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Copper electrochemistry in the choline chloride-oxalic acid based deep eutectic solvent at glassy carbon electrode

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- ✓ Nuclei density.

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Abstract

Electrodeposition of copper is carried out on a glassy carbon (GC) electrode from deep eutectic solvent (DES) consisting of a mixture of choline chloride and oxalic acid dihydrate (ChCl-Ox) containing the salt $Cu(NO_3)_2.3H_2O$ as source of Cu^{2+} ions precursor. Cyclic voltammetry and chronoamperometry were used to study the ChCl-Ox + 30 mmolal $Cu(NO_3)_2.3H_2O$ system at 70°C. The voltammograms recorded show that the copper deposition process reveals the Cu^{2+}/Cu^+ and Cu^+/Cu redox couples, respectively reversible and quasi-reversible. The electrochemical reactions that take place at the glassy carbon electrode are controlled by diffusion. The mechanism of nucleation and growth was studied by chronoamperometry. The use of chronoamperograms and the tracing of current transients from chronoamperometry studies confirms an instantaneous nucleation and 3D-type growth model controlled by diffusion according to the Scharifker and Hills model. The diffusion coefficients of the Cu^{2+} and Cu^+ ions, determined by cyclic voltammetry and chronoamperometry according Scharifker and Hills models are respectively $2.56 \pm 0.09 \times 10^{-7}$ $cm^2.s^{-1}$ and $5.503 \pm 0.330 \times 10^{-7}$ $cm^2.s^{-1}$. These values are consistent with values of D_{Cu^+} and $D_{Cu^{2+}}$ found in other eutectic solvents based on choline chloride by authors listed in the literature.The chronoamperometry measurements have also made it possible to determine the maximum density of nuclei (N_0) in the order of 3. $10^7/cm^2$ reached at a potential of -0.46V. This potential would be well indicated for the electrodeposition of copper in ChCl-Ox + 30 mmolal $Cu(NO_3)_2.3H_2O$ media.

1. Introduction

Copper is one of the most widely used metals in many applications because of its numerous physical properties coupled with its exceptional thermal and electrical conductivity [1-4]. Such a metal characterized by very interesting properties needs the development of viable technical and economic processes for its recovery in ores and other compounds.

For this reason, the electrodeposition of copper has been a long time an interesting subject due to the interest in its alloys in various fields of application such as the electronics industry [5-7]. It is currently attracting a lot of attention, as the method does not require sophisticated instruments. In addition, in emerging fields such as electronics requiring the development of thin-film materials, electrodeposition appears to be the most promising technology, to reduce manufacturing costs, which are inherently high in vacuum methods, while being also more efficient in terms of reagent and energy consumption. To do this, solvents which are compatible with a sustainable environment are needed to make this technology even more attractive. However, current processes for extracting and recovering copper on an industrial scale use acidic aqueous solvents [8-10]. These media are toxic, corrosive, [11] and have restricted potential windows. In addition, aqueous solvents have been shown to affect the composition and morphology of deposits and therefore affect their electrical and mechanical properties [12]. All these undesirable effects have prompted the search for new solvents such as ionic liquids (ILs). Since the discovery of these ILs, their use in electrochemical processes for copper deposition is increasingly widespread [13-18].

Thus, copper has been intensively studied in ionic liquids based on chloroaluminates [15, 16], then in ionic liquids concentrated in chlorides such as 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][Cl][BF_4]) [17]. Electrodeposition of copper has also been performed from metal salts (CuCl and $CuCl_2$) in 1-ethyl-3-methylimidazolium ionic liquids based on dicyanamide anions ([EMIM][DCA]) or bis(trifluorométhylsulfonyl)imide ([EMIM][TFSI]) [18]. All these studies show that copper is reducible to the metallic state and that it is oxidizable to Cu(I) and Cu(II). However, it should be noted that ionic liquids are sometimes expensive in terms of cost. In addition, studies have shown that certain ionic liquids have limits with regard to the dissolution of certain metals [19].

For these reasons, investigations have made it possible to find a category of solvents similar to ionic liquids called deep eutectic solvents (DESs). They can be prepared by properly mixing various quaternary ammonium salts with different hydrogen donors such as an alcohol or a carboxylic acid [13, 20-26]. In addition, the cost of the basic components to design such solvents is cheaper compared to ILs. DES are biodegradable and less toxic [27, 28].

Several works have been carried out on the electrodeposition of copper in DES. In this sense, we can cite the group of Abbott [29] who studied the electrochemical behavior of copper (II) chloride dihydrate ($CuCl_2.2H_2O$) in the mixture of choline chloride-urea (1: 2) at platinum electrode. They have shown that the kinetics of copper deposition as well as the complexation of copper ions are different from those in aqueous media under comparable conditions. A similar electrochemical study was performed by A. M. Popescu et al. with an anhydrous copper (II) chloride salt ($CuCl_2$) [30] and anhydrous copper (I) chloride (CuCl) [12]. The shape of the voltammograms characteristic of the precursors CuCl and $CuCl_2$ dissolved in ChCl-U reveals a disproportionation between the Cu(I) and Cu(II) ions. In both cases, the voltammograms clearly show the reduction of copper (II) to copper (I), that of copper (I) to copper (0) as well as the corresponding oxidation reactions. Other groups of researchers such as Tsuda et al. [31] chose a copper (I) oxide (Cu_2O) precursor to study in detail the nucleation mechanism associated with the electrodeposition of copper in ChCl-U at glassy carbon electrode. They also elucidated the reversibility kinetics of the Cu^{2+}/Cu^{+} couple on a rotating disk electrode. In the same vein, Paula Sebastiána et al. [32] also carried out an in-depth study on the mechanism of nucleation and growth of copper in ChCl-U. They showed that in the presence of chloride ions, the copper deposition process involves two redox couples namely (Cu^{2+}/Cu^{+}) and (Cu^{+}/Cu).

In addition, studies carried out in DES have revealed very interesting properties regarding the dissolution of metals present in ores [24]. In this sense, authors listed in the literature have studied the electrochemistry of copper from chalcocite ore 5 (Cu_2S), chalcopyrite ore pyrite ($CuFeS_2$) from DES based on choline-ethylene glycol chloride (1: 2) [33-35] sometimes with additives such as iodine used as an electrocatalytic agent.

In view of the work listed in the literature, the main factors influencing the electrochemistry of copper in DES depend on the solvent, the precursor, the electrode substrate and sometimes chemicals complexing additives or dissolution accelerators. The most frequently used solvent is choline chloride-urea (ChCl-U) and to a lesser extent the mixture of choline chloride-ethylene glycol (ChCl-EG). Metal chloride-based salts (CuCl, $CuCl_2$, $CuCl_2.2H_2O$) have most often been used because of the determining role of chloride ions in the copper deposition process. Thus, the present study is distinguished by the nature of the precursor which is a salt of copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and the DES used which is a mixture of choline chloride-oxalic acid dihydrate (ChCl-Ox). A Deep Eutectic Solvent already used in the literature for the study of copper but electrochemical aspects has not been extended [36]. The present work is therefore an electrochemical contribution of the electrodeposition of copper in ChCl-Ox. In addition to cyclic voltammetry, it aims to use chronoamperometry to study the mechanism of nucleation and growth of copper at glassy carbon (GC) electrode.

