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Optimization of Electrochemical Copper Recovery Process: Effect of the Rotation Speed in Chloride Medium of pH=3

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Potentiostatic copper electrodeposition at a graphite electrode from synthetic 0.05 M copper (II) sulfate solution was studied at pH 3. Sodium chloride was added to increase the conductivity of the solution and catalyze the process. Cyclic voltammograms had shown that copper was deposited though the two step reduction processes Cu(II)/CuCl and CuCl/Cu(0). The effect of the electrolyte rotation using magnetic stirrer during deposition at -500 mV_{SCE} has been studied. The current efficiency and the copper removal percentage increase with the increase of the rotation speed and at 1500 rpm reached a maximum of 94% and 99% respectively after four (4) hours of process. Without rotation, XRD results illustrate a heterogeneous deposit that consists of pure copper with copper oxide, hydroxide and chloride species. The deposit became more pure with the increase of the rotation speed. SEM results show, that initially, the deposit was compact and uniform while at later deposition times, the structure and morphology changed to delicate deposit characterized by dendritic growth. This deposit was easily removable from the cathode suiting the purpose of copper recovery.

Keywords: copper recovery, potentiostatic copper electrodeposition, rotation, chloride medium, current efficiency, dendritic growth.

1. INTRODUCTION

Metallic copper is produced in many countries. The continuously higher demand of copper has led to an increase in the production in the last decades due to potential application in several new technological fields. Copper and its alloys take a big part in green energy which are considered a promising option in today's search for suitable replacements for fossil fuels to counter global warming

[1]. High electrical conductivity and resistance to corrosion make copper unique as an electrical conductor.

Nearly 500 pounds of copper is produced in the world each second. At the current rate of consumption, there are copper reserves of 25 to 30 years in nonrenewable resources.

Along with the increased production, copper quantities in the environment have increased. Wastewater pollution by heavy metals including copper, remains today one of the biggest environmental problems to solve in industrialized countries, which still poses a threat to society. Various conventional methods are used to remove heavy metals from wastewater. They are based on chemical precipitation phenomena, ion exchanges, adsorption or biosorption. These systems are often unsuitable due to their complexity and expensive cost of operation and maintenance. Electrodeposition of metals, particularly from aqueous solutions, is an attractive method for the recovery of metal ions from different industrial effluents such as plating, metal finishing and electronics [2].

Electrodeposition is usually applied for the recovery of copper from wastewater [3]. The recovery process is considered of great importance for reducing environmental emissions and for substantial savings. 12% to 16% of copper is obtained by recycling copper from wastes [1]. Indeed, copper can be recycled without loss of quality or performance. There is no difference in quality of copper between recycled metal and the metal from mining. This property of copper is unique in the world of recycling. Copper is virtually 100% recyclable [4].

A lot of research has been carried out in different media and under various conditions to study and optimize the recovery of copper. Electrodeposition of copper has been investigated in media containing sulfates [5,6,7] ammonia [8,9] and ionic liquids[10,11,12]. Organic additives, such as thiourea, gelatine, animal glue and a mixture of ethoxyacetic alcohol and triethyl-benzyl-ammonium chloride (TEBA) are widely used in copper electrodeposition since they can produce smooth and bright copper deposits [13].

The most widely used electrolyte for copper deposition is sulphuric acid. Generally, cathodic deposition of copper in sulphuric acid solution is proposed to occur through two consecutive charge transfer steps involving the soluble intermediate Cu^+ [14].

Chloride ion is well known accelerator for the plating reaction in acid copper baths; it was shown that the plating rate is much faster at low overpotentials when chloride ions are present. Generally, chloride ions are added in the concentration range of a few mM. David M. Soares and Sabine Wasle studied cathodic reduction of copper in the absence and in the presence of chloride ions ($1.10^{-3} \leq C_{cl} \leq 8.10^{-3}$ M) in an electrolyte that is comparable to galvanic copper baths (2.2 M H_2SO4 +0.3 M $CuSO_4$). A mechanism of Cu (II) reduction with intermediate formation of CuCl has been postulated [15].

Without chlorides, Cu^+_{ads} ion are produced at the interface and these act as an electrostatic barrier to further Cu^{+2} discharge. Chloride ions evidently reduce the height of this barrier, probably by bonding to the adsorbed cation species [16]. The increase in the concentration of Cl^- ions (0.1 M-1 M) shifts potentials of cathodic and anodic peaks in positive and negative directions, respectively. This behavior is characteristic of both the binding into a complex of the reduced form of the system $Cu^{+2}/CuCl^{-2}$ and the formation of a difficultly soluble form of the system $Cu^{+2}/CuCl_m$ [17].

