

# The influence of surface preparation on the electrochemistry of boron doped diamond: A study of the reduction of 1,4-benzoquinone in acetonitrile

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## Abstract

The reduction, at boron doped diamond electrodes, of 1,4-benzoquinone dissolved in acetonitrile is investigated. It is shown that the mechanism of reduction is dependent on electrode pre-treatment. Whilst the response at an oxygenated diamond electrode surface resembles that at platinum and carbon electrodes, the  $i$ - $E$  curve at a hydrogenated diamond surface is indicative of protonation of intermediates. The cyclic voltammograms obtained suggest that the sub-surface hydrogen present in the hydrogenated diamond lattice is able to participate in electrochemical processes. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Diamond; Cyclic voltammetry; Benzoquinone; Surface modification

## 1. Introduction

Electrodes based on polycrystalline diamond are presently generating significant interest. Polycrystalline diamond possesses physical properties that suggest that electrodes fabricated from suitably doped samples of this material will exhibit advantageous attributes. For example, Compton and co-workers [1] have shown that in sonoelectrochemical experiments diamond electrodes are resistive to surface damage. In addition it has been claimed that boron doped diamond electrodes possess advantageous electrochemical characteristics that include: a wide potential window in aqueous electrolyte [2], low background currents [3] and excellent resistance to surface fouling [4].

A range of redox processes have been studied at highly boron doped diamond electrodes. It has been reported that at a diamond electrode those inorganic redox couples that are oxidised and reduced via an outer sphere electron transfer mechanism show reversible electrochemical behaviour [5]. Electrochemical impedance spectroscopy of diamond electrodes immersed in

solutions containing reversible redox couples indicates that the mechanism of electron transfer is dependent on the surface termination [6]. The redox electrochemistry at highly boron doped diamond electrodes has been investigated for a range of organic species in aqueous solution. For a number of couples oxidation and reduction have been observed within the available potential window, these include phenol [7], dopamine [8] and anthraquinonedisulphonate [9]. Studies in which the surface termination of the diamond electrodes has been considered indicate that the overpotential for the oxidation of ascorbic acid increases when the surface is oxygenated [8]. However, the majority of studies of organic oxidation have focused on electrodes biased at a positive potential that lies in the water breakdown region. Investigations have shown that remediation of polluted water may be achieved using a positively biased diamond electrode [10]. It has been suggested that the organic species are oxidised by OH radicals which are generated on the oxidation of water [10]. For example, Iniesta et al. [7] have reported that when low overpotential is applied the electrochemical oxidation of phenol at synthetic boron doped diamond electrodes in acidic media occurs via direct electron transfer and results in a polymeric film on the surface. Whilst during electrolyses in the potential region of water decomposition indirect

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oxidation reactions take place which, depending on the applied current and phenol concentration, may result in the complete combustion of phenol to CO or the partial oxidation of phenol to other aromatic compounds.

Studies of diamond electrodes in non-aqueous electrolytes are more limited. It has been reported that diamond electrodes in non-aqueous electrolyte possess an increased potential window, allowing a fifth peak for the reduction of C<sub>60</sub> to be observed [11]. In addition diamond electrodes have been employed in the generation of solvated electrons in ammonia [12]. This paper is concerned with electrochemistry of boron doped diamond electrodes immersed in acetonitrile. Specifically, boron doped diamond electrodes are employed in a study of the cyclic voltammetry of benzoquinone reduction. The importance of diamond electrode surface preparation in determining the mechanism of reduction is described.

## 2. Experimental

Continuous diamond films were deposited on a 1.5 cm<sup>2</sup> undoped silicon (100) wafer substrate by hot-filament chemical vapour deposition (*cvd*). Briefly, the substrate was manually abraded with 1–3 μm diamond grit and then ultrasonically cleaned in propan-2-ol. Then the substrate was placed in a *cvd* chamber containing a hydrogen/methane/diborane gas mixture at a pressure of 20 Torr. The boron concentration employed corresponded to a dopant density of 10<sup>21</sup> cm<sup>-3</sup>, i.e., the samples were degenerately doped. The gas mixture was activated by heating two 0.25 mm diameter tantalum coil filaments, in series. Deposition was performed for 16 h, giving a film thickness of approximately 5 μm. The film was cooled in the chamber under a hydrogen atmosphere. Electrical contacts were made to the samples using silver paint, applied on top of the diamond and protected using epoxy resin. The quality of the diamond films was assessed using Raman spectroscopy (Renishaw confocal imaging systems) and scanning electron microscopy, *sem* (JEOL JSM 5600LV).