2. Experimental details

2.1 Electrolytes preparation

The deep eutectic solvent (DES) used was prepared by mixing choline chloride (ChCl) (Alfa Aesar, + 98%, MW: 139.62 g/mol) and oxalic acid dihydrate (VWR NORMAPUR, 100, 2%, MW: 126.07 g/mol) in a 1:1 molar ratio. Choline chloride (ChCl) is purified by recrystallization from absolute ethanol (VWR Chemicals, NORMAPUR), then filtered and dried in vacuum before use while oxalic acid (Ox) is used as received. The mixture (ChCl-Ox) is maintained at 70°C for 30 minutes with constant magnetic stirring until a homogeneous and transparent liquid is obtained.The precursor salt $Cu(NO_3)_2.3H_2O$ (Acros Organics, 99%, MW: 241,6 g/mol) was weighed and added directly to the ChCl-Ox mixture without prior treatment. The whole is heated for two hours (2 h) at a temperature of 70°C on a heating plate (VWR Advanced, VMS-C10) equipped with a temperature probe until the complete melting of all the constituents of the mixture.

2.2 Experimental methods

The electrochemical experiments were performed using a three-electrode system connected to an Autolab PGSTAT302N potentiostat (Metrohm). NOVA 2.1 software was used for data acquisition and processing. The working electrode is a glassy carbon (GC) disc (BASI, geometric area = 0.0707 cm^2) and the counter electrode is a large area of platinum grid. A silver wire isolated in a mixture of choline chloride-oxalic acid (ChCl-Ox) was used as a pseudo-reference electrode. Before each set of experiments, the working electrode is polished with a 1.0 µm alumina-water suspension on a smooth polishing cloth. The electrode is then treated in an ultrasonic bath twice for five (5) minutes before being rinsed with Milli-Q water, to remove all traces of alumina, then dried under nitrogen. The platinum counter electrode is cleaned with a red flame using a torch. The silver wire used as the pseudo reference electrode is polished with silicon carbide polishing paper and insulated in a CoralPor MF-2042 glass tube. Bubbling the solution with nitrogen gas is carried out before the electrochemical measurements.

3. Results and discussion

3.1 Potentiodynamic study of the ChCl-Ox + $Cu(NO_3)_2.3H_2O$ mixture on glassy carbon (GC) electrode

Before adding the precursor $Cu(NO_3)_2.3H_2O$ to the ChCl-Ox mixture, we first investigated its range of electroactivity potential. The green cyclic voltammograms of the figure 1 show that the electrochemical window potential of ChCl-Ox at the glassy carbon electrode is between 1.15 V and -0.70 V. This DES is therefore very suitable for the study of the ChCl-Ox (1: 1) + $Cu(NO_3)_2.3H_2O$ system. Its wide range potential coupled with its leaching power in metal extraction processes [24, 37] could make it a good solvent for the study of a number of electrochemical systems.

After adding the $Cu(NO_3)_2.3H_2O$ precursor, the red voltammogram of figure 1 related to the $Cu(NO_3)_2.3H_2O$ 30 mmolal + ChCl-Ox mixture was recorded. The representation on the same graph of it curve and that related to the solvent clearly show that this DES makes it possible to demonstrate all the electrochemical responses of the precursor.

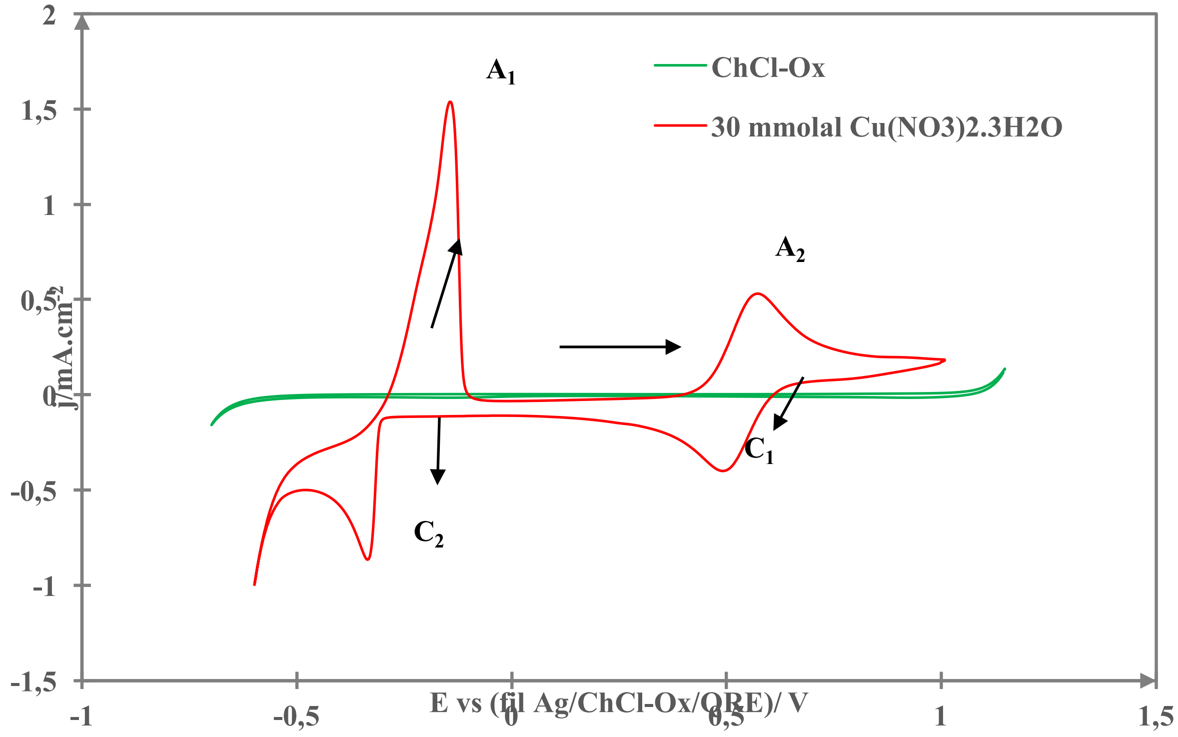

Figure 1. Cyclic voltammograms (3rd scan) of ChCl-Ox (green curve) and ChCl-Ox with 30 mmolal of $Cu(NO_3)_2.3H_2O$ (red curve) at GC electrode; v = 10 mV/s and T= 70°C.

