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

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A B S T R A C T

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 potentiostatic step signal was employed to record j–t 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 Sharifker-Hills model, $j_m^2 t_m$ products and rising part analysis including the calculated parameters, which are strengthened as valuable tools for complete copper electrodeposition analysis in these media.

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## 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 potentiostatic 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 electroreduction 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

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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:

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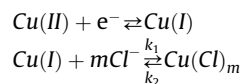
where $k_1$ and $k_2$ indicate the forward and backward kinetic constants of the chemical reaction taken to be of pseudo-first order and $m = 2$ or 3 (i.e $Cu(Cl)_m = Cu(Cl)_2^-$ or $Cu(Cl)_3^{2-}$).

When a constant potential, $E_1$, 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:

$$\left. \begin{array}{l} \hat{\delta}_{Cu(II)} = 0 \\ \hat{\delta}_{Cu(I)} = -k_1 c_{Cu(I)}(x,t) + k_2 c_{Cu(Cl)_m}(x,t) \\ \hat{\delta}_{Cu(Cl)_m} = k_1 c_{Cu(I)}(x,t) - k_2 c_{Cu(Cl)_m}(x,t) \end{array} \right\} \tag{1}$$

being

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \frac{\partial^2}{\partial x^2} \tag{2}$$

$$\left. \begin{array}{l} t = 0, x \le 0 \\ t \ge 0, x \to \infty \end{array} \right\} c_{Cu(II)}(x,t) = c^*, c_{Cu(I)}(x,t) = 0, c_{Cu(Cl)_m}(x,t) = 0 \tag{3}$$

$$x = 0, t > 0$$

$$D_{Cu(II)} \left( \frac{\partial c_{Cu(II)}(x,t)}{\partial x} \right)_{x=0} = -D_{Cu(I)} \left( \frac{\partial c_{Cu(I)}(x,t)}{\partial x} \right)_{x=0} \tag{4}$$

$$D_{Cu(Cl)_m} \left( \frac{\partial c_{Cu(Cl)_m}(x,t)}{\partial x} \right)_{x=0} = 0 \tag{5}$$

$$c_{Cu(II)}(0,t) = c_{Cu(I)}(0,t)e^\eta \tag{6}$$

with $\eta$ given by

$$\eta = \frac{F}{RT} \left( E_1 - E^{0'}_{Cu(II)/Cu(I)} \right) \tag{7}$$

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. $D_{Cu(II)} = D_{Cu(I)} = D_{Cu(Cl)_m}$ 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 $\left( \phi(x,t) = c_{Cu(I)}(x,t) - K c_{Cu(Cl)_m}(x,t) \right)$ does not depend on time (i.e. assuming kinetic steady state conditions (kss)) [28,37] the following expression for the j/E/t response is derived

$$\frac{j_{EC}}{j_d} = \frac{(1+K)}{1 + K + K\gamma e^\eta} F(\chi^{EC}) \tag{8}$$

where $\chi^{EC}$, $K$ and $\gamma$ are given by

$$\chi^{EC} = \frac{2\sqrt{\chi}}{\gamma e^\eta} (1 + K + K\gamma e^\eta) \tag{9}$$

$$K = k_2/k_1 \tag{10}$$

and

$$\gamma = \sqrt{\frac{D_{Cu(II)}}{D_{Cu(I)}}} \tag{11}$$

with $\chi$ being the dimensionless rate constant of the complexation reaction