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Effect of Potential on the Early Stages of Nucleation and Growth during Silver Electrocrystallization in Ammonium Medium on Vitreous Carbon

Margarita Miranda-Hernández^{a,*,z} and Ignacio González^{b,*}

^aCoordinación de Superficies, Interfaces y Materiales Compuestos, Departamento Materiales Solares, Centro de Investigación en Energía-UNAM, Temixco, Mor 62580, México
 ^bDepartamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, 09340 México, D. F., México

In this work, a systemic study of silver electrocrystallization process was performed on a vitreous carbon (VC) electrode in a medium of 1.6 M NH₃, 1 KNO₃ at pH 11. The analysis of current transients, using different theoretical models, shows that the systematic evolution of electrocrystallization process is observable through the gradual modification of energetic conditions of the interface by either changing the concentration of electroactive species $[10^{-4} \text{ to } 0.1 \text{ M Ag}(\text{NH}_3)_2^+]$ or the potential imposed to the electrode. At low concentrations of electroactive species ($\leq 10^{-3}$ M) and not so negative potentials, 2D-2D growth of silver may be observed forming deposits less than the monolayer coverage. At more negative potentials 2D-3D growths are obtained. In this type of transition, two kinds of silver growth sites are identifiable, first on the VC and afterward, on the recently deposited silver. At concentrations $\geq 10^{-2}$ M and less negative potentials, 3D growth of nuclei can be seen, forming deposits far beyond a monolayer. Their growth is influenced by either diffusion of Ag(NH₃)₂⁺ or the incorporation of silver adatoms into the substrate lattice, depending on the conditions of imposed potential. At concentrations $\geq 10^{-1}$ M and very negative potentials, where the deposited silver. It is worth noting that this is the first time, that in the same chemical system, the systematic evolution of electrocrystallization of 2D and 3D stages of nuclei growth on heterogeneous VC surfaces can be observed, through the gradual modification of electroactive species or the potential imposed to the electrode.

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In general, electrocrystallization studies reported in the literature are performed at small intervals of applied potential and therefore take into account only one type of nucleation and growth in the current-transient response analysis. This type generally fits the model of three-dimensional (3D) growth limited by diffusion of the electroactive species proposed by Scharifker and Hills.¹⁻⁹ In the case of a complex response of current transients (presence of more than one current maximum), these are not quantitatively analyzed¹⁰ or the studies investigating that kind of response are very few^{11,12} and only show the effect of the electroactive species concentration in nucleation and growth stages at small intervals of applied potential. In these studies, other models¹³⁻¹⁸ associating transient responses with simple or multiple growths (growth transitions) are used. These models describe two-dimensional (2D) or 3D growths that comprise different limiting stages, such as adatoms incorporation into substrate lattice. Another study¹⁹ shows a methodology for quantitative analysis of experimental current transients that display complex shapes.

The aim of this work is to show that after modifying energetic conditions of the electrode/electrolyte interface, it is possible to describe the evolution of electrocrystallization process (nucleation and growth changes). It is demonstrated that transient responses may be analyzed by applying different theoretical models without the limitation of a single model commonly reported in the literature.^{1-10,20-22}

It is well known that the initial stages of the nucleation are determined by substrate surface properties: Step edges, defects, and inhomogeneities. The influence of surface properties on the electrode of vitreous carbon (VC) in ammonia medium has been described previously^{11,12,23} therefore that effect is not discussed in this paper. This work associates the quantity of monolayers formed on the substrate with the type of growth analyzed. Hence its importance, because to our knowledge, there are no similar results reported in the literature. The study was carried out using a VC electrode and ammonium baths with different concentrations of

^z E-mail: mmh@cie.unam.mx

electroactive species, from very dilute to the concentrated (10^{-4} to 0.1 M). For each system, potential pulses were applied in a wide range (-0.03 to -0.7 V vs. standard calomel electrode, SCE).

Experimental

The studies were carried out in a typical three-electrode cell consisting of a SCE as reference, a graphite bar as auxiliary electrode and VC disc with 0.071 cm² area as working electrode. The system was $x \operatorname{Ag}(\operatorname{NH}_3)^+/1.6 \operatorname{M} \operatorname{NH}_3$, 1 M KNO₃ at pH 11, with x representing different concentrations of complex metallic ion (10^{-4} M to) 0.1 M). The electrochemical techniques employed were cyclic voltammetry and chronoamperometry. Each system of different concentration was characterized by voltammetry with scan rate of 50 mV/s in the potential range between 0.7 to -0.7 V vs. SCE. The sweep potential was always initiated in negative direction. Chronoamperometric studies were performed in the same Ag(I) concentration range as the voltammetric study, in a wide range of electrode potentials (-0.03 to -0.7 V vs. SCE) with increases of 20 mV. The study was always initiated applying a potential pulse in negative direction for 2 s (for concentrations above 10^{-3} M, the pulse time was 5 s); after the potential was reversed to the value E_{anodic} = 0.7 V vs. SCE. On the other hand, before each sequence of perturbation, the working electrode was submitted to cleaning described in Ref. 11 and 24 which assured realization of each experiment on a clean surface. A PAR 270 potentiostat was coupled to a computer for data acquisition and analysis by M-270 software.

Results

Figure 1 shows typical voltammograms corresponding to the systems 10^{-3} and 10^{-2} M Ag(NH₃)⁺₂ obtained at the potential range between 0.7 to -0.7 V vs. SCE at 50 mV/s. In both cases, the reduction peak C₁ was detected in the direct sweep potential (negative direction), corresponding to the reduction of Ag(NH₃)⁺₂ species to metallic silver. In the reverse sweep potential, two crossovers are observed, one at more negative potentials and the other at zero current, characteristic of metal deposition onto substrates of different nature. There is also a sharp peak A₁ associated with the thorough dissolution of metal on the substrate surface. Voltammetric re-

^{*} Electrochemical Society Active Member.



