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Influence of Chloride and Nitrate Anions on Copper Electrodeposition in Ammonia Media

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Copper electrodeposition onto a glassy carbon electrode (GCE) was investigated using linear sweep voltammetry and a potential step technique in 5×10^{-2} M $Cu(NH_3)_4{}^{2+}$, 1 M NH_3 and pH 10.5, in the presence of chloride and nitrate anions. Voltammetric analysis showed that copper electrodeposition is carried out in two steps. The first step corresponds to $Cu(NH_3)_4{}^{2+}/Cu(NH_3)_2{}^{+}$ couple managed by diffusion control, whereas in the second, the reduction of $Cu(NH_3)_{2+}$ to Cu(0) is influenced by Cl^- and $NO_3{}^-$ anions. In the case of chloride and chloride and nitrate baths, it may be observed that only 40-60% of deposited copper is oxidized in the reverse potential sweep; these low charge recoveries are due to an disproportionation stage: the newly deposited copper reacts with the Cu(II) present in the reaction layer to form Cu(I). For baths containing only nitrates, the efficacy of charge recovery is even smaller (20%) due to an interaction between newly deposited copper and nitrate ions that could include a direct redox reaction and/or nitrate reduction on the surface of copper nuclei, this reaction provokes an additional dissolution of copper nuclei. The presence of chlorides in nitrate-containing baths seems to block said interaction between nitrates and newly deposited copper. Through the analysis of current transients, copper electrocrystallization on GCE is shown to be performed by means of a three-dimensional nucleation growth diffusion-limited mechanism in the presence of the three electrolytes studied here. However, the presence of anions directly influences the magnitude and dependence of kinetic parameters of copper electrocrystallization with the applied potential.
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The use of electrodeposition in the preparation of new materials with specific characteristics (thin layers, dispersed materials, nanostructures) requires deep comprehension of different phases of the electrodeposition process. Nucleation kinetics and the growth of the first metallic nuclei formed on the initial substrate are critical steps which determine the physicochemical properties of the electrodeposited materials[1] and are, therefore, crucial points for understanding and control. Electrochemical characterization of the nucleation process is generally performed by collecting different forms of current transients obtained when pulses are imposed on the substrate/electrolyte interface.[2] Recent studies have suggested that our understanding of the chemical and electrochemical reactions associated with the electrocrystallization process is still incomplete.[3]

Our research group has previously reported studies on complex cases of electrocrystallization for silver electrodeposition from two alternative noncyanide electrolyte baths. An important adsorption of electroactive species has been observed in an ethylamine aqueous medium.[4] On the other hand, the mechanism of nucleation and growth of the silver nuclei deposited from ammonia media depends on the chemical composition of the electrolytic bath.[5-7]

The influence of metallic ion concentration and pH effect on copper electrodeposition[8] has also been studied; however, it was established that the predominant chemical form of the electroactive species involved in the reduction process influences the type of nucleation.[8,9] Studies with cobalt[10] showed that the modification in the sphere of coordination of cobalt complexes also produces changes in the cobalt electrocrystallization mechanism. These changes are related to the nature of the ligand. In the gold electrodeposition in ammonia media it has been observed that temperature influences different mechanisms of nucleation.[11] The influence of substrate treatment on electrocrystallization has been investigated as well.[12,13] Likewise, it was possible to determine the influence of simultaneous reactions occurring in the electrocrystallization process, such as hydrogen evolution and catalytic reactions of the newly formed deposition. In particular, catalytic reactions of anions present in the solution with newly formed metal deposit modify deposition conditions and characteristics as shown in the case of cobalt.[14] In this respect, we have established the importance of studying the influence of chloride and nitrate anions present in the deposition bath containing 1 M NH_3 at 10.5 pH on the copper electrocrystallization mechanism. In these baths, we have selected such operating conditions as to make the sphere of Cu(II) coordination the same ($Cu(NH_3)_4{}^{2+}$) in the three baths studied.

Experimental

Electrochemical studies were made in a typical three-electrode cell. Hg/HgO/KOH was used as a reference electrode, specially recommended for basic media; the contact with the working solution was made through a Luggin capillary. The electrode used had the experimental potential of 0.213 V *vs.* normal hydrogen electrode (NHE). As an auxiliary electrode, we used a graphite rod introduced into a separate porous-glass compartment. As a working electrode, we used a glassy carbon (GC) disk electrode with an area of 0.16 cm^2. The exposed surface was polished by Microcloth (Buehler) to a mirror finish with alumina powders down to 5 μm and treated in an ultrasonic bath with pure water for 10 min. Three different media were treated at 5×10^{-2} 1 M $Cu(NH_3)_4{}^{2+}$ and 1 M NH_3. All solutions were prepared from analytical grade reagents using ultrapure Millipore-Q water (Millipore-Q system). The first bath contained 1 M NaCl; the second, 1 M $NaNO_3$ and 1 M NaCl; whereas the third contained only 1 M $NaNO_3$. The pH used was 10.5, regulated with NaOH or HNO_3 in the case of nitrates, or with HCl in the case of chlorides.

