

Effect of additives on Cu electrodeposits: electrochemical study coupled with EQCM measurements

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Abstract The effect of polyethylene glycol (PEG) and chloride ions on Cu electrodeposition mechanism is investigated. Using blank electrolyte, electrochemical measurements show that PEG adsorbs more or less on the electrode surface depending on the nature of this surface (copper, gold). Alternative current techniques and electrochemical quartz crystal microbalance (EQCM) experiments are performed at open circuit and under polarisation. They show that the PEG adsorption on the Cu electrode is weak at open circuit, but increases under polarisation. In complementary EQCM tests made on Au and on electrodeposited Cu, we conclude that the H₂ gas production reduces the apparent mass of the gold surface. In contrary on Cu, H₂ entrapped in the Cu deposit increases the mass. In all cases, there is an important mass hysteresis. Whatever the substrate, the addition of PEG + Cl⁻ to solution has a beneficial effect by reducing this hysteresis due to the H₂ production. For Cu electrolytes, the PEG addition to solution has little effect, while the simultaneous PEG + Cl⁻ addition inhibits both the Cu²⁺ reduction current and the mass increase. Atomic force microscopy (AFM) images made on the deposits confirm the beneficial effect of the two additives in solution.

Keywords Copper · PEG · Chloride · Additives · Voltametry

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1. Introduction

Acid copper baths containing CuSO₄ in high concentration are often used to obtain Cu electrodeposits [1].

Traditionally and especially for nanotechnology applications, organic substances are added to the electrolyte in low concentration (in the order of parts per million) to enhance the quality of the deposit by forming smooth and shiny deposits. Therefore, the chemical composition of the electrolyte bath has been the topic of numerous studies and various organic or inorganic substances have been tested. Many additives used alone or in a mixture have been studied to elucidate their effect on the nucleation mechanism and on the deposit properties.

In particular, many investigations show that polyethylene-glycol (PEG) and chloride ions act in a synergistic way improving the performance of the galvanic baths and the properties of the deposit. The influence of those additives on the Cu electrodeposition mechanisms has thus widely been discussed.

When both PEG and Cl⁻ are present, a surface layer forms on the copper electrode that constitutes a barrier for charge transfer [2–4]. Healy et al. suggested that the polymer can adsorb in two different ways. One predominates close to the open circuit potential and may well be a copper chloride complex with the polyethylene glycol as a ligand. The other prevails at more negative potentials where copper plating is carried out; this species is likely to be the simple, neutral polymer molecule.

In a previous publication [5] we used electrochemical and non electrochemical methods (atomic force microscopy (AFM), ellipsometry, X-ray diffraction (XRD)) to have insight into the mechanism of PEG and PEG + Cl⁻ action during copper deposition. We concluded that the adsorption

is potential dependent and that the texture of the deposit is modified and the roughness is significantly decreased to $0.5 \mu\text{m}$.

Doblhofer et al. [3] showed that the inhibiting layer forms by reaction between the adsorbate-covered copper electrode and PEG, i.e., neither Cu^+ nor Cu^{2+} from the electrolyte are required.

Moreover, in recent studies [6] PEG and Cl^- co-adsorption has been investigated on Pt in acid baths and one finds that the adsorption of PEG occurs via a non faradic process and that no adsorption is observed at the open circuit potential.

In spite of numerous studies on the influence of PEG and Cl^- precisely on the copper electrodeposition process, their adsorption mechanisms remain a subject of research to understand better their modes of action.

The aim of the present work is to study the influence of additives (PEG 10000, Cl^-) and their co-adsorption during copper electrodeposition from a sulphuric acid bath.

The study is carried out using a combination of the electrochemical quartz crystal microbalance (EQCM) technique and classical electrochemical methods (linear sweep and cyclic voltametry). AFM and capacitance measurements are also performed.

2. Experimental

A classical three-electrode cell is used for all electrochemical experiments. The working electrode consists of a 0.28 cm^2 pure copper rod (99.999% purity). It is prepared by extensive polishing using emery paper to a grade of 1200, followed by a diamond paste polishing on polishing clothes of grain size 6 and $1 \mu\text{m}$ and then washed in an ultrasonic bath with pure water. For EQCM measurements, quartz crystals of nominal frequency $f_0 = 5 \text{ MHz}$, gold plated on both sides (Maxtek, CA) are employed. The geometric area of the gold surface in contact with the electrolyte is 1.37 cm^2 . The counter electrode is a platinum grid and all potentials are recorded with respect to a saturated calomel electrode (SCE).

The study of the influence of polyethylene glycol (PEG, $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OH}$ average molar mass 10,000, supplied by Merck) and chloride ions (added by using NaCl) is carried out by introducing them in the common formulation bath ($\text{pH} = 0$): $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$ 0.1 M + H_2SO_4 1 M. In the aim to determine the influence of each additive, several solutions are prepared using dionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) treated by a millipore system, containing no, one or both additives (see below). The weak concentration of the additives used does not change the pH value.

Blank experiments are carried out without Cu^{2+} in solution, in electrolytes referenced as followed:

S_0 : pure H_2SO_4 1 M solution
 S_p : S_0 + PEG 0.5 g/l
 S_c : S_0 + Cl^- 50 ppm
 S_{pc} : S_0 + PEG 0.5 g/l + Cl^- 50 ppm

The copper solutions are used as listed below:

Cu_0 : CuSO_4 0.1 M + H_2SO_4 1 M
 Cu_p : Cu_0 + PEG 0.5 g/l
 Cu_c : Cu_0 + Cl^- 50 ppm
 Cu_{pc} : Cu_0 + PEG 0.5 g/l + Cl^- 50 ppm

Electrochemical experiments are performed in direct current mode (d.c. mode) and in alternative current mode (a.c. mode). The d.c. experiments consist of cyclic voltametry or linear sweep polarization. The equipment is a EG&G-PAR model 273 potentiostat-galvanostat. The potential sweeps start from the rest potential of the substrate in the solution and continue in the cathodic direction. In the case of a.c. measurements, the equipment consists of a frequency response analyzer 1260 Solartron coupled with a potentiostat 1287 Solartron. The interfacial-layer capacitance C is calculated from the imaginary part of the impedance Z_{im} obtained by high frequency measurements ($f = 10 \text{ kHz}$), according to the relationship:

$$Z_{\text{im}} = \frac{1}{C\omega j} \quad \text{with } \omega = 2\pi f \quad (1)$$

When the capacitance evolution is followed in function of time, the time of acquisition has to remain small with respect to the time interval separating two points; this precaution is absolutely necessary.

