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

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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 electroreduction 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,  $j_m t_m$  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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Barcelona, January 11, 2015

Dear Prof. Birbilis,

Please find enclosed the revised version of the manuscript entitled “*Advances in Copper Electrodeposition in a Chloride Excess. A Theoretical and Experimental Approach*” by P. Sebastián, E. Torralba, E. Vallés, A. Molina and E. Gómez, referenced as **NB14-440**.

After a careful reading of the reviewer’s comments we agree with reviewer 1 in the partial reduction of the experimental content of the manuscript. In this line:

- a) Experimental section has been removed and merely specifies the different working temperature in DES, justifying the selection.
- b) The 4.1. General behaviour section has been reduced and concisely new DES related results are included. Figures 2 and 3 in the old version have been removed as well and only the corresponding results are included.
- c) An effort to reduce the text related to previously published results has been made along the text.
- d) Figures 9 and 12 in the old version have also been removed and the reader is referred to the previous paper (ref[26]) for more information about experimental procedures.

All changes are highlighted in yellow in the new version.

On the other hand, we would like to state that the experimental content of this manuscript was performed according to the conditions advised by the theoretical model. For this reason the results included do not coincide with those previously published. We consider that the rest of experimental figures are necessary to follow the argument of the manuscript.

Please find attached the answers concerning to the questions raised by referees 1 and 2 in the document "Response to the reviewers"

We hope that, this new version is now suitable to be published in *Electrochimica Acta*.

Thank you in advance for your interest.

Yours sincerely,

The authors

Reviewer #1

First of all we would like to thank the reviewer for his/her constructive comments. In the following we answer to his/her questions and suggestions explaining the modifications we have made in this revised version following them.

*Reviewer #1: The manuscript by P. Sebastian et al present in depth study of the nucleation and growth mechanism of copper electrodeposition with stabilization of intermediate through chloride complexation. Authors expand on their previous finding of "Copper electrodeposition in a deep eutectic solvent. First stages analysis considering Cu(I) stabilization in chloride media" which was published recently in Electrochim. Acta, 123 (2014) 285 earlier this year.*

*Well written, the manuscript adds new details on intermediates involves in the Cu reduction, but experimentally, is trails path of the previous publication, along with similar experimental approach. As a matter of fact, same concentration of Cu ( 0.05 M CuCl<sub>2</sub> in DES solvent) were used in both published and current experimental.*

In this manuscript, the results derived for the Cu(II) electrodeposition in DES solvent correspond to a working temperature of 40°C, lower than that previously used in reference 26 of 70°. This lower temperature was selected in order to prevent the possible decomposition of the solvent at long working times. For this reason experimental results related to DES solvent were included in the text.

*Some parts of the manuscript (especially experimental) were copy-pasted from the previous publication, the authors also carried over misprints. For instance, p.4 "Higroscopicity" instead of hygroscopicity into the current manuscript. Same misprint can be found on page 286 of published manuscript.*

The experimental procedure was included in order to avoid the reader searching for the other paper. We apology for the misprint.

In this new version, the content of Experimental section has been removed, and merely specifies the working temperature in DES, justifying its selection.

*I feel it would be more appropriate to focus only on theoretical parts of the modeling, referencing previous experimental results.*

According to the reviewer suggestions, in this new version the *4.1. General behaviour section* has been reduced and concisely DES related results are included. Figures 2, 3 in the old version have been removed as well. An effort to reduce the drafting of some paragraphs related to previous work has been made along the text.

With respect to the nucleation and growth section we would like to clarify that its experimental content is related to different residence times at the potential E1, according to the conditions needed to test the theoretical model, and so it corresponds to different experimental results that those previously obtained and published in *Electrochim. Acta*, 123 (2014) 285. Nevertheless, following the referee's suggestions Figures 9 and 12 of the old version related to the rising part analysis of the j-t transients have been removed and only their results are briefly presented. The reader is referred to the previous manuscript for more information about the experimental procedures.

Reviewer #2:

We would like to thank the reviewer 2 for his/her in-depth reading of the manuscript. In the following we answer to his/her questions in the same order that he/she stated them.

*Reviewer #2: This paper presents an analysis of pulsed electrodeposition of copper in two concentrated chloride solutions - an aqueous NaCl solution and a deep eutectic choline chloride solvent (DES). High Cl<sup>-</sup> concentration stabilizes the Cu(I) intermediate, so the Cu<sup>+2</sup>/Cu<sup>+</sup> and Cu<sup>+</sup>/Cu reactions occur at significantly different potentials. In the double pulse experiments, Cu<sup>+</sup> species are produced at the first potential E1 and Cu deposited at the second potential E2. The Cu<sup>+2</sup>/Cu<sup>+</sup> reaction at E1 is modeled by a classic EC mechanism with diffusion controlled electrode reaction and Cl<sup>-</sup> complexation the chemical step. The deposition process at E2 is treated by the Sharifker-Hills diffusion-controlled electrochemical nucleation and growth model. The analysis appears to be successful, so that apparently these high Cl<sup>-</sup> concentration experiments remove the ambiguity typically produced when the potential ranges of the two processes overlap significantly. The model and results are presented clearly and the paper is generally well written.*

*Copper electrodeposition is important in fabrication of interconnects for semiconductor devices, and chloride at low concentrations is an important additive in the damascene baths for this process. In particular, chloride appears to accelerate deposition by an unknown mechanism*

*(even without other additives). Also, there is a lot of recent work on electrodeposition from non-aqueous solutions. Therefore, there is considerable interest in this topic and so the paper is appropriate for Electrochimica Acta. I recommend publication with minor revisions.*

*This paper seems to constitute progress towards quantitative treatment of chloride effects on electrodeposition. From the results, both the  $\text{Cu}^{+2}/\text{Cu}^{+}$  reactions and the growth of nuclei are under diffusion control, with only the chloride complexation reaction controlled by kinetics. In fact, it is shown that after sufficient time at E1, the complexation reaction is also at equilibrium. Would the model apply at the low chloride concentrations of greater technological interest? Does the model provide insight into possible acceleration mechanisms at low chloride concentration?*

In the development of our theoretical model we assume that the bulk concentration of chloride ion in solution is large enough compared with that of Cu(I) in order to a pseudofirst-order kinetics is satisfied. If this condition is not fulfilled our model could not be applied and the mass transport should be solved numerically. So, high chloride concentrations are required.

*The authors mention that the voltammetric peak separation in DES is much larger than expected for diffusion-controlled reactions, and suggest that the ohmic resistance of the solution may be significant. It seems that proper inclusion of ohmic effects could dramatically change the model. Migration terms in the species balances and the electroneutrality condition would be included to fully account for migration effects. Why is this model still valid if migration is important?*

One of the main disadvantages of sweep voltammetric techniques like CV is the distortion caused by the combination of the double layer charging process with the ohmic drop, related with the uncompensated resistance of the solution. This distortion is much less severe in pulse techniques, due to the discrete nature of the recorded current [V. Mirceski, S.Komorsky-Lovric, M. Lovric in Square-Wave Voltammetry, Theory and Application, Springer, Heidelberg 2007]. Our theoretical model is derived for the application of a single potential pulse (Normal pulse voltammetry) so it is expected that under the experimental conditions selected the IR effect is not significant on the NPV response. Moreover, the ionic concentration of inert electrolyte in both aqueous and DES medium is so high in comparison with the copper concentration that it can be expected

that the migration effects will not have significant influence [J. Phys. Chem. 2009, 113, 11157-11171]

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

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4 **Abstract**  
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7 This is an in depth study in the knowledge of the nucleation and growth mechanism that  
8 governs copper electrodeposition in excess chloride media. In these conditions copper  
9 electro-reduction takes place via two well-separated steps, since the Cu(I) intermediate  
10 is stabilized through chloride complexation. The process was studied in two media, a  
11 deep eutectic solvent (DES) based on a mixture of urea and choline chloride, and in  
12 excess chloride aqueous solution, in order to also analyse solvent influence on the early  
13 stages of the deposition process. In both media, copper electrodeposition follows a  
14 nucleation and a diffusion controlled three-dimensional growth mechanism. In line with  
15 a previous work a double potentiostatic step signal was employed to record j-t transients  
16 associated to both nucleation and growth stages, and from them, the whole mechanistic  
17 analysis of the copper electrodeposition was performed. This analysis involved the  
18 calculation of the surface concentrations of Cu(II), free Cu(I) and complexed Cu(I) for  
19 any time and potential required and the application of Sharifker-Hills model,  $j_m^2 t_m$   
20 products and rising part analysis including the calculated parameters, which are  
21 strengthened as valuable tools for complete copper electrodeposition analysis in these  
22 media.  
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47 *Keywords:* copper electrodeposition, first stages, surface concentration, chloride effect,  
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4 **1. Introduction**  
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7 Copper electrodeposition has been for a long time an important topic due to the interest  
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9 that copper coatings have in a wide range of applications. This has been heightened yet  
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11 more by the massive use of copper in the electronics industry [1-4].  
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15 As it is well known, the presence of free or complexed cations in solution has an  
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17 important role on the overall deposition process, as they strongly affect both nucleation  
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19 and growth. In the copper's case, for instance, some commercial and laboratory copper  
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21 deposition baths incorporate species which can act as complexing agents, some of them  
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23 (such as ammoniac, chloride, bromide, cyanide, thiocyanide, etc.) acting as well as  
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25 complexing agents for the Cu(I) intermediate [5-7].  
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29 Due to its fundamental and theoretical importance there is no lack of reports related to  
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31 the Cu deposition mechanism [8-14]. However, to the best of our knowledge, there is no  
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33 literature with takes into consideration a possible intermediate stabilization when  
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35 performing the mechanistic analysis via chronoamperometric method. The mechanistic  
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37 analysis of the first deposition stages using chronoamperometric data has usually been  
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39 performed by recording the response after the application of a typical single  
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41 potentiostatic step. This procedure, however, does not lead to reliable results when  
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43 stabilization of the intermediate occurs, so that comments related to divergent or  
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45 unexpected results have been included in some of the reports [4,15-17].  
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50 Recently it has been proved that ionic liquids based on eutectic mixtures of choline  
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52 chloride and hydrogen bond donors (known as deep eutectic solvents (DES)) can be  
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54 used for copper electrodeposition [18-21]. In these media, chloride is present in excess  
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56 (about 5M) and the intermediate Cu(I) is stabilized by complexation with it, such that  
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58 the complete electroreduction process takes place via two well-separated one-electron  
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4 stages. This behaviour is similar to that previously observed in aqueous concentrated  
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6 chloride solutions [22-25]. In a previous work the first stages of Cu(II) reduction were  
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8 studied in two chemical systems having in common a chloride excess (DES and  
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10 aqueous concentrated chloride solution) [26]. In both media, it was proposed to apply a  
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12 double-step signal in the chronoamperometric study as an adequate procedure to obtain  
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14 reproducible results on nucleation and growth processes. The overall profile of the  $j$ - $t$   
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16 response obtained by using this double-step signal presents two clear zones related to  
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18 Cu(II) to Cu(I) reduction and to the Cu electrodeposition from Cu(I). The purpose of  
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20 this work is to extend the previous studies and to deepen the knowledge of the  
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22 mechanism governing Cu(II) electro-reduction by carrying out the complete quantitative  
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24 analysis of the two reduction processes mentioned above. This requires knowing the  
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26 surface concentration of the ionic species of interest on the electrode at the instant in  
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28 which the second potential step is applied, which enables the proper selection of the  
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30 residence time value at the first applied potential and so the control of the conditions at  
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32 which the electrodeposition starts. In this line, a quantitative study that allows  
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34 evaluation of the surface concentrations of the species involved in the first stages of the  
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36 deposition process (i.e. Cu(II), free Cu(I) and complexed Cu(I)) has been carried out in  
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38 both media (aqueous solvent and DES), using analytical equations for the  
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40 current/potential response and surface concentrations obtained assuming that these first  
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42 stages follow an EC reaction scheme [27, 28]. The equations obtained enable us to  
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44 estimate the formal potential of the Cu(II)/Cu(I) couple and the complexation reaction  
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46 rate constant values between Cu(I) and chloride in the two media by nonlinear fitting  
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48 between experimental data and theoretical equations. Once the process has been  
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50 characterized, the surface concentration values of Cu(II), free Cu(I) and complexed  
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52 Cu(I) at any experiment time are readily obtained. Afterwards, the non-dimensional  
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4 Scharifker and Hills (S-H) model [29, 30] has been used to analyze the nucleation and  
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6 growth deposition processes, an approach that has already been applied recently to  
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8 deposition processes in ionic liquids [26, 31-34]. As will be shown, the knowledge of  
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10 surface concentration values allows the complete quantitative analysis to be  
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12 accomplished.  
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## 15 16 17 18 19 **2. Experimental**

