Advances in Copper Electrodeposition in Chloride Excess. A Theoretical and Experimental Approach

P. Sebastián a, E. Torralba b, E. Vallés a, A. Molina b, E. Gómez a, *

* Corresponding author. Tel.: +34 934 021 234; fax: +34 934 021 231. E-mail address: e.gomez@ub.edu (E. Gómez).

ARTICLE INFO

Article history:
Received 24 November 2014
Received in revised form 13 January 2015
Accepted 24 February 2015
Available online 26 February 2015

Keywords:
copper electrodeposition
first stages
surface concentration
chloride effect
DES

ABSTRACT

This is an in depth study in the knowledge of the nucleation and growth mechanism that governs copper electrodeposition in excess chloride media. In these conditions copper electro-reduction takes place via two well-separated steps, since the Cu(I) intermediate is stabilized through chloride complexation. The process was studied in two media, a deep eutectic solvent (DES) based on a mixture of urea and choline chloride, and in excess chloride aqueous solution, in order to also analyse solvent influence on the early stages of the deposition process. In both media, copper electrodeposition follows a nucleation and a diffusion controlled three-dimensional growth mechanism. In line with a previous work a double potentialstatic step signal was employed to record t−1 transients associated to both nucleation and growth stages, and from them, the whole mechanistic analysis of the copper electrodeposition was performed. This analysis involved the calculation of the surface concentrations of Cu(II), free Cu(I) and complexed Cu(I) for any time and potential required and the application of Sharifi-er-Hills model, l∞, vr products and rising part analysis including the calculated parameters, which are strengthened as valuable tools for complete copper electrodeposition analysis in these media.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Copper electrodeposition has been for a long time an important topic due to the interest that copper coatings have in a wide range of applications. This has been heightened yet more by the massive use of copper in the electronics industry [1–4].

As it is well known, the presence of free or complexed cations in solution has an important role on the overall deposition process, as they strongly affect both nucleation and growth. In the copper's case, for instance, some commercial and laboratory copper deposition baths incorporate species which can act as complexing agents, some of them (such as ammoniac, chloride, bromide, cyanide, thiocyanide, etc.) acting as well as complexing agents for the Cu(I) intermediate [5–7].

Due to its fundamental and theoretical importance there is no lack of reports related to the Cu deposition mechanism [8–14]. However, to the best of our knowledge, there is no literature with takes into consideration a possible intermediate stabilization when performing the mechanistic analysis via chronoamperometric method. The mechanistic analysis of the first deposition stages using chronoamperometric data has usually been performed by recording the response after the application of a typical single potentialstatic step. This procedure, however, does not lead to reliable results when stabilization of the intermediate occurs, so that comments related to divergent or unexpected results have been included in some of the reports [4,15–17].

Recently it has been proved that ionic liquids based on eutectic mixtures of choline chloride and hydrogen bond donors (known as deep eutectic solvents (DES)) can be used for copper electrodeposition [18–21]. In these media, chloride is present in excess (about 5 M) and the intermediate Cu(I) is stabilized by complexation with it, such that the complete electrodeposition process takes place via two well-separated one-electron stages. This behaviour is similar to that previously observed in aqueous concentrated chloride solutions [22–25]. In a previous work the first stages of Cu(II) reduction were studied in two chemical systems having in common a chloride excess (DES and aqueous concentrated chloride solution) [26]. In both media, it was proposed to apply a double-step signal in the chronoamperometric study as an adequate procedure to obtain reproducible results on nucleation
and growth processes. The overall profile of the j-t response obtained by using this double-step signal presents two clear zones related to Cu(II) to Cu(I) reduction and to the Cu electrodeposition from Cu(I). The purpose of this work is to extend the previous studies and to deepen the knowledge of the mechanism governing Cu(II) electro-reduction by carrying out the complete quantitative analysis of the two reduction processes mentioned above. This requires knowing the surface concentration of the ionic species of interest on the electrode at the instant in which the second potential step is applied, which enables the proper selection of the residence time value at the first applied potential and so the control of the conditions at which the electrodeposition starts. In this line, a quantitative study that allows evaluation of the surface concentrations of the species involved in the first stages of the deposition process (i.e. Cu(II), free Cu(I) and complexed Cu(I)) has been carried out in both media (aqueous solvent and DES), using analytical equations for the current/potential response and surface concentrations obtained assuming that these first stages follow an EC reaction scheme [27,28]. The equations obtained enable us to estimate the formal potential of the Cu(II)/Cu(I) couple and the complexation reaction rate constant values between Cu(I) and chloride in the two media by nonlinear fitting between experimental data and theoretical equations. Once the process has been characterized, the surface concentration values of Cu(II), free Cu(I) and complexed Cu(I) at any experiment time are readily obtained. Afterwards, the non-dimensional Scharifker and Hills (S-H) model [29,30] has been used to analyze the nucleation and growth deposition processes, an approach that has already been applied recently to deposition processes in ionic liquids [26,31–34]. As will be shown, the knowledge of surface concentration values allows the complete quantitative analysis to be accomplished.

