

The Influence of Anions on the Underpotential Deposition of Copper on a Polycrystalline Gold Substrate

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Received: March 29, 1995; October 16, 1995

Neste trabalho é descrito o estudo da deposição, em regime de subtensão, de cobre sobre ouro policristalino em dois diferentes meios: 0.5 M H₂SO₄ + 1 mM CuSO₄ and 0.5 M HClO₄ + 1 mM Cu(ClO₄)₂, utilizando voltametria cíclica e espectroscopia diferencial de reflectância de UV-visível. Os experimentos de voltametria mostram diferenças significativas entre os dois sistemas, as quais podem estar associadas à adsorção mais forte do ânion sulfato com a superfície do eletrodo. Os espectros de UV-visível apresentam uma banda a $\lambda = 490$ nm para o sistema contendo perclorato e duas bandas a $\lambda = 490$ e 630-660 nm para o de sulfato. Os refletogramas mostram variações na refletividade da superfície do eletrodo para o sistema de perclorato que correspondem aos picos de corrente observados nos voltamogramas. Os resultados demonstram a conveniência de se ter somente um tipo de ânion presente na solução.

This work describes the study of underpotential deposition (UPD) of copper on polycrystalline gold in two different media, 0.5 M H₂SO₄ + 1 mM CuSO₄ and 0.5 M HClO₄ + 1 mM Cu(ClO₄)₂, using cyclic voltammetry and UV-visible differential reflectance spectroscopy techniques. The voltammetric experiments show significant differences between the two systems which may be associated with the stronger adsorption of the sulfate anion at the electrode surface. The UV-visible spectra present one band at $\lambda = 490$ nm for the perchlorate system and two bands at $\lambda = 490$ and 630-660 nm for the sulfate one. The reflectograms show that the changes in the reflectivity of the electrode surface for the perchlorate system correspond to the current peaks observed in the voltammograms. The results point to the convenience of having only one anion present in the solution.

Keywords: underpotential deposition, copper, UV-visible spectroscopy

Introduction

Underpotential deposition (UPD) is the process of the deposition of a metal on a foreign metal substrate at potentials positive to the Nernst potential for the corresponding bulk metal deposition^{1,2}. The main characteristic of this process is that the adsorbate-substrate interactions are stronger than the adsorbate-adsorbate ones, and this has a strong influence on the further growth of the deposit, as well as on the catalytic properties of the surface. Among

the metals investigated, the UPD of copper has received special attention especially in platinum substrates³⁻⁶. Previous studies presented many interesting conclusions concerning the early stages of UPD. The so-called "weakly-bonded" hydrogen adsorption is preferentially inhibited by Cu(0) with a 1:1 site relationship⁵, and close to the equilibrium potential a perfect 2-D structure is formed with the Cu atoms uniformly distributed over the Pt surface⁶. The influence of the anion on the UPD of copper on platinum was also studied in acid media containing sulfate

and chloride by cyclic voltammetry and a.c. impedance techniques⁷. In this work, the authors concluded that in hydrochloric acid solution the adsorption reaction, $\text{Cu}_{\text{ads}} \leftrightarrow \text{Cu}(\text{II}) + 2\text{e}^-$, follows the kinetic response of the diffusion-controlled specific adsorption of the reactant and that the contribution of the Warburg impedance and the adsorption capacitance are smaller than those in sulfuric acid solution.

The UPD of copper on gold has been studied in different media by various techniques⁸⁻¹². A study using polycrystalline gold in alkaline media revealed details about its effect on the oxygen reduction reaction⁸. In acidic media the UPD of copper was studied on gold single crystals by electron diffraction techniques (LEED and RHEED)^{9,10}. The main conclusion of the studies on single crystals in a solution containing $\text{HClO}_4 + \text{CuSO}_4$, using different anions for the acid and the salt, is that the UPD of Cu presents a $(\sqrt{3} \times \sqrt{3}) \text{R } 30^\circ$ super-structure and a coverage of $2/3$ of a monolayer on Au(111). It was also noted that there is a strong effect of the orientation of the single crystal surface used as a substrate on the profile of the current-potential curves¹⁰. A comparison between the cyclic voltammograms shown by Nakai *et al.*¹⁰ and those presented by Dickermann *et al.*¹¹ on Au(111) reveals some discrepancies. The differences between these two experiments are in the concentrations of the acid and the salt, so that the discrepancies can be interpreted as evidence of the influence of the nature of the anion on the UPD process. Recently, a systematic study on the coadsorption of copper with chlorine, bromine and iodine on Au(111) electrodes by STM demonstrated a strong dependence of the structure of the deposit on the size of the halogen atom¹².