The electrochemical techniques used were voltammetry and chronamperometry. Electrode potentials were controlled with an EG&G PARC 273A potentiostat connected to a microcomputer with EG&G M270 software. The voltammetry was performed at a potential interval of 400 to −900 mV *vs.* Hg/HgO and at sweep rates of 5, 20, and 100 mV/s, for the three systems mentioned above. The chronamperometry was performed using potential pulses within an interval of 600 to −1000 mV *vs.* Hg/HgO. All experiments were made with an initial oxygen purge using a N_2 current and N_2 bub-

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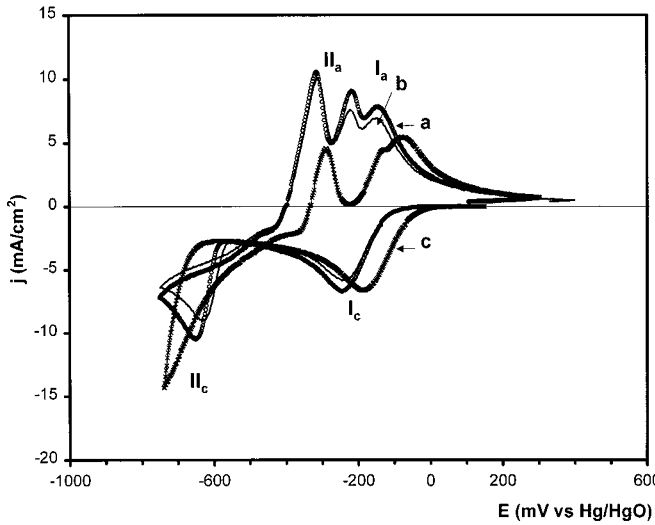

Figure 1. Typical CVs for copper deposition obtained on GCE, from 5×10^{-2} M $Cu(NH_3)_4^{2+}$, 1 M NH_3, pH 10.5, with different anions present in the deposition bath: (a) 1 M chloride, (b) 1 M chloride and 1 M nitrate (c) 1 M nitrate. Scan rate: 20 mV/s. All anions were supplied as sodium salts.

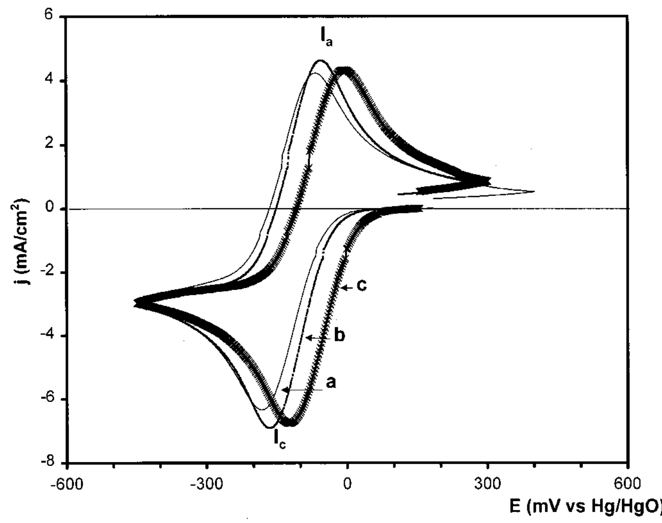

Figure 2. Typical CVs for copper deposition obtained on GCE, from 5×10^{-2} M $Cu(NH_3)_4^{2+}$, 1 M NH_3, pH 10.5, with different anions present in the deposition bath (a) 1 M chloride, (b) 1 M chloride and 1 M nitrate, (c) 1 M nitrate. The negative potential scan was inverted before the Cu(I) reduction. Scan rate: 20 mV/s. All anions were supplied as sodium salts.

bling was maintained during the whole experiment.

Results and Discussion

This paper describes a study of initial Cu deposition states in different alkaline media in the presence of ammonia and different anions such as Cl^- and NO_3^- on a GC disk. The stability constant of copper with ammonia[15] allows the latter to be used as a complexation agent and determines the coordination sphere of Cu soluble in the electrolytic system. In the experimental baths used here (1 M NH_3, pH 10.5 and Cu(II) 5×10^{-2} M) the predominant chemical species of copper[9] are $Cu(NH_3)_4^{2+}$ for Cu(II), and $Cu(NH_3)_2^+$ for Cu(I). It is important to note that neither the presence of 1 M NO_3^- nor that of Cl^-, modifies these predominant chemical species. A detailed study of the above can be found in Nila and González.[9]

Voltammetric study.—Figure 1 shows the typical cyclic voltammograms (CVs) obtained on the GC electrode (GCE) for $Cu(NH3)_4^{2+}$ reduction in different electrolytes. Generally, in the reduction region of the three media two important cathodic processes are observed, indicated by $\mathbf{I_c}$ and $\mathbf{II_c}$. The first process, $\mathbf{I_c}$, is the one corresponding to $Cu(NH3)_43^{2+}$ reduction toward $Cu(NH_3)_2^+$, Reaction 1. It may be observed that the three systems have very similar behaviors, although in the experiment with nitrate media, the peak of the cathodic reduction is found to be at slightly less negative potentials.

