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Fabrication and characterization of gold ultra and microelectrodes

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Abstract

Gold disk ultramicroelectrodes of 10 μm and microelectrodes of 60 μm diameter were fabricated using gold wires. These ultra and microelectrodes were characterized by electrochemical measurements and using scanning electron microscopy (SEM) for determining the real shape of the surface, and obtaining information about the quality of the seal at the electrode material-insulating material interface.
Keyword: Cyclic voltammetry; gold ultramicroelectrodes; microelectrodes; scanning electron microscopy
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Fabricación y caracterización de ultra y microelectrodos de oro

Resumen

Microelectrodos de oro de 10 y 60 μm de diametro fueron fabricados utilizando alambres de oro. Estos microelectrodos fueron caracterizados electroquimicamente y utilizando microscopía de barrido electrónico para determinar la forma real de la superficie y obtener información acerca de la calidad del sello entre la interface del metal y el material aislante utilidado en la construcción del electrodo.
Palabras claves: Voltametria cíclica; ultramicroelectrodos de oro; microelectrodos; microscopía de barrido electrónico

Introduction

Gold was selected as it is reasonably inert and allows substrates to be manipulated in air with less concern for contamination. In contact with an aqueous electrolyte, it is covered with an oxide film in a broad range of anodic potentials. On the other hands the use of gold substrates is important to the molecular self-assembly process of thiols since this kind of chemical compound produces high quality films due to the spontaneous adsorption of thiol units on its surface [1-4]. The application of highly organized organic monolayers constitutes a promising approach to electrode modification and the gold substrate seems to be the best for obtaining this goal. A series of factors must be considered when an electrode is fabricated. Parameters such as geometry, electrode material and insulating material, are the main factors that control the fabrication of these devices [5-7]. A very good geometry is required to obtain a well defined diffusion field around the electrode surface. Moreover the electrode material and the insulating material must be stable in the electrolyte media used.

Different materials have been used as insulating material around metal wires. The most common of these materials is glass. This type of material has been successfully used due to its mechanical strength, which protects fragile metal wires. Moreover, glass materials are stable in most electrolytes, which is an advantage for maintaining a very clean electrode surface. The seal between the electrode material and the glass is generally obtained by melting the glass around the electrode material. The methods for doing this depends on the melting point of the electrode material. The quality of the seals between the electrode materials and the insulating materials depends on the difference of the thermal expansion coefficient between them, which must be small or zero, so that the electrode material does not shrink away from the insulating material as the assembly cools. The formation of air bubbles around the interface, between the electrode material and the insulating material can affect the quality of the seal. For that reason, the process of sealing is

generally carried out under vacuum when glass materials are used as insulators.

Other insulating materials such as epoxy resin are formed around the electrode material without the need to use high temperatures for obtaining the seal. This type of insulating material is much softer than glass materials.

Information about the quality of the seal between the material used as electrode and the insulating material and the shape of the disk can be obtained by micrographs of the surfaces of the disk and the boundaries of the interface between the electrode material and the insulating substrate. Scanning electron microscopy (SEM) is particularly useful for mapping the morphology of the microelectrode surface. The quality of the seal may also be evaluated by capacitance measurements.

In the present work, some *in situ* methods (cyclic voltammetry and capacitance measurements) and an ex situ method (scanning electron microscopy) were utilized for the characterization of the gold disk fabricated.

Experimental

Concentrated reagent grade 70% $HClO_4$, KF, was obtained from Fluka; this chemical was used as received. A supporting electrolyte solution of $HClO_4$ was treated with purified active charcoal for gas adsorption (particle size 0.85-1.70 mm) from BDH to eliminate organic impurities, which can be adsorbed on the electrode surface. Gaseous N_2 was passed through the solution in the cell for 15 min before measurements were made.

