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ORIGINAL PAPER

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Influence of the degree of surface oxidation of polycrystalline Rh electrodes on the underpotential deposition of Cu

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Abstract The underpotential deposition of copper onto polycrystalline rhodium was studied as a function of the degree of oxidation of the electrode surface in acidic media using potentiodynamic techniques. Surface oxidation of the rhodium electrode was carried out using a triangular sweep potential between E_L (lower limit) and E_U (upper limit: $0.94 \leq E_U \leq 1.4$ V). Cu electrodeposition was performed at the same time as the total or partial reduction of the oxidized species. The surface oxides produced at $E_U \leq 1.09$ V were completely reduced during Cu electrodeposition. In this case, the potentiodynamic *I-E* patterns for oxidative dissolution of Cu were characterized by three anodic peaks located at 0.41 V (peak I), 0.47 V (peak II) and 0.59 V (peak III) and the coverage degree by Cu, θ_{Cu}, was on the order of a monolayer. Surface oxides produced at $E_U > 1.09$ V were partially reduced during the copper electrodeposition. In this case, the *I-E* profiles exhibited only two anodic peaks (II and III) and θ_{Cu} was < 1. The Rh-oxygen species that remain on the electrode surface block the active sites of lower energy and modify the binding energy of strongly adsorbed Cu.

Keywords Underpotential deposition · Copper · Rhodium

Introduction

The underpotential deposition (UPD) of metals on metallic substrates (mono- and polycrystalline) that differ in nature from the deposited metal has been widely studied as an important theoretical and applied aspect of electrocatalysis [1, 2, 3, 4]. However, few studies have examined the UPD of metals with interference of the oxygen electrosorption process produced on electrodes of metals of Groups 8–10 [5]. The interference of these two processes – UPD of the metal and electrosorption of oxygen over the substrate – is favored when the thermodynamic potential of the redox pair M/M^{n+} is sufficiently positive and/or when the oxygen electrosorption process occurs at relatively low potentials. The presence of oxygen species over the electrode surface could have an important influence on the formation process of the layer of metal. Therefore, the elucidation of the influence of electroadsorbed oxygen on the process of UPD of metals is fundamental to clarifying the mechanisms of electrochemisorption and electrocatalysis in these systems.

Metal UPD with interference from oxygen electrosorption has been widely studied in the system Pt/Ag^{+} [6, 7, 8, 9, 10, 11] and to a lesser extent in systems such as Ru/Cu^{2+} [12], Pt/Zn^{2+} [13] and Rh/Cu^{2+} [14].

In the case of Rh/Cu^{2+}, the electrochemical characterization of the UPD process of Cu in an acidic medium has been reported by several authors [15, 16, 17, 18, 19]. In this system, in contrast to the Pt/Cu^{2+} system, it is not possible to discard the possibility that the UPD process of Cu is affected by the existence of oxide traces on the Rh surface, as has been suggested by Parajon et al. [15] and Horanyi et al. [18]. More recently, we reported the UPD of Cu onto partially oxidized Rh electrodes [14]. In that work, the partially oxidized Rh electrodes were produced at an upper potential limit of 0.94 V/SHE. The results showed that the UPD process of Cu is accompanied by the partial or complete reduction of the oxidized species. The partial reduction of the surface oxides causes surface blocking of the electrode that leads to low values of the coverage degree by Cu, and to a possible chemical reaction between adatoms of Cu and adsorbed oxygen at long deposition times. The complete reduction of surface oxides that occurs at the same time

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as the UPD of Cu leads to a redistribution of active sites and favors the formation of low-energy active sites. These observations show that oxygen adsorbed onto Rh has an important influence on the UPD process of Cu. However, surface oxidation on Rh electrodes in the interval of the thermodynamic stability of water can involve the formation of several Rh-oxygen species. Species of type RhOH, $Rh(OH)_3$, RhO, Rh_2O and Rh_2O_3 have been considered to be probably involved in the surface oxidation of Rh electrodes [21, 22, 24]. To date, no general consensus has been reached regarding the types of Rh-oxygen species formed at a given potential. However, in order to understand the electrosorption properties of the Rh/Cu^{2+} system it is interesting to analyze the influence of surface oxides produced at different potentials on the formation process of the Cu monolayer on rhodium electrodes.