2. Experimental

The preparation of solutions and the electrochemical experiments were performed in the same way that had been previously described in references [26,35]. The selected temperature in DES solvent was 40 °C, lower than in [26], in order to assure liquid stability at long working times.

3. Theory

It has been demonstrated that in a excess of chloride medium the intermediate Cu(I) coming from the Cu(II) reduction in the first stage of the reduction process stabilizes by complexation, and so the complete electrochemical process occurs by means two well separated one-electron stages (Cu(II)–Cu(I) and Cu(I)–Cu(0)) [26].

3.1. Theoretical model for the first stage of the copper electrodeposition in excess of chloride medium: Cu(II)/Cu(I) reduction facilitated by chloride complexation.

In this section we focus in the theoretical model of the mass transport problem corresponding to the first stage of the copper electrodeposition under chloride excess (Cu(II)/Cu(I) reduction facilitated by chloride complexation) by assuming that it takes place via an EC process:

\[ Cu(II) + e^- \rightarrow Cu(I) \]
\[ Cu(I) + mCl^- \rightarrow k_2 CuCl_m \]

where \( k_1 \) and \( k_2 \) indicate the forward and backward kinetic constants of the chemical reaction taken to be of pseudo-first order and \( m = 2 \) or \( 3 \) (i.e. \( Cu(Cl)_2^- \) or \( Cu(Cl)_3^{2-} \)).

When a constant potential, \( E_s \), is applied to this system at a planar electrode, mass transport can be described by the following diffusive-kinetic equation system and boundary value problem:

\[
\begin{align*}
\dot{c}_{Cu(II)} &= 0 \\
\dot{c}_{Cu(I)} &= -k_1 c_{Cu(I)}(x,t) + k_2 c_{Cu(I)}(x,t) \\
\dot{c}_{CuI_m} &= k_1 c_{Cu(I)}(x,t) - k_2 c_{Cu(I)}(x,t)
\end{align*}
\]

(1)

being

\[
\dot{c} = \frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2}
\]

(2)

\[ t = 0, x \leq 0 \]
\[ t \geq 0, x \to \infty \]
\[ c_{Cu(II)}(x,t) = c^*, c_{Cu(I)}(x,t) = 0, c_{CuI_m}(x,t) = 0 \]

(3)

\[ x = 0, t > 0 \]
\[ D_{Cu(II)} \left( \frac{\partial c_{Cu(II)}(x,t)}{\partial x} \right)_{x=0} = -D_{Cu(I)} \left( \frac{\partial c_{Cu(I)}(x,t)}{\partial x} \right)_{x=0} \]

(4)

\[ D_{CuI_m} \left( \frac{\partial c_{CuI_m}(x,t)}{\partial x} \right)_{x=0} = 0 \]

(5)

\[ c_{Cu(I)}(0,t) = c_{Cu(I)}(0,t)e^\eta \]

(6)

with \( \eta \) given by

\[ \eta = \frac{F}{RT} \left( E_s - E_{Cu(II)/Cu(I)} \right) \]

(7)

In these equations, \( c_i(x,t) \) and \( D_i \) are, respectively, the concentration of the species \( i \) and its diffusion coefficient, \( c^* \) is the bulk concentration of species Cu(II) and other symbols have their usual meaning.

The solution for this problem has been derived rigorously for spherical and planar electrodes by assuming equal diffusion coefficients for all the species involved in the EC process [36] (i.e. \( D_{Cu(II)} = D_{Cu(I)} = D_{CuI_m} \) in this particular case). If different diffusion coefficients are considered for species Cu(II) and Cu(I) and supposing that the function perturbation of the chemical equilibrium \( (\phi(x,t) = c_{Cu(I)}(x,t) - K c_{CuI_m}(x,t) ) \) does not depend on time (i.e. assuming kinetic steady state conditions [kss]) [28,37] the following expression for the \( J/E \) response is derived

\[ \frac{J_{EC}}{J_d} = \frac{1 + K}{1 + K + \chi \gamma e^\eta} F(\chi_{EC}) \]

