

Boron-doped diamond electrodes in organic media: Electrochemical activation and selectivity effects

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Abstract

This study highlights the effects of the electrochemical surface pre-treatment of polished polycrystalline boron-doped diamond electrodes in ethanol on electron transfer to organic redox systems. A novel “activation” procedure based on cathodic polarisation in ethanol (0.01 M NBu₄PF₆) is proposed and shown to be highly effective in promoting electron transfer to the aqueous Fe(CN)₆^{3-/4-} redox system. For redox systems in acetonitrile, effects on electron transfer processes are strongly dependent on the type of electron transfer process. For decamethylferrocene⁺⁰, decamethylcobaltocene⁺⁰, methylviologen^{2+/+}, and for methylviologen⁺⁰ redox systems essentially reversible electron transfer is observed irrespective of the pre-treatment of the boron-doped diamond electrode. For the benzoquinone^{0/-} redox system insignificant changes occur but for the benzoquinone^{-/2-} process a more dramatic change in electron transfer kinetics is observed (after cathodic polarisation in ethanol) consistent with an improved interfacial electron transfer (a 4.6 × increase in peak current occurs). Finally, the tetraethyl-ethylenetetra-carboxylate^{0/-} system is investigated as a model olefin redox system. Again changes in reactivity occur (a 4.0 × increase in peak current) at the cathodically pre-treated boron-doped diamond electrode. XPS surface analysis data reveal only insignificant changes in the chemical composition of the boron-doped diamond surface before and after activation and therefore a predominantly electronic mechanism for the “activation” process is proposed. In future selectivity effects for electron transfer at boron-doped diamond electrode surfaces could be introduced intentionally and used beneficially for chemo-selective electro-organic processes. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Boron-doped diamond is an exceptional electrode material introduced into electrochemistry two decades ago [1–3] as n-type semiconductor [4] or as degenerate semiconductor material [5] with properties depending on the boron-doping level and surface functionalities. Applications of boron-doped diamond electrodes have been proposed in

anodic waste degradation [6] and decoloration [7], hydroxyl radical [8] and ozone [9] generation, production of peroxophosphates [10] and peroxocarbonates [11], analytical sensing [12–17], in bio-sensors [18], but also electro-organic synthesis [19–21]. The use and benefits of boron-doped diamond electrodes in organic solvent systems was proposed first by Fujishima et al. [22] and later work was expanded to include both anodic [23] and cathodic processes [24]. A recent publication highlighted the perhaps surprising ability of boron-doped diamond to yield unexpected electro-synthesis products such as *ortho*-coupled 2,4-dimethylphenols generated at a diamond anode during oxidation

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of 2,4-dimethylphenol [25]. Clearly there is a lot of potential in employing mechanically robust boron-doped diamond electrodes as anode or cathode with properties complementary to conventional electrode materials in organic solvent media.

In this study, the effects are explored of the boron-doped diamond surface “activation” step on the electron transfer to a range of non-aqueous redox couples. The change in reactivity of boron-doped diamond surfaces (or “activation”) after potential pre-treatment in aqueous solutions is well known [26]. Here, a novel and more effective “activation” procedure employing an ethanol rather than an aqueous electrolyte solution is proposed. Surface “activation” of electrodes has been widely used to improve the rate of heterogeneous electron transfer at both glassy carbon [27] as well as at boron-doped diamond electrodes [28]. A cathodic pre-treatment usually results in a more reversible voltammetric response (or faster electron transfer). Both a shift in the flat band potential [29] and the degree of hydrogen termination on the boron-doped diamond electrode surface have been correlated with this effect [30]. In this report, it is suggested that chemical changes at the boron-doped diamond surface accompanying the “activation” process remain insignificant after reduction in ethanol solution and that only minor (local) chemical modification of the boron-doped diamond surface or electronic effects are the main cause of the change in the rate of electron transfer.

2. Experimental details

2.1. Chemical reagents

Potassium hexacyanoferrate(II), methylviologen dichloride hydrate, bis(pentamethylcyclopentadienyl)iron, bis(pentamethylcyclopentadienyl)cobalticinium hexafluorophosphate, benzoquinone (all Aldrich), tetrabutylammonium hexafluorophosphate (electrochemical grade, Fluka), and tetraethyl-ethylenetetraacboxylate (Lancaster) were purchased commercially and used without further purification. HPLC grade ethanol and acetonitrile were obtained from Aldrich. The electrochemical modification of the BDD surface was conducted using 0.01 M tetrabutylammonium hexafluorophosphate dissolved in ethanol.

2.2. Instrumentation

Electrochemical experiments were conducted with a PGSTAT 30 Autolab system (Eco Chemie, Netherlands) in a 50 cm³ capacity three-electrode single compartment cell. Free-standing polycrystalline boron-doped diamond electrodes with a mirror finish polish (Diafilm™, mineral acid treated, doping level ca. 10²⁰ cm⁻³, Windsor Scientific, Slough, UK) were obtained in the form of 3 mm diameter discs or 5 mm × 5 mm plates for electrochemical experiments (mounted in epoxy resin and coated with silver-epoxy as a back electrical contact). The counter electrode

was platinum gauze and the reference electrode was a KCl saturated calomel electrode (SCE, Radiometer). The solutions were thoroughly de-aerated with argon (BOC) for about 30 min prior to conducting experiments. Experiments were conducted at 22 ± 2 °C.