In the present work, the deposition of Cu onto polycrystalline Rh electrodes is studied in acidic medium under the influence of surface oxides of Rh produced at different values of the upper potential limit E_U.

Experimental

A glass electrochemical cell with three electrodes, suitable for working in a nitrogen atmosphere, was used. The working electrode was a polycrystalline Rh wire (Johnson Matthey, 99.99%) of geometric area 0.10 cm^2, previously treated with hot chromic acid followed by thorough washing in triple-distilled water. A carbon rod (spectroscopic grade) was used as a counter electrode and the reference was an $Hg/Hg_2SO_4/K_2SO_4$ saturated electrode connected to the cell by means of a Luggin capillary. In this work, all potentials are referenced to the standard hydrogen electrode (SHE).

The experiments were performed at room temperature in 1 M H_2SO_4, which was prepared from sulfuric acid (Merck AR) and triple-distilled water deionized with a Millipore system. The deaerated electrolytes satisfied the purity criterion established by the cyclic voltammetric *I-E* response of $Pt/H_2SO_4(aq)$ [23].

Prior to the copper deposition experiments, the working electrode in 1 M H_2SO_4 was subjected to triangular potential cycling between 0.04 and 1.4 V at 20 mV s^{-1} until no change was observed in the voltammogram (~25 cycles). The real surface area of the rhodium electrode was determined by hydrogen adsorption [24], and the roughness factor, f_r, was calculated ($f_r = 7.8$).

The potential-time program shown in Fig. 1 was applied in order to prepare the oxidized surfaces of the Rh electrode, to carry out the electrochemical characterization of the surface oxides in 1 M H_2SO_4 and, subsequently, to accomplish the formation of surface oxides in situ in a working solution of 1 M $H_2SO_4 + 1.9\times 10^{-3}$ M $CuSO_4$ with the subsequent deposition of Cu.

As shown in the E-τ diagram in Fig. 1, the first stage consists of stabilizing the electrode by continuous cycling of the potential between values of E_L (lower limit) and E_{U1} (upper limit 1) until a constant *I-E* profile is obtained. After this, the upper potential limit is gradually modified, 0.94 V $\leq E_U \leq$ 1.4 V, while the lower potential limit, E_L (0.15 V), remains fixed. Each cycle was registered after holding the potential E_L for $\tau = 1$ s. The surface oxidation of the electrode is produced during the anodic scan between the values of E_L and E_U. These oxidation procedures produce different degrees of surface oxidation for each potential E_U [24], thereby establishing the base surface conditions for the Cu deposition. The surface oxides of the Rh electrode formed at different values of E_U were characterized by cyclic voltammetry in 1 M H_2SO_4.

The surface oxides of the Rh electrode were formed in situ in a working solution of 1 M $H_2SO_4 + 1.9\times 10^{-3}$ M $CuSO_4$ with the subsequent deposition of Cu, following the potential-time program