(8)

where \( \chi_{EC}, K \) and \( \gamma \) are given by

\[ \chi_{EC} = 2\sqrt{\frac{\gamma e^\eta(1 + K + \chi \gamma e^\eta)}{F(\chi_{EC})}} \]

(9)

\[ K = k_2/k_1 \]

(10)

\[ \gamma = \sqrt{\frac{D_{Cu(II)}}{D_{Cu(I)}}} \]

(11)

with \( \chi \) being the dimensionless rate constant of the complexation reaction.
\[ \chi = (k_1 + k_2)t \]  
\[ j_d \text{ the diffusion limited current density} \]  
\[ j_d = -FA \sqrt{\frac{D_{\text{Cu(II)}}}{\pi t} \rho^c} \]  
and \( F(x) \) being given by
\[ F(x) = \sqrt{\frac{X}{\pi}} e^{x/2} \text{erf} \left( \sqrt{\frac{X}{2}} \right) \]  
Eq. (8) is applicable for any \( K \) value provided \((k_1 + k_2)t \geq 5\) [38].

Note that \( K \) given by Eq. (10) represents the inverse of the equilibrium constant taken of pseudo-first order with respect to \( \text{Cu (II)} \). The expression for the real equilibrium constant of the complexation reaction is
\[ K_{\text{real}} = \frac{1}{K(E^c)^m} = \frac{c_{\text{Cu(I)a}}}{(c_{\text{Cu(II)}})^m} \]

The expression for the surface concentrations for all the species involved in the first stage of the electrodeposition process are obtained by following a similar procedure to that used in Ref [28] and have the following form

| Table 1 |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( v \) in mV s\(^{-1} \) | \( E_{\text{pa}} \text{V} \) | \( E_{\text{pc}} \text{V} \) | \( |E_{\text{pc}} - E_{\text{pa}}|/V \) | \( j_p \text{ in mA cm}\(^{-2} \) |
| 5 | 0.393 | 0.307 | 0.086 | 0.1698 |
| 10 | 0.397 | 0.295 | 0.102 | 0.22 |
| 20 | 0.401 | 0.286 | 0.115 | 0.3085 |
| 50 | 0.407 | 0.288 | 0.119 | 0.4912 |
| 70 | 0.417 | 0.283 | 0.134 | 0.5166 |
| 100 | 0.424 | 0.26 | 0.164 | 0.5906 |
| 150 | 0.434 | 0.248 | 0.186 | 0.7871 |

\( \text{E vs Ag/AgCl} \)

Fig. 1. Voltammetric curves at 50 mV s\(^{-1} \) from: a) 0.05 M CuCl\(_2\) in DES solvent and b) 0.01 M CuCl\(_2\)+3 M NaCl aqueous solution. Inset: voltammetric curves in DES solution: solid line 0.05 M CuCl\(_2\) and dashed line 0.05 M CuCl.

Fig. 2. (A) Scheme of the applied double step signal. B) Potentiostatic current transients for the electro-reduction of Cu (II) to Cu(I) from 0.05 M solutions of CuCl\(_2\) in DES solvent at 40 °C at different \( t \): a) 400, b) 380, c) 370, d) 350, e) 340, f) 330, g) 300, h) 250, i) 150, j) 0, k) −100 and m) −200 mV.

\[ c_{\text{Cu(II)}(0,t)} = 1 + \frac{1}{1 + K + K \gamma e^0} \left( 2 \sqrt{\pi} \chi^c \right) - 1 \]  
\[ c_{\text{Cu(I)a}}(0,t) = c_{\text{Cu(II)}}(0,t)/e^0 \]  
\[ c_{\text{Cu(II)a}}(0,t) = c_{\text{Cu(II)}}(0,t)/e^0 \]  
When \( \chi^c \geq 21.5 \), the diffusive-kinetic steady state (dkss) approximation applies [22,33]. Under these conditions, \( F(\chi^c) = \sqrt{\pi} \chi^c / (2 + \sqrt{\pi} \chi^c) \) and Eq. (8) for the \( j/E/t \) response simplifies to
\[ \frac{j_{\text{EC}}}{j_d} = \frac{1 + K}{1 + K + \gamma e^0 (K + 1/\sqrt{\pi} \chi)} \]  
This response is quite interesting since it can be linearized in an identical way to that corresponding to a simple \( E \) process, so we have
\[ E = E_{1/2} + \frac{RT}{F} \rho (\frac{j_d - j_{\text{EC}}}{j_{\text{EC}}}) \]
with $E_{1/2}$ being the half-wave potential

$$E_{1/2} = E^0_{{\text{Cu(II)}}/\text{Cu(I)}} + \frac{RT}{n \ln(1 + K)}$$

(19)

Expressions (17)–(19) could be used for a general good description of the system instead of those deduced under kss conditions [28,37] and are very helpful to estimate the values of $E_{1/2}$, $K$ and/or $\chi$ avoiding numerical fitting, as is shown in Fig. 6.