Prior to the electrochemical studies the as-prepared hydrogen terminated samples were stored under vacuum. Oxygen terminated surfaces were prepared by immersing the diamond electrodes in a hot chromic acid solution [13]. Regeneration of a hydrogenated surface was achieved by placing the electrodes in aqueous 1 mol dm<sup>-3</sup> KCl solution and applying a potential in the hydrogen evolution region for 6 h. The sample was then dried for 1 h in an oven at 100 °C and then stored under vacuum.

Electrochemical studies of benzoquinone reduction were performed in a dry box in which the amount of water vapour was less than 5 ppm. In all experiments a 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> 1,4-benzoquinone/anhydrous aceto-

nitrile (99.9% pure) solution was studied in which 0.1 mol dm<sup>-3</sup> of tetrabutylammonium perchlorate (TBAP) was dissolved as supporting electrolyte. A three electrode system was used; a diamond or a glassy carbon working electrode, a platinum gauze counterelectrode and a 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> FeCp<sub>2</sub><sup>+</sup>/FeCp<sub>2</sub> reference electrode. All potentials are reported relative to FeCp<sub>2</sub><sup>+</sup>/FeCp<sub>2</sub> reference couple. The diamond electrode was mounted in the cell such that 0.4 cm<sup>2</sup> of the diamond surface was exposed to electrolyte. Cyclic voltammetry measurements were performed using an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273; controlled using Research Electrochemistry software (version 4.3).

## 3. Results and discussion

The results of Raman and *sem* studies have been published previously [13]. The Raman spectrum displays a sharp sp<sup>3</sup> peak at 1332 cm<sup>-1</sup> and shows no evidence of sp<sup>2</sup> carbon lines between 1500 and 1700 cm<sup>-1</sup>. The *sem* images show well-faceted crystallites of dimension *ca.* 1–5 μm with no evidence of graphitic regions, cracks in the film or extensive pitting.

At the beginning of the experiment a cyclic voltammogram was recorded using a glassy carbon working electrode. A typical *i*-*E* curve for a glassy carbon electrode immersed in the 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> benzoquinone/0.1 mol dm<sup>-3</sup> TBAP/acetonitrile solution is shown in Fig. 1. The curve shows two reversible reduction peaks the first at -1.40 V and the second at -2.29 V, these correspond to the formation of Q<sup>•-</sup> and Q<sup>2-</sup> respectively, where Q represents 1,4-benzoquinone. The behaviour observed is typical for the reduction of benzoquinone in an aprotic solvent [14,15] and confirms

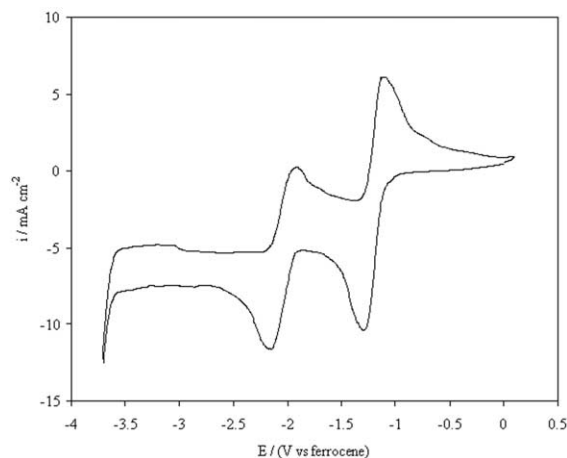


Fig. 1. A cyclic voltammogram recorded at a glassy carbon electrode immersed in 1 × 10<sup>-3</sup> mol dm<sup>-3</sup> 1,4-benzoquinone/0.1 mol dm<sup>-3</sup> TBAP in anhydrous acetonitrile. The *i*-*E* curve was recorded at scan rate of 0.1 V s<sup>-1</sup>.

that the electrolyte employed in the experiments was dry. Cyclic voltammograms for a glassy carbon working electrode were taken periodically during the studies and in all cases curves similar to that in Fig. 1 were observed. This indicates that at no stage, even following ex situ surface processing, was water introduced into the electrolyte.

