

Electrocrystallization of Cu and Hg on Pt Ultramicroelectrodes

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Received: April 30, 1994; November 30, 1994

A eletrodeposição de Cu e Hg sobre ultramicroeletrodos de Pt foi estudada por cronoamperometria e por voltametria cíclica. Utilizando-se um modelo desenvolvido com equações I-t especialmente derivadas para microdiscos, obteve-se uma grande concordância dos valores calculados com os dados experimentais. Esta concordância indica nucleação instantânea para o Cu e progressiva para o Hg, ambas controladas pelo transporte difusional de massa. Os transientes apresentaram máximos pouco pronunciados. Esta característica foi associada: a) à forma de transporte de massa e b) ao número reduzido de núcleos, devido à pequena área do eletrodo, que após a coalescência não altera significativamente as áreas totais das superfícies. O número de núcleos de Cu formados na Pt foi calculado e mostrou ser fortemente dependente do potencial, variando de 11 a 67 no intervalo pesquisado. Já no caso do Hg, foi calculada a taxa de formação de núcleos resultando em valores entre 1.9×10^7 e $55.0 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ segundo o potencial aplicado.

The electrocrystallization of copper and mercury was studied on platinum ultramicroelectrodes by potentiostatic transients and cyclic voltammetry. Using a model involving proper I-t equations derived for microdisk electrodes, a good fitting with the experimental data was obtained which indicated an instantaneous nucleation for Cu and a progressive one for Hg, both being controlled by mass transport. The transient responses showed rather small current maxima, a fact that was attributed to: a) the form of mass transport, and b) the small number of nuclei, which after coalescence do not significantly alter the total surface area of the electrode. The actual number of Cu nuclei formed on Pt was calculated and found to be strongly dependent on potential, with values varying from 11 to 67 in the potential interval under investigation. In the case of Hg, the rate of nuclei formation was evaluated showing values between 1.9×10^7 and $55.0 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ according to the applied potential.

Keywords: *electrocrystallization, nucleation, ultramicroelectrodes*

Introduction

Ultramicroelectrodes (UMEs) are being used with increasing frequency in electrochemistry and electroanalytical chemistry due to their well-known properties¹. The enhanced rates of mass transport by spherical diffusion together with a very low ohmic drop make their utilization in several cases decisive in investigating electrochemical processes. As such, for highly resistive solutions like organic solvents or aqueous systems without supporting electrolytes, as well as for gas evolving reactions, the UME is becoming an essential instrument. A Pt UME ($\phi = 40 \mu\text{m}$) has been recently used in our laboratory to study the hydrogen evolution reaction in 0.5 M H₂SO₄ solutions^{2,3}. The results obtained lead to advances in the discussion of the kinetics and mechanism of the reaction. Therefore, it is very

important to extend those results to the electrocatalytic materials usually employed in water electrolysis, such as nickel and its alloys (electrodeposited on Cu), iron, and other interesting surfaces like mercury.

However, the preparation of UMEs involves severe difficulties in sealing metallic wires in Pyrex glass or epoxy resins. The appropriate material for this application is platinum. Metals like Ni or Fe need inert gas atmospheres to prevent the formation of surface oxides which give rise to cracks which in turn cause infiltration. A good alternative is the electrodeposition of metals on Pt previously sealed in Pyrex glass.

The early stages of an electrochemical reaction involving phase formation are usually associated with two- or three-dimensional nucleation processes. A number of works have been published in this area. Initially, Abyaneh and Fleischmann⁴ proposed a scheme where the nuclei

were treated as circular cones growing either in the perpendicular or in the parallel directions. To explain the presence of a current maximum in potentiostatic transients, this model needs the addition of the concepts of the "death" and "rebirth" of active centers for nuclei formation. This simple model was contested by Amblard *et al.*⁵ based on transmission electron microscopy which showed the spherical growth of the crystallites. Thus, the coalescence of nuclei is responsible for the maximum by diminishing the surface area. This approach was further developed by Abyaneh⁶ with a more elaborated mathematical treatment.