Figure 1. Typical cyclic voltammetric curves obtained in the x/M Ag(NH₃)₂⁺/1.6 M NH₃ 1 M KNO₃ at pH 11 system on vitreous carbon electrode, at two different concentrations of electroactive species (a) $x = 10^{-3}$ (b) $x = 10^{-2}$ M. The scan potential rate was 50 mV/s.

sponses for other systems of different concentrations were similar to the above-described behavior. It is important to note that the current response is characteristic of the concentration of the system. These results show that the reduction reaction at the electrode in all systems is the following

$$Ag(NH_3)_2^+ + e^- \to Ag^o + 2NH_3$$
$$E' = E^{o'} + 0.06 \log \frac{[Ag(NH_3)_2^+]}{[NH_3]^2}$$
[1]

where E' is the conditional potential represented by the Nernst Eq. 1, which depends on the electroactive species and $[NH_3]$ concentrations. In this case, $[NH_3] = 1.6 \text{ M}$ and $E_{Ag(NH_3)_2^+/Ag^o}^{o} = 0.136 \text{ V} vs.$ SCE. E' refers to the silver complexes in the ammonia bath. The estimated values of E' for each experimental condition are reported in Table I. More details of E' determination have been reported elsewhere (see Appendix, Ref. 11). In order to made a energetic comparison, in all cases the overpotentials were considered (evaluated from imposed potentials and the potentials of Table I).

Below results are shown corresponding to the chronoamperometric study obtained for systems at different concentrations, applying a wide range of potentials.

Table I. Values of conditional potential (E') as a function of concentration the electroactive species $Ag(NH_3)_2^+$.

$\left[\operatorname{Ag}(\operatorname{NH}_3)_2^+\right]/M$	E'/V vs. SCE
10^{-4} 10^{-3}	-0.128 -0.068
10^{-2}	-0.008
10^{-1}	0.052

System: $10^{-4} M Ag(NH_3)_2^+/1.6 M NH_3$, $1 KNO_3$ at pH 11.—Figure 2 shows potentiostatic current transients obtained in a solution with $10^{-4} M Ag(NH_3)_2^+/1.6 M NH_3$, $1 KNO_3$ at pH 11 in different overpotential pulses between 0.078 and -0.572 V. All transients show a similar behavior: first the transient current declined sharply due to the double-layer (dl) charging process; after a current maximum M_1 observed within the time range of 0.04-0.1 s. At longer times, the current transients present another maximum M_2 .

On comparing the transients of Fig. 2 with the theory reported in the literature, this suggests that both maxima $(M_1 \text{ and } M_2)$ can be analyzed by the model proposed by Bewick *et al.*²⁵⁻²⁷ That model describes the kinetics of electrolytic phase formation at the early stages of 2D growth determined by the lattice incorporation of adatoms to the periphery of a growing nucleus, taking into account the overlap of nuclei. This model considers two kinds of nucleation processes, instantaneous and progressive, which can be described by Eq. 2 and 3, respectively

$$i_{\text{instantaneous}} = \frac{2\pi n F M h N_o k_g^2 t}{\rho} \exp\left(-\frac{\pi N_o M^2 k_g^2 t^2}{\rho^2}\right) \qquad [2]$$

$$j_{\text{progressive}} = \frac{\pi n F M h A N_o k_g^2 t^2}{\rho} \exp\left(-\frac{\pi A N_o M^2 k_g^2 t^3}{3 \rho^2}\right) \qquad [3]$$

where, N_0 is the number density of active sites, k_g is the growth rate constant of a nucleus, A corresponds to the nucleation rate constant, M is the molar mass, ρ is density of the deposited material, nF is the molar charge transferred during electrodeposition and h is height of the monolayer.

A quick way to demonstrate the applicability of this model to the transient responses shown in Fig. 2 is to undertake a comparative diagnosis between the theoretical response, in dimensionless coordinates, of Eq. 2 and 3 $(I/I_{\rm m} vs. t/t_{\rm m})$ and the experimental response,^{26,27} where $I_{\rm m}$ and $t_{\rm m}$ are the coordinates of the current



Figure 2. Family of current transients for the electrodeposition of silver onto vitreous carbon from 10^{-4} M Ag(NH₃)₂⁺/1.6 M NH₃, 1 KNO₃ solution at pH 11, obtained at different overpotentials η /V: (\diamond) 0.078, (\odot) –0.022, (\bigcirc) –0.122, (\blacktriangle) –0.322, (\bigtriangleup) –0.372, (\blacksquare) –0.472, and (\Box) –0.572.