3.2. Treatment for the Nucleation and Growth

The mechanistic analysis of the Cu(I)–Cu(0) electrodeposition was performed from the chronoamperometric results using the well-known Scharifker and Hills (S-H) model, developed for nucleation and three-dimensional growth diffusion controlled, whose basis are well-established and which can be consulted elsewhere [29,30]. The two non-dimensional equations given by Eqs. (20) and (21) and correspond to the limiting cases of progressive and instantaneous nucleation, respectively. The former is associated with nuclei sequential appearance whereas the latter identifies with simultaneous nuclei formation:

$$\left( \frac{j}{j_m} \right)^2 = 1.2254 \left( \frac{t}{t_m} \right)^{-1} \left[ 1 - \exp \left( -2.3367 \left( \frac{t}{t_m} \right)^2 \right) \right]^2$$

(20)

$$\left( \frac{j}{j_m} \right)^2 = 1.9542 \left( \frac{t}{t_m} \right)^{-1} \left[ 1 - \exp \left( -1.2564 \left( \frac{t}{t_m} \right)^2 \right) \right]^2$$

(21)

where $j$ and $t$ represent, respectively, the current density and the time during the nucleation and growth stages, and $j_m$ and $t_m$ are the values of these magnitudes at which the potentiostatic maximum is attained.

By assuming that the charge-transfer rate for copper deposition is sufficiently high for a continued growth of nuclei through mass transfer control to be established and that there is no overlapping of the nuclei randomly distributed on the surface, the rising part of the $j$–$t$ transients can also be used as an adequate tool for mechanistic analysis. The corresponding equations derived for progressive and instantaneous nucleation, respectively, are the followings:
Fig. 5. Potentiostatic current transients at different residence times (t₁): a) 15 b) 30 and c) 45 s from: A) 0.05 M solution of CuCl₂ in DES solvent, E₁ = −100 mV, E₂ = −390 mV. B) 0.01 M solution of CuCl₂ + 3 M NaCl aqueous solution, E₁ = 0 mV, E₂ = −390 mV.

\[ j = \frac{2}{3}ZF(2DC)^{1/2}M^{1/2} \rho^{-1/2}N_cAt^{1/2} \]  

(22)

where \( D \) is the diffusion coefficient of the depositing species, \( c, M \) and \( 2F \) are its concentration, molecular weight, and molar charge, respectively, \( \rho \) is the density of the solution, \( N_c \) the maximum number of nuclei obtainable under the prevailing conditions and \( A \) the steady state nucleation rate constant per site [29].

As an extra diagnostic criterion to study the nucleation mechanism governing the process, the \( J_{mf}t_m^2 \) products for the limiting cases of progressive and instantaneous nucleation (Eqs. (24) and (25), respectively) can be used to determine whether the nucleation process is progressing or has been arrested, by taking advantage of the surface concentration values previously obtained. The \( J_{mf}t_m^2 \) products do not contain quantities related to kinetic parameters, fact that makes them valuable [29].

\[ J_{mf}t_m = 0.260(Fcz)^2D \]  

(24)

\[ J_{mf}t_m = 0.163(Fcz)^2D \]  

(25)

4. Results and discussion

4.1. General behaviour

The voltammetric curves recorded in both media (Fig. 1) showed similar profile, the peaks corresponding to the Cu(II)-Cu(I) reduction were followed by a second group of features at more negative potentials related to Cu(I) electrodeposition [26].

In aqueous chloride medium the peaks related to Cu(I) electrodeposition were sharper and less negative than those recorded in the DES. The inset in Fig. 1 shows a good coincidence between the voltammetric curves recorded from Cu(II) and Cu(I).
solutions in the potential range where copper electrodeposition takes place.

The diffusion coefficients of Cu(II) and Cu(I) in the DES solution at 40 °C were respectively determined from voltammetric experiments and potentiostatic electrodeposition transients as described in reference [26]. Cyclic voltammograms were recorded at different scan rates. The differences \( \Delta E_{p,c} - \Delta E_{p,a} \) between the cathodic and anodic peak potentials (Table 1) approached 85 mV at the lowest scan rates and increased as the scan rate did, behaviour that can be ascribed to the resistance of organic media [21]. The Cu(II) diffusion coefficient calculated according to Eq. (26) [27]

\[
jp c \approx 0.4463 \times \left( \frac{F^3}{RT} \right)^{1/2} \times n^{3/2} \times D_{Cu(II)} \times \frac{\delta}{\delta}
\]

was 2.24 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}, consistent with previously reported values at other temperatures [21,26].

