Trends in Analytical Chemistry 77 (2016) 203–213

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

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

Antimony- based electrodes for analytical determinations

Núria Serrano, José Manuel Díaz-Cruz, Cristina Ariño, Miquel Esteban *

Departament de Química Analítica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain

ARTICLE INFO

Keywords:
Analytical determination
Antimony film, Antimony-coating method
Antimony modified glassy carbon electrode (SbGCE)
Antimony modified carbon paste electrode (SbCPE)
Antimony modified screen-printed electrode (SbSPE)
Environment-friendly sensor

ABSTRACT

This review summarizes analytical determinations carried out using antimony film electrodes (SbFEs), an environmentally safe option that constitutes an alternative not only to the most conventional Hg-based electrodes but also to Bi-based electrodes. SbFEs offer some interesting characteristics such as favorably negative overvoltage of hydrogen evolution, wide operational potential window, convenient operation in acidic solutions of pH 2 or lower and a very small Sb stripping signal. The substrate on which the Sb was plated is used to classify the types of SbFEs. Moreover, we detail the method of coating the substrate with Sb as well as the Sb modifiers. We present tables with the most important information from the accessible literature.

Contents

1. Introduction

Stripping techniques are particularly suitable for trace and species analysis due to their high sensitivity and selectivity, their capacity to multielement determination and their simple but complete instrumentation and their relative low cost, being particularly suitable for the determination of trace heavy metal ions in environmental samples [1]. The performance of the stripping techniques is strongly influenced by the working electrode material. Mercury-based electrodes have been extensively used not only for inorganic compounds determination, such as for heavy metal analysis, but also for the determination of many organic compounds, since they are very reproducible and have a wide cathodic window [2]. However, in the last years the potential toxicity of mercury vapors and mercury salts, and the European Regulations on banning exports and safe storage of metallic mercury have led to the development of alternative electrodes that exhibit an analogous electrochemical behavior but lower toxicity. In 2000 bismuth film electrodes (BiFE) were introduced by Wang et al. as substitutes of mercury electrodes demonstrating their applicability for heavy metals analysis [3]. Since their presentation, bismuth-based electrodes became a valuable, attractive and widely used alternative to common mercury-based electrodes for electroanalytical purposes being environment friendly and offering the features closest to those of mercury [4–6]. With the aim of developing new electrode materials, in 2007 Hocevar and coworkers introduced the antimony film electrodes (SbFEs) for the determination of metal ions. SbFEs feature some interesting characteristics such as favorably negative overvoltage of hydrogen evolution, wide operational potential window, convenient operation in acidic solutions of pH 2 or lower (which is superior to that reported for BiFEs) and a very small stripping signal for antimony itself under some conditions [7,8]. Moreover, although antimony does not belong to the group of "green elements", its toxicity is markedly lower than that of mercury.

As in the case of Bi electrodes and among other considerations, two important aspects have to be taken into account in the

* Corresponding author. Tel.: 0034934039117; Fax: 0034934021233.
E-mail address: miquelestebanc@ub.edu (M. Esteban).

http://dx.doi.org/10.1016/j.trac.2016.01.011
0165-9936/

preparation of a Sb electrode: i) The substrate on which the Sb will be plated; and ii) the selected antimony-coating method.

Sb can be plated on different supports being the carbon substrate in its diverse forms (carbon paste, glassy carbon, screen-printed carbon ink . . .) the most important support for the preparation of the Sb film, revealing a clear advantage over the metal electrode materials [9], although gold and platinum disk electrode as well as boron doped diamond (BDD) were also used.

Regarding on Sb-coating methods, they are similar to those used for the preparation of BiFEs [10]: (i) *In-situ* plating method: the electrode is immersed directly into the sample solution containing Sb(III) ions and antimony is electrochemically deposited on the electrode surface during the analysis; (ii) *ex-situ* plating or preplated method: the electrode is immersed into a Sb(III) solution and, after the application of an appropriate potential, Sb(III) ions are reduced to metallic Sb and electroplated on the electrode surface; later, the SbFE is rinsed carefully with ultra-pure water and then immersed into the sample solution; (iii) the "bulk" method: the modification with Sb takes place during the preparation of the electrode and involves the preparation of a mixture of carbon paste and antimony precursor (Sb_2O_3); Sb precursor is later electrochemically reduced to metallic Sb at a selected potential; and (iv) the sputtering method: the thin film of antimony is obtained by the antimony sputtering on a silicon substrate.

Fig. 1 shows the SEM images of a bare (commercial) screen-printed carbon electrode (SPCE), as an example of carbon support for the preparation of the Sb electrodes, and different antimony-coated screen-printed electrodes (SbSPE). The scanning electron micrograph of the bare SPCE (Fig. 1A) shows a uniform carbon surface compared to the other SbSPE surfaces (Fig. 1B–D). The SEM image of an *in-situ* SbSPCE (Fig. 1B) shows that its surface is different from that of the *ex-situ* SbSPCE (Fig. 1C), in which the Sb particles are bigger, brighter and more randomly dispersed than those observed on the *in-situ* approach. The surface morphology of $Sb_{sputtered}$SPE (Fig. 1D) was the most different from the rest of SbSPE. The main differences are that the substrate of this electrode is ceramic instead of carbon and that the Sb was sputtered directly on it, showing Sb particles of different sizes which are bigger and more compact than those observed on the *ex-situ* SbSPCE.