System 10^{-4} M Ag(I)								
	Λ	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	M_2					
η (V)	$\frac{t_{\rm m}I_{\rm m}\times10^5}{({\rm C~cm^{-2}})}$	$^{*h \times 10^8}$ (cm)	$\frac{t_{\rm m}I_{\rm m}\times10^5}{({\rm C~cm^{-2}})}$	$^{*h} \times 10^{8}$ (cm)		Nucleation and growth		$^{**h} \times 10^8$ (cm)
0.078	1.94	0.20	1.09	0.11		Transition		0.18
0.028	1.46	0.15	1.12	0.12		2D-2D		0.23
-0.022	1.57	0.16	1.23	0.13		progressive		0.29
-0.072	1.74	0.18	1.48	0.15				0.37
-0.122	1.94	0.20	1.72	0.17				0.43
-0.172	1.83	0.19	1.95	0.20				0.55
-0.192	1.61	0.17	1.95	0.20				0.57
-0.222	1.72	0.18	2.04	0.21				0.61
-0.272	1.89	0.20	2.44	0.25				0.69
-0.322	1.89	0.20	2.34	0.24				0.67
-0.372	3.91	0.41	3.82	0.40				1.09
-0.422	3.03	0.31	3.43	0.35				0.98
-0.472	3.54	0.37	4.52	0.47				1.18
-0.522	5.54	0.57	4.90	0.51				1.35
-0.572	6.53	0.68	6.29	0.65				1.56
-0.122	2.12	0.22	4.04	0.42				
-0.572	2.28	0.24	4.88	0.51				
		M_{1}			M_2			dl
η (V)	$\stackrel{A_1}{(\mathrm{s}^{-1})}$	$No_1 \times 10^{-3} \ (cm^{-2})$	$k_{g1} \times 10^{3}$ (mol cm ⁻² s ⁻¹)		$No_2 \times 10^{-3}$ (cm ⁻²)	$k_{\rm g2} \times 10^3 \ ({\rm mol} \ {\rm cm}^{-2} \ {\rm s}^{-1})$	$\begin{array}{c} k_{\rm ads} \times 10^3 \\ ({\rm A~cm^{-2}}) \end{array}$	k_{des} (s ⁻¹)
-0.122	19.04	1.58	33.46	2	0.2	78.1	2.33	90.21
-0.572	25	1.98	31.62	2.86	0.27	67.08	7.8	109

Table II. Types of growth, nucleation, and kinetic parameters corresponding to the mechanism of silver electrocrystallization obtained for the 10^{-4} M Ag(NH₃)⁺/1.6 M NH₃, 1 M KNO₃ system at pH 11, as a function of the overpotential (η).^a

^a The thickness of a monolayer of silver deposited is 1.59×10^{-8} cm (this term was evaluated from characteristics parameters). The thickness (**h*) of silver layer was obtained for $I_{\rm m}t_{\rm m}$ using Eq. 6. The thickness of the silver formed (***h*) was evaluated from the charge associated to the deposit (area under the curve of the corresponding current transient).

maximum and t_m is the time associated to this maximum. The analysis of each successive maximum M_1 and M_2 (Fig. 2) allows the association with a progressive 2D growth which suggests a 2D-2D transition for all of the transient current responses.

A detailed analysis is presented below of the transient responses shown in Fig. 2, in order to demonstrate if a 2D-2D transitions may effectively be associated with progressive growth.

Considering Eq. 3, the maximum current occurs at a time defined by

$$t_{\rm m} = \left(\frac{2\rho^2}{\pi M^2 A N_{\rm o} k_{\rm g}^2}\right)^{1/3}$$
 [4]

the maximum current density is given by

$$I_{\rm m} = zF \left(\frac{4\pi A N_{\rm o} k_{\rm g}^2 \rho}{M}\right)^{1/3} h \exp(-2/3)$$
 [5]

the product $I_{\rm m}t_{\rm m}$ yields

$$I_{\rm m}t_{\rm m} = \frac{2zF\rho h \exp(-2/3)}{M}$$
[6]

As may be observed, the product $I_m t_m$ should be a constant determined by the height of the silver monolayer independent of the electrode potential, concentration and pH.

Table II shows the values of the product $I_m t_m$ and of h (height of the deposited layer) evaluated with Eq. 6. It may be observed that both $I_m t_m$ and h are relatively constant only up to a certain value of overpotential (0.078 to -0.322 V). For more negative overpotentials, the product $I_m t_m$ changes. With this it is demonstrated that over a large interval of overpotentials, the maxima M_1 and M_2 observed in the transient current response may be associated with 2D growth.

It also is very important to note that, in the entire range of overpotentials (Table II), the thickness (*h*) of the deposit is less than a monolayer. The monolayer is estimated to have a thickness of 1.59×10^{-8} cm, considering the number of silver atoms required to cover the geometric area of the electrode (0.0707 cm²) and the area of a silver atom is 9.62×10^{-16} cm². Therefore, the charge needed to form a monolayer (7.35×10^{13} atoms) is 1.19×10^{-5} C.

The reason that this does not strictly obey the product of Eq. 6 is due precisely to the fact that there are different contributions to the total current: the current necessary to charge the dl $(I_{\rm dl})$ and for the 2D-2D growth transition, the current which corresponds to 2D progressive growth in the maximum M_1 ($I_{\rm 2DP(M1)}$) and the current of the 2D progressive growth in the maximum M_2 ($I_{\rm 2DP(M2)}$). In this manner, the total current may be represented as follows

$$I_{\text{total}} = I_{\text{dl}} + I_{2\text{DP}(\text{M1})} + I_{2\text{DP}(\text{M2})}$$
 [7]

In order to separate each of the contributions in the total current response, a nonlinear fit of Eq. 7 (see details of nonlinear fit processes in the Appendix) was made to the experimental results and presented in its completely developed form in the following equation, where $I_{\rm dl} = k_{\rm ads} \exp(-k_{\rm des}t)$ and $I_{\rm 2DP}$ are defined for Eq. 3

$$I = k_{ads} \exp(-k_{des}t) + \left[\frac{n\pi F M h_1 A_1 N_{o_1} k_{g_1}^2 t^2}{\rho} \exp\left(-\frac{\pi M^2 A_1 N_{o_1} k_{g_1}^2 t^3}{3\rho^2}\right)\right] + \left[\frac{n\pi F M h_2 A_2 N_{o_2} k_{g_2}^2 t^2}{\rho} \exp\left(-\frac{\pi M^2 A_2 N_{o_2} k_{g_2}^2 t^3}{3\rho^2}\right)\right] [8]$$

At the initial stage of the silver deposition transient, a sharp decline in the current normally occurs (Fig. 2). According to the



