ELECTROCHEMICAL OXIDATION OF BENZOIC ACID ON BORON DOPED DIAMOND ELECTRODES

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Abstract

The oxidation of benzoic acid has been performed on boron doped diamond electrodes supported on silicon substrate. The voltammetric behaviour has shown that during the oxidation of benzoic acid at 2.7V (RHE), a polymeric film is formed on the electrode surface that is oxidized at higher potential values.

Bulk electrolysis of benzoic acid in $HClO_4$, under galvanostatic conditions results in an instantaneous current efficiency (ICE) near 100% at low current densities and high benzoic acid concentrations. Electrolysis at high current densities and low benzoic acid concentrations results in a decrease of ICE due to mass transport limitations.

Keywords: diamond electrodes, benzoic acid, electrooxidation.

1. Introduction.

The electrochemical oxidation is a promising technique in the treatment of waste water containing organic pollutants [1-2]. Aromatic compounds are highly pollutants produced or used in many industrial processes. Anodic oxidation has been widely studied with a variety of anode materials: porous carbon felts, PbO_2, SnO_2, etc. [3-7].

Boron doped diamond electrodes are emerging as unique material for several applications due to its properties including acceptable conductivity, high resistance to corrosion, high thermal stability, etc. Several papers described this material as a non-active electrode, generator of hydroxyl radicals adequate for oxidation of organic compounds [2,8,9].

Benzoic acid presents a low current efficiency (defined also as electrochemical oxidation index (EOI)) during anodic oxidation on platinum electrodes, like other aromatic compounds with electron withdrawing groups.

This work studies the electrochemical oxidation of benzoic acid on boron doped diamond electrodes in perchloric acid medium by cyclic voltammetry and bulk electrolysis.

2. Experimental.

The boron doped diamond electrodes (Si/BDD) were provided by the Swiss Center for Electronics and Microtechnology. The diamond film was grown on p-Si sustrate by chemical vapour deposition technique, and the thickness was about 1 µm.

The Ti/IrO$_2$/SnO$_2$ electrodes were prepared according to the method described previously [10]. The total loading of active layer was 39 g/m^2 of SnO$_2$-Sb.

The test solution was 0.5M HClO$_4$ Merck prepared from Merck Suprapur concentrated acids. Benzoic acid was Fluka p.a.

Voltammetric measurements were obtained with an EG&G potentiostat model 273 controlled by Echem M270 software. As working electrode a Si/BDD plate of 1 cm^2 of geometric area was used. The reference electrode was a reversible hydrogen electrode.

The anodic oxidation of benzoic acid was carried out using an undivided electrochemical flow cell of a volume of 500 cm^3. The mass-transfer coefficient in the cell was $1.5.10^{-5}$ m s^{-1}, determined using the ferri/ferrocyanide couple. A Si/BDD disc and a zirconium disc was used as anode and cathode respectively, both of 50 cm^2. The electrolysis were performed in galvanostatic mode. Chemical Oxygen Demand (COD) was determined by a HACH DR200 analyser and the Total Organic Carbon (TOC) was determined by a TOC-5050 Shimadzu equipment.

The instantaneous current efficiency was calculated using the following relation [11]:

$$I = 4FV \frac{[(COD)_t - (COD)_{t+\Delta t}]}{I\Delta t}$$

where (COD)$_t$ and (COD)$_{t+\Delta t}$ are the chemical oxygen demand (in mol O$_2$ dm^{-3}) at time t and t+Δt, I is the current in Ampers, F is the Faraday constant and V is the volume of electrolyte (dm^3).

3. Results and Discussion.

Figure 1 shows the voltammogram of boron doped diamond electrode in 0.5M HClO$_4$. It can be observed that there is not any noteworthy faradic current in the potential range between -0.7 and 2.4V. Then, this type of electrodes shows a large potential range of stability.