The Cu(I) diffusion coefficient was determined in a 0.05 M CuCl2 solution. The ends of the descending part of the recorded transients overlapped as befits a diffusion controlled process. Adjustment according to the well-known Cotrell equation led to an average value of 2.08 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}.

**Table 2**

<table>
<thead>
<tr>
<th>( E ) in mV</th>
<th>( t_m ) in s</th>
<th>( J_m ) ( \times 10^3 ) A cm(^{-2} )</th>
<th>( J_m t_m ) ( \times 10^3 ) A cm(^{-2} ) s</th>
</tr>
</thead>
<tbody>
<tr>
<td>-360</td>
<td>2.55</td>
<td>-5.24</td>
<td>7.00</td>
</tr>
<tr>
<td>-370</td>
<td>1.47</td>
<td>-6.5</td>
<td>6.21</td>
</tr>
<tr>
<td>-390</td>
<td>0.76</td>
<td>-8.95</td>
<td>6.09</td>
</tr>
<tr>
<td>-395</td>
<td>0.61</td>
<td>-10.2</td>
<td>6.35</td>
</tr>
<tr>
<td>-400</td>
<td>0.39</td>
<td>-12.8</td>
<td>6.38</td>
</tr>
</tbody>
</table>

\( E \) vs (Ag/AgCl)

### 4.2. Surface concentration

The complete analysis of copper reduction was made by an accurate potentiostatic study using the double step signal proposed previously [26]. At first the potential was jumped from a potential \( E_0 \) where no process occurred to a potential \( E_1 \) at which only the reduction of Cu(II) to Cu(I) took place (Fig. 2A). After a residence time \( t_1 \) in the potential \( E_1 \), the potential was switched to a potential \( E_2 \) at which electrodeposition occurred. The recorded current showed two clear features, at first the current decayed monotonically to a quasi-stationary value (Fig. 2B) and, after applying the E2 potential, the transient showed the typical profile of a nucleation and 3D growth process (see Figs. 5, 6A and 8A).

A quantitative study was carried out to obtain information about the surface concentrations on the electrode along the residence time \( t_1 \). Fig. 3 displays the dependence on time of the surface concentrations of the species participating in the first stage of the copper reduction (i.e. Cu(II) to Cu(I) facilitated by chloride complexation) in the two media selected (aqueous solvent and DES, Fig. 3A and B respectively) obtained by applying Eq. (16). The \( E_1 \) values selected, 0 V in aqueous solution and -0.1 V in DES, were chosen according to the previous voltammetric results.

To build these plots it was taken into account that Cu(I) can bind either two or three chloride ions, giving rise to two different chloride complexes Cu(Cl)\(^m\) (where \( m = 2 \) or 3, solid and dotted lines, respectively, in the Fig. 3). The stability constant of the two different complexes was estimated in water using the information given in Ref [39] as \( K_{\text{complexation}}^{\text{water}} \approx 10^{5.5} \) for the complex with \( m = 2 \) and \( 10^{5.7} \) for the complex with \( m = 3 \). For the theoretical calculations, the equilibrium between the complexed and uncomplexed Cu(I) in DES was considered to be highly displaced towards the complexed species \( K_{\text{complexation}}^{\text{DES}} \approx K_{\text{complexation}}^{\text{water}} \).

The values of \( k_1 + k_2 \approx k_1 \) for these complexation reactions highly displaced to the products) required for \( \chi_{\text{EC}} \) to be known (Eq. (9)) and to plot the surface concentrations were obtained by non-linear fitting between the experimental Normal Pulse Voltammetric (NPV) signals and the theoretical ones (Eq. (8)) as depicted in Fig. 4. Chronoamperometric experiments at different potentials at which only the facilitated Cu(II) to Cu(I) reduction took place were used to build the experimental NPV responses.

Tentative initial values for \( k_1 \) were obtained by introducing experimentally determined \( E_{1/2} \) values in Eq. (19). These \( E_{1/2} \) values were estimated by the linearized \( E_1 \) versus \( (j_t - j_{EC})/j_{EC} \) plots (Eq. (18)) as shown in the inset figures. The tentative initial value used for \( E_{1/2}^{\text{Cu(II)/Cu(I)}} \) was 159 mV, obtained from the literature [27].