Figure 3. (\diamond) Experimental current transient recorded at: (a) η = -0.122 V, (b) η = -0.572 V, for the system 10^{-4} M Ag(NH₃)₂⁺/1.6 M NH₃, 1 KNO₃ at pH 11, and (*) a theoretical curve for the 2D-2D nucleation transition (Eq. 8). Contributions to the transient current from the double layer charging phenomenon (I_{dl}) and two consecutive 2D progressive nucleation processes (I_{2DP}) are shown separately.

literature,^{1,13} this is related to the electrode dl charging effect initiated by the potential pulse employed. Although this phenomenon has been recognized and described qualitatively, a quantitative characterization has rarely been performed. Kolb and co-workers showed that such a charging effect can be correlated quantitatively to the adsorption-desorption process of ions on the electrode surface.¹³ To estimate quantitatively the dl charge contribution in this silver overpotential deposition, the same approach as Kolb¹³ was employed. The estimation of the current density contribution $(I_{\rm dl})$ in current transients due to the dl charging effect was based on a Langmuir-type adsorption-desorption equilibrium and previously established mathematical formalisms.^{28,29} From I_{dl} , k_{ads} is related to the total charge of the adsorption process Q_{ads}

$$I_{\rm dl} = k_{\rm ads} \exp(-k_{\rm des} t)$$
[9]

where $k_{ads} = k_{des} Q_{ads}$ In Fig. 3a-b, the result of the nonlinear fit is shown as an example for two overpotentials -0.122 and -0.572 V. Also, the contribution of each of the events described in Eq. 8 to the current as well as the total current (the sum of all of the contributions) are illustrated. Considering the response for each event, it was observed that the transient response corresponding to the maximum M_1 is the largest contribution to the total current, for I_{dl} as well as for $I_{2DP(M2)}$ during the entire time interval in which the M_1 was formed. At the



Figure 4. Potentiostatic current transients obtained for the deposition of silver on a VC electrode from 10^{-3} M Ag(NH₃)₂⁺/1.6 M NH₃, 1 KNO₃ solution at pH 11. The overpotential of the electrode was different; see in the figures

end of Table II, the value of $I_m t_m$ for M_1 and M_2 is shown, obtained from each individual fit, in other words without contributions. In this table, the parameters found with the nonlinear fit of Eq. 3 ($AN_0 k_g$, $k_{\rm ads}$ and $k_{\rm des}$) are also reported, where the subscripts 1 and 2 are used to denote the maxima M_1 and M_2 . The magnitude of these parameters show a tendency very similar to those reported in Ref. 11 and 12. The thickness of the silver formed (**h) was evaluated from the charge associated to the deposit (area under the curve of the corresponding current transient). The values obtained in this manner are always less than that required to form the monolayer.



Figure 5. (\diamond) Experimental current transient recorded at: (a) $\eta = -0.432 \text{ V}$, (b) $\eta = -0.6372 \text{ V}$, for the system 10^{-3} M Ag(NH₃)₂⁺/1.6 M NH₃, 1 KNO₃ at pH 11, and (*) a theoretical curve for the 2D-2D nucleation transition (Eq. 11). Contributions to the transient current from the dl charging phenomenon (I_{dl}) and two consecutive 2D instantaneous nucleation processes (I_{2DIns}) are shown separately.

Considering the results of Table II, the presence of 2D-2D growth on the polycrystalline surface of (VC) is confirmed.

System: $10^{-3} M Ag(NH_3)^+/1.6 M NH_3$, $1 KNO_3$ at pH 11.-Figure 4a-c shows potentiostatic current transients obtained in a solution with 10^{-3} M Ag(NH₃)⁺/₂/1.6 M NH₃, 1 KNO₃ at pH 11, corresponding to different overpotentials between -0.032 and -0.632 V. These responses have complex shapes, different from each other. Figure 4a-b, for the same transient, shows more than one current maximum $(M_1 \text{ and } M_2)$; after the dl charge. Note that the current of M_2 in Fig. 4b is observed to be constant unlike that of M_2 in Fig. 4a. Figure 4c shows just one maximum, M_1 . All transients were analyzed using the model described for 2D growth proposed by Bewick in dimensionless coordinates from Eq. 2 and $3.^{25-27}$ The analysis reports a progressive 2D-2D transition for the overpotential range between -0.032 and -0.132 V (Fig. 4a). The overpotential range of -0.182 to -0.382 V (Fig. 4b) shows another 2D-3D transition. They are both limited by adatoms incorporation into the substrate lattice (see detailed analysis in Ref. 12 and 24). At overpotentials between -0.432 and -0.632 V (Fig. 4c), an instantaneous 2D-2D transition is present. In Fig. 5a-b, nonlinear fits of two experimental current transients are presented (-0.432 and -0.632 V), using Eq. 10 and considering Eq. 2, which describes an instantaneous nucleation 2D ($I_{2\text{DIns}}$) and Eq. 9 for I_{dl}

$$I_{\text{total}} = I_{\text{dl}} + I_{2\text{DIns}(\text{M1})} + I_{2\text{DIns}(\text{M2})}$$
[10]

The fully developed form of Eq. 10 is shown in Eq. 11

$$I = k_{ads} \exp(-k_{des}t) + \left[\frac{2n\pi F M h_1 N_{o_1} k_{g_1}^2 t}{\rho} \exp\left(-\frac{\pi M^2 N_{o_1} k_{g_1}^2 t^2}{\rho^2}\right)\right] + \left[\frac{2n\pi F M h_2 N_{o_2} k_{g_2}^2 t}{\rho} \exp\left(-\frac{\pi M^2 N_{o_2} k_{g_2}^2 t^2}{\rho^2}\right)\right]$$
[11]

Table III summarizes the results obtained for this system. It is important to mention that in this table the values of $t_{\rm m}$ and $I_{\rm m}$ for the overpotential range of -0.432 to -0.632 are not reported because in the experimental results it is difficult to appreciate the presence of a second maximum (M_2). This becomes evident only after the different contributions to the total current have been separated through the nonlinear fit of the transient current responses of Fig. 4c, in such a form that the product $t_{\rm m}I_{\rm m}$, which is practically constant, has been evaluated (see Table III). In the same manner as the last case, **h (the thickness of the deposited silver) was evaluated. As before, this is less than that required to form the monolayer, which is in agreement with the corresponding value of *h obtained from $t_{\rm m}I_{\rm m}$, for overpotentials from -0.032 to -0.382. At more negative overpotentials, *h as well as **h present values that correspond to the formation of more than a monolayer (3D growth).