The mechanism of copper deposition in a sulphuric acid–sulfate bath in the presence of chlorides was also investigated by C. Gabrielli and P. Mocoteguy. A catalytic action of chloride ions, not limited by mass transport, was proposed. This shows that the observed mass transport limitation is due to the diffusion of cupric ions and that, at high current densities, copper deposition is mainly due to a mechanism involving CuCl formation on the electrode [14].

Nekrasov and Berezina used a rotating ring disk electrode and found that the Cu^+ ion is more stable in the presence of Cl^- ion compared to the absence of Cl^- ion [7].

The influence of chlorides and three different additives (polyethylene glycol, a thiocompound and a quaternary ammonium salt) on structure and morphology of copper electrodeposits from a solution of 0.8 M copper sulfate at pH 3 has been investigated by A.Vicenzo and P.L. Cavallotti [5]. The results have shown that chlorides behave as a surface stabilizing agent, promoting epitaxial growth of copper. Deposition from sulphate solution of pH3 was shown to be a valuable alternative to copper deposition from standard acid bath ($CuSO_4$ 0.25 M, H_2SO_4 1.5 M) [5]. L. Doulakas and K. Novy investigated the recovery of copper and other metals from a chloride solution. The goal was to recover each heavy metal with high purity, yield and reaction rate, under potentiostatic conditions. The quality of the deposits obtained depended strongly on the overpotential and less on the pH [3]. The mechanism of copper deposition at -450 mV and -500 mV from a solution with 2.48 M of NaCl indicated an intermediate Cu^{+1} stabilized by chloride ions as a complex CuCl. Efficiency close to 100% has been obtained [3].

Our goal was to optimize the recovery of copper by potentiostatic deposition from aqueous sulphate solution of pH 3 containing 0.1 M of chloride ions with a prospect of facilitating copper removal via a Cl^- catalyzed electrochemical process. Copper, thus obtained, may be recycled by direct recuperation (use) or by oxidation process of the deposit.

2. EXPERIMENTAL

The electrochemical study of the recovery of copper was carried out in a conventional three-electrode with graphite working electrode (area = $2cm^2$). A graphite bar with an exposed area twice greater than the working electrode was used as an auxiliary electrode. A saturated calomel electrode (SCE) was used as a reference. All potentials refer to SCE scale. All solutions were prepared from analytical reagent grade chemicals without further purification using double distilled water. PH was adjusted by adding dilute hydrochloric acid (HCl). All experiments were performed at room temperature.

Electrochemical experiments were performed by potentiostat/galvanostat PG model 263A. Before each experiment the working electrode was polished and held in the electrolyte at the open circuit potential during 20 min in order to stabilize the system. All measurements for copper electrodeposition were performed under potentiostatic conditions except one galvanostatic experiment that was done for comparison. Ohmic resistance between the reference and the working electrode was measured at 10^5 Hz and found to be 10.7 Ω. The data are shown without the ohmic drop correction.

Cyclic voltammetry (CV) experiments were performed in a cell of 250 ml with a distance of 4 cm between the working and the auxiliary electrode. The scan was started from the anodic potential of 1200 mV towards the cathodic potential of -2000 mV. The scan rate was varied from 10 mV $s^{-}1$ to 500 mV s^{-1}.The effect of the electrolyte movement on cyclic voltammograms has been investigated through the use of magnetic stirrer at different rotation speeds equal to: 500, 1000 and 1500 rpm.

Chronoamperometry was applied during deposition from the solution at -500 mV. After electrolysis, the electrode was taken out with special care so that the shear force between the solution and electrode surface did not break the deposit. All deposits were washed with double distilled water and dried with nitrogen gas. X-ray diffraction (XRD) measurement was used to characterize the composition of the deposits. XRD measurements were performed using Shimadzu diffractometer XRD 6000 with CuKα radiation. Data was collected for 2θ between 2 and 80°, in a step scan mode with steps of 0.02° and counting time of 0.6 s.

The efficiency of copper deposition was measured in a potentiostatic experiment that lasted for four hours and was performed at -500 mV, in a cell of 50 ml with distance of 2.5 cm between the working and the auxiliary electrode. Samples from the electrolyte were taken every one hour for the determination of the decrease in copper concentration by spectrophotometric measurements. Copper concentration was determined by complexation with 1,10-phenanthroline reagent. The absorbance was measured after 24 hours of incubation at 317 nm using JENWAY 6300 spectrophotometer.

Scanning electron microscopy (SEM) was used to characterize the surface morphology during the process of deposition. For that purpose the deposition was performed for 1, 2, 3 and 4 hours. The deposits were examined by scanning electron microscope PEG QUANTA 250 SEM FEI at an acceleration voltage of 20 kV. The structure of the deposit obtained by galvanostatic deposition at -10 mA for one (1) hour was also examined.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

Cyclic voltammetry is the first step to investigate copper electrodeposition in 0.05M $CuSO_4$ copper sulphate bath of pH 3 containing 0.1M NaCl. Literature on copper electrodeposition in sulphuric acid medium shows that the reduction of copper in the presence of chloride ions occurs in two stages [14,15,17,18,19] presented by two cathodic peaks which are more or less separated in the voltammetric curve depending on the ratio Cl^{-}/Cu^{+2} [17].