One way to better understand the process of UPD is through the analysis of the competitive adsorption which occurs at the metal / solution interface. This kind of approach was used for systems presenting coadsorption of Cu^{2+} and SO_4^{2-} by applying electrochemical and spectroscopic techniques¹³⁻¹⁷. Some interesting conclusions were derived from these works, including the suggestion that the interpretation which has been made in UPD studies regarding the two-state character of Cu adsorption at the Au(111) surface may not be correct¹⁷. However, these authors¹⁷ also used a solution containing a mixture of the anions SO_4^{2-} and ClO_4^- , which may introduce competitive adsorption of the anions, and may consequently lead to erroneous interpretations.

Apart from the electrochemical and electroreflectance investigations mentioned here, to the authors' knowledge no reflectance studies in the UV-visible range have been performed on UPD processes. So, the aim of the present work is to investigate the influence of sulfate and perchlorate anions on the copper UPD process on gold by cyclic voltammetry and *in situ* UV-visible reflectance spectroscopy and also to evaluate the potentialities of this

spectroscopic technique in UPD studies. It is well known that the low index faces of gold single crystals present superficial reconstruction when the potential is made negative enough. The UPD of copper occurs in this region of negative potentials, so some contamination of the gold surface may occur by trapped copper atoms in the first layers of gold during the reconstruction. If this happens*, the single gold crystal surface will not be suitable for electrochemical studies. Thus, as a first approach and in order to assess the potentiality of the UV-visible technique, polycrystalline gold was chosen as the substrate. Furthermore, considering that one of the reasons for the problems and discrepancies observed in previous studies on this subject may be the presence of two different anions with different adsorption characteristics in the solution, the UPD of copper on polycrystalline gold was studied in solutions containing only one type of anion. The electrolytic media used in the present study contained either perchloric acid / copper perchlorate or sulfuric acid / copper sulfate.

Experimental

The electrochemical set up consisted of a Wenking MP81 potentiostat, a X-Y recorder and a three electrode / one compartment cell. A polycrystalline gold rod was prepared by melting 99.95% gold wire in a graphite crucible. One of its faces to be exposed to the electrolyte with a geometric area of 0.166 cm², was polished with emery paper (from 320 to 1500) and alumina (from 1 to 0.05 μm). Between each step of this treatment the electrode was cleaned in an ultrasonic bath, and just before the introduction of the electrode into the cell, the surface was flame treated, cooled in ultra pure water, and protected with a drop of water before the transference to the electrochemical cell. The counter electrode was a gold spiral which was flame treated before immersion in the cell. All potentials were measured in relation to a commercial mercury-mercurous sulfate electrode (MSE) joined to the main compartment of the cell by a glass bridge. The solutions, 0.5 M $\text{H}_2\text{SO}_4 + 1 \text{ mM CuSO}_4$ and 0.5 M $\text{HClO}_4 + 1 \text{ mM Cu}(\text{ClO}_4)_2$, were prepared with suprapur (Merck) acids, *p.a.* grade salts and water from a Milli-Q system (Millipore). All the experiments were performed at room temperature.

The UVDRS experiments were carried out using a Harrick RSS-C rapid scan spectrometer^{18,19}. The incident light, produced by a quartz-halogen lamp, was separated by a grate mounted on the mobile frame of a small galvanometer. All the movements of the grate were monitored by an electronic module RSS-C signal processor. The monochromatic light, which was unpolarized, was split into a reference beam and a sample beam and collected by two identical Hamamatsu R955 photomultipliers. The resulting output signals were then processed and further stored in a

* The existence of superficial contamination was observed by Dickermann *et al.*¹¹, but recently Hachiya *et al.*¹³ reported that no positive evidence for the existence of other phases had been found.

