

PROCEEDINGS OF
**THE 16th INTERNATIONAL SYMPOSIUM ON
ANALYTICAL AND ENVIRONMENTAL PROBLEMS**

28 September 2009

Edited by
Zoltán Galbács



SZAB
SZEGED, HUNGARY

THE 16th INTERNATIONAL SYMPOSIUM ON ANALYTICAL AND
ENVIRONMENTAL
PROBLEMS

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978-963-482-975-1

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THE ELECTROCHEMICAL BEHAVIOUR OF DSA AND BDD ELECTRODES DURING DICLOFENAC ELECTROOXIDATION

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ABSTRACT

The electrooxidation of anti-inflammatory drug diclofenac (DCF) on Dimensionally Stable Anodes (DSA) and Boron Doped Diamond (BDD) electrode was investigated by cyclic voltammetry. The experiments were carried out in aqueous solutions by using 0.1 M Na₂SO₄ supporting electrolyte. The DSA electrodes were prepared by thermal decomposition of appropriate precursors, while the BDD electrode was commercially produced. The DSA electrodic compositions were Ti/RuO₂-TiO₂ and Ti/RuO₂/SnO₂-Sb₂O₅. The recorded voltammograms showed that DCF direct oxidation did not occur on DSA and the oxidation could occur in the potential range of oxygen evolution. The electrooxidation of DCF on BDD electrode was possible by direct oxidation.

INTRODUCTION

As part of conventional wastewater treatment technology, which involves physical, chemical and biological processes employing conventional activated sludge, most of pharmaceutically active compounds (PhACs) have not been removed.

The above finding has been confirmed by many studies that indicated the occurrence of PhACs at low levels of concentrations (ng-µg/L) on large scale in different compartments of the aquatic environment, and without doubt their presence within surface waters has proved that the removal of PhACs in sewage treatment plants has been incomplete [1-3]. However, the presence of pharmaceuticals at low levels of concentrations in the environment can have adverse effects on aquatic organisms [4].

Consequently, the advanced wastewater treatment solutions for pharmaceuticals effluents have been studied intensively in the recent years in order to provide appropriate influents for sewage treatment plants: Fenton-like system in combination with lime coagulation [5], Fenton's oxidation [6], membrane bioreactor process [7], and combination of anodic oxidation with ozonation [8].

Diclofenac (DCF) belongs to non-steroidal anti-inflammatory drugs that are a special group of pharmaceuticals that are often found as a persistent toxic waste and are one of the most widely available drugs in the world. DCF is used in the treatment of inflammatory and degenerative diseases of the articulations [9].

The aim of this paper was to investigate the electrochemical behaviour of Dimensionally Stable Anodes (DSA) and Boron Doped Diamond (BDD) electrode during the electrooxidation of DCF envisaging the treatment of pharmaceutically effluents by electrochemical methods.

MATERIALS and METHODS

The DSA electrodes used in these experiments were Ti/RuO₂-TiO₂ and Ti/RuO₂/SnO₂-Sb₂O₅. The electrodes were prepared by thermal decomposition of appropriate precursors. For Ti/RuO₂-TiO₂ the precursors were RuCl₃·nH₂O (Fluka) and TiCl₄ (Carlo Erba). The molar ratio Ru:Ti in the precursors solution was 30:70 and the decomposition temperature was 450 °C. For the electrocatalytic layer of Ti/RuO₂/SnO₂-Sb₂O₅ the precursors were SnCl₄·5H₂O (Aldrich) and SbCl₃ (Aldrich) and the decomposition temperature was 550 °C. The molar ratio Sb:Sn in precursors solution was 3:97. The intermediate layer of RuO₂ (from Ti/RuO₂/SnO₂-Sb₂O₅) was obtained by thermal decomposition of RuCl₃·nH₂O (Fluka) at 450 °C. The BDD electrode was commercially provided by Windsor Scientific Ltd.

DCF (2-[2',6'-dichlorophenyl]amino]phenylacetic acid) was supplied by Amoli Organics Ltd as sodium salt and sodium sulphate by Merck. Distilled water was used for the preparation of the solutions.

The cyclic voltammetric experiments were performed by using an EcoChemie Autolab-PGSTAT 302 potentiostat-galvanostat controlled by GPES 4.9 software. A saturated calomel electrode was used as a reference electrode. DSA electrode with active surface area of 1 cm² and BDD electrode with active surface area of 0.07 cm² were used as working electrodes. The counter electrode was a platinum plate of 1 cm². Experiments were carried out at 50 mVs⁻¹ potential scan rates at room temperature in solution of 0.1 M Na₂SO₄ supporting electrolyte and solutions of DCF of 10 - 25 ppm in 0.1 M Na₂SO₄.

RESULTS

The voltammetric response of DSA and BDD electrodes will provide useful information concerning their electrochemical behaviour during DCF oxidation, as well as the window potential and oxygen evolution.

The cyclic voltammograms of DSA electrodes in the potential range from -0.5 V to 1.5 V vs. SCE and BDD electrode in the potential range from -0.5 V to 1.25 V vs. SCE in 0.1 M Na₂SO₄ supporting electrolyte are shown in Fig. 1-3.