Although there is little in the literature on quantitative treatments for the electrocrystallization of metals on platinum, some related research can be found. Hills *et al.*⁷ studied the electrodeposition of single nuclei of Ag, Cu and Hg on Pt ($\phi = 10 \mu\text{m}$) and C ($\phi = 8 \mu\text{m}$) UMEs at low overpotentials. The observed currents were always proportional to $t^{1/2}$, without any apparent maximum. The authors concluded, from microscopic observations, that the crystallites formed were spherical in the case of Hg, and microscopic single crystals in the case of solid metals. The rate constants for nucleation were associated with the inverse of the mean value of the induction time which precedes the birth of each crystallite, and were shown to be directly proportional to the overpotential.

Gunawardena *et al.*⁸ studied the electrodeposition of mercury on vitreous carbon (VC) electrodes in solutions of 1 M KNO_3 with different concentrations of $\text{Hg}_2(\text{NO}_3)_2$. The authors proposed that nucleation is progressive in the initial stages, becoming instantaneous at longer times. The calculation of the number of nuclei on the VC surface as a function of overpotential was a difficult task, leading to a high degree of dispersion in the results. Tsakova *et al.*⁹ studied the influence of organic additives on the nucleation of mercury on platinum. Organic molecules such as different types of polypropyleneglycols, safronic dyes and sulfo-organic aliphatic compounds usually inhibited the formation of nuclei. Chierchie *et al.*¹⁰ investigated the electrochemical nucleation of Cu on palladium, applying the potential step technique. A progressive form of nucleation was found, with the calculated nucleation rate varying from 9.3×10^2 to $2.2 \times 10^4 \text{ cm}^{-2} \text{ s}^{-1}$ with overpotential. Kolb *et al.*¹¹ used *in situ* scanning tunneling microscopy to study the electrodeposition of Cu on Au(111) and Au(100) electrodes. The very initial stages occurred predominantly at surface defects, such as step edges of the substrate surface. An instantaneous mechanism was proposed.

The aim of this work is to study the electrocrystallization of Cu and Hg on Pt UMEs by voltammetric and potentiostatic transients to determine the characteristics of the processes that, in turn, will allow the preparation of surfaces adequate for future studies of the hydrogen evolution reaction.

Experimental

The electrochemical measurements were performed in a Pyrex cell with one compartment and two electrodes, the Pt UME and, unless otherwise mentioned, a saturated calomel electrode as the auxiliary/reference. The UME was constructed by sealing a $40 \mu\text{m}$ Pt wire in a Pyrex glass tube. The electrode surface was polished with 600 grid emery paper until the microdisk was exposed, and then with $0.1 \mu\text{m}$ alumina powder.

The electrolytic solutions were: (a) 0.1 M $\text{CuSO}_4 + 0.5 \text{ M H}_2\text{SO}_4$, and (b) $1.26 \times 10^{-3} \text{ M Hg}(\text{NO}_3)_2 + 0.1 \text{ M KNO}_3$. The reagents were from Merck P.A., and the water was purified by a Milli-Q system from Millipore. The solutions were deaerated with N_2 (White Martins, SS).

The instrumentation used was composed of an EGG & PARC potentiostat-galvanostat model 273 linked to a microcomputer PC-AT 386, with M270 software from EGG & PARC. The surface was periodically observed with an Olympus metallographic microscope.

Results and Discussion

Figure 1 shows cyclic voltammograms for the deposition and redissolution of Cu (1A) and Hg (1B) on Pt at 100 mV/s in the solutions described above. Both curves present the crossing-over of cathodic and anodic branches characteristic of nucleation processes, which are related to