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22 The preparation of solutions and the electrochemical experiments were performed in the  
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24 same way that had been previously described in reference [26]. The selected  
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26 temperature in DES solvent was 40°C, lower than in [26], in order to assure liquid  
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28 stability at long working times.  
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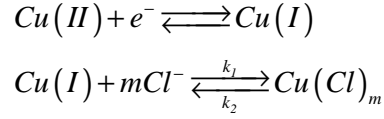
## 35 36 **3. Theory**

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38 It has been demonstrated that in a excess of chloride medium the intermediate Cu(I)  
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40 coming from the Cu(II) reduction in the first stage of the reduction process stabilizes by  
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42 complexation, and so the complete electrochemical process occurs by means two well  
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44 separated one-electron stages (Cu(II)-Cu(I) and Cu(I)-Cu(0)) [26].  
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### 48 49 ***3.1. Theoretical model for the first stage of the copper electrodeposition in excess of*** 50 51 ***chloride medium: Cu(II)/Cu(I) reduction facilitated by chloride complexation.*** 52

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



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.  $\text{Cu(Cl)}_m = \text{Cu(Cl)}_2^-$  or  $\text{Cu(Cl)}_3^{2-}$ ).

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:

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

being

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

$$\left. \begin{aligned} t=0, \quad x \leq 0 \\ t \geq 0, \quad x \rightarrow \infty \end{aligned} \right\} c_{\text{Cu(II)}}(x,t) = c^*, \quad c_{\text{Cu(I)}}(x,t) = 0, \quad c_{\text{Cu(Cl)}_m}(x,t) = 0 \quad (3)$$

$$x=0, \quad t > 0$$

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

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

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

with  $\eta$  given by

$$\eta = \frac{F}{RT} (E_1 - E_{Cu(II)/Cu(I)}^{0'}) \quad (7)$$

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

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

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

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

$$K = k_2 / k_1 \quad (10)$$

and

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

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4 with  $\chi$  being the dimensionless rate constant of the complexation reaction  
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$$\chi = (k_1 + k_2)t \quad (12)$$

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10  $j_d$  the diffusion limited current density  
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$$j_d = -FA\sqrt{\frac{D_{Cu(II)}}{\pi t}} c^* \quad (13)$$

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18 and  $F(x)$  being given by  
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$$F(x) = \sqrt{\pi} \frac{x}{2} e^{(x/2)^2} \operatorname{erfc}\left(\frac{x}{2}\right) \quad (14)$$

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27 Equation (8) is applicable for any  $K$  value provided  $(k_1 + k_2)t \geq 5$  [38].  
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30 Note that  $K$  given by Eq. (10) represents the inverse of the equilibrium constant taken of  
31 pseudo-first order with respect to Cu(II). The expression for the real equilibrium  
32 constant of the complexation reaction is  
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$$K^{real} = \frac{I}{K(c_{Cl^-})^m} = \frac{c_{Cu(Cl)_m}}{(c_{Cu(I)})(c_{Cl^-})^m} \quad (15)$$

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44 The expression for the surface concentrations for all the species involved in the first  
45 stage of the electrodeposition process are obtained by following a similar procedure to  
46 that used in Ref [28] and have the following form  
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$$\left. \begin{aligned}
\frac{c_{Cu(II)}(0,t)}{c^*} &= I + \frac{I+K}{I+K+K\gamma e^\eta} \left\{ \frac{2}{\sqrt{\pi}} \frac{F(\chi^{EC})}{\chi^{EC}} - I \right\} \\
c_{Cu(I)}(0,t) &= c_{Cu(II)}(0,t) / e^\eta \\
\frac{c_{Cu(Cl)_m}(0,t)}{c^*} &= -\frac{I}{e^\eta} \left[ I + \frac{(I+K)(1+\gamma e^\eta)}{I+K+K\gamma e^\eta} \left\{ \frac{2}{\sqrt{\pi}} \frac{F(\chi^{EC})}{\chi^{EC}} - I \right\} \right]
\end{aligned} \right\} \quad (16)$$

When  $\chi^{EC} \geq 21.5$ , the diffusive-kinetic steady state (*dkss*) approximation applies [22, 33]. Under these conditions,  $F(\chi^{EC}) = \sqrt{\pi}\chi^{EC} / (2 + \sqrt{\pi}\chi^{EC})$  and Eq. (8) for the  $j/E/t$  response simplifies to

$$\frac{j_{EC}}{j_d} = \frac{1+K}{1+K+\gamma e^\eta (K+1/\sqrt{\pi\chi})} \quad (17)$$

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

$$E = E_{1/2} + \frac{RT}{F} \ln \left( \frac{j_d - j_{EC}}{j_{EC}} \right) \quad (18)$$

with  $E_{1/2}$  being the half-wave potential

$$E_{1/2} = E_{Cu(II)/Cu(I)}^{0'} + \frac{RT}{F} \ln \left( \frac{1}{\gamma} \right) + \frac{RT}{F} \ln \left( \frac{(1+K)\sqrt{\pi\chi}}{1+K\sqrt{\pi\chi}} \right) \quad (19)$$

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 Figure 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) 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:

$$\left(\frac{j}{j_m}\right)^2 = 1.2254 \left(\frac{t}{t_m}\right)^{-1} \left[ 1 - \exp\left(-2.3367 \left(\frac{t}{t_m}\right)^2\right) \right]^2 \quad (20)$$

$$\left(\frac{j}{j_m}\right)^2 = 1.9542 \left(\frac{t}{t_m}\right)^{-1} \left[ 1 - \exp\left(-1.2564 \frac{t}{t_m}\right) \right]^2 \quad (21)$$

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

$$j = \frac{2}{3} zF \pi (2Dc)^{3/2} M^{1/2} \rho^{-1/2} N_o A t^{3/2} \quad (22)$$

$$j = zF \pi (2Dc)^{3/2} M^{1/2} \rho^{-1/2} N_o t^{1/2} \quad (23)$$

where  $D$ , is the diffusion coefficient of the depositing species,  $c$ ,  $M$  and  $zF$  are its concentration, molecular weight, and molar charge, respectively,  $\rho$  is the density of the solution,  $N_o$  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  $j_m t_m^2$  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  $j_m t_m^2$  products do not contain quantities related to kinetic parameters, fact that makes them valuable [29].

$$j_m^2 t_m = 0.260 (Fcz)^2 D \quad (24)$$

$$j_m^2 t_m = 0.163 (Fcz)^2 D \quad (25)$$

## 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].

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4 <Figure 1>  
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7 In aqueous chloride medium the peaks related to Cu(I) electrodeposition were sharper  
8 and less negative than those recorded in the DES. The inset in Figure 1 shows a good  
9 coincidence between the voltammetric curves recorded from Cu(II) and Cu(I) solutions  
10 in the potential range where copper electrodeposition takes place.  
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16 The diffusion coefficients of Cu(II) and Cu(I) in the DES solution at 40°C were  
17 respectively determined from voltammetric experiments and potentiostatic  
18 electrodeposition transients as described in reference [26]. Cyclic voltammograms were  
19 recorded at different scan rates. The differences  $|E_{p,c}-E_{p,a}|$  between the cathodic and  
20 anodic peak potentials (Table 1) approached 85 mV at the lowest scan rates and  
21 increased as the scan rate did, behaviour that can be ascribed to the resistance of organic  
22 media [21]. The Cu(II) diffusion coefficient calculated according to eq (26) [27]  
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$$j_{p,c} = 0.4463 * \left(\frac{F^3}{RT}\right)^{1/2} * n^{3/2} * D^{1/2}[Cu(II)]v^{1/2} \quad (26)$$

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38 was  $2.24 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ , consistent with previously reported values at other temperatures  
39 [21, 26].  
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42

43 <Table 1>  
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45  
46 The Cu(I) diffusion coefficient was determined in a 0.05 M CuCl solution. The ends of  
47 the descending part of the recorded transients overlapped as befits a diffusion controlled  
48 process. Adjustment according to the well-known Cottrell equation leads to an average  
49 value of  $2.08 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ .  
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#### 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  $E_2$  potential, the transient showed the typical profile of a nucleation and 3D growth process (see Figures 5, 6A and 8A).

<Figure 2>

A quantitative study was carried out to obtain information about the surface concentrations on the electrode along the residence time ( $t_1$ ). Figure 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, Figs. 3A and 3B respectively) obtained by applying Eq. (16). The  $E_1$  values selected, 0V in aqueous solution and -0.1V in DES, were chosen according to the previous voltammetric results.

<Figure 3>

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 Figure 3). The stability constant of the two different complexes was estimated in water using the information given in Ref [39] as

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4  $K_{water}^{real} = 10^{5.5}$  for the complex with  $m = 2$  and  $10^{5.7}$  for the complex with  $m = 3$ . For the  
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7 theoretical calculations, the equilibrium between the complexed and uncomplexed Cu(I)  
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9 in DES was considered to be highly displaced towards the complexed species (  
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11  $K_{DES}^{real} \approx K_{water}^{real} \gg 1$ ).