Raman spectroscopy studies of the electrode surface were carried out with a Renishaw Raman microscope system with a resolution of around 2 cm⁻¹ and using an excitation energy of 5.08 eV (244 nm) provided by a frequency-doubled continuous-wave argon ion laser. This excitation energy is a popular choice for studies of diamond and diamond-like carbon as it offers a high sensitivity to sp³-bonded carbon. The area of the sample that could be sampled was a disc of approximately 10 μm in diameter, and the excitation intensity was kept low (below 100 μW over this area) in order to minimise heating or damage to the sample. Raman spectra were recorded at several points on the boron-doped diamond surface.

XPS data were obtained using a Scienta ESCA300 photoelectron spectrometer fitted with an Al Kα source, operating at an effective system resolution of ~0.3 eV, and all spectra were recorded using an angle of photoelectron emission of 45° with respect to the surface normal.

2.3. Electrochemical activation procedure for boron-doped diamond and surface characterisation

Boron-doped diamond electrodes were cathodically treated in order to modify their surface reactivity. A vigorously stirred solution of 0.01 M NBu₄PF₆ in ethanol was employed and the potential was set to -4 V vs. SCE (current density ca. -0.6 A cm⁻²). After 30 min the electrode was removed from the solution, rinsed with ethanol, and dried in air. The “activation” effect was observed independent on storage and exposure to air (several hours). However, anodic current treatment under the same conditions immediately changed the behaviour of the boron-doped diamond electrode back to the “non-activated” state.

Fig. 1 shows an optical micrograph and a Raman spectrum (244 nm excitation) for the diamond surface. In the optical micrograph the polycrystalline nature of the diamond surface is clearly resolved and individual crystals of 5–50 μm size can be seen, due to the differing electronic and electron emission properties of the differing crystallites. Dark spots are due to small crevices at crystal boundaries. Differences in electrochemical reactivity in different zones on the boron-doped diamond surface have been reported in the literature [31,32]. The Raman spectrum shows the F_{2g} diamond band at 1333 cm⁻¹ as well as a weaker signal centered at 2450 cm⁻¹. Raman data were obtained on a 10 μm diameter sample spot and entirely consistent with a detailed Raman investigation published recently [33]. The pre-treatment in ethanol (cathodic or anodic) had no effect on the optical appearance or Raman signals of the diamond surface, indicating the effect of the electrochemical treatments is restricted to the surface region.

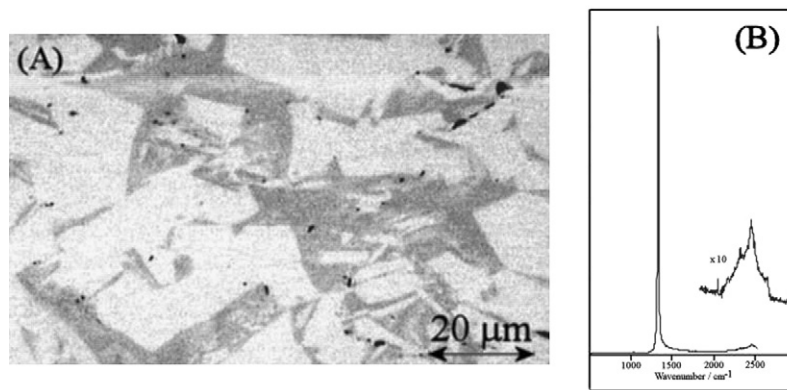


Fig. 1. (A) Optical micrograph of the surface of a polished polycrystalline boron-doped diamond electrode showing areas of low (brighter) and high (darker) boron-doping level. Dark spots are due to crevices at crystal boundaries. (B) Raman spectrum of the polycrystalline boron-doped diamond surface.

3. Results and discussion

3.1. Comparison of activation procedures for boron-doped diamond electrodes in aqueous acids and in ethanol for the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system

The effect of cathodic and anodic pre-treatment on the reactivity of boron-doped diamond electrode surfaces is known for example for the reduction of dioxygen [34] and has been observed in media such as aqueous HNO_3 [35], HClO_4 , or H_2SO_4 [36]. A chemical change on the surface of the diamond electrode consistent with hydrogenation has been observed and proposed as the reason for the observed change in reactivity [37].

