

## Correspondence

## The 5-V Window of Polarizability of Fluorinated Diamond Electrodes in Aqueous Solutions

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Heavily doped diamond films are quite actively studied for their promising applications in industrial as well as in fundamental electrochemistry (both for physicochemical studies and in the field of electroanalysis), because of their very high stability toward chemical and electrochemical oxidative attacks. Fluorinated diamond electrodes exhibit an exceptionally lower electrocatalytic activity toward reactions involving adsorbed intermediates, as a result of the F-termination of the surface dangling bonds. This feature allows the investigation of the widest range of potentials for an electrode material in aqueous solution, being limited only by the formation of free hydrogen [ $E^{\circ}(\text{H}^+/\text{H}_2) = -2.3 \text{ V}_{\text{SHE}}$ ] and hydroxyl [ $E^{\circ}(\text{OH}, \text{H}^+/\text{H}_2\text{O}) = 2.74 \text{ V}_{\text{SHE}}$ ] radicals, at the two boundaries of the  $\sim 5\text{-V}$  polarization window.

In electrochemistry, the potential range in which an electrode material can be used, in a given medium, is generally referred to as the “window of ideal polarizability”, and the evaluation of new electrode materials, especially for applications in electroanalysis and as electrochemical sensors, is often focused on the background current. In aqueous media, a wide potential window of  $\sim 3 \text{ V}$  has been found for highly conductive, high-quality boron-doped diamond (BDD) films, the window becoming much narrower with increasing  $\text{sp}^2$  carbon content.<sup>1,2</sup> Depending on the supporting electrolyte, the positive potential limit has been proved to depend on water oxidation (leading to hydroxyl radicals<sup>3</sup> and, finally, to the evolution of gaseous oxygen) or on powerful oxidants production,<sup>4</sup> such as peroxodisulfuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ ) and peroxy-monosulfuric acid (Caro’s acid,  $\text{H}_2\text{SO}_5$ ), as well as ozone and hydrogen peroxide. In the absence of an electrochemically active supporting electrolyte, the hydroxyl radical formation ( $E^{\circ} = +2.74 \text{ V}_{\text{SHE}}$  in acidic solution)<sup>5</sup> represents the deciding reaction for anodic potential buffering. On the other hand, the cathodic limit is generally due to the hydrogen evolution reaction (HER), which

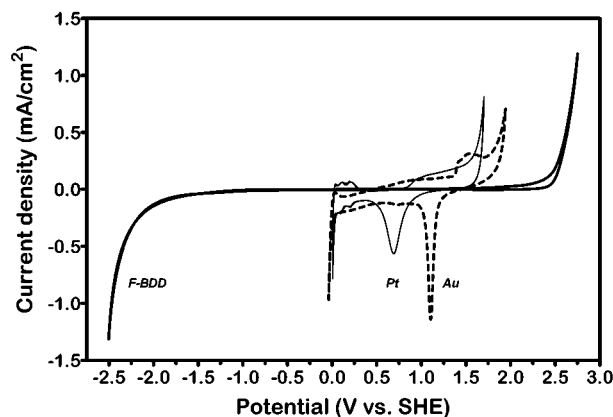
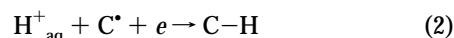
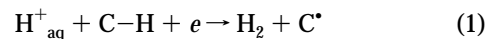
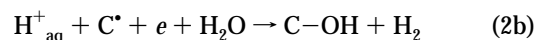


Figure 1. Comparison of CV curves for fluorinated BDD, platinum, and gold electrodes, in degassed 1 M  $\text{HClO}_4$ . Scan rate,  $0.2 \text{ V s}^{-1}$ .

has been reported to take place, at rates of the order of magnitude of the  $\text{mA}/\text{cm}^2$ , at  $\sim -1.25 \text{ V}_{\text{SHE}}$  at BDD,<sup>6</sup> in  $0.5 \text{ M H}_2\text{SO}_4$ . As observed by Angus and co-workers,<sup>6</sup> the HER should take place at  $-2.11 \text{ V}_{\text{SHE}}$  (a value of  $-2.30 \text{ V}_{\text{SHE}}$  has been reported in ref 7), in the absence of stabilizing interactions with the electrode surface. At Pt, on the contrary, the reaction occurs at  $\sim 0 \text{ V}_{\text{SHE}}$ , as a consequence of the formation of adsorbed  $\text{H}^*$  species. To account for the significant anticipation of the HER at BDD, with respect to the thermodynamic value, some sort of interactions have been hypothesized also with the hydrogen-terminated BDD surface, and the following mechanism has been suggested:<sup>8</sup>



The second equation could be better replaced with the following, which would account for an increase in hydrophilicity of the BDD surface:



While the recent research of Comminellis and co-workers<sup>3</sup> has

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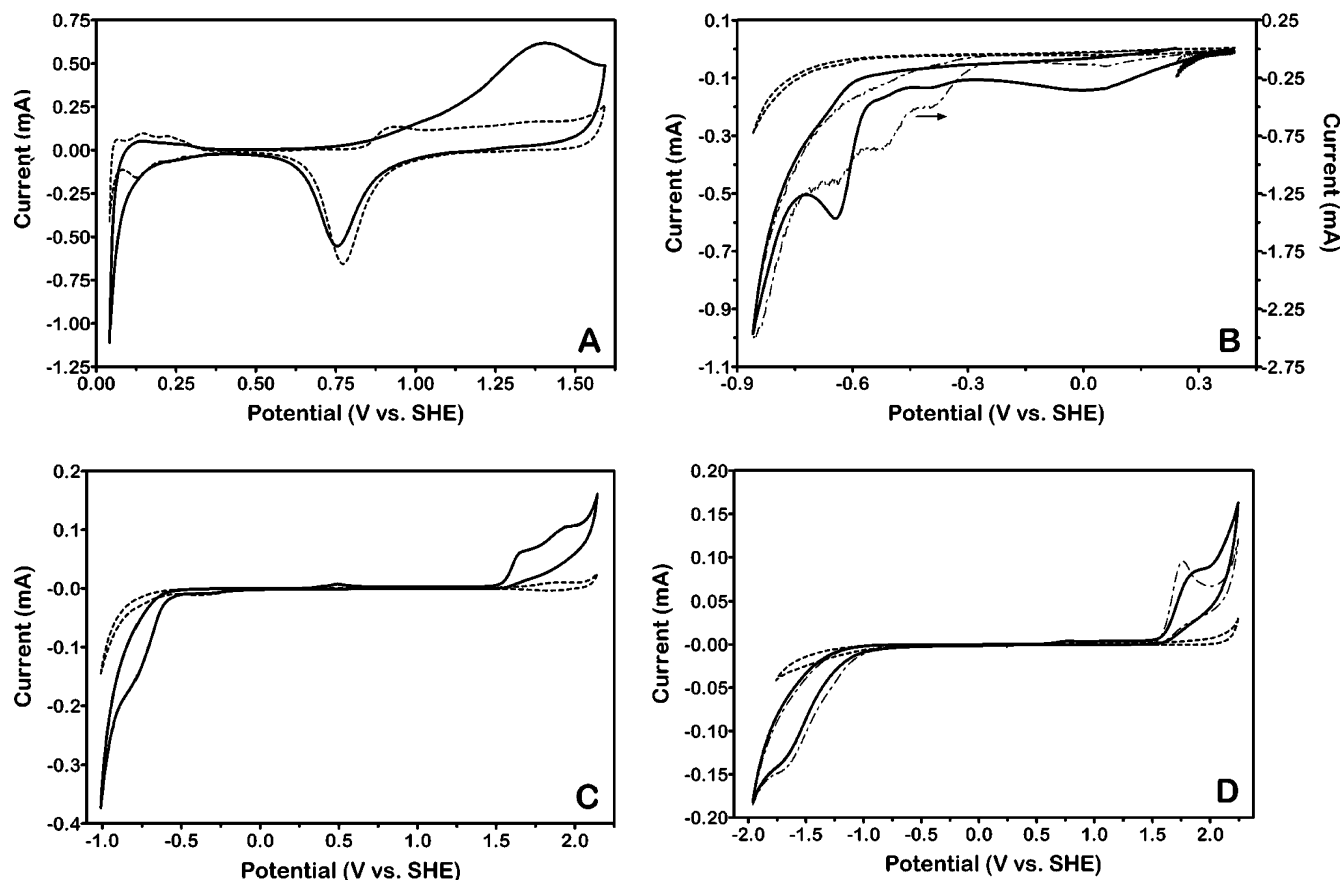


Figure 2. CV curves recorded at the different electrode materials, in degassed 1 M HClO<sub>4</sub> (dashed line) and in the presence of 1 mM PBN (solid line): (A) platinum, (B) mercury, (C) H-terminated, boron-doped diamond, and (D) surface-fluorinated, boron-doped diamond. First scan data (broken line) are also presented in (B) and (D). Scan rate, 0.1 V s<sup>-1</sup>.

supplied convincing explanation for the high oxygen evolution overpotentials (in the absence of other electrochemically active substances), the cathodic region has been scarcely investigated.

**Results and Discussion.** In a recent work,<sup>9</sup> a physicochemical investigation on the properties of highly stable, fluorinated, conducting diamond (F-BDD) films has been described. Also Angus et al. have reported on the electrochemical features of F-BDD electrodes,<sup>10</sup> but their specimens were said to lose fluorine under polarization. As shown in Figure 1 (which reports data from Figure 4 in ref 9), a “window of ideal polarizability” of ~5 V, in degassed 1 M HClO<sub>4</sub>, was investigated at the F-BDD electrode, representing an extension of the already wide potential window of BDD of another 2 V in the cathodic potential direction. Compared with BDD,<sup>6,8</sup> the HER takes place significantly at potentials close to the thermodynamic value for direct discharge of proton,<sup>7</sup> witnessing the absence of any interaction between the electrode surface and the intermediates of the cathodic reaction.