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15 The values of  $k_1 + k_2$  ( $\approx k_1$  for these complexation reactions highly displaced to the  
16  
17 products) required for  $\chi^{EC}$  to be known (Eq. (9)) and to plot the surface concentrations  
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19 were obtained by non-linear fitting between the experimental Normal Pulse  
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21 Voltammetric (NPV) signals and the theoretical ones (Eq. (8)) as depicted in **Figure 4**.  
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24 Chronoamperometric experiments at different potentials at which only the facilitated  
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26 Cu(II) to Cu(I) reduction took place were used to build the experimental NPV  
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28 responses.  
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33 <Figure 4>  
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36 Tentative initial values required for  $k_1$  were obtained by introducing experimentally  
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38 determined  $E_{1/2}$  values in Eq.(19). These  $E_{1/2}$  values were estimated by the linearized  $E_1$   
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40 versus  $(j_d - j_{EC}) / j_{EC}$  plots (Eq. (18)) as shown in the inset figures. The tentative  
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42 initial value used for  $E_{Cu(II)/Cu(I)}^{0r}$  was 159 mV, obtained from the literature [27].  
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48 The optimum values of  $E_{Cu(II)/Cu(I)}^{0r}$ ,  $E_{Cu^{+2}/Cu^{+1}}^{0r}$  and  $k_1$  that yielded the best fitting were 162  
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50 mV and  $29 \times 10^3 \text{ s}^{-1}$  for the data obtained in the aqueous solvent, and 168 mV and  $12 \times$   
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52  $10^3 \text{ s}^{-1}$  for that obtained in DES. From these, the values for the real forward kinetic  
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54 constant of the complexation reaction  $k_1^{real} \left( = k_1 / (c_{CF})^m \right)$  were obtained in the two  
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56 media for the two possible complexes considered (i.e. those with  $m = 2$  or  $3$ ) as  $k_1^{real} \approx$   
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4  $3.2 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$  and  $1.1 \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$  for the complexes with  $m = 2$  and 3, respectively,  
5  
6 in the aqueous solvent, and  $k_i^{real} \approx 4.8 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}$  and  $10^2 \text{ M}^{-3} \text{ s}^{-1}$  for the complexes in  
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8 DES.  
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11 Several conclusions can be drawn from the analysis of the plots given in **Figure 3**. First,  
12  
13 it can be seen that the surface concentration of Cu(II) is almost always zero at any time  
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15 of the experiment in both water and DES. These applied potentials correspond to  
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17 conditions of diffusion controlled current for the Cu(II)/Cu(I) reduction, beneficial  
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19 conditions to the generation of Cu(I). Besides, it is observed that as time increases the  
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21 concentration at the electrode surface of complexed Cu(I) increases, at the expense of a  
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23 decrease in the surface concentration of free Cu(I). The observed variation is slight for  
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25 both media, such that  $c_{Cu(Cl)_m}(0,t)$  approximates quickly to the limiting value of  $\gamma c^*$   
26  
27 (Eq. (27)), which corresponds to  $4.946 \cdot 10^{-3}$  and  $16.393 \cdot 10^{-3} \text{ M}$  in the aqueous media and  
28  
29 in DES (**Figs. 3A and 3B**), respectively.  
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36 Under diffusion controlled conditions ( $E_I \ll E_{Cu(II)/Cu(I)}^{0'}$ ) and for complexation  
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38 reactions highly displaced toward the products ( $K^{real} \gg 1$  or  $K (= k_2/k_1) \ll 1$ ), the  
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40 surface concentrations involved in the EC mechanism simplify to  
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$$\left. \begin{aligned}
 \frac{c_{Cu(II)}(0,t)}{c^*} &= 0 \\
 \frac{c_{Cu(I)}(0,t)}{c^*} &= \frac{\gamma}{\sqrt{\pi\chi}} \\
 \frac{c_{Cu(Cl)_m}(0,t)}{c^*} &= \left(1 - 1/\sqrt{\pi\chi}\right)\gamma
 \end{aligned} \right\} \quad (27)$$

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4 with  $c^*$  being the initial concentration of Cu(II) in solution and  $\gamma$  and  $\chi$  given by Eqs.  
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7 (11) and (12), respectively. From Eq. (27) it can be seen that when time increases and  
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9  $\chi(=(k_1+k_2)t) \gg 1$ , the surface concentrations of free and complexed Cu(I) tend to  
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11 zero and to  $\gamma c^*$ , respectively. Equation (27) constitutes a simple set of expressions that  
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13 are adequate to obtain the evolution of the surface concentration with time in our  
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15 system.  
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19 Note that, under the conditions selected there is no difference between the curves  
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21 corresponding to the complex with  $m = 2$  and  $m = 3$ , which coincides with the  
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23 behaviour predicted by Eq. (27).  
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### 26 27 **4.3. Nucleation and growth**

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30 In order to address the study of the electrodeposition process in both media, different  
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32 residence times within the time range in which the surface concentrations showed a  
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34 quasi-stationary value were selected ( $t_1 = 15, 30$  and  $45$ s). After the  $E_2$  application, new  
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36  $j$ - $t$  transient appeared showing the typical nucleation and 3D growth controlled by  
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38 diffusion profile.  
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42 For the three residence times selected the comparison of the transients recorded at a  
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44 given  $E_2$  did not reveal significant differences in the rate of the deposition process (Fig.  
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46 5A and 5B). Indeed, quasi coincidence was observed in the current profiles, the current  
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48 maxima ( $j_m$ ) and the time elapsed ( $t_m$ ) between the  $E_2$  application, and also on the  
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50 achievement of the current maximum. These results are in agreement with those  
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52 provided by the theory, with the Cu(I) concentration reaching a constant value from a  
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54 certain  $t_1$ .  
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59 <Figure 5>  
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#### 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 0V. 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.

Figures 6A and 6B 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.

<Figure 6>

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  $t_1=45$ s appeared farther to the



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4 instantaneous limiting case than those recorded after 15s or 30s. This can be explained  
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6 by taking into consideration that extending the residence time in the Cu(II)-Cu(I)  
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8 electro-reduction zone could favour, in the aqueous medium, the formation of a low  
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10 amount of insoluble CuCl species, which could perturb the deposit growth. Thus, the  
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12 data recorded after 15s were considered more reliable for the mechanistic analysis.  
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16 <Figure 7>  
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19 The knowledge of surface concentrations of Cu(I) (see Fig. 3) at the instant that  $E_2$  was  
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21 applied allowed the use of the products  $j_m^2 t_m$  as an extra tool to analyze the nucleation  
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23 mechanism. For  $t_1=15s$  the surface concentration was  $4.9 \cdot 10^{-3}$  M, which together with a  
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25 value for the Cu(I) diffusion coefficient of  $1.5 \cdot 10^{-5} \text{cm}^2 \text{s}^{-1}$  [26] yielded  $j_m^2 t_m$  products of  
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27  $8.87 \cdot 10^{-7}$  and  $5.56 \cdot 10^{-7} \text{A}^2 \text{cm}^{-2} \text{s}$  for progressive and instantaneous nucleation,  
28  
29 respectively. The obtained  $j_m^2 t_m$  products (Table 2) evolved on increasing the  
30  
31 overpotential from  $7 \cdot 10^{-7}$  to  $6 \cdot 10^{-7} \text{A}^2 \text{cm}^{-2} \text{s}$ , values close to those predicted for  
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33 instantaneous mechanism. These results in good agreement with both those obtained  
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35 from the overall S-H adjustment and those from rising part analysis, also indirectly  
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37 support the results derived from the theoretical treatment of the potentiostatic curves  
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39 recorded at  $E_1$ , which predict the appropriate concentration value of complexed Cu(I)  
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41 species on the surface of the electrode.  
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47 <Table 2>  
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#### 50 51 4.3.2. Copper electrodeposition in the DES solvent 52

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54 Proceeding in a similar way as in the aqueous medium, sets of  $j$ - $t$  transients were  
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56 recorded in DES at different residence times within the time zone at which the surface  
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58 concentrations attained a stationary value. In the DES solvent a wide overpotential  
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60 range was needed to observe significant changes in the recorded currents.  
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<Figure 8>

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

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4 and the specific nature of this ionic solvent that benefits the intermediate Cu(I)  
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6 complexation, avoiding the possible non-soluble Cu(I) species formation.  
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9 Using the surface concentration at the beginning of the electrodeposition process  
10 (0.01694 M) and the calculated diffusion coefficient, the products  $j_m^2 t_m$  predicted by  
11 equations (24) and (25) for the limiting cases were calculated and compared with those  
12 obtained from the extracted parameters from the experimental j-t curves. All the  $j_m^2 t_m$   
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14 products obtained from the experimental data reproduced the magnitude order predicted  
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16 by theory, although they were slightly higher than the value corresponding to  
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18 progressive nucleation (not shown), which is always the highest value.  
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26 According to the literature, in DES solvent copper species are entirely complexed by  
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28 chloride [40], but no information about the equilibrium constants values is provided,  
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30 neither of the  $E^0$  value of the couple Cu(II)/Cu(I) at DES. So, we used the  $K$  and  $E^0$   
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32 values corresponding to aqueous medium as the initial guess values in the subsequent  
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34 non-linear fitting of the experimental data. This first approximation could explain the  
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36 slight discrepancy between the  $j_m^2 t_m$  products from experimental values with those  
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38 calculated theoretically.  
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43 The coherency between the results provided by the complete analysis with the S-H  
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45 model and the analysis of the rising part of the transients confirms that an appropriate  
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47 control of the initial conditions in the first stages of the electrodeposition and in the  
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49 stationary concentration of Cu(I) on the surface was achieved, although in the DES  
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51 medium this concentration value seems to be slightly underestimated.  
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## 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

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4 providing the stationary surface concentration theoretically predicted is enough for the  
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6 appropriate mechanistic analysis.  
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9 The incorporation of the calculated surface concentrations in the  $j_{\text{m}}^2 t_{\text{m}}$  products  
10 provides excellent concordance in aqueous medium, conditions at which  
11 thermodynamic parameters are available, showing the performance of the theoretical  
12 treatment. A slight displacement between experimental and calculated  $j_{\text{m}}^2 t_{\text{m}}$  values is  
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14 observed in the DES medium, in which underestimated concentration values seem to  
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16 have been obtained probably due to the uncertainty in the estimation of the formal  
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18 potential.  
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26 The results obtained sustain the use of the double step mode as a very good  
27 approximation to analyze accurately the Cu electrodeposition in both water and DES  
28 when considering the stabilization of the Cu(I) intermediate by complexation, avoiding  
29 the uncertainty associated with the application of a single step. Additional studies that  
30 not only rely on voltammetric data would be highly beneficial to know more of the  
31 physicochemical properties of this novel solvent and to understand how better it affects  
32 thermodynamic and kinetic parameters of the charge transfer and complexation reaction  
33 so as to refine model predictive abilities.  
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45 The strategy developed here for the analysis of the copper electrodeposition by using  
46 experimental data of the two electrochemical steps involved can be extended to any  
47 deposition process in which the overall reduction take place via two well separated  
48 stages.  
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4 **References**  
5