Here a novel approach for the electrochemical activation of the boron-doped diamond surface is proposed based on the use of ethanol as an organic electrolyte medium. In contrast to earlier studies, in ethanol the surface hydrogenation of the diamond surface appears to be less significant (vide infra) and the rate of the accompanying hydrogen evolution process is reduced. The cathodic pre-treatment (see Section 2) is very effective as shown in Fig. 2A. The $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system is known to provide a sensitive probe for the surface state and reactivity of the boron-doped diamond electrode [38,39]. Curve (i) in Fig. 2A shows a typical cyclic voltammogram observed for the oxidation and re-reduction of $\text{Fe}(\text{CN})_6^{4-}$ in aqueous 0.1 M KCl. After cathodic pre-treatment of the boron-doped diamond electrode surface in ethanol (see Section 2) the voltammetric response becomes much more reversible (see curve (ii)). The peak-to-peak separation under these conditions (2 mM $\text{Fe}(\text{CN})_6^{4-}$ in 0.1 M KCl, scan rate 0.1 V s^{-1}) changes from 500 mV to 83 mV consistent with close to reversible electron transfer conditions after the cathodic pre-treatment in ethanol. A similar experiment employing the traditional activation method in aqueous HNO_3 [35] (–5 V vs. SCE in 1 M HNO_3 under vigorous stirring for 30 min) was less effective and under similar conditions (the same electrode and test solution) resulted in a

peak-to-peak separation of typically 160 mV for the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system after activation (not shown).

It was observed that the “activation” of the boron-doped diamond electrode surface was reversed after short anodic polarisation. In order to explore this effect, voltammograms were recorded at different states of “activation”. In acetonitrile (0.1 M NBu_4PF_6) a characteristic peak at ca. 1.2 V vs. SCE is observed (see Fig. 2B).

With continuing cathodic pre-treatment this voltammetric response is gradually increasing (see Fig. 2C) and remained constant after ca. 30 min. After applying a potential higher than this anodic process the effect of cathodic pre-treatment is removed. This effect is repeatable and unlikely to result from impurities. It appears likely that the oxidation at 1.2 V vs. SCE is removing states from the diamond surface which aid electrical conductivity and electron transfer. The charge under the fully developed oxidation peak at 1.2 V vs. SCE, ca. 1–2 μC , suggests less than a mono-layer effect with a site-to-site separation of ca. 1 nm at the boron-doped diamond surface.

In order to study the effects of the cathodic pre-treatment on the surface composition, XPS experiments were conducted. XPS spectra relating to the modifications brought about by cathodic polarisation in ethanol-based media are shown in Fig. 3. Three types of electrode were examined, (i) in the as-received state, (ii) after cathodic treatment, and finally (iii) after subsequent anodic polarisation. Very little difference in the wide-scan spectra were observed for these three samples; as shown in Fig. 3A, the only elements present in significant quantities are carbon and oxygen, as detected by the 1s spectral signals associated with these elements.

Measurement of peak area ratios, corrected for sensitivity factors, of the two main peaks indicates an O:C concentration ratio of around 0.11, essentially identical within 10% for all three samples (see Table 1). The concentration ratio calculated in this way is averaged over the XPS sampling depth, which for diamond is around 10 atomic layers. The actual surface concentration of oxygen on the