System: 10^{-2} M Ag(NH₃)⁺/1.6 M NH₃, 1 KNO₃ at pH 11.—Figure 6a-b shows potentiostatic current transients obtained in 10^{-2} M Ag(NH₃)⁺/1.6 M NH₃, 1 KNO₃ solution at pH 11, upon the application of different overpotential pulses in the range of -0.09 to -0.69 V. The transient responses shown in Fig. 6a, are similar to the those described by the theoretical model proposed by Scharifker and Hills.^{1,5,6} Their models describe the kinetics of electrolytic phase formation in the early stages when diffusion of the electroactive species from bulk to the interface is the slowest step of the process. The growth of the nuclei is considered to be 3D, taking into account overlap of diffusion zones. The instantaneous and progressive-type nucleation is described by Eq. 12 and 13

$$j_{\text{instantaneous}} = \frac{nFD^{1/2}}{\pi^{1/2}t^{1/2}} [1 - \exp(-N_0\pi kDt)]$$
[12]

$$k = \left(\frac{8\pi cM}{\rho}\right)^{1/2}$$
[12a]

$$j_{\text{progressive}} = \frac{nFD^{1/2}}{\pi^{1/2}t^{1/2}} \left[1 - \exp\left(-\frac{AN_{o}\pi k_{g}Dt^{2}}{2}\right) \right]$$
[13]

$$k_{\rm g} = \frac{4}{3} \left(\frac{8 \,\pi c M}{\rho} \right)^{1/2} \tag{[13a]}$$

where D is the diffusion coefficient, and c is the bulk concentration of the silver species. Other parameters were described above for Eq. 2 and 3.

This model is used to analyze experimental transients (Fig. 6a) and it shows that there is a progressive 3D growth limited by diffusion of the electroactive species from the bulk dissolution toward the interface (see details in Ref. 11). Figure 6b exemplifies two transients, one obtained at -0.49 V and the other at -0.69 V. The current maxima are displaced at short times and cannot be analyzed by the above model. Moreover, regarding the shape of the transient changes (-0.69 V); first there is a current maximum that rapidly decreases, then a small shoulder appears followed by an asymptotic current drop which does not reach zero. This type of transient is scarcely reported in the literature. Budevski *et al.*^{17,27} consider that this kind of response is due to a 2D growth of crystals on the periphery of the electrode. Table IV summarizes the results obtained as a function of the potential applied.

	<i>M</i> ₁ 2D	progressive	System 10^{-3} M Ag(I) M_2 2D progressive		System 10^{-3} M Ag(I) M_2 2D progressive				
η (V)	$\begin{array}{c}t_{\rm m}I_{\rm m}\\\times10^5\\({\rm C~cm^{-2}})\end{array}$	${}^{*h} \times 10^{8}$ (cm)	$\begin{array}{c}t_{\rm m}I_{\rm m}\\\times10^5\\({\rm C~cm^{-2}})\end{array}$	$^{*h} \times 10^{8}$ (cm)	Nuclea and gro	tion owth	$^{**h}_{(cm)} \times 10^{8}$		
-0.032	1.43	0.15	1.09	0.11	Transit	tion	0.32		
-0.082 -0.132	1.51 1.68	0.16 0.17	1.20	0.12 0.16	2D-2 progres	D sive	0.38 0.46		
-0.182	2.84	0.29	M_2 3D progressive		Transit	tion	0.50		
-0.232	3.11	0.32			2D-3	D	1.00		
-0.232	5.87 3.17	0.40			progres	Sive	0.75		
-0.332	3.93	0.41					1.08		
-0.382	4.37	0.45					1.42		
	M_1 2D instantaneous		M_2 2D instantaneous		Transit	ion			
-0.432	6.09	1.07			instantar	D	1.90		
-0.482	7.95	1.39			11000011001	loous	2.35		
-0.532	9.19	1.61					2.70		
-0.582	12.07	2.12					3.06		
-0.632	14.95	2.62					3.40		
-0.432	2.53	0.44	13.31	2.33					
-0.632	2.61	0.46	13.52	2.37	dl				
	$N_{o_1} \times 10^{-3}$ (cm ⁻²)	$k_{\rm g1} \times 10^3 \ ({\rm mol} \ {\rm cm}^{-2} \ {\rm s}^{-1})$	$N_{ m o_2} imes 10^{-3}$ (cm ⁻²)	$k_{g2} \times 10^3$ (mol cm ⁻² s ⁻¹)	$\substack{k_{\rm ads} \times 10^3 \\ ({\rm A \ cm}^{-2})}$	k_{des} (s ⁻¹)			
$-0.432 \\ -0.632$	0.70 10.13	38.85 10.05	0.62 1.08	10.39 9.21	8.9 9.5	188.72 121.24			

Table III. Types of growth, nucleation and kinetic parameters corresponding to the mechanism of silver electrocrystallization obtained for the 10^{-3} M Ag(NH₃)⁺/1.6 M NH₃, 1 M KNO₃ system at pH 11, as a function of the overpotential (η).