Gold disk electrodes were fabricated with gold wires of 0.01 mm and 0.06 mm diameter, 99.99% (Goodfellow Metal). The fabrication of gold ultramicroelectrodes proved to be a difficult task. Several attempts were made using different types of glass and epoxy to obtain a good seal between the gold and the insulating material. The main difficulty for reproducing a good seal stems from the relatively large difference between the thermal expansion coefficients of the gold and glass, which produces a large gap at the gold-glass interface. A mix of soft glasses was employed to obtain a material with a thermal expansion coefficient near to that of the metal (14.2×10^{-6} m/m ^{o}C). However, this method was not successful when gold wires of 0.01 mm were used. It was found that using a composite of AralditeTM CY1301 + Hardener HY 1300 from Ciba-Geigy Plastic, very good seals between the gold and the composite could be obtained. The gold wires were cleaned chemically with 1:1 concentrated H_2SO_4/H_2O. This solution reacts violently with most organic materials and must be handled with extreme care. The wires were rinsed with ultrapure water and dried in an oven for 30 min. Each gold wire was then soldered to a nickel wire and threaded through a glass pipette until the gold projected out of the pipette tip by at least 2 mm. The composite was then added to the pipette. The epoxy was allowed to harden at room temperature for 24 hours and then in an oven at 70 ^{o}C for 5 hours. The glass tube was cut flat to obtain the gold ultramicrodisk. The ultramicroelectrode was polished with different grades of aluminum oxide sheet (lapping Film, 3M; 30 and 3 μm) and with 0,3 μm alumina Buehler), using ultrapure water as lubricant. After this cleaning procedure, they were rinsed and sonicated for a few seconds in ultrapure water to remove alumna from the electrode surface. In addition, the gold ultramicroelectrodes and gold microelectrodes were treated electrochemically by cycling between 0 and 1.45 V vs. SCE in 0.2 mol dm^{-3} $HClO_4$. The ultramicroelectrodes were rinsed with ultrapure water and transferred to the cell where the experiment was carried out, taking care to leave a drop of water on the electrode surface during the transfer.

Electrochemical experiments were carried out using a single compartment cell with a two electrodes configuration. The cell was cleaned by using a solution of H_2O/H_2SO_4 (1/1), and rinsing with ultra pure water to remove residual organic. A saturated Calomel electrode (SCE), model K4040 from Radiometer Electrodes, and a platinum quasi-reference electrode were used as reference electrodes in different experiments.

Cyclic voltammetry experiments were carried out using a waveform generator (Hitek Instruments) coupled to a current amplifier with a low pass filter (sensitivity of 0.01 μA V^{-1}), built in-house. The amplifier and the cell were placed in an earthed metal Faraday box.

The solutions were deoxygenated before each experiment and all the experiments were carried out at 20 °C.

Results and Discussion

The characterization of gold electrodes was carried out using physical and electrochemical measurements. The quality of the seal between the electrode material and the insulating material as well as the shape of the microdisk were investigated by scanning electron microscopy. Capacitance measurements were also used to check the quality of the seal and an oxygen adsorption method from acid solutions was used for determining the effective area of the electrodes.

Figure 1 shows the cyclic voltammogram recorded using a gold disk of 5 μm radius

(sealed in epoxy composite), for a blank solution of 0.2 mol dm^{-3} $HClO_4$.

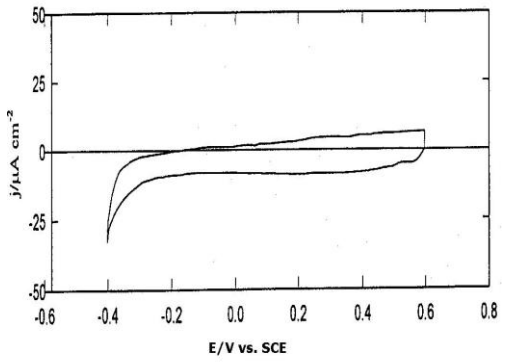

Figure 1. Cyclic voltammogram at a gold ultramicroelectrode of 5 μm radius (sealed in epoxy composite), in 0.2 mol dm^{-3} $HClO_4$; ν = 60 mV s^{-1}