The voltammograms recorded at different scan rates without electrolyte mixing are presented in Figure 1. The general shape of the cyclic voltammograms obtained is similar to that reported in literature for electrodeposition of copper from acidic copper sulphate solutions containing chlorides [17, 19]. During the cathodic scan at a scan rate of 50 mV.s^{-1}, two broad peaks “A” and “B” were observed, respectively, at –0.2V and –0.5 V . The former is due to the reduction of Cu^{+2} to Cu^{+1} and the latter due to the reduction of Cu^{+1} to metallic Cu^{0} [18,20,21]. During the reverse scan, two separate

peaks that merge with the increase in scan rate were observed; both resulting from oxidation of copper deposit.

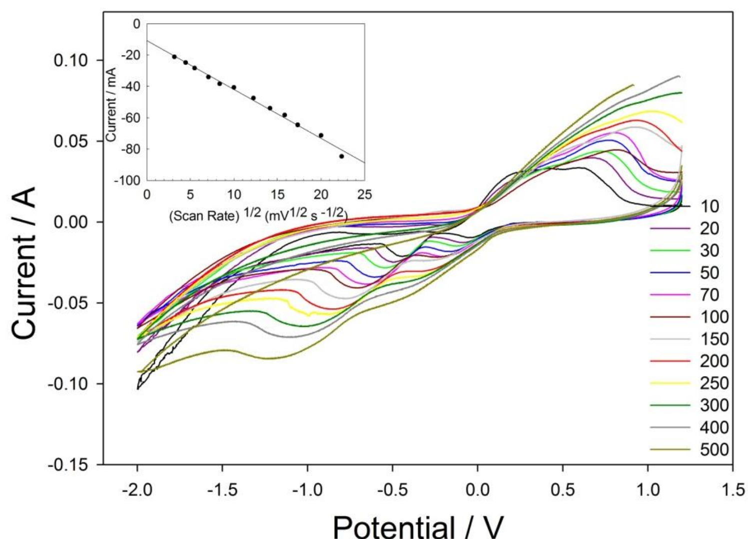

Figure 1. Cyclic voltammograms obtained in the solution of 0.05 M Cu^{2+} (copper sulphate) + 0.1 M NaCl of pH 3 at different scan rates.

Figure 2 illustrates that the first anodic peak at approximately 0.1 V corresponds to the oxidation of Cu^0 to Cu^{+1} and the second at more positive potential of 0.217 V corresponds to the oxidation of Cu^{+1} to Cu^{+2}. Thus, the combination of the two anodic peaks is the result of simultaneous processes of oxidation due to the presence of chloride complexes in the deposit. This effect is pronounced in the presence of Cl^-, which causes the stabilization of copper(I) on the electrode surface.

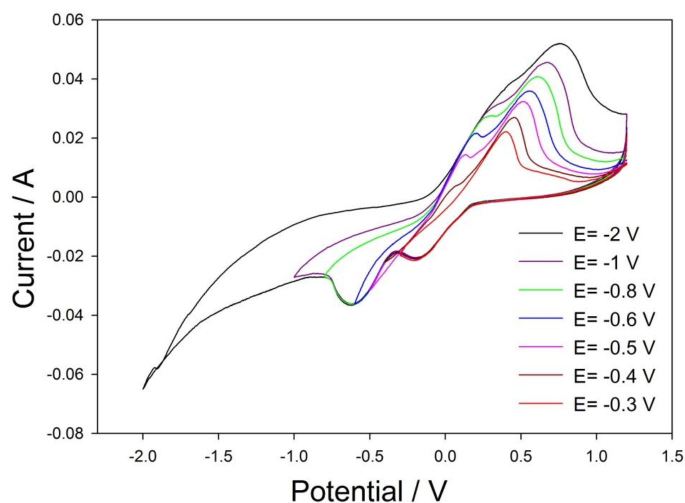

Figure 2. Cyclic voltammograms obtained in the solution of 0.05 M Cu^{2+} (copper sulphate) + 0.1 M NaCl of pH 3 with different cathodic inversion potentials. Scan rate equals 50 mV s^{-1}.

Inset of Figure 1 shows that the second cathodic peak current increases linearly with the square root of the scan rate. This result establishes that the reduction of Cu^{+1} to metallic Cu^0 is a diffusion controlled process [19, 22].