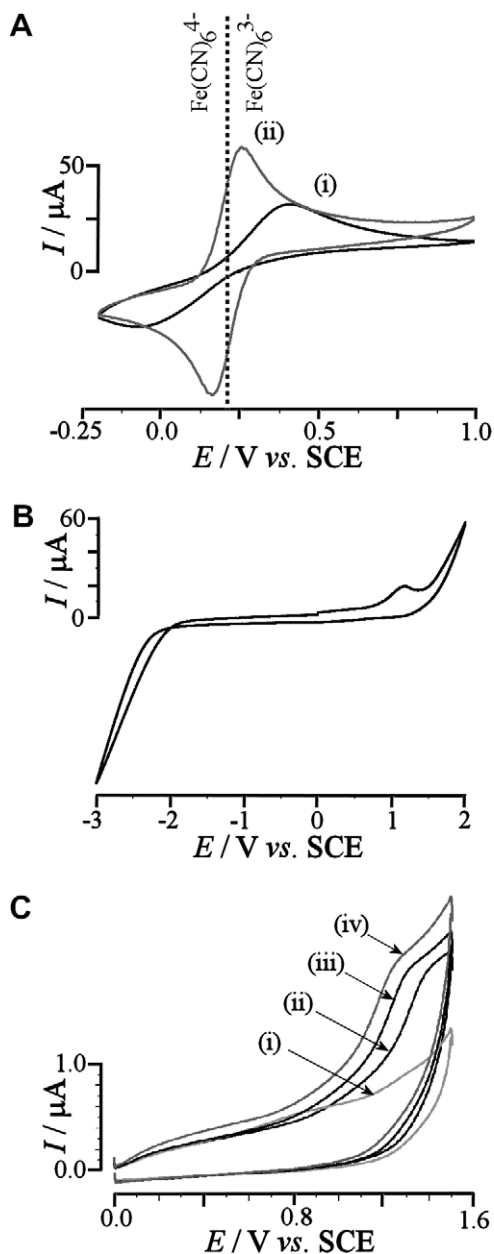


Fig. 2. (A) Cyclic voltammograms (scan rate 100 mV s^{-1}) for the oxidation of $2 \text{ mM Fe(CN)}_6^{4-}$ in aqueous 0.1 M KCl at a 3 mm diameter boron-doped diamond (i) without and (ii) with cathodic pre-treatment. (B) Cyclic voltammograms (scan rate 100 mV s^{-1}) for the solvent background in acetonitrile ($0.1 \text{ M NBu}_4\text{PF}_6$) at a 3 mm diameter boron-doped diamond with cathodic pre-treatment. (C) Cyclic voltammograms (scan rate 100 mV s^{-1}) for the solvent background in acetonitrile ($0.1 \text{ M NBu}_4\text{PF}_6$) at a 3 mm diameter boron-doped diamond with (i) 5 min, (ii) 10 min, (iii) 20 min, and (iv) 30 min cathodic pre-treatment.

diamond interface can be estimated if the inelastic mean free path of the C 1s photoelectrons is known. This parameter is not known accurately but probably lies in the range $1.5\text{--}2.2 \text{ nm}$; the smaller value yields an O surface concentration of around $0.8 \text{ O atoms per surface C atom}$, whereas the latter yields a value of about 1.2 . It is clear that all three electrodes are essentially oxygen terminated at the electrode surface and that the cathodic treatment in ethanol

does not significantly hydrogenate or chemically modify the interface. The differences in electrochemical behaviour noted above (and illustrated further below) must therefore depend on more subtle changes at the diamond surface (e.g. filling of irreversible electronic states or chemical modification of dopant sites).

Chemical changes which do occur can be judged from the narrow scan C 1s spectra which are also shown in Fig. 3. The C 1s XPS spectra for oxidised diamond surfaces have been investigated in some detail [40–42], and normally display spectral components (in order of increasing binding energy) around 283.2 eV (graphitic bonding), 284.5 eV (diamond), 285.1 eV (C-H_x), 285.8 eV (C-O), 286.8 eV (O-C-O , C=O) and 288 eV (O-C=O). Spectral fits to these six components are included in the C 1s spectra in Fig. 3. Close inspection shows some clear differences between the concentrations of these chemical species, as measured by the peak areas, in the different samples. In particular, the “as-received” electrode shows much higher concentrations of the C-H_x bonding component, believed to be due to the presence of strongly bound hydrocarbon species at the interface. In comparing the anodically treated and cathodically treated samples, the only discernable difference is the relative concentrations of C-O and C=O species, typically representing alcohol and carbonyl functionalities, respectively; on the cathodically treated sample, the former is more abundant than the latter by about 8% whereas on the anodically treated sample the C=O dominate over the former by about 12% . It would appear that the cathodic activation process in ethanol frees the electrode from the bound hydrocarbons and produces a largely oxygen-terminated surface where alcohol functionalities dominate. The anodic treatment then deactivates the interfaces by producing C=O as the most abundant oxygen containing functionality. Surface dipole arguments may suggest that the former surface may attract anionic species more than the latter, or alternatively chemical changes only in the vicinity of boron surface states may occur. So it may be this subtle effect which is largely responsible for the sometimes quite dramatic (vide infra) differences between the anodically and cathodically treated electrodes. The overall surface chemical differences between these two differently treated electrodes are however surprisingly small.

3.2. The absence of effects of cathodic activation on the methylviologen $^{2+/+0}$, the decamethylcobalticenium/decamethylcobaltocene, and the decamethylferricenium/decamethylferrocene redox systems

In order to explore the effect of surface activation on redox systems in non-aqueous solutions a range of test experiments with model redox systems were conducted in acetonitrile. From experiments in aqueous solution it is known that redox systems with a very fast rate of electron transfer, e.g. aqueous $\text{Ru(NH}_3)_6^{3+/2+}$ [35], are not affected by the electrochemical surface pre-treatment. Reversible