The second reduction process, $\mathbf{II_c}$, corresponds to the $Cu(NH_3)_2^+$ reduction to Cu(0), Reaction 2. These voltammograms display characteristic features of nucleation phenomena, namely, large peak separation and crossover on the cathodic branches, due to the presence of nucleation and growth processes.[16] A well-defined reduction peak may be seen in the systems with the presence of chlorides (chloride, and chloride and nitrate, Fig. 1a, b). However, in the experiment in nitrate-containing medium (Fig. 1c), the well-defined reduction peak is not observed, but on the contrary, with the potential varying toward more negative values, the current keeps growing

$$Cu(NH_3)_4^{2+} + 1e = Cu(NH_3)_2^+ + 2NH_3$$

$$E = E^0 + 0.06 \log[Cu(NH_3)_4^{2+}]/[Cu(NH_3)_2^+][NH_3]^2$$
$$= -0.173 \text{ V } vs. \text{ Hg/HgO} \quad [1]$$

$$Cu(NH_3)_2^+ + 1e = Cu^0 + 2NH_3$$

$$E = E^0 + 0.06 \log[Cu(NH_3)_2^+]/[NH_3]^2$$
$$= -0.403 \text{ V } vs. \text{ Hg/HgO} \quad [2]$$

Voltammetric behaviors such as those observed in Fig. 1c for nitrates are related to an additional supply of electroactive species on the reduction process. This behavior is typically associated with catalytic reactions. In the case of Co reduction, a secondary chemical reaction with nitrates[14] has been observed in the same way that it may be occurring in our case of copper reduction.

The potentials (E) of Eq. 1 and 2 are calculated from the values reported for E^0 [8,17,18] also taking into consideration the experimental conditions of the solution. In a chemical speciation study, we have shown that in the presence of 1 M nitrates and 1 M chlorides, the Cu and ammonia complexes are not modified in their sphere of coordination to basic pHs, thus preventing the formation of chlorocomplexes.

If the potential is reversed after reducing Cu(II) and before reducing Cu(I), only one oxidation peak appears (Fig. 2). The half-wave potential ($E_{1/2}$) is evaluated as a half sum of the cathodic peak potential (E_{pc}) and the anodic peak potential (E_{pa}) for the peaks shown in Fig. 2. The values of $E_{1/2}$ within the experimental interval do not vary considerably, thus indicating that the electroactive species are the same in the three electrolytes. On the other hand, these values are also similar to the thermodynamic equilibrium potential associated with the passage of Cu(II)/Cu(I) for Eq. 1, thereby indicating that in said experimental conditions, the sphere of Cu(II) coordination with NH_3 does not change; furthermore, these values appear, in all cases, as the ammonia complexes described in Eq. 1, in such a way that Cl^- and NO_3^- anions added to the baths always behave as supporting electrolytes. The modification of E_{pc} in these processes in the presence of nitrates, may be due to charge transfer rate changes probably associated with the modification of the GCE/electrolyte interphase. However, this is not the objective of this work.

In the region of anodic current in Fig. 1 different oxidation processes showing a great complexity are observed: production of hydroxides, oxides, and/or chlorides that may be adsorbed or forming soluble species. These anodic processes, peaks $\mathbf{I_a}$ and $\mathbf{II_a}$ in Fig. 1, may be related as corresponding systems to the reductions $\mathbf{I_c}$ and $\mathbf{II_c}$. It has been proposed that at this pH (around 10.5), three oxida-

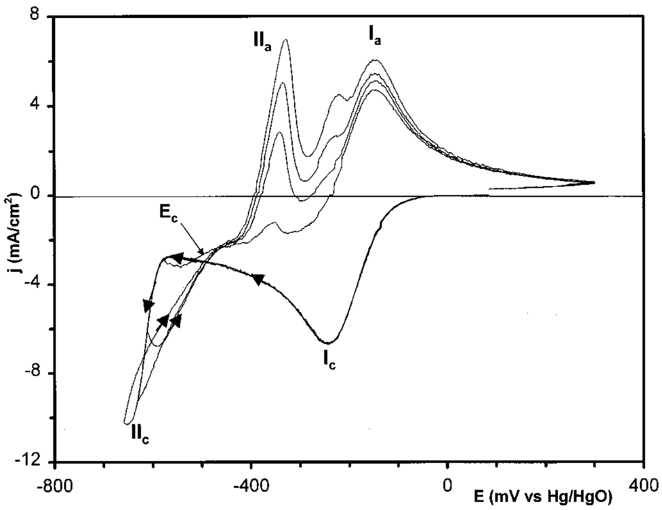

Figure 3. Typical set of voltammograms obtained for different negative switching potentials $E_{-\lambda}$, at a scan rate of 20 mV s^{-} for copper deposition onto GCE, from 5×10^{-2} M $Cu(NH_3)_4^{2-}$, 1 M NH_3, pH 10.5, in 1 M NaCl.