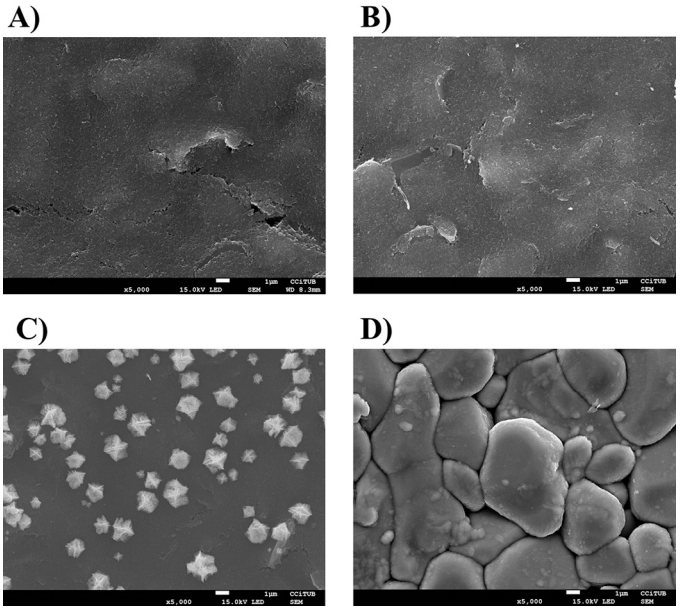

Fig. 1. Scanning electron micrographs: (A) Commercial screen-printed carbon electrode (SPCE); (B) antimony film coated *in-situ* on a commercial SPCE; (C) antimony film coated *ex-situ* on a commercial SPCE; (D) commercial antimony sputtered screen-printed electrode. Resolution of 1 μm, magnification of 5,000× and accelerating potential of 15.0 kV were used. Reproduced with permission from [10].

The possibility of preparation of Sb electrodes in a great variety of supports and suitable substrate electrodes combined with the different methods for coating the substrate with Sb significantly extends the scope and applicability of the antimony-based electrodes to different environmental challenges.

2. Antimony film electrodes

Despite both the quantity of substrates available and the different coating methods, in most cases the antimony film is plated on a carbon substrate via *in-situ* or *ex-situ* leading to an antimony working electrode that is placed in a typical electrochemical cell together with a platinum counter electrode and a conventional silver / silver chloride reference electrode. Particularly, the screen-printed electrode approach usually integrates in a same strip a carbon working electrode, whose surface is modified with antimony, a carbon counter electrode, and a silver or silver / silver chloride reference electrode. However, the antimony screen-printed working electrode can also be placed in a conventional electrochemical cell.

For this review, SbFEs were categorized in four groups in agreement with the substrate on which the Sb was plated. Moreover, the method of coating the substrate with Sb and the Sb modifiers were also itemized.

The four considered categories are:

(1) Antimony modified glassy carbon electrode (SbGCE)
(2) Antimony modified carbon paste electrode (SbCPE)
(3) Antimony modified screen-printed electrode (SbSPE)
(4) Miscellaneous

2.1. Antimony modified glassy carbon electrode (SbGCE)

A major part of the investigations related to the applicability of a SbFE was performed using the glassy carbon electrode (GCE) as a substrate for the antimony film. The significant applications of antimony modified glassy carbon electrode (SbGCE) are reported in Table 1. As it can be seen, in a significant percentage of the studies the antimony was coated on the glassy carbon substrate by means of the *in-situ* approach. Prior to the formation of the Sb film via *in-situ*, the GCE should be polished using a suspension of alumina particles of 50–300 nm diameter rinsed with purified water and methanol or ethanol for 5 min in an ultrasonic bath, and dried. In stripping measurements with *in-situ* SbGCE, Sb(III) ions are directly added into the sample solution containing usually hydrochloric acid (pH 2.0), in the concentration range 0.3–2 ppm being 1 ppm the most common, and Sb is codeposited onto the bare glassy carbon electrode together with the target metal /metals [7,9,12,13,15–17,23,24,30,31]. The potential and the time of deposition are defined by the own analytical determination. Most of the authors, before each stripping measurement, perform a cleaning step by keeping the working electrode at usually 0.3 V during 30 s. In other cases, a (1–5%) Nafion solution [14,28] was placed on the surface of the GCE prior to the modification with Sb, or the Sb was plated on a GCE through the poly p-aminobenzene sulfonic acid poly (p-ABSA) film [20] resulting in the formation of the NSbFE and Sb/poly(p-ABSA)FE, respectively. In other studies the addition of tartrate to the measurement solution is also considered, on the one hand a saturated solution of hydrogen potassium tartrate (pH 3.6) is used as a complexing supporting electrolyte [19] to prevent the precipitation of SbOCl that may otherwise occur in diluted hydrochloric acid media [32]. On the other hand, in mildly alkaline solution (pH 9.0), potassium sodium tartrate is added to stabilize the Sb(III) [22]. The main use of the *in-situ* SbGCE is the determination of heavy metals, especially Pb(II), Cd(II) and Zn(II), in water samples,