

Effect of metals on silver electrodeposition Application to the detection of cisplatin

David Hernández-Santos, María Begoña González-García,
Agustín Costa-García*

*Departamento de Química Física y Analítica, Facultad de Química,
Universidad de Oviedo, 33006 Oviedo, Asturias, Spain*

Received 26 January 2004; received in revised form 3 May 2004; accepted 28 August 2004
Available online 30 November 2004

Abstract

In the present work, the influence of several metals (Co, Ru, Pd, Os, Pt, Cu, Pb), deposited on a carbon paste electrode, towards silver electrodeposition was tested. First, adequate conditions for the electrodeposition of metals on the electrode were found. Then, the cyclic voltammograms registered (silver deposition curves and analytical signals) showed that Co, Cu, Pt and Pd were able to accelerate silver electrodeposition. Finally, a valid methodology for the detection of cisplatin was established. It is based on the deposition of silver on a Pt (from cisplatin) modified electrode and the analytical signal corresponds to the anodic stripping of the deposited silver. A limit of detection of $3.2 \times 10^{-9} \text{ mol dm}^{-3}$ (1 ng cm^{-3}) cisplatin was obtained.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Cisplatin; Silver electrodeposition; Carbon paste electrodes; Cyclic voltammetry

1. Introduction

The modification of an electrode surface employing metals or metallic complexes can give rise to electrodic surfaces able to facilitate and/or accelerate electrochemical processes and also to provoke electrocatalytic reactions. These surfaces can usually be formed by means of chemical deposition of the metal or metallic complex or by means of metal electrodeposition.

Such layers can be formed by just placing a solution of the metallic complex on the surface of the electrode for a time. Cobalt metalophthalocyanines are commonly employed in this way, as they are able to catalyse electrochemical reactions. Electrodes so modified have been employed for the detection of formaldehyde [1], trichloroacetic acid [2] or hydrazine [3]. Also, osmium, rhodium and ruthenium phthalocyanines have been deposited on glassy carbon electrodes for the electrooxidation of cysteine [4].

The bulk electrodeposition of metals on the surface of electrodes can also form electrocatalytic layers. In some cases, the electrocatalytic properties do not rely on the metal itself but on derivatives such as metallic oxides. Wang et al. [5] electrodeposited Pd and Pt on a glassy carbon electrode for the electrocatalytic detection of formaldehyde, acetaldehyde and propionaldehyde in a FIA system. Casella et al. [6] employed Pd modified glassy carbon electrodes as detectors in chromatography for oxalic acid. Pt is also commonly employed for the electrocatalytic detection of different analytes [7,8].

The underpotential deposition (upd) process, discovered by Rogers et al. [9], is known as the phenomenon in which up to a monolayer of metal deposits onto a foreign metal substrate (usually the electrode) at potentials positive from the reversible Nernst potential due to distinct interaction between them. The upd of a metal can form on the electrode

* Corresponding author. Tel.: +34 985 103 488; fax: +34 985 103 125.
E-mail address: costa@fq.uniovi.es (A. Costa-García).

surface a metallic layer that shows high catalytic activity towards several electroodic processes. Thus, cyclopentanol was electrocatalytically oxidised employing Pt electrodes modified with underpotentially deposited Co, Ge and Pb [10]. Moreover, Pauling and Jüttner [11] showed that the upd co-electrodeposition of Tl and Ag modifies the catalytic properties of a gold electrode.

In our research group, carbon paste electrodes have been modified with colloidal gold by physical adsorption and has been demonstrated that it accelerates silver electrodeposition [12–14]; however, in this case the modification of the electrode was employed to detect colloidal gold and not the reagent that suffers the electrochemical reaction (silver). Colloidal gold facilitates the electrodeposition of silver because silver reduction process occurs at a less negative potential than in the absence of gold on the surface of the electrode. This fact generates a range of potentials in which silver reduction only occurs when the metal is adsorbed on the electrode; therefore, if an anodic scan is performed in 1.0 mol dm^{-3} NH_3 after silver electrodeposition at one of these potentials, an oxidation peak of silver at $+0.100 \text{ V}$ is obtained. The amount of electrodeposited silver is proportional to that of the adsorbed metal, so silver stripping allows the detection of colloidal gold.

Other strategies based on silver amplification for DNA detection (using colloidal gold) [15,16] or for conducting purposes [17] have been described.

