



Electrocatalytic oxidation and flow detection analysis of semicarbazide at based IrO_x chemically modified electrodes



Innocenzo G. Casella*, Michela Contursi

Dipartimento di Scienze dell'Università degli Studi della Basilicata, Via dell'Ateneo Lucano 10, 85100 Potenza, Italy

ARTICLE INFO

Article history:

Received 23 July 2014

Received in revised form 14 October 2014

Accepted 13 November 2014

Available online 21 November 2014

Keywords:

Iridium oxide

Modified electrode

Amperometry

Semicarbazide

ABSTRACT

An IrO_x modified electrode was characterized and proposed as an amperometric sensor for the detection of semicarbazide using cyclic voltammetry, chronoamperometry and amperometry techniques. The modified electrode was characterized as sensing probe in both acid and alkaline medium toward the electrocatalytic oxidation and detection of semicarbazide. A liquid chromatography approach based on the strong cation exchange mode (LC-SCX column) was used in acid conditions for the separation and analysis of semicarbazide in a synthetic mixture. Operating under a constant applied potential of 1.1 V vs. Ag/AgCl and using HClO₄ as carrier electrolyte, the limit of detection (LOD) is attested at level of 0.1 μM (i.e., 7.5 μg L⁻¹), while an excellent precision and temporal stability of the amperometric signal, was observed. The linear ranges spanning over three order of magnitude of the detection limit with a correlation coefficients higher than 0.995.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Iridium oxide films have been a subject of considerable research interest due to potential applications in many fields, from basic science to industry contexts, such as: pH sensors in highly aggressive media and/or temperature [1–4], electrochromic devices [5,6], electroodic substrates for neural stimulation or material for cardiovascular applications [7–9]. The excellent biocompatibility and good electrical conductivity, coupled to corrosion resistance and chemical stability in both acidic and alkaline medium, makes these oxide materials (IrO_x) particularly attractive and interesting for biotechnological applications. In addition, iridium oxides exhibit interesting electrocatalytic activity for the reduction or oxidation of various electroactive molecules in a wide range of pH and experimental conditions [10–12]. As consequence, IrO_x and/or its based modified surface electrodes have been studied and characterized as sensing probes for amperometric detection of several electroactive molecules [13–16].

Numerous methods have been devoted for IrO_x preparation, including thermal salt decomposition, reactive sputtering, pulsed laser ablation and electrochemical deposition techniques. Among these methods, electrochemical techniques are very attractive, because they do not require severe experimental conditions (i.e., temperature, etc.) or expensive apparatus; they are also

compatible with a wide range of substrate materials, favoring the formation of high effective surface areas and defined morphology of the deposit. As consequence, electrochemical technique for the deposition processes of metal oxides, and/or its alloys, are widely studied in order to obtain new materials with specific physical, chemical and/or morphological properties. Thin films of electrodeposited metal oxides with defined composition, morphology and mechanical properties can be easily prepared by modulating experimental deposition conditions such as: potentials, current density, temperature, supported electrode materials, composition (i.e., presence of additives and their concentration, etc.) and pH of the electrolyte bath, time of the electrolysis. Thus, electrochemical techniques for the deposition process of IrO_x species are proposed in order to obtain new iridium-based materials with specific physical, chemical and/or morphological properties [2–4,7,14,16–20]. The use of such materials can be particularly suited to electroanalytical applications in the areas of the biology, foods, pharmaceutical and environmental contexts.

Semicarbazide (SEM, H₂NNHCONH₂) has been demonstrated as a stable metabolite of nitrofurazone in animal tissues and has been used as a marker residues for the illegal use of this drug in animal food production [21]. Moreover, the deliberate adulteration of milk with SEM as high nitrogen source, creates problems in food safety or ethical and legal implications [22]. In addition, it has been shown that SEM in foods may originate from other sources including environmental and those associated with food processing and packaging materials derived from industrial processes associated to azodicarbonamide treatment. Thus, sensitive,

* Corresponding author. Tel.: +39 971 202399.

E-mail address: innocenzo.casella@unibas.it (I.G. Casella).

selective, robust and inexpensive analytical methodologies for the routine determination of this molecule, are needed. Several analytical methods based on liquid chromatography coupled with mass spectrometry detection have been proposed for the determination of SEM in various real contexts [21–27]. Nevertheless, studies regarding detection schemes characterized by simplicity in the use, non-derivatization procedures, low cost, and good level of sensitivity should be particularly encouraged. Thus, electrochemical detection strategies based on the direct SEM electrooxidation process that does not require complex procedures of sample treatment or expensive instrumentation, when available, can be proposed in analytical context. In this respect, there are few reports regarding the voltammetric behavior of SEM in HClO_4 employing a Pt (100) working electrode [28] or using graphene modified electrode in acetate buffer solution [29]. The present study describes the electrochemical preparation of an IrO_x modified electrode and its characterization as sensing probe for the amperometric detection of semicarbazide in acid and alkaline medium. A glassy carbon electrode substrate modified by anodic deposition of IrO_x deposit (GC/IrO_x), was characterized by cyclic voltammetry and chronoamperometry toward the electrooxidation of SEM. In addition, flow injection analysis (FIA) and liquid chromatography were used to characterize the sensor under constant applied potentials (DC) for the determination of SEM. To the best of our knowledge, this study reports the first example regarding the use of IrO_x modified electrode as amperometric sensor for the electrooxidation and detection of SEM.