The voltammogram has two cathodic responses and two anodic responses. In fact, when scanning "out" towards negative potentials, a first C1 peak is observed linked to the reduction of copper (II) to copper (I) around 0.49 V according to equation (Eqn.1). The deposition of copper related to the reduction of copper (I) to metallic copper Cu(0) takes place at C2 to -0.34 V according to equation (Eqn. 2). When scanning back to oxidation, metallic copper oxidizes to copper (I) with an intense A1 peak around -0.14 V (equation (Eqn. 3)) then copper (I) in turn oxidizes to Cu(II) at a potential of 0.57 V (peak A2) according to equation (Eqn. 4).

C_1: $\mathrm{Cu(II)} + e^- \rightarrow \mathrm{Cu(I)}$ (Eqn. 1)

C_2: $\mathrm{Cu(I)} + e^- \rightarrow \mathrm{Cu(0)}$ (Eqn. 2)

A_1: $\mathrm{Cu(0)} \rightarrow \mathrm{Cu(I)} + e^-$ (Eqn. 3)

A_2: $\mathrm{Cu(I)} \rightarrow \mathrm{Cu(II)} + e^-$ (Eqn. 4)

It appears that the process of copper deposition in ChCl-Ox on the glassy carbon electrode essentially passes through two stages linked to equations (Eqn. 1) and (Eqn. 2) respectively relating to the reduction of Cu(II) to Cu(I) and Cu(I) to Cu(0). Similar results have already been observed in the work of A. M. Popescu et al. [12] using an anhydrous copper chloride (CuCl) salt in choline chloride-urea (ChCl-U) media with a platinum electrode. According to these authors, the reduction reaction corresponding to the Cu(II)/Cu(I) couple takes place at potential of 0.20 V followed by the reduction of Cu(I) to Cu(0) at -0.68 V compared to values found in this work which are respectively 0.49 V and

-0.34 V. Thus the reduction potentials depend on the electrode substrate but also on the electrolytic media.

In addition these, same authors [30] studied the electrochemical behavior of copper (II) from a salt of anhydrous copper chloride ($CuCl_2$) dissolved in a ChCl-U mixture. The two cathodic responses previously obtained, respectively corresponding to the couples Cu(II)/Cu(I) and Cu(I)/Cu(0) are observed. The investigations resulting from studies of the ChCl-U + CuCl [12] and ChCl-U + $CuCl_2$ [30] systems highlight the important role of chloride ions (Cl^-) in the metallic copper (Cu(0)) deposition process which necessarily passes through the intermediary Cu(I). Indeed, when the salt of copper (II) precursor is dissolved in ChCl-U, the Cu^+ ions formed as a result of the reduction of the Cu^{2+} ions are complexed by the Cl^- ions in the media, thus promoting the deposition of metallic copper (Cu(0)).

Other authors listed in the literature such as Paula Sebastián et al. [32], ME. Obeten et al. [33], R. Bernasconi et al. [38] and many other authors [39-41] have found similar results in solvents based on choline chloride -urea (ChCl-U), choline chloride -ethylene glycol (ChCl-EG), dihydrogencitrate choline and ethylene glycol (CDHC-EG 1: 4).

In view of the works listed in the literature, we could retain that chloride ions play a determining role in the process of copper ions reduction in DES. However, the results obtained in this work show that their origin is not necessarily linked to the precursor used since the one ($Cu(NO_3)_2.3H_2O$) used in this work does not contain sources of chloride ions. Chloride ions would come from DES. Thus the ChCl-Ox mixture like the DESs formed from choline chloride as ChCl-EG or ChCl-U type are well suited for the electrochemical study of copper with a view to its recovery from samples of compounds which contain it with regard to its high degree of solubility in these DES. This study could be applied on other types of metals. In addition, the ChCl-Ox mixture as ChCl-EG or ChCl-U also can release chloride ions (Cl^-) from choline chloride, a chemical species which complexes Cu(I) ions thus easily promoting their reduction. The choice of ChCl-Ox electrolyte is therefore appropriate for the study of copper electrodeposition even if other parameters such as the electrode substrate, the precursor salt or the study conditions are required to be taken into account.

After analysis of the electrochemical responses, the characteristics of the recorded voltammograms were analyzed. Considering the reduction (C2) and oxidation (A1) peaks of the Cu(I)/Cu(0) couple in figure 1, we can see a very small difference between the start potential of the cathodic wave and that of the anodic wave. In addition, a current is quickly observed whether in oxidation or reduction as soon as one crosses the equilibrium potential of the system. There is almost a cross between the anodic wave and the cathode wave. This is the hallmark of an electrochemical system marked by rapid kinetics (Figure 1). This phenomenon was the subject of a chronoamperometry study presented in paragraph 3.1.2.

For the same couple, the voltammogram recorded at 10 mV/s gives values of cathodic (E_{pc}) and anodic (E_{pa}) peak potentials of -333 mV and -144 mV respectively; with a potential difference ΔEp ($E_{pa} - E_{pc}$) of 189 mV. However, the theoretical value calculated according to A. J. Bard et al [42] and B. Fethi et al [43] is 65 mV; expected value for a reversible system. It turns out that $\Delta Ep > 65$ mV, the Cu(I)/Cu(0) pair corresponding to A1/C2 is therefore not reversible.

However, we notice that ΔEp increases with the scanning speed. Indeed, the values of ΔEp calculated at 20 mV/s, 30 mV/s, 40 mV/s and 50 mV/s are respectively 200 mV, 226 mV, 237 mV and 248 mV. These values increase as a function of the scanning speed and therefore justify a quasi-reversible behavior of the Cu(I)/Cu(0) couple according to references [42, 43]. In addition, the voltammogram recorded at 10 mV/s in figure 1 shows respectively for the Cu(II)/Cu(I) couple values of cathodic (E_{pc}) and anodic (E_{pa}) peak potentials of 494 mV and 570 mV. We notice that the values of the cathodic (E_{pc}) and anaodic (E_{pa}) peak potentials vary a little with the scanning speed and the ratio of the peaks ($RJ_p = \left|\frac{j_{pA_2}}{j_{pC_1}}\right|$) ($RJ_p = 1{,}13; 1{,}06; 1{,}03; 1{,}04; 1{,}02$ respectively at 10 mV/s, 20 mV/s, 30 mV/s, 40 mV/s and 50 mV/s) is substantially equal to 1. Then, the Cu(II)/Cu(I) couple is reversible.

Figure 2 below presents a study of the system as a function of the scanning speed. We note the influence of the scanning speed on the rate of cyclic voltammograms. All of the peaks (C1, C2, A1 and A2) increase in intensity. In addition, there is a slight shift on either side of the oxidation and reduction peaks of the A1/C2 and A2/C1 pairs. As in Figure 1, for all the scanning speed, there is almost a cross between the reduction and oxidation waves corresponding to peaks C2 and A1.

This would highlight a phenomenon of nucleation and growth which will be studied in paragraph 3.1.2 by chronoamperometry measurements. These results are in agreement with those obtained in other DESs based on choline chloride (ChCl-EG [33, 38], ChCl-U [12, 30]).