The  $i$ - $E$  curve for the reduction of benzoquinone at an oxygenated boron doped electrode is displayed in Fig. 2. The plot essentially resembles that at a glassy carbon electrode but differs in two respects. First the peaks occur at lower potentials, this is due to the fact that  $iR$  compensation was not employed when recording the data and hence the voltammogram is distorted as a result of the potential drop across the diamond. Second the current density is almost an order of magnitude less than at glassy carbon, such behaviour is usual for diamond electrodes and has been assigned to the fact that the majority of charge transfer occur at the grain boundaries [5]. The voltammogram implies that benzoquinone undergoes two reversible one-electron reductions at an oxygenated boron doped diamond surface. In contrast, the benzoquinone reduction at the as-prepared boron doped diamond surface differs markedly from that at a glassy carbon electrode. The cyclic voltammogram for the reduction of benzoquinone at an as-prepared electrode is shown in Fig. 3. Similar cyclic voltammograms, see Fig. 4, were found for the initial cycles of benzoquinone reduction at boron doped electrodes at which, following chromic acid treatment, hydrogen had been generated in aqueous solution. However, it is of note that following a period of one hour of continual cycling the  $i$ - $E$  curve at the re-hydrogenated electrode surface began to resemble that of the oxygenated surface. The cyclic voltammograms

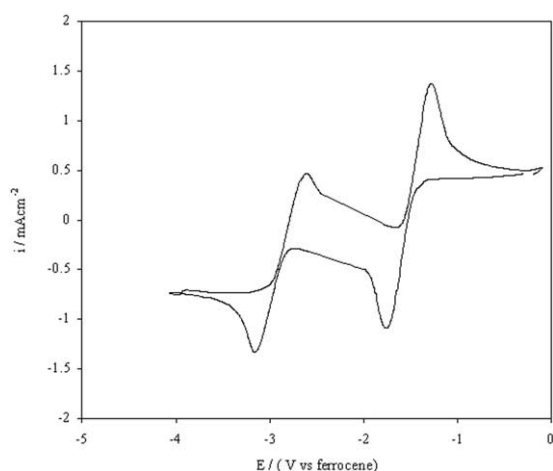


Fig. 2. A cyclic voltammogram recorded at an oxygen terminated, high boron doped, diamond electrode immersed in  $1 \times 10^{-3}$  mol dm $^{-3}$  1,4-benzoquinone/0.1 mol dm $^{-3}$  TBAP in anhydrous acetonitrile. The  $i$ - $E$  curve was recorded at scan rate of 0.1 V s $^{-1}$ .

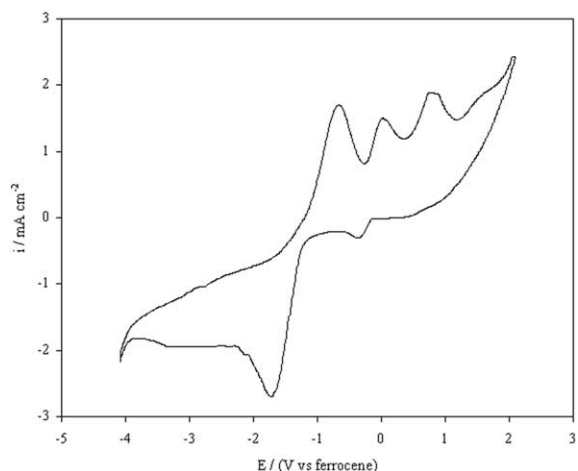


Fig. 3. A cyclic voltammogram recorded at an as-grown, high boron doped, diamond electrode immersed in  $1 \times 10^{-3}$  mol dm $^{-3}$  1,4-benzoquinone/0.1 mol dm $^{-3}$  TBAP in anhydrous acetonitrile. The  $i$ - $E$  curve was recorded at scan rate of 0.1 V s $^{-1}$ .

