

Influence of some additives on Cu layer formation in underpotential and overpotential regions in acidic CuSO_4 solutions

11. Investigation of the early stages of Cu electrocrystallisation onto sulphur-modified Pt(poly) electrode

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Copper electrodeposition from 0.5 M H_2SO_4 + 0.1 M CuSO_4 solution has been studied on clean Pt(poly) and S-modified Pt(poly) substrates by a potential step technique. Analysis of the chronoamperometric results has indicated that the Cu electrodeposition onto these substrates begins through the instantaneous 3D nucleation and diffusion-controlled growth mechanism proposed by Scharifker and Hills. The nuclei number density (N) has been shown to decrease and, the average radius of nuclei (r_{av}), on the contrary, to increase slightly when the clean Pt(poly) electrode was replaced by an S-modified Pt(poly) electrode. The possible reasons for these experimental findings have been discussed.

Key words: Cu OPD, early stages of deposition, sulphur-modified Pt, chronoamperometry

INTRODUCTION

Of particular importance in the metal plating practice is the electrodeposition of Cu on different substrates, especially from acidic Cu(II) solutions, not only because of its industrial usefulness for protection of metals in corrosive environments and the surface finishing processes, but also of great suitability for the examination of general features of metal ion discharge reactions and metal new phase formation. In particular, the early stages in deposition of Cu onto Pt and Au substrates considered commonly as one of the model systems are still of specific research interest.

A new interest in the application of Cu deposits and, consequently, in a more detailed re-examination of Cu deposition and Cu layer formation mechanisms arose due to the steady extension of such high-technology fields as nanotechnology, production of multilevel Cu interconnections for logic ultralarge-scale integrated (ULSI) circuits, on-chip metallisation shift from Al to Cu, deposition of ultrathin and thin Cu layers with desired properties, *e.g.*, as a barrier layer onto semiconducting materials, etc.

Various inorganic and organic compounds have been proposed as additives for bulk Cu deposition and extensively studied to the present day to obtain relatively thick, bright and ductile coatings mainly for the corrosion prevention of steel and zinc alloy products and for fabricating different kinds of printed circuit boards [1–12]. These compounds even in small amounts have been recognized to exert a crucial influence on the properties of Cu coatings and on the performance of galvanic baths.

An important aspect of the electroplating practice (in deposition of not only Cu but other metals as well) involves examination of the early stages of metal electrodeposition onto various substrates in the absence of additives (reviews have been recently published by Budevski, Staikov and Lorenz [14] and Gamburg [15]) or in their presence (see the literature relating to Cu deposition [1, 4, 6, 11, 16–21]). It has been generally recognized that the final quality of metal coatings depends to a large extent on many factors including solution composition, the presence of additives, the structure and pretreatment of the substrate, the mechanism and kinetics of metal electrocrystallisation [14, 15]. Although the addition agents in Cu (and other metals) electrop-

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lating have been used for decades, there are still many unknown aspects concerning their mode of action, and much of today's knowledge in this area is not sufficiently deep and systematic [1, 14].

Traditionally, the additives are added to an electrolyte. Of specific interest is the examination of metal deposition onto modified electrodes in an additive-free solution. Such experiments have been shown to be particularly helpful in studying electrocatalysis in various redox reactions (see a review by Somorjai [22]) and studies on the dependence of the formation of a new phase on the state of a foreign substrate [14, 15].

In this context, chemisorption of S and of S-containing compounds continues to be of considerable interest in modifying the surface properties of electrodes suitable for a variety of functional applications among which, in particular, is the investigation of charge transfer (*e.g.*, the reaction $\text{Fe}^{3+} + e = \text{Fe}^{2+}$ at Pt covered with chemisorbed S [23], electrochemical oxidation and evolution of hydrogen at sulphurized Pt [24–26] and Ir [27] electrodes; Cu deposition on thiol-modified Au electrodes [28–30]). However, to our knowledge, there have been no systematic studies designed to the mechanism of early stages of Cu deposition onto a foreign substrate independently precovered with sulphur species.

In this work, the effect of sulphur species adsorbed onto polycrystalline Pt (Pt(poly)) upon the early stages of electrodeposition of Cu from acidic CuSO_4 solution was studied using the current transient technique. The results were compared with those for a clean Pt(poly) electrode.