The quartz crystal microbalance (Maxtek model 710), and the potentiostat-galvanostat EG&G-PAR model 273, are controlled by independent computers running the software PM 710 and EG&G M270, respectively. In that way, electrochemical parameters and resonance frequency of the quartz crystal are simultaneous measured as function of the applied potential, or in function of time. The relation between the change in surface mass and the resonance frequency for an EQCM electrode, is given by the Sauerbrey equation [7]

$$\Delta m = -C_f \Delta f \quad (2)$$

with Δf : frequency change in Hz, Δm : surface mass change in $\text{ng}\cdot\text{cm}^{-2}$, C_f : sensitive factor of the EQCM in $\text{ng}\cdot\text{cm}^{-2}\text{Hz}^{-1}$.

EQCM is an useful method for adsorption at a monolayer level because of its high sensitivity ($18 \text{ ng} \cdot \text{cm}^{-2} \cdot \text{Hz}^{-1}$), and also because adsorption can not be directly detected by voltametry since it is a non faradic process. Two kinds of experiments are performed with this technique. The first one consists of measuring the mass variation in function of the applied potential (called voltmassogram) and the second, the change of mass as a function of the immersion time, for three different polarisations, before and after a PEG addition.

Bulk deposits are obtained under galvanostatic conditions, from copper solutions with and without the additives. In that case, the substrate consists in a 2 cm^2 pure copper sample (99.9% purity), soldered on a conductive sheet isolated from the solution by an araldite film. In this way the substrates are easily removed from the support to be analyzed. Morphology and roughness of the deposits are determined by optical microscopy and atomic force microscopy (AFM) performed in air using a commercial instrument (CP Autoprobe provided by Park Scientific Instruments) in contact mode. AFM images are recorded over scan areas of $12 \times 12 \mu\text{m}^2$, with 512×512 data points. The root mean square roughness R_{RMS} , which is defined as the standard deviation of the surface height profile from the mean height, is given by:

$$R_{\text{RMS}} = \sqrt{\frac{\sum_{n=1}^N (Z_n - \bar{Z})^2}{N - 1}} \quad (3)$$

where \bar{Z} is the mean z height, N the number of data points of the image.

3. Results and discussion

3.1. Blank electrolytes without Cu^{2+}

3.1.1. Linear sweep polarizations on Cu

Because a modification of the hydrogen evolution reaction (h.e.r.) is dependent on an adsorbed layer, the first experiments are made on blank solutions without Cu^{2+} , with or without additives. Indeed, the pH value being unchanged whatever the solution used, if a change of h.e.r. ($E_{\text{eq,H}^+/\text{H}_2} = -0.24 \text{ V/ECS}$) is performed, that can not be due to a complex formation with the proton but rather to an adsorbed layer on the electrode surface. It is also simpler than with Cu^{2+} in solution, because in that case no deposit is formed on the surface with polarization.

The Fig. 1 reports the linear sweep polarization curves carried out on copper at 20 mV/s , from open circuit to -1 V , in S_0 , S_p , S_c , S_{pc} solutions. For S_0 , no significant current is performed until the potential reaches -700 mV , corresponding to the h.e.r. The over-potential η for the proton reduction

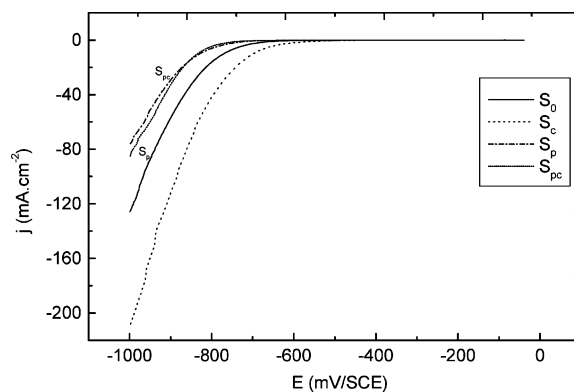


Fig. 1 Influence of additives on the linear sweep polarizations for H^+ reduction on Cu from: (S_0): pure H_2SO_4 1 M solution, (S_p): S_0 + PEG 0.5 g/l, (S_c): S_0 + Cl^- 50 ppm, (S_{pc}): S_0 + PEG 0.5 g/l + Cl^- 50 ppm

on the copper substrate is then about 450 mV . From the other solutions, it can be noticed that:

- no supplementary current is observed until the h.e.r.; the PEG and Cl^- additives are not electroactive, at least in this potential range.
- when the additives are added to the S_0 solution, a supplementary over-voltage η for the h.e.r. is obtained on the curves S_p and S_{pc} in comparison to S_0 . These additives present a blocking effect on the proton reduction reaction. With Cl^- alone in solution, an opposite result is obtained with a decrease of η . This is called the ion bridging effect by T.C. Franklin [8, 9] and leads to an acceleration of the proton reduction. The mechanism consists of the ability of a complexed ion to accelerate the rate of electron flow through the additive from the electrode to the cation. Besides this, Cl^- is known for its high adsorption power [10–12], and the formation of a cuprous chloride layer adsorbed on the copper surface is also involved [13–15].

It can be concluded that these two additives can adsorb on the copper substrate, at least in the potential range where the h.e.r. occurs.