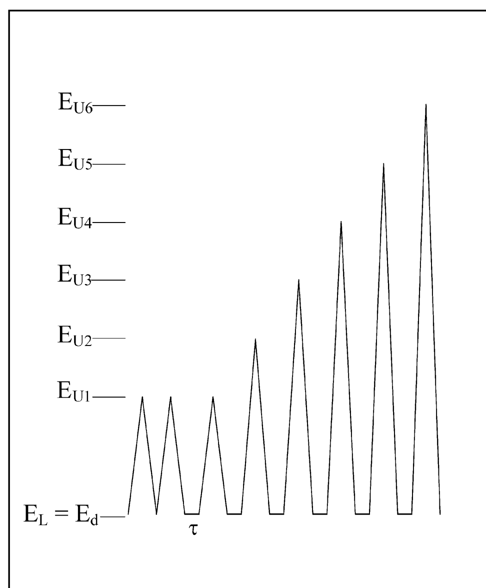


Fig. 1. Potential-time pattern used to prepare surface oxides of a Rh electrode by different values of the potential E_U (upper limit, 0.94 V $\leq E_U \leq$ 1.4 V); E_L is constant (0.15 V) and $\tau = 1$ s. The program was applied in (1) Rh/1 M H_2SO_4 and (2) Rh/1 M $H_2SO_4 + 1.9\times 10^{-3}$ M $CuSO_4$ for in situ formation of surface oxides and subsequent Cu deposition; $E_L = E_d$ (deposition potential) and $\tau = t_d$ (deposition time)

shown in Fig. 1. In this case, the potential E_L (0.15 V) corresponds to the deposition potential, E_d, and the deposition time $t_d = \tau$ was 1 s. The effect of surface oxides on the Cu UPD process is discussed from the potentiodynamic *I-E* profiles (20 mV/s) for the oxidative dissolution of copper adatoms.

A potentiostat (PAR 263A) controlled by M270 software running on a PC computer was used.

Results and discussion

Electrochemical characteristics of the surface oxides of Rh in 1 M H_2SO_4 as a function of E_U

Figure 2 shows the potentiodynamic *I-E* profiles of the Rh electrode in 1 M H_2SO_4 in the potential interval 0.15–1.4 V registered at 20 mV s^{-1} with increments of 0.1 V in E_U from 0.94 to 1.4 V, as shown in Fig. 1.

The *I-E* curves in Fig. 2 (anodic region) show a peak at 0.18 V associated with the desorption of small amounts of adsorbed H. The electrosorption of oxygen starts at 0.5 V and is characterized by a broad peak around 0.8 V (peak O_a) followed by an increase in current with increasing the potential up to 1.4 V. The reduction of surface oxides occurs during the potential scan in a negative direction and is characterized by the cathodic peak O_c, which shows a marked dependence on E_U. The progressive increase of E_U causes the displacement of the cathodic peak, E_{pc}, to more negative potentials and the increase of the current cathodic peak, I_{pc}, as can be seen in Fig. 2. Thus, the surface oxides produced at more positive potentials are electroreduced at less positive potentials than those required by the

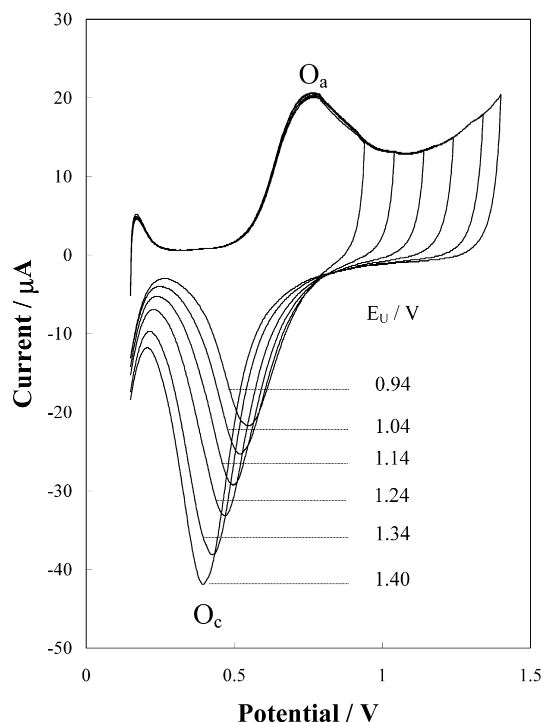


Fig. 2. Voltammograms of a Rh electrode in 1 M H_2SO_4 at 20 mV s^{-1}, between E_L (lower limit) and E_U (upper limit): 0.94 V ≤ E_U ≤ 1.4 V