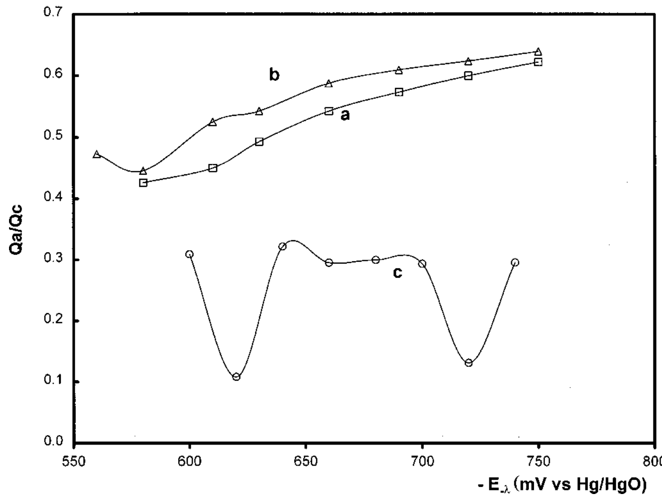

Figure 4. Relationship between the charge associated with anodic (Q_a) and cathodic (Q_c) branches for copper voltammetric deposition and different switching potentials ($E_{-\lambda}$) obtained from the system: 5×10^{-2} M $Cu(NH_3)_4^{2+}$, 1 M NH_3, pH 10.5, with different anions: (a) 1 M chloride, (b) 1 M chloride and 1 M nitrate, (c) 1 M nitrate.

tion peaks are observed for one medium with 1 M NH_4Cl. Since the copper appears to have reversible behavior when inverting the potential sweep in the first reduction peak (Fig. 2), the oxidation of newly deposited Cu(0) produces at least two oxidation peaks. It can be explained as follows: the oxidation of Cu(0) at the interface is not limited by diffusion, so a high concentration of Cu(I) appears at the interface and Cu_2O or CuCl is formed.[8]

With the purpose of ensuring diffusion control conditions, we performed a study with a rotating disk to analyze the process of $Cu(NH_3)_4^{2+}/Cu(NH_3)_2^{+}$. A constant potential of -0.4 V *vs.* Hg/HgO was fixed for 10 s, then the potential was inverted to a value of 0.6 V for 10 s as well. This program of potential is applied to different rotation rates (ω) of the electrode for the three different electrolytes. The reduction density current (j) is measured at 10 s and it varies linearly with $\omega^{1/2}$, in a typical diffusion control of the current. The diffusion coefficients of the order of 6×10^{-6} cm^2/s, obtained for the three systems, are very similar among each other reported in the literature.[19]

In the case of a Cu(I)/Cu(0) system, the experiment is carried out at a reduction potential of -0.75 *V vs.* Hg/HgO. For chloride, and chloride and nitrate baths, the relations of (j) *vs.* $\omega^{1/2}$ are linear and correspond to a diffusion control; however, for a nitrate-containing system this linear behavior is not observed, and this different behavior suggests a coupled chemical reaction.

Influence of the switching potentials ($E_{-\lambda}$).—The study focuses on the second reduction region where the electrocrystallization occurs. In order to determine the type of kinetic control which is taking place during the growth of nuclei, a voltammetric study using different switching potentials ($E_{-\lambda}$) was carried out. The analysis was limited in the potential region at the cathodic deposition peak $\mathbf{II_c}$ on GCE. Figure 3 shows a typical set of the obtained voltammograms using different switching cathodic potentials $E_{-\lambda}$, at a scan rate of 20 mV s^{-1}. In this figure, the overcrossing potential (E_c) was indicated.

The overcrossing potential remains constant at approximately -500 mV *vs.* Hg/HgO for the case of chloride, and chloride and nitrate solutions, regardless of the change of E_{λ}, indicating, according to Fletcher,[16] charge transfer control during the copper electrocrystallization process. Fletcher[16] proposed that for this type of control, E_c values should correspond to the reversible potential (E') of the metal redox couple $Cu(NH_3)_2^{+}/Cu^0$ which is theoretically equivalent to -403 mV *vs.* Hg/HgO (Eq. 2). In a previous[8] study we have shown that E_c values are quite close to the thermodynamic E' values (differences of 20 mV at most) when analyzing the Cu reduction in ammonia media at acid pH: we have also found differences of the order of 100 mV when the deposition is made in basic media. The difference in experimental potential might be due to the fact that in basic media of pH 10.5 some chloride and hydroxide precipitates would appear in the interphase. Given these conditions we may say that there is an acceptable correlation between E_c and E', and that Reaction 2 describes metallic copper formation. On the other hand, in the case of a nitrate/solution system, the E_c varies considerably with $E_{-\lambda}$, so it is not possible to associate it with thermodynamic potential.

Charges due to the cathodic (Q_c) and anodic (Q_a) processes can be obtained by integrating the cathodic and anodic branches of the $I - E_{-\lambda}$ curves, respectively. Figure 4 shows plots of the Q_a/Q_c ratio as a function of $E_{-\lambda}$ for copper deposition from different solutions considered. It should be noted that these recoveries are low (40 to 60%) for the systems containing chlorides, and chlorides and nitrates (Fig. 4a-b), but they are even lower for systems containing only nitrates (Fig. 4c). Generally, when only metal deposition is present in several stages, that is, through successive charge transfers, these low recoveries are due to a reaction of disproportionation,[20] which would, in this case, be the following reaction

$$Cu(NH_3)_4^{2+} + Cu(0) = 2Cu(NH_3)_2^{+} \qquad [3]$$

It is important to emphasize that the influence of this disproportionation reaction on the metal deposition stability has scarcely been mentioned, since there is a general tendency to analyze cases with no intermediate species between the metallic ion to deposit and the deposited metal, as in the case of Ag(I)/Ag(0), Au(I)/Au(Au(0), or the Cu(II)/Cu(0) system itself where Cu(I) is not stable, *e.g.*, in sulfuric acid media.

