



Gold oxide films grown in the confined aqueous layer between gold and organic solvents



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ABSTRACT

The properties of anodic passive films potentiostatically formed on polycrystalline gold in aqueous phosphate solutions were studied using voltammetry, electrochemical impedance spectroscopy, and contact angle measurements. The nature of the gold oxide layer was analyzed as a function of a potential holding in the aqueous double layer charge region at the interface between gold and the aqueous layer confined by insoluble organic solvents (hexane, chloroform, anisole, butyl acetate, xylene, and isopropyl ether). Different growth conditions change the homogeneity of the oxide layer leading to different passive properties. A synergetic effect on the gold oxidation of hydrogen dissolved in both the bulk metal and the confined aqueous layer is discussed.

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1. Introduction

Gold and gold nanoparticles are employed either as substrate or additive in electrochemical sensors in order to improve the analytical selectivity of membranes. On the other hand, drops of organic solvents immiscible in water work as template for the production of gold nanoparticles [1–5]. Besides, the contact angle (CA) of captive drops (CD) allows evaluation of the surface energy, as in the case of nanofiltration, and the development of less fouling membrane materials [6,7]. The CD technique involves placing bubbles or droplets against a solid surface where they are held captive in a cell filled with some immiscible fluid. The effect of the electrochemical potential on the surface properties of electrodes and membranes can be measured “*in situ*”. Under these conditions the complete hydration of the surface avoids hydrophobic contributions to the surface tension produced by adsorbed air or empty vacuoles [8–10].

This paper investigates the effect of the applied potential program on the structure of oxide films formed on gold using voltammetry, electrochemical impedance spectroscopy (EIS) and CA measurement. The anodization is carried out in both phosphate solutions at pH 6.7 and in the same electrode in contact with the confined water layer forms when the metal is covered by several organic immiscible solvents.

The comparison of the capacitance obtained in different growth conditions contributes to providing a deep insight into the different processes involved in the catalytic behavior of this complex interface.

2. Experimental

The experimental set-up has been described in previous works [11–13]. Polycrystalline gold rods (99.999% purity, area 0.5 cm²) were used as working electrodes. Before each experiment, the electrodes were mechanically polished to a mirror finish with alumina of 0.3 and 0.05 μm. The counter electrode was a platinum wire placed around the working electrode. A Pt/H₂ electrode coupled to a Luggin–Haber capillary tip was used as reference electrode for all potential measurements.

The experiments were performed at room temperature and under bubbling nitrogen in phosphate buffer solutions of 0.25 M K₂HPO₄ + 0.25 M KH₂PO₄ pH 6.7 with and without the addition of a drop of different insoluble organic solvent like hexane, chloroform, butyl acetate, *m*-xylene, benzene, toluene and anisole. In all the cases the electrode was horizontally dipped into the solution and covered by the drop of solvent that tends to float in the electrolyte solution. Only in the case of chloroform, due to its higher density, the electrode was placed at the bottom of the cell and then became covered by the sunken drop.

The fresh polished electrode dipped in the cell was scanned by five cycles from the potentials $E_c = 0.04$ V up to $E_a = 1.7$ V at a

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sweep rate $v = 0.1 \text{ V s}^{-1}$ followed by a holding at open circuit $E_{oc} = 0.6 \text{ V}$.

In the case of CA measurements a drop of solvent was introduced in the cell at E_{oc} using a micro syringe and the image of the bubble was registered by optical magnification. The CA was then calculated by the programme ImageJ and an appropriate subroutine plug-in [14–17]. Finally, several measurements were performed holding at different potentials in the $0.04 \text{ V} \leq E \leq 1.2 \text{ V}$ potential range for 5 min and during the growth of the gold oxide monolayer at 1.7 V.

The impedance measurements were carried out using a Zahner Im6d. EIS were started in the frequency range of $65 \text{ kHz} \leq \omega \leq 1 \text{ MHz}$ at the E_{oc} potential. After a holding of about $\tau = 20 \text{ s}$ at $E = 0.6 \text{ V}$ stationary values of the current were obtained. The EIS data and the current i were simultaneously recorded. Similar EIS data were obtained in the double layer potential region and during the growth of the gold oxide monolayer at 1.7 V, starting after a time of $\tau = 3, 10, \text{ and } 20 \text{ min}$. Two potential programs were employed. Program 1, labeled “DL holding and 1.7 V” involved successive holds of 10 min in steps of 0.1 V towards cathodic and anodic E potentials in the double layer charge region, that is, in the $0.6 \text{ V} \geq E \geq 0.04 \text{ V}$ and then in $0.6 \leq E \leq 1.2 \text{ V}$ potential regions. Next, the three successive EIS spectra at 1.7 V were taken. Program 2, labeled “OC and 1.7 V”, after measuring at $E_{oc} = 0.6 \text{ V}$, the three EIS spectra at 1.7 V were taken. Comparative measurements were made with the cycled gold electrode totally covered with a larger drop of the different organic solvents.

3. Results

3.1. Voltammetric data

Fig. 1 shows the simultaneous current, i , and the potential, E , detection during repetitive cycling at 0.1 V/s with the formation (anodic scan peak) and reduction (cathodic scan peak) of the Au_2O_3 monolayer.

When at the end of the anodic scan the potential is held at $E_a = 1.7 \text{ V}$, i decreases rapidly in the time τ from $450 \mu\text{A}$ to less than $20 \mu\text{A}$ after 20 s (see arrow). During the subsequent cathodic scan, narrower reduction peaks result with only a very small current increase after longer holding times at 1.7 V with $\tau = 2, 10$ and 20 min (dashed curves).

