightarrow Ru(NH_3)_6^{2+} \qquad (1)$$

The well defined voltammetric responses remain symmetric even at fast potential scan rates of up to 1 V $s^{-1}$. The separation between the peak potentials for the cathodic and the anodic

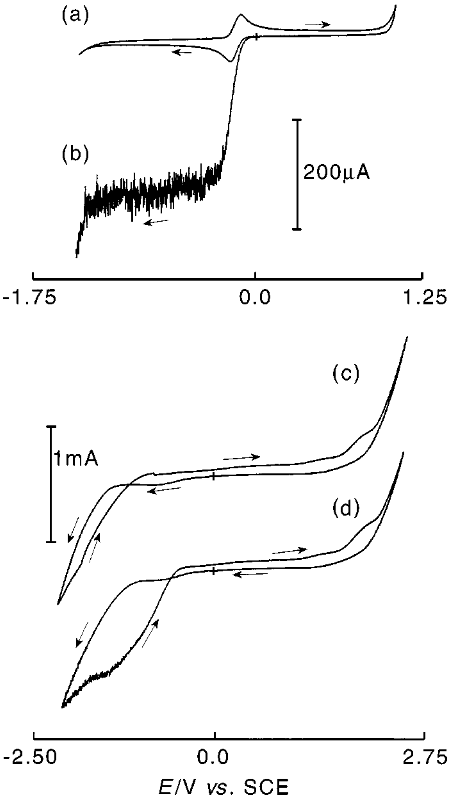

**Fig. 2** (a) Cyclic voltammogram obtained for the reduction of 1 mM $Ru(NH_3)_6^{3+}$ in 0.1 M KCl at a polished 5 × 5 mm diamond electrode with a scan rate of 0.1 V $s^{-1}$. (b) Sonovoltammogram obtained under the same conditions with 90 W $cm^{-2}$ ultrasound intensity and 10 mm electrode to horn distance. Cyclic sonovoltammograms obtained in 0.1 M phosphate buffer at pH = 2 (c) in the absence and (d) in the presence of *ca.* 0.87 mM dioxygen.

**Table 1** Electrochemical data obtained from cyclic voltammograms for the reduction of 1 mM $Ru(NH_3)_6^{3+}$ in 0.1 M KCl at a polished highly boron-doped diamond electrode at $T = 20 \pm 2$ °C

| Scan rate/ V s$^{-1}$ | $E_{1/2}{}^{a}$/V *vs.* SCE | $\Delta E_p$/mV | $I_{p,cath.}$/ $10^{-6}$ A | $k^{\circ b}$/cm s$^{-1}$ |
|---|---|---|---|---|
| 0.02 | −0.18 | 72 | 22 | $9.5 \times 10^{-3}$ |
| 0.05 | −0.18 | 81 | 34 | $9.4 \times 10^{-3}$ |
| 0.10 | −0.18 | 84 | 47 | $11 \times 10^{-3}$ |
| 0.20 | −0.18 | 96 | 66 | $10 \times 10^{-3}$ |

[a] Obtained as mid potential $E_{1/2} = 0.5(E_{p,cath.} + E_{p,anod.})$. [b] Standard rate constant for heterogeneous electron transfer calculated from $\Delta E_p$.[10]

current responses increases with scan rate from 66 mV at a scan rate of 10 mV s$^{-1}$ in agreement with a quasi-reversible electron transfer process with $k° = 0.01 \pm 0.003$ cm s$^{-1}$ similar to standard rate constants for electron transfer observed on other diamond and glassy carbon type materials.[9] Data are summarised in Table 1.

