Available online at www.sciencedirect.com

ScienceDirect

Electrochimica Acta 53 (2008) 2355–2361

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Phthalocyanines and porphyrins linked to gold adatoms and their catalytic property towards hydroxide oxidation

Karolien De Wael*, Annemie Adriaens

Ghent University, Department of Analytical Chemistry, Krijgslaan 281 S12, B-9000 Ghent, Belgium

Received 7 August 2007; received in revised form 21 September 2007; accepted 26 September 2007

Abstract

This paper describes the electrochemical formation and detection of gold adatoms, by recording successive cyclic voltammograms of a gold electrode in base, and their ability to function as an anchor for phthalocyanine or porphyrin adsorption. The values of the redox potential of the adatom reactions are linked to the redox potential of the adsorbed central metal ion, cobalt or copper, of the phthalocyanine or porphyrin compound. In addition, when using a phthalocyanine or porphyrin immobilized on a gold electrode, the detection of hydroxide can be improved by electrocatalysis. The catalytic current was found to vary linearly with the hydroxide concentration and a detection limit of 11×10^{-6} mol L^{-1} for a 5,10,15,20-tetrakis-(4-carboxyphenyl)-porphyrin-Co(II) modified gold electrode could be calculated.

Keywords: Electrocatalysis; Phthalocyanines; Porphyrins; Adatoms; Hydroxide

1. Introduction

The metastable state of metals is well known in metallurgy [1,2], but largely ignored in surface electrochemistry. Adatoms are so-called metastable, active (or low lattice coordination state) surface metal atoms, such as terrace, step, ledge and kink atoms [3–6]. It has been pointed out that some metals, e.g. gold [7], undergo a premonolayer oxidation in which these adatoms are oxidized at potentials well below the potential required for regular monolayer α-oxide formation. Gold adatoms give thus rise to faraday currents in the premonolayer region; they undergo oxidation to yield low-coverage hydrous oxide species that can mediate oxidation and reduction processes at the electrode surface. Therefore, these species can play an important role in electrocatalytic reactions [7–10]. Next to the classical ways to obtain a certain number of adatoms, there are several alternative procedures to gain metastable species, including gas deposition, laser treatment, ion sputtering and potential cycling [1,2]. The latter involves a surface roughening. As will be presented in this article, this roughening step is also needed to immobilize macrocyclic compounds, such as tetrapyrroles. Here, phthalocyanines and porphyrins were selected as tetrapyrroles. The former have been widely used as dyestuffs and colours. Nowadays they are also commonly used in high-tech applications, such as photovoltaic, electronic and sensing devices [11–14]. Porphyrins are widespread compounds in nature. They are important for several mechanisms in life: they catalyse enzymatic reactions and are, for instance, responsible for the oxygen transport in the human body [15]. The major characteristics of the phthalocyanine and porphyrin macrocycle are their thermal and chemical stability, coupled with their extensive redox chemistry. The aromatic ring structure can be electrochemically oxidized and/or reduced [11]. More than 70 different metal ions can form a complex by coordinating with the ring. When the central metal is a transition metal, its ion can also be electrochemically active. The immobilization of these compounds on an electrode surface can lead to modified electrodes with electrocatalytic properties. As a result, the charge transfer kinetics of the oxidation or reduction of some molecules, e.g. sodium dithionite, can be increased by modifying bare electrodes by phthalocyanines or porphyrins [16]. Electrodeposition is the method used in this study to deposit a film of phthalocyanine or porphyrin onto a gold electrode. A continuous potential cycling of the electrode between two potentials in a phthalocyanine or porphyrin solution can lead to a modification of a bare electrode in a very reproducible way [17]. By

---

* Corresponding author at: Postdoctoral Fellow of the Research Foundation, Flanders, Belgium. Tel.: +32 9 264 48 20; fax: +32 9 264 49 60.

E-mail address: Karolien.DeWael@UGent.be (K. De Wael).

0013-4686/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2007.09.049

measuring the current, it is possible to follow the adsorption process in situ.

This paper describes the electrochemical formation and detection of gold adatoms by recording successive cyclic voltammograms of a gold electrode in base and their ability to function as an anchor for phthalocyanine or porphyrin adsorption. The authors will also show that the detection of hydroxide on bare gold electrodes can be improved by electrocatalysis using a phthalocyanine or porphyrin as catalyst.

2. Experimental

A saturated calomel electrode with two compartments (SCE, Radiometer, Copenhagen) and a carbon stick were used as the reference and counter electrode. The working electrodes were gold electrodes from BAS (West Lafayette, USA) (diameter 1.6 mm) and were pretreated by mechanical and electrochemical polishing. Before its first use, the electrode surface was scoured briefly on 1200 grit SiC-emery paper to obtain a fresh surface. To smoothen this relatively rough surface, it was further subjected to sequential polishing on a polishing cloth covered with alumina (Buehler, Illinois, USA) powder of 1, 0.3 and 0.05 μm particle size for respectively 5, 10 and 20 min. To remove any adherent Al_2O_3 particles, the electrode surface was rinsed thoroughly with doubly deionised water and cleaned in an ultrasonic bath (Branson 3210) for 2 min. Finally, the electrode was pretreated electrochemically by scanning it in a Na_2HPO_4/NaOH buffer solution (pH 12, purchased from Riedel-de Haën) between −1.2 and 0.6 V versus SCE until five subsequent scans were identical. The scan rate for all cyclic voltammetric experiments was $50\,mV\,s^{-1}$. Before each experiment, pure nitrogen was bubbled through the cell solution for 20 min.