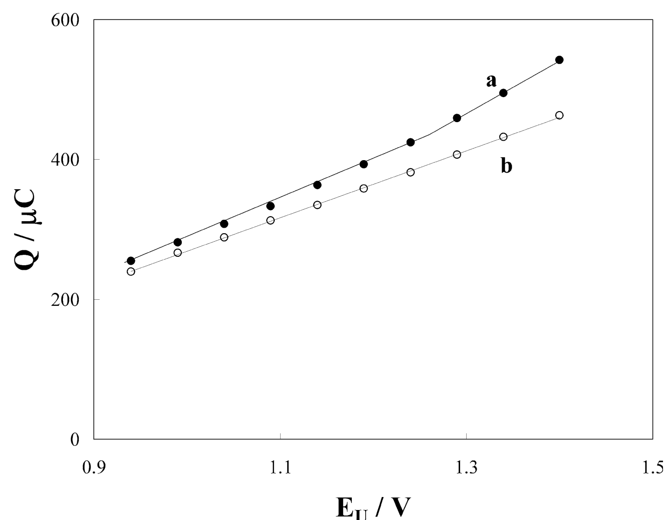


Fig. 3. Surface oxidation charge (Q_{ox}) and surface reduction charge (Q_{red}) of a Rh electrode as a function of E_U resulting from *I-E* profiles depicted in Fig. 2: (*a*) (Q_{ox}) vs. E_U and (*b*) (Q_{red}) vs. E_U

oxides formed using low potentials. The negative displacement of the potential peak O_c becomes greater with increasing E_U; when $E_U = 1.4$ V the maximum displacement of $E_{pc(Oc)}$ is 160 mV with respect to that obtained at $E_U = 0.94$ V. This indicates that the Rh-oxygen species formed at more positive values of E_U are more stable than those formed at less positive values.

The amount of oxides formed over the electrode surface at the potential E_U, and the corresponding amount of oxides reduced in the inverse potential scan, were estimated indirectly using measurements of the charges Q_{ox} and Q_{red} from the area below the anodic and cathodic curves in the potentiodynamic *I-E* profiles in Fig. 2. The dependence of the charges Q_{ox} and Q_{red} on E_U is shown in curves a and b in Fig. 3, respectively. The charges Q_{ox} and Q_{red} progressively increase with increasing E_U, indicating that the proportion of oxides formed and reduced increases as the value of E_U is made more positive. The curve $Q_{ox} = f(E_U)$ (curve a, Fig. 3) shows two linear sections, one from 0.9 to 1.25 V and the other from 1.25 to 1.4 V. The change in the slope of $Q_{ox} = f(E_U)$ at around 1.25 V is associated with the change in the stoichiometry of the Rh-oxygen species, suggesting that at least two types of oxide are involved in the oxidation process [21]. However, the curve $Q_{red} = f(E_U)$ (curve b, Fig. 3) exhibits a linear dependence over the range of E_U considered (0.9–1.4 V). Comparison of curves a and b in Fig. 3 shows an imbalance between the charges Q_{ox} and Q_{red} at every value of E_U (Q_{red} is always less than Q_{ox}), and the difference between Q_{ox} and Q_{red} increases on going to more positive values of E_U. Similar results have been reported by other authors [20, 21]. Woods et al. [20] demonstrated, using coulometry and direct analytical techniques, that the dissolution of Rh in sulfuric acid solution is the principal factor responsible for the charge imbalance. More recently, Pallota et al. [21] have explained the increase in the difference (Q_{ox}–Q_{red}) with increasing E_U by taking into account the electrodissolution of Rh as well as the partial chemical dissolution and possible redox reactions of electroadsorbed Rh-oxygen species. These authors argue that the chemical formation of O-electrosorbed species are only partially electroreduced during the potential scan in the negative direction, which is closely related to the overlapping of the O-electrodesorption and the H-electrosorption potential ranges. For this reason, it is highly probable that the Rh-oxygen species interfere with the UPD process of Cu.