- 6 [1] P. Leisner, P. Moller, M. Fredenberg, I. Belov, Recent progress in pulse reversal  
7 plating of copper for electronics applications, Transactions of the Institute of Metal  
8 Finishing, 85 (2007) 40.  
9  
10  
11  
12 [2] M. Cortés, E. Gomez, A. Pérez-Rodríguez, C. Serre, E. Valles, Optimisation of  
13 copper electrodeposition processes for Si technology based inductive microsystems, J.  
14 Electroanal. Chem., 619 (2008) 176.  
15  
16  
17 [3] S. Miura, H. Honma, Advanced copper electroplating for application of electronics,  
18 Surf. & Coat. Technol. 169 (2003) 91.  
19  
20  
21 [4] A. Ramos, M. Miranda-Hernández and I. González, Influence of Chloride and  
22 Nitrate Anions on Copper Electrodeposition in Ammonia Media, J. Electrochem. Soc.,  
23 148 (2001) C315.  
24  
25  
26 [5] IUPAC Stability constants database (SC Database) compiled by L.D. Pettit and K.J.  
27 Powell. –Timble: Academic Software Pub.2001 version 5.16. Univ Christchurch. New  
28 Zealand.  
29  
30  
31 [6] D. Jagner, E. Sahlin, L. Renman, Experimental and computational study of species  
32 formed during electrochemical stripping oxidation of copper in chloride media.  
33 Determination of copper (II) in  $\text{ng l}^{-1}$  range by stripping potentiometry, Talanta 42  
34 (1995) 1447.  
35  
36  
37 [7] The chemistry of monovalent copper in aqueous solution. In Rudi van Eldik, Ivana  
38 Ivanovic-Burmazovic, Ed. Advances in Inorganic Chemistry, Vol. 64, Burlington,  
39 Academic Press, 2012, pp.219-261.  
40  
41  
42 [8] M. Gu, Q. Zhong, Copper electrocrystallization from acidic sulfate electrolyte  
43 containing MPS additive, J Appl Electrochem., 41 (2011) 765.  
44  
45  
46  
47  
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3  
4 [9] G. Vazquez,; C.M. Roldan-Fernandez, I. Gonzalez, The effect of the anion on  
5  
6 copper electrocrystallization. Impedance analysis, ECS Transactions, 15 (2008) 171.  
7  
8 [10] G. Gunawardena, G. Hills, I. Montenegro, Electrochemical nucleation partIV.  
9  
10 Electrodeposition of copper onto vitreous carbon, J. Electroanal. Chem., 184 (1985)  
11  
12 357.  
13  
14 [11] D. Grujicic, B. Pesic, Electrodeposition of copper: the nucleation mechanisms,  
15  
16 Electrochim. Acta, 47 (2002) 2901.  
17  
18 [12] Ch.A. Gunawan, B.H.R. Suryanto, C. Zhao, Electrochemical study of copper in  
19  
20 room temperatura protic ionic liquids ethylammonium nitrate and triethylammonium  
21  
22 methylsulfonate, J. Electrochem. Soc., 159 (2012) D611.  
23  
24 [13] C. Gabrielli, P. Moçoteguy, H. Perrot, R. Wiart, Mechanism of copper deposition  
25  
26 in a sulphate bath containing chlorides, J. Electroanal. Chem., 572 (2004) 367.  
27  
28  
29  
30  
31 [14] K.R. Hebert, S. Adhikart, J.E. Houser, Chemical mechanism of suppression of  
32  
33 copper electrodeposition by poly(ethylene glycol), J. Electrochem. Soc. 152(5) (2005)  
34  
35 C324.  
36  
37  
38  
39 [15] D. Grujicic, B. Pesic, Reaction and nucleation mechanisms of copper  
40  
41 electrodeposition from ammoniacal solutions on vitreous carbon, Electrochim. Acta, 50  
42  
43 (2005) 4426.  
44  
45 [16] S. Figueroa, M.Miranda, Copper electrodeposition on carbon film electrodes, ECS  
46  
47 Trans., 15(1) (2008) 181.  
48  
49  
50  
51 [17] W-Z. Xu, J-B. Xu, H-S. Lu, J-X. Wang, Z-J. Hu, X-P. Qu, Direct copper plating on  
52  
53 ultra thin sputtered cobalt film in an alkaline bath, J. Electrochem. Soc. 160(12) (2013)  
54  
55 D3075.  
56  
57  
58  
59  
60  
61  
62  
63  
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65

- 1  
2  
3  
4 [18] S. Xing, C. Zanella, F. Deflorian, Effect of pulse current on the electrodeposition of  
5  
6 copper from choline chloride-ethylene glycol, *J Solid State Electrochem.*, 18 (2014)  
7  
8 1657.  
9
- 10 [19] P.Y. Chen, Y.T. Chang, Voltammetric study and electrodeposition of copper in 1-  
11  
12 butyl-3-methylimidazolium salicylate ionic liquid, *Electrochim. Acta*, 75 (2012) 339.  
13  
14 [20] Z. El Abedin, S. Prowald, A. Endres, Fabrication of highly ordered macroporous  
15  
16 copper films using template-assisted electrodeposition in an ionic liquid, *Electrochem.*  
17  
18 *Commun.*, 18 (2012) 70.  
19  
20 [21] A.P. Abbott, K.E. Tabib, G. Frisch, K.J. Mckenzie, K.S. Ryder,  
21  
22 Electrodeposition of copper composites from deep eutectic solvents based on choline  
23  
24 chloride, *Phys. Chem. Chem. Phys.*, 11 (2009) 4269.  
25  
26 [22] L. M. S. G. A. Applegarth, Ch. R. Corbeil, D. J. W. Mercer, C. C. Pye, P. R.  
27  
28 Tremaine, Raman and ab Initio Investigation of Aqueous Cu(I) Chloride Complexes  
29  
30 from 25 to 80 °C, *J. Phys. Chem. B*, 118 (2014) 204.  
31  
32 [23] R. Drissi-Daoudi, A. Irhzo, A. Darchen, Electrochemical investigations of copper  
33  
34 behaviour in different cupric complex solutions: Voltammetric study, *J. Appl.*  
35  
36 *Electrochem.*, 33 (2003) 339.  
37  
38 [24] S. Ivanov, V. Tsakova, Influence of copper anion complexes on the incorporation  
39  
40 of metal particles in polyaniline Part I: Copper citrate complex, *J. Appl. Electrochem.*  
41  
42 32 (2002) 701.  
43  
44 [25] H. Zhao, J. Chang, A. Boika, A. J. Bard, Electrochemistry of high concentration  
45  
46 copper chloride complexes, *Anal. Chem.*, 85 (2013) 7696.  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
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- 1  
2  
3  
4 [26] P. Sebastián, E. Vallés, E. Gómez, Copper electrodeposition in a deep eutectic  
5 solvent. First stages analysis considering Cu(I) stabiliztion in chloride media,  
6 Electrochim. Acta, 123 (2014) 285.  
7  
8  
9  
10 [27] A. J. Bard and L. R. Faulkner, Electrochemical Methods, Wiley, New York, 2nd  
11 edn, 2000.  
12  
13  
14 [28] I. Morales, A. Molina, Analytical expressions of the  $I-E-t$  curves of a CE process  
15 with a fast chemical reaction at spherical electrodes and microelectrodes, Electrochem.  
16 Commun., 8 (2006) 1453.  
17  
18  
19  
20 [29] G. Gunawardena, G. Hills, I. Montenegro, B. Sharifker, Electrochemical  
21 nucleation. Part I. General Considerations, J. Electroanal. Chem., 138 (1982) 225.  
22  
23  
24 [30] B. Scharifker, G. Hills, Theoretical and experimental studies of multiple  
25 nucleation, Electrochim. Acta, 28 (1983) 879.  
26  
27  
28 [31] X. He, B. Hou, Ch. Li, Q. Zhu, Y. Jiang, L. Wu, Electrochemical mechanism of  
29 trivalent chromium reduction in 1-butyl-3-methylimidazolium bromide ionic liquid,  
30 Electrochim. Acta, 130 (2014) 245.  
31  
32  
33 [32] P. Sebastián, E. Vallés, E. Gómez, First stages of silver electrodeposition in a deep  
34 eutectic solvent. Comparative behavior in aqueous medium, Electrochim. Acta, 112  
35 (2013) 149.  
36  
37  
38 [33] N.M. Pereira, P.M. Fernandes, C.M. Pereira, A.F. Silva, Electrodeposition of zinc  
39 from choline chloride-ethylene glycol deep eutectic solvent: effect of the tartrate ion, J.  
40 Electrochem. Soc., 159 (2012) D501.  
41  
42  
43 [34] X.H. Xu, Ch. L. Hussey, Electrodeposition of silver on metallic and nonmetallic  
44 electrodes from the acidic aluminum chloride-1-methyl-3-ethylimidazolium chloride  
45 molten salt, J. Electrochem. Soc., 139 (1992) 1295.  
46  
47  
48  
49  
50  
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54  
55  
56  
57  
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- 1  
2  
3  
4 [35] E. Gomez, P. Cojocar, L. Magagnin, E. Valles, Electrodeposition of Co, Sm and  
5  
6 SmCo from a Deep Eutectic Solvent, *J. Electroanal. Chem.*, 658 (2011) 18.  
7  
8 [36] A.Molina, F. Martínez-Ortíz, E. Laborda, Rigorous Analytical Solution for EC  
9  
10 Mechanism in Normal Pulse Voltammetry at Spherical Electrodes and Microelectrodes,  
11  
12 *Int. J. Electrochem. Sci.*, 4 (2009) 1395.  
13  
14  
15 [37] A. Molina, I. Morales and M. Lopez Tenés, Chronoamperometric behaviour of a  
16  
17 CE process with fast chemical reactions at spherical electrodes and microelectrodes.  
18  
19 Comparison with a catalytic reaction, *Electrochem. Commun.*, 8 (2006) 1062.  
20  
21  
22 [38] E. Torralba, A. Molina, C. Serna, J. A. Ortuño, Rigorous Characterization of the  
23  
24 Facilitated Ion Transfer at Ities in Normal Pulse Voltammetry. Comparison with the  
25  
26 Approximated Treatments, *Int. J. Electrochem. Sci.*, 7 (2012) 6771.  
27  
28  
29 [39] MEDUSA-Chemical Diagrams (2.0) and HYDRA-Hydrochemical Database  
30  
31 (2.0).Softwares of I. Puigdomenech. <http://www.kemi.kth.se/medusa/>.  
32  
33  
34  
35 [40] P. de Vreese, N.R. Brooks, K. van Hecke, L. van Meerven, E. Mattheijs, K.  
36  
37 Binnemans, R. van Deun, Speciation of Copper(II) Complexes in an Ionic Liquid Based  
38  
39 on Choline Chloride and in Choline Chloride/Water Mixtures, *Inorganic Chemistry*, 51  
40  
41  
42  
43  
44 (2012) 4972.  
45  
46  
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4 **Figure captions**  
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7 Fig. 1. Voltammetric curves at  $50 \text{ mVs}^{-1}$  from: a)  $0.05 \text{ M CuCl}_2$  in DES solvent and b)  
8  $0.01\text{M CuCl}_2 + 3\text{M NaCl}$  aqueous solution. Inset: voltammetric curves in DES solution:  
9 solid line)  $0.05 \text{ M CuCl}_2$  and dashed line)  $0.05 \text{ M CuCl}$ .  
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14 **Fig. 2.** A) Scheme of the applied double step signal. B) Potentiostatic current transients  
15 for the electro-reduction of Cu(II) to Cu(I) from  $0.05\text{M}$  solutions of  $\text{CuCl}_2$  in DES  
16 solvent at  $40^\circ\text{C}$  at different  $E_1$ : a) 400, b) 380, c) 370, d) 350, e) 340, f) 330, g) 300, h)  
17 250, i) 150, j) 0, k) -100 and m) -200mV.  
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24 **Fig. 3.** Time dependence of the surface concentrations of the species participating in the  
25 first stage of the copper electrodeposition in the two media selected (aqueous solvent  
26 and DES, **Figs. 3A and 3B** respectively) for the cases in which Cu(I) is complexed by  
27 two or by three chloride ions ( $m= 2$  and  $m= 3$ , respectively, indicated by solid and  
28 dotted lines) obtained from Eq. (16). A) for aqueous solution:  $(k_1 + k_2) = 29 \times 10^3 \text{ s}^{-1}$ ,  
29  $D_{\text{Cu(II)}} = 3.67 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$   $D_{\text{Cu(I)}} = 1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $K (m=2) = 3.5 \times 10^{-7}$ ,  $K (m=3)$   
30  $= 7.4 \times 10^{-8}$ ,  $E_1 = 0 \text{ mV}$  and  $c^* = 10 \text{ mM}$ . B) for DES:  $(k_1 + k_2) = 12 \times 10^3 \text{ s}^{-1}$ ,  $D_{\text{Cu(II)}} =$   
31  $2.24 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$   $D_{\text{Cu(I)}} = 2.08 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ,  $K (m=2) = 1.3 \times 10^{-7}$ ,  $K (m=3) = 1.6 \times$   
32  $10^{-8}$ ,  $E_1 = -100 \text{ mV}$  and  $c^* = 50 \text{ mM}$ .  
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48 **Fig. 4.** Experimental (symbols) and theoretical (lines) NPV responses at three different  
49 times of the experiment ( $t = 0.5, 1.5$  and  $2.5 \text{ s}$ , indicated by crosses, circles and  
50 diamonds, respectively) for the Cu(II) to Cu(I) reduction facilitated by chloride  
51 complexation in: A) the aqueous solution and B) in DES. Theoretical curves were  
52 obtained by non-linear fitting of Eq. (8) to the experimental data by means of the Miner  
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4 function implemented in Mathcad. Tentative initial values for  $(k_1 + k_2)$ : 28700 and  
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7 12600 s<sup>-1</sup> for Fig. 4A and 4B, respectively. Tentative  $E_{Cu(II)/Cu(I)}^{0'}$  = 159 mV for both  
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10 media. Other parameters were as stated in Figure 3. Inset: Linearized  $E$  vs  
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12  $(j_d - j_{EC})/j_{EC}$  responses at the three times selected.  
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16 Fig. 5. Potentiostatic current transients at different residence times ( $t_1$ ): a) 15 b) 30 and  
17  
18 c) 45 s from: A) 0.05M solution of CuCl<sub>2</sub> in DES solvent,  $E_1 = -100$  mV,  $E_2 = -1050$  mV.  
19  
20 B) 0.01M solution of CuCl<sub>2</sub> + 3M NaCl aqueous solution,  $E_1 = 0$  mV,  $E_2 = -390$  mV.  
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24 Fig. 6. A) Potentiostatic current transients for the deposition of copper from 0.01M  
25  
26 CuCl<sub>2</sub> + 3M NaCl aqueous solution, using the double step signal,  $E_1 = 0$  mV,  $t_1 = 15$  s  
27  
28 and different  $E_2$ : a) -360, b) -370, c) -390, d) -395, e) -400, f) -405 and h) -410 mV. B)  
29  
30 Non-dimensional plots of  $(j/j_m)^2$  vs  $t/t_m$  for some of the j-t transients of Fig. 6A.  
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34 Fig. 7. Non-dimensional plots of  $(j/j_m)^2$  vs  $t/t_m$  for the copper electrodeposition j-t  
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36 transients recorded at different residence times ( $t_1$ ): a) 15 b) 30 and c) 45 s from: A)  
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38 0.01M CuCl<sub>2</sub> + 3M NaCl aqueous solution applying  $E_1 = 0$  mV and  $E_2 = -405$  mV. B)  
39  
40 0.05M CuCl<sub>2</sub> in DES solution applying  $E_1 = -100$  mV and  $E_2 = -1050$  mV.  
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43  
44 Fig. 8. A) Potentiostatic current transients for the deposition of copper from a 0.05M  
45  
46 CuCl<sub>2</sub> solution in DES, using the double step signal,  $E_1 = -100$  mV,  $t_1 = 15$  s and  
47  
48 different  $E_2$ : a) -950, b) -960, c) -975, d) -1000, e) -1050, f) -1100 and h) -1150 mV. B)  
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50 Non-dimensional plots of  $(j/j_m)^2$  vs  $t/t_m$  for some of j-t transients of Fig. 8A.  
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**Table 1**