Therefore, low charge recoveries observed in the medium containing nitrate solution indicate an additional or different contribution from that of disproportionation that could be explained in terms of some process coupled to the cathodic reaction. In other words, this evidence supports the simultaneous presence of another cathodic process (that may consume electrons or recently deposited copper) besides copper reduction. The main characteristic of this second process is that its charge transfer product cannot undergo oxidation during an anodic scan. It is likely that an interaction between newly deposited copper and nitrate ions in solution might be taking place. This interaction seems to be prevented by the presence of chloride anions. It may also include a direct redox reaction and/or nitrate reduction on the surface of the copper nuclei. The former reaction would consume the copper deposit, and the latter would provide electrons to the external circuit. Jointly or separately, these reactions explain the low copper recovery efficiency for a nitrate bath.

In a solution containing only nitrates, the following mechanism of copper deposition may be proposed according to the following faradic reactions (4, 5, 6)

$$Cu(NH_3)_{2(aq)}{}^{+} + 1e^{-}(GCE) = Cu/GCE + 2NH_3 \qquad [4]$$

$$2NH_{3(aq)} + Cu(0)/GCE = Cu(NH_3)_{2(aq)}{}^{+} + 2e^{-}(Cu) \qquad [5]$$

Considering Reaction 5, we propose simultaneous nitrate reduction during the cathodic process according to the following reaction

$$6H_2O_1 + NO_{3(aq)}{}^{-} + 8e^{-}(Cu) = NH_{3(aq)} + 9\ OH_{(aq)}{}^{-} \qquad [6]$$

The proposed Reactions 5 and 6 are based on the solution pH and thermodynamic diagrams of predominant nitrogen species.[17] The direct catalytic reaction of $NO_3{}^{-}$ to NH_3 has been reported for the case of Tl reduction in nitrate-containing media.[21]

Note that the addition of chlorides to nitrate baths somehow prevents this catalytic reaction. Probably, a specific adsorption of chlorides on GCE or on newly deposited copper atoms may be the cause. This hypothesis requires a more profound analysis. Chronamperometry studies are shown here with the aim of demonstrating the influence of solution anions on the nucleation and growth in the process of Cu electrocrystallization.

Potential step study.—Figure 5 shows current transient curves for all three systems representing the region corresponding to copper electrocrystallization. It is important to emphasize that the imposed potential pulses are found in the region of greater negative potentials than those corresponding to the reduction of $Cu(NH_3)_4{}^{2+}$ to $Cu(NH_3)_2{}^{+}$ (Fig. 1). For the system containing only nitrates, the potentials applied were far more negative.

In all cases, the first sudden change of current is attributed to the double layer charge and immediately afterward, the typical response of nucleation and growth takes place. As for the case of chloride media (Fig. 5a and b), there is an increase of current reaching its maximum, followed by a slow decrease that ends in a constant state above zero current. This is a typical behavior of three-dimensional (3-D) nucleation diffusion-limited growth.[22,23] On the other hand, Fig. 5c, where only nitrates are present, also shows a maximum current, followed by a decrease toward different currents in accordance with the potentials applied. These different currents may be the consequence of the presence of a nitrate chemical reaction. For the purposes of identification of the electrocrystallization process we apply the theoretical model corresponding to 3-D nucleation-growth proposed by Scharifker and Hills.[22]

Figure 6 shows the comparison, in nondimensional coordinates,[22] of experimental transients with the corresponding theoretical plots for extreme cases (instantaneous and progressive) of 3-D nucleation growth diffusion-limited cases. It may be observed that the nondimensional experimental transients range within the interval delimited by instantaneous and progressive nucleation. As for the solution containing only nitrates, it may be seen that at times threefold greater than t_{max}, experimental curves go beyond the domain of 3-D growth.

Once the theoretical model satisfactorily describes the entire transient, the relevant information about the kinetic parameter can be obtained from the current and the time corresponding to the potentiostatic maximum. As an alterative method, Sharifker's general equation[23] (Eq. 7) for time evolution of the current density via the 3-D nucleation with growth limited by diffusion was used. This