The surface coverage of the Rh electrode by oxygen for different values of E_U was evaluated from the equivalence between Q_{ox} and $2Q_{Hs}$ [24], where Q_{Hs} is defined as the charge for the adsorption of a hydrogen monolayer, and it is assumed that one hydrogen atom is adsorbed onto one metal atom in the surface. Table 1 shows the values of the surface coverage of the Rh electrode by oxygen in the potential interval 0.94 V ≤ E_U ≤ 1.4 V. The values obtained indicate that the oxygen monolayer is formed at around 1.14 V and reaches 1.5 monolayers at the maximum upper limit potential of 1.4 V.

These results show that the potential applied at the upper potential limit, E_U, produces different degrees of surface oxidation [21, 24] and that the Rh-oxygen species produced increase in stability on going to more positive values of E_U. Consequently, each value of the potential E_U establishes a distinct condition of the oxidized surface, which differs in the degree of surface coverage of oxygen and the stability of the oxygenated

Table 1. Surface coverage of a Rh electrode by oxygen in the potential interval $0.94 \leq E_U \leq 1.4$ V, as obtained from $Q_{ox}/2Q_{H,s}$

E_U / V	$Q_{ox}/2Q_{Hs}$
0.94	0.72
0.99	0.80
1.04	0.87
1.09	0.94
1.14	1.01
1.19	1.11
1.24	1.20
1.29	1.30
1.34	1.40
1.4	1.53

species. The process of Cu electrodeposition was analyzed under these conditions of the base surface.

Deposition of Cu onto Rh as a function of E_U

Figure 4 shows the potentiodynamic *I-E* profiles of Rh in 1 M $H_2SO_4 + 1.9\times10^{-3}$ M $CuSO_4$ for a number of values of E_U in the range $0.94\ V \leq E_U \leq 1.4$ V. The potential and deposition time were constant in all experiments ($E_d = 0.15$ V, $t_d = 1$ s), as indicated in the diagram in Fig. 1.

When the upper potential limit was 1.04 V, the anodic region of the potentiodynamic profile (Fig. 4) exhibits three anodic peaks, located at 0.41 V (peak I), 0.47 V (peak II) and 0.59 V (peak III). Peak I dominates over peaks II and III. The anodic peaks II and III coincide with those reported for the oxidation of Cu UPD onto Rh electrodes [14, 15], which have been associated with the desorption of Cu bound in active sites of low and high energy, respectively. This represents the first observation of peak I, located in the underpotential region, and does not correspond to massive Cu oxidation. When the deposition time was increased to $t_d = 5$ s (dashed curve in Fig. 4), an additional peak appears at 0.23 V (peak m), characteristic of the oxidation of bulk Cu. Therefore, the presence of peak I in the potentiodynamic *I-E* profiles suggests the existence of other types of active site, onto which Cu is adsorbed with a binding energy weaker than the Cu binding energy that gives rise to peaks II and III.

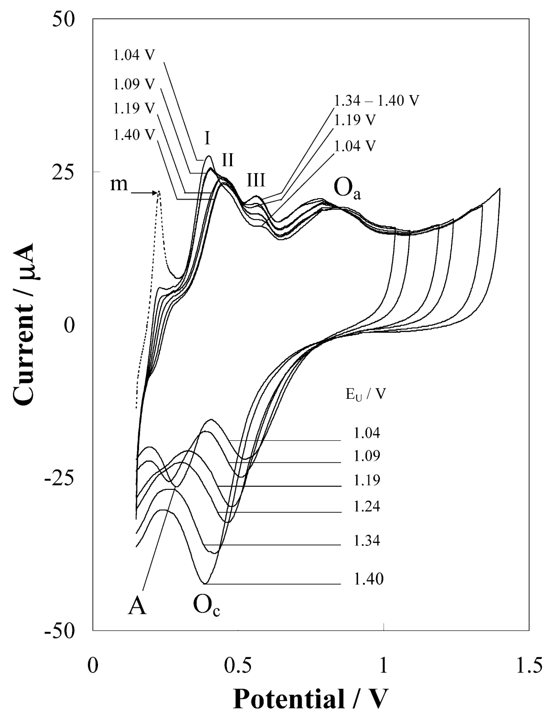


Fig. 4. Potentiodynamic *I-E* profiles of a Rh electrode in 1 M $H_2SO_4 + 1.9\times10^{-3}$ M $CuSO_4$ at 20 mV s^{-1}, with increments in E_U potential (upper limit, $1.04\ V \leq E_U \leq 1.4$ V). Deposition potential $E_d = E_L = 0.15$ V during the deposition time $t_d = 1$ s