Characteristic values of  $E_{pa}$ ,  $E_{pc}$ ,  $|E_{pc}-E_{pa}|$ , and  $j_{pc}$  for the anodic and cathodic peaks of the different CV voltammograms recorded from a 0.05 M solution of  $CuCl_2$  in DES

$v / mV s^{-1}$	$E_{pa} / V$	$E_{pc} / V$	$ E_{pc}-E_{pa}  / V$	$j_{pc} 10^3 / A cm^{-2}$
5	0.393	0.307	0.086	0.1698
10	0.397	0.295	0.102	0.2200
20	0.401	0.286	0.115	0.3085
30	0.407	0.288	0.119	0.4192
50	0.417	0.283	0.134	0.5166
70	0.424	0.260	0.164	0.5906
100	0.429	0.256	0.173	0.6379
150	0.434	0.248	0.186	0.7871

solvent at different scan rates

E vs (Ag/AgCl)

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**Table 2**

Characteristics values for the potentiostatic current maximum and  $j_m^2 t_m$  products for the j-t transients obtained from [Cu(II)]=0.01M + [NaCl]=3M in aqueous medium.

E/mV	$t_m$ / s	$j_m 10^3 / A \text{ cm}^{-2}$	$j_m^2 t_m 10^7 / A^2 \text{ cm}^{-4} \text{ s}$
-360	2.55	-5.24	7.00
-370	1.47	-6.50	6.21
-390	0.76	-8.95	6.09
-395	0.61	-10.2	6.35
-400	0.39	-12.8	6.38

E vs (Ag/AgCl)

**Table 1**

Characteristic values of  $E_{pa}$ ,  $E_{pc}$ ,  $|E_{pc}-E_{pa}|$ , and  $j_{pc}$  for the anodic and cathodic peaks of the different cyclic voltammograms recorded from a 0.05 M solution of  $CuCl_2$  in DES solvent at different scan rates

$v / mV s^{-1}$	$E_{pa} / V$	$E_{pc} / V$	$ E_{pc}-E_{pa}  / V$	$j_{pc} 10^3 / A cm^{-2}$
5	0.393	0.307	0.086	0.1698
10	0.397	0.295	0.102	0.2200
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150	0.434	0.248	0.186	0.7871

E vs (Ag/AgCl)



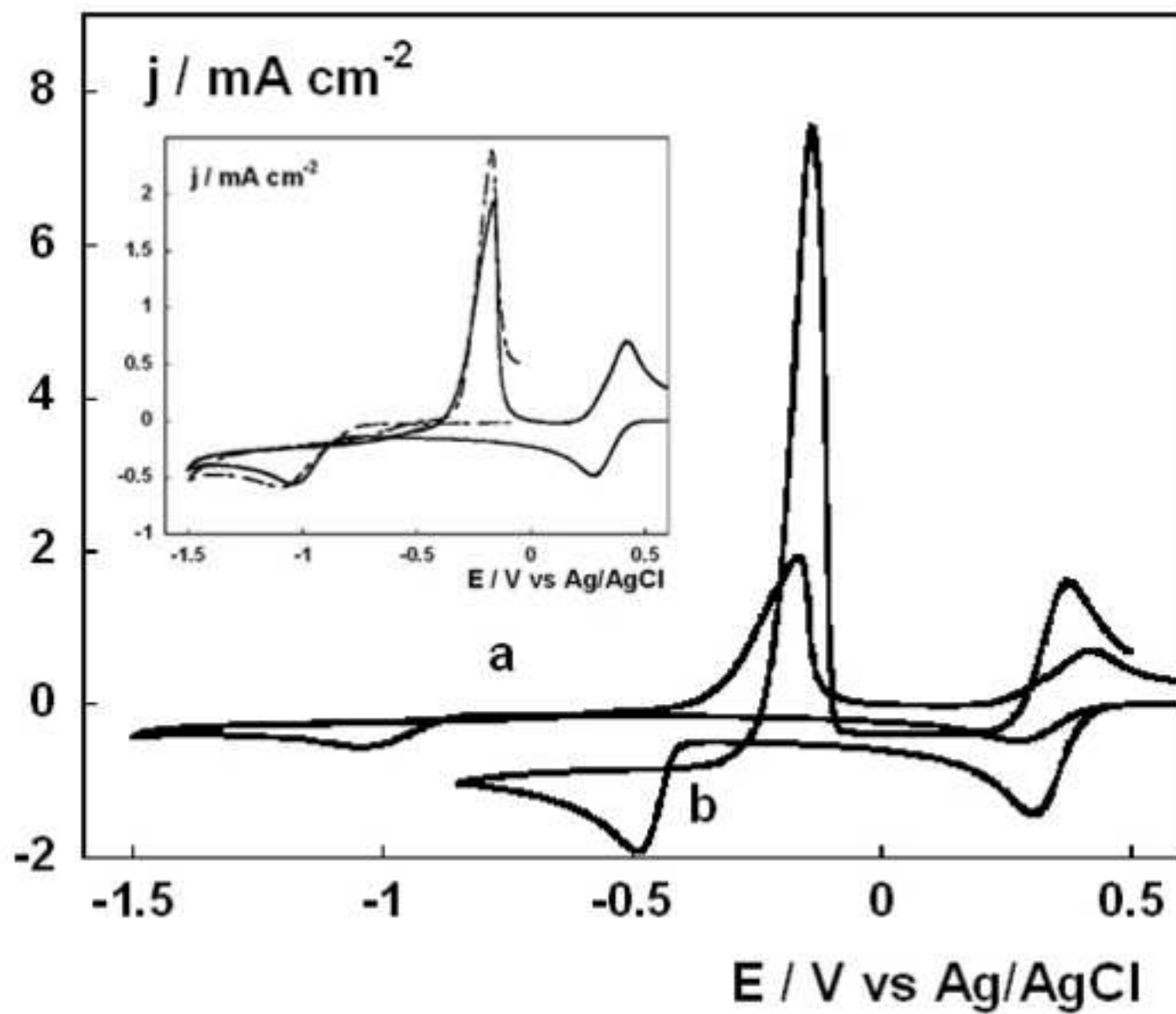


**Table 2**

Characteristics values for the potentiostatic current maximum and  $j_m^2 t_m$  products for the j-t transients obtained from [Cu(II)]=0.01M + [NaCl]=3M in aqueous medium.