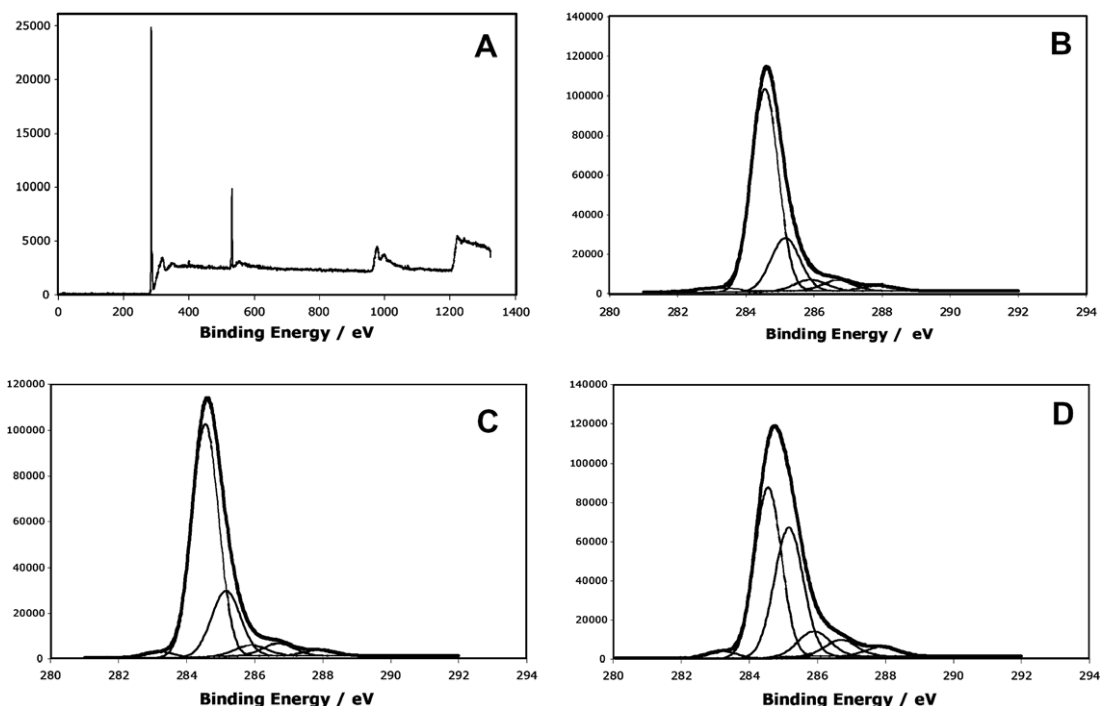


Fig. 3. (A) Wide scan XPS spectrum of cathodically pretreated sample (-4 V vs. SCE in ethanolic 10 mM NBu_4PF_6 , 30 min) showing C 1s (285 eV), O 1s (532 eV), C Auger (1216 eV) and O Auger (976 eV) peaks. (B–D) C 1s narrow scan spectra of the cathodically treated (B), anodically treated (after cathodic pre-treatment a potential of $+1.5$ V vs. SCE was applied for 2 min) (C) and “as-received” samples (D). The bold lines denote the spectral envelope and non-bold lines denote the fitted spectral components (see Table 1).

Table 1

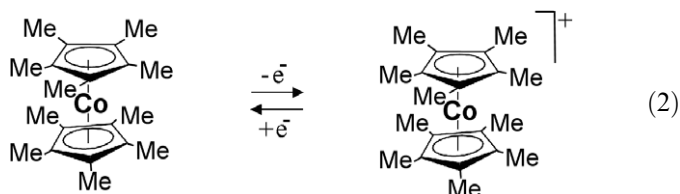
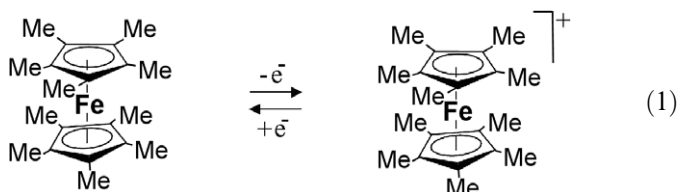
Relative intensity data from XPS surface analysis for boron-doped diamond samples with and without surface pre-treatment in ethanol (0.01 M NBu_4PF_6)

Peak assignment	C^{graph}	C-H_x	C–O	C=O and O–C–O	O–C=O
“As-received”	0.047	0.82	0.18	0.11	0.066
Cathodic treatment	0.038	0.28	0.064	0.060	0.030
Anodic treatment	0.028	0.31	0.056	0.064	0.030

Chemical forms are noted and normalised to the diamond peak intensity for each sample.

cyclic voltammograms are obtained independent of the history of the boron-doped diamond electrode surface. This effect is confirmed here for several reversible (neutral and cationic) redox systems in organic solvent media.

Fig. 4A shows cyclic voltammograms (curve (i) is the background) for the oxidation of decamethylferrocene and for the reduction of decamethylcobalticenium in acetonitrile. Both processes involve fast one electron transfer steps (Eqs. (1) and (2)).



In Fig. 4A a typical cyclic voltammogram obtained at a cathodically pretreated boron-doped diamond electrode is shown. The oxidation of decamethylferrocene occurs at -0.02 V vs. SCE and the reduction of decamethylcobalticenium is observed at -1.46 V vs. SCE. Comparison with Fig. 4B shows that no significant differences are observed with or without electrochemical activation of the boron-doped diamond electrode surface consistent with fast electron transfer under all conditions.

Fig. 4B also shows the effect of scan rate on the voltammetric signal. Increasing the scan rate from 25 to 150 mV s^{-1} does lead to a slight increase in peak-to-peak separation but the shape of the voltammetric signals suggests that a solution resistance effect (due to low concentration of supporting electrolyte) and not a kinetic effect is responsible in this case.

Next, the methylviologen $^{2+/+0}$ redox couples are investigated. In acetonitrile, both reduction steps of the methylviologen $^{2+}$ cation occur at boron-doped diamond electrodes with fast electron transfer kinetics (Eqs. (3) and (4)).