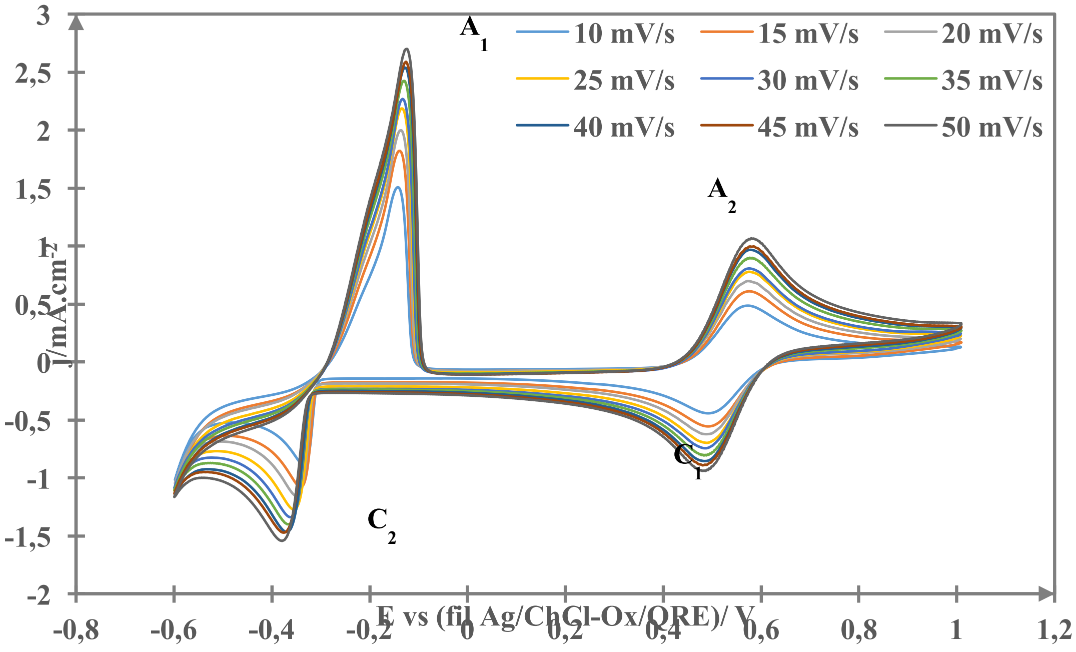

Figure 2. Cyclic voltammograms (3rd scan) of ChCl-Ox with 30 mmolal of $Cu(NO_3)_2.3H_2O$ at GC electrode recorded at different scan rate and T= 70°C.

To better understand the electrochemical behavior of Cu(II)/Cu(I) and Cu(I)/Cu(0) couples, a limited study of the system on the potential intervals surrounding the reduction and oxidation waves (A1/C2 and A2/C1) was made according to the scanning speed.

Thus, in the potential interval between 1 V and 0.1 V, the peak current density is normalized against the square root of the slew rate for all voltammograms recorded between 10 and 50 mV.s^{-1} (Figure 3a). It is clear showed that the oxidation and reduction waves are symmetrical or even superimposable. This implies a perfectly reversible system. As for the Cu(I)/Cu(0) couple, the study is carried out in the potential interval between 0.1 V to -0.6 V (Figure 3b). The shapes of the voltammograms show a displacement of the peak C2 corresponding to the reduction of Cu(I) into Cu(0) towards negative potentials when the speed increases. In contrast, the A1 peak corresponding to the oxidation of Cu(0) to Cu(I) shifts towards positive potentials. Thus, ΔEp necessarily becomes high, hence the quasi-reversible nature of the Cu(I)/Cu(0) couple.

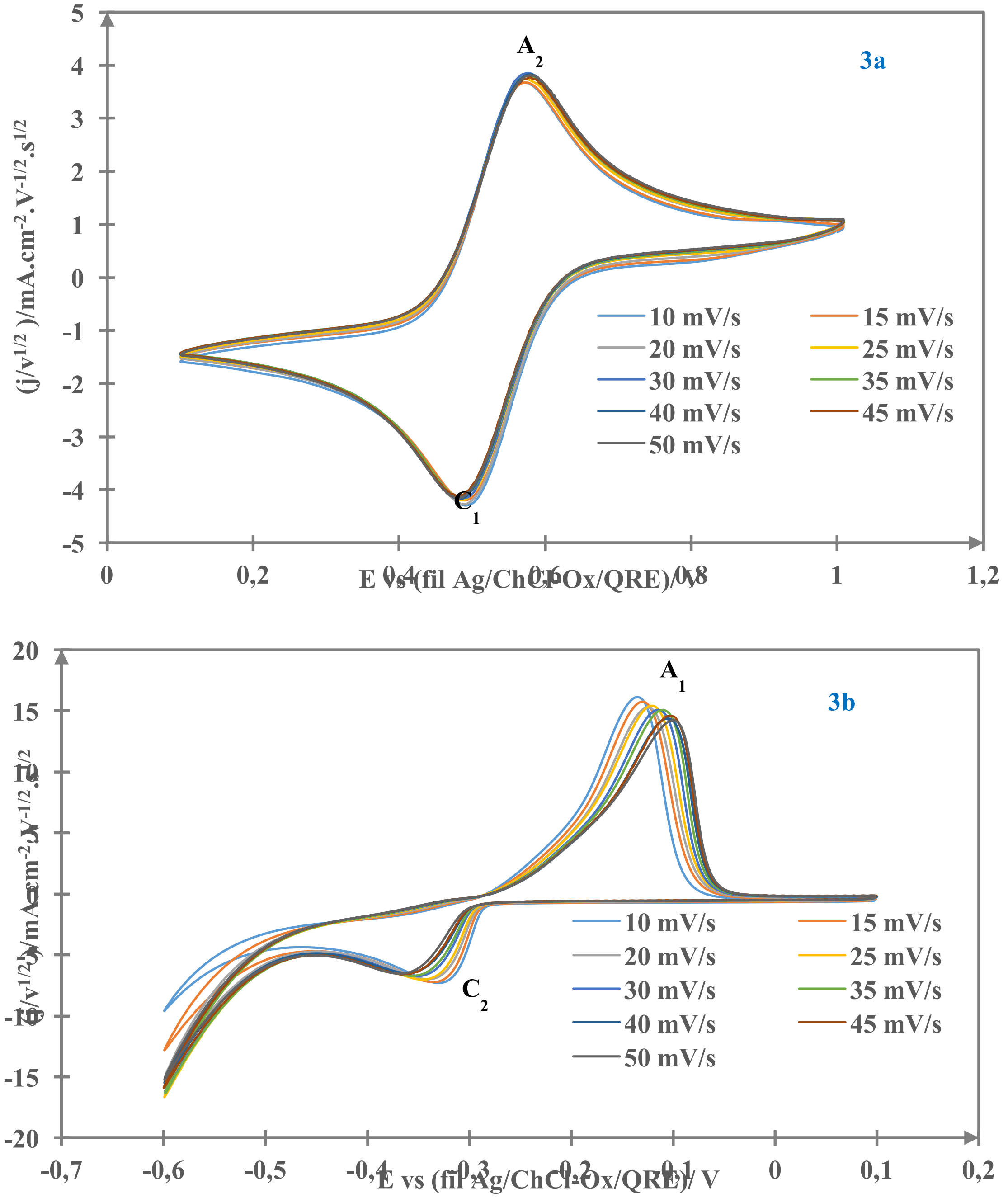

Figure 3. (3a) Current density normalized with respect to the square root of the scan rate $(\frac{j}{v^{1/2}} = f(E))$ vs potential between potential range of 0.1 V and 1 V. Current density from cyclic voltammograms (3rd scan, figure 1) of ChCl-Ox with 30 mmolal of $Cu(NO_3)_2.3H_2O$ at GC electrode recorded at different scan rate and T= 70°C.