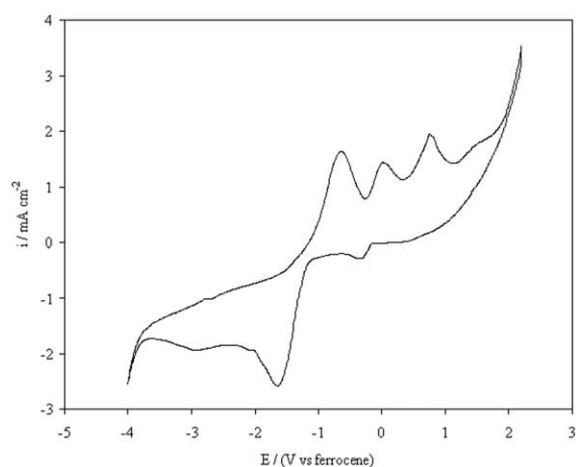
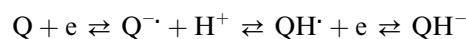
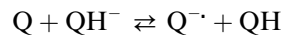


Fig. 4. A cyclic voltammogram recorded at a re-hydrogenated, high boron doped, diamond electrode immersed in  $1 \times 10^{-3}$  mol dm $^{-3}$  1,4-benzoquinone/0.1 mol dm $^{-3}$  TBAP in anhydrous acetonitrile. The  $i$ - $E$  curve was recorded at scan rate of 0.1 V s $^{-1}$ .

displayed in Figs. 3 and 4 are very similar to those reported for benzoquinone reduction in the presence of a weak acid [14,16]. This suggests that the small oxidation peak at the start of the scan, at a potential of  $-0.2$  V corresponds to the reduction of protonated quinone (the scan depicted is not the first of the series) whilst the peak at  $-1.73$  V is due to the ECE process,



which may be accompanied by the disproportionation reaction,



The shoulder at more negative potentials appears to result from the irreversible reduction of  $Q^-$ . In the cyclic

voltammetry of benzoquinone in the presence of a weak acid the three oxidation peaks are assigned as the oxidation of  $Q^{\cdot-}$  ( $-0.55$  V),  $QH^{\cdot-}$  ( $0.00$  V) and  $QH_2$  ( $+0.75$  V), respectively.

The observation that the redox behaviour of benzoquinone at the hydrogenated boron doped diamond surface resembles that normally observed only in the presence of a weak acid is surprising. As mentioned above, cyclic voltammetry was regularly performed at a glassy carbon electrode in order to assess if the solution remained dry during the experiments. For these control experiments no evidence of a weak acid in the solution was found, suggesting that the diamond surface is responsible for protonation of the  $Q^{\cdot-}$  radical and not a solution phase species. This inference is supported by the observation that in a common solution the reaction at the oxygenated surface is markedly different to that at the hydrogenated surface. It has been established [17] that there is a sub-surface layer of hydrogen at as-grown *cvd* diamond that may be responsible for the high surface conductivity of the material. Treatment of the diamond with oxidising acids results in an oxygenated surface and a loss of hydrogen from the sub-surface region, resulting in a lowering of the surface conductivity [18]. The sub-surface hydrogen in diamond is restored when hydrogen gas is electrochemically generated at the electrode/electrolyte interface. It appears that the hydrogen in the sub-surface may act as a source of protons in electrochemical reactions.

#### 4. Conclusions

It has been demonstrated that benzoquinone can be reduced and oxidised at boron doped diamond electrodes in non-aqueous solvents. The mechanism of reduction is dependent on the preparation of the diamond surface. At a surface treated with hot chromic acid, oxygen terminated, the electrochemistry resembles that at glassy carbon, i.e., two reversible reduction processes are observed. In contrast, at an as-prepared electrode or one at which hydrogen has been generated, hydrogen terminated surface, the electrochemistry indicates the presence of a source of protons. Rigorous tests showed

that the electrolyte was not contaminated and suggest that hydrogen in the diamond sub-surface may participate in electrochemical processes.

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