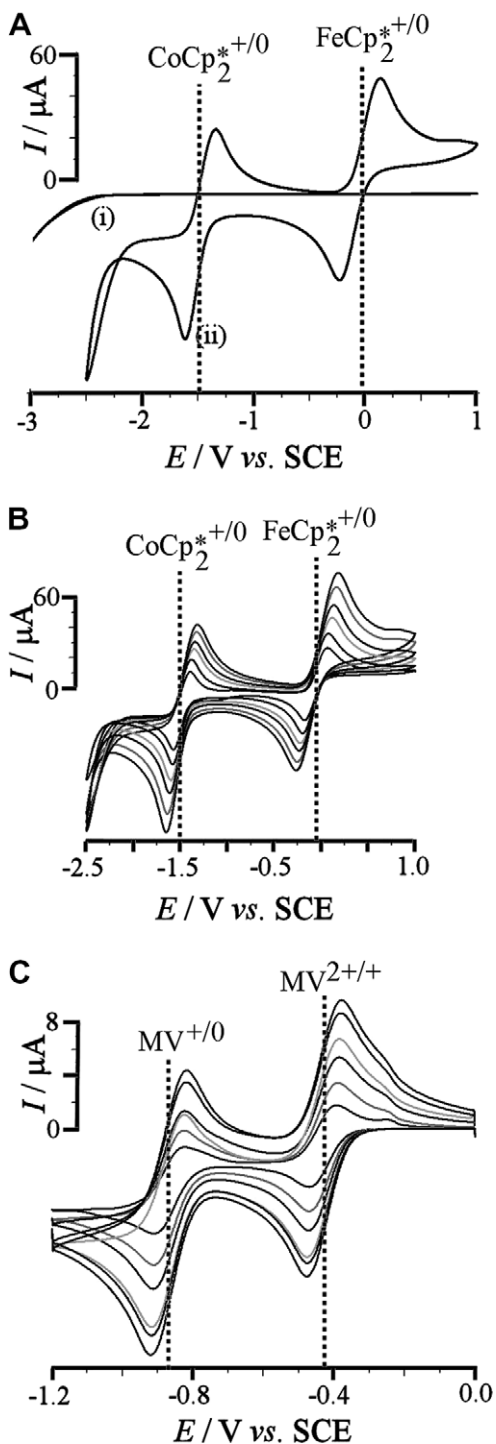


Fig. 4. (A) Cyclic voltammograms (scan rate 100 mV s^{-1}) for (i) the solvent background and (ii) the oxidation of 2 mM decamethylferrocene and for the reduction of 2 mM decamethylcobalticenium hexafluorophosphate in acetonitrile (0.01 M NBu_4PF_6) at a 3 mm diameter boron-doped diamond electrode with cathodic pre-treatment. (B) Cyclic voltammograms (scan rate 25, 50, 75, 100, 125, and 150 mV s^{-1}) for the oxidation of 2 mM decamethylferrocene and for the reduction of 2 mM decamethylcobalticenium hexafluorophosphate in acetonitrile (0.01 M NBu_4PF_6) at a 3 mm diameter boron-doped diamond electrode without cathodic pre-treatment. (C) Cyclic voltammograms (scan rate 25, 50, 75, 100, 125, and 150 mV s^{-1}) for the reduction of 0.2 mM methylviologen in acetonitrile (0.01 M NBu_4PF_6) at a 3 mm diameter boron-doped diamond electrode without cathodic pre-treatment.

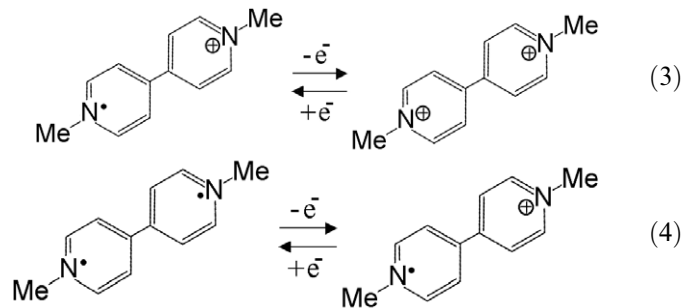


Fig. 4C shows cyclic voltammetry data obtained at a range of scan rates showing the $\text{MV}^{2+/+}$ process at -0.42 V vs. SCE and the $\text{MV}^{+/0}$ process at -0.87 V vs. SCE. The peak-to-peak separation is typically 70–80 mV and there is again no indication of slow electron transfer kinetics with (not shown) or without cathodic pre-treatment of the boron-doped diamond electrode. Next, it will be shown that interfacial electron transfer processes in organic solvents may indeed be strongly affected by the electrode pre-treatment when systems with inherently slower electron transfer (or processes involving anionic species) are investigated.

3.3. The effects of cathodic activation on the benzoquinone/hydroquinone and the tetraethyl-ethylenetetra-carboxylate^{0/-} redox systems

The benzoquinone redox system is well known and may be regarded as a model for the reduction of quinoidic carbon–oxygen double bonds. In the absence of a proton source and in organic solvent media the reduction of benzoquinone proceeds in two single electron transfer steps (Eqs. (5) and (6)). The process has been studied at boron-doped diamond electrodes and is sensitive to the state of the boron-doped diamond surface [43].

