

# Mechanistic studies on boron-doped diamond: Oxidation of small organic molecules



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## ABSTRACT

The electro-oxidation of ethanol, acetone, i-propanol, its fluorinated analogue hexafluoroisopropanol (HFIP) and cyclohexane in 1 M HClO<sub>4</sub> was studied on a boron doped diamond (BDD) electrode by on-line differential electrochemical mass spectrometry (DEMS), using a dual thin layer cell. One can distinguish two oxidation pathways: at potentials below 2.5 V a direct electron transfer to the BDD takes place, while at potentials above 2.5 V OH radicals are produced and scavenged by the reactants. As a consequence, the oxygen evolution reaction is at least partially suppressed. The direct electron transfer to the electrode is observed for i-propanol, ethanol and cyclohexane. For acetone and HFIP, only the second, indirect, pathway with the participation of OH radicals is effective. For all the reactants except HFIP CO<sub>2</sub> formation was observed generally at 2.5 V or higher, the potential for the oxygen evolution reaction (OER) in the pure supporting electrolyte. Hence OH radicals are instrumental in the cleavage of C–C bonds. For HFIP, the cyclic voltammograms of the supporting electrolyte with and without the reactant are identical. This indicates that the oxidation of HFIP is initiated by OH radicals followed by a further electron transfer to the electrode, similarly to the oxidation of CO (I. Kisacik, A. Stefanova, S. Ernst and H. Baltruschat, PCCP, 15 (2013) 4616). For both pathways, the reactivity follows the same trend as the homogeneous hydrogen abstraction reaction rates with OH radicals. The intermediate radicals formed in the reaction with the electro-generated OH radicals can react with oxygen present in the solution.

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## 1. Introduction

Differently from the catalytically active Pt-group metals [1,2], Boron doped diamond electrodes (BDD) interact only weakly with organic molecules. They exhibit high stability in acidic medium, high oxygen evolution overpotential and formation of strong oxidants, therefore they find an application for wastewater treatment and electrosynthesis [3–7].

During anodic polarization of the BDD, hydroxyl radicals are generated from water discharge and react further to oxygen, or participate in the oxidation process of the compounds. The formation of hydroxyl radicals on BDD electrodes was confirmed by spin-trapping experiments [8], coumarin oxidation [9], and a Tafel-slope of 120 mV/dec in the potential region above 2.4 V for the oxygen evolution reaction (OER) in perchloric acid [10] and for the oxidation of methanol and formic acid [11]. The oxidation of H<sub>2</sub>O<sub>2</sub> as well as carbon monoxide and small aliphatic organic molecules such as MeOH, EtOH, formic and acetic acid, was studied in order to clarify the oxidation processes on BDD electrodes in aqueous

media [12–14]. The oxygen evolution reaction was suppressed in the presence of organic molecules, which can be explained with the competition for the OH radicals. This is another evidence for the role of OH radicals in the oxidation of the compounds. In the case of aromatic compounds, a direct oxidation at the electrode takes place at potentials about 1 V below 2.3 V [15–17].

The oxidation via hydroxyl radicals generated at the electrode is a fast process, controlled by the mass transport of the organic species to the electrode surface and the production rate of the hydroxyl radicals [18]. Experiments with acetic acid in the presence of isotopically labelled oxygen in the solution showed that not only OH radicals, but also molecular oxygen, if present in the solution, takes part in the oxidation of the compounds [5]. This finding opens the possibility to an electrochemically initiation of waste water treatment with oxygen from the air, which could largely reduce the amount of necessary electricity.

The aim of this work was to understand better the oxidation process of organic molecules at BDD electrodes. Fluorinated alcohols, such as hexafluoroisopropanol (HFIP), were of interest as they are more stable than water. Another reason to investigate the behaviour of HFIP is the fact that it is used as a solvent in the electrosynthesis on BDD, because it is able to stabilize radicals [6,7,19,20]. In a parallel publication [21], we investigated the

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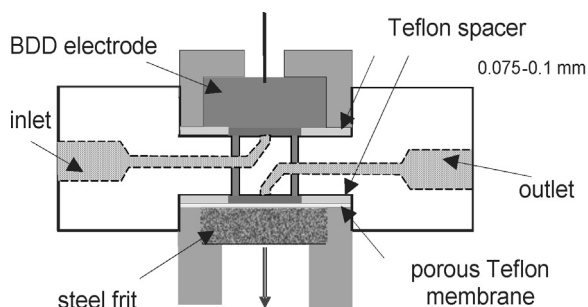


Fig. 1. Schematic of the electrochemical cell used for DEMS.

oxidation of water and primary, secondary, and tertiary alcohols in HFiP as a solvent, which on oxidation does not form OH radicals.

Here, in addition to HFiP, its analogue *i*-propanol and other small organic molecules, acetone, ethanol and the alkane cyclohexane were also investigated. As a small organic molecule *i*-propanol is well suited as a test compound to understand better the processes occurring at BDD. The electro-oxidation of *i*-propanol on Pt has been already studied by DEMS and the main product is known to be acetone, without total oxidation to CO<sub>2</sub> [22,23]. Oxidation of acetone to CO<sub>2</sub> at a Pt electrode is only possible after its preceding adsorption, i.e. from the adsorbed state [24]. The thermodynamic potential of oxidation of *i*-propanol to acetone was calculated to be 0.13 V and 0.10 V for the complete oxidation to CO<sub>2</sub>, using the tabulated values for the Gibbs energies [25,26] without taking into account solution effects. To further the understanding of the *i*-propanol oxidation also that of acetone, as a product of this reaction, and that of ethanol, as simple primary alcohol, was investigated. As an aliphatic saturated compound also cyclohexane was studied. Understanding of the oxidation of these relatively simple compounds will help in the general understanding of reactions on BDD electrodes.