E/mV	$t_m / s$	$j_m 10^3 / A \text{ cm}^{-2}$	$j_m^2 t_m 10^7 / A^2 \text{ cm}^{-4} s$
-360	2.55	-5.24	7.00
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-395	0.61	-10.2	6.35
-400	0.39	-12.8	6.38

E vs (Ag/AgCl)



**Figure 1**

Figure 2  
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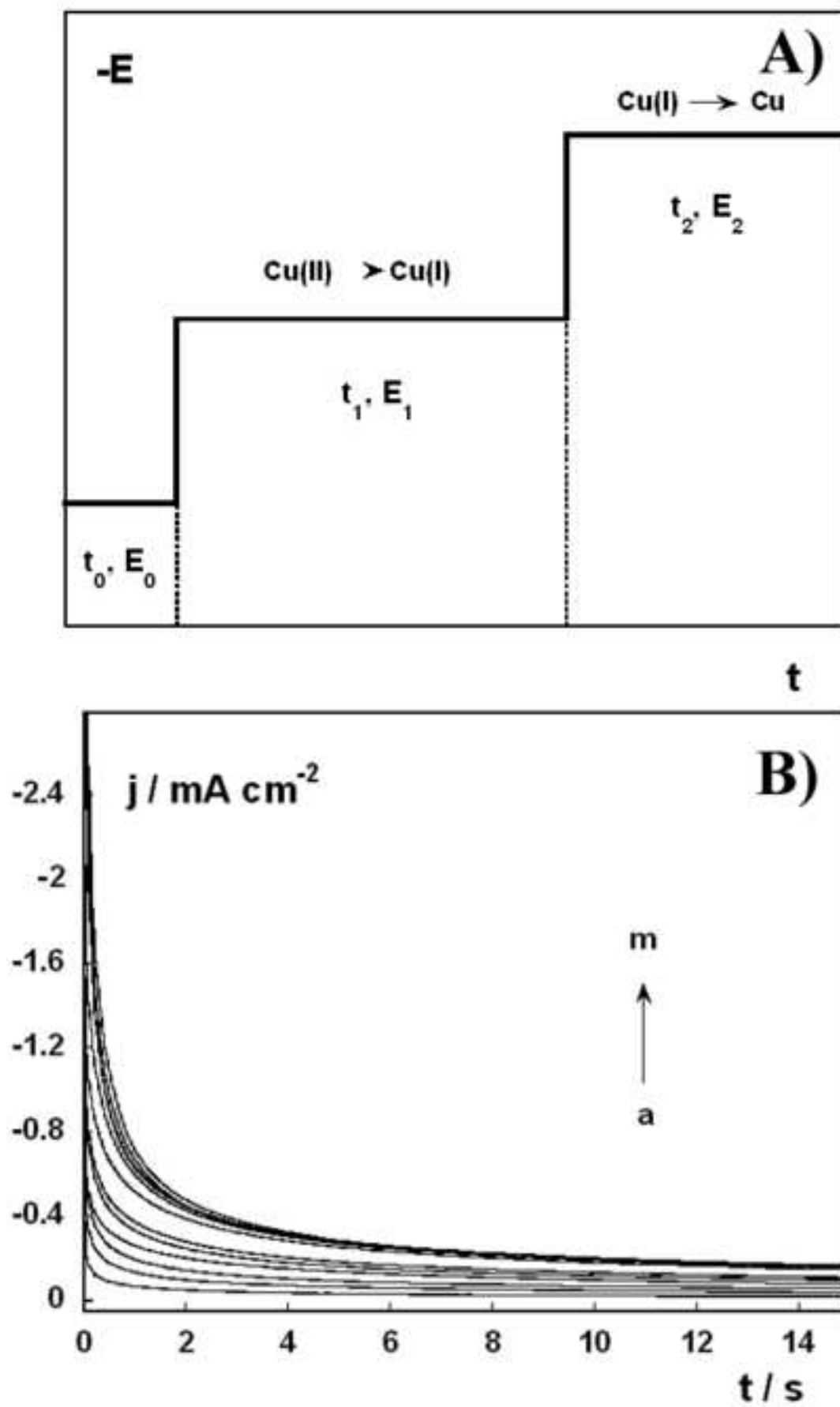
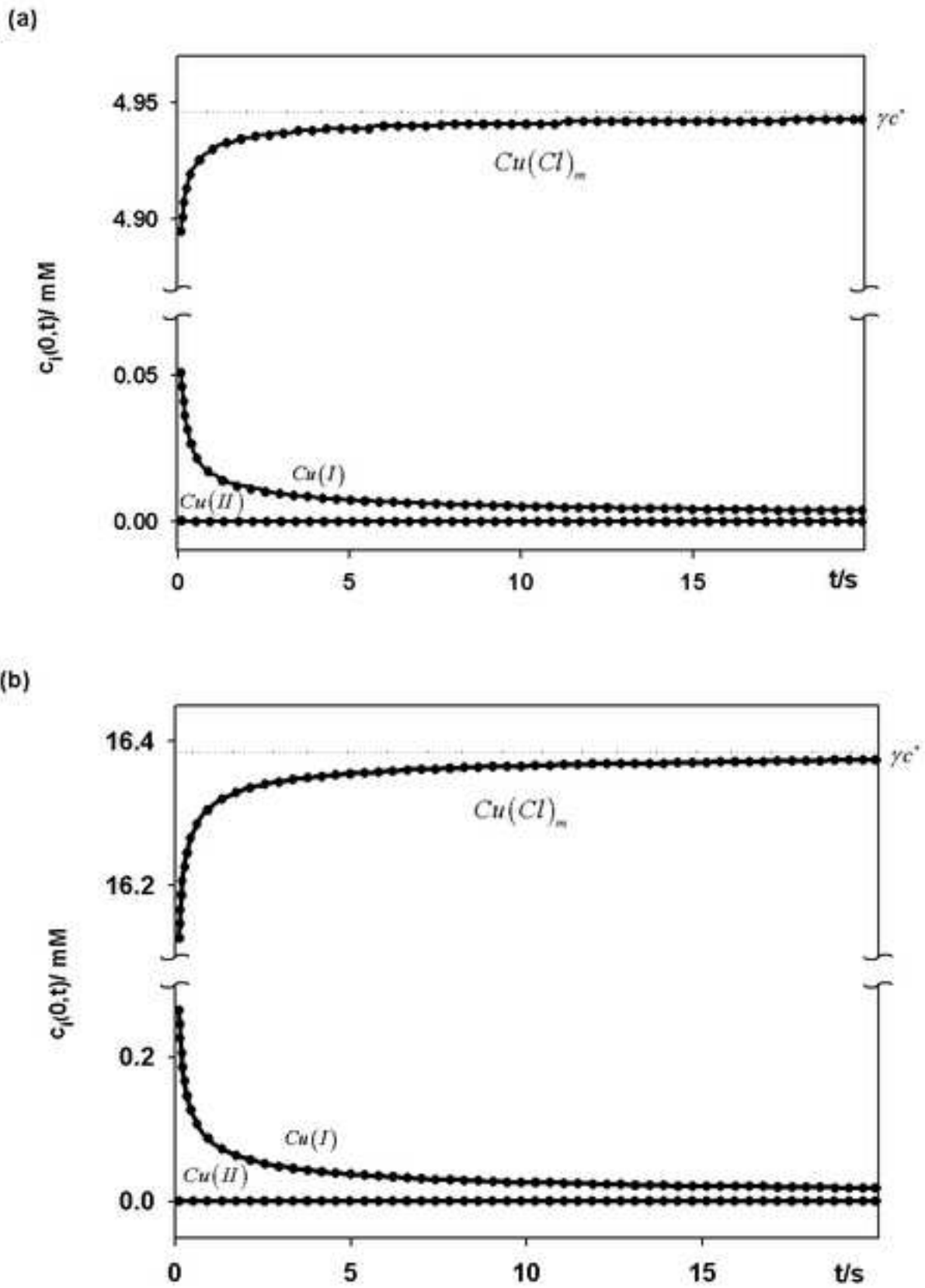


