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There are a number of systems for which a complete 2-D monolayer of Me on a foreign substrate can be coupled [141. These monolayers, whose structures are formed at potentials more positive than the reversible potential $E_\text{r}$, seem to be completed before the nucleation and 3-D growth of bulk Me occurs at potentials $E_\text{r}$ more negative than $E_\text{r}$. Accordingly, the growth model for the Me electrodeposits implies the successive growth of 2-D domains under quasi-equilibrium followed by the electrodeposition of Me monolayer becomes unstable, and during a certain initial period of the electrodeposition process, free substrate and 2-D Me domains can coexist with 3-D Me nuclei.

In these cases, bulk Me can be detected when the degree of Pt surface coverage by Cu atoms exceeds 0.5.

Key words: electrocrystallization, metal electrodeposition, electrode roughness, growth models, columnar structured metal electrodes.

INTRODUCTION

There are a number of systems for which a complete 2-D monolayer of Me on a foreign substrate can be formed at potentials more positive than the reversible potential $E_\text{r}$ of the corresponding Me/Me$^+$ redox couple[1-4]. These monolayers, whose structures have been ascribed to a 2-D gas[5], seem to be completed before the nucleation and 3-D growth of Me occurs at potentials $E_\text{r}$ more negative than $E_\text{r}$. Accordingly, the growth model for the Me electrodeposits implies the successive growth of 2-D domains under quasi-equilibrium followed by the growth of the 3-D Me phase. In a number of electrochemical systems this situation can be approached when the electrodeposition of Me proceeds on well-defined smooth substrates at potentials close to $E_\text{r}$.

The early stages of Cu electrodeposition on a foreign metal substrate are particularly interesting for understanding the mechanism of electrocrystallization of metals, including the transition from 2-D submonolayers to bulk Me deposits. From the standpoint of electrochemical kinetics the most relevant works on the cathodic formation of monolayers and multilayers of metal atoms were carried out by using polycrystalline Pt surfaces[6], platinized Pt[7] and well-defined crystallographic faces[5, 8], although the latter, as recently shown from scanning tunnelling microscopy (STM), contain a relatively large number of defects[3]. A different situation arises when the electrodeposition of Me takes place on a rough conducting substrate far from equilibrium conditions as often occurs in applied electrochemistry. In this case the validity of the preceding model is far from proven. This fact encourages the investigation of both the influence of the surface roughness of the substrate and the electrodeposition conditions on the early stages of Me electrocrystallization.

Data on Cu[9] and Ag electrodeposition[10] on polycrystalline Pt at potentials $E_\text{r}$ more negative than $E_\text{r}$ showed that the nucleation and 3-D metal overlayer growth involves a 2-D to 3-D rearrangement at growing sites. Hence, under those conditions the electrodeposited Me monolayer becomes unstable, and during a certain initial period of the electrodeposition process, free substrate and 2-D Me domains can coexist with 3-D Me nuclei.

Recently the influence of surface roughness on both underpotential (upd) and overpotential (opd) electrodeposition of Ag has been studied on columnar structured Pt electrodes[11]. The structure of these electrodes has been solved through the application of STM at the nanometre level[12, 13] and their use is particularly attractive for detecting surface rearrangements and other dynamic aspects of the Me surface at the early stages of electrocrystallization. Usually these features cannot be observed on smooth conducting surfaces.

This work refers to the electrodeposition of Cu on columnar structured Pt electrodes comprising a rather wide range of roughness factors. The physical picture derived from the present results for the early stages of Me electrodeposition under relatively fast perturbing potential conditions is consistent with the simultaneous presence of bulk Cu, 2-D Cu domains and free Pt sites. This conclusion can be compared with previously reported data for Me electrodeposition at potentials close to $E_\text{r}$[9, 10]. Furthermore, when $E < E_\text{r}$, the growth of bulk Me deposits can occur when the surface coverage of the substrate by 2-D Cu domains exceeds 0.5.

EXPERIMENTAL

The starting working electrode was a polycrystalline (pc) Pt wire (99.99% purity, 0.05 cm$^2$ geometric area) encased in a glass holder. The electrochemical cell was completed with a Pt counter electrode (4 cm$^2$ geometric area). A reversible hydrogen...
The voltammograms obtained in $10^{-3}$ M CuSO$_4$ + 0.5 M H$_2$SO$_4$ at $v = 0.02$ V s$^{-1}$ (Fig. 2a-c) depend on the value of $R$. Thus, for $R = 2$, the negative potential going scan shows peak Ic which involves the simultaneous contributions from the O adatom monolayer electroreduction and the first stage of Cu upd, followed by a small and broad cathodic peak (11c) located positively with respect to the reversible potential of the Cu/Cu$^{2+}$ electrode ($E_r = 0.250$ V). Peak IIc is related to the second stage of Cu upd on Pt[9].