(3b) Current density normalized with respect to the square root of the scan rate $(\frac{j}{v^{1/2}} = f(E))$ vs potential between potential range of -0.6 V and 0.1 V. Current density from cyclic voltammograms (3rd scan, figure 1) of ChCl-Ox with 30 mmolal of $Cu(NO_3)_2.3H_2O$ at GC electrode recorded at different scan rate and T= 70°C.

The graphical representation of the cathodic (C1, C2) and anodic (A1, A2) peaks resulting from the electrochemical processes at the electrode as a function of the square root of the scanning speed gives straight lines. This means that all the processes at the electrode are controlled by diffusion (Figure 4).

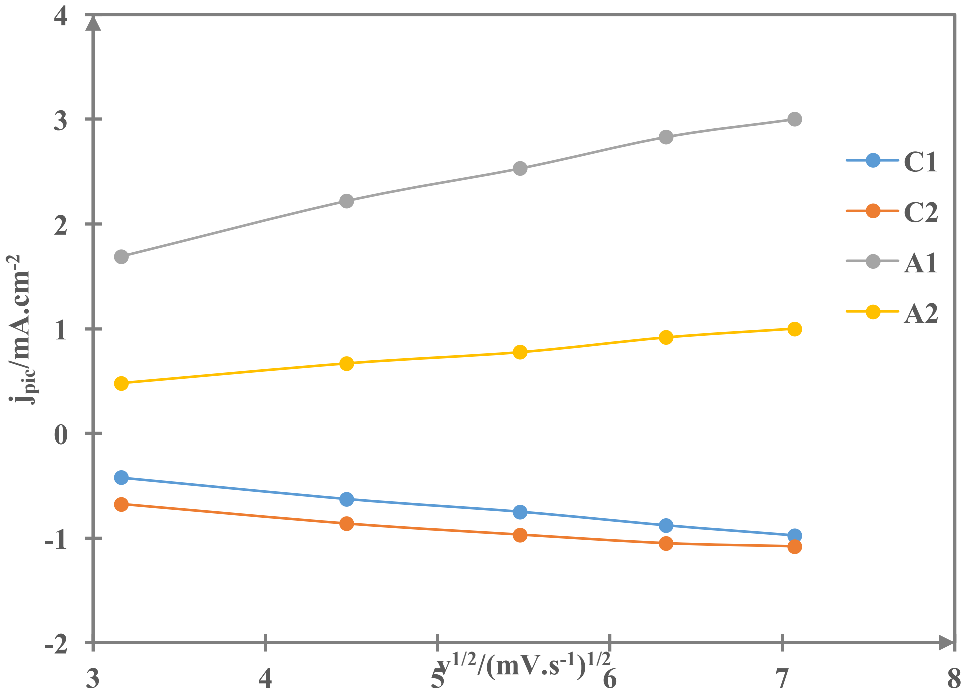

Figure 4. Current density at the peaks C1, C2, A1 and A2 vs square root of the scan rate ($j_{peak} = f\left(v^{1/2}\right)$ of ChCl-Ox with 30 mmolal of $Cu(NO_3)_2.3H_2O$ at GC electrode recorded at different, T= 70°C.

Since the transport of matter is governed by diffusion, it is necessary to determine the diffusion coefficient of the electroactive species. Thus, the diffusion coefficient of Cu^{2+} ions is calculated according to the equation of A. J. Bard and L. R. Faulkner [44] below:

$$j_{pc} = 0.4463 * \left(\frac{F^3}{RT}\right)^{1/2} * n^{1/2} * D^{\frac{1}{2}} * [Cu(II)] * v^{\frac{1}{2}} \qquad \text{(Eqn. 5)}$$

$$\text{with } D = \frac{(j_{pc})^2}{(0.4463)^2 * \left(\frac{F^3}{RT}\right).n^3.[Cu(II)].v} \qquad \text{(Eqn. 6)}$$

with j_{pc}: the peak current density (C1) in $A.cm^{-2}$; $[Cu(II)] = C_0^*$: the concentration of the ion in mol/cm^3; D: the diffusion coefficient; F: Faraday's constant (96485 $C.mol^{-1}$); n: the number of electrons exchanged: the scanning speed in $mV.s^{-1}$; R: the ideal gas constant (8.314 $J.K^{-1}.mol^{-1}$) and T: the temperature in Kelvin (343 K).

The results obtained by using the data of the voltammograms recorded at different speeds are presented in table 1 below.

Table 1. Values of cathodic peak C_1 potential (Epc) and anodic peak A_2 (Epa) potential, the difference |Epc-Epa|, the current density corresponding to the reduction of Cu^{2+} to Cu^{+} from voltammograms recorded at variable scan rate potential in ChCl-Ox with 30 mmolal of $Cu(NO_3)_2.3H_2O$ at GC electrode, T= 70°C

$v/V.s^{-1}$	E_{pa}/V	E_{pc}/V	$\lvert E_{pc}-E_{pa}\rvert/V$	$j_{pc}.10^4/A.cm^{-2}$	$(j_{pc})^2.10^7$	$D_{Cu^{2+}}.10^7/cm^2.s^{-1}$
0.010	0.57037	0.49393	0.076	-4.23	1.790	2.425
0.020	0.57159	0.49280	0.079	-6.27	3.925	2.660
0.030	0.57434	0.4879	0.086	-7.49	5.607	2.532
0.040	0.57495	0.4873	0.088	-8.79	7.727	2.617
0.050	0.57953	0.48639	0.093	-9.76	9.532	2.583

The difference $|E_{pc}-E_{pa}|$ between the potentials of the cathode and anode peaks at the scanning speed of 10 mV/s is 76 mV. This value increases with the scanning speed (Table 1). This development could be justified by the resistance of the ChCl-Ox mixture, a behavior which is observed for most DES based on choline chloride [29, 32].

The average value of the diffusion coefficient of Cu^{2+} ions is $2.563 \pm 0.09 \times 10^{-7}$ $cm^2.s^{-1}$. This value is almost of the same order of magnitude as those found in other deep eutectic solvents based on choline chloride (Table 2). It will be later compared to D_{Cu^+} as a result of the chronoamperometry study of the ChCl-Ox + $(Cu(NO_3)_2.3H_2O)$ system. This will allow us to draw a conclusion on the charge transfer kinetics of Cu^{2+} and Cu^+ ions at the glassy carbon electrode.