Nicolet 370 data acquisition system connected to a personal computer. The data treatment was made with the software described elsewhere¹⁸. This equipment made the acquisition of a single UV-visible spectrum possible in 10 ms. The electrochemical control of the system was made with the same potentiostat used in the voltammetric experiments, and the cell used had a cylindrical compartment with a glassy-carbon counter-electrode (diameter *ca.* 2 cm) and a MSE reference electrode. The working electrode used in the spectroscopic measurements was mounted in a syringe welded to the cell to facilitate its positioning in the cell.

Results and Discussion

Cyclic voltammetry

The initial information about the influence of the anion on the UPD of copper was obtained from purely electrochemical experiments. One aspect to be considered in this work is the comparison of the results with those previously obtained by Dickermann *et al.*¹¹ using copper perchlorate and sulfuric acid. Because of this comparison, cyclic voltammetric experiments were carried out at $20 \text{ mV}\cdot\text{s}^{-1}$, though a scan rate of $1 \text{ mV}\cdot\text{s}^{-1}$ would have been more appropriate for guaranteeing equilibrium conditions in the perchlorate system. However, a rate of $1 \text{ mV}\cdot\text{s}^{-1}$ was used here in the UV-visible experiments. The cyclic voltammograms, recorded at $20 \text{ mV}\cdot\text{s}^{-1}$, for the gold polycrystalline electrode in contact with a $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ mM CuSO}_4$ solution, are shown in Fig. 1 for different inversion potentials. In the underpotential region (between -0.1 and -0.5 V) three distinct peaks (A: -0.21 V ; B: -0.23 V ; C: $\approx -0.4 \text{ V}$) appear during the negative deposition scan, and five peaks (A': -0.2 V ; B': -0.23 V ; C': $\approx -0.28 \text{ V}$; D': -0.34 V ; E': \approx

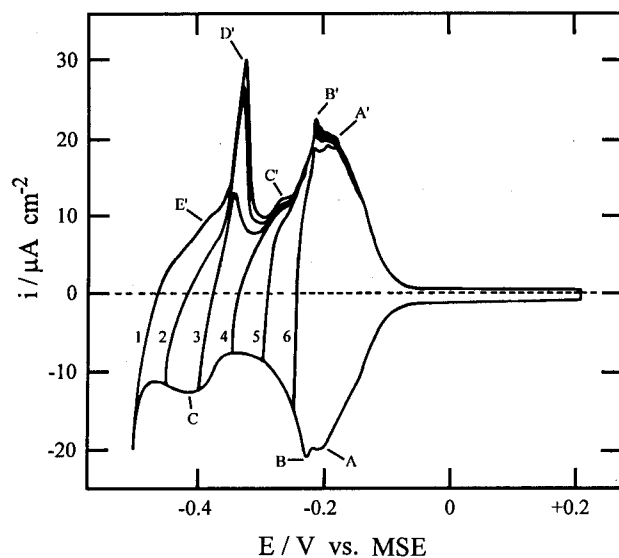


Figure 1. Cyclic voltammograms for polycrystalline gold at $20 \text{ mV}\cdot\text{s}^{-1}$ in $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ mM CuSO}_4$ for different potential ranges from $+0.2 \text{ V}$ to -0.5 V vs. MSE. to: -0.5 (1); -0.45 (2); -0.4 (3); -0.35 (4); -0.3 (5) and -0.25 (6) V vs. MSE.

-0.39 V) appear during the dissolution scan. It can be observed that peaks A and B are symmetrical to A' and B', respectively, with a peak current of *ca.* $22 \mu\text{A cm}^{-2}$. Additional experiments showed that the size of these peaks is independent of the number of cycles, and that the peak potentials are independent of the sweep rate. As expected, the peak currents are strongly dependent on the scan rate. On the other hand, when the number of cycles increases, peaks C, D' and E' increase and peak C' decreases, and their positions in the potential axis change.

Peaks A, B, A' and B' were already observed by Kolb and co-workers¹⁰ and attributed to a deposit having a strong interaction with the substrate. At more negative potentials on the basis of measured charges it was assumed that the degree of coverage (θ) of the gold surface by copper adatoms is equal to $1/2$ ¹⁰. In a preliminary analysis, peak C was associated with a deposit of copper with $\theta > 1/2$, with peaks D' and C' being the corresponding dissolution peaks. The small peak E' in Fig. 1 increases when the potential range increases to more negative values, and can be associated with deposits on the electrode surface exceeding one monolayer.