The optimum values of \( E_{1/2}^{\text{Cu(II)/Cu(I)}} = \frac{E_{1/2}^{\text{Cu(I)}} - \frac{1}{2} E_{1/2}^{\text{Cu(II)}}}{j_{Cu(I)}} = \frac{1}{2} E_{1/2}^{\text{Cu(II)}} \) and \( k_1 \) that yielded the best fitting were 162 mV and \( 29 \times 10^3 \text{ s}^{-1} \) for the data obtained in the aqueous solvent, and 168 mV and \( 12 \times 10^3 \text{ s}^{-1} \) for that obtained in DES. From these, the values for the real forward kinetic constant of the complexation reaction \( K_{\text{complexation}}^{\text{water}} \approx K_1^{\text{water}} \) were obtained in the two media for the possible complexes...
considered (i.e. those with \( m = 2 \) or \( 3 \)) as \( k_1^{\text{red}} \approx 3.2 \times 10^3 \text{M}^{-2} \text{s}^{-1} \) and \( 1.1 \times 10^5 \text{M}^{-3} \text{s}^{-1} \) for the complexes with \( m = 2 \) and \( 3 \), respectively, in the aqueous solvent, and \( k_1^{\text{red}} \approx 4.8 \times 10^2 \text{M}^{-2} \text{s}^{-1} \) and \( 10^2 \text{M}^{-2} \text{s}^{-1} \) for the complexes in DES.

Several conclusions can be drawn from the analysis of the plots given in Fig. 3. First, it can be seen that the surface concentration of Cu(II) is almost always zero at any time of the experiment in both water and DES. These applied potentials correspond to conditions of diffusion controlled current for the Cu(II)/Cu(I) reduction, beneficial conditions to the generation of Cu(I). Besides, it is observed that as time increases the concentration at the electrode surface of complexed Cu(I) increases, at the expense of a decrease in the surface concentration of free Cu(I). The observed variation is slight for both media, such that \( c_{\text{Cu}(I)}(0, t) \) approximates quickly to the limiting value of \( yc^+ \) (Eq. (27)), which corresponds to 4.946 \( 10^{-3} \) and 16.393 \( 10^{-3} \) M in the aqueous media and in DES (Fig. 3A and B), respectively.

Under diffusion controlled conditions \( (E_1 \ll E_2^{\text{p}} \text{of} \text{Cu(II)/Cu(I)}) \) and for complexation reactions highly displaced toward the products \((K_{\text{red}} \gg 1 \) or \( K = k_2/k_1 < 1\), the surface concentrations involved in the EC mechanism simplify to

\[
\begin{align*}
\frac{c_{\text{Cu(II)}(0, t)}}{c} &= 0 \\
\frac{c_{\text{Cu(II)}(0, t)}}{c^+} &= \gamma \sqrt{\pi \chi} \\
\frac{c_{\text{Cu}(I)(0, t)}}{c^+} &= (1 - 1/\sqrt{\pi \chi}) \gamma
\end{align*}
\]

(27)

with \( c^+ \) being the initial concentration of Cu(II) in solution and \( \gamma \) and \( \chi \) given by Eqs. (11) and (12), respectively. From Eq. (27) it can be seen that when time increases and \( \chi(= k_1 + k_2 \gamma \tau) \gg 1 \), the surface concentrations of free and complexed Cu(I) tend to zero and to \( yc^+ \), respectively. Eq. (27) constitutes a simple set of expressions that are adequate to obtain the evolution of the surface concentration with time in our system.

Note that, under the conditions selected there is no difference between the curves corresponding to the complex with \( m = 2 \) and \( m = 3 \), which coincides with the behaviour predicted by Eq. (27).

4.3. Nucleation and growth

In order to address the study of the electrodeposition process in both media, different residence times within the time range in which the surface concentrations showed a quasi-stationary value were selected \( (t_1 = 15, 30 \) and \( 45 \) s). After the E_2 application, new \( j \)-t transient appeared showing the typical nucleation and 3D growth controlled by diffusion profile.

For the three residence times selected the comparison of the transients recorded at a given \( E_2 \) did not reveal significant differences in the rate of the deposition process (Fig. 5A and B). Indeed, quasi coincidence was observed in the current profiles, the current maxima \( (j_{\text{m}}) \) and the time elapsed \( (t_{\text{m}}) \) between the \( E_2 \) application, and also on the achievement of the current maximum. These results are in agreement with those provided by the theory, with the Cu(I) concentration reaching a constant value from a certain \( t_1 \).