The thickness of a monolayer of silver deposited is 1.59×10^{-8} cm (this term was evaluated from characteristics parameters). The thickness (**h*) of silver layer was obtained for $I_{\rm m}t_{\rm m}$ using Eq. 6. The thickness of the silver formed (***h*) was evaluated from the charge associated to the deposit (area under the curve of the corresponding current transient).

System: $10^{-1} M Ag(NH_3)^+_2/1.6 M NH_3$, 1 KNO₃ at pH 11.—Figure 7a-b shows the potentiostatic current transients obtained in 10^{-1} M Ag(NH₃)⁺/1.6 M NH₃, 1 KNO₃ solution at pH 11 upon the application of different overpotential pulses in range of -0.08 to -0.75 V. The transient response shown in each figure is different and depends on the interval of the overpotential. Figure 7a shows a family of current transients corresponding to the potential range of -0.08 to -0.20 V. For all potentials, the rise of the deposition current as a function of the deposition time was observed. In the final stage, the current reached a steady-state condition. Figure 7b shows that the shape of current transients are modified as the applied overpotential becomes more negative. Within the overpotential range between -0.22 and -0.35 V, a current maximum is well defined, whereas at overpotentials ranging from -0.4 to -0.75 V, an increase in current is observed which later decreases asymptotically to a determined value different of zero.

The transients of Fig. 7a were analyzed using the model proposed by Armstrong.^{18,26} That model describes a 3D instantaneous or progressive nucleation, limited by the lattice incorporation of adatoms, and takes into account the overlapping of growing nuclei with a specific geometry (right-circular cones). Each nucleus is treated as a well-defined circular cone which grows on a foreign substrate in a direction parallel to the surface with a rate constant (k_1) . In the direction perpendicular to the substrate surface, nuclei grow with a different rate constant defined as (k_2) . Equations 14 and 15 describe instantaneous and progressive nucleation, respectively, in this model

$$j_{\text{instantaneous}} = nFk_2 \left[1 - \exp\left(\frac{-\pi M^2 k_1^2 N_0 t^2}{\rho^2}\right) \right]$$
[14]

$$j_{\text{progressive}} = nFk_2 \left[1 - \exp\left(\frac{-\pi M^2 k_1^2 A N_0 t^3}{3\rho^2}\right) \right]$$
[15]

All parameters mentioned in these equations were described previously. The values obtained for kinetic parameters of nucleation are reported in Ref. 11. The transients obtained in the interval of -0.22 to -0.35 V (Fig. 7b, i-v) were analyzed by the model proposed by Scharifker and Hills,^{1,5,6} and Eq. 12 and 13 describes 3D growth of nuclei limited by diffusion of the electroactive species. The current transient obtained at overpotentials between -0.4 and -0.75 V (vi, vii), shows that t_m corresponding to current maxima (I_m) occurred a very short time and furthermore these cases are not possible to evaluated through by Eq. 12 and 13, however similar responses are reported for to 2D growth limited by diffusion.^{17,30} Interestingly, in this case as well as in the previous case of 10^{-2} M (high concentrations of Ag(NH₃)⁺₂ species), current transient responses, at more negative overpotentials, shows the 2D growth; this behavior is curious because for these conditions (high concentrations and more negative overpotential), a 3D growth is expected. In order to elucidate the results, a detailed discussion of Tables II-V is given below.

Discussion

Tables II and III corresponding to 10^{-4} and 10^{-3} M of Ag(I) respectively, show that for the overpotential range between 0.078 to -0.382 V, a 2D-2D transition are described. Furthermore, these cases were reported to have formed less than a monolayer, not only at less negative potential ranges but also at the intermediate and more negative ranges. The low concentration of electroactive species might be the cause of 2D growth on the VC surface. It is



Figure 6. Potentiostatic current transients obtained for the deposition of silver on a VC electrode from 10^{-2} M Ag(NH₃)⁺₂/1.6 M NH₃, 1 KNO₃ solution at pH 11. The overpotential of the electrode was different; see in the figures.

important to note that the electrocrystallization processes occur in underpotential region (0.078, 0.028 V) in the solution of 10^{-4} M Ag(I), this is probably due to the specific interaction between the adatoms and substrate, provoked by the coordination sphere of silver ions $[Ag(NH_3)_2^+]$ and the electrolyte (NH₃). As the applied potential becomes more negative, the tendency to form the monolayer increases, which indicates that new types of growth are induced by changes in the potential conditions. The fact that growth zones may be modified through the changes of potential shows that new silver nuclei constantly develop in energetically preferential sites. This justifies the progressive nucleation in these cases. It is also likely to be one of the causes of transitions observed in the growth (2D to 2D and 2D-3D). Moreover, the growth transitions may also be attributed to overlap effects between the deposited silver nuclei. For more drastic energetic conditions (more negative overpotentials, Table III), the growth of silver nuclei on silver can be observed because more than one monolayer is formed. Therefore, the type of nucleation probably changes from progressive (Ag⁰/VC) to instantaneous $(Ag^{o}/Ag^{o}).$

On the other hand, a 3D growth is observed for 10^{-2} M concentration of electroactive species (Table IV) at overpotentials range between -0.09 to -0.19 V, whereas the number of monolayers and thickness of the formed deposit is much greater than a monolayer, which justifies the 3D growth. It is also worth noting that the number of monolayers and thickness of the formed deposit are practically constant at all overpotentials, indicating that once the nuclei have grown and diffusion layers have overlapped, no additional nucleation centers are formed, not even at more negative potentials.