As indicated by the calculated charges, the potential of -0.48 V corresponds to $\theta = 1$, which is in agreement with previously presented results¹⁰. For potentials more negative than -0.48 V the current increases due to the bulk deposition of copper. In order to calculate the real surface area, a study of oxide formation on this electrode was performed as previously described²⁰, and a roughness factor close to 1.5 was estimated. With this information, the calculation of the charge density from Fig. 1, considering this roughness factor and correcting for the double layer charging, shows that for $\theta = 1$ the charge transferred at $E \approx -0.48 \text{ V}$ is around $207 \mu\text{C cm}^{-2}$. So, for $\theta = 1/2$ the charge at $E \approx -0.28 \text{ V}$ would be $103 \mu\text{C cm}^{-2}$. From these results it is possible to conclude that in the dissolution direction half a monolayer of copper deposited on gold from a purely sulfate medium is present at a potential corresponding exactly to the position of peak C'.

Figure 2 shows cyclic voltammograms for the same gold electrode in contact with a $0.5 \text{ M HClO}_4 + 1 \text{ mM Cu}(\text{ClO}_4)_2$ solution for different inversion potentials. Considering the potential range between $+0.5 \text{ V}$ and -0.65 V , in this system there is a broad peak in both directions (deposition and dissolution) between $+0.47$ and 0 V . In the deposition direction (negative sweep), a wide peak occurs around -0.2 V (peak A) and a small shoulder appears at *ca.* -0.45 V (peak B). On the other hand, in the dissolution direction (positive sweep), two peaks (D' and C') appear at -0.4 and -0.27 V , respectively, corresponding to the dissolution of the bulk deposit ($\theta > 1$). Using the same parameters as for the sulfate system and considering a double layer correction, it was possible to determine that peak B' corresponds to the dissolution of the first half of the monolayer

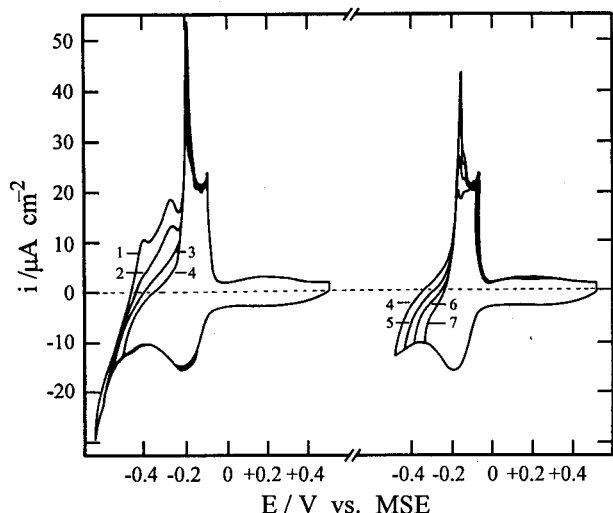


Figure 2. Cyclic voltammograms for polycrystalline gold at $20 \text{ mV}\cdot\text{s}^{-1}$ in $0.5 \text{ M HClO}_4 + 1 \text{ mM Cu(ClO}_4)_2$ for different potential ranges from $+0.5 \text{ V}$ to: -0.65 (1); -0.6 (2); -0.55 (3); -0.5 (4); -0.45 (5); -0.4 (6) and -0.35 (7) V vs. MSE .

($1 > \theta > 1/2$) with the corresponding peak B in the deposition direction. Peak A' is in fact composed of four different peaks which correspond to the dissolution of the last half of the copper monolayer deposited on the gold surface, with the corresponding peak A in the deposition direction ($1/2 > \theta > 0$).

Very interesting features can be observed when the cyclic voltammograms in the sulfate solutions are compared with those obtained in perchlorate media. A comparison between Figs. 1 and 2 clearly shows that both systems have completely different behavior. The first aspect is that for the perchlorate system, the dissolution of a complete monolayer of copper is located between -0.2 and

-0.1 V , while for the sulfate system the potential range for the complete dissolution is between -0.37 and -0.1 V . This can be explained by the stronger adsorption of the sulfate anions when compared with perchlorate, which means that as the interaction of the anion with the gold surface increases it is necessary to apply a stronger field to dissolve the copper layer. The difference in the adsorption characteristics of the anions can also explain the fact that the current density corresponding to the deposition and dissolution peaks in perchlorate is larger than in sulfate. These observations are in agreement with those described by Manne *et al.*²¹ using atomic force microscopy, where the authors emphasize that Cu UPD in perchlorate occurs at potentials $\approx 110 \text{ mV}$ more positive than the same process in sulfate.