4.3.1. Copper electrodeposition in aqueous chloride excess medium

In aqueous chloride excess medium several \( j \)-t transients were recorded by means of the double step signal for all the \( t_1 \) selected, at different values of \( E_2 \) keeping \( E_1 \) at 0 V. On increasing the overpotential applied the recorded current increased and the maximum was attained at a lower time. Note that a narrow potential range (c.a. 20 mV) was sufficient to observe relevant changes in the recorded \( j \)-t transients.

Fig. 6A and B show, respectively, the \( j \)-t transients recorded at \( t_1 = 15 \) s and the corresponding adjustment to the non-dimensional S-H model. The adjustment of the \( j \)-t transients was made once the current related to Cu(II)–Cu(I) reduction was subtracted from the total current to avoid overestimation of the current related to copper electrodeposition. The S-H adjustment showed that the nucleation mechanism was intermediate and close to instantaneous even at the lowest overpotentials applied.

The analysis of the rising part of the experimental transients (Eqs. (22) and (23)) revealed that, for the lowest overpotentials applied, the slopes were close to 0.7, and on increasing overpotential, the slope tended to 0.5, as corresponds to instantaneous nucleation (see also reference [26]). These results are in well agreement with those provided by S–H adjustment, so, in aqueous chloride excess the nucleation was close to the instantaneous one.

In order to analyse the possible influence of the residence time on the nucleation mechanism, the adjustment of S–H model for several \( j \)-t curves recorded at a fixed \( E_2 \) and different \( t_1 \) values were compared (Fig. 7A). Non relevant differences were found in the
time range previous to the maximum. However, the adjusted data from \( t > t_m \) showed slight differences. The curve corresponding to \( t_1 = 45 \text{s} \) appeared farther to the instantaneous limiting case than those recorded after 15 s or 30 s. This can be explained by taking into consideration that extending the residence time in the Cu(I)–Cu(II) electro-reduction zone could favour, in the aqueous medium, the formation of a low amount of insoluble CuCl species, which could perturb the deposit growth. Thus, the data recorded after 15 s were considered more reliable for the mechanistic analysis.

The knowledge of surface concentrations of Cu(I) (see Fig. 3) at the instant that \( E_2 \) was applied allowed the use of the products \( j_m^2t_m \) as an extra tool to analyze the nucleation mechanism. For \( t_1 = 15 \text{s} \) the surface concentration was \( 4.9 \times 10^{-7} \text{M} \), which together with a value for the Cu(I) diffusion coefficient of \( 1.5 \times 10^{-5} \text{cm}^2 \text{s}^{-1} \) [26] yielded \( j_m^2t_m \) products of \( 8.87 \times 10^{-7} \) and \( 5.56 \times 10^{-7} \text{A}^2 \text{cm}^{-2} \text{s} \) for progressive and instantaneous nucleation, respectively. The obtained \( j_m^2t_m \) products (Table 2) evolved on increasing the overpotential from \( 7 \times 10^{-7} \) to \( 6 \times 10^{-7} \text{A}^2 \text{cm}^{-2} \text{s} \), values close to those predicted for instantaneous mechanism. These results in good agreement with both those obtained from the overall S–H adjustment and those from rising part analysis, also indirectly support the results derived from the theoretical treatment of the potentiostatic curves recorded at \( E_2 \), which predict the appropriate concentration value of complexed Cu(I) species on the surface of the electrode.

4.3.2. Copper electrodeposition in the DES solvent

Proceeding in a similar way as in the aqueous medium, sets of j–t transients were recorded in DES at different residence times within the time zone at which the surface concentrations attained a stationary value. In the DES solvent a wide overpotential range was needed to observe significant changes in the recorded currents.

The comparison between experimental (Fig. 8A) and theoretical curves obtained from the S–H model (Fig. 8B), proved that in the DES solvent the nucleation mechanism was intermediate, near to progressive at the lowest applied overpotential, but without fully attainment of the instantaneous limit with significant \( E_2 \) increase. Therefore, from the non-dimensional analysis, the effect of the solvent nature on the mechanism seems clear. The growth of the nucleus formed was slowed by DES even for moderate temperatures (40 °C), effect observed previously for the deposition of other metals [32].

Complementary analysis of the mechanism which governs the formation of the first nucleus was also made by logarithmic analysis of the rising part of the j–t curves at short deposition times in the same way depicted in reference [26]. The slopes calculated evolved from 1.0 to 0.6 on increasing the overpotential, i.e. the nucleation tended to instantaneous nucleation when considerably increasing the overpotential but this limit was not fully attained as observed with the S–H fittings.