For the same value of $E_U = 1.04$ V, the cathodic region of the voltammogram (Fig. 4) shows two current peaks, one at 0.51 V (peak O_c), corresponding to the electroreduction of Rh-oxygen species, and another at 0.27 V (peak A), associated with the reduction of Cu^{2+} ions. Because the potential of the anodic peak for the oxidation of Cu/Cu (0.23 V) is less positive than the potential of cathodic peak A (0.27 V), we conclude that peak A is related to the UPD of Cu onto Rh. This result is consistent with the work of Canullo et al. [17] on the system of Cu over faceted Rh, which showed the presence of the cathodic peak for UPD of Cu in the potentiodynamic *I-E* profiles. In our results, the heights of the peaks O_c and A (Fig. 4) are similar; this should be because of the overlapping of the peaks.

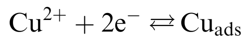
Increasing the upper potential limit, E_U, produces significant changes in the structure of the potentiodynamic *I-E* profiles shown in Fig. 4. In the anodic region, peaks I, II and III for the oxidation of UPD Cu show a significant redistribution with increasing E_U. As E_U is increased, the peak I current decreases and this peak is not observed at values of E_U greater than or equal to 1.19 V, while peak III increases and is displaced to less positive potentials. For values of E_U greater than 1.19 V, peak II becomes well defined and dominates over peak III. The subsequent increase in E_U causes a slight decrease in the height of peak II, while peak III increases in height once again and is displaced to less positive potentials. For values of E_U greater than or equal to 1.34 V, peaks II and III do not vary in height or position. In addition, when $E_U \leq 1.19$ V the potential of peak O_a is localized at 0.84 V, i.e. 60 mV more positive than the value obtained for the same peak in a solution which is 1 M H_2SO_4 and is free of Cu^{2+} and adsorbed Cu (Fig. 2). In this case, it is important to notice that the peak O_a potential is independent of the increase of E_U (ca. 0.78 V). From the potentiodynamic *I-E* profiles of Fig. 4 it is again observed that for $E_U > 1.19$ V the potential of peak O_a is displaced to less positive potentials and tends to reach the value of 0.78 V, which corresponds to peak O_a shown in Fig. 2. This suggests that Cu adsorbed on the electrode sur-

face influences the surface oxidation process and, reciprocally, that Rh-oxygen species affect the Cu adlayer formation process.

In the cathodic region of the potentiodynamic profiles (Fig. 4) the peaks O_c and A are well defined when $E_U \leq 1.09$ V. However, when E_U is increased (>1.09 V), only peak O_c is observed. The dominant contribution of the current of peak O_c, and the displacement of this peak to lower potential, obscures the presence of peak A.