EXPERIMENTAL

The working solution consisted of 0.5 M H_2SO_4 and 0.1 M CuSO_4 and was prepared from doubly distilled water, copper sulphate salt $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Fluka) preheated for 4 h at 400 °C and highest purity sulphuric acid H_2SO_4 (Russia). Prior to each experiment, the working solution was deaerated with argon gas for 0.5 h.

All electrochemical experiments were performed at 20 ± 0.1 °C in a conventional three-electrode cell with a Pt plate of *ca.* 4 cm² in area as the counter electrode and a Ag/AgCl/KCl(sat.) electrode as the reference electrode. The working electrode was a vertical disc made from a Pt(poly) foil (99.99% purity). The geometric area of the working electrode was 1 cm². In the text, all potentials are reported with respect to the standard hydrogen electrode (SHE). The Nernst potential for a couple Cu^{2+}/Cu was estimated measuring an open-circuit potential (OCP) of a bulk Cu deposit in an unstirred 0.5 M H_2SO_4 + 0.1 M CuSO_4 solution at 20 °C and was found to be +0.292 V.

The pretreatment of the working Pt(poly) electrode prior to the electrochemical measurements and the modification procedure was described elsewhere [31]. The true surface area was evaluated from the hydrogen adsorption current-potential profile recorded in 0.5 M H_2SO_4 solution at a sweep rate (ν) of 50 mV s⁻¹, following the method proposed by Biegler et al. [32]. The roughness factor (*f*) was obtained to be 1.9 ± 0.05 .

The quality of the surface of Pt(poly) electrode prepared for the subsequent measurements was checked by a comparison of the cyclic voltammogram (CV) recorded in a supporting 0.5 M H_2SO_4 solution at 50 mV s⁻¹ with that presented in the literature [33, 34] and claimed to be characteristic of a clean Pt surface.

The modification of the working Pt(poly) electrode by adsorbed sulphur species was achieved by immersion in 0.5 M H_2SO_4 + *x* mM Na_2SO_3 solution (*x* = 0.5, 3, 5 or 10) for 2 min at an adsorption potential $E_{\text{ads}}^0 = +0.65$ V followed by a single potential sweep from E_{ads}^0 to different values of *E* in the region +0.45 to 0.0 V (mainly to *E* = +0.25 V) at $\nu = 50$ mV s⁻¹, in accordance with the procedure described in [35], then rinsing and a transfer to another cell with the working solution. The transfer was carried out under the protection of a droplet of water (the loss of ad-species was not evaluated). After the modification, the degree of coverage by sulphur species was determined in separate experiments from a decrease in the quantity of adsorbed hydrogen, following the recommendation proposed in [36]. In the potential region of hydrogen adsorption onto Pt(poly), a decrease of the two main peaks for adsorption hydrogen occurred due to an inhibiting action of deposited sulphur species [36, 37]. The quantity of adsorbed hydrogen, displaced by the adsorption of sulphur, was determined as the difference $\Delta Q_{\text{H}} = Q_{\text{H}}^0 - Q_{\text{H}}^{\text{S}}$, where Q_{H}^0 and Q_{H}^{S} are the charge quantities associated with hydrogen adsorption in the absence and in the presence of adsorbed sulphur, respectively. The degree of coverage by sulphur (Θ_{S}) was calculated: $\Theta_{\text{S}} = \Delta Q_{\text{H}} / Q_{\text{H}}^0$. The calculated values of Θ_{S} can be illustrated here as follows: 0.54, 0.60, 0.66, 0.89 and *ca.* 1.0 when a single *E* sweep was performed from $E_{\text{ads}}^0 = +0.65$ V to *E* = +0.45, +0.35, +0.25, +0.15 and +0.05 V, respectively, in the 0.5 M H_2SO_4 solution containing 3 mM Na_2SO_3 .

The chronoamperometric measurements were carried out using a PI 50–1 potentiostat (Belarus) interfaced through a home-made analogue to a digital converter with a PC (Siemens) and a PR-8 programmer (Belarus). In all cases, the working electrode first was kept in a solution at a starting potential $E_{\text{start}}^0 = +0.35$ V for 2 min. The experimental data acquisition was in a numerical form with time resolution of 50 ms per point.