It is seen in Figure 1 that, with the increase of the scan rate, the anodic and cathodic peaks become higher. This can be justified by the increase of the rate of deposition controlled by Cu^{2+} diffusion and the increase in the amount of chloride ions used for complexation. It was shown that the voltammetric behavior of coper deposition significantly depends on the concentration of chloride ions. The separation of the two redox couples Cu^{+2}/Cu^{+1} and Cu^{+1}/Cu^0 increases with increasing the concentration of chlorides and correspondingly to the enhanced formation of CuCl complex [23]. The second peak of reduction differs from the first in form, which is connected with the participation of some insoluble species in the Cu^{+1}/Cu^0 process which are detected in the deposit by XRD and FTIR measurements [17].

The effect of the rotation speed on cyclic voltammograms was recorded and presented in Figure 3. A pronounced increase in cathodic and anodic peaks is observed with the increase in rotation speed, indicating acceleration in the process of deposition. Also, rotation induces a progressive shift of both cathodic and anodic peaks to more negative and positive values respectively. The diffusion limited cathodic current (plateau) is observed for the highest rotation speed. The observed cathodic current behavior can be justified by the enhanced diffusion of Cu^{+2} to the cathode in the steered electrolytes yielding a higher amount of Cu^{+1} near the cathode after the first step of reduction. More chloride ions are used for the complexation with Cu^{+1}, which yields wider separation between the cathodic and anodic peaks with the increase in rotation speed.

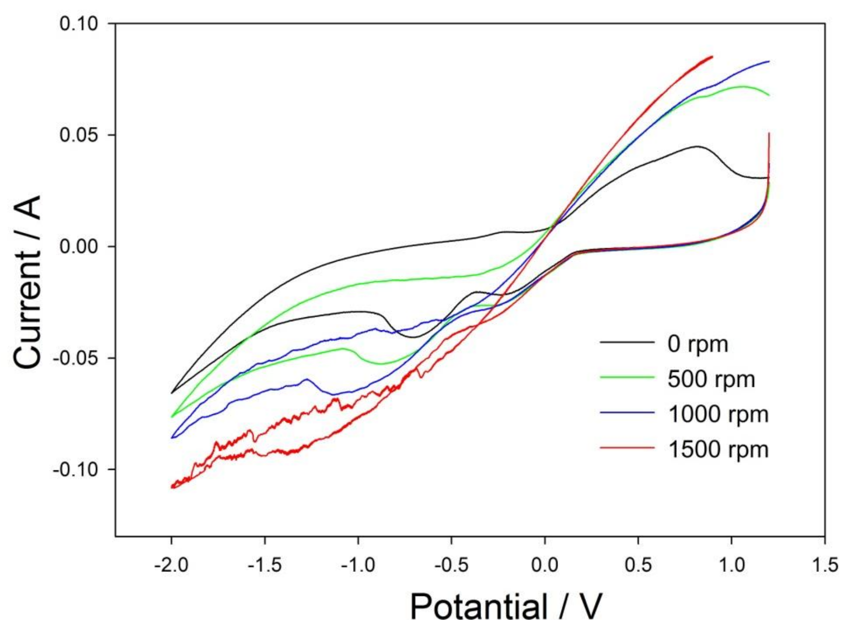

Figure 3. Cyclic voltammograms obtained in the solution of 0.05 M Cu^{2+} (copper sulphate) + 0.1 M NaCl of pH 3 for different rotation speeds. Scan rate equals 100 mV. s^{-1}.

On the other hand, anodic current behavior can be understood by taking into account the oxidation of deposited metallic copper.

3.2. Chronoamperometry

Chronoamperometry was applied to obtain a deposit potentiostatically at -500 mV with and without electrolyte rotation during four hours of deposition in a cell of 50 ml with a distance of 2.5 cm between the working and the auxiliary electrode.

Figure 4 shows cronoamperograms obtained for various rotation speeds. It can be seen that there are two separate time intervals of current behavior, during the first interval the current increases indicating intensification of the displacement of copper from the electrolyte bulk to the surface of the graphite electrode resulting in a large amount of deposit and larger surface area of the electrode.

After two hours of deposition without rotation and an average of three hours with rotation, the current starts decreasing and correspondingly a smaller amount of copper deposit is formed. This can be related to the diminution of copper concentration in the solution. The decrease of the current can also be affected by the ratio Cu^{+2}/Cl^{-}, which affects the stability of the CuCl complex.

The increase of the deposition rate and the duration of the current rise with rotation can be justified by the competing effects the mass transfer of copper from the solution to the electrode enhanced by agitation and the depletion of copper from the solution. From Figure 4 it can be seen that the deposition at the rotation speed of 1000 rpm shows the longest current increase period which makes the deposition more uniform, giving more pure and compact deposit with respect to other measurements.

