Research Paper

Electrochemical sensing of copper employing tellurium film electrode

Andrzej Bobrowski[*], Agnieszka Królicka, Julia Śliwa, Jerzy Zarębski

Department of Building Materials Technology, Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow, Poland

A B S T R A C T

An ASV procedure featuring a new tellurium film electrode deposited *in-situ* on a glassy carbon substrate in 0.1 M HCl is presented. The electrochemical behavior of the tellurium film electrode with regard to its applicability in the ASV determination of copper(II) was thoroughly studied and discussed. It was found that during the accumulation step in 0.1 M HCl, Cu(II) is co-deposited with tellurium at -0.5 V in the form of a Cu-Te alloy. When SW-ASV is used, Cu(II) accumulated *in-situ* with Te(IV) on the GC electrode yields a stripping peak at a potential ca. 240 mV more positive than that obtained at a bare GC; this peak is also 3.65 times higher. The key parameter that determines the performance of the TeF/GC electrode in the ASV determination of Cu(II) is the concentration of Te(IV) present in the supporting electrolyte. For higher concentrations of Cu(II) in the range from 25 to 125 μg L^{-1} and a time of accumulation equal to 60 s, the Te(IV) concentration of 150 μg L^{-1} is recommended. In the Cu(II) concentration range from 0.5 to 25 μg L^{-1} and a longer accumulation time of 300 s, 50 μg L^{-1} of Te(IV) is optimal. These conditions allow a relatively positive potential window to be applied and, consequently, make the TeF/GC electrode a viable alternative to the BiFE and SbFE in the determination of Cu(II) traces via anodic stripping voltammetry. The application of the tellurium film electrode under the optimized conditions (supporting electrolyte containing 0.1 M HCl and 50 μg L^{-1} Te(IV), 300 s of accumulation at -0.5 V, square wave voltammetric mode) assures a sensitive stripping voltammetric response for Cu within the concentration range of 0.5 to 25 μg L^{-1}, good precision (RSD = 4%), and a low detection limit (0.18 μg L^{-1} Cu). Possible interferences from the co-existing ions and surface-active substance were investigated. The proposed method of copper determination was successfully applied and validated with the use of mineral water sample.

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1. Introduction

Stripping voltammetry (ASV) is a well-known electrochemical technique used for the quantification of selected metals at the hanging mercury drop or mercury film electrodes [1,2], which remain the best voltammetric sensors in terms of sensitivity and reproducibility. Unfortunately, their main drawback is the toxicity of mercury vapour and the relatively complex maintenance and handling of the mercury system.

Although the application of amalgam electrodes [3–6] reduced or even entirely neutralized the toxicity of mercury, the use of mercury alloys or salts in chemical laboratories has been strongly restricted in some countries. The above restriction led to a search for alternative electrode materials that would replace mercury. Great progress in the development of new electrodes was achieved

when Wang's team introduced the bismuth film electrode (BiFE) to electrochemical practice [7]. The BiFEs have found widespread application in the determination of several metals (Cd, Pb, Tl, In, Zn, Ni, Co) and organic substances by means of anodic and adsorptive stripping voltammetry [8–11]. At a later point, some other metals, such as Sb [12–14], Sn [15,16] and Pb [17–20], were proposed as film-forming materials to be used in stripping voltammetry. According to the reported results, solid metallic film electrodes performed well in many of the applications that mercury electrodes have traditionally been employed for. The most frequently highlighted advantages of film electrodes are their ability to provide well-defined and well-separated stripping signals, a wide cathodic potential range, and insensitivity to dissolved oxygen. However, they do have a considerable disadvantage. Namely, the accessible potential windows of the majority of modern metal film electrodes are limited from the positive side, due to the oxidation of the metal-forming film.

Therefore, some metals accumulated during ASV determination (e.g. Cu or Hg) are oxidized at more positive potentials than metals

* Corresponding author.
E-mail addresses: abobrow@agh.edu.pl, gcbobrow@cyf-kr.edu.pl (A. Bobrowski).

forming films, such as Bi or Sb. Nevertheless, some attempts to quantify Cu at the SbFE [21–28] or even BiFE [29–33] were also undertaken. To overcome this problem, a selenium film electrode was applied by Nagaosa [34] to determine Cu, which dissolves at a more negative potential than selenium film.

The electrochemical properties of tellurium are similar to those of selenium. It is oxidized in acidic media at positive potentials. Hence, the in-situ generation of a tellurium film may also make the quantification of copper ions possible.

Due to its photoelectric properties, elemental tellurium and its compounds are widely employed in semiconductors and electronics [35]. The element is also used to improve the properties of some alloys. The thin tellurium layers manufactured on an industrial scale are deposited mainly by physical and chemical vapor deposition methods, but electrochemically plated layers have also become increasingly important lately [36,37]. The electrochemical behaviour of tellurium and its compounds has been investigated for many years now [38]. The electrochemistry of tellurium is very complex and pH dependent [39–43]. Because of the low solubility of Te(IV) in a neutral solution, most reported experiments were conducted in very acidic solutions. In acidic media Te(IV) occurs as the $HTeO_2^+$ ion, while for alkaline media the TeO_3^{2-} form is predominant. Generally, both $HTeO_2^+$ and TeO_3^{2-} ions can be electrochemically reduced to $Te_{(s)}$ and eventually to Te^{-2}, but the reaction pathways and intermediate steps are different [38].

