Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Sparked-bismuth oxide screen-printed electrodes for the determination of riboflavin in the sub-nanomolar range in non-deoxygenated solutions

Daniel Riman^a, Apostolos Avgeropoulos^b, Jan Hrbac^{c,*}, Mamas I. Prodromidis^{d,*}

^a Department of Analytical Chemistry, Palacky University, 77146 Olomouc, Czech Republic

^b Department of Materials Science Engineering, University of Ioannina, Ioannina 451 10, Greece

^c Department of Chemistry, Masaryk University, 625 00 Brno, Czech Republic

 $^{\mathrm{d}}$ Department of Chemistry, University of Ioannina, Ioannina 451 10, Greece

ARTICLE INFO

Article history: Received 4 February 2015 Received in revised form 6 March 2015 Accepted 7 March 2015 Available online 11 March 2015

Keywords: electric discharge spark deposition bismuth electrode riboflavin screen printed electrodes

ABSTRACT

Despite their outstanding performance for the stripping voltammetric detection of trace metals, bismuth electrodes show poor sensitivity for the cathodic detection of organic compounds. Moreover, oxygen removal from samples is recommended to lower the background signal, which limits their application to on-site analysis. Herein, we propose recently introduced sparked-bismuth oxide screen printed electrodes for the cathodic detection of riboflavin, a reducible organic compound. The ultra-sensitive determination of riboflavin in the sub-nanomolar range in the presence of dissolved oxygen is demonstrated. After electroless preconcentration for 60 s, electrodes showed a linear response over the concentration range 1–100 nmol L⁻¹ riboflavin, while the limit of detection (S/N=3) was found to be 0.7 nmol L⁻¹ riboflavin, ca. 140-fold lower than that has been achieved with electroplated bismuth electrodes. Excellent interelectrode reproducibility and application to a pharmaceutical sample are also demonstrated.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Various types of bismuth electrodes, such as bismuth-bulk electrodes, bismuth-film electrodes (BiFEs), and bismuth precursor compounds-modified electrodes have been widely used for the stripping voltammetric determination of metals, and, without doubt, they are considered as the most successful alternative of ecologically questionable mercury electrodes [1,2]. The scope of the use of bismuth electrodes in electroanalysis is continuously enriched by applications to the cathodic electrochemical determination of organic compounds [3], benefiting from the high hydrogen overpotential and the relatively low background signal in the negative potential region. Different types of bismuth electrodes (mostly BiFEs) can serve as suitable surfaces for the electroanalysis of pharmaceuticals [4–8], pesticides [9–13], hormones [15], nitrocompounds [16,17] etc. However, the achieved detection capabilities are considerably lower compared with those that have been reported for the stripping voltammetric

E-mail addresses: jhrbac@atlas.cz (J. Hrbac), mprodrom@cc.uoi.gr (M.I. Prodromidis).

determination of metals thus hampering the widespread application of bismuth electrodes for the detection of reducible organic compounds.

An extra obstacle is the electrocatalytic activity of bismuth electrodes to the reduction of dissolved oxygen, which limits their application to deoxygenated samples. Moreover, practical difficulties associated with sample deaeration outside the laboratory, also prevent their use to on-site applications. The few examples of BiF [10–12,15,18] and bismuth-carbon paste [14] electrodes dealing with applications at non-deoxygenated solutions also suffer from poor performance. The magnitude of the background signal regulates the achieved detection capabilities, while reliable analytical signals over oxygen reduction voltammetric wave can be obtained only in relatively high i.e., sub-micromolar [15,18] and, more commonly, micromolar [10–12,14] concentrations of the target analytes.

Therefore, the development of new bismuth surfaces to allow the detection of reducible organic compounds in the nanomolar range and in the presence of dissolved oxygen is highly desirable. In view of this analytical challenge, sparkedbismuth oxide graphite screen-printed electrodes (sparked-BiSPEs), recently devised by our group [19] were examined using riboflavin (vitamin B2) as a model compound.





CrossMark

^{*} Corresponding authors. Tel.: +26 510 08301; fax: +26 510 08796.

It has been demonstrated that highly effective BiSPEs can be prepared by a simple sparking process between a flat electrode substrate (graphite screen-printed electrode) and a tip counter electrode (bismuth wire) [19]. Sparking process is conducted in the absence of any electrolyte, while a typical sparking procedure requires ca. 20-30 s to prepare the modified electrode surface. The modification of the electrode surface through the sparking process relies on the application of an electric field capable of producing an electric discharge when the two conductors (the substrate and the tip electrodes), being connected with an external power supply, are brought into close proximity. The ensuing dielectric breakdown produces free electrons and ions originating from ionized molecules of air constituents, which in turn, bombard the sparked electrodes. Heat, introduced due to the flow of electricity leads to the formation of air plasma and vaporized (nano) particles by each electrode material (i.e. carbon and bismuth) at the closest points between them. The vaporized electrodes' material, eventually transformed by the reactions with the environment, e.g. oxidation in the presence of air, is positioned in the space between the two electrodes and upon the termination of the discharge, solidifies and deposited on the surface of the electrodes, unless carried away by dielectric fluid or inert gas flowing through the gap between the electrodes [19–21].

The facile and "green" fabrication procedure along with the attractive analytical performance of sparked-BiSPEs for the determination of riboflavin in the sub-nanomolar range, in the presence of dissolved oxygen, suggest that the developed sensors have the potential to be used for the on-site sensitive detection of a wide range of reducible organic compounds.