The double layer capacitance was determined from the relationship:

$$C_{dl} = \frac{j_{dl}}{\upsilon} \qquad (1)$$

where j_{dl} is the current density in the double layer region. The value of about 50 μF cm^{-2} is in agreement with the values reported in the literature [8]. The values of capacitance obtained using other microelectrodes qualitatively show the quality of the seal between the gold and the glass or epoxy composite. According to these values and the shape of the voltammograms obtained, the electrodes fabricated were classified into two groups. The first group of electrodes with values of capacitance less than 70 μF cm^{-2}, exhibited very flat voltammograms. The second group, in which the values of capacitance are higher than 1 mF cm^{-2}, gave voltammograms that were tilted indicating that solution was penetrating between the gold and the glass or epoxy composite.

By using the oxygen adsorption method, it is assumed that oxygen is chemisorbed on a monoatomic layer prior to O_2 evolution with a one to one correspondence with surface metal atoms. Knowing that gold has well-developed regions for oxide monolayer formation and reduction [9], this method may be used to determine surface areas. However, the cleanliness of the surface of the ultramicrodisk and the solution must be ensured. During adsorption (positive potential sweep), the measured anodic charge may include oxidizable impurity effects and some charge associated with oxygen evolution. On the other hand, the charge measured during adsorbed oxygen reduction may correspond to multilayers (oxide film) of undefined stoichiometry.

The successful application of this method entails a careful selection of the limits of the potential range where the charge corresponding to oxidation or reduction should be determined. Different methods for cleaning the electrodes were tested and extreme care was taken when preparing the solution. The gold electrodes were repolished with 3 and 0.3 alpha alumina, followed by rinsing and sonication with ultra pure water for 1 min. Then they were electrochemically treated by cycling in acid media in the potential range where the formation of gold oxide and its reduction occur. In experiments carried out in 0.5 mol dm^{-3} H_2SO_4, the onset of the formation of gold oxide and its reduction are shifted to more positive potentials than in 0.2 mol dm^{-3} aqueous solutions of $HClO_4$. This behavior has also been reported by Kozlowska et al. [10], and it has been attributed to the sulfate ion which is adsorbed more strongly than the perchlorate ion. On the other hand, when the electrode is cycled at a high sweep rate in the potential range where the formation of gold oxide and its reduction occur, the voltammogram changes after the first cycle, and it was found that the roughness of the microsurface increases with cycling time.

Following these results, the characterization of these electrodes was performed using $HClO_4$ as supporting electrolyte because the range of potential where oxide formation and its reduction occur can be reduced, hence increased surface roughening avoided**. Figure 2** shows the voltammogram obtained at a gold ultramicroelectrode in $HClO_4$ aqueous solution. The potential scan includes the double layer region (0.1 to 1 V), as well as the region of oxide formation (1 to 1.4 V). In the double layer region, an electrode process is observed around 0.65 V. This shoulder is attributed to the adsorption of the ClO_4^- anion [10]. In the region of oxide formation, replacement of the adsorbed anions by OH^- occurs and two peaks are observed. The first peak at 1.25 V is attributed to the formation of the first sublattice of OH^- deposited in between adsorbed anions [10]:

$$\blacksquare M_x A^- \underline{M} + H_2O \rightarrow \blacksquare M_x A^- \underline{M}OH + H^+ + e^- \qquad (2)$$

The second peak at 1.35 V has been attributed to the deposition of OH^- accompanied by desorption of the anions [11]:

$$M_xA^- + H_2O \Leftrightarrow M_{x-1} + MOH + A^- + H^+ + e^- \qquad (3)$$

A peak is observed on the cathodic side of the voltammogram between 0.85 and 0.9 V, which corresponds to the reduction of adsorbed oxygen (oxide stripping).