RESULTS AND DISCUSSION

When the nucleation/growth process of Cu was investigated chronoamperometrically in 0.5 M H₂SO₄ + 0.1 M CuSO₄ solution using a clean Pt electrode and a S-modified Pt electrode, both these electrodes were initially held at $E_{\text{start}} = +0.35$ V, where a Cu adlayer was deposited underpotentially [37–39], and then stepped to a sufficiently negative deposition potential (E_{dep}) to initiate Cu nucleation. The amount of Cu deposited underpotentially (Cu_{UPD}) at +0.35 V has been shown to range up to about one monolayer [21]. When an S-modified Pt(poly) electrode was used, the potentiostatic current–time curves suitable for a subsequent analysis were recorded in the range of more negative E_{dep} .

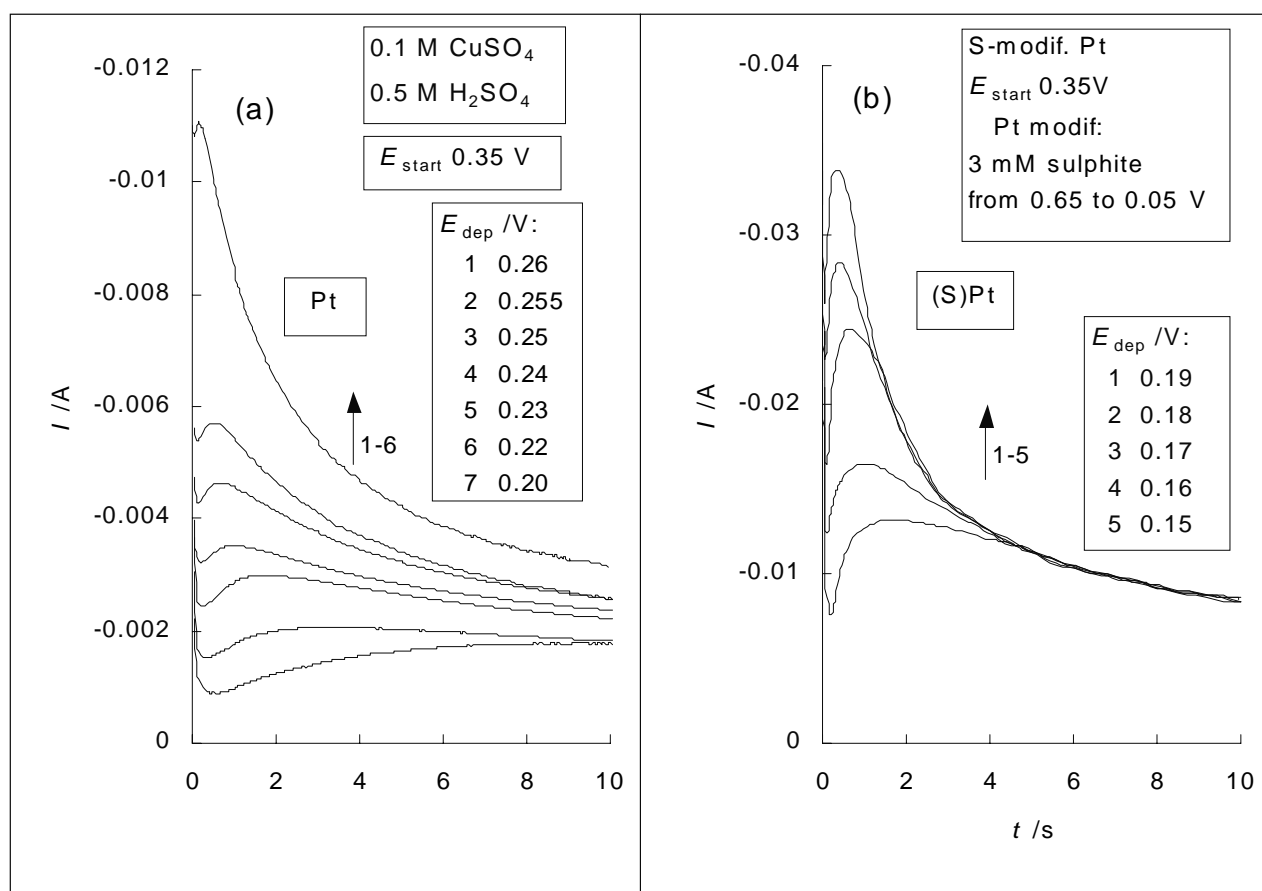


Fig. 1. Potentiostatic current transients for Cu deposition onto a clean Pt(poly) substrate (a) or an S-modified Pt(poly) substrate (b) at different values of deposition potential E_{dep} in 0.5 M H₂SO₄ + 0.1 M CuSO₄ solution. The conditions of modification are presented in (b)

A series of typical potentiostatic current transients are shown in Fig. 1. All of them are typical of a diffusion-limited metal nucleation/growth process onto a foreign substrate [40–44].