The above evidence supports the hypothesis that, at F-BDD, the hydrogen evolution takes place through formation of free hydrogen radicals, since any other possible mechanism would allow the HER to occur at less negative potentials. To afford independent experimental evidence of this possibility, attempts

have been made to identify H<sup>•</sup> atoms via their ESR spectrum,<sup>11</sup> housing a F-BDD electrode directly in the ESR cavity. No convincing signals could be obtained, neither (I) during a cathodic polarization in 1 M HClO<sub>4</sub> nor (II) in the presence of  $\alpha$ -phenyl *N-tert*-butyl nitron (PBN), probably as a consequence of radicals reactivity (which rapidly lead to H<sub>2</sub> formation) that considerably limits both the free (case I) and the trapped (case II) H<sup>•</sup> concentration. Accordingly, only indirect evidence could be obtained, and at first, the cyclic voltammetric behavior of the PBN spin trap was studied. Investigations have been carried out at platinum, mercury, BDD, and F-BDD, recording CV curves in the pure supporting electrolyte solution (1 M HClO<sub>4</sub>, degassed with argon), as well as in the presence of 1 mM PBN; the different results are shown in Figure 2. With the spin trap in solution, a general increase in current could be observed, in the cathodic region, at all electrode materials, and adsorption of the organic molecule seems to take place at platinum (Figure 2A) and mercury (Figure 2B). McIntire and co-workers examined the electrochemistry of different spin traps, at the former electrode material,<sup>12</sup> in aqueous and nonaqueous solutions, giving an account for the direct reduction of PBN at a cathodic potential of  $-1.88 V_{SCE}$  ( $\sim -1.64 V_{SHE}$ ), in aqueous 0.1 M LiClO<sub>4</sub>. Figure 2A shows that, in the presence of PBN in solution, a significant faradic process

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takes place in the hydrogen adsorption region (potential values  $\leq 0.125 V_{\text{SHE}}$ ), i.e., before the onset of the hydrogen evolution reaction but just after the H underpotential deposition (UPD). Since, according to Conway and Jerkiewicz,<sup>13</sup> the kinetically significant adsorbed intermediate in the HER would not be the strongly bound (UPD-type) hydrogen layer but, rather, the weakly bound H atoms, which form on the preexisting UPD layer, the above-discussed PBN-related process appears unequivocally attributable to the capture of  $\text{H}^\bullet$  by the spin trap. At the mercury electrode (Figure 2B), the process occurs with a different mechanism, as H adsorption does not take place at Hg; however, in the presence of PBN, cathodic currents are more than tripled and the required overpotentials are also significantly reduced. Panels C and D of Figure 2 concern the BDD and F-BDD electrodes, respectively; in both cases, the presence of PBN in solution considerably modify the current responses. Noteworthy is the displacement of the phenomenon under investigation at the different electrode materials: if the measured currents were due to a direct reduction of PBN, such potential differences could not be justified; the contrary applies for a reaction “mediated” by hydrogen radicals, since the different catalytic properties of Pt, Hg, BDD, and F-BDD fully rationalize the above picture.

A second indirect evidence for the production of free hydrogen radicals has been obtained, based on a work by Kobosev and Nekrasov:<sup>14</sup> in the presence of free H atoms, their reducing action should change the color of a tungstic oxide suspension, from yellow ( $\text{WO}_3$ ) to blue ( $\text{W}_2\text{O}_5$ , as reported in ref 14; however, more recent work<sup>15</sup> referred to the tungsten bronze  $\text{H}_x\text{WO}_3$ , with  $x \leq$

1). Accordingly, in the frame of the present work, a F-BDD electrode was placed in the cathodic compartment of a divided cell, containing a  $\text{WO}_3$  suspension in deoxygenated 0.5 M  $\text{H}_2\text{SO}_4$ , which caused a transition from yellow to blue for the  $\text{WO}_3$  suspension color. Interestingly, no color change was observed upon hydrogenation of a  $\text{WO}_3$  suspension with hydrogen gas, while a sudden effect could be obtained by simply adding a small amount of palladiated carbon to the test solution.

**Conclusions.** The fluorinated diamond electrode represents the first material at which both the positive and the negative boundaries of the “window of ideal polarizability” only depend on solvent stability ( $\sim 5$  V in aqueous solution, according to the  $E^\circ(\text{H}^\bullet/\text{H}_2) = -2.3 V_{\text{SHE}}$  and  $E^\circ(\cdot\text{OH}, \text{H}^+/\text{H}_2\text{O}) = 2.74 V_{\text{SHE}}$  reduction potentials<sup>5,7</sup>). Such a result has to be related to the lack of any stabilizing interaction between the electrode surface and species undergoing electrochemical oxidation or reduction.

Beyond the attempt of interpretation of experimental results above exposed, they certainly indicate that F-terminated, boron-doped diamond electrodes add the advantage of a high negative ideal polarization limit (i.e., higher than mercury) to the feature, already observed at H-terminated BDD electrodes, in the positive direction. The very low ability of the F-BDD surface in stabilizing reaction intermediates, along with its low capacitive currents, is responsible for the very low residual currents and makes this material an excellent candidate for electroanalytical applications.

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