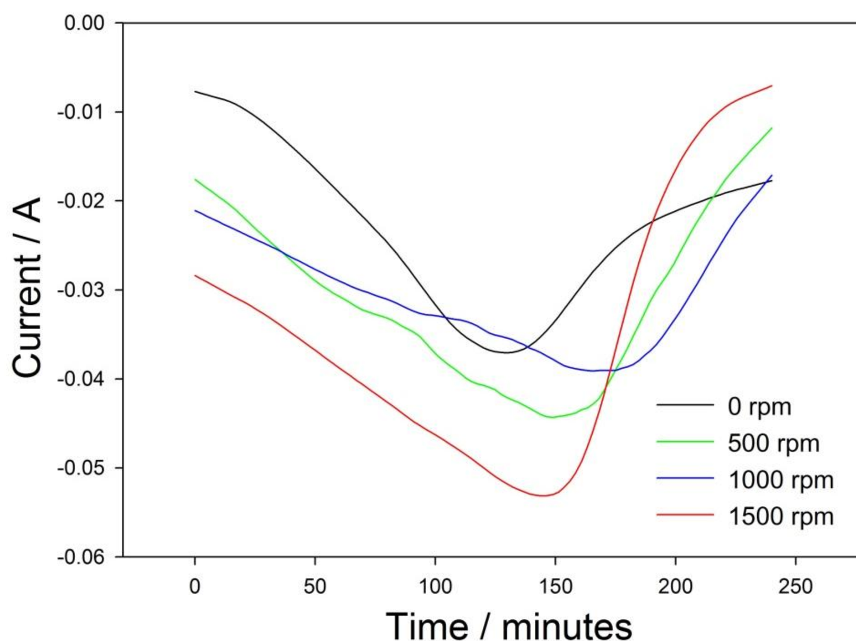

Figure 4. Cronoamperograms obtained at different rotation speeds during the deposition of copper from the solution of 0.05 M Cu^{2+} (copper sulphate) + 0.1 M NaCl of pH 3 at -500 mV.

Despite a considerable number of works devoted to the cathodic copper deposition in acid solutions with chlorides, the reduction mechanism is still unclear because of the effect of a large number of parameters that influence the stability of chloride complexes that can be formed in the first stage of the reduction. Studies indicated that in dilute chloride solutions (0.001– 0.1 M Cl^-), the predominant complex is CuCl, and in more concentrated solutions, $CuCl_2$ and $CuCl_3^{2-}$, complexes are predominant [24]. Hence, in the present case it may be assumed that reaction mechanism follows a two-step process. First, Cu^{+2} ions arrive to the cathodic surface by bulk diffusion and react through a one-electron transfer, leading to the formation of Cu^{+1}, its complexation with chloride anion and adsorption onto the surface:

$$Cu^{+2}_{sol} + Cl^-_{sol} + é = CuCl_{ads} \quad E= -0.112V \quad (A)$$

The cuprous complex reacts via a second one-electron transfer and metallic copper deposits on graphite electrode is formed:

$$CuCl_{ads} + é = Cu_m + Cl^-_{sol} \quad E= -0.513 \quad (B)$$

The Cu^{+1} ion is considered as soluble species, which electrode coverage does not have to be considered [14]. As Cu^+ ions are not consumed at the electrode, their action is not limited by mass transport and they are efficient even at low concentrations. The observed mass transport limitation is due to the diffusion of cupric ions [14].

It is assumed that in Cl^- free solutions a partial discharge state is attained, e.g. Cu^+_{ads}, which functions as a barrier to further Cu^{2+} reduction at low overpotentials [16]. Cl^- is assumed to interact strongly with Cu^+_{ads}, thereby reducing the electrostatic repulsion barrier between Cu^+_{ads} and Cu^{2+}_{sol} at the interface. Consequently, the plating rate is much faster at low overpotentials when chloride ions are present.

3.3. XRD

XRD studies have been carried out to characterize the deposits obtained after 2 hours of deposition at -500 mV. The deposits were rinsed and dried before each measurement. The results substantiate the mechanism of copper deposition proposed, according to the presence of the intermediate complex CuCl adsorbed on the surface of the copper. Significant effect of rotation in on chemical composition of deposit was observed.

Figure 5 shows the XRD patterns. In general the patterns show the presence of three compounds: pure copper, cuprous oxide Cu_2O, copper chloride CuCl and $Cu(OH)_2 \times H_2O$ [25,26,27]. It was demonstrated previously that small crystals of CuCl are formed on a copper surface when it is exposed to a copper sulfate solution containing a few mM chloride ions [15]. In the present case, CuCl in the deposit can be related to the later phenomenon or to CuCl adsorption during deposition [14].