The cyclic voltammograms of Ti/RuO₂-TiO₂ in the potential range from -0.5 V to 1.5 V vs. SCE (Fig. 1.) showed that the oxidation current was almost steadfast below the oxygen evolution potential of 1.1 V vs. SCE and then it increased sharply as the oxygen evolution occurred. Low voltammetric background current was observed and neither anodic nor cathodic peaks were identified below 1.1 V vs. SCE, reflecting the easily polarisable nature of the solid-electrolyte interface. The shape of the voltammogram was similar to that reported by Motheo et al. [10] and C. Feng et al. [11].

As for Ti/RuO₂-TiO₂, the cyclic voltammogram of Ti/RuO₂/SnO₂-Sb₂O₅ in the potential range from -0.5 V to 1.5 V vs. SCE (Fig. 2) revealed an almost constant oxidation current below the oxygen evolution and followed by a rapid increase. As compared to Ti/SnO₂-Sb₂O₅ that has an oxygen evolution potential of 1.4 V vs. SCE [12], for Ti/RuO₂/SnO₂-Sb₂O₅ the oxygen evolution potential became 1.06 V vs. SCE. The shift of oxygen evolution potential towards less positive values could be due to the intermediate layer of RuO₂ introduced in the electrode composition to increase the service life of DSA with film of non-noble metal oxides.

The cyclic voltammogram of Ti/RuO₂/SnO₂-Sb₂O₅ showed a cathodic peak at 0.7 V vs. SCE that could be attributed to the reduction process of the intermediate as resulted within the oxidation process of the electrode surface under the oxygen potential range [13].

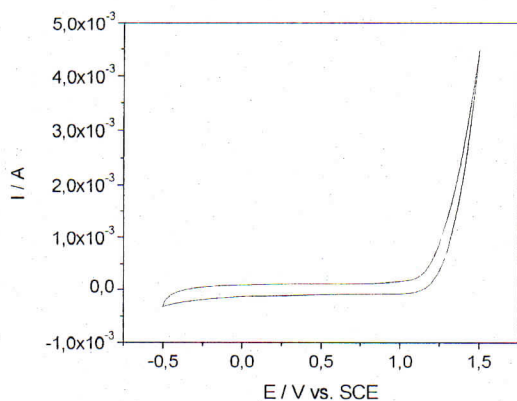


Fig.1. Cyclic voltammogram of Ti/RuO₂-TiO₂ in 0.1 M Na₂SO₄; scan rate 0.05 V/s; potential range: - 0.5 V → + 1.5 V vs. SCE

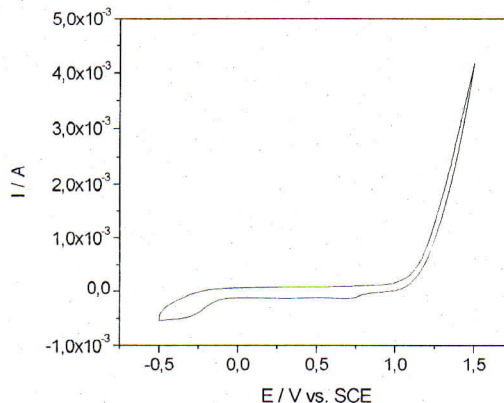


Fig.2. Cyclic voltammogram of Ti/RuO₂/SnO₂-Sb₂O₅ in 0.1 M Na₂SO₄; scan rate 0.05 V/s; potential range: - 0.5 V → + 1.5 V vs. SCE

The cyclic voltammogram of BDD recorded in the potential range from -0.5 V to 1.25 V vs. SCE (Fig.3) showed that oxygen evolution potential occurred at 1.05 V vs. SCE. Below this potential, no anodic or cathodic peaks appeared and low voltammetric current was observed, reflecting the easily polarisable nature of the solid-electrolyte interface. The rapid increase of the anodic current in the high potential region was attributed to oxygen evolution.

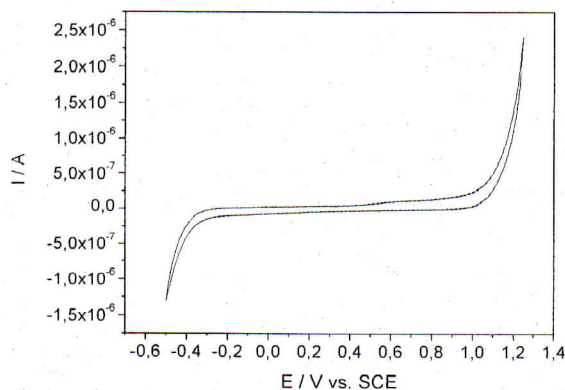


Fig.3. Cyclic voltammogram of BDD in 0.1 M Na₂SO₄; scan rate 0.05 V/s; potential range: - 0.5 V → + 1.25 V vs. SCE

The electrochemical response of DCF on DSA and BDD electrodes is presented in Fig.4-6. Examination of the voltammograms of DSA electrodes with film of noble or non-noble metal oxides (Fig. 4 and 5) in the potential range from - 0.5 V to 1.5 V vs. SCE in the presence and absence of DCF showed their overlap. This suggested that no direct oxidation occurred and the oxidation of the pollutant could occur under simultaneous O₂ evolution.