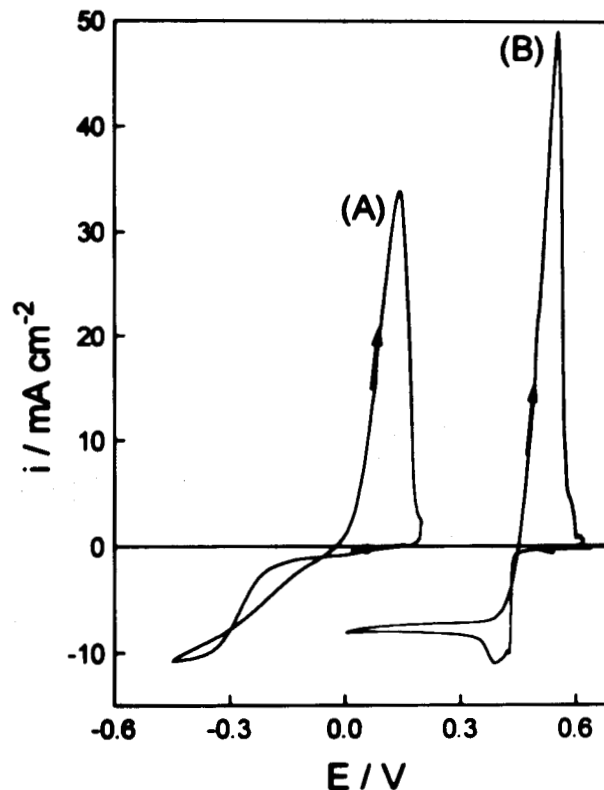


Figure 1. Cyclic voltammograms for Cu (A) and Hg (B) deposition and redissolution on Pt UMEs. $v = 100 \text{ mV/s}$. Electrolytic solutions as indicated in the text.

the increase in the active area of the surface during deposition. The potentials used in the potentiostatic transients were selected from the cathodic sweep in these voltammograms. The best range for Cu deposition is from -0.22 to -0.35 V, while for Hg the potential region is from 0.42 and 0.34 V. Furthermore, the initial potentials for conditioning the surfaces after polishing and prior to deposition were selected to be anodic to the dissolution process, that is, 0.2 V for Cu and 0.6 V for Hg, respectively.

To analyze the nucleation processes detected in the voltammograms of Fig. 1, potentiostatic steps using the potential values given above were performed. The results obtained for Cu are presented in Fig. 2 for different final potentials, as indicated, and the results for Hg are presented in Fig. 3. The shapes of the transients are somewhat particular because: a) not very pronounced maxima are observed, and b) the limiting currents are dependent on the final potentials. The former characteristic can be associated with the small number of nuclei initially formed (to be

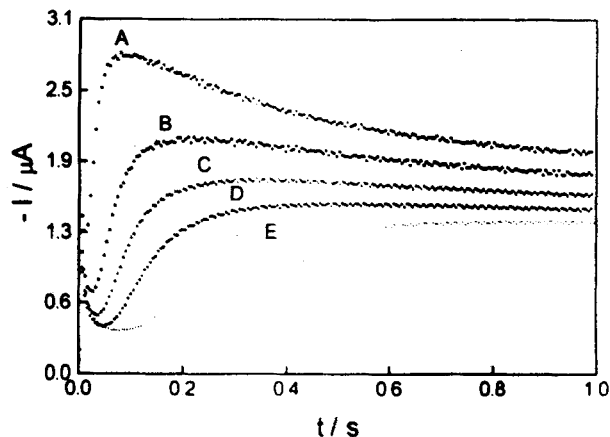


Figure 2. Potentiostatic transients for Cu electrocrystallization on Pt UMEs in 0.1 M CuSO₄ + 0.5 M H₂SO₄ aqueous solution at room temperature. Initial potential = 0.2 V. Final potentials: (A) -0.35, (B) -0.30, (C) -0.27, (D) -0.25, and (E) -0.22 V.

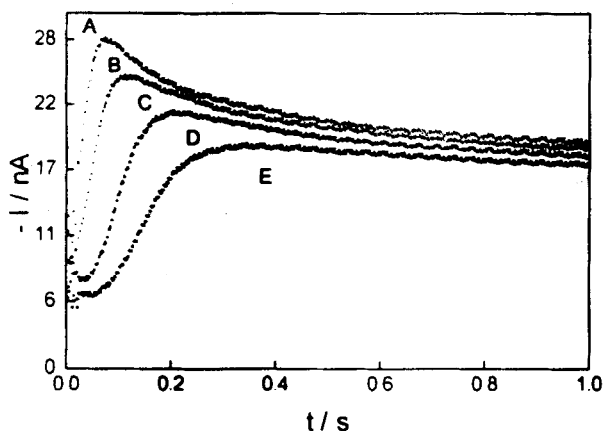


Figure 3. Potentiostatic transients for Hg electrocrystallization on Pt UMEs in 1.26×10^{-3} M Hg(NO₃)₂ + 0.1 M KNO₃ aqueous solution at room temperature. Initial potential = 0.6 V. Final potentials: (A) 0.35, (B) 0.36, (C) 0.38, (D) 0.39, and (E) 0.40 V.

discussed) and with the spherical form of diffusion towards the UME surface, while the latter is related to the variation of the surface area with the number of nuclei formed during the step. This latter effect is much less pronounced in Hg because of the nearly unitary roughness factor of the surface covered with this metal.

