Detection of Hydroxyl Radicals during the Electrochemical Oxidation of Organic Compounds at BDD Electrodes

B. Marselli and Ch. Comninellis
Section of Chemistry and Chemical Engineering, ISP - UGEC
Swiss Federal Institute of Technology, CH - 1015 Lausanne, Switzerland.

Oxidation processes at BDD occur at high anodic potential, in the region of water discharge. The oxidation of formic acid at BDD electrodes shows a decrease in the starting potential of water decomposition with the acid concentration meaning that the oxidation pathway involves hydroxyl radicals as electrogenerated intermediates. These are produced by the water discharge according to the following equation:

$$H_2O \rightarrow HO^{\bullet} + H^+ + e^-$$

The detection of these radicals is possible by spin trapping. In this work, the radicals were trapped with different scavengers (DMPO, RNO and salicylic acid) in order to produce stable adducts, which were investigated by several techniques (Electron Spin Resonance, UV-visible measurements and liquid chromatography).

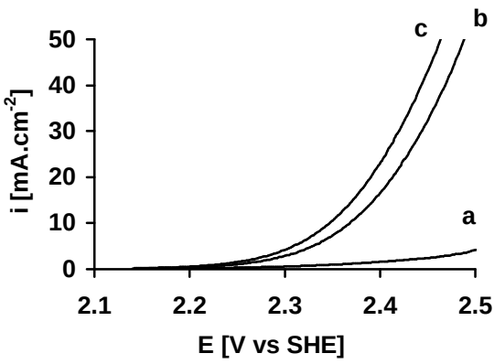

Figure 1: Voltammetric i-E curve obtained at BDD electrode in (a) $HClO_4$ 1M, (b) HCOOH 0.25M + HClO4 1M and (c) HCOOH 0.5M + $HClO_4$ 1M. Scan rate 20 mVs^{-1}, T=25°C

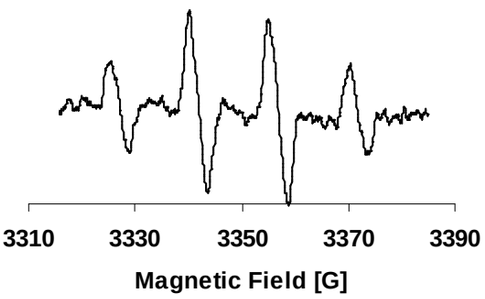

Figure 2: ESR spectrum of DMPO adduct obtained after
electrolysis of a 10 mM DMPO solution in $HClO_4$ 1M for
2 hours on BDD electrode at 0.1 $mA.cm^{-2}$ T = 25°C