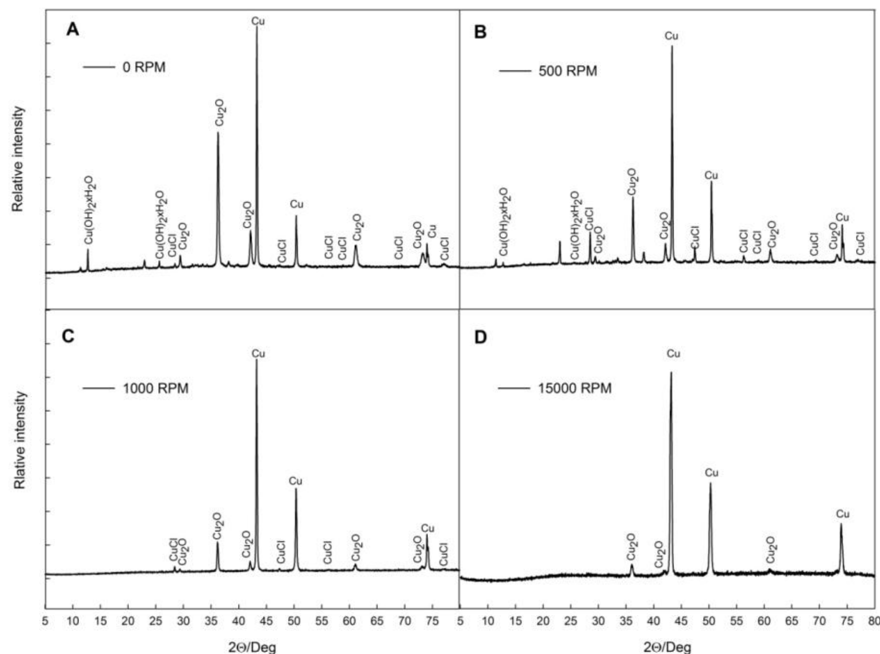

Figure 5. XRD patterns of deposits obtained after 2 hours of deposition and for various rotation speeds from the solution of 0.05 M Cu^{2+} (copper sulphate) + 0.1 M NaCl of pH 3 at -500 mV.

From XRD patterns, shown in Figure 6, it can be deduced that the intensity of the diffraction peaks of impurities decreases with increasing the rotation speed. All the impurities except Cu_2O totally disappear in the deposit obtained at 1500 rpm. The XRD patterns show that the increase of the rotation speed and hence, the increase of the Cu^{2+} transport to the electrode, leads to the improvement in purity of copper deposits [1]. The residual Cu_2O can from the surface oxidation of Cu powder particles [25] or co-deposition of cuprous oxide with copper metallic [28, 29].

3.4 Current efficiency of deposition

During potentiostatic deposition of copper at -500 mV, samples of electrolyte were taken once per hour and the decrease of copper concentration was followed by spectrophotometry. The current efficiencies **(η)** of the process and the conversion factor **(χ)** of the recovery were calculated using the following equations [2]:

$$\eta = \frac{zVF\left(C_0 - C_f\right)}{Q_t} \times 100 \qquad (1)$$

$$\chi = \frac{\left(C_0 - C_f\right)}{C_0} \times 100 \qquad (2)$$

Where **Z** is the number of electrons, **V** is the volume of electrolyte, $\mathbf{C_0}$ and $\mathbf{C_f}$ are the initial and final concentrations of copper, respectively, and **Qt** is the total charge calculated from chronoamperograms. The current efficiencies and the conversions factors presented in Table 1.

Cu^{+2} ion concentration decreased by increasing the time of deposition. The use of bath agitation is improved the mass transport in the electrolyte and therefore enhanced the rate of Cu^{+2} depletion from the solution. However, in terms of cathode deposition, bath agitation was found to enhance the percentage of the recovery.

Table 1. Cathodic current efficiency and conversion factor of a copper deposition process obtained at different rotation speeds.

Rotation	0rpm			500rpm			1000rpm			1500rpm		
Time	$C_f(M)$	η %	χ %	$C_f(M)$	η %	χ %	$C_f(M)$	η %	χ %	$C_f(M)$	η %	χ %
1h	0.0459	89.98	8.2	0.042	87.55	16	0.0413	92.54	17.4	0.0384	92.89	23.2
2h	0.0361	92.18	27.8	0.0302	88.74	39.6	0.0298	94.76	40.4	0.0219	96.67	56.2
3h	0.0282	80.26	43.6	0.0196	79.35	60.8	0.0184	89.55	63.2	0.003	92.2	94
4h	0.0220	80.65	56	0.0117	82.15	76.6	0.008	91.32	84	0.0005	94.0	99

From the decrease of copper quantity in solution after the deposition experiment, the mass transport coefficient, K_m was calculated using the equation presented below [2]:

$$\frac{C(t)}{C_0} = \frac{-K_m A}{Vt} \qquad (3)$$

The result showed an increase of the masse transport coefficient with the rotation speed during four hours of deposition. Supposing a surface area of 2 cm^2, a value of $1,42\times10^{-3}$ cm s^{-1} was calculated for the system without rotation and the values of 2.52×10^{-3}, 3.18×10^{-3} and 7.99×10^{-3} cm s^{-1} have been calculated for 500 rpm, 1000 rpm and 1500 rpm, respectively. The highest efficiencies**,** conversion factor and transport coefficient were observed for the highest rotation speed.