Comparing Figs. 1 and 2 of this work with Fig. 3 in Ref. 10, it is evident that the results observed with Au(111) in HClO_4 solutions containing CuSO_4 present the characteristics of the sulfate system in the potential region corresponding to $0 < \theta < 1/2$. This points to the need for careful control of the solution composition in order to obtain the correct response of the system.

UV-visible reflectance spectra

The UVDRS experiments were performed in the same region of potentials used to record the cyclic voltammograms, in the wavelength (λ) range from 350 to 750 nm , with a sweep rate of $1 \text{ mV}\cdot\text{s}^{-1}$. Two types of analysis are possible from these experiments: the dependence of the adsorbance change, δA (which is equal to $-\delta R/R$, the relative reflectivity change of the electrode surface) at a fixed wavelength (reflectogram) on the applied potential and the dependence of δA on the wavelength at a fixed potential (spectrum)¹⁸. The variation of absorbance of the electrode-

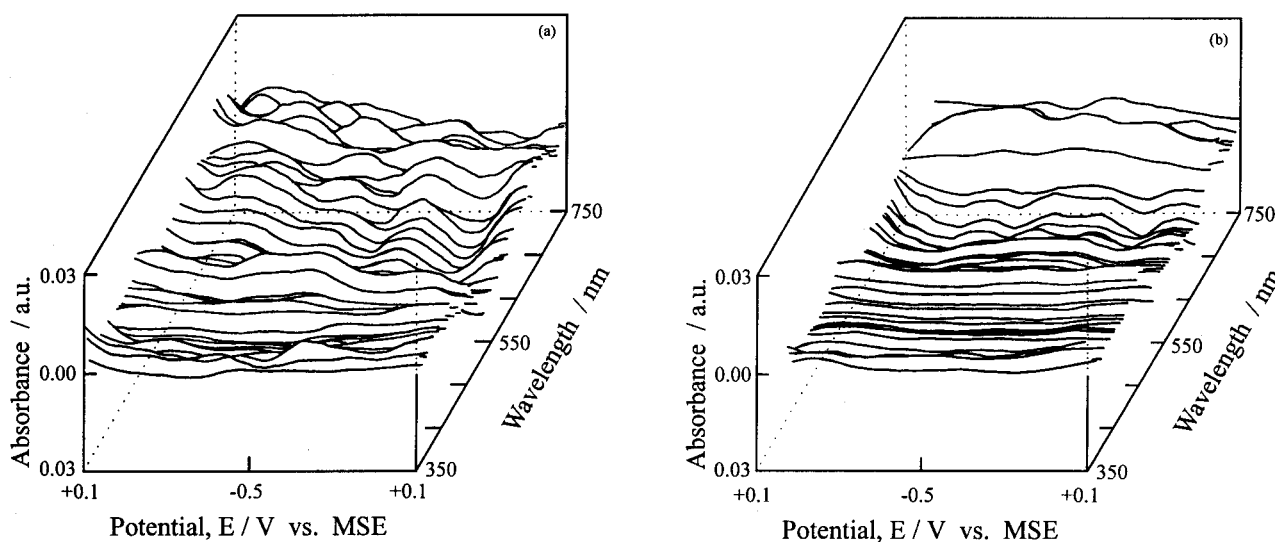


Figure 3. Three-dimensional reflectograms ($\delta A, E, \lambda$) recorded at $1 \text{ mV}\cdot\text{s}^{-1}$ for the UPD of copper on a polycrystalline gold electrode in contact with aqueous solutions having the following compositions: (a) $0.5 \text{ M HClO}_4 + 1 \text{ mM Cu(ClO}_4)_2$ and (b) $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ mM CuSO}_4$.

solution interface can be plotted in either two or three dimensions. Spectra and reflectograms are displayed in three-dimensional diagrams ($(\delta A, \lambda, E)$ and $(\delta A, E, \lambda)$, respectively).