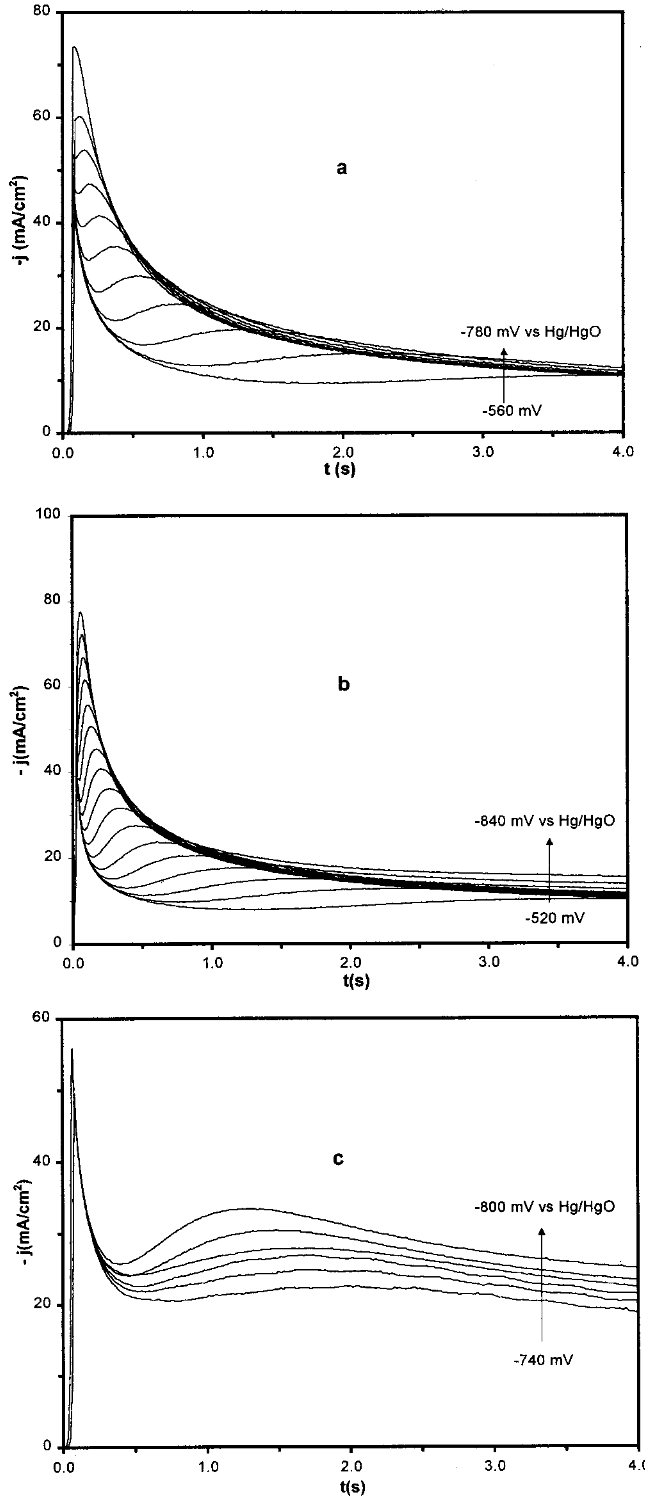

Figure 5. Experimental current transients obtained on GCE, in 5×10^{-2} M $Cu(NH_3)_4{}^{2+}$, 1 M NH_3, pH 10.5 deposition bath, with different anions: (a) 1 M chloride, (b) 1 M chloride and 1 M nitrate, (c) 1 M nitrate. In each case, different potential ranges were imposed to GC electrode, these ranges are marked on figure.

equation is also valid for describing instantaneous and progressive nucleation and does not require classification of the nucleation mechanism prior to its use

$$I(t) = \frac{zFD^{1/2}C}{\pi^{1/3}t^{1/2}}\left[1 - \exp\left(-N_o\pi\kappa D\left[t - \frac{1 - \exp(-At)}{A}\right]\right)\right] \qquad [7]$$