Recently, Scharifker with co-workers [44] has critically examined several theoretical descriptions of potentiostatic current transients for the diffusion-controlled three-dimensional (3D) metal electrocrystallisation and compared with experimental and

computer-simulated data. In all the cases examined, the overall current has been obtained from a material flux to free, noninteracting growing centres considering the overlap of circular diffusion zones expanding around them. It has been also shown that essential differences among the examined approaches occurred from the calculations of a growth rate of these diffusion zones, yielding significantly different values of the rate of the nucleation process (A) and the number of the density of sites for nucleation (N_0). The most recent review of the models of multiple metal nucleation with diffusion controlled growth onto a foreign substrate given by Hyde and Compton [45] has shown that the models developed by Scharifker and Hills (SH) [41] and by Scharifker and Mostany (SM) [42] are still most popular

in analyzing the potentiostatic current transients, which are related to the early stages of electrocrystallisation. With this in mind, the approach by Scharifker et al. was also used here.

For the 3D nucleation with nuclei growth controlled by localized hemispherical diffusion, it has been generally accepted [40–44] that this process is well described by two limiting cases of the 3D nucleation, instantaneous or progressive. Instantaneous

nucleation represents a fast nucleation on a relatively small number of active sites, with all nucleation sites activated instantly at $t = 0$, whereas progressive nucleation describes a slow nucleation on a virtually infinite number of active sites, which gradually increases with time.

According to Thirsk and Harrison [46], during the early stages of metal deposition onto a foreign substrate, a relationship between the current and the deposition time allows to gain a certain information about the mode of nucleation. A linear relationship between I and $t^{0.5}$ corresponds to instantaneous nucleation, followed by 3D growth under diffusion control, and the linear relationship between I and $t^{1.5}$ corresponds to the progressive nucleation and a 3D growth of the nuclei limited by a slow diffusion process. As shown in Figs. 2 and 3, an approximate linear relationship between I and $t^{0.5}$ was found for the initial ascen-

ding portion of each current transients for both types of the working electrodes. In principle, experimental times needed to be corrected for a small delay time (t_0) prior to a measurable faradaic current [46]. However, in all the data sets examined, the magnitude of t_0 was not detected. The minor deviation from a straight line might be caused by such factors as *e.g.*, nuclei overlap, irregular growth on a certain area of the electrode surface or birth and death of nuclei at the early nucleation stage. So, the analysis of the I vs. t^n relationships (Figs. 2 and 3) suggests that the instantaneous 3D nucleation of Cu seems to dominate on the clean Pt(poly) electrode and also on the S-precovered Pt(poly) electrode.

In order to distinguish these two cases, the dimensionless experimental plots $(I/I_{\max})^2$ vs. t/t_{\max} are commonly used and compared with the theoretical plots, which for the limiting cases of instantaneous