The shape of the voltammogram is similar to that reported for polycrystalline gold [9]. The effective area of the gold ultramicroelectrode was calculated taking into account that the cathodic charge in aqueous solutions of $HClO_4$ increases almost linearly with the applied potential above 1.2 V and that this charge is independent of pH [12].

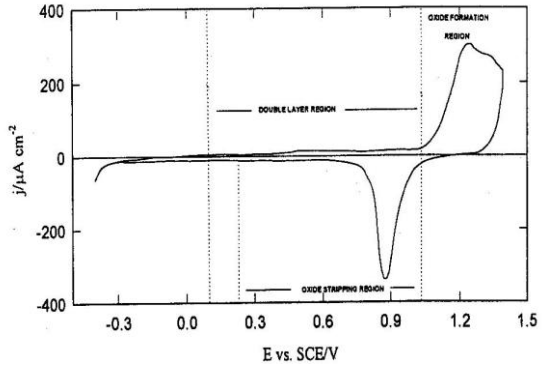

Figure 2. Cyclic voltammogram at a gold ultramicroelectrode of 5 μm radius (sealed in epoxy composite), in 0.2 mol dm^{-3} $HClO_4$; ν = 70 mV s^{-1}

The charge value (Q_B) used was taken from the curve cathodic charge vs anodization potential reported by Brummer et.al. [12]. This value and the charge obtained experimentally by integration of the oxide stripping peak (**figure 3)** were used to calculate the real area of the microdisc from the ratio:

$$A_{real} = \frac{Q_{exp}}{Q_B} \qquad (4)$$

The apparent radius was calculated by assuming that the ultramicroelectrode is an ideal disk:

$$r = \sqrt{\frac{A_{real}}{\pi}} \qquad (5)$$

For a series of experiments carried out at 60 mV s^{-1}, using gold wires of 10 μm diameter, the value of apparent radius obtained was 4.80 ± 0.13 μm. This value corresponds closely to the nominal value of 5 μm.

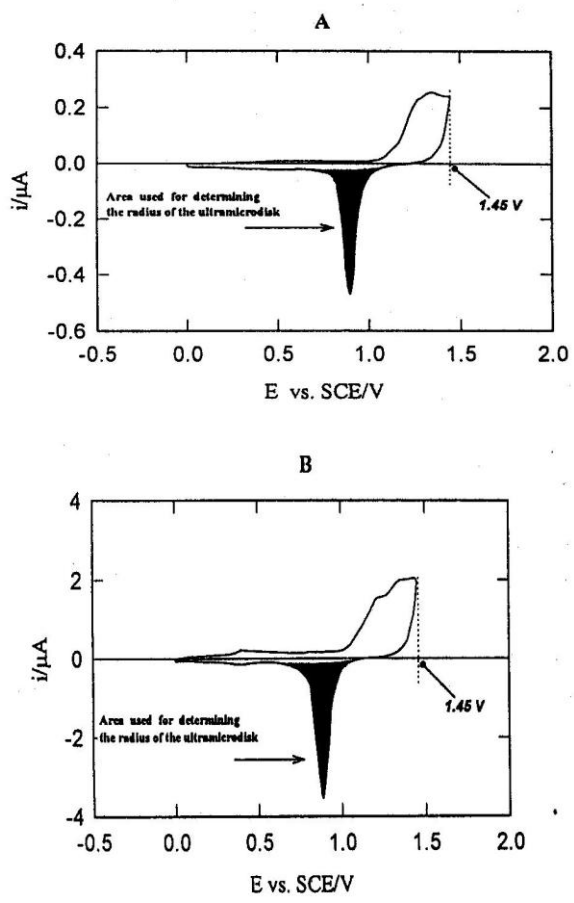

Figure 3. Cyclic voltammograms at: A) a gold ultramicroelectrode of 5 μm radius (sealed in epoxy composite); B) a gold microelectrode sealed in glass (60 μm diameter) in 0.2 mol dm^{-3} $HClO_4$; ν = 60 mV s^{-1}

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