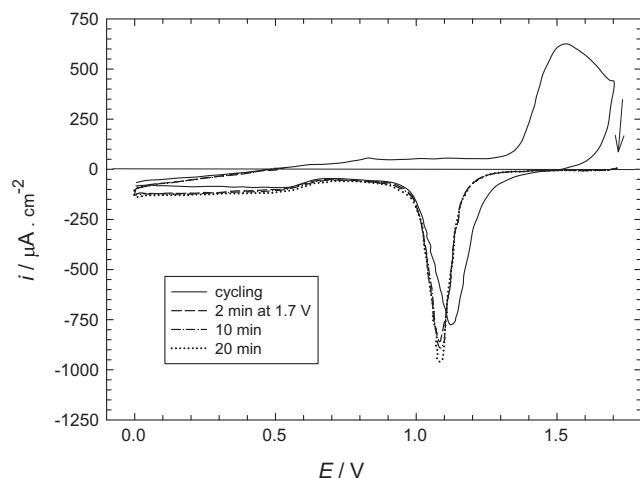


Fig. 1. Current i vs. potential E voltammograms in phosphate buffer solution obtained scanning at 100 mV/s between $E_c = 0.04 \text{ V}$ and either $E_a = 1.7 \text{ V}$. Full line show the repetitive voltammogram observed after five cycles and dotted lines show different scans after holding at $E_a = 1.7 \text{ V}$ during either $\tau = 2, 10$ or 20 min.

3.2. Contact angle measurements

Fig. 2 shows a plot of the contact angle θ vs. radius R plot of several immiscible solvents dipped in the buffer solution. The plotted radius concerns immiscible drops spontaneously detached from the micro syringe dipped in the phosphate solution. For all the solvents the angle is very high with values between 150° and 180° . In spite of the dispersion on the results, a tendency to reduce the angle with increasing radius is observed. The highest measured contact angle corresponds to the anisole and the lowest to the isopropyl ether drop.

3.3. Electrochemical impedance spectroscopy data

Fig. 3 shows the Nyquist and the Bode φ vs. ω plots of the spectra obtained on gold at $E_{oc} = 0.60 \text{ V}$ and those at 1.7 V starting after a holding time of either $\tau = 3, 10$ or 20 min. The Bode impedance diagram exhibits a capacitive semicircle (3a–c) at high frequencies followed by another incompletely defined contribution at intermediate or low frequencies ($\omega \leq 0.1 \text{ Hz}$). Previously reported EIS results on gold in 0.5 M HClO_4 show very similar diagrams [18].

For the electrode initially held at 0.6 V and then at 1.7 V the Nyquist plots show decreasing curvature and this tendency still continues for longer times τ at 1.7 V. The decrease in the curvature is stressed when the electrode remains in the potential region $0.04 \text{ V} \leq E \leq 1.2 \text{ V}$ for more than 60 min.

All the impedance experimental data can be well described by the following transfer function:

$$Z(j\omega) = R_\Omega + \frac{1}{[\text{CPE}]_1 + (R_{t1} + Z')^{-1}} \quad (1)$$

where $\omega = 2\pi f$. The high frequency limit R_Ω corresponds to the ohmic resistance of the electrolyte, whereas $[\text{CPE}]_1$ denotes the constant phase element given by $[\text{CPE}]_1 = [C_1(j\omega)^{\alpha_1}]^{-1}$, C_1 is the capacitance at high frequencies, α_1 takes into account the distribution of the time constants due to surface inhomogeneities, and R_{t1} is the charge transfer resistance probably related to proton reduction [19]. Z' is associated with a diffusion process [13].

$$Z' = Z_w = R_{DO}(jS)^{-1/2} \tanh(jS)^{-1/2} \quad (2)$$

where the diffusion resistance R_{DO} is the limit of $Z_w(j\omega)$ at $\omega \rightarrow 0$ and the parameter $S = d^2(\omega/D)$, being D the diffusion coefficient. This diffusion process probably occurs in the aqueous solution.

Non-linear least square fitting routines [20] provide good agreement between experimental results and simulated data. C_1 and R_{t1} values are determined from the optimum fit procedure in the region of high frequencies, obtaining $C_1 = 104 \pm 10 \mu\text{F cm}^{-2}$ and $\alpha_1 = 0.94 \pm 0.02$, while R_{t1} values are in the range $14,200 \leq R_{t1} \leq 78,000 \Omega \text{ cm}^{-2}$. A clear increase in R_{t1} results during the potential holding at 1.7 V. This effect is stressed when a previous holding in the double layer region is applied (Table 1).

Similar experiments are shown for the gold electrode covered with an extended drop of either hexane (Fig. 4) or chloroform (Fig. 5). For increasing holding time at 1.7 V analogous trends in R_{t1} are observed. However, a remarkable and unexpected split in the Bode plot is noticed at about 4 Hz (see arrow in Fig. 4a, b and 5a, b). This is practically unseen in the Nyquist plot, where the capacitive semicircle is only slightly distorted. In the same way, any change is noticed in the Bode modulus plot (not shown), which remains invariable in the high frequency range and independent of the application of Procedure 1 or 2.

Table 2 shows the fitted C_1 , C_2 , R_{t1} and R_{t2} values obtained in the region of high frequencies using Eq. (1) with the transfer function Z' :

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