Attempts to quantitatively analyze the results using the equations developed for hemispherical growth on conventional size electrodes under diffusion control conditions¹² were unsuccessful. The existing treatment for UMEs⁸ corresponds to situations where very low overpotentials are applied, thus promoting the formation of a single nucleus on the surface. Therefore, it was necessary to develop new equations¹³ for the I-t transients based on the same principles used by Scharifker and Hills¹², but correcting the current with a term that takes spherical diffusion to a microdisk surface into account^{14,15}. The detailed calculation is beyond the scope of this work and will be the subject of a separate publication.

The results of these calculations showed¹³ that for an instantaneous nucleation process occurring on a UME surface the current transient can be described by:

$$I = (4nFDC^\infty r + 8nFc^\infty r^2 D^{1/2} \pi^{-3/2} t^{-1/2}) [1 - \exp(-N\pi kDt)] \quad (1)$$

where I is the current, n the number of electrons, F the Faraday, D the diffusion coefficient, c^∞ the bulk concentration, r the microdisk radius, t the time, N the number of nuclei, and k a constant given by:

$$k = \left(\frac{8\pi c^\infty M}{\rho} \right)^{1/2} \quad (2)$$

with M being the molecular weight of the metal ion and ρ its density.

In the case of progressive nucleation, Eq. 1 becomes:

$$I = (4nFDC^\infty r + 8nFc^\infty r^2 D^{1/2} \pi^{-3/2} t^{-1/2}) [1 - \exp(-0.5AN_\infty \pi k' Dt^2)] \quad (3)$$

where AN_∞ is the rate of nuclei formation and k' is given by:

$$k' = \frac{4}{3} \left(\frac{8\pi c^\infty M}{\rho} \right)^{1/2} \quad (4)$$

Equations 1 and 3 show a single maximum after which the current approaches a limiting diffusional value, but in contrast to conventional relationships, they cannot be easily extrapolated for $t = 0$ or converted into a non-dimensional plot for the analysis of experimental data. To evaluate the results, an iterative procedure was used in which N (or AN_∞) was taken as the variable to adjust the calculated I-t values to the experimental ones. Figures 4 and 5 illustrate such a procedure for the electrocrystallization of Cu at

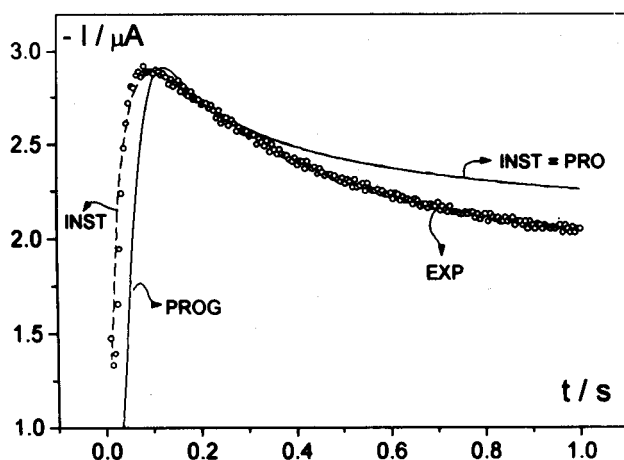


Figure 4. Experimental (o) and calculated transients for instantaneous (dashed line) and progressive (solid line) nucleation processes. The experimental transient refers to Cu at $E = -0.35$ V.