Figure 2 shows the voltammogram obtained in presence of benzoic acid in 13 mM concentration. A peak appears during the first positive scan at approximately 2.6V that does not appear with the BDD electrode in absence of benzoic acid in the solution. This peak increases with the benzoic acid concentration indicating that is consequence of the oxidation of benzoic acid in the solution. After the first cycle in subsequent scans, a remarkable decrease of the current of this peak appears, indicating that the electrode suffers a deactivation during the oxidation of benzoic acid. During the second cycle there is no peak.
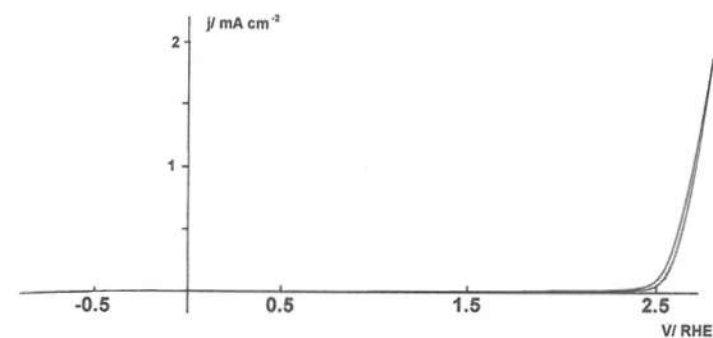
Figure 1: Stabilised voltammogram of a Si/BDD electrode in 0.5M HClO$_4$. The polarisation program was: initial potential 0.5 V, upper limit 2.7 V, lower limit –0.7 V. Counter electrode Pt wire. Scan rate 100 mV s^{-1}.
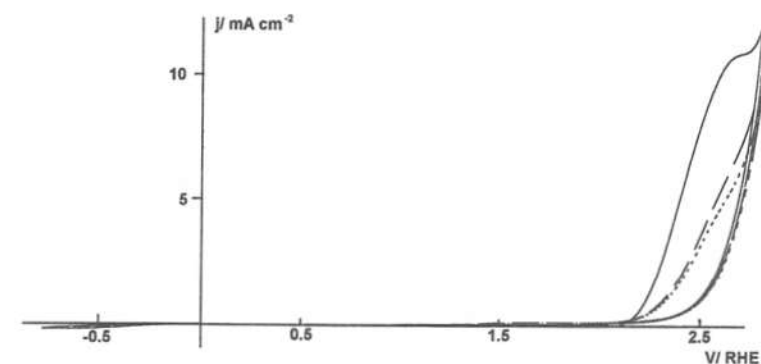

Figure 2: Cyclic voltammograms for the oxidation of 0.013M benzoic acid in 0.5M HClO$_4$. Working electrode Si/BDD. Counter electrode Pt wire. Scan rate 100 mV s^{-1}. Filled line 1st scan. Dashed line 2nd scan. Doted line 5th scan.

Table 1 shows the peak potential during the first cycle, the current densities during the first and the fifth cycle and the percentage of deactivation at different benzoic acid concentrations. In all cases, it can be observed that the electrode deactivation is enhanced at high benzoic acid concentrations. The deactivation of the electrode should be due to the formation of a polymeric product during the oxidation of benzoic acid. It could be observed a yellowish product attached on

the electrode surface. If the positive potential limit is changed to higher values the percentage of deactivation decreases. That is if the positive potential limit is 3.05V, the percentage of deactivation is 11% during the fifth cycle. This decrease of the deactivation indicates that the polymeric product formed during the oxidation of benzoic acid at 2.8V is oxidized at higher potential values. The electrode surface remains blocked by the polymeric product if the surface is rinsed with water or isopropanol. In order to clean the electrode surface, it should be subjected to a positive polarization during 10 minutes at 10 mA cm^{-2}.

Table 1 : Peak potential, current density of the first and in the fifth scan and percentage of deactivation of the oxidation peak of benzoic acid, measured during cyclic voltammetry of different solutions of benzoic acid in 0.5M HClO$_4$. Working electrode Si/BDD. Scan rate 100 mV s^{-1}, T= 25°C.

c(mM)	E_{peak} (V/RHE)	$j(mAcm^{-2})$		% of deactivation
		1st scan	5th scan	
1.6	2.51	3.06	2.46	20
3	2.53	5.60	3.67	34
7	2.61	10.03	4.97	50
13	2.64	13.73	5.36	61

The oxidation of benzoic acid was performed in a electrochemical flow cell in 0.5M HClO$_4$ at constant current of 1.5 A. The concentration of benzoic acid was changed from 2.11 mM to 8.86 mM. Figure 3 shows the evolution with time of the COD during the electrochemical oxidation of benzoic acid as a function of the initial concentration of this organic compound. It can be observed in this figure that at the beginning of the electrolysis, the COD decreases linearly with specific charge and after passing a value of critical charge, this factor decreases following an exponential trend as the model proposed by Panizza et al. [9]. This model predicts the evolution of the COD and current efficiency during the electrochemical oxidation of organic compounds. The model makes an estimation of the limiting current density from the COD value considering complete oxidation of the organic compounds to CO$_2$.

Figure 3, inset, shows the evolution of the Instantaneous Current Efficiency (ICE) during the electrolysis. It can be observed that at high concentration of benzoic acid, the instantaneous current efficiency (ICE) is near 100% and the reaction is under current limiting control, however, when the concentration decreases this value is lower than 100% because of a mass transfer control.