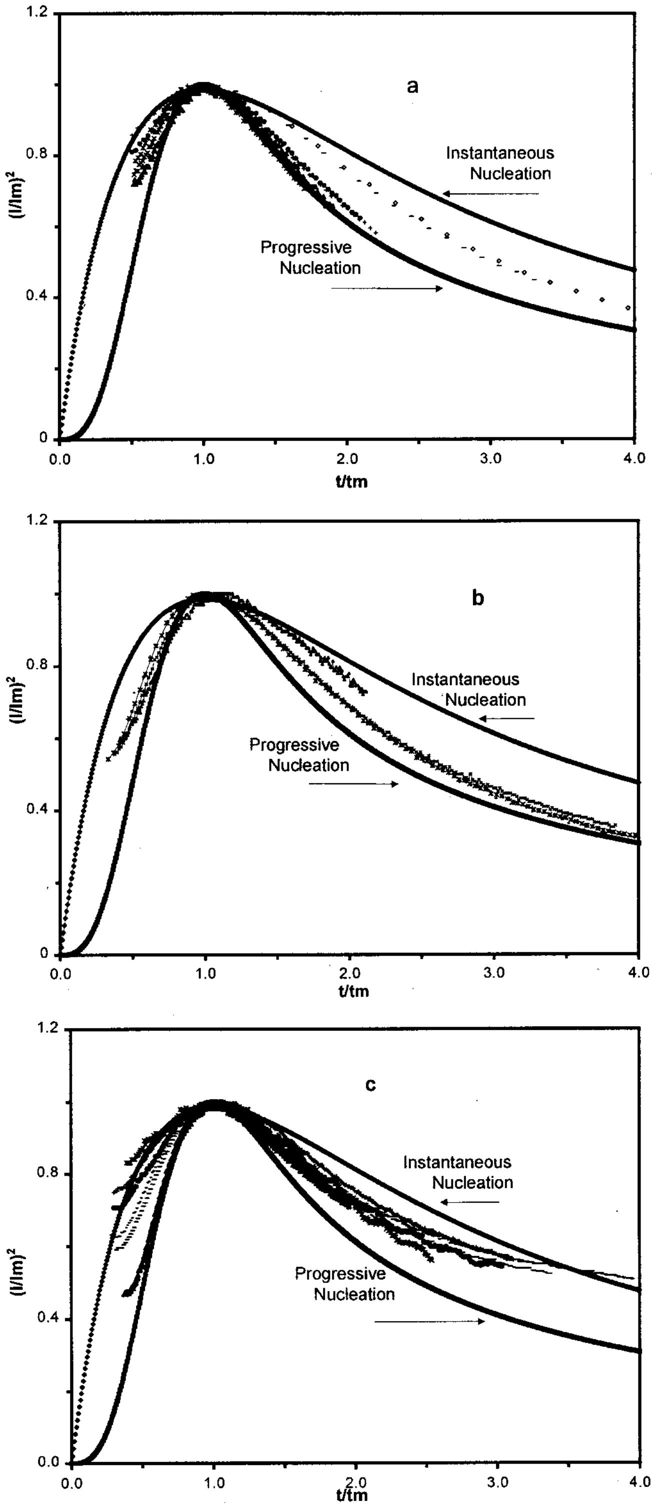

Figure 6. Comparison of theoretical nondimensional plots $(I/I_m)^2$ *vs.* t/t_m, for instantaneous and progressive nucleation (calculated according to the Scharifker[22] model for 3-D growth) with experimental data corresponding to Fig. 5. Deposition was carried out from 5×10^{-2} M $Cu(NH_3)_4^{2+}$, 1 M NH_3, pH 10.5, with different anions: (a) 1 M chloride, (b) 1 M chloride and 1 M nitrate, (c) 1 M nitrate.

Where the number density of active sites is N_o, the nucleation rate constant is A, the diffusion coefficient is D, the concentration is C, the time is t, z is the equivalent number, F is Faraday constant, and Eq. 8 defines κ

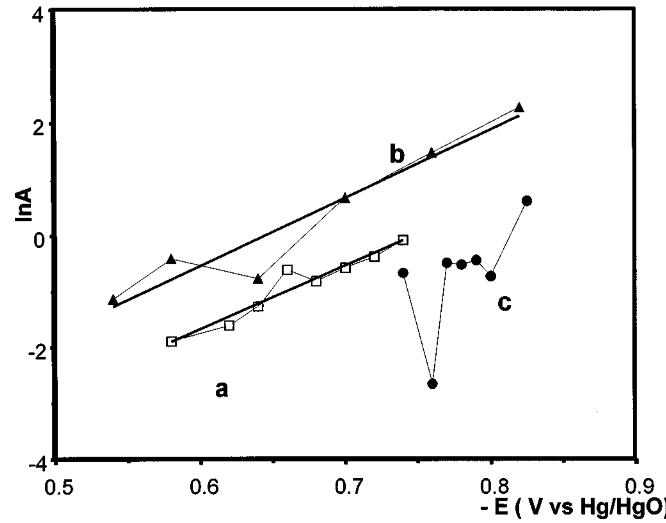

Figure 7. Dependence of nucleation rate (A) with applied potential for copper electrocrystallization onto GCE from 5×10^{-2} M $Cu(NH_3)_4^{2+}$, 1 M NH_3, pH 10.5, with different anions present in the deposition bath: (a) 1 M chloride, (b) 1 M chloride and 1 M nitrate, (c) 1 M nitrate.

$$\kappa = \frac{4}{3}\left[\frac{8\pi CM}{\rho}\right]^{1/2} \quad [8]$$

M and ρ are atomic weight and density deposited material, respectively. The saturation number density of the formed copper N_s was calculated using Eq. 9

$$N_s = (AN_o/2\kappa D)^{1/2} \quad [9]$$

The experimental data were adjusted by the nonlinear fitting equation, using the EQ001 program furnished by Scharifker and Mostany.[23] From this procedure, we have obtained the N_o, N_s, and A values for the copper electrocrystallization as function of applied potential from different electrolyte solutions.

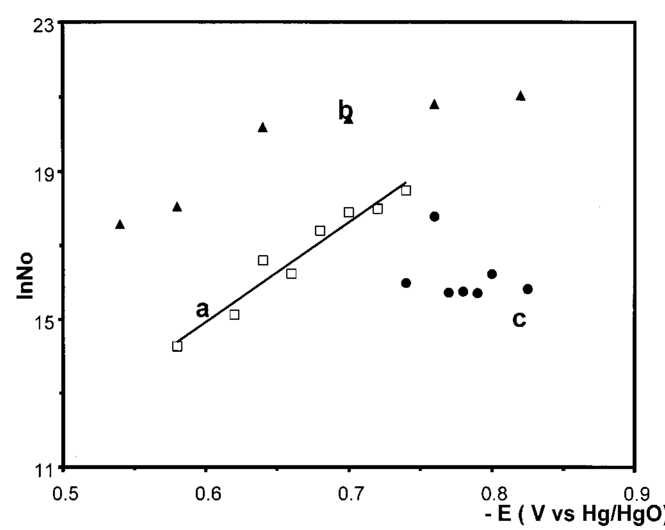

Figure 8. Dependence of number density of active sites (N_o) with applied potential for copper electrocrystallization onto GCE from 5×10^{-2} M $Cu(NH_3)_4^{2+}$, 1 M NH_3, pH 10.5, with different anions present in the deposition bath: (a) 1 M chloride, (b) 1 M chloride and 1 M nitrate, (c) 1 M nitrate.