In the presence of power ultrasound the current observed for the reduction of 1 mM $Ru(NH_3)_6^{3+}$ in aqueous 0.1 M KCl is considerably enhanced [Fig. 2(b)]. This mass transport enhanced current response now exhibits 'steady-state' characteristics and the limiting current which can be controlled by changing the ultrasound intensity or the horn to electrode distance may be described by eqn. (2):

$$I_{lim} = n\,F\,A\,D\,[\text{substrate}]\,/\,\delta(D) \qquad (2)$$

In this expression the limiting current, $I_{lim}$, is related to the number of electrons transferred per substrate molecule, $n$, the Faraday constant, $F$, the electrode area, $A$, the diffusion coefficient, $D$, and the diffusion layer thickness, $\delta(D)$, which in aqueous media has been shown[8] to be proportional to $D^{1/3}$. The resulting limiting currents from the sonovoltammetric measurements for the reduction of $Ru(NH_3)_6^{3+}$ with $D = 0.91 \times 10^{-9}$ m$^2$ s$^{-1}$ may therefore be used for the calibration of the diffusion layer thickness at constant ultrasound intensity and over a range of different electrode to horn distances.

It has recently been shown that the sonoelectrochemical reduction of oxygen at Ni–Cu alloy materials[11] (also known to be very hard and erosion resistant) and at Ti alloy sonotrodes[12] predominantly leads to the 4-electron reduction from dioxygen to water. Sonovoltammograms obtained by scanning the potential over a wide range in the absence [Fig. 2(c)] and in the presence [Fig. 2(d)] of dioxygen in 0.1 M phosphate buffer at pH = 2 at a highly boron doped diamond electrode show some characteristic features different to those previously observed at metal alloy electrodes. A wide solvent window with dioxygen evolution beginning to occur at a potential of +2.2 V *vs*. SCE is observed. Hydrogen evolution commences at a very negative potential of −1.5 V *vs*. SCE. However, after scanning the potential negative and reversing the scan direction the current appears to be increased and a 'crossing' occurs at −1.2 V *vs*. SCE. This feature is a 'tell-tale' sign for a chemical change at the electrode/solution interface, *e.g*. the reduction of surface functional groups of the polished diamond which then cause an increase in the rate of the proton reduction process.

This chemical change on the surface of the polished diamond electrode causes even more pronounced changes in the kinetics for the reduction of *ca*. 0.87 mM dioxygen in aqueous 0.1 M phosphate buffer at pH = 2 [Fig. 2(d)]. After the onset of the reduction process at a potential of −1.2 V *vs*. SCE and reversing the scan direction at −2.1 V *vs*. SCE a sustained limiting current with $I_{lim} = -0.86$ mA can be detected which finally decays with a half wave potential of −0.8 V *vs*. SCE. The calculation of the number of transferred electrons, $n$, per dioxygen molecule based on eqn. (2) and the above calibration procedure with a diffusion coefficient[14] for dioxygen of $D = 1.65 \times 10^{-9}$ m$^2$ s$^{-1}$ gives $n = 2.1 \pm 0.1$ consistent with the two electron reduction of oxygen to hydrogen peroxide [eqn. (3)].

$$O_2 + 2\,e^- + 2\,H^+ \rightarrow H_2O_2 \qquad (3)$$

A colorimetric test reaction with iodide[13] was used to confirm the formation of hydrogen peroxide after a period of 20 minutes electrolysis at an applied potential of −2.0 V *vs*. SCE. In contrast, under the same experimental conditions but without electrolysis the sonolytic formation of $H_2O_2$ was found to be negligible. The change of the surface properties of the boron-doped diamond electrode which has been reported to be present to a much smaller extent for 'as grown' boron-doped diamond[14] was found to be reversed by scanning into the region of positive potentials and the nature and mechanistic significance of the surface functional groups on the surface of the polished highly boron-doped diamond is currently the topic of a more detailed study by both electrochemical and spectroscopic techniques.

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## Notes and References

† In electrochemical experiments an Autolab PGSTAT 20 system (Eco Chemie, NL) was used for recording voltammetric data in conjunction with a special thermostated three-electrode cell of 25 cm$^3$ volume which has been described recently.[8] Experimental details for Raman and AFM measurements have been published.[3] Industrially polished boron-doped diamond was treated with oxidising acid in order to remove sp$^2$ type carbon from the polished surface and has been used as received from De Beers Industrial Diamond Division. Experiments were carried out after degassing with pure argon or dioxygen (BOC) at a temperature thermostated to 20 ± 2 °C.

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