3.1.2. Interfacial capacity measurement

The interface between the electrode and the solution can be modelled by a dielectric which is characterized by a capacity as follows:

$$C = \epsilon \epsilon_0 S / e \quad (4)$$

with

- C : capacitance in Faraday
- $\epsilon \epsilon_0$: electrolyte and air permittivity ($8.85 \times 10^{-8} \mu\text{F cm}^{-1}$)
- S : surface of the dielectric in cm^2
- e : thickness of the dielectric in cm.

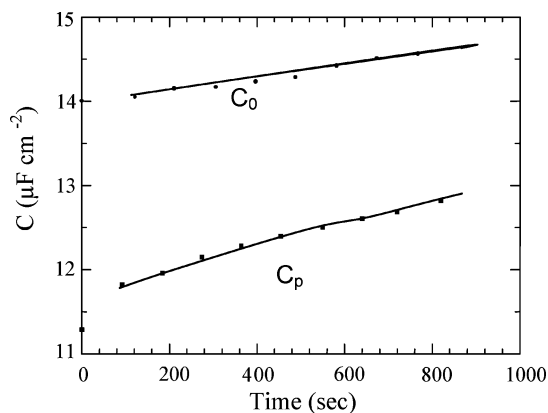


Fig. 2 Interfacial capacitance evolution as a function of the immersion time at open potential, from S_0 ((S_0) : 1 M H_2SO_4) and S_p ((S_p) is $S_0 + 0.5$ g/l PEG) solutions

Consequently, when a blocking additive (such as an organic molecule) adsorbs on an electrode surface the capacitance is lowered due to a decrease of the reactive surface S [12, 16].

The capacitance versus immersion time (total time of about 13 min) is shown in Fig. 2. In our case, it appears that the values of the capacitance in the two solutions (about 12 and $14 \mu F cm^{-2}$) are very close. The slight difference could be due to a variation in the surface state induced by the electrode polishing. These values are close and reproducible to $\pm 1 \mu F cm^{-2}$ and indicate no or a very weak PEG adsorption on the copper substrate, at least at open potential. At first sight, this conclusion might be considered in total contradiction to the first electrochemical experiments described above. But, if the electrochemical and the optical results are interpreted together, then the conclusion must be that the PEG adsorption does not occur at open circuit but at a more cathodic potential.

The subsequent capacitance measurements are made under cathodic polarization conditions from the rest potential to a potential before the hydrogen evolution reaction (Fig. 3).

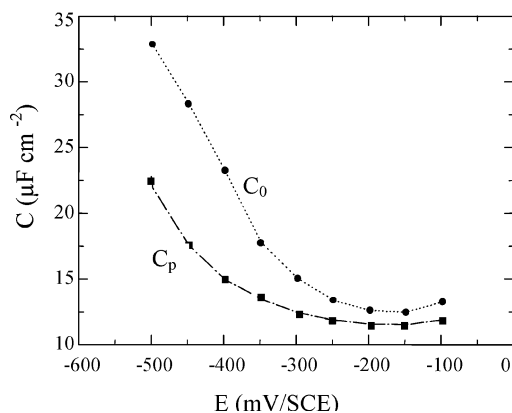


Fig. 3 Interfacial capacitance evolution as a function of the applied potential, from S_0 ((S_0) : 1 M H_2SO_4) and S_p ((S_p) is $S_0 + 0.5$ g/l PEG) solutions

Table I Capacitance evolution from S_0 and S_p blank electrolytes, as a function of the potential

E (mV/SCE)	$E_{i=0}$	-300	-400	-450	-500
C_0 ($\mu F cm^{-2}$)	14	15	23.7	28.5	33
C_p ($\mu F cm^{-2}$)	12	12.5	15	17.5	23
C_p/C_0	0.86	0.83	0.64	0.62	0.70

With (S_0): 1 M H_2SO_4 and (S_p): $S_0 + 0.5$ g/l PEG.

For S_0 , the interfacial capacity C_0 is about $14 \mu F cm^{-2}$ at the beginning of the cathodic polarization and then increases to $33 \mu F cm^{-2}$. This corresponds to an activated state of the electrode.

With PEG, the capacitances C_p are very close to those obtained without additive, until -250 mV/SCE. For more cathodic potentials, the two curves follow the same trend but in a different way, C_p being weaker than C_0 . This result obtained from blank electrolytes shows an adsorption of the PEG molecule on the copper surface, because no complexation can be envisaged. In Table I, the interfacial capacity values C_0 , C_p and the C_p/C_0 ratio are given as function of the potential. The error margin is estimated at $\pm 1 \mu F cm^{-2}$. The C_p/C_0 ratio evolution is weak but meaningful. It shows an increase of inhibition with the cathodic potential, reaching the lowest C_p/C_0 value at about -450 mV/SCE, which corresponds to the maximum efficiency. In conclusion, PEG adsorption on the electrode surface is clearly potential dependent.

3.1.3. EQCM measurements

Figure 4 presents the voltamograms and Fig. 5 the voltasograms obtained simultaneously in blank electrolyte on the quartz/gold surface, with and without additives. If one looks at the two curves S_0 , no reaction is apparent until the potential reaches -700 mV. Below that value, a continuous mass

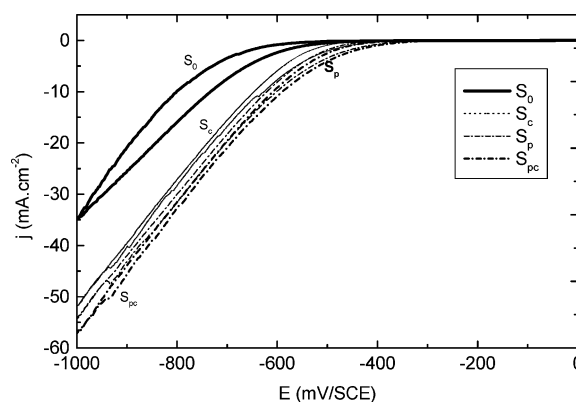


Fig. 4 Influence of additives on the voltamograms for H^+ reduction on quartz/gold from: (S_0): pure H_2SO_4 1 M solution, (S_p): $S_0 +$ PEG 0.5 g/l, (S_e): $S_0 + Cl^-$ 50 ppm, (S_{pe}): $S_0 +$ PEG 0.5 g/l + Cl^- 50 ppm