The 3-D reflectograms obtained for the systems used in this work are shown in Fig. 3 in the potential range from +0.1 to -0.5 V, using the spectrum recorded at +0.1 V as a reference. This reference spectrum is subtracted from all the spectra in a given set. This method allows accurate localization of band maxima and easy characterization of their potential dependence. Results of the UVDRS experiments are always difficult to interpret and the most convenient way is to directly compare the reflectograms with the voltammograms. For this purpose, Fig. 4 presents three typical reflectograms at 500, 510 and 520 nm, together with the corresponding developed voltammograms in a 2-D plot, for the sulfate system (Fig. 4a) and the perchlorate system (Fig. 4b). From such a comparison it is possible to follow

the deposition and the dissolution of the copper layer, and to see the modification of the reflectivity at the same time. It is clear from Fig. 4 that the changes in reflectivity with the potential are much more important for the system containing perchlorate in the specific wavelength range considered (500-520 nm). These wavelengths correspond to the absorption of radiation with the green color, which has as its complement the dark red (purple) color. This is expected because the sulfate anion presents a strong adsorption on the gold surface, and with copper on the surface, it forms an ordered overlayer structure in which the ratio of the adsorbed copper to the adsorbed sulfate is equal to two¹⁷. So, it is expected that this arrangement on the gold surface will keep the reflectivity at almost the same level in the whole potential range.

Another way to analyze the spectroscopic data is to draw 3-D spectra, as shown in Fig. 5. From this figure it is possible to observe that for both systems, sulfate and per-

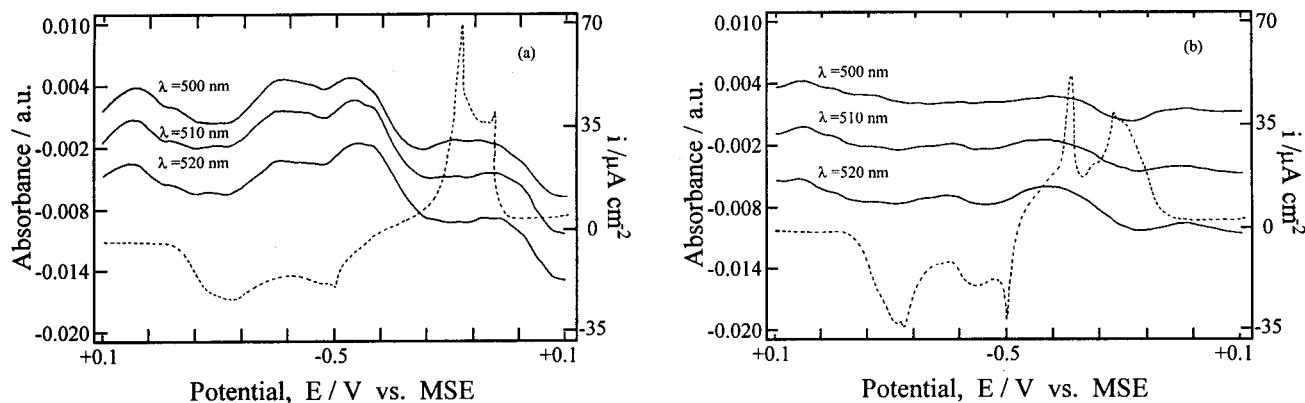


Figure 4. Two-dimensional reflectograms ($\delta A, E$) at $\lambda = 500, 510$ and 520 nm and the corresponding developed voltammogram for the UPD of copper on a polycrystalline gold electrode in the solutions: (a) 0.5 M $HClO_4 + 1$ mM $Cu(ClO_4)_2$; and (b) 0.5 M $H_2SO_4 + 1$ mM $CuSO_4$.