3.5. SEM

Surface morphology of copper deposits at different rotation speeds during four 4 of deposition at -500 mV were analyzed using SEM measurements.

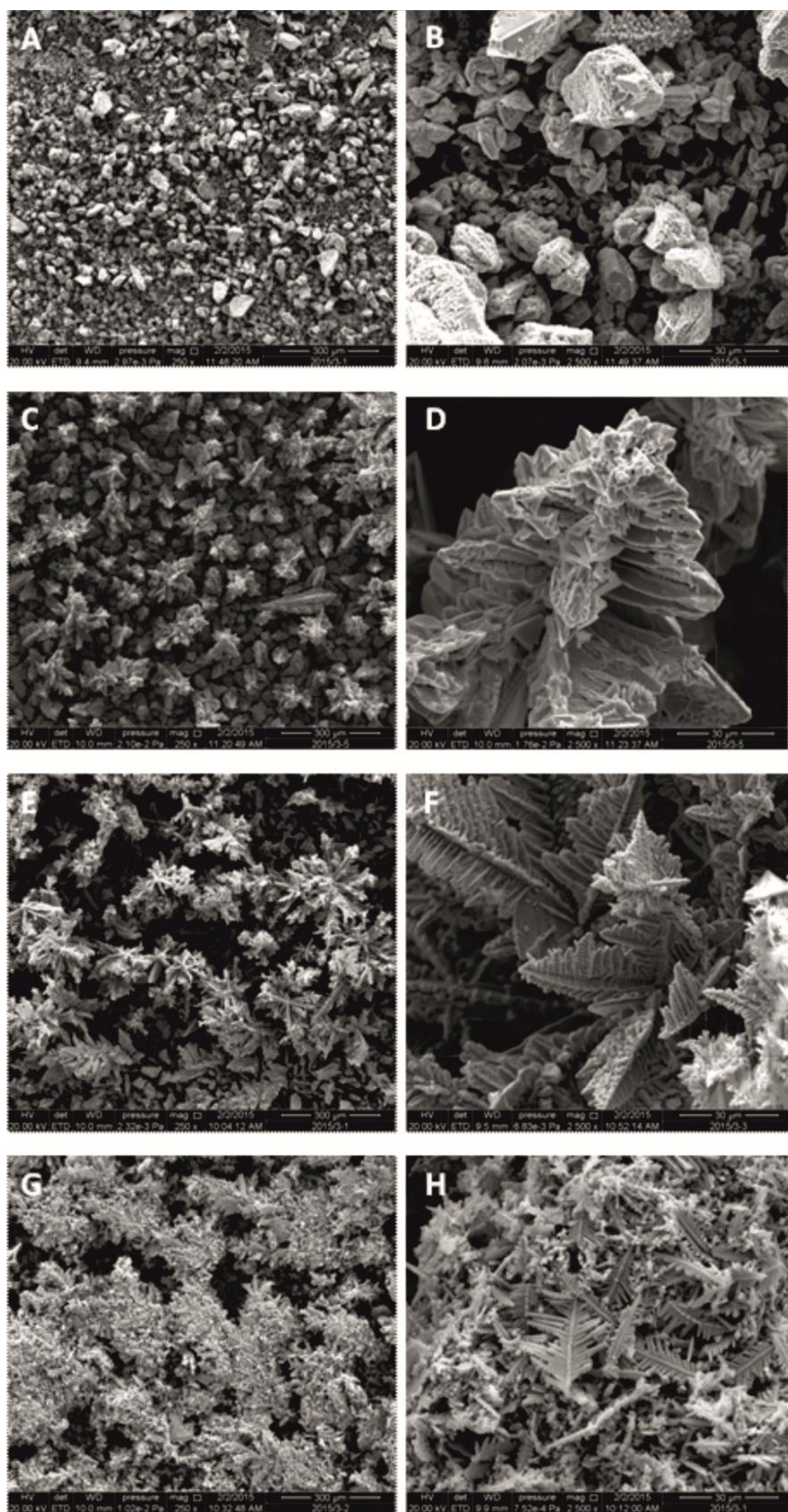

Figure 6. SEM images of deposits formed during 4 hours of deposition from the solution of 0.05 M Cu^{2+} (copper sulphate) + 0.1 M NaCl of pH 3 at -500 mV with electrolyte rotation.