The electro-oxidation of these compounds was studied by quantitative differential electrochemical mass spectrometry (DEMS). The detailed determination of the current efficiencies and of the relative product yields allows a better insight into the underlying reactions.

## 2. Experimental

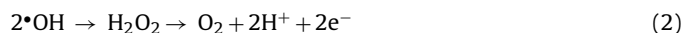
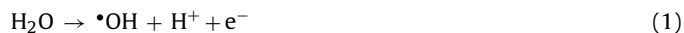
The potential dependent formation of volatile products was monitored on-line, i.e. simultaneously with cyclic voltammetry, using differential electrochemical mass spectrometry (DEMS) [27]. The electrochemical cell used here was a dual thin layer cell, manufactured from Kel-F. It consists of two compartments, connected by six capillaries [28,29]. A schematic is reproduced in Fig. 1. The electrode was placed in the upper compartment. The products of the electrochemical reaction pass through the capillaries into the (lower) detection compartment, from where they can diffuse through a porous Teflon membrane into the mass spectrometer (a quadrupole mass spectrometer Pfeiffer–Balzers QMG-422). The time constant of the detection is determined by the transport of the species from the electrode to the Teflon membrane, and at the flow rate of 5 μl/s it is about 1–2 s.

The surface area of the electrode (0.28 cm<sup>2</sup>) and the thickness of the electrochemical compartment (100 μm) were defined by a thin Teflon spacer, placed on the electrode. The flow of the electrolyte was controlled by a peristaltic pump at the outlet. As a reference electrode a reversible hydrogen electrode (RHE) was used. Two gold wires, placed at the inlet and the outlet of the cell were used as counter electrodes and connected to the potentiostat via two different resistors in order to optimize the current distribution in the cell and to minimize the IR-drop. The experiments were

performed at room temperature. The BDD electrodes, 10 mm diameter, 1 μm diamond doped with 6000 ppm B on a 1 mm thick Si-substrate, were obtained from Adamant, La-Chaux-de-Fonds, Switzerland. The supporting electrolyte was 1 M HClO<sub>4</sub>, except for the ethanol measurement, where 0.5 M H<sub>2</sub>SO<sub>4</sub> was used. Before preparing the solutions, the perchloric acid was deaerated with highly pure argon (99.99% firm Acros), except for the measurement with oxygen containing *i*-propanol, afterwards the analyte was added to the deaerated HClO<sub>4</sub>. Introducing Ar to the solution during the measurement for an extended period would change the concentration by extracting *i*-propanol or acetone from the solution, therefore, these analyte containing solutions were not continuously bubbled with Ar. The HFiP and the ethanol solutions were deaerated with Ar before and during the measurement. The saturated (ca. 0.7 mM[26]) cyclohexane solution was prepared by introducing Ar through a cyclohexane containing vessel, and then further bubbling the cyclohexane saturated Ar for 1 h into a 1 M HClO<sub>4</sub> solution, deaerated with pure Ar before.

All solutions were prepared with Millipore-Q water. The perchloric acid was obtained from Acros, HFiP (hexafluoroisopropanol) from Fluorochem, *i*-propanol and acetone from Sigma–Aldrich, cyclohexane, sulphuric acid and ethanol from Merck.

The system was calibrated for O<sub>2</sub> in the supporting electrolyte (HClO<sub>4</sub>), where no other reaction than O<sub>2</sub> evolution takes place by sweeping to 2.7 V at a scan rate of 10 mV/s for the three flow rates used here. The calibration has to be performed separately for each flow rate because the transfer efficiency  $f_2$  (the probability for a species formed at the electrode to reach the Teflon membrane and enter the vacuum system of the mass spectrometer, cf. below) depends on the flow rate. At 2.7 V, the oxygen evolution reaction (OER) from water takes place, initiated by the generation of OH radicals at the BDD electrode:



The overall reaction is



The calibration constant  $K^*$ , giving the ratio of the detection signal of the mass spectrometer (as ion current  $I_{\text{MS}}$ ) and the amount of produced oxygen molecules (as given by the Faraday current) was calculated by the equation

$$K^* = z \frac{Q_{\text{MS}}}{Q_{\text{F}}} \quad (4)$$

where  $Q_{\text{MS}}$  is the ionic charge of the signal for the mass/charge ratio  $m/z = 32$  (oxygen),  $Q_{\text{F}}$  is the corresponding Faraday charge during oxygen evolution in a cyclic voltammetry experiment,  $\Delta n$  the corresponding number of mols, and  $z$  the number of electrons involved in the reaction (see Eq. (3), in this case  $z = 4$ ). The charges give the average currents and therefore they were used to determine the calibration constant for oxygen.

The calibration for CO<sub>2</sub> was performed with a polycrystalline Pt electrode using the electro-oxidation of adsorbed CO with a known number of electrons transferred as the source as described elsewhere [27,30]. The calibration of O<sub>2</sub> and CO<sub>2</sub> showed that  $K_{\text{CO}_2}^* = 2.0 K_{\text{O}_2}^*$ .

For the other compounds, such as HFiP, *i*-propanol and acetone, there is no electrode reaction with a known current efficiency. Thus, a different calibration procedure had to be used. The ionic currents for  $m/z$  ratios of 51, 45 and 58, respectively, were measured for solutions of these compounds with known concentrations. For each of the flow rates  $u = dV/dt$ , the ionic current  $I_{\text{MS}}$  was plotted versus the concentration  $c$ , since  $I_{\text{MS}} = (K^* f_2 u) \cdot c$ , where  $K^*$  is the ratio of the number of fragment ions detected and the number of molecules

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