The behaviour of DCF during the oxidation on BDD was different with respect to DSA electrodes. The cyclic voltammogram (Fig.6) revealed that the oxidation of DCF on BDD occurred up to the oxygen evolution potential that corresponded to a direct oxidation by charge transfer on the electrode surface. Four oxidation peaks could be identified on the anodic curve, i.e., 0.1, 0.33, 0.6 and 0.97 V vs. SCE.

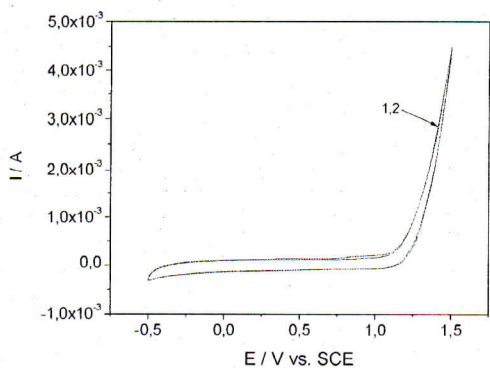


Fig.4. Cyclic voltammograms of Ti/RuO₂-TiO₂; scan rate 0.05 V/s; potential range: - 0.5 V → + 1.5 V vs. SCE; 1- 0.1 M Na₂SO₄; 2 – 25 ppm DCF in 0.1 M Na₂SO₄

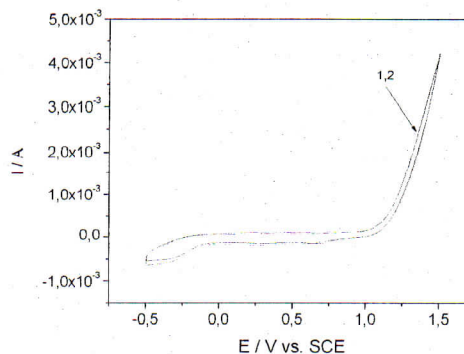


Fig.5. Cyclic voltammograms of Ti/RuO₂/SnO₂-Sb₂O₅; scan rate 0.05 V/s; potential range: - 0.5 V → + 1.5 V vs. SCE; 1- 0.1 M Na₂SO₄; 2 – 25 ppm DCF in 0.1 M Na₂SO₄

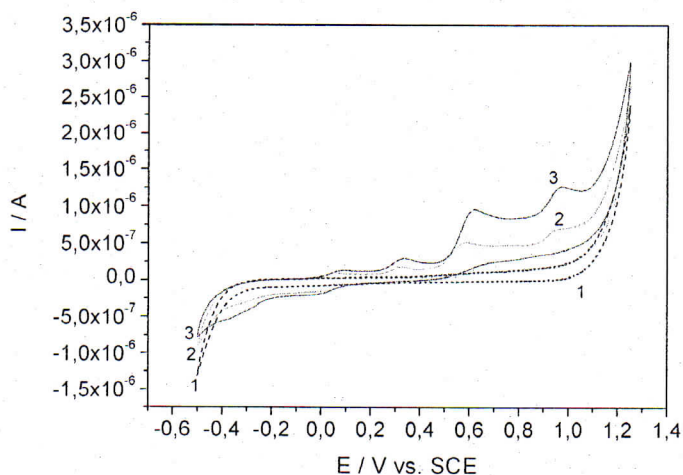


Fig.6. Cyclic voltammograms of BDD in supporting electrolyte 0.1 M Na₂SO₄ and in presence of DCF at various concentration: 1 – 0 ppm; 2- 10 ppm; 3 – 20 ppm; scan rate 0.05 V/s; potential range: - 0.5 V → + 1.25 V vs. SCE

CONCLUSIONS

This study dealt with the electrooxidation of non-steroidal anti-inflammatory drug DCF on DSA (Ti/RuO₂-TiO₂ and Ti/RuO₂/SnO₂-Sb₂O₅) and BDD electrodes envisaging the application of the electrochemical methods in pharmaceutical wastewater treatment. The electrochemical behaviour of DSA and BDD electrodes during the electrooxidation of DCF was assessed by cyclic voltammetry. The oxygen evolution potential in 0.1 M Na₂SO₄ for Ti/RuO₂-TiO₂ was 1.1 V vs. SCE and 1.06 V vs. SCE for Ti/RuO₂/SnO₂-Sb₂O₅. The cyclic voltammograms of the DSA and BDD electrodes recorded in 0.1 M Na₂SO₄ supporting electrolyte and in the presence of DCF pointed out that the drug was not directly oxidised on DSA electrodes, the oxidation could occur under simultaneous oxygen evolution.

On BDD electrode, DCF was oxidised directly in four steps at 0.1, 0.33, 0.6 and 0.97 V vs. SCE, up to 1.05 V vs. SCE oxygen evolution potential in 0.1 M Na₂SO₄. These findings are important to upscale the working conditions for bulk electrolysis of DCF within pharmaceutical wastewaters.

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