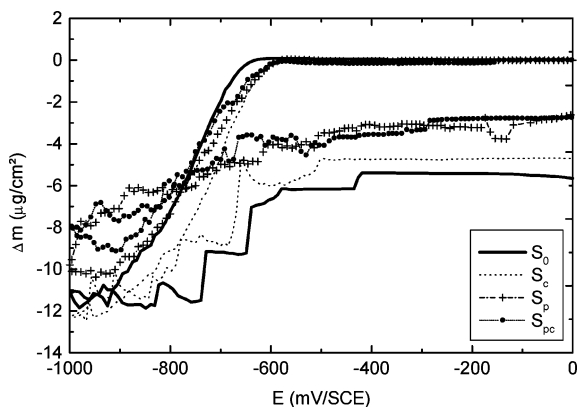


Fig. 5 Influence of additives on the voltmassograms for H^+ reduction on quartz/gold from: (S_0): pure H_2SO_4 1 M solution, (S_p): S_0 + PEG 0.5 g/l, (S_c): S_0 + Cl^- 50 ppm, (S_{pc}): S_0 + PEG 0.5 g/l + Cl^- 50 ppm

decrease is observed when the potential is scanned in cathodic direction. This apparent mass loss is probably due to the H_2 bubbles adsorbed on the gold. When the scan is reversed, H^+ reduction and in consequence H_2 production are decreased and the mass gain is increased. There is an important hysteresis between the final and the initial mass of about $-6 \mu g cm^{-2}$. This hysteresis can be explained by the fact that H_2 adsorbed on the gold surface is always present, even if the polarization is stopped.

When the additives are in solution, the curves obtained on Figs. 4 and 5 are modified compared to S_0 . The voltammograms and the voltmassograms both show a decrease of the proton overvoltage. In comparison to the polarization obtained on copper in Fig. 1, the influence of the substrate is obvious. With PEG and PEG + Cl^- , it appears that the H_2 production is more important (at a given potential the current with additives is more important than that without additive) while the amount of H_2 staying on the electrode is reduced (the apparent mass loss is less important with the two additives). The mass hysteresis obtained in that case is also reduced ($-3 \mu g \cdot cm^{-2}$). We can conclude that on gold the additives adsorb on the surface without diminishing the H_2 production. Nevertheless, they allow evacuating more easily the H_2 bubbles from the surface.

1 μm thick Cu is electrodeposited on the quartz/gold surface, by applying a $-250 mV$ potential. The thickness of the deposit is obtained both from the faraday law (the current obtained during the polarization is performed) and from the mass change directly obtained from the microbalance. On Fig. 6, whatever the solution used, the voltammograms are the same. The effect of the additives is weak on this electrodeposited Cu substrate. Nevertheless, the voltmassograms performed at the same time, present some big differences. First of all, in that case, Δm increases with the H^+ reduction as shown in Fig. 7: the H^+ reduction leads to a mass gain instead of a loose of mass previously obtained on gold. That could

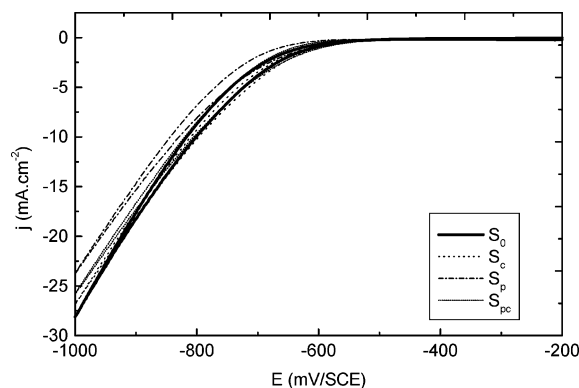


Fig. 6 Influence of additives on the voltammograms for H^+ reduction on Cu deposited on quartz/gold from: (S_0): pure H_2SO_4 1 M solution, (S_p): S_0 + PEG 0.5 g/l, (S_c): S_0 + Cl^- 50 ppm, (S_{pc}): S_0 + PEG 0.5 g/l + Cl^- 50 ppm

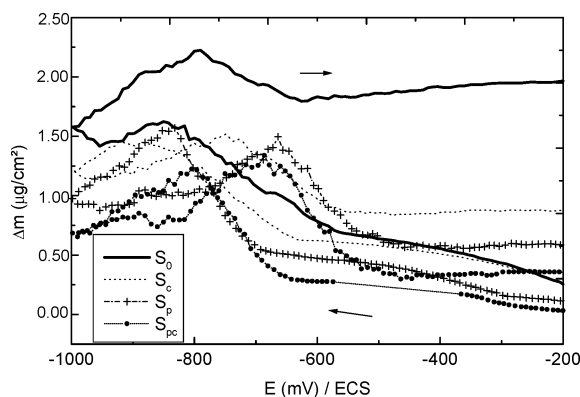


Fig. 7 Influence of additives on the voltmassograms for H^+ reduction on Cu deposited on quartz/gold from: (S_0): pure H_2SO_4 1 M solution (S_p): S_0 + PEG 0.5 g/l, (S_c): S_0 + Cl^- 50 ppm, (S_{pc}): S_0 + PEG 0.5 g/l + Cl^- 50 ppm

be due to hydrogen entrapped in the porous Cu deposit that makes the surface heavier. A hysteresis between the initial and the final surface mass, of about $2 \mu g \cdot cm^{-2}$, is performed, that is less important than the value obtained on gold (see Fig. 5). With additives, although the currents performed stay the same than from the pure solution, the gain of mass and the hysteresis are reduced. The more important decrease is obtained with PEG + Cl^- in solution. These results show that, if the H^+ reduction stays the same with and without additives, the amount of hydrogen entrapped in the Cu deposit is reduced. There is a beneficial effect of the additives.