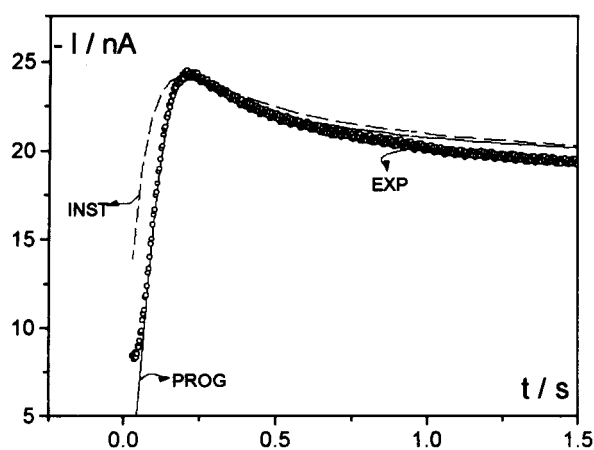


Figure 5. Experimental (o) and calculated transients for instantaneous (dashed line) and progressive (solid line) nucleation processes. The experimental transient refers to Hg at $E = 0.36$ V.

-0.35 V and Hg at 0.36 V, respectively. The fitting is very good in both cases only showing some deviation for long times, for Cu in particular. This may be due to a diminishment in the electrode area after coalescence of the nuclei which is not totally accounted for by Avrami's theorem. The same procedure was applied to all the transients presented in Figs. 2 and 3 and indicates an instantaneous nucleation for Cu and a progressive one for Hg, with the nucleation and growth processes being controlled by diffusion in both cases. The values of N and AN_{∞} obtained for Cu and Hg, respectively, are presented in Table 1.

Another important characteristic of such transients is the values of current and time associated with the maximum. These parameters can be theoretically evaluated by equating the first derivative of the I - t relationships to zero¹³. The results are transcendental equations analogous to those obtained by Gunawardena *et al.*⁸. By determining the zero

Table 1. Potentiostatic transient parameters obtained for the processes of electrocrystallization of Cu and Hg on Pt UMEs.

(A) Cu

E (V vs. SCE)	t_{\max} (s)		I_{\max} (μ A)		$10^{-5} N$ (cm^{-2})
	Exp	Calc	Exp	Calc	
-0.22	0.87	1.14	1.30	1.35	8.8
-0.25	0.56	0.67	1.55	1.59	15.0
-0.27	0.35	0.46	1.77	1.63	21.0
-0.30	0.22	0.19	2.15	2.15	32.0
-0.35	0.10	0.11	2.92	2.83	54.0

(b) Hg

E (V vs. SCE)	t_{\max} (s)		I_{\max} (nA)		$10^{-7} AN_{\infty}$ ($\text{cm}^{-2}\text{s}^{-1}$)
	Exp	Calc	Exp	Calc	
0.40	0.83	0.75	16.0	16.6	1.9
0.39	0.57	0.58	18.0	18.4	3.0
0.38	0.33	0.34	21.0	21.2	8.0
0.36	0.21	0.21	25.0	24.5	20.0
0.35	0.13	0.12	28.0	27.5	55.0

of such functions it is possible to derive the equations below. Thus, for instantaneous nucleation:

$$t_{\max} = \frac{x}{N\pi kD} \quad (5)$$

$$I_{\max} = 4nFDc^{\infty}r(1 - e^{-x})\left[2r\left(\frac{kN}{\pi^2}\right)^{1/2} + 1\right] \quad (6)$$

where x corresponds to the zero of the transcendental equation. For progressive nucleation the equations are:

$$t_{\max} = \left(\frac{x}{AN_{\infty}\pi k'D}\right)^{1/2} \quad (7)$$

$$I_{\max} = 4nFDc^{\infty}r(1 - e^{-x})\left[2r\left(\frac{AN_{\infty}k'}{2D\pi^5x}\right) + 1\right] \quad (8)$$

The values of $D_{\text{Cu}} = 1.56 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ and $D_{\text{Hg}} = 1.04 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ were determined from linear plots of I vs. $t^{1/2}$ obtained from independent potentiostatic experiments on the same systems but involving very cathodic potential steps (-0.4 V for Cu and 0.0 V for Hg) which effectively nucleate the surface, imposing instantaneous spherical diffusion towards the entire electrode surface⁸. With these values and Eqs. 5-8 the parameters for instantaneous (Cu) and progressive (Hg) nucleation at several potentials were calculated, and the results are presented in Table 1. The agreement between experimental and calculated values for I_{\max} and t_{\max} also indicates an instantaneous nucleation for Cu and a progressive one for Hg. The concordance ob-

served in Table 1 between the calculated and experimental values of I_{\max} and t_{\max} is remarkable for all transients which show well-defined current maximum. For those that do not present a maximum, the model becomes less precise and the values less coincident.