Tellurium is rarely used as a sensing layer material in voltammetry [44–47]. In reference [44], the authors observed that Pb and Cd signals benefited from the presence of a high Te(IV) concentration (1.2 $mg L^{-1}$) in the supporting electrolyte. The authors attributed the amplification of Cd and Pb signals to the deposition of a tellurium film, but no definitive evidence of film formation was provided, which is especially important if it is considered that the potentials applied for film deposition (i.e. −1.2 V or −1.3 V) were typical of H_2Te evolution and not Te(0) deposition. Moreover, the authors of the above-cited paper did not precisely define the pH of the standard solution of tellurium and the final pH of the investigated solution, which may have a decisive effect on the electrochemical behaviour of Te(IV).

The aim of the presented paper was to generate tellurium film electrode in-situ on a glassy carbon support (TeFE-GC) and to evaluate its performance in the quantification of Cu, which is oxidized in a range of relatively positive potentials. The study focuses predominantly on the determination of Cu(II) at the TeFE-GC; however, the electrochemistry of the Cu-Te pair has been also investigated.

2. Experimental

2.1. Apparatus

Electrochemical measurements were performed using an Autolab PGSTAT20 potentiostat (EcoChemie, The Netherlands) controlled by GPES 4.9 software, with a standard three-electrode configuration. The working electrode used in all experiments was tellurium film electrode plated in-situ at a glassy carbon substrate. A coil of platinum wire (wire diameter 0.5 mm) served as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. Glassy carbon (GC) electrode (diameter 3 mm, Mineral, Poland), was polished before measurement by 0.3 μm and 0.05 μm alumina slurry on a polishing pad and rinsed with water before use. Photolysis was performed using a UV digestion system with a 150 W lamp (Mineral, Poland).

The morphology of the deposits was evaluated using a Nova NanoSEM 200 (FEI, USA) scanning electron microscope (SEM).

2.2. Reagents

All solutions were prepared using deionized water with a resistivity of 18.2 MΩ (Millipore, Simplicity UV). Standard solution containing Te(IV) at a concentration of 1 $g L^{-1}$ was prepared by dissolution of 0.1 g Te in the mixture of 2 mL concentrated HNO_3 and 2 mL of water. The solution was then evaporated to dryness, the residue was dissolved by an addition of 2 mL 1 M KOH and made up to 100 mL. The standard solution of 1 $g L^{-1}$ was kept in the refrigerator. Standard solutions of other elements at a concentration of 1 $g L^{-1}$ were obtained from Merck and diluted as required. Suprapur grade reagents were used to prepare supporting electrolytes. Purging solutions with argon was used to remove oxygen.

2.3. Procedure

Prior to the experiments, the polished GC electrode was preconditioned electrochemically in 0.1 M HCl by applying 5 cycles of potential scans run in the positive direction from −1.0 V to 0.5 V with a scan rate of 0.5 $V s^{-1}$. After conditioning, the GC electrode was transferred to a 0.1 M HCl solution, and the latter was spiked with 50 or 150 $\mu g L^{-1}$ Te(IV). Before each deposition, the surface of the GC was cleaned by applying the potential of 0.5 V for 10 s. Immediately after cleaning, the potential was changed to −0.5 V, which was maintained for 60 s (Te(IV) solution of 150 $\mu g L^{-1}$) or 300 s (Te(IV) solution of 50 $\mu g L^{-1}$) to deposit the tellurium film and, at the same time, accumulate copper on the surface of the working electrode. Then, after a rest period of 15 s, a square wave anodic stripping voltammogram (SW-ASV) was recorded within the range of −0.5 V to 0.5 V. The parameters of the SWV mode were as follows: frequency − 150 Hz, amplitude − 50 mV, step potential − 4 mV. During cleaning and accumulation, the solution was stirred using a magnetic bar.

When performing analyses of the real mineral water sample, its aliquot was put in a voltammetric cell and acidified with Suprapur hydrochloric acid to obtain a concentration of 0.1 M. After the addition of Te(IV) at a concentration of 50 $\mu g L^{-1}$, a SW-ASV measurement was executed, as described above. To evaluate the results, an ET-AAS unit was used in the standard way.
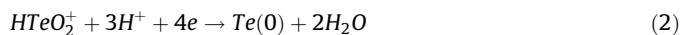
3. Results

3.1. Voltammetric behaviour of Te(IV) at the glassy carbon electrode

In solutions of hydrochloric acid, Te(IV) may be present in the form of $HTeO_2^+$ or H_2TeO_3 [48–51], as represented by the reaction:

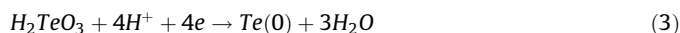$$H_2TeO_3 + H^+ \rightleftarrows HTeO_2^+ + H_2O \quad (1)$$

Fig. 1 presents the cyclic voltammograms of solution containing Te(IV) ions and 0.1 M HCl, in which two reduction peaks and one oxidation peak of Te(IV) were detected.

The cathodic CV peak observed at −0.4 V (Fig. 1, peak C1) is attributed to the following reactions:

$$HTeO_2^+ + 3H^+ + 4e \rightarrow Te(0) + 2H_2O \quad (2)$$

or

$$H_2TeO_3 + 4H^+ + 4e \rightarrow Te(0) + 3H_2O \quad (3)$$

In moderately acidic solutions containing 0.1 M HCl (Fig. 1), both forms $HTeO_2^+$ and H_2TeO_3 may co-exist in the solution, and reactions (2) and (3) may occur simultaneously.

The more negative CV peak at ca. −0.73 V (Fig. 1, peak C2) is the result of the reduction of the deposited elemental Te to hydrogen telluride:

$$Te(0) + 2H^+ + 2e \rightarrow H_2Te \quad (4)$$