These results show that the process of Cu UPD onto Rh is influenced by the conditions of the surface oxidation of the electrode produced at different limits of the potential E_U. For $E_U \leq 1.09$ V, the Rh surface with low oxygen coverage ($\theta_O < 1$) favors the adsorption of UPD Cu onto three types of active site with different energies (peaks I, II and III in Fig. 4), whereas for $E_U > 1.09$ V, where the Rh surface has a higher oxygen coverage ($\theta_O > 1$), only two types of active site are available for the adsorption of Cu (peaks II and III in Fig. 4). This behavior can be reasonably explained by taking into account the observation that the complete or partial reduction of surface oxides proceeds simultaneously with the electrodeposition of Cu. The complete reduction of Rh-oxygen species that occurs in conjunction with the electrodeposition of Cu is possible at a low coverage of surface oxygen ($\theta_O < 1$) and a low stability of the Rh-oxygen species. In this case, the fact that the Rh surface is free of surface oxides makes possible the Cu adsorption onto three types of active site of different energies. On the other hand, the partial reduction of surface oxides during the Cu electrodeposition only allows Cu adsorption onto two types of active site. In this case, it is necessary to know the effect of the oxides that remain on the surface. As a starting point we will consider two possibilities: (1) that the surface oxides remaining on the electrode surface block the active sites of lower energy, leading to the observation of two oxidation peaks of Cu UPD (peaks II and III), and/or (2) that the increase in surface oxides provokes a surface rearrangement that favors the formation of high-energy active sites, which would justify the increase of the peak III current with increasing E_U. To test these hypotheses, the amount of Cu coating the Rh surface was calculated as a function of the potential E_U.

The electric charge due to the process of desorption of adatoms of Cu (Q_{Cu}) was calculated from the integral under the oxidation peaks of UPD Cu in Fig. 4, after correction for surface oxidation. The coverage by Cu was evaluated from the relation $Q_{Cu}/2Q_{H,s}$, assuming that the reduction of Cu^{2+} occurs via the reaction



$$Cu^{2+} + 2e^- \rightleftarrows Cu_{ads}$$

. In addition, it is important to consider that the adsorption of HSO_4^- (SO_4^{2-}) anions does not cause significant changes in the formation of the adlayer of Cu [18]. The dependence of $Q_{Cu}/2Q_{H,s}$ on the potential E_U (Fig. 5) shows that the degree of surface coverage by Cu

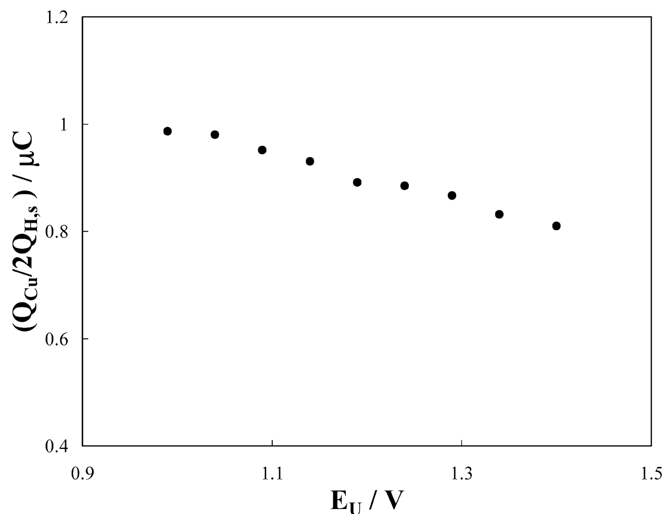


Fig. 5. Dependence of the surface coverage degree on a Rh electrode by Cu ($Q_{Cu}/2Q_{H,s}$) vs. EU

is influenced by the magnitude of the potential E_U. For $E_U = 0.94$ V the coverage by Cu, θ_{Cu}, is of the order of 1. However, the increase of E_U causes a progressive decrease in θ_{Cu} to a value of 0.8 at $E_U = 1.4$ V (Fig. 5). The formation of a monolayer of Cu over the Rh suggests that the Rh-oxygen species had been completely reduced during the process of Cu electrodeposition, while the decrease in θ_{Cu} for more positive values of E_U indicates that a fraction of the active sites for Cu adsorption had been blocked. In these conditions, the Cu and adsorbed oxygen coexist on the electrode surface. XPS measurements of the UPD of Cu onto partially oxidized Rh electrodes have corroborated the coexistence of Cu and adsorbed oxygen [14]. Consequently, the behavior of peak O_a shown in Fig. 4 can be reasonably justified, considering that the formation of the Cu monolayer on Rh displaces surface oxidation to more positive potential values. However, when the amount of adsorbed Cu decreases with E_U, the oxidation of the Rh surface tends to be developed at less positive potentials, as in the case of Rh/1 M H_2SO_4 free of adsorbed Cu.