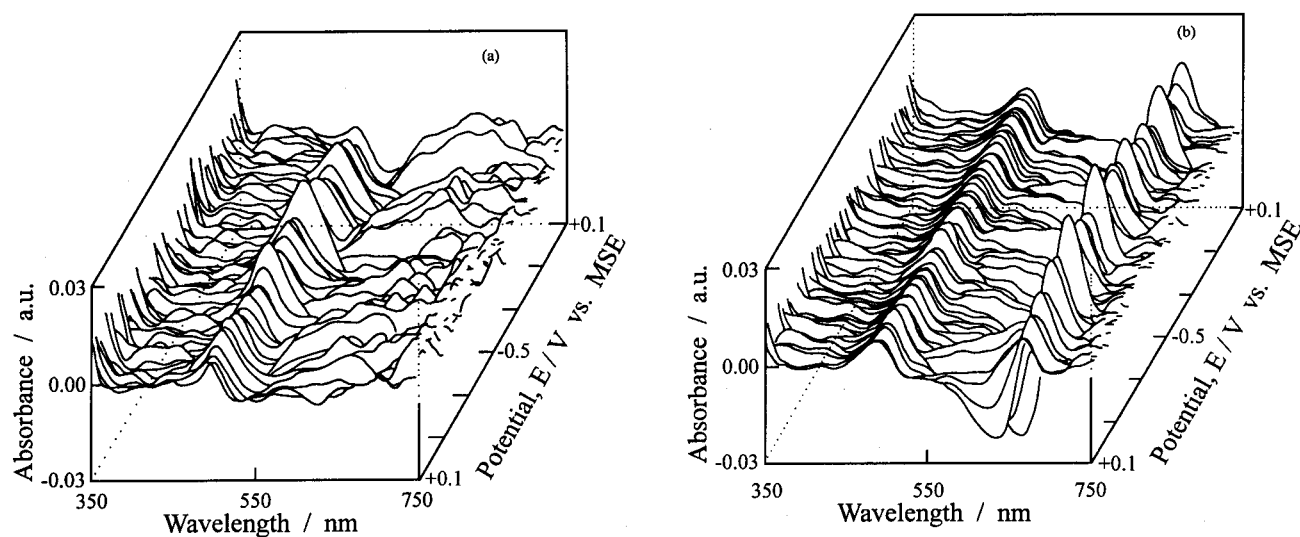


Figure 5. Three-dimensional spectra ($\delta A, \lambda, E$) for the UPD of copper on a polycrystalline gold electrode in contact with aqueous solutions having the following compositions: (a) 0.5 M $HClO_4 + 1$ mM $Cu(ClO_4)_2$ and (b) 0.5 M $H_2SO_4 + 1$ mM $CuSO_4$.

chlorate, a well-defined band appears at $\lambda \approx 490$ nm, which corresponds to a blue color, and can be associated with the gold surface covered with copper atoms, which will be seen as the complementary red-orange color. The shape of this band in sulfate medium is well defined and almost independent of potential, while in perchlorate medium the shape of the band changes with potential in an irregular manner. The region $550 \text{ nm} < \lambda < 750 \text{ nm}$ for the perchlorate system seems to have no well-defined bands. However, for the sulfate system two bands are present: one with a negative absorbance at 630 nm, and the other with a positive absorbance at 660 nm. This bipolar band is probably a by-product of the technique, because a reference spectrum was subtracted from the other spectra. This band appears at ca. 630-660 nm, which corresponds to red radiation having blue as its complementary color. So, this band can be associated with Cu(II) atoms close to the electrode surface which are attracted by the stronger adsorbed sulfate anions.

Considering that the copper structure on the gold surface is more open in the presence of sulfate than in perchlorate²¹, it is expected that this structure will be less dependent on the applied potential than in the presence of perchlorate. So, in the presence of sulfate, the reflectivity of the copper layer will depend more smoothly on the applied potential.

Conclusions

The present investigation demonstrates that the characteristics of the UPD process are strongly influenced by the adsorption of anions. Thus, when using copper sulfate in a perchlorate medium the characteristics are dominated by the stronger adsorption of the sulfate anion, even though it may be present at a much lower concentration. Because of this, extreme care must be exercised in the interpretation of results when a mixture of anions is present in the solutions. Evidence of the influence of the anion on the UPD process is also obtained from the UV-visible differential reflectance spectroscopy (UVDRS) experiments. The main difference in the spectra is the occurrence of two well-defined positive absorbance bands for the sulfate system, and just one band in perchlorate medium, which is a consequence of the different degree of adsorption of these two anions. Also, the reflectograms indicate that the response of the sulfate system is less dependent on potential, also due to the stronger adsorption of this anion. These differences establish the potential of the UVDRS technique to detect the characteristics of the overlayer formed in a UPD process. Additional studies are in progress to analyze other mixtures of acids with their corresponding copper salt.

Acknowledgments

This work was supported by a bilateral exchange program between CNPq, Brazil and CNRS, France. The

authors thank Eveline De Robertis for helping with the analysis of the results.

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