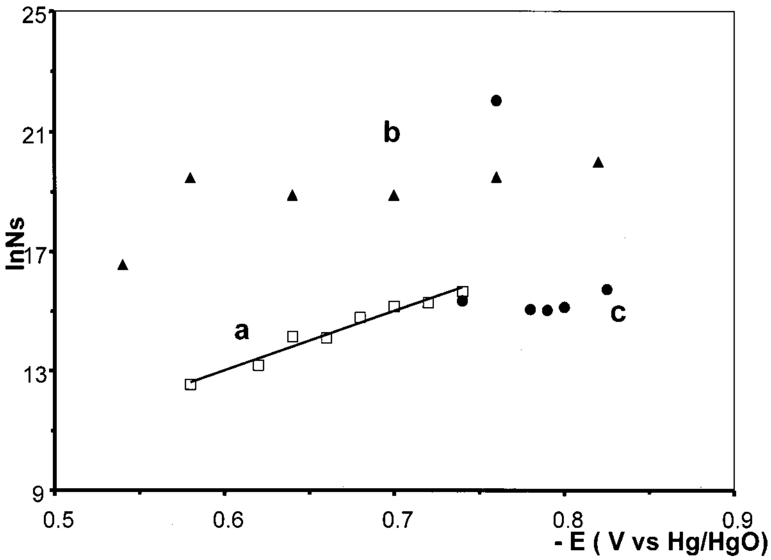

Figure 9. Dependence of number density of the formed copper nuclei (N_s) with applied potential for copper electrocrystallizatin onto GCE from 5×10^{-2} M $Cu(NH_3)_4^{2+}$, 1 M NH_3, pH 10.5, with different anions present in the deposition bath: (a) 1 M chloride, (b) 1 M chloride and 1 M nitrate, (c) 1 M nitrate.

In the case where the deposition is made in the presence of chloride, kinetic parameters of nucleation increase as the potential becomes more negative nucleation rate A (Fig. 7a) and the number of formed and active sites N_o and N_s, respectively (Fig. 8a and 9a) increase exponentially with the potential, thus complying with the theory of 3-D nucleation growth diffusion-control.[23,24] When there is chloride and nitrate in solution it is no longer possible to consider exponential increase (Fig. 7b, 8b, and 9b), probably because of the competition among ions, namely, chloride's tendency to get adsorbed on the GCE surface or on the newly deposited copper nuclei, and the competence of secondary reaction of nitrates with copper.

Likewise, another important fact is the magnitude of kinetic parameters in which the presence of nitrates and chlorides allows both N_o and N_s to increase considerably. On the other hand, for the case in which the deposition is made in the presence of $NaNO_3$, N_o and N_s vary chaotically with applied potential (Fig. 8c and 9c), indicating the existence of a reaction in addition to the 3-D nucleation mechanism in the Cu electrocrystallization process. This will also be corroborated by the fact that at high potentiostatic pulse times, the associated currents go beyond the two extreme cases of nucleation (Fig. 6c). Moreover, in the voltammetric study, the same Cu deposition behavior is detected to be different from the other media. Said behavior might be attributed to the presence of a coupled reaction between newly deposited copper and NO_3^- in solution.[14]

Conclusions

The voltammetry study shows the anions influence on the reduction process of $Cu(NH_3)_4^{2+}$ on the GCE. In these voltammograms, two reduction stages (reaction 1 and reaction 2) are made evident. Reaction 1 is controlled by diffusion in all baths studied, and the thermodynamic potential could have been associated with the half-wave potential ($E_{1/2}$). Under the conditions of the experiment, the predominant species was that of copper ammonia complex, $Cu(NH_3)_4^{2+}$ and $Cu(NH_3)_2^{+}$, so that the anions's only function is that of supporting electrolyte.

Upon imposing different switching potentials ($E_{-\lambda}$) in the study, thermodynamic potentials associated with overcrossing potential for experiments were observed for chloride, and chloride and nitrate baths; this was not the case of the baths with nitrates alone. A low charge recovery (Q_a/Q_c) was also observed probably due to the presence of a successive electron transfer system in which a copper disproportionation process takes place. Lower charge recoveries associated with the nitrate bath as well as the reduction process without the appearance of a voltammetry defined peak, call to mind a secondary chemical reaction or one coupled with the copper electrocrystallization. According to the reports in literature, we have proposed that the nitrates present in solution oxidize the newly deposited copper. The presence of chlorides in the nitrate bath seems to diminish this reaction considerably.

As a result of the chronoamperometry study, it was possible to determine that in the presence of $NaNO_3$, copper electrocrystallization probably follows a 3-D nucleation diffusion-limited growth mechanism, which is modified by the appearance of a simultaneous reaction, possibly one between nitrates and newly deposited Cu. The chaotic behavior of kinetic parameters A, N_o, and N_s, depending on the potential applied, supports this assumption. In the case of a chloride bath, there is also a 3-D nucleation diffusion-limited growth mechanism; the kinetic parameters have an exponential behavior depending on the potential applied, and their values are of lesser magnitude. The aforementioned is probably a result of an adsorption of chlorides on the GCE or of the newly deposited Cu nuclei. The addition of NaCl to the nitrate bath inhibits the secondary reaction described above, just as nitrates can inhibit the chloride adsorption. The magnitude of kinetic parameters and their tendency in accordance with the applied potential show this conjugated effect. Thus, Cu electrocrystallization in the nitrate and chloride bath follows a nucleation that approximates progressive 3-D nucleation diffusion-limited growth mechanism more closely.

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