2. Experimental

2.1. Chemicals

Bismuth foil (0.5 mm thick, purity 99.99%) was purchased from Goodfellow and cut into narrow strips. Bismuth(III) nitrate pentahydrate and riboflavin were obtained from Sigma. The stock solution of riboflavin in double distilled water (DDW) was prepared weekly in a stoppered dark vial and kept at 4 °C. Working solutions of riboflavin were daily prepared by diluting the stock solution in DDW and kept in dark. 0.1 mol L^{-1} buffer solutions of acetate (pH 4.5), phosphate (pH 7) and ammonia (pH 9.2) were used as supporting electrolytes. Samples of "B-Komplex Forte" (Zentiva) tablets containing B1, B2, B3, B5 and B6 vitamins were prepared as follows: An accurately weighed amount of ca. 100 mg grinded tablets was sonicated in DDW for 5 min. The suspension was filtered through a 0.45 µm filter and after successive washings with DDW the filtrate was diluted to an expected concentration of 15 μ mol L⁻¹. For the recovery studies, samples were fortified with $35 \,\mu mol \, L^{-1}$ riboflavin.

2.2. Apparatus

Electrochemical measurements were conducted with the PGSTAT12 (Metrohm Autolab) analyzer in a three-electrode cell. Bare, electroplated or sparked SPEs were used as the working electrodes. A Pt-wire and a Ag/AgCl, 3 M KCl electrode (IJ Cambria) served as auxiliary and reference electrodes, respectively. All potentials reported hereafter refer to this reference electrode. Cyclic voltammograms (CVs) were obtained at a scan rate of 0.1 V s^{-1} . The preconcentration of riboflavin was performed in an electroless mode under stirring and then, after 10 s equilibration time, both the diffusing and adsorbed species were reduced by means of a square wave (SW) voltammetry scan using the following waveform: frequency: 50 Hz, step potential: 0.0015 V, amplitude: 0.050 V.

Transmission electron microscope (TEM) images were obtained at 200 kV using a JEOL-2100 microscope. Samples were deposited on a carbon grid, after dispersing the active layer of sparked-BiSPEs in ethanol.

2.3. Modification of the electrode surface

The modification of graphite screen-printed electrodes was conducted with an in-house built power supply at 1.2 kV DC by applying a number of twenty electric discharge (sparking) cycles, under atmospheric conditions. Sparking cycles, evenly distributed over the surface of SPEs, were implemented by bringing into close proximity a bismuth wire, connected to the positive pole of the power supply, and the substrate (graphite screen-printed electrode) connected to the negative pole of the power supply. Details on the development of sparked-BiSPEs as well as the effect of the sparking polarity on the morphological characteristics of the sensing surfaces, the size of the bismuth oxide nanoparticles and the bismuth loading are given in an earlier work [19]. For comparison studies, electroplated bismuth SPEs were prepared by electrolysis of an acetate buffer solution (pH 4.5) containing 20 mg L⁻¹ Bi(III) at -1.2 V for 180 s under stirring [22].

3. Results and Discussion

3.1. Electrocatalytic performance

At the offset, bare and sparked-BiSPEs were examined in their efficiency to probe the electro reduction of riboflavin by performing comparative cyclic voltammetry experiments in three different electrolytes. All measurements were performed in non-deoxyganated solutions and after the cathodic polarization of the sparked-BiSPEs at -1.6 V for 5 min, which aimed to produce bismuth nanoparticles at their surface by the reduction of bismuth oxide formed by sparking process [19]. Based on a previous research, which has shown that certain electrochemical treatments might alter the electrochemical behavior, or even to endow chemical sensor properties at graphite SPEs [23], the CV behavior of sparked-BiSPEs was compared with that of both electrochemical treated (-1.6V for 5 min) (Fig. 1) and untreated (Fig. S1) bare graphite screen-printed electrodes. Eventually, both types of bare electrodes exhibited almost identical CV patterns.

CVs illustrated in Figs. 1A-C show that the unmodified screenprinted electrodes (scans a, black lines) serve as suitable electrocatalytic surfaces for the electro reduction of riboflavin possessing well-defined peaks at -0.262 V (Fig. 1A), -0.451 V (Fig. 1B) and a broad peak centered at -0.386 V (Fig. 1C) in acetate, ammonia and phosphate buffer solutions, respectively. Most importantly, these peaks are considerably higher at the CVs obtained by sparked-BiSPEs (scans b, red lines) indicating that the as-formed bismuth nanoparticles [19] exhibit an enhanced electrocatalytic activity to the riboflavin reduction. Other peaks appeared during the cathodic scan attributed to the reduction of bismuth species produced during the anodic scan (for comparison the CVs obtained with sparked-bismuth graphite screen-printed electrodes in the absence of riboflavin in each electrolyte are illustrated with dashed lines) and to the reduction of dissolved oxygen. During the anodic scan, the first peak corresponds to the oxidation of riboflavin while the second peak is assigned to the stripping of bismuth ions according to previous studies [19] and the control CVs (dashed lines) in each electrolyte. In ammonia buffer, Fig. 1C, the double peak can be attributed to the stepwise oxidation (reduced hydroquinone à semiquinone à oxidized quinone) of the isoalloxazine ring in the molecule of riboflavin [24].

The efficiency of sparked-BiSPEs to probe the electro reduction of riboflavin was also investigated by performing SW voltammetry Download English Version:

https://daneshyari.com/en/article/6611918

Download Persian Version:

https://daneshyari.com/article/6611918

Daneshyari.com