An interesting feature of the values presented in Table 1 is the number of nuclei formed on the ultramicroelectrode surface. In the case of Cu nucleation, the minimum number of nuclei per square centimeter was 8.8×10^5 . This value corresponds to a total of 11 nuclei, showing that the present situation is as close to the nucleation of a single nucleus as that studied by Hills *et al.*⁷, thus explaining the lack of a maximum in some of the transients presented in Fig. 2.

Finally, Fig. 6 presents voltammograms of the surfaces modified by Cu and Hg deposition taken in 0.5 M NaOH at 100 mV/s and using a NHE as an auxiliary/reference, after the recording of the more cathodic transients, together with the curve for pure Pt. The alteration of the original shape (curve C), which shows among other things the total inhibition of the H-adsorption peaks on Pt (curves A and B), is a clear indication that the surface coverage of Pt by the deposited metal is complete, thus attending the future objectives of this work.

Conclusions

The results presented here indicate that ultramicroelectrodes have considerable advantages when used as substrates in electrocrystallization studies. The single-maximum current transients obtained were successfully analyzed with equations properly derived for UMEs. For this purpose, a model for diffusion controlled nucleation and three-dimensional growth of hemispheres which, after a given period of time, undergo a process of coalescence forming a continuous surface was used.

Under the present experimental conditions, the electrocrystallization of Cu follows an instantaneous nucleation mechanism, while Hg presents a progressive one, both being controlled by diffusion.

The range of potential steps explored in these experiments was adequate to promote the formation of a relatively small number of nuclei (when compared with those obtained on conventional sized electrodes), thus approaching the conditions for single nucleus deposition and minimizing the interactions between nuclei.

Finally, the voltammograms in NaOH solutions showed that the coverage of the Pt surface with Cu and with Hg is complete at the end of the more cathodic transients.

Acknowledgments

The authors wish to thank the Conselho Nacional de Pesquisa e Desenvolvimento (CNPq) and the Financiadora de Estudos e Projetos (FINEP) for financial support.

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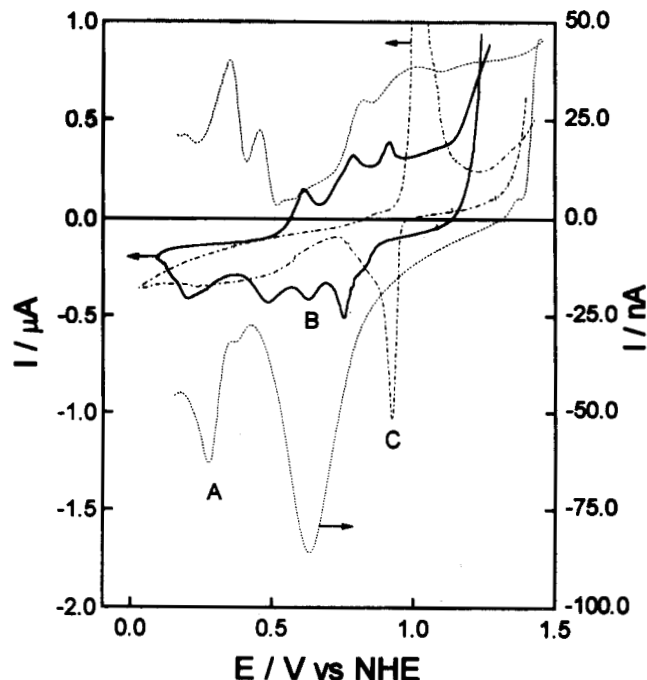


Figure 6. Cyclic voltammograms for the Pt surfaces, smooth (A) and covered with Cu (B) and Hg (C) in 0.5 M NaOH solutions at 100 mV/s. Potentials measured against NHE.

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