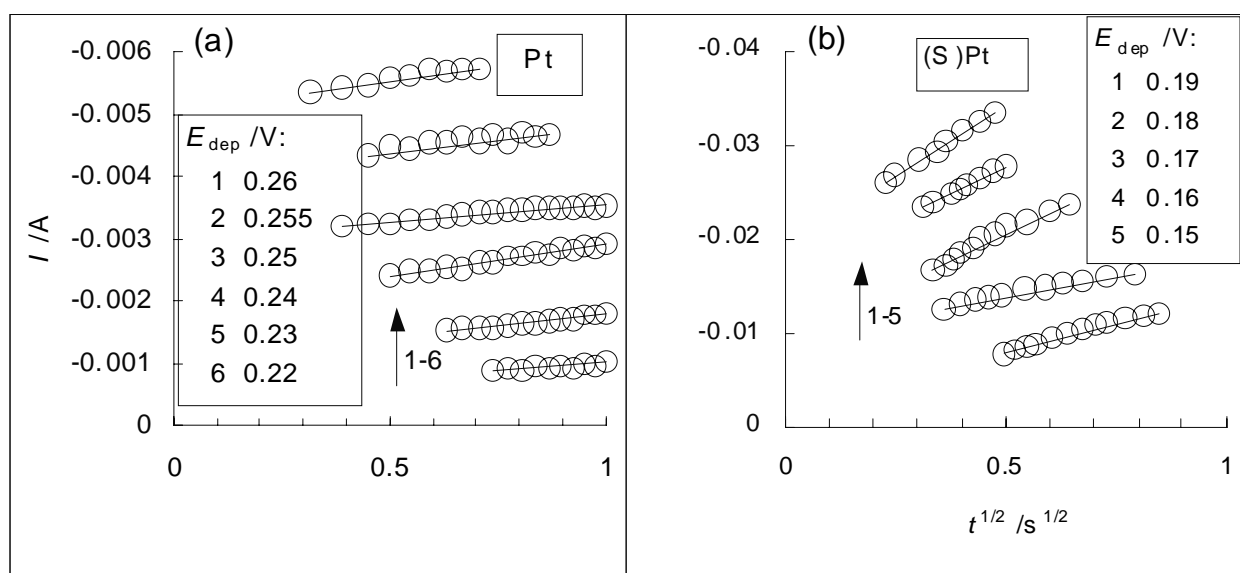


Fig. 2. Current (I) vs. $t^{0.5}$ plots for chronoamperometric data (from Fig. 1)

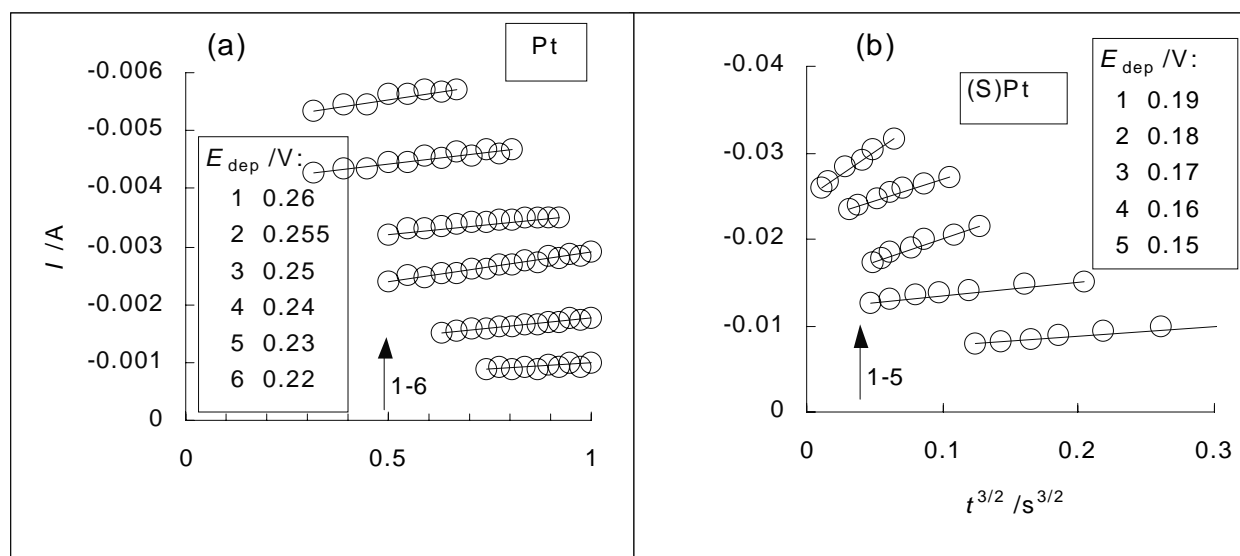


Fig. 3. Current (I) vs. $t^{1.5}$ plots for chronoamperometric data (from Fig. 1)

(Eq. 1) and progressive (Eq. 2) nucleation are represented, respectively, [40, 41] by

$$(I/I_{\max})^2 = 1.9542(t/t_{\max})^{-1}\{1-\exp[-1.2564(t/t_{\max})]\}^2, \quad (1)$$

$$(I/I_{\max})^2 = 1.2254(t/t_{\max})^{-1}\{1-\exp[-2.3367(t/t_{\max})^2]\}^2. \quad (2)$$

These expressions correlate the normalized current (I/I_{\max}) to the normalized time (t/t_{\max}) for each type of nucleation, and a comparison of the dimensionless experimental current-time transients with this theory provides a definitive clue for differentiating between the two nucleation models ([40, 41] and a review [45]).