Table IV. Types of growth and nucleation corresponding to the mechanism of silver electrocrystallization obtained for the 10^{-2} M Ag(NH₃)⁺₂/1.6 M NH₃, 1 M KNO₃ system at pH 11 on VC, as a function of the overpotential (η).^a

		10 ⁻² M Ag	g(I)	
η (V)	Nucleation	Growth	No. of monolayers	** $h \times 10^{6}$ /cm
-0.09	Progressive	3D Controlled	59	0.94
-0.14		by the diffusion of	65	1.03
-0.16		electroactive species	62	0.98
-0.18		1	70	1.11
-0.19			71	1.13
-0.24	Indefinite	2D Limited	72	1.15
-0.29		by the growth	69	1.10
-0.31		on electrode periphery	66	1.05
-0.34			69	1.10
-0.39			67	1.07
-0.44			61	0.98
-0.49			60	0.96
-0.54			70	1.12
-0.59			62	0.98
-0.69			73	1.16

^a The thickness of a monolayer of silver deposited is 1.59×10^{-8} cm (this term was evaluated from characteristics parameters). The thickness of the silver formed (***h*) was evaluated from the charge associated to the deposit (area under the curve of the corresponding current transient). The charge needed to form a monolayer (7.35 $\times 10^{13}$ atoms) is 1.19×10^{-5} C.

These results prove the hypothesis proposed for this theory by Hills, Sharifker, and Mostany regarding the diffusion-limited 3D growth.^{1,6} At more negative overpotentials (-0.24 to -0.69 V), the nucleation and growth are not "defined." Following with a logical behavior, for these experimental conditions, a 3D growth is expected, however distinctly transients, similar to those described by the model of Budevski,¹⁷ appear. The shapes of these transients correspond to a 2D growth limited by the substrate environment.

It is important to emphasize that when the Ag(I) concentration is 10^{-3} M an instantaneous 2D growth is observed at more negative overpotentials (-0.432 to -0.632 V), associated with the growth of silver nuclei on silver. This indicates that for the 10^{-2} M Ag(I) system at the overpotential of -0.24 to -0.69, the transient response may be related to the nucleation and silver growth on silver. Therefore, it could be speculated that at less negative potentials, the response *I* vs. *t* is associated with the growth and nucleation of silver on VC, whereas at more negative potentials, the growth and nucleation of silver on silver is described.

The results reported in Table V $[10^{-1} \text{ M de Ag(I)}]$, for less negative overpotentials (-0.08 to -0.2 V), the type of growth reported is 3D, limited by adatoms incorporation into the substrate lattice. Moreover, the number of estimated monolayers is quite large, which justifies the type of growth analyzed. Yet, in the description of experimental current transients using the model reported by Armstrong¹⁸ it was considered that at very short times (below 1 s, Fig. 7) no overlap of formed nuclei takes place. Therefore, for such conditions of overpotential, the initial growth of silver nuclei is supposed to take place on VC.¹¹ Furthermore, this model suggests that at greater times, overlap effects show up through the formation of a great number of monolayers (see Table V) that result in the silver deposition onto silver. Unlike the 3D growth presented in Table IV, the thickness and the number of monolayers grow considerably as the overpotential becomes more negative. It is surprising



Figure 7. Potentiostatic current transients obtained for the deposition of silver on a VC electrode from 10^{-1} M Ag(NH₃)₂⁺/1.6 M NH₃, 1 KNO₃ solution at pH 11. The overpotential η /V was different; Fig. 7a: (i) -0.08, (ii) -0.10, (iii) -0.12, (iv) -0.15, (v) -0.17, (vi) -0.20. Figure 7b: (i) -0.22, (ii) -0.24, (iii) -0.25, (iv) -0.30, (v) -0.35, (vi) -0.45, (vii) -0.75.

that for overpotentials between -0.22 to -0.35 V, a 3D growth limited by diffusion of electroactive species appears. The nuclei grow onto silver independent the amount of the monolayers formed (Table V); yet, the energetic conditions are such that the process is limited by diffusion. Once the conditions become energetically more severe (-0.4 to -0.75), the amount of deposited metal becomes significant and 2D growth of silver onto silver is observed again.

Conclusion

In this work, a systemic study of silver electrocrystallization process was performed on a VC electrode in a medium of 1.6 M NH₃, 1 KNO₃ at pH 11. It was carried out for a wide range of concentrations of electroactive species $[Ag(NH_3)_2^+]$ and the potentials applied. It is important to emphasize that the potential pulse times for these experiments are short (from 2 to 5 s), whereas in the literature the times reported are much longer.

In order to evaluate the kinetic parameters of nucleation and growth, it was necessary to establish a methodology for identification and analysis of current transients using different theoretical models.

For low concentrations of electroactive species $(10^{-4}, 10^{-3} \text{ M})$ and not so negative overpotentials, it is possible to observe 2D-2D and 2D to 3D growths. In these transitions, two types of silver growth sites were identifiable, first on VC and after, on the recently deposited silver. Concentrations greater than or equal to 10^{-2} M and not so negative overpotentials, 3D growth was observed of nuclei forming deposits beyond a monolayer that depended on the diffusion

Table V. Types of growth and nucleation corresponding to the mechanism of silver electrocrystallization obtained for the 10^{-1} M Ag(NH₃)₂⁺/1.6 M NH₃, 1 M KNO₃ system at pH 11 on VC, as a function of the overpotential (η).^a

		$10^{-1} M \text{ Ag}$	(I)	
η (V)	Nucleation	Growth	No. of monolayers	** $h \times 10^{6}$ /cm
-0.08	Instantaneous	3D	147	2.33
-0.10		Controlled by the	132	2.09
-0.12		lattice	191	3.04
-0.14		incorporation of adatoms	198	3.14
-0.15			301	4.79
-0.16			250	3.96
-0.17			262	4.16
-0.20			332	5.28
-0.22	Progressive	3D Controlled	381	6.06
-0.24		by the diffusion of	429	6.81
-0.25		electroactive species	458	7.27
-0.30		1	448	7.11
-0.35			518	8.22
-0.40	Indefinite	2D	526	8.35
-0.45			508	8.07
-0.50			512	8.13
-0.55			513	8.15
-0.60			506	8.03
-0.75			547	8.68