**RESULTS**

The voltammograms recorded for different EDPtEs in 0.5 M H$_2$SO$_4$ (Fig. 1) at $v = 0.1$ V s$^{-1}$ exhibit the cathodic and the anodic O-electrosorption current peaks located at 0.75 V (peak 1c) and 0.7-1.4 V (peaks 1a), respectively. Besides, the current peaks related to H atom electrosorption are observed in the 0.05-0.35 V potential range. No marked voltammetric differences in 0.5 M H$_2$SO$_4$ can be detected for EDPtEs with $R$ ranging from 2 to 200.
Early stage of Cu electrodeposition

Data depicted in Fig. 3 indicate that under non-equilibrium conditions such as Cu electrodeposition on rough Pt surfaces \((R > 30)\) the formation of 3-D Cu deposits decreases as \(R\) and \(v\) are increased. Thus, for \(v > 0.02\ \text{V s}^{-1}\), the charge related to 3-D Cu deposits is beyond the possibilities of its electrochemical detection. The decrease of \(q_h\) is accompanied by the simultaneous changes in \(\theta_{ni}\) and \(\theta_{hi}\), the latter becoming independent of \(v[16]\). Furthermore, the decrease of \(\theta_{ni}\) and the simultaneous increase of \(\theta_{hi}\) with increasing \(R\) indicate that under certain conditions three processes are competing for reacting sites at the Pt substrate, namely the growth of 2-D Cu domains, the growth of bulk Cu, and the H-atom electrosorption.

For explaining the preceding results one has to first consider that the structure of EDPtEs \((30 < R < 200)\) involves pores of \(3 \times 10^{-5} - 2 \times 10^{-4}\ \text{cm}\) length and \(10^{-6}\ \text{cm}\) average width[12, 13]. For the sake of simplicity, let us consider an intermediate value of \(R\) such as \(R \approx 50\) with an average length of pores equal to \(5 \times 10^{-5}\ \text{cm}\). Then the average number of Cu\(^{2+}\) ions contained in the pore volume for the electrolyte solution used in the present experiments is close to 10, in contrast to \(10^4\) Pt surface atoms constituting the wall of the pore. Furthermore, from the standpoint of electrochemical kinetics, both the relatively high exchange current density \((j_e)\) value for Cu\(/\text{Cu}^{2+}\) reaction[17] and the time required for the relaxation of the Nernst diffusion layer for a columnar structure equal to \(5 \times 10^{-5}\ \text{cm}\) height, which is of the order of \(0.1\ \text{s}[18, 19]\), have to be considered.

Under the present circumstances the electrodeposition of Cu is diffusion controlled by Cu\(^{2+}\) ions moving from the bulk of the solution towards the tips of the columnar Pt structure, ie the active Pt electrode surface is mainly constrained to the 'envelope' of the rough substrate. Accordingly, the simplest physical picture for the early stages of Cu electrodeposition would imply the formation of 2-D Cu domains at tip sites whose average area can be estimated as \(3 \times 10^{-12}\ \text{cm}^2\). The formation of 2-D Cu domains is followed by the growth of 3-D Cu deposits over those domains. Consequently, the bare Pt sites at the wall of the pores would remain as possible sites for H atom electrosorption when the applied potential is set accordingly. This first mechanistic approach can be described as a "frozen particle" model as surface displacements of the depositing particles are not allowed. A scheme of the early stages of Me electrodeposition on the rough substrate in the absence of Me atom surface diffusion is illustrated in Fig. 4a-d. Unfortunately this model, which has been used to interpret the \(\text{upd}\) of Mes on different smooth conducting electrodes, fails to explain the initial stages of Cu electrodeposition on the EDPtEs, as the "frozen particle" model predicts a smooth decrease of \(q_h\) with potentials more negative than \(E_e\), a diffusion current peak (IIIc) related to bulk Cu electrodeposition \((\text{opd})\) is observed[9]. This peak partially overlaps the HER current which initiates at ca 0.0 V. Furthermore, the positive potential-going scan displays a large anodic peak (IIIa) due to the stripping of bulk Cu followed by three small current peaks Ia, I'a and I''a located at 0.45, 0.62 and 0.75 V, respectively, all these peaks being related to the anodic stripping of \(\text{upd}\) Cu. Similarly to the blank, at potentials more positive than 0.85 V the complex anodic peak Ia can be observed.