A PGSTAT20 potentiostat (ECO Chemie, The Netherlands) controlled by GPES 4.9 software package running on a Pentium II computer (Eknadata) was used to perform the potential cycling and to obtain the voltammetric data. Measurement of the pH of the solution was done using a Model 420A Orion Benchtop pH-meter. The phthalocyanine compounds, more specific 3,4′,4″,4‴Cu(II) tetrasulphonated phthalocyanine sodium salt (CuTSPc) and Co(II)tetrasulphonated phthalocyanine sodium salt (CoTSPc) were purchased respectively from Sigma Aldrich (USA) and Rhodes University of Grahamstown, Eastern Cape (South Africa). The porphyrin compounds were purchased from Porphyrin Systems (Lübeck, Germany): 5,10,15,20-tetrakis-(4-carboxyphenyl)-porphyrin-Cu(II) (CuTCPor), 5,10,15,20-tetrakis-(4-carboxyphenyl)-porphyrin-Co(II) (CoTCPor), 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin-Co(II) tetrasodium salt (CoTSPor). Sodium hydroxide (NaOH) and sodium sulphate (Na_2SO_4) were purchased from Sigma Aldrich (USA).

Electrode modification was performed by recording successive cyclic voltammetric scans (60 scans) in a potential window from −1.2 to 0.6 V versus SCE in a Na_2HPO_4/NaOH pH 12 buffer solution containing $1 \times 10^{-3}\,mol\,L^{-1}$ phthalocyanine or porphyrin. An analogous experiment was done in the same pH 12 buffer solution not containing phthalocyanine or porphyrin to investigate the formation of adatoms at a gold electrode.

3. Results and discussion

3.1. Electrochemical detection of gold adatoms

It was already suggested in the introduction that by repetitive cycling in a potential window the amount of adatoms at a gold electrode increases. To investigate this statement, a gold electrode was subjected to successive cyclic voltammetry in a pH 12 buffer solution. Fig. 1 represents a selection of the 5000 cyclic voltammetric scans recorded at a bare gold electrode from −1.2 to 0.6 V versus SCE with a scan rate of $50\,mV\,s^{-1}$. The peaks corresponding to the oxidation of the gold surface (A_a) and the reduction of the gold α-oxide formed during surface oxidation (A_c) decrease with growing scan number [7,8,18,19]. In contrast, the current of the redox couples B and C grows during the potential cycling experiment. A literature study [7–9,18,20] revealed that these pairs of peaks are attributed to gold surface reactions of so-called adatoms (Au*) and their corresponding Au(III) incipient hydrous oxides. The more reactive adatoms (those of lowest lattice coordination number) oxidize first, the less active oxidize later, at more anodic potentials. These species have unique properties as they do not belong to the crystallographic structure; they are assumed to take place mainly at different defect sites on the electrode, including steps, grain boundaries or terraces. Therefore, the reactivity of adatoms depends on its nature. It is clear that at scan 5000 the sum of the charges of all six processes equals the sum of the charges of peak A_a and A_c in scan 10. This illustrates that the redox processes B and C originate from the gold α-oxide process A. A prerequisite to observe those adatom peaks is that the potential cycling includes the α-oxide potential region, more specific 0.3–0.6 V versus SCE, in order to roughen the gold surface and create surface defects and thus adatoms which are possible ‘anchors’ for other molecules. This effect is also called the place-exchange phenomenon [20]. When the repetitive cycling is performed in the potential region from −1.2 until 0.2 V versus SCE (just before α-oxide formation), none of the adatom peaks appear.

3.2. Adatoms as anchors for phthalocyanine or porphyrin adsorption

Running through this roughening procedure (0.3–0.6 V versus SCE) is also a necessity to deposit phthalocyanines or porphyrins onto a gold electrode. As the authors have shown previously, these compounds can be immobilized onto electrodes by recording successive cyclic voltammograms in a potential window from −1.2 until 0.6 V versus SCE [16,21–25]. When the potential cycling is done in the range of −1.2 to 0.3 V or from −0.7 to 0.3 V, no adsorption of the phthalocyanine or porphyrin occurs. Fig. 2 represents this phenomenon. Curve 1 is the 10th cyclic voltammogram of a bare gold electrode in a pH 12 buffer solution. Curve 2 represents the 50th cyclic voltammogram of a gold electrode in a pH 12 buffer solution containing $1 \times 10^{-3}\,mol\,L^{-1}$ CoTCPor recorded in a potential window from −0.7 to 0.3 V versus SCE. No oxidation or reduction process occur in this potential range, which means that by excluding the α-oxide formation no deposition takes