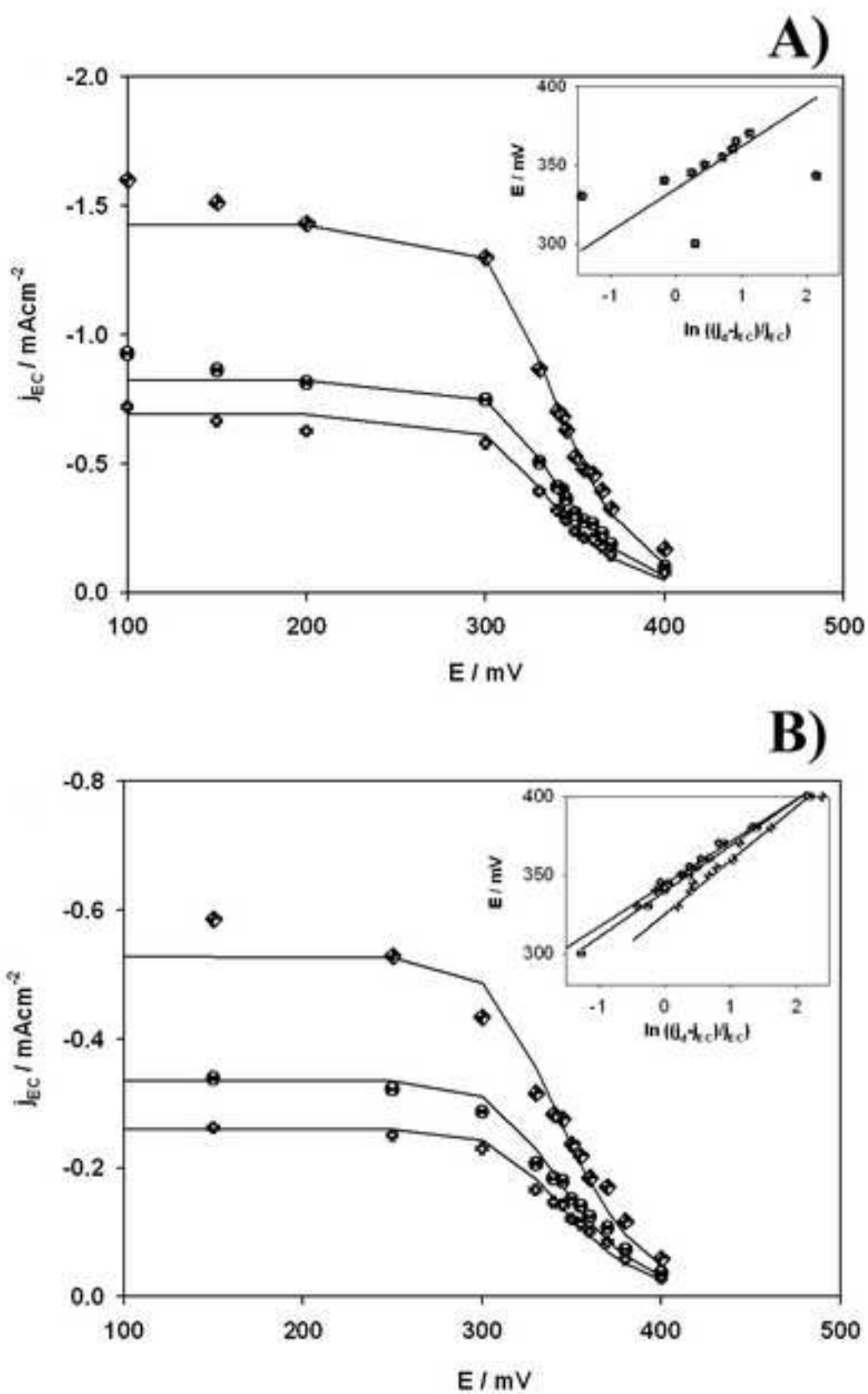
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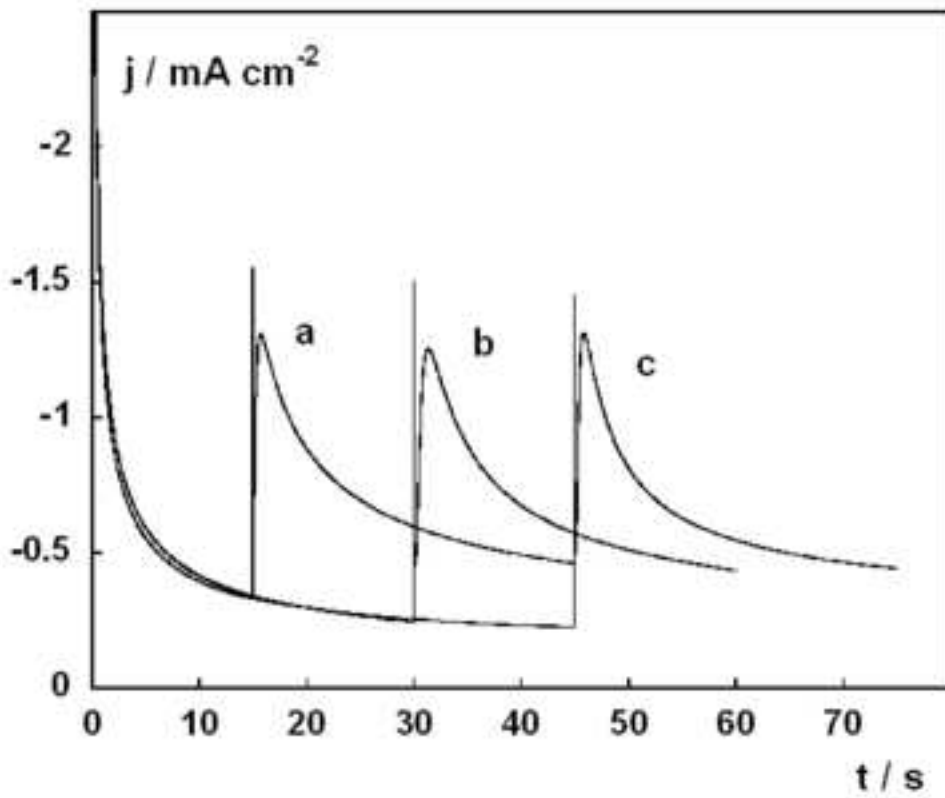
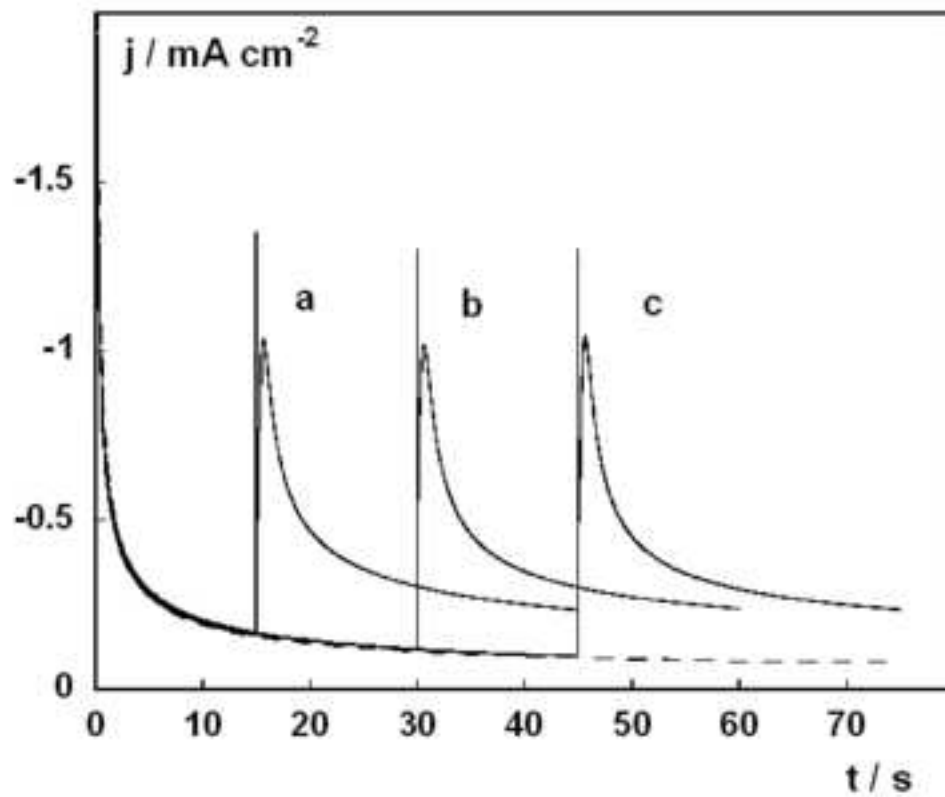
**Figure 3**