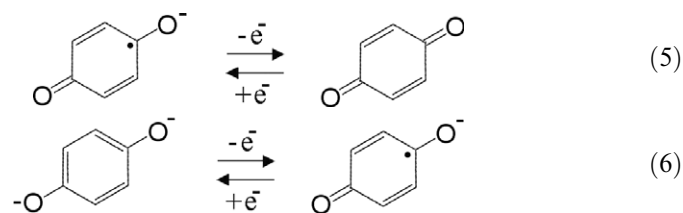


Fig. 5 shows typical voltammograms obtained for the reduction of 2 mM benzoquinone in acetonitrile. Data in Fig. 5A was recorded at a non-activated (anodically treated) boron-doped diamond electrode and voltammograms in Fig. 5B were obtained after cathodic pre-treatment in ethanol (see Section 2). The first reduction step (Eq. (5)) remains essentially reversible. However, the second reduction is strongly affected. The peak-to-peak separation for the benzoquinone^{2-/·} redox system is widened to approximately 0.7 V and interestingly the midpoint potential ($E_{\text{mid}} = 1/2E_{\text{p,a}} + 1/2E_{\text{p,c}}$) appears to be shifted to more negative potentials (presumably due to coupled homogeneous electron transfer steps). After cathodic pre-treatment of the boron-doped diamond electrode surface the

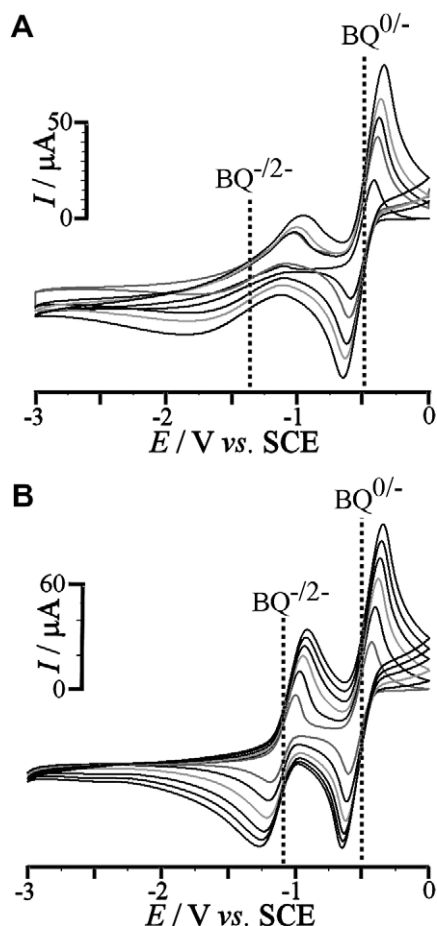


Fig. 5. (A) Cyclic voltammograms (scan rate 25, 50, 75, 100, and 125 mV s^{-1}) for the reduction of 2 mM benzoquinone in acetonitrile (0.01 M NBu_4PF_6) at a 3 mm diameter boron-doped diamond without cathodic pre-treatment. (B) Cyclic voltammograms (scan rate 25, 50, 75, 100, 125, and 150 mV s^{-1}) for the reduction of 2 mM benzoquinone in acetonitrile (0.01 M NBu_4PF_6) at a 3 mm diameter boron-doped diamond with cathodic pre-treatment.

peak-to-peak separation is markedly reduced (ca. 0.2 V) although tailing of the voltammetric peak still suggests a kinetic effect.

There are literature reports on the rate of electron transfer slowing down at more negative potentials consistent with a p-type semiconductor material [44] and this must be part of the effect observed here. However, the shape of voltammograms observed for the benzoquinone reduction are more complex and they may reflect in addition the electronic heterogeneity of the boron-doped diamond electrode surface. In some experiments the freshly activated electrode was used in acetonitrile and then “deactivated” by scanning the potential of the electrode to +1.5 V vs. SCE (see Fig. 2C). The in situ re-activation of the boron-doped diamond in the acetonitrile environment (by setting the potential to -4 V vs. SCE) was not successful and therefore protons (from ethanol) are likely to be involved in the surface chemical process responsible for the activation process.