Table 2. Diffusion coefficients of Cu^{2+} in choline chloride-based DES

Authors	Methods	Solvent	T (°C)	$D_{Cu^{2+}}/cm^2.s^{-1}$
Abbot et al. [29]	CV	ChCl-EG	25	2.40×10^{-7}
P. Sebastián et al. [32]	CA	ChCl-U	40	2.24×10^{-8}
R. Bernasconi et al. [38]	CV	ChCl-EG	80	1.39×10^{-8}
David Lloyd et al. [45]	CA CV	ChCl-EG ChCl-EG	25 25	$1.60 \pm 0.10 \times 10^{-7}$ $1.45 \pm 0.02 \times 10^{-7}$
David Lloyd et al. [46]	CV	ChCl-EG	25	$1.32 \pm 0.50 \times 10^{-7}$
A-S Catrangiu [36]	CV	ChCl-Ox	60	1.02×10^{-7}
This work	CV	ChCl-Ox	70	$2.56 \pm 0.09 \times 10^{-7}$

CA = chronoamperometry ; CV = Cyclic voltammetry

3.2 Chronoamperometry study of the ChCl-Ox + $(Cu(NO_3)_2.3H_2O)$ system on a glassy carbon electrode

To elucidate nucleation and growth mechanism, a study of the system was carried out by chronoamperometry. To do this, the working electrode is maintained at 0.40 V for 20 seconds in order to enrich the solution in Cu^+ ions by reduction of Cu^{2+} to Cu^+, and consequently to promote the subsequent deposition of metallic copper Cu(0) by reduction of these ions thus highlighting the phenomenon of nucleation.

Before starting the chronoamperometry study, a characteristic cyclic voltammogram plot in the potential range between 0.40 V and -0.50 V was done to set the working potential. Subsequently, chronoamperograms were obtained by recording the transient currents (Figure 5).

The shape of these chronoamperograms indicates the growth of copper nuclei deposited on the glassy carbon electrode to the point of collision (Figure 5) followed by a considerable decrease to a constant plateau. However, the recorded chronoamperograms do not provide sufficient information on the mode and nature of copper nucleation during its electrodeposition on the electrode. These electrochemical phenomena are elucidated by determining the nucleation and growth modes by comparing the experimental results with those of theoretical models. In general, these theoretical models have been already applied in previous studies related to mechanisms of nucleations and growth [47-50]. In particular, they have been applied in the framework of studies related to the electrodeposition of copper by certain authors in aqueous media [32, 39], ionic liquid [48] and in DES [32].

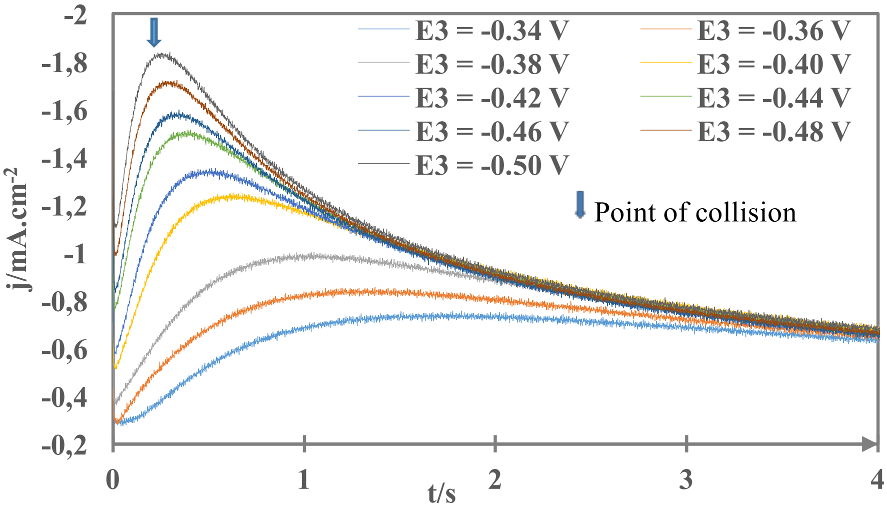

Figure 5. Experimental current density transients recorded from ChCl-Ox with 30 mmolal of $Cu(NO_3)_2.3H_2O$ at GC after a potential step from -0.3 V to various final potentials indicated in the legend. T = 70°C.

Several models exist but that of Scharifker and Hills [47] has been used. The two types of nucleation and growth mechanisms notably instantaneous nucleation (IN) and progressive nucleation (PN) given by this theory are described by the following equations:

$$\left(\frac{j}{j_m}\right)^2 = 1.9542 * \left(\frac{t_m}{t}\right) * \left\{1 - \exp\left[-1,2564 * \left(\frac{t}{t_m}\right)\right]\right\}^2 \qquad \text{IN (Eqn. 7)}$$

$$\left(\frac{j}{j_m}\right)^2 = 1.2254 * \left(\frac{t_m}{t}\right) * \left\{1 - \exp\left[-2,3367 * \left(\frac{t}{t_m}\right)^2\right]\right\}^2 \qquad \text{PN (Eqn. 8)}$$

j_m and t_m are respectively the current density and the deposition time. These values take into account the grain coverage. The application of these models to the data of the chronoamperograms of figure 5 makes it possible to obtain the curves resulting from the plot of the transients $\left(\frac{j}{j_m}\right)^2 = f\left(\frac{t}{t_m}\right)$ presented in figure 6.

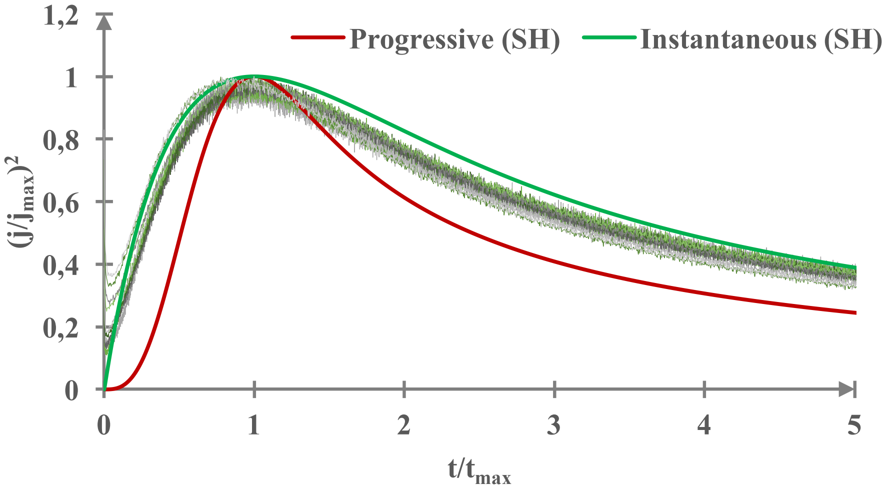

Figure 6. Non-dimensional plot of the current density transients for Cu deposition from 30 mmolal of $Cu(NO_3)_2.3H_2O$ in ChCl-Ox at T = 70°C.