It is worth noting that in DES both the j–t curves recorded a fixed \( E_2 \) after different residence times (\( t_1 \)) and the corresponding non-dimensional adjustments did not show significant differences with respect to the \( t_1 \) value selected, as occurred in aqueous medium. The non-dependence between the residence time in \( E_1 \) and the electrodeposition process once the surface concentration of Cu(I) behaves in a stationary manner was confirmed by comparison of the S–H adjusted curves obtained at the different residence times selected (Fig. 7B). In DES medium good agreement between experimental and adjusted curves was found even at long deposition times. This behaviour could be related to both the higher chloride concentration in the DES and the specific nature of this ionic solvent that benefits the intermediate Cu(I) complexation, avoiding the possible non-soluble Cu(I) species formation.

Using the surface concentration at the beginning of the electrodeposition process (0.01694 M) and the calculated diffusion coefficient, the products \( j_m^2t_m \) predicted by Eqs. (24) and (25) for the limiting cases were calculated and compared with those obtained from the extracted parameters from the experimental j–t curves. All the \( j_m^2t_m \) products obtained from the experimental data reproduced the magnitude order predicted by theory, although they were slightly higher than the value corresponding to progressive nucleation (not shown), which is always the highest value.

According to the literature, in DES solvent copper species are entirely complexed by chloride [40], but no information about the equilibrium constants values is provided, neither of the \( E^0 \) value of the couple Cu(II)/Cu(I) at DES. So, we used the \( K \) and \( E^0 \) values corresponding to aqueous medium as the initial guess values in the subsequent non-linear fitting of the experimental data. This first approximation could explain the slight discrepancy between the \( j_m^2t_m \) products from experimental values with those calculated theoretically.

The coherency between the results provided by the complete analysis with the S–H model and the analysis of the rising part of the transients confirms that an appropriate control of the initial conditions in the first stages of the electrodeposition and in the stationary concentration of Cu(I) on the surface was achieved, although in the DES medium this concentration value seems to be slightly underestimated.

5. Conclusions

In chloride excess medium the stabilization of the Cu(I) intermediate by chloride complexation slows down the second reduction stage and implies an extra overpotential to get electrodeposited copper. The double step potential method allows to study accurately the kinetics related to each step of the reduction. From the j–t curves recorded along the first reduction step and by applying the appropriate equations which describe the kinetics of the Cu(II)–Cu(I) reduction, the surface concentration versus time functions are deduced for a fixed potential, and the values of the surface concentrations of Cu(II), free Cu(I) and complexed Cu(I) present in the electrode are estimated in any condition. As these surface concentrations achieve a stationary value, it is shown that residence times greater than this stationary value are suitable to initiate the electrodeposition process at controlled conditions. From this knowledge, the length of the first step is selected by setting the residence time at which electrodeposition begins. Under these conditions, the analysis of the mechanism related to the first stages of the copper electrodeposition from Cu(I) is performed successfully in an aqueous concentrated chloride solution and in a Deep Eutectic Solvent (DES) providing reliable results, in agreement with those expected. In DES at the selected temperature progressive nucleation to intermediate is observed in a wide potential range, whereas in aqueous medium instantaneous nucleation is easy to get, a behaviour which is always supported by the logarithmic analysis of the rising part of the j–t transients.

The S–H non-dimensional analysis at a fixed \( E_2 \) value shows slight dependence on the growth mechanism between the results obtained at different residence times in aqueous medium and none in DES, so the selection of a residence time value close to that providing the stationary surface concentration theoretically predicted is enough for the appropriate mechanistic analysis.

The incorporation of the calculated surface concentrations in the \( j_m^2t_m \) products provides excellent concordance in aqueous medium, conditions at which thermodynamic parameters are available, showing the performance of the theoretical treatment. A slight displacement between experimental and calculated \( j_m^2t_m \) values is observed in the DES medium, in which underestimated
concentration values seem to have been obtained probably due to the uncertainty in the estimation of the formal potential. The results obtained sustain the use of the double step mode as a very good approximation to analyze accurately the Cu electrodeposition in both water and DES when considering the stabilization of the Cu(I) intermediate by complexation, avoiding the uncertainty associated with the application of a single step. Additional studies that not only rely on voltammetric data would be highly beneficial to know more of the physicochemical properties of this novel solvent and to understand how better it affects thermodynamic and kinetic parameters of the charge transfer and complexation reaction so as to refine model predictive abilities.

The strategy developed here for the analysis of the copper electrodeposition by using experimental data of the two electrochemical steps involved can be extended to any deposition process in which the overall reduction take place via two well separated stages.

References