The metal electrodeposition/anodic stripping voltammograms run at 0.02 V s\(^{-1}\) (Fig. 2b and c) show that the increase of \(R\) simultaneously produces a decrease in the charge density related to \(\text{upd}\) Cu, an increase in the H atom electrosorption charge, and a considerable decrease in the anodic stripping charge related to \(\text{opd}\) Cu. These results are largely comparable with those recently reported for \(\text{upd}\) and \(\text{opd Ag}\) on the same types of electrode[16].

Data derived from voltammetric runs in the 0.02 V s\(^{-1}\) < \(v\) < 0.1 V s\(^{-1}\) range are summarized in Fig. 3a-c. In those plots \(\theta_{hi}\) stands for the degree of surface coverage by H adatoms, \(\theta_{ni}\) the degree of surface coverage by \(\text{H adatoms}\), \(\theta_{hi}\) the degree of surface coverage by \(\text{H adatoms}\), and \(q_h\) denotes the charge density of \(\text{opd metal}\) referred to the real rough Pt surface. For the evaluation of \(\theta_{hi}\) and \(\theta_{ni}\), the corresponding monolayer charge density values were taken as 0.210 and 0.420 mC cm\(^{-2}\), respectively.

**DISCUSSION**

Data derived from those voltamgrams run at different vs \((v)\) values, \(v = 0.02\ \text{V s}^{-1}\) (Fig. 2b and c) and \(v = 0.1\ \text{V s}^{-1}\) (Fig. 3a-c) are presented in Table 1.
increasing values of \( R \). This means that some traces of \( q_b \) would have to be detected even for those electrodes with the highest values of \( R \) rather than the apparent complete inhibition of 3-D Cu growth actually observed within the possibilities of the voltammetric technique.

The explanation of the kinetics of the initial Cu electrodeposition on EDPtEs can be improved by considering that the arriving Cu atoms can diffuse on 2-D Cu domains formed at tip sites reaching free Pt sites at the wall of the pores. This approach implies that the surface mobility of Cu atoms at 2-D Cu domains is greater than their mobility on the Pt substrate. This assumption is consistent with the fact that the Cu–Cu bonding energy appears to be weaker than the Cu–Pt bonding energy, as deduced from the electrochemical data, i.e., from the potential values of the Cu upd and Cu opd anodic stripping peaks. The high mobility of Cu surface atoms in contact with the electrolyte solution at room temperature is further supported by the STM imaging of the initial stages of Cu electrodeposition[5]. Correspondingly, the mobility of Cu surface atoms on 2-D Cu domains tends to produce a spillover effect which hinders the 3-D Cu growth (Fig. 4). A scheme of this reaction pathway is depicted in Fig. 4a, b', c', d.

It should be noted that this type of surface atom rearrangement involving the relaxing and the reconstruction of metal deposits has been extensively studied on well-defined surfaces under either ultra-high-vacuum conditions or in contact with a gas phase[20].

On the other hand, for experimental conditions far from equilibrium there is a threshold value of \( \theta_{ml} \) for the formation of 3-D Cu deposits. This critical value of \( \theta_{ml} \) is about 0.5, a figure which coincides with the...
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degree of Pt surface coverage by strongly bound Cu adatoms on Pt[9]. This means that for $E_d \ll E_r$, the appearance of the 3-D Cu phase takes place when a fraction of the 2-D Cu monolayer involving strongly bound Cu adatoms has been formed.

CONCLUSIONS

1. The voltammetric electrodeposition of Cu at different $\nu$ values on columnar structured Pt electrodes shows that at relatively high $\nu$s, as the roughness of the electrode is increased, the presence of bulk Cu electrodeposits tends to disappear, the amount of electroadsorbed H atoms increases, and the coverage of Pt substrates by 2-D Cu domains decreases.

2. For fast Cu electrodeposition ($E \ll E_r$) from a diluted Cu$^{2+}$ ion containing solution on EDPtEs involving a large roughness factor, there is an initial stage of the process in which 3-D Cu nuclei, 2-D Cu and free Pt domains are simultaneously present in the system.

3. The early stages of Cu electrodeposition on EDPtEs reveal that both Cu atom surface diffusion and 2-D $\Rightarrow$ 3-D reversible changes at the growing Cu layer play an important role in the overall process.

4. At high Cu$^{2+}$ ion discharge rates bulk Cu can be detected when the EDPtE surface coverage by 2-D Cu domains exceeds 0.5. This figure represents the maximum Pt surface coverage by strongly bound Cu adatoms on Pt.

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