These curves are superimposed with the theoretical instantaneous nucleation curve (IN) which corresponds to a slow growth of copper nuclei on a limited number of active sites. All nuclei are formed from the first moments of deposition. Saturation is then quickly reached followed by a rapid decrease until the saturation level is reached. In short, the copper is deposited on the glassy carbon electrode following a model of instantaneous nucleation and 3D type of growth mechanism controlled by diffusion. These results are consistent with those obtained in previous works by some authors [32, 39, 48]. After determining the type of nucleation and growth, the next step is devoted to determining the diffusion coefficients of Cu^+ ions, that of Cu^{2+} ions having already been determined by cyclic voltammetry measurements (Table 1). To do this, the following equation from Scharifker and Hills [47] related to instantaneous nucleation is used:

$$j_m^2 . t_m = 0.1629 * (nFC_0^*)^2 D \qquad \text{(Eqn. 9)}$$

with D: the diffusion coefficient, C_0^*: the ion concentration in $mol.cm^{-3}$, F: the Faraday constant (96485 $C.mol^{-1}$), n: number of electrons exchanged which corresponds to one (1).

The values of $j_m^2 t_m$ were determined for the values of the potential E ranging from -0.34 V to -0.50 V. The calculation gives an average diffusion coefficient of $D_{Cu^+} = 5.503 \pm 0.330 \times 10^{-7}\ cm^2.s^{-1}$ (Table 3).

Table 3. Characteristic of transients j(t) for the determination of the diffusion coefficient of Cu^+ ions in ChCl-Ox with values 30 mmolal of $Cu(NO_3)_2.3H_2O$ at GC electrode, T= 70°C

E/V	$j_m.10^4/A.cm^{-2}$	t_m/s	$j^2_m.10^7/A^2.cm^{-4}$	$j^2_m.t_m.10^7/A.cm^{-4}.s$	$D_{Cu^+}.10^7/cm^2.s^{-1}$
-0.34	-7.567	1.821	5.726	10.426	5.847
-0.36	-8.547	1.369	7.304	10.000	5.608
-0.38	-10.019	1.051	10.037	10.549	5.916
-0.40	-12.509	0.628	15.648	9.827	5.511
-0.42	-13.545	0.535	18.347	9.816	5.505
-0.44	-15.134	0.391	22.903	8.955	5.022
-0.46	-15.975	0.345	25.521	8.805	4.938
-0.48	-17.214	0.334	29.633	9.897	5.550
-0.50	-18.388	0.297	33.813	10.042	5.632

This value (average) was confirmed by the use of the Cottrell equation which gives the evolution of the current as a function of time when a stationary working electrode is immersed in a solution according to the equation [51] below:

$$i = \frac{nFSD^{1/2}C_0^*}{\pi^{1/2}} . t^{-1/2} \qquad \text{(Eqn. 10)}$$

$$\text{and } j = \frac{nFD^{1/2}C_0^*}{\pi^{1/2}} . t^{-1/2} \qquad \text{(Eqn. 11)}$$

With j: the current density ($A.cm^{-2}$), n: number of electrons exchanged (1 for the reduction of Cu (I) to Cu (0)), F: Faraday constant (96485 C. mol^{-1}), C_0^*: the concentration of the ion in mol / cm^3, t: the time (s), D: the diffusion coefficient ($cm^2.s^{-1}$)

The evolution of the current density (j) as a function of $.t^{-\frac{1}{2}}$ makes it possible to determine the diffusion coefficient from the slope (p) of the linear part of the curve $j = f(t^{-\frac{1}{2}})$ according to the following relation:

$$D = \frac{\pi p^2}{n^2F^2{C_0^*}^2} \qquad \text{(Eqn. 12)}$$

The calculations give a slope value around -0.0014 for n = 1, F = 96485 C.mol^{-1} and $C_0^* = 3.43 \times 10^{-5}\ \mathrm{mol.cm^{-3}}$. The use of this slope value gives a diffusion coefficient $D_{Cu^+} = 5.622 \times 10^{-7}\ \mathrm{cm^2.s^{-1}}$. A value approximately equal to that calculated above by the Scharifker and Hills (SH) method. This result is in agreement with those already found in other deep eutectic solvents based on choline chloride by other authors listed in Table 4. In summary, the values of the diffusion coefficients (2.563 ± 0.09 × 10^{-7} cm^2.s^{-1}) of Cu^{2+} ions and Cu^+ (5.622 × 10^{-7} cm^2.s^{-1} and 5.503 ± 0.330 × 10^{-7} cm^2.s^{-1}) ions are conform to those found in the literature for deep eutectic solvents based on choline chloride (Tables 2 and 4). We note that D_{Cu^+} is slightly higher than $D_{Cu^{2+}}$. The difference between the two values of diffusion coefficient makes it possible to differentiate the kinetics transfer charge of the two species (Cu^+ and Cu^{2+}) at the level of the electrode substrate. The charge transfer process of Cu^{2+} ions to the electrode substrate in the $Cu(II) + e^- \rightarrow Cu(I)$ reaction is slow compared to that of Cu^+ ions in the $Cu(I) + e^- \rightarrow Cu(0)$. These results are in agreement with the work of G. Saravanan et al. [48], E. Mattson et al. [52] and G. Gunawardena et al. [41].

Table 4. Diffusion coefficients of Cu^+ ions in choline chloride-based DES

Authors	Methods	Solvent	T (°C)	D_{Cu^+}/cm^2.s^{-1}
A. M. Popescu et al. [12]	CV	ChCl-U	70 et 80	1.22 × 10^{-8}
P. Sebastián et al. [32]	CA	ChCl-U	40	2.08 × 10^{-7}
R. Bernasconi et al. [38]	CV	ChCl-EG	80	1.39 × 10^{-8}
David Lloyd et al. [45]	CA CV	ChCl-EG ChCl-EG	25 25	2.80 ± 0.10 × 10^{-7} 2.70 ± 0.06 × 10^{-7}
This work	CA (SH) Cottrel	ChCl-Ox ChCl-Ox	70 70	5.50 ± 0.33 ×10^{-7} 5.622 ×10^{-7}

CA = chronoamperometry), CV = Cyclic voltammetry, SH = Scharifker and Hills

3.3 Nuclei density

The nuclei density relating to the formation of nuclei (N_0) from the first instants of the reaction $Cu(I) + e^- \rightarrow Cu(0)$ was calculated from the values of j_m and t_m according to the following relation [53]:

$$N_0 = 0.0652 \left(\frac{\rho}{8\pi CM}\right)^{1/2} . \frac{(nFC)^2}{j_m^2 . t_m^2} \qquad \text{(Eqn. 13)}$$

With: N_0: the density of nuclei (cm^{-2}), n: the number of electrons exchanged, F: the Faraday constant, C the sum of concentrations (C^*_0 (mol.cm^{-3})) of the reduced cations, M: the compound molar mass (M (Cu) = 63.54 g.mol^{-1}) and ρ: the material density (ρ (Cu) = 8.92 g. cm^{-3}), j_m: the current density (A.cm^{-2}), t_m: the deposition time.