The capacitance measurements have shown that PEG adsorption is potential dependent. We want to verify this result by using the EQCM technique. For that we performed the mass variation of the quartz/gold/Cu electrode in function of time, from the pure solution, for 3 cathodic polarizations lying between -150 and $-300 mV$. After 1200 s, 0.5 g/l of PEG is added to the solution rapidly shaken while continuing the experiment. The results are shown in Fig. 8. Without

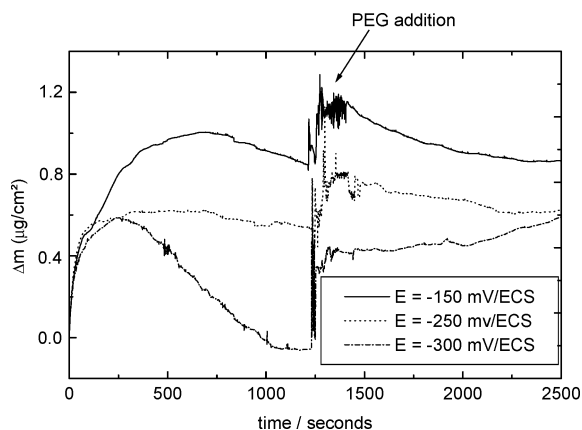


Fig. 8 Δm change in function of time, before and after a 0.5 g/l addition of PEG in the solution. Tested for 3 polarizations of the Quartz/gold/Cu surface

PEG in solution, whatever the polarization, there is a rapid mass increase due to either the copper surface oxidation, or a modification to the substrate—electrolyte interface under polarization. Then the stabilization of the mass is obtained, except for -300 mV. Here, we get a mass decrease for which we do not have an explanation. From the 3 curves, as soon as PEG is added to the solution, there is a jump of mass followed by a decrease and then a stabilization. It is obvious that the mass jumps increase with the potential, reaching respectively $0.4 \mu\text{g}/\text{cm}^2$ at -300 mV and $0.2 \mu\text{g}/\text{cm}^2$ at -150 mV. These EQCM results confirm the previous capacitance measurements. Moreover, in the literature some authors have already shown by other techniques that PEG adsorption is potential dependent [2, 5, 6, 17].

3.2. Cu^{2+} Containing electrolytes

3.2.1. Voltametry on Cu

It is interesting to see the additives influence on the electrode surface, without Cu^{2+} in solution. But copper solutions have also to be studied, because in that case the active sites on the surface could be reached either by Cu^{2+} cations or by the additives.

Figure 9 shows the voltamograms obtained from copper solutions on copper with and without additives. First, in an additive free bath (curve Cu_0), no current is observed until $E_r = -100$ mV, which corresponds to the reduction of Cu^{2+} . Below that value, there is an increase in cathodic current, due to the copper crystallization, followed by a current plateau, at about 32 mA cm^{-2} indicating a mass transfer control of the process. By reversing the sweep, a crossover is observed between the backward and the forward currents, characteristic of a nucleation mechanism [18, 19]. This shape of voltamogram was already obtained from sulfuric acid solutions, but

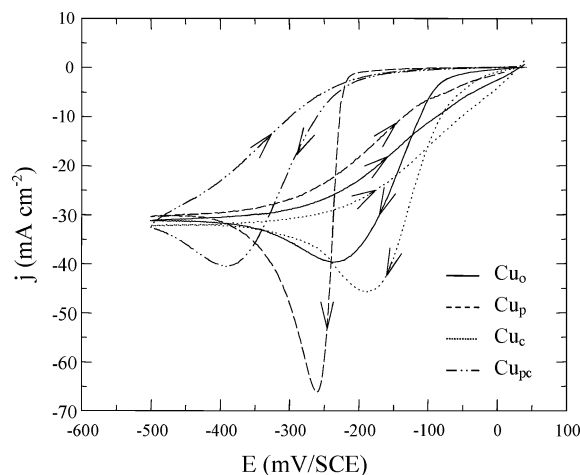


Fig. 9 Influence of additives on the cathodic part of the voltamograms obtained on copper from several solutions: (Cu_0): CuSO_4 0.1 M + 1 M H_2SO_4 ; (Cu_p) is Cu_0 + 0.5 g/l PEG; (Cu_c) is Cu_0 + 50 ppm Cl^- ; (Cu_{pc}) is Cu_0 + 0.5 g/l PEG + 50 ppm Cl^-

on vitreous carbon and not on copper, the substrate used for this study [20].

In solution Cu_p the shape of the voltamogram obtained is modified. A strong inhibiting effect can be noticed because the additive shifts the deposition potential to more negative values creating an over-voltage of 150 mV. The slope of reduction is higher than before corresponding to faster kinetics. The limiting current is the same with or without PEG: this removes the possibility of a complex formation in solution between PEG and the Cu^{2+} species because in this case the diffusion coefficient of Cu^{2+} in solution would have been modified, and consequently the limiting current [21]. Anyway, the complexation of 0.1 M of Cu^{2+} ions by a small PEG quantity seems unlikely. By reversing the scan, it appears that the backward currents obtained with and without the additive are very close. This result may suggest that the change at the copper surface due to the additive adsorption is reversible: once copper deposition begins, PEG loses its ability to inhibit the deposit. A similar conclusion was already proposed in reference [2].

Figure 9 also shows the influence of Cl^- (solution Cu_c) on the copper reduction mechanism. In that case, the Cu^{2+} reduction is shifted towards more positive potentials. An inverse effect is thus obtained with Cl^- with regards to that obtained with PEG, and already obtained from blank solution (see Fig. 1). On the other hand the shape of the curves Cu_c and Cu_0 with and without Cl^- , remains unchanged: they keep the same slope. It can be concluded that the presence of Cl^- leads to an acceleration of the copper reduction but without modification of the mechanism.