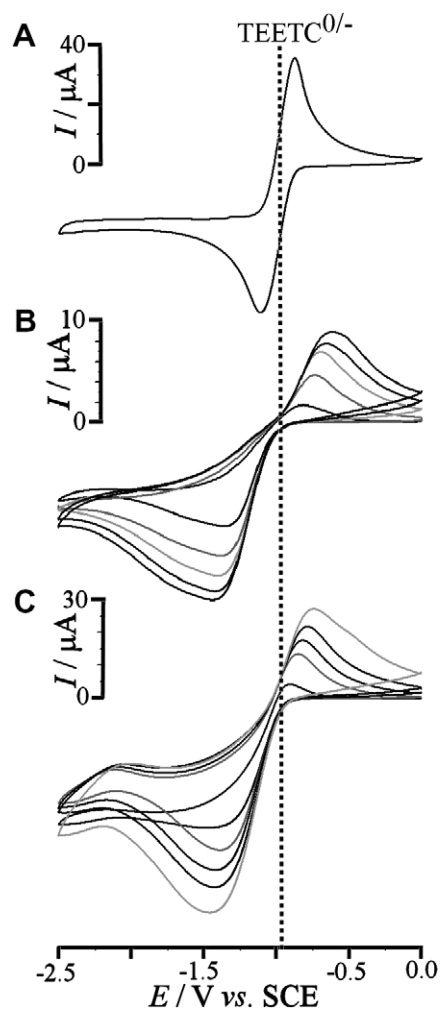
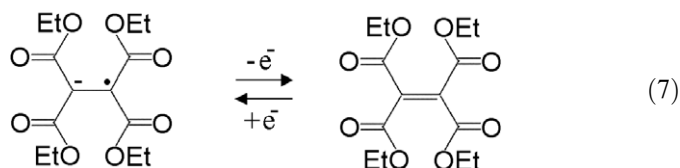


Fig. 6. (A) Cyclic voltammogram (scan rate 100 mV s^{-1}) for the reduction of 2 mM tetraethyl-ethylenetetracarboxylate in acetonitrile (0.01 M NBu_4PF_6) at a 3 mm diameter glassy carbon electrode. (B) Cyclic voltammograms (scan rate 25, 50, 75, 100, and 125 mV s^{-1}) for the reduction of 2 mM tetraethyl-ethylenetetracarboxylate in acetonitrile (0.01 M NBu_4PF_6) at a 3 mm diameter boron-doped diamond without cathodic pre-treatment. (C) Cyclic voltammograms (scan rate 25, 50, 75, 100, and 125 mV s^{-1}) for the reduction of 2 mM tetraethyl-ethylenetetracarboxylate in acetonitrile (0.01 M NBu_4PF_6) at a 3 mm diameter boron-doped diamond after cathodic pre-treatment.

The electrochemical reduction of $\text{C}=\text{C}$ double bonds is a facile process (in particular for activated electron-deficient olefins) and in the presence of a proton source hydrogenation and the formation of alkanes is observed [45]. Tetraethyl-ethylenetetracarboxylate (or TEETC) is a model olefin redox system which is known to undergo clean reduction and hydrogenation without radical coupling or other side reactions [45].



At glassy carbon electrodes, at a potential of -0.99 V vs. SCE a reversible one electron transfer occurs leading to the TEETC radical anion (see Eq. (7)). This reduction occurs as a highly reversible process (see Fig. 6A). At boron-doped diamond electrodes, this reduction process is observed within the same potential range but as a highly irreversible process.

Without cathodic pre-treatment a cathodic peak current of ca. -16 μ A is observed suggesting that large parts of the boron-doped diamond electrode surface remain inactive. The associated anodic peak is small consistent with a spherical diffusion effect (see Fig. 6B) causing some of the TEETC⁻ radical anion to escape into the bulk solution.

After cathodic pre-treatment of the boron-doped diamond electrode, both the cathodic and the anodic responses are improved (see Fig. 6C) indicating a more active surface and a substantially enhanced rate of electron transfer to TEETC. The remaining difference between cathodic and anodic response may be interpreted in two ways: (i) there is still a strong electronic heterogeneity at the boron-doped diamond surface and the “active” regions may simply have been expanded leaving some non-planar diffusion character and (ii) it may be possible that the negatively charged anion is more difficult to oxidise due to unfavourable interaction with a negatively charged surface state.

4. Summary

- Boron-doped diamond electrodes change their electron transfer reactivity upon reduction or oxidation in ethanol. In organic solvents this is most sensitively observed with anionic redox systems such as benzoquinone^{-/2-}.
- XPS surface analysis of the boron-doped diamond after cathodic or anodic pre-treatment in ethanol shows only a minor modification in the chemical composition of the surface. The originally proposed cathodic surface hydrogenation does not occur under these conditions although the effect on the electron transfer reactivity (e.g. for aqueous Fe(CN)₆^{3-/4-}) is dramatic. Therefore, it seems likely that reduction/oxidation of surface states (e.g. boron centers) rather than all of the surface is responsible for the activation effect.
- The heterogeneity of the boron-doped diamond electrode surface (due to a crystal growth mosaic pattern) in conjunction with electron transfer kinetics is responsible for the complex shape of voltammetric signals obtained under mixed kinetic-diffusion control. Fully diffusion controlled processes involving cationic redox systems are not affected.
- The selectivity towards certain types of cathodic redox processes should allow electrode processes at boron-doped diamond immersed in organic media to be used as regio- or chemo-selective reduction tools. However, a more uniform reactivity across the electrode surface

e.g. employing homoepitaxially grown or patterned diamond [46] will be required.

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