For the treatment of benzoic acid solutions a Ti/IrO$_2$/SnO$_2$-Sb electrode was prepared. Figure 4 shows the COD obtained during an experiment using this Ti/IrO$_2$/SnO$_2$ electrode. It can be

observed the different behaviour of this electrode in comparison to the obtained in the case of Si/BDD electrodes (dashed line of Figure 4). The COD is practically constant during the electrolysis. Figure 4 inset shows the value of ICE obtained during the electrolysis showing a value lower than 2 %, a value very low in comparison with the observed in the case of Si/BDD electrode.
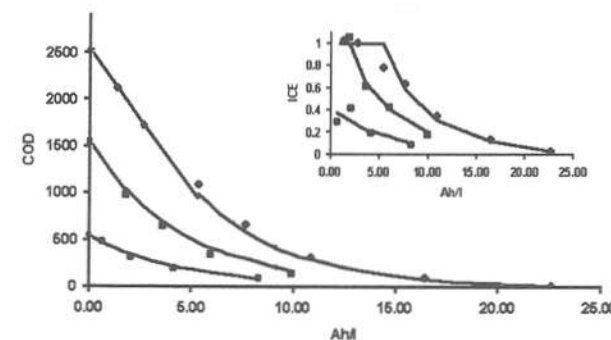

Figure 3: Evolution of Chemical Oxygen Demand (COD) and Instantaneous Current Efficiency (ICE) (inset) during electrolyses of benzoic acid in 0.5M HClO$_4$. Initial concentration of benzoic acid, (◆) 8.86 mM, (■) 4.76 mM, (●) 2.11 mM. Anode: Boron-doped diamond electrode. Cathode Zr plate.T=25 °C. j= 24 mA cm^{-2}. The solid lines represent the model prediction.
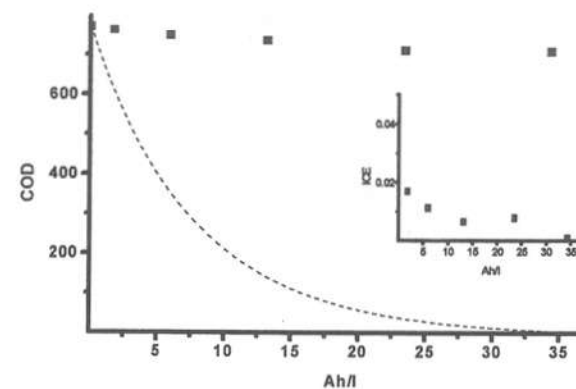

Figure 4: Evolution of Chemical Oxygen Demand (COD) and Instantaneous Current Efficiency (ICE) (inset) during electrolyses of benzoic acid in 0.5M HClO$_4$. Initial concentration of benzoic acid 2.4 mM. Anode: Ti/IrO$_2$/SnO$_2$. Cathode Zr plate.T=25 °C. j= 24 mA cm^{-2}. The dashed line represents the model prediction.

4. Conclusions.

The Si/BDD electrodes have been used in the treatment of benzoic acid in perchloric acid solutions. These electrodes have shown a very good performance in the oxidation of this organic compound in comparison with the behaviour observed with a tin dioxide electrode. The chemical oxygen demand using Si/BDD electrodes decreases during the electrolysis in a good agreement with the model proposed by Panizza et al. [9].

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6. References.

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NIMESULIDE AMPEROMETRIC DETERMINATION IN PHARMACEUTICALS WITH A PARALLEL CHANNEL FIA SYSTEM

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ABSTRACT

The development of a FIA procedure with amperometric detection for nimesulide determination is described. The method is based on the oxidation of nimesulide at a glassy carbon electrode and was applied to the quantification of this drug in pharmaceutical preparations. The calibration graph, linear within the range 5.0×10^{-5} - 3.0×10^{-4} M was possible to obtain by using a FIA manifold with a leaping detector with two parallel channels: one used for the nimesulide measurement and the other for conditioning the working electrode surface. The determinations were performed in an ethanol/ pH=6.1 Britton-Robinson buffer mixture 30/70 (%, v/v), at a potential of 1.2 V versus an AgCl/Ag (KCl, 3 M) reference electrode. The sampling rate was 60 samples h^{-1} and the percentage recovery of nimesulide from the tablets was within 99.1 – 102.8 %.

Keywords: Nimesulide; Pharmaceutical products; Amperometry; FIA; Tubular electrodes.

1. INTRODUÇÃO

O nimesulide N-(4-nitro-2-fenoxifenil)metanosulfonamida é um anti-inflamatório não esteróide administrado no tratamento de uma vasta gama de estados de inflamação e de dor. Este princípio activo, tem-se mostrado eficaz na redução dos referidos sintomas associados à osteoartrite, artrite reumatóide, tromboflebite, infecções do tracto respiratório e da cavidade oral [1].

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