On Fig. 9, the curve Cu_{pc} is obtained using a bath containing both additives PEG + Cl^- . It seems that addition of Cl^- to the PEG solution leads to the same over-voltage than

with PEG alone (curve Cu_p) but with a reduction of the copper deposition rate. One finds the same reduction slope as for copper alone (curve Cu_0) and for copper deposition in presence of chloride (curve Cu_c). Besides this, the limiting current remains always the same with or without additive. This confirms that the reduction mechanism remains under mass-transfer control and that the effect of additives does not intervene through a complex formation of copper in solution. A significant difference with PEG alone is recorded on the backward scan of the curve Cu_{pc} : in that case the backward current is smaller than the forward current, without nucleation loop. This shows that the influence of the two additives continues during the growth of the copper deposit while, with only PEG in solution, there is a reduction of the PEG effect during thickening of the deposit. Therefore, it may be concluded that PEG and Cl^- act in a synergistic way, leading to a strong inhibition of the deposit with change of deposition mechanism.

3.2.2. Interfacial capacity measurements

The capacitance measurements are made under cathodic polarization using the copper solutions Cu_0 , Cu_p and Cu_{pc} , from the rest potential to a potential before the hydrogen evolution reaction (Fig. 10). From Cu_0 bath, i.e. without additive, the capacity value decreases slowly until -100 mV/SCE. For this value there is a steep increase in capacitance that rises from $20 \mu F cm^{-2}$ to about $55 \mu F cm^{-2}$. This potential corresponds to the beginning of the reduction of Cu^{2+} determined by the previous voltametry study (Fig. 9). The capacitance then stabilises, before increasing again for more cathodic potentials than -450 mV/SCE where the hydrogen evolution reaction begins.

With PEG alone in solution (Cu_p), the same trend as previously is observed on the curve. However, the capacitance

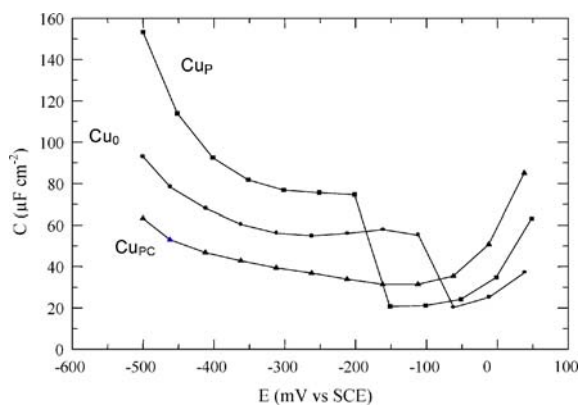


Fig. 10 Interfacial capacitance evolution as a function of the applied potential, from several copper containing solutions: (Cu_0): $CuSO_4$ 0.1 M + 1 M H_2SO_4 ; (Cu_p) is Cu_0 + 0.5 g/l PEG; (Cu_{pc}) is Cu_0 + 0.5 g/l PEG + 50 ppm Cl^-

jump that indicates the beginning of copper reduction, occurs for a more cathodic potential than before (-200 mV). This result outlines the blocking effect of PEG on copper reduction well known in the literature [2, 4, 5].

With both PEG + Cl^- additives (solution Cu_{pc}), the trend of the curve is really different: at the beginning there is a more rapid decrease in the capacity value from 80 down to $40 \mu F cm^{-2}$. Then, after -150 mV/SCE, there is a slow increase in capacity without abrupt variation. The capacitance values measured under these conditions are always lower than those obtained from the other solutions. The absence of an abrupt variation in interfacial capacity values let us predict a smoother deposit than those obtained from the other baths.

Finally the order of magnitude of capacities measured in the various PEG containing baths (tens of $\mu F cm^{-2}$) indicates another kind of adsorption than a film type. Indeed, in the case of painting [22, 23] or other organic coatings, the capacities are lower by two to three orders of magnitude.

3.2.3. EQCM experiments on gold

In Fig. 11, we have put together the voltamogram and the voltmassogram obtained without additive that means from Cu_0 solution. In the first region, before the formation of the copper deposit, neither current nor mass variations are observed, until the potential reaches the copper reduction potential of -100 mV. Then, a continuous mass increase is observed as the potential is scanned in cathodic direction. This trend is conserved when the scan is reversed, as long as the potential stays in the cathodic region with regards to the copper equilibrium potential. When the potential is more anodic than the copper equilibrium potential, the current becomes anodic, and the mass variation is reversed: the copper dissolution is obvious. Finally, when all the copper deposit in the cathodic part is dissolved, the current and the mass decrease to zero. The voltamogram and the voltmassogram are in good agreement.

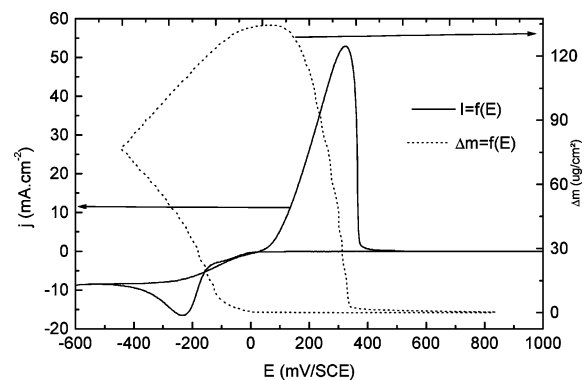


Fig. 11 Comparison of the voltamogram and the voltmassogram obtained from Cu_0 solution: $CuSO_4$ 0.1 M + 1 M H_2SO_4

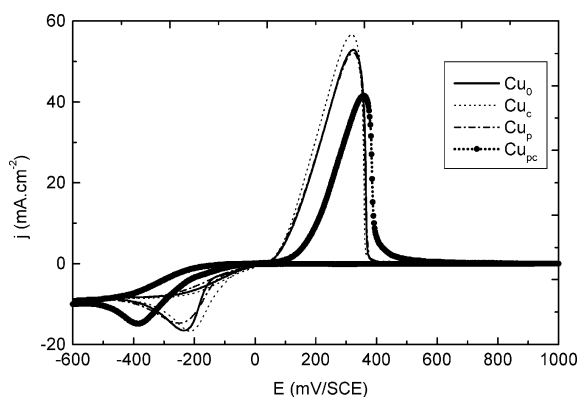


Fig. 12 Influence of additives on the voltamograms for Cu^{2+} deposition on quartz/gold from: (Cu_0): CuSO_4 0.1 M + 1 M H_2SO_4 ; (Cu_p) is Cu_0 + 0.5 g/l PEG; (Cu_{cl}) is Cu_0 + 50 ppm Cl^- ; (Cu_{pc}) is Cu_0 + 0.5 g/l PEG + 50 ppm Cl^-