Once it is established, the instantaneous 3D nucleation with diffusion controlled model is applicable to Cu electrodeposition under our experimental conditions, the number of nuclei (N_i) can be calculated from the values of t_{\max} [41]:

$$N_i = 1.2564/t_{\max} \pi k_e D, \quad (3)$$

where $k_e = (8\pi cM/\rho)^{0.5}$, M and ρ are the molar weight and density of the depositing metal (the parameter k_e for Cu is equal to 0.024). The calculated values of N_i depending on the E_{dep} and the type of the working electrode are shown on Fig. 5. One

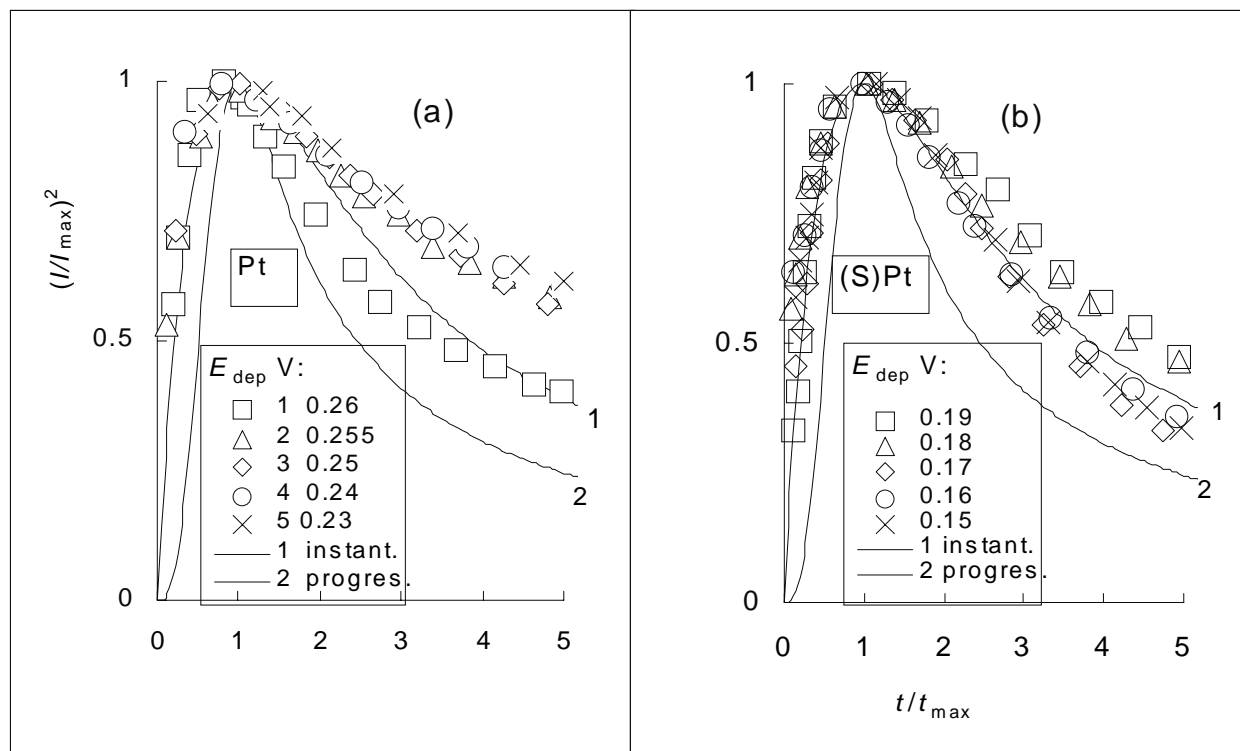


Fig. 4. Comparison of the experimental normalized current-time dependences for Cu nucleation and growth onto Pt(poly) and S-modified Pt(poly) in 0.5 M H_2SO_4 + 0.1 M CuSO_4 solution to the calculated normalized current-time dependences for the 3D nucleation models developed by Scharifker and Hill

The dimensionless experimental and theoretical plots (I/I_{\max})² vs. t/t_{\max} are shown in Fig. 4. All these plots clearly suggest that the deposition of Cu onto both types of the working electrodes agrees rather well with the limiting model of instantaneous nucleation within the given range of Cu overpotentials. In this regard, the S-modified electrode behaves quite similarly as the Se-modified Pt(poly) electrode [47]. The deviation from the predicted responses observed after the maximum, when the experimental points are placed above the theoretical line for instantaneous nucleation and the process is expected to be controlled purely by linear diffusion, may be associated with a different transition of the hemispherical diffusion to the linear one at different areas of the Pt(poly) electrode surface [47].

can see that N_i being of the order of 10^5 to 10^6 cm^{-2} implies a rather low coverage for the Cu nuclei formation, because the calculated values of N_i correspond to less than one or *ca.* one in 10^9 surface atoms from a density of atomic sites (about 10^{15} cm^{-2}) for Pt(poly). Similar results were obtained for the other values of Θ_s . So, it can be concluded that only a small fraction of the total number of atomic sites of the Pt(poly) surface is available for the initiation of Cu nucleation and subsequent growth. This is in good agreement with the observations of other authors [48].

Assuming that the Cu particles deposited are of a spherical shape, an average nuclei radius (r_{av}) can be evaluated from the following relationship [49]:

$$r_{\text{av}} = (3QV_m / 4\pi zFN)^{1/3}, \quad (4)$$

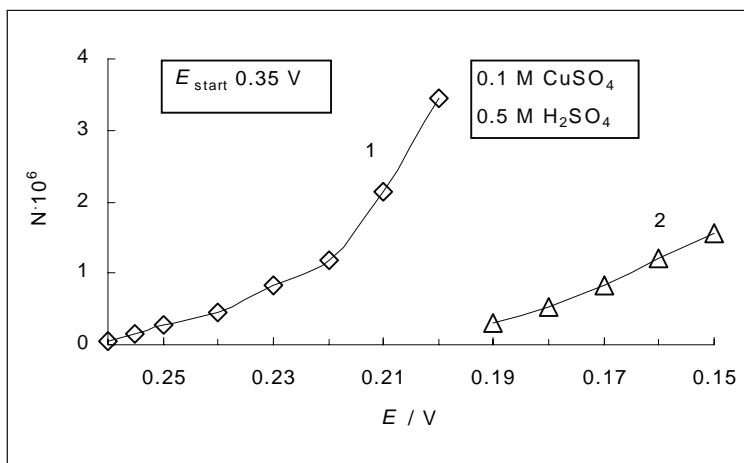


Fig. 5. Variation of the nuclei number density (N) with E_{dep} for the clean Pt(poly) electrode (1) and the S-modified Pt(poly) electrode (2)

where Q is a charge per unit area consumed during metal electrodeposition and v_m is the molar volume of the depositing metal (for Cu $v_m = 7.1 \text{ cm}^3 \text{ mol}^{-1}$). Q was evaluated here by integration of a corresponding chronoamperogram over a time interval up to $t = t_{\text{max}}$ assuming that the contribution of parasitic processes is negligible under the given experimental conditions.

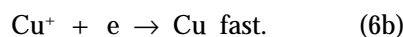
Considering the instantaneous 3D nucleation process and the Scharifker and Hills model [41], it is possible to recalculate the diffusion coefficient (D) for Cu^{2+} ion from the product $I_{\text{max}}^2 \cdot t_{\text{max}}$:

$$I_{\text{max}}^2 \cdot t_{\text{max}} = 0.1629(zFc)^2 D. \quad (5)$$

The calculated values of D for a Cu^{2+} ion, N_t and r_{av} are listed in Table. N_t increases with the negative shift of E_{dep} (Fig. 5 and Table) as expected. The data obtained also clearly show that N_t decre-

ases with going from the clean Pt(poly) electrode to the S-modified Pt(poly) electrode. A similar picture has been observed for a Se-modified Pt(poly) electrode in $0.5 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M CuSO}_4$ [47] or for a bare Pt(poly) electrode in $0.5 \text{ M H}_2\text{SO}_4 + 0.01 \text{ M CuSO}_4$ solution containing H_2SeO_3 in amounts of $1 \cdot 10^{-3}$ to $5 \cdot 10^{-2} \text{ mM}$ [21].

From the chronoamperometric data presented above it is not sufficiently clear to what extent the parameters N_t and r_{av} correlate with the value of Θ_s estimated from the change of the amount of H onto Pt(poly) in a range of underpotentials. Nevertheless, this must be firstly considered taking into account the blocking effect of adsorbed sulphur species, especially in relation to the more active Pt sites. On the other hand, another explanation relating the decrease in N_t and the slight increase in r_{av