In addition to blocking low-energy active sites, the presence of adsorbed oxygen over the Rh surface may promote high-energy active sites. Rh-oxygen species on the electrode surface modify the electronic properties of the neighboring metallic Rh sites, favoring the interaction of these sites with adatoms of metallic Cu. According to Kolb et al. [25], the potential difference between the stripping peak of the bulk deposit and the most positive stripping peak of the UPD deposit in the cyclic voltammogram is a measure of the bond strength of the substrate surface atoms and the UPD species. They correlated this underpotential shift (ΔE_p) to the work function difference, $\Delta\phi$, between the substrate and the adsorbate and showed that a simple relation exists between the two, for many UPD reactions on polycrystalline substrates: $e\Delta E_p = 0.5(\phi_{substrate} - \phi_{adsorbate})$.

Taking into account the above, the potentiodynamic *I-E* profiles (Fig. 5) show that as E_U is increased to more positive values the most positive anodic peak (peak III) increases in height and its peak potential ($E_{pa(III)}$) is displaced to less positive values. In agreement with the displacement of the potential of peak III with E_U, it is possible to establish that the binding force of Cu adatoms (strongly adsorbed) and Rh is a direct function of the degree of surface coverage by oxygen. It is clear that the displacement at underpotential (ΔE_p) of Cu/Rh when the rhodium surface has low oxygen coverage, or in its absence ($\theta_{Cu}=1$), exhibits more positive values ($\Delta E_p=0.36$ V) than in the case of Rh surfaces with greater oxygen coverage ($\Delta E_p=0.33$ V). This suggests that the Cu-Rh binding energy decreases as the quantity of oxygen on the electrode surface increases. This is reasonable if we consider that the adsorbates of type O and OH are attracted toward the interior of the substrate surface and donate electric charge to the surface when the applied electric field is positive [26]. Consequently, the Rh metallic sites adjacent to the species that contain oxygen may modify the work function. It is probable that the work function of these metallic sites diminishes and therefore the Cu-Rh binding energy decreases.

The result is interesting from a phenomenological viewpoint, as it allows us to consider the influence of the adsorbed oxygen on the first stages of the formation of the Cu monolayer on Rh. Additional studies aimed at determining the variability of the work function induced by the presence of Rh-oxygen species are necessary in order to understand the electronic properties of Rh electrodes that have been modified by adsorbed oxygen. This type of study has the potential to reveal relevant details regarding the influence of surface oxides on the UPD process in other systems with noble metal substrates.

Conclusion

The influence of surface oxides of rhodium on the copper UPD process onto polycrystalline Rh electrodes was analyzed. The surface oxides of the electrode were produced by cyclic voltammetry with different amplitudes of the potential E_U. The electrochemical characterization of the surface oxides shows that each value of E_U produces a surface state characterized by a particular degree of covering of oxygen and stability of Rh-oxygen species.

The Cu UPD process was accompanied by the simultaneous complete or partial reduction of oxidized species. The complete reduction of surface oxides during the process of Cu electrodeposition occurs when the surface oxides are produced at values of $E_U \leq 1.09$ V. In this case, a monolayer of Cu is produced and the oxidation of UPD Cu is characterized by three anodic peaks, located at 0.41 V (peak I), 0.47 V (peak II) and 0.59 V (peak III). Anodic peak I, for which there was previously no clear evidence, suggests the existence of another type of active site, at which Cu is adsorbed with a weaker Rh-Cu binding energy than that corresponding to the anodic peaks II and III. The partial reduction of oxidized species occurs for surface oxides formed at more positive values of E_U (>1.09 V). In this case, the oxidized species that remain on the electrode surface block the active sites of lower energy and favor the formation of high-energy active sites. The presence of surface oxides modifies the Rh-Cu binding energy (strongly adsorbed), as can be deduced from the values of the displacement of the anodic peak III.

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