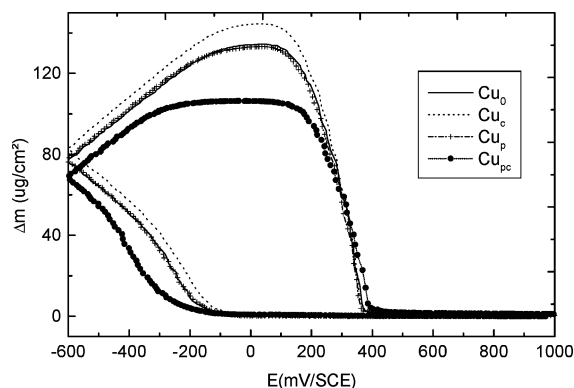


Fig. 13 Influence of additives on the voltmassograms for Cu^{2+} deposition on quartz/gold from: (Cu_0): CuSO_4 0.1 M + 1 M H_2SO_4 ; (Cu_p) is Cu_0 + 0.5 g/l PEG; (Cu_{cl}) is Cu_0 + 50 ppm Cl^- ; (Cu_{pc}) is Cu_0 + 0.5 g/l PEG + 50 ppm Cl^-

Figure 12 presents the voltamograms obtained from the four copper electrolytes, on quartz/gold substrates. In this case, the shape of the voltamograms is the same as those obtained on the copper substrate (Fig. 9), except for PEG in solution that presents the same curve as without additives.

The effect of the additives on the voltmassograms obtained on quartz/gold, from copper electrolytes, is shown in Fig. 13. PEG alone in solution has no effect, neither on voltamograms nor on voltmassograms. The curves with PEG follow those obtained from the additive free bath. With chloride ions, there is an accelerating effect, shown by the voltamogram: copper reduction is obtained at a more anodic potential leading to a longer deposition time and consequently to a thicker deposit. This increases the anodic current for copper dissolution. On the voltmassogram, the gain of mass appears more significant. With the two additives in solution, the retarding effect is obvious, the over-potential to reduce Cu^{2+} being more important and thus the anodic peak. On the voltmassograms this trend is observable because the mass increase appears

for more cathodic potentials, leading to a total mass gain less important than those obtained from the other electrolytes.

In Table II, the maximum gain of mass obtained from the 4 baths is shown, in agreement with the comments above.

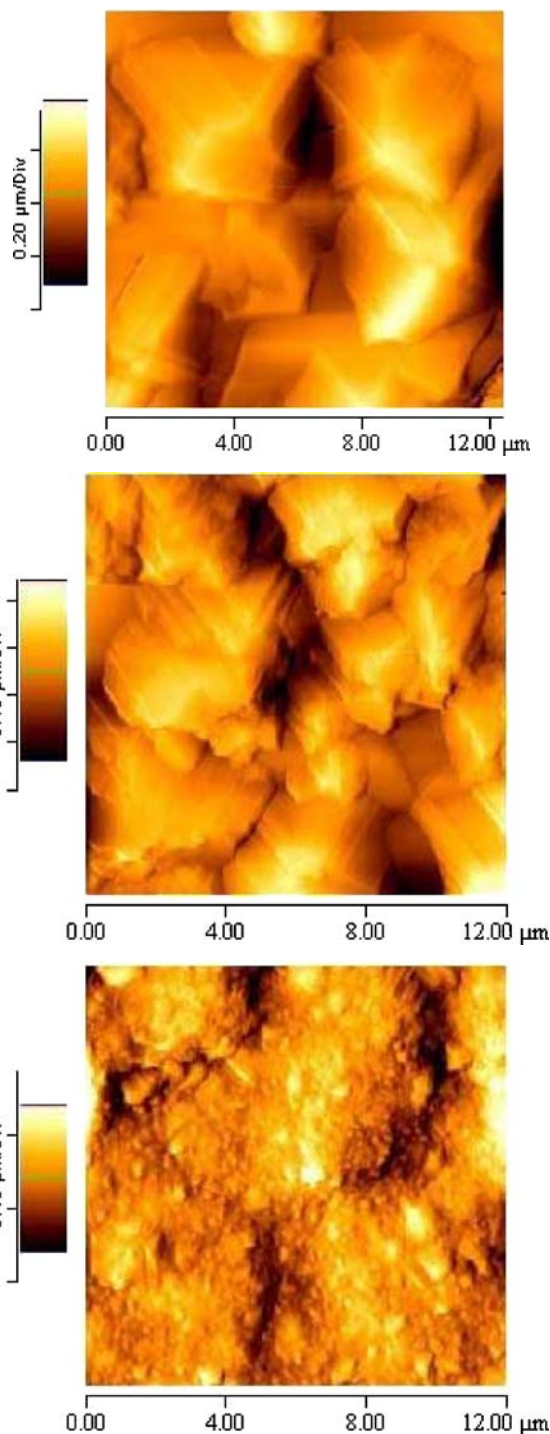


Fig. 14 AFM 2D images of 3 samples ($12 \times 12 \mu\text{m}$) obtained from 3 different copper electrolytes on Cu substrate, at 10 mA cm^{-2} : (a) D_0 is obtained from Cu_0 : CuSO_4 0.1 M + 1 M H_2SO_4 . (b) D_p is obtained from Cu_p : Cu_0 + 0.5 g/l PEG. (c) D_{pc} is obtained from Cu_{pc} : Cu_0 + 0.5 g/l PEG + 50 ppm Cl^-

Table II Maximum gain of mass deduced from EQCM results from copper solution

Solution	Cu ₀	Cu _p	Cu _C	Cu _{PC}
Δm ($\mu\text{g}/\text{cm}^2$)	136.1	133.2	146.1	106.2

(Cu₀): CuSO₄ 0.1 M + 1 M H₂SO₄; (Cu_p) is Cu₀ + 0.5 g/l PEG; (Cu_C) is Cu₀ + 50 ppm Cl⁻; (Cu_{PC}) is Cu₀ + 0.5 g/l PEG + 50 ppm Cl⁻.