^a The thickness of a monolayer of silver deposited is 1.59 $\times 10^{-8}$ cm (this term was evaluated from characteristics parameters). The thickness of the silver formed (***h*) was evaluated from the charge associated to the deposit (area under the curve of the corresponding current transient). The charge needed to form a monolayer (7.35 $\times 10^{13}$ atoms) is 1.19 $\times 10^{-5}$ C.

of $Ag(NH_3)_2^+$ or the incorporation of silver adatoms into the substrate lattice. Likewise, for these concentrations and very negative overpotentials at which the amount of deposited silver is much greater than a monolayer, 2D growths are observable, possibly associated with the growth of Ag^o on the previously deposited silver.

It is worth noting that, for the first time in the same chemical system, the systematic evolution of electrocrystallization of 2D-3D stages of nuclei growth on heterogeneous VC surfaces can be observed through gradual modification of energetic conditions of the interface by either changing the concentration of electroactive species or the potential imposed to the electrode.

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Appendix

Nonlinear Fit Procedure

The equations used for the nonlinear fit of the experimental current transients contain different parameters that can be varied during the fitting procedure. In this Appendix, the nonlinear procedure used in this work is shown for the case of Eq. 8 (as an example).

As described in the text, the total current for this case may be represented as follows

$$I_{\text{total}} = I_{\text{dl}} + I_{2\text{DP}(\text{M1})} + I_{2\text{DP}(\text{M2})}$$
 [A-1]

where

$$I_{\rm dl} = k_{\rm ads} \exp(-k_{\rm des}t)$$
 [A-2]

and

$$j_{2\text{DP}} = \frac{\pi n F M h A N_o k_g^2 t^2}{\rho} \exp\left(-\frac{\pi A N_o M^2 k_g^2 t^3}{3\rho^2}\right)$$
[A-3]

 M_1 and M_2 in Eq. 1 correspond to each one maximum in the experimental current transient and this equation is completely developed as

$$I = k_{ads} \exp(-k_{des}t) + \left[\frac{n\pi F M h_1 A_1 N_{o_1} k_{g_1}^2 t^2}{\rho} \exp\left(-\frac{\pi M^2 A_1 N_{o_1} k_{g_1}^2 t^3}{3\rho^2}\right)\right] + \left[\frac{n\pi F M h_2 A_2 N_{o_2} k_{g_2}^2 t^2}{\rho} \exp\left(-\frac{\pi M^2 A_2 N_{o_2} k_{g_2}^2 t^3}{3\rho^2}\right)\right]$$
[A-4]

this equation is parametrized such as

$$I = k_1 \exp(-k_2 t) + [P_1 P_2 P_3 P_4 t^2 \exp(P_5 P_2 P_3 P_4 t^3)] + [P_9 P_6 P_7 P_8 t^2 \exp(P_5 P_6 P_7 P_8 t^3)]$$
[A-5]

where

$$k_1 = k_{ads}, \ k_2 = k_{des}, \ P_1 = \frac{n\pi F M h_1}{\rho}, \ P_2 = A_1, \ P_3 = No_1, \ P_4 = k_{g1}^2,$$

 $P_5 = \frac{\pi M^2}{3\rho^2}$
 $P_6 = A_2, \ P_7 = No_2, \ P_8 = k_{g2}^2, \ P_9 = \frac{n\pi F M h_2}{\rho}$

Kinetic parameters $(P_1, P_2, P_3, \dots, P_9)$ were obtained as a result of the best fit (nonlinear regression) of Eq. A5 to experimental data. We performed the nonlinear fit using the Statistica StatSoft software. This software requires the initial values of each parameter in Eq. A5, and these were estimated considering the following the maximum current occurs at a time defined by

$$t_{\rm m} = \left(\frac{2\rho^2}{\pi M^2 A N_0 k_{\rm g}^2}\right)^{1/3} \qquad [A-6]$$

the maximum current density is given by

$$I_{\rm m} = zF \left(\frac{4\pi A N_{\rm o} k_{\rm g}^2 \rho}{M}\right)^{1/3} h \, \exp(-2/3)$$
 [A-7]

the product $I_m t_m$ yields

$$I_{\rm m}t_{\rm m} = \frac{2zF\rho h\,\exp(-2/3)}{M}$$
[A-8]

Using the experimental current transients, we obtained the different values of $t_{\rm m}$ (A6), $I_{\rm m}$ (A7), and the product of Eq. A8, for each applied potential; these values are specific and allowed to fix the initial limits of parameters in Eq. A5. Likewise, the convergence criterion, means, and standard deviation for the fitting procedure was fixed in a factor of 10^{-4} . Furthermore the convergence criterion, means and standard deviation for the fitting, the values obtained in this manner, are accepted only when the magnitude obtained for P_5 , P_1 , and P_9 parameters (see below) are equals to those obtained by the direct evaluation using previously reported values for: M (molecular weight of silver) and ρ (silver density).

$$P_5 = \text{constant} \text{ value} = 110.37 = \frac{\pi M^2}{3\rho^2}$$

$$P_1$$
 and P_9 are defined as equal to $\frac{n\pi FMh}{\rho} = 3.1124 \times 10^6 h$

This procedure allows one to obtain the values of N_o , A, k_g with physical meaning. Furthermore, this procedure allows to independently determine values of k_g and N_o . This is the importance of this procedure.

The strategies used for the nonlinear fit procedure for different electrocrystallization processes are more deeply discussed in a previous works.

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