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**Figure 4**

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**Figure 5**

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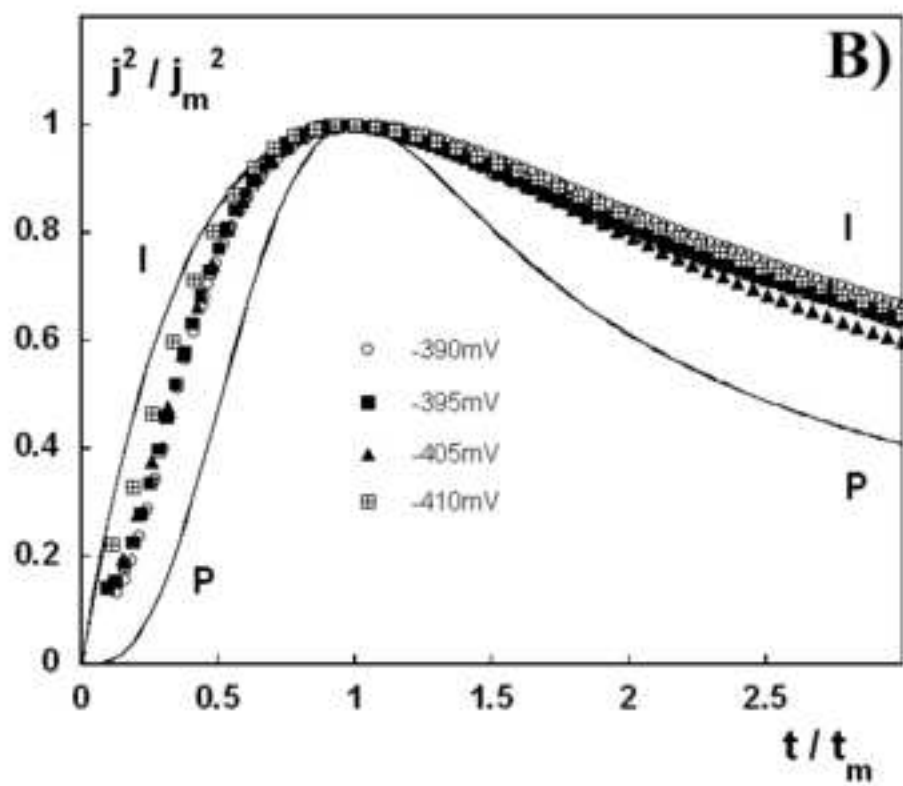
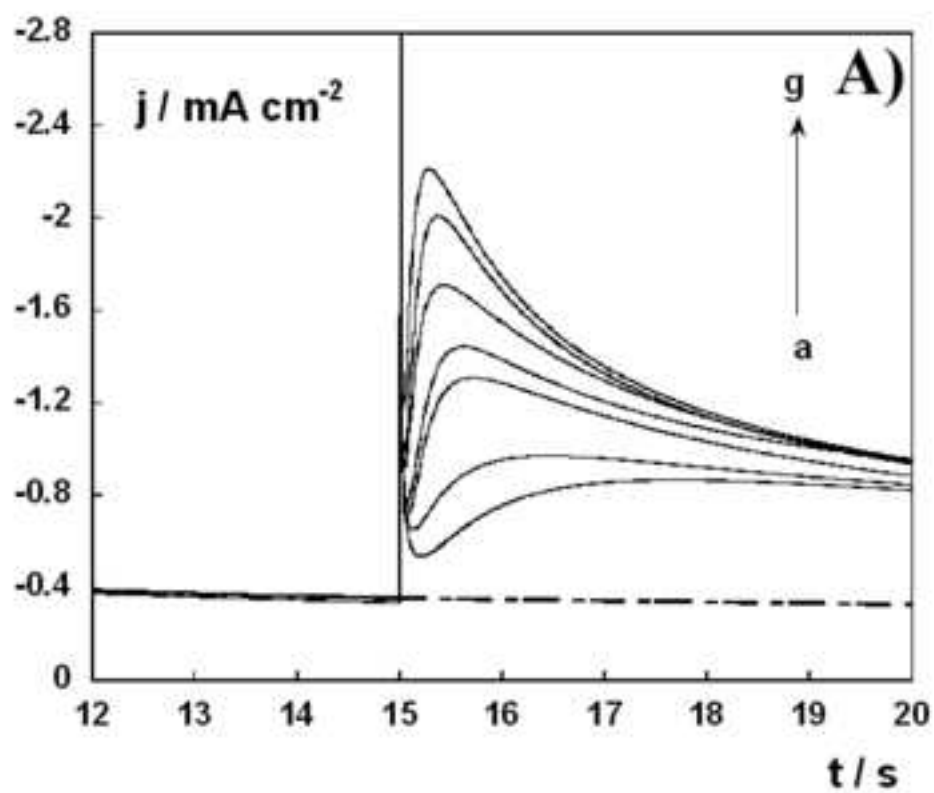
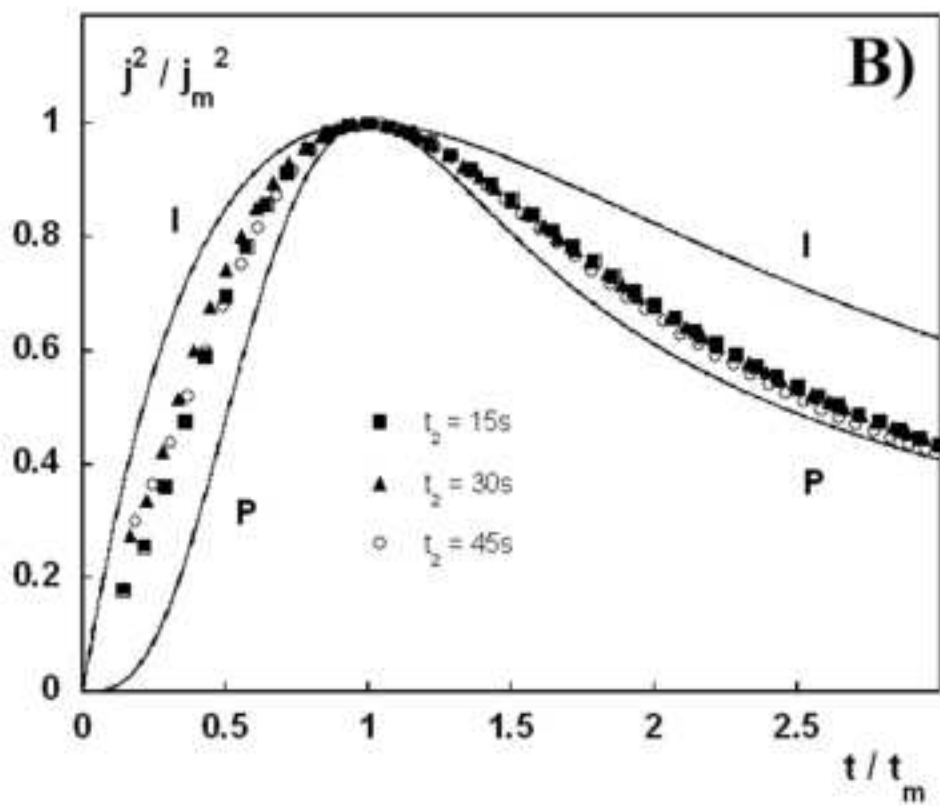
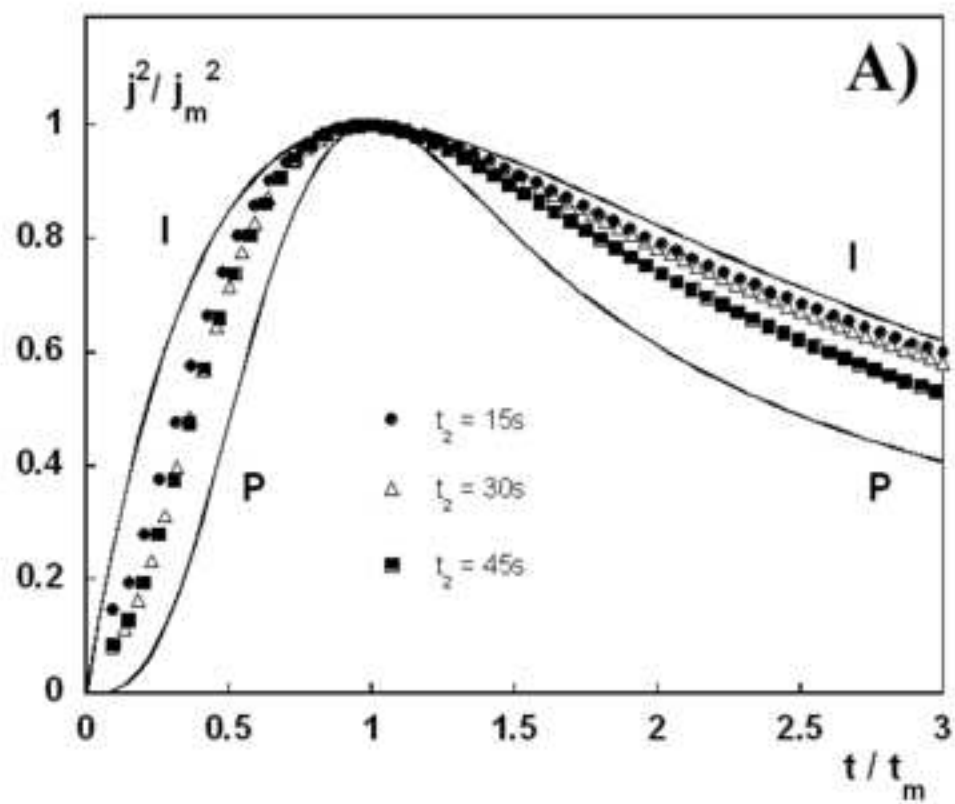


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**Figure 7**



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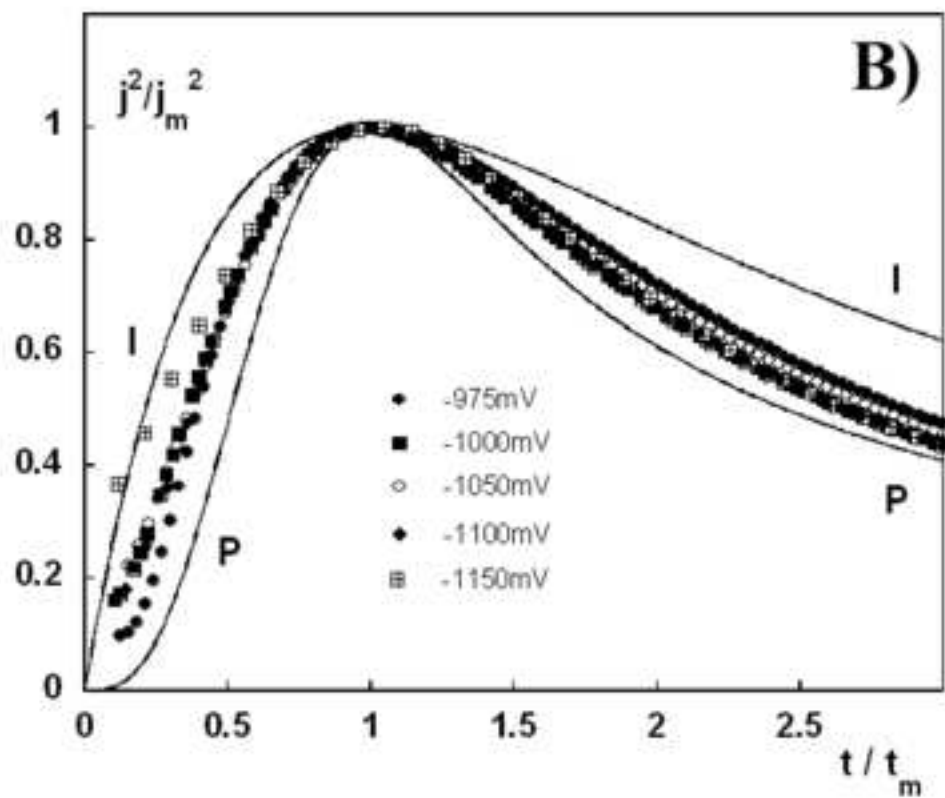
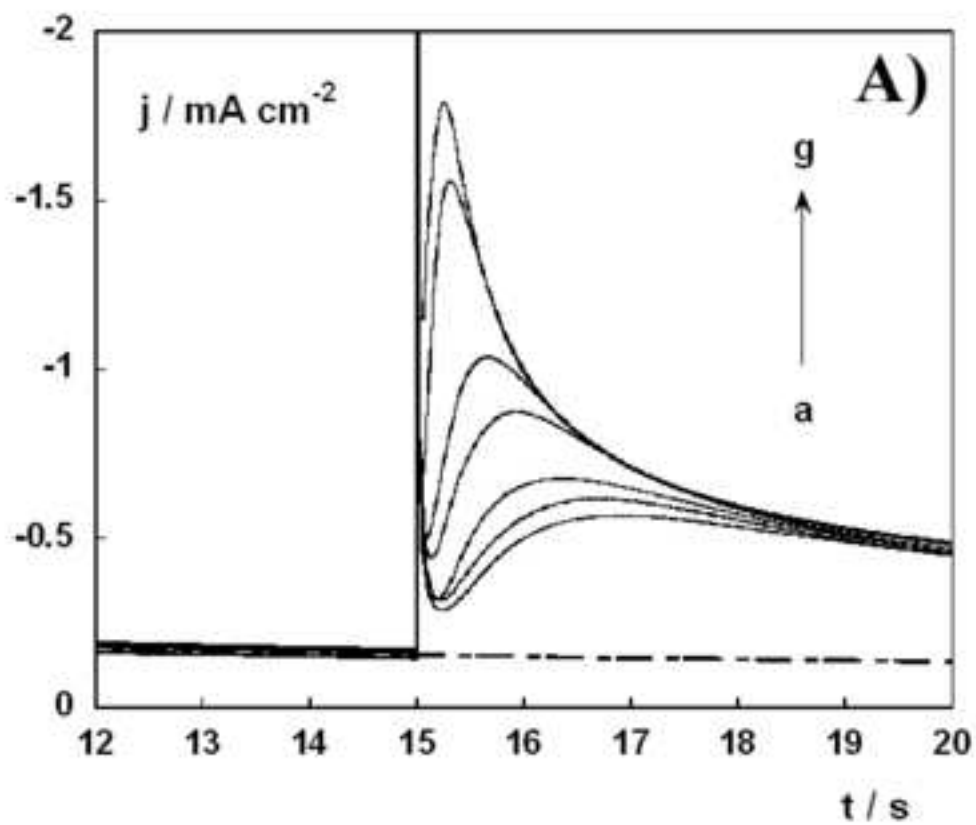


Figure 8