3.2.4. Bulk deposits characterization

To support the electrochemical and EQCM studies, bulk copper coatings are obtained on a 2 cm² copper substrate under galvanostatic conditions ($j = -10 \text{ mA cm}^{-2}$), with a theoretical thickness of 10 μm . Depending on the Cu²⁺ bath used, Cu₀ without any additive, Cu_p with PEG only or Cu_{PC} with PEG and Cl⁻, these deposits are respectively identified by D₀, D_p and D_{PC}.

Morphological examination of the deposits is achieved by optical microscopy and AFM. In the case of the additive-free solution, the sample D₀ appears as a dull and a powdery coating, with poor aspect and coarse grains. AFM observations are difficult because of the high roughness of this deposit; an AFM image of this deposit (Fig. 14(a)) shows some large faceted crystallites with a length of about 5 μm . The R_{RMS} is quite large (about 120 nm).

The presence of PEG in the bath (Fig. 14(b)), reduces the crystallite size (varying from 1 to 5 μm) and divides the R_{RMS} by a factor 2 (60 nm). The crystallites keep a faceted aspect

In the case of D_{PC} (Fig. 14(c)) the micro-structure of the coating shows small grains (300 nm). In comparison to the results obtained from Cu_p solution, the mean roughness is significantly reduced to 34 nm.

4. Conclusion

A combination between electrochemical and non electrochemical investigations gives insight into the mechanism of action of PEG and Cl⁻ + PEG during copper electrodeposition. The first results show that EQCM is a valuable instrument for interpretation of electrodeposition mechanisms. The experiments made on proton reduction show an adsorption of PEG molecules on the copper surface. This adsorption is weak at open circuit potential and increases under cathodic polarization. Even if the additive effects are not always seen on the voltamograms, their beneficial action like the decrease of the amount of adsorbed or entrapped hydrogen on the surface is seen on EQCM curves. The presence of PEG in the copper bath leads to a shift of copper deposition potential to more negative values. The copper reduction process is then hindered. However, PEG alone is not able to produce a bright coating, due to the release effect during copper growth. The

addition of small amounts of Cl⁻ to the copper and PEG electrolyte has a substantial effect. The nucleation mechanism of Cu²⁺ on the copper substrate is no more involved, probably due to a bridging effect of Cl⁻. In that case the influence remains with time, showing a synergetic effect between the two additives, resulting in a quite good compact copper deposit, with disappearing of large grains obtained from additive-free baths and with PEG alone in solution.

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References

1. M. Schlesinger and M. Paunovic, *Modern Electroplating*, 4th ed., Chap. 2, (Jonh Wiley & Sons, Inc, New York, 2000).
2. J. Healy, D. Pletcher, and M. Goodenough, *J. Electroanal. Chem.*, **338**, 155 (1992).
3. K. Doblhofer, S. Wasles, D.M. Soares, K.G. Weil, and G. Ertl, *J. Electrochem. Soc.*, **150**, C657 (2003).
4. J. Kelly and C. West, *J. Electrochem. Soc.*, **145**, 3472 (1998).
5. L. Bonou, M. Eyraud, R. Denoyel, and Y. Massiani, *Electrochim. Acta*, **47**, 4139 (2002).
6. E. Bahena, P.F. Mendez, Y. Meas, R. Ortega, L. Salgado, and G. Trejo, *Electrochim. Acta*, **49**, 989 (2004).
7. G. Sauerbrey, *Z. Phys.*, **178**, 457 (1964).
8. T.C. Franklin, *Plat. Surf. Finish.*, **4**, 62 (1994).
9. T.C. Franklin, *Surf. and Coat. Tech.*, **30**, 415 (1987).
10. W. Paik, M.A. Genshaw, and J.M. O’Bockris, *J. Phys. Rew.*, **74**, 4266 (1970).
11. L. Vracar and D.M. Drazic, *J. Electroanal. Chem.*, **339**, 269 (1992).
12. T. Murakawa, S. Nagura, and N. Hackerman, *Corros. Sci.*, **7**, 79 (1967).
13. L. Mirkova and St Rashkov, *J. Appl. Electrochem.*, **24**, 420 (1994).
14. D.M. Soares, S. Wasle, K.G. Weil, and K. Doblhofer, *J. Electroanal. Chem.*, **532**, 357 (2002).
15. K. Doblhofer, S. Wasle, D.M. Soares, K.G. Weil, G. Weinberg, and G. Ertl, *Z. Phys. Chem.*, **217**, 490 (2003).
16. M. Eyraud, M. Andrei, F. Soto, and J. Crousier, *Organic and Inorganic Coatings for Corrosion Prevention* (Published for The EFC by The Institute of Materials, 1997), p. 160.
17. J. Healy, D. Pletcher, and M. Goodenough, *J. Electroanal. Chem.*, **338**, 167 (1992).
18. G. Gunawardena, G. Hills, and I. Montenegro, *J. Electroanal. Chem.*, **184**, 357 (1985).
19. D. Grujicic and B. Pesic, *Electrochim. Acta*, **47**, 2901 (2002).
20. I. Bimagrha and J. Crousier, *Materials Chem. and Phys.*, **21**, 109 (1989).
21. A.J. Bard and L.R. Faulkner, *Electrochimie, principes méthodes et applications*, edited by Masson, Paris, New York, Barcelone, Milan, Mexico, Sao Paulo, 1983).
22. K. Jütner, *Electrochim. Acta*, **35**, 1505 (1990).
23. L. Bonou, Y. Massiani, and J. Crousier, *British Corrosion J.*, **29**, 201 (1994).