The results have shown little difference in appearance among deposits obtained with different rotation speeds. Contrarily, with the increase in the time of deposition, morphology of copper deposit changes visibly from a continuous and compact deposit to a delicate and brittle dendritic deposit. Deposition starts with the appearance of small polyhedral particles on the surface of graphite electrode.

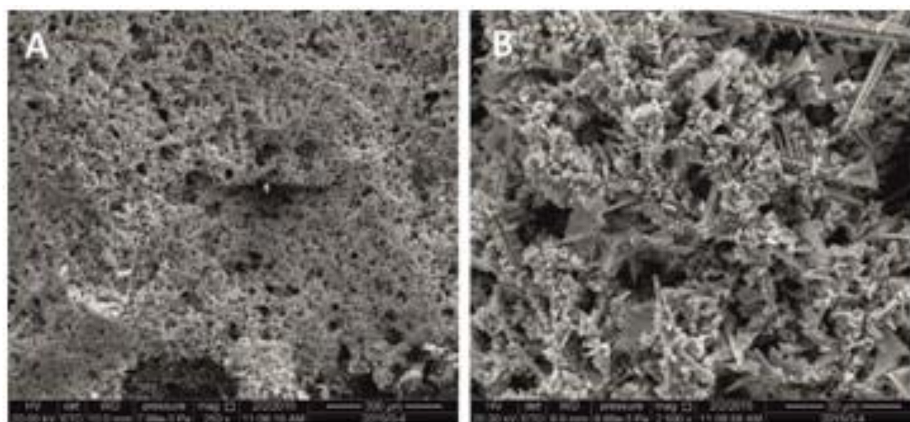

Figure 7. SEM images of deposits formed during 4 hours of deposition at -500 mV in the electrolyte without rotation.

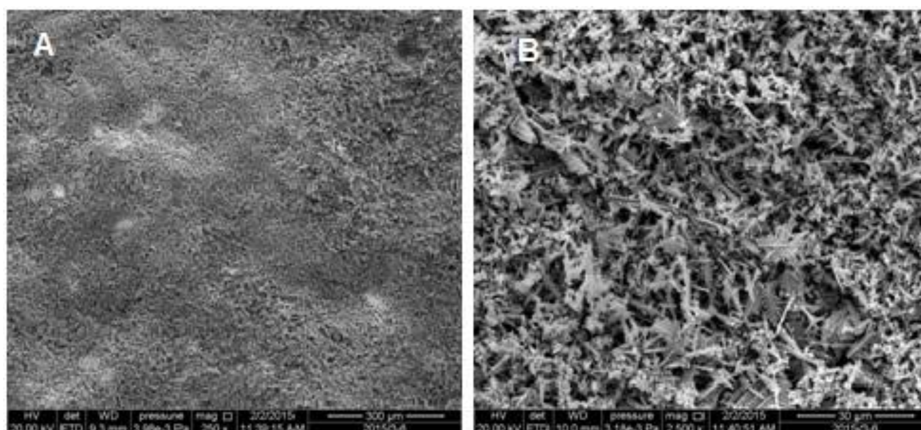

Figure 8. SEM images of deposits formed during 4 hours of deposition at -10 mA in the electrolyte without rotation.

The particles grew with visible crystallographic facets and their size varied between 1 and 5μm (Figure 6, A and B). After 40 minutes, growth of small dendritic nodules from the surface of each particle was observed (Figure 6, C and D). From 90 minutes onwards, the dendritic structure began to proliferate as an overgrowth of randomly branched dendrites [27] developing later into fern-like foliage (Figure 6, E and F). Finally at longer electrolysis times, the presence of discontinuous available electroactive surface due to ramified dendritic growth [3] causes an agglomerate growth of dendritic particles around the gaps (Figure 6, G and H) as the concentration of copper becomes smaller. As

expected [30], in potentiostatic regime, dendrites of deposited metal appeared in the limiting diffusion current density range and hydrogen co-deposition was not a necessary factor for the powder formation.

In the system without rotation the morphology of the deposit is significantly different (Figure 7) and a sponge-like structure is obtained. For comparison, deposition was done galvanostatically at -10 mA. The deposition process was accompanied by vigorous hydrogen evolution and only a thin porous copper deposit was formed even after hours of deposition (Figure 8).

4. CONCLUSION

An excellent recovery of copper (99%) by potentiostatic deposition at -500mV with deposit easily removable from the electrode by scratching and tapping without removing the cathode material has been achieved in this present work. The deposition is characterized by good current efficiency (94%) and especially, at sufficient electrolyte agitation rate, an almost pure copper deposit has been obtained. Under the same experimental conditions, galvanostatic deposition at -10 mA has shown to be inefficient.

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