In this work, the effect of several metals (electrodeposited on a carbon paste electrode) towards silver electrodeposition is studied. Then, cisplatin (*cis*-[Pt(NH₃)₂Cl₂]) is selected as a model metallic complex that could act as electrochemical label and that contains one of the metals able to accelerate silver electrodeposition. Thus, an adequate methodology, based on the electrodeposition of silver, is developed in order to quantify this complex.

Cisplatin has been employed as an anticancer drug since 1969, when Rosenberg et al. [18] discovered its chemotherapeutic properties. When cisplatin enters into the cells it coordinates to different molecules such as enzymes (affinity for sulphur groups), RNA or DNA, being the interaction with DNA the responsible of the therapeutic action. Cisplatin can coordinate to N7 of two neighbouring guanine and/or adenine bases, as this nitrogen does not form H bonds with other bases, in the same or in opposite DNA strands. As a consequence of the employment of cisplatin in cancer treatment, it became necessary to detect the molecule in biological samples [19–26]. The most employed technique has been HPLC coupled to different kinds of detection (electrochemical, spectrophotometric) but the electrochemical detection of cisplatin, by differential pulse polarography, without previous separation has also been described [26]. Moreover, Sadik and co-workers [27–29] have described some silver based methodologies for the electrochemical sensitive detection of cisplatin on avidin covered, silver coated (electrochemically deposited) gold electrodes modified with biotinylated double-stranded DNA.

The employment of platinum complexes as electrochemical labels in biological assays is based on the ability of square planar Pt(II) complexes with a free coordination site to bind to DNA (as previously described) or to proteins. This is commonly employed to attach markers, i.e. enzymes or fluorochromes previously coordinated to the Pt complex, to the target molecule via the proprietary Universal Linkage System (ULS™) labelling technology from Kretech Biotechnology [30].

2. Experimental

2.1. Reagents

Carbon paste was prepared by thorough mixing of 0.24 cm^3 of Uvasol paraffin oil (Merck) with 1 g of Ultra “F” purity graphite powder (Ultra Carbon). It was prepared weekly.

Water was obtained from an ultrapure Millipore Milli-Q water system.

Analytical grade (Merck) H_2SO_4 , HNO_3 , HCl , NH_3 , NaCl and AgNO_3 were used.

The following reagents were employed: $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (all of them from Fluka), OsCl_3 , $(\text{NH}_4)_2[\text{PtCl}_4]$ (both from Riedel-de Haën), $\text{Pb}(\text{NO}_3)_2$ (from Merck) and *cis*-[Pt(NH₃)₂Cl₂] “cisplatin” (from Sigma). Solutions were prepared in 0.1 mol dm^{-3} HNO_3 , excepting the $(\text{NH}_4)_2[\text{PtCl}_4]$ solutions, which were prepared in 0.1 mol dm^{-3} HCl ; solutions of cisplatin were prepared daily in NaCl 0.9% and stored at 4°C protected from light with aluminium foil.

The 0.04 mol dm^{-3} silver nitrate solutions were made daily and 0.134 cm^3 were added to a 25 cm^3 cell containing 1.0 mol dm^{-3} NH_3 to obtain a final concentration of $2 \times 10^{-4} \text{ mol dm}^{-3}$ Ag^+ for each experiment.

2.2. Apparatus

Voltammetric measurements were performed with an ECO CHEMIE μ Autolab Type II potentiostat/galvanostat coupled to a PC and controlled by Autolab GPES software version 4.6 for Windows.

The electrochemical arrangement used was a conventional three-electrode cell. A homemade carbon paste electrode with a surface diameter of 3 mm was used as the working electrode. It is made of a hollow Teflon tube in which the carbon paste is packed under pressure into a 2 mm deep well; a stainless steel rod acts as the electrical contact between the carbon paste and the potentiostat; the paste is further compacted by polishing manually on a sheet of paper. The reference electrode was an Ag/AgCl electrode; the counter electrode was a $1.5 \text{ mm} \times 1 \text{ mm}$ platinum wire. Cells were protected from light with aluminium foil when silver solutions or cisplatin solutions were employed.

Download English Version:

<https://daneshyari.com/en/article/10269547>

Download Persian Version:

<https://daneshyari.com/article/10269547>

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