

## Underpotential Deposition of Cu on Partially Oxidized Rhodium Electrodes and the Influence of PH

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The underpotential deposition (UPD) of foreign metals onto substrates has been widely studied as an important theoretical and applied facet of electrocatalysis [1,2]. Nevertheless, very little attention has been directed towards examining the UPD of metals with interference of the oxygen electroadsorption process that are produced on electrodes of the group VIII metals [3]. The presence of the oxygen-species on the surface electrode, either by simultaneous adsorption of oxygen with the UPD of metal or pre-existing due to the preparation method of the electrodes before the UPD of metal, might have an important effect on the formation of metal layer, as at Pt/Ag system [4].

Recently the UPD of Cu on partially oxidized Rhodium was studied [6]. The presence of oxidized species on the rhodium electrode surface caused important effects on the copper UPD process. The UPD process was simultaneously performed with reduction of the oxidized species and such reduction was partial or total. In the case of partial reduction, the remaining oxidized species provoked a blocking effect on the electrode surface that led to low values of coverage degrees; besides, a chemical reaction on the electrode surface is possible between the copper adatoms and oxygen existing on the electrode surface. On the other hand, when the reduction of the oxidized species was simultaneously completed with the UPD process, it caused a redistribution process of the active sites and favored the formation of the low energy active sites.

In this work the UPD of Cu on partially oxidized rhodium electrodes was studied in  $\text{H}_2\text{SO}_4$  solutions (0.01M to 1.0 M) using potentiodynamic techniques. The process is analyzed within different potential amplitudes where occurred the oxygen electroadsorption and UPD Cu process. The process is too analyzed as a function of the potential and time of deposition.

The results show that the increasing electrolyte concentration produces changes on E-I profiles of Rh electrodes associated with changes in the energy distribution of the adsorbed species related to both the H and O electroadsorption process [6]. So, the decreasing in the electrolyte concentration favoured the interference of oxygen electroadsorption process with the UPD Cu.

For the study of the influence of Rh oxide on the Cu deposit, the electrode was submitted to different positive potential limits. With the increasing on upper potential limit between 0.2 and 0.7 V/SME, the structure and distribution of current peaks of Cu UPD oxidation are changed drastically, as is observed in Fig. 1.

The UPD process of copper was studied as a function of the deposition time at two fixed potentials (-0.4 and -0.3V/SME) on four conditions of partial surface oxidation. Two of these correspond to the partially oxidized rhodium electrode obtained by cyclic voltammetry with upper potential limits of 0.24 and 0.7

V/SME, respectively. Other conditions correspond to the electrodes prepared by anodic polarization at -0.24 and 0.7 V/SME, respectively, during the oxidation time  $t_{\text{ox}}$ . The effect of pH was analyzed on these conditions.

The results show that the UPD process of copper follows a typical behavior pattern on these conditions of surface at relatively low values of  $t_d$ . However, at the highest  $t_d$  values the electrochemical behaviour of the oxidation peaks differs from that reported for the same adsorbate; in addition, on most oxidized surface (polarized electrodes) the oxidation of Cu UPD is accomplished for a one new anodic current peak to more positive potential, which is associated with the decrease at peak II. This effect is more important with low concentration of electrolyte.

Therefore, the UPD of Cu on these types of electrodes start on equivalent active sites, but the subsequent deposition steps (high  $t_d$  values) involve the formation of more stable adsorbed species, which could be due to the interaction between the Cu adatoms and the oxygen existing on the electrode surface.

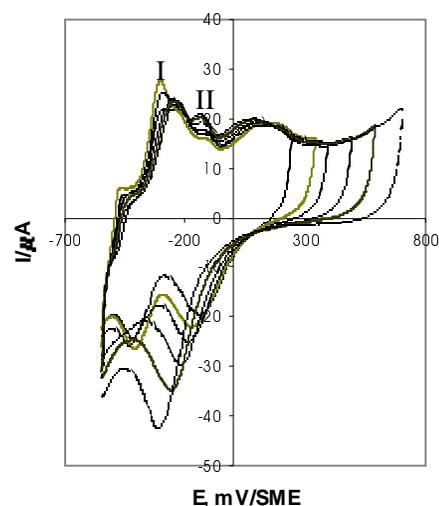


Fig.1 Influence of the initial oxidation state of the electrode on the electrodeposition of Cu monolayer. 1.0 M  $\text{H}_2\text{SO}_4$  +  $4.7 \times 10^{-3}$  M  $\text{CuSO}_4$ .  $E_d = -0.5\text{V}$ ,  $t_d = 30$  s. I and II current peaks of Cu UPD oxidation.

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