Figure 7 shows a graphical representation of the nuclei density as a function of the reduction potential of copper (I) to copper (0) in the potential range between -0.34V and -0.50 V. We note a sawtooth variation of the nuclei density as a function of the potential between -0.34 V and -0.46V with a maximum nuclei density in order of 3 × 10^7/cm^2 reached at -0.46 V. After this value, the nuclei density decreases before increasing slightly for a value of approximately 3.055 × 10^7/cm^2 at -0.50 V. We can split the potential interval between -0.50V and -0.34 V in half with the one where the nuclei density increases progressively between -0.34 V and -0.46 V. Between the interval -0.46 V and -0.50 V, the variation of the nuclei density is not progressive. The potential of -0.46 V would therefore be suitable for carrying out an electrochemical deposition of copper in a ChCl-Ox + 30 mmolal $Cu(NO_3)_2.3H_2O$ media on a glassy carbon electrode. At this potential, the cluster or nucleus would contain the maximum number of atoms. The results obtained are in agreement with certain results listed in the literature notably with those of D. Grujicic and B. Pesic [39] in the case of the nucleation of copper on vitreous carbon in a dilute sulfuric acid media. They found a nuclei density of 2.09. 10^6 cm^{-2} at the potential of -0.45 V for a concentration of 0.05 mol. L^{-1} in Cu^{2+} ions. It is certainly difficult to compare the two media, but the value found in this work (3 × 10^7 cm^{-2}) compared to 2.09 × 10^6 cm^{-2} showed that the value in ChCl-Ox is about 10 times greater than that found in a dilute sulfuric acid media. So the growth of copper nuclei by electrodeposition on glassy carbon electrode is more favorable with ChCl-Ox.

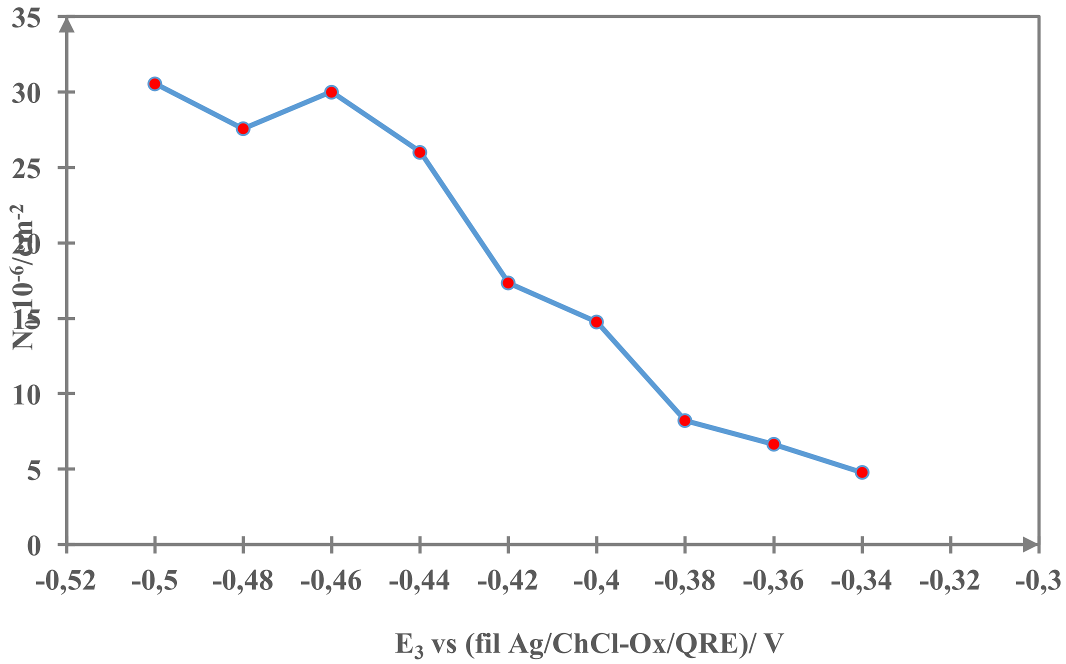

Figure 7. Evolution of the nuclei density vs the reduction potential of copper (I) to copper (0) in ChCl-Ox with 30 mmolal of $Cu(NO_3)_2.3H_2O$ at GC electrode, T= 70°C.

4. Conclusion

It emerges from this study that it is possible to use the mixture of choline chloride-oxalic acid dihydrate (ChCl-Ox) for the electrodeposition of copper by using 30 mmolal $Cu(NO_3)_2.3H_2O$ as precursor. Cyclic voltammetry indicates two essential steps in this process. The first step, kinetically determining which corresponds to the reduction of the cupric ions Cu^{2+} into cuprous ions Cu^{+} then the second stage corresponding to the reduction of cuprous ions Cu^{+} into metallic copper Cu(0). All electrochemical oxidation and reduction reactions that take place at the electrode are controlled by diffusion. The results also show that the reaction involving the Cu(II)/Cu(I) couple is reversible while that involving the Cu(I)/Cu(0) couple is almost reversible.

The mechanism of nucleation and growth was studied by chronoamperometry. The use of chronoamperograms and the tracing of current transients confirms an instantaneous nucleation and 3D-type growth model controlled by diffusion according to the Scharifker and Hills model. The diffusion coefficients of the Cu^{2+} and Cu^{+} ions, are determined by cyclic voltammetry and chronoamperometry. On the one hand, by using cyclic voltammetry, $D_{Cu^{2+}} = 2.56 \pm 0.09 \times 10^{-7}\ cm^2.s^{-1}$. On the other hand, by using chronoamperometry and according to Scharifker and Hills models $D_{Cu^{+}} = 5.503 \pm 0.330 \times 10^{-7}\ cm^2.s^{-1}$; According to the Cottrell model, $D_{Cu^{+}} = 5.622 \times 10^{-7}\ cm^2.s^{-1}$.These values are consistent with values of D_{Cu^+} and $D_{Cu^{2+}}$ found in other eutectic solvents based on choline chloride by other authors listed in the literature.

These results have shown that the charge transfer kinetics of Cu^{2+} ions is slow compared to that of Cu^+ ions. The chronoamperometry measurements have also made it possible to determine the maximum density of nuclei N_0 in the order of $3 \times 10^7 cm^{-2}$ reached at a potential of -0.46V. This potential would be suitable for the electrodeposition of copper in ChCl-Ox +30 mmolal $Cu(NO_3)_2.3H_2O$ media. In short, the study shows that the ChCl-Ox mixture prepared using oxalic acid dihydrate as a hydrogen bond donor is well indicated, as well as other DESs prepared on the basis of choline chloride and other hydrogen bond donors such as ChCl-U and ChCl-EG, for the electrodeposition of copper from compounds which contain it.

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