2. Experimental procedures

2.1. Chemicals

All chemicals were of analytical-reagent grade and were purchased from Sigma–Aldrich (Steinheim, Germany). The chemicals were used without further purification and solutions were prepared by using ultrapure water supplied by a Milli-Q RG unit from Millipore (Bedford, MA, USA). The working solutions were prepared fresh each day.

2.2. Apparatus

Voltammetric experiments were performed with an Autolab PGSTAT 30 Potentiostat/Galvanostat (Eco Chemie, Utrecht, The Netherlands) and data were acquired using an Autolab GPES software package version 4.9. A three-electrode cell consisting of a working glassy carbon electrode modified superficially with electrodeposited IrO_x defined GC/IrO_x , a SCE reference electrode and a counter Pt electrode. All used electrodes and electrochemical cell were purchased from Amel (Italy).

Amperometric measurements in flowing streams were performed by using a PAR Model 400 Electrochemical Detector and a flow-through thin-layer electrochemical cell consisting of the GC/IrO_x as working electrode, an Ag/AgCl (4 M KCl) reference electrode and a stainless steel counter electrode. Experiments were performed using a metal free pump Mod. PU-1580i (Jasco Corporation, Tokyo, Japan) equipped with a rotary injection valve Mod. 7125i (Rheodyne, Cotati, CA, USA) with a 20 μL sample loop.

Chromatographic separation of SEM was achieved with a cation exchange Supelcosil LC-SCX column, 5 μm 250 mm \times 4.6 mm (Supelco, Bellefonte, PA, USA). A personal computer equipped with an in-house software allowed acquisition and processing of chromatograms.

The mobile phase was protected from oxygen and other gaseous dissolved species by an on-line degasser system (Waters In-Line Degasser).

2.3. Electrode preparation

Prior to each electrode preparation, traces of iridium oxide were removed from the electrode by polished the surface with 0.05 μm α -alumina powder on a polishing micro-cloth and washed with HCl (15%) and finally with ultrapure water. The composition of the deposition solution was 55 mM NaOH containing 6 mM IrCl_6^{3-} and 20 mM Cl^- . The resulting solution was allowed to stabilize over one week at room temperature. During this aging time, the solution changed from pale yellow to pale green and finally became blue. The deposition solution, was stored in a transparent borosilicate bottle at room temperature and the same solution had been used up to 3–4 months after its preparation. The GC/IrO_x was obtained electrochemically by voltage cycling (100 mV s^{-1}) between -0.7 V and 1.0 V vs. SCE for 50 cycles.

The resulting modified electrode GC/IrO_x was rinsed with pure water and transferred to an electrochemical cell for the electrochemical or amperometric measurements in FIA and chromatographic contexts.

3. Results and discussion

3.1. Electrodeposition of IrO_x active film and voltammetric measurements

The IrO_x film is deposited on glassy carbon electrode surface from aged blue alkaline 55 mM NaOH solution containing 6 mM IrCl_6^{3-} and 20 mM Cl^- by voltage cycling (100 mV s^{-1}) between -0.7 V and 1 V (SCE) for 50 cycles. A typical example of growth of iridium oxide particles on the glassy carbon electrode surface is shown in Fig. 1. According to the conducting character of the IrO_x deposited, two complexes cathodic waves comprised between -0.6 V and 0.75 V vs. SCE, grow with the scans as new iridium species are electrodeposited. Under these conditions, after 40–50 cycles of potentials a uniform and adherent bluish film is observed on the electrode surface. The average thickness of the IrO_x deposit obtained in this study is approximately comprised between 50 nm and 80 nm, considering a surface density of $7.8 \times 10^{-7} \text{ mol cm}^{-2} \mu\text{m}^{-1}$ [17,30]. It is interesting to observe that, electrodeposited films of IrO_x can be also obtained under anodic potentiostatic conditions at an applied potential of 1.0 V (SCE) for 10–15 min. In fact, the electrodeposition process carried

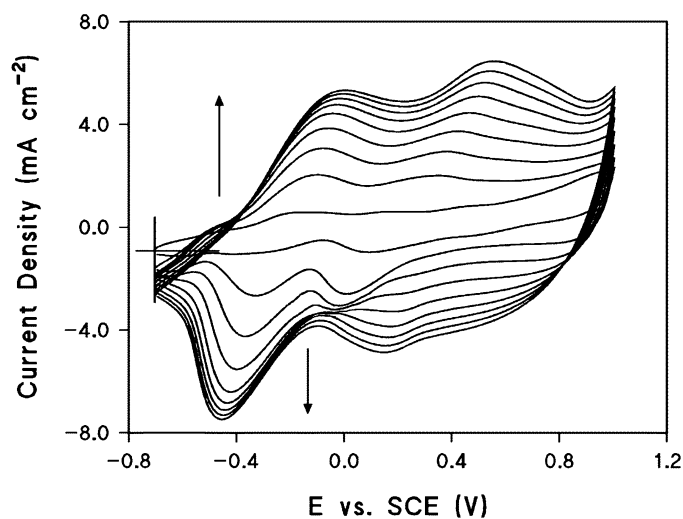


Fig. 1. Consecutive cyclic voltammograms of IrO_x film growth on a glassy carbon substrate in an alkaline 55 mM NaOH solution containing 6 mM IrCl_6^{3-} and 20 mM Cl^- . Scan rate, 100 mV s^{-1} . The voltammograms refer to the 5th, 10th, 15th, 20th, 25th, 30th, 35th, 40th, and 45th cycle of the potential.

Download English Version:

<https://daneshyari.com/en/article/7146008>

Download Persian Version:

<https://daneshyari.com/article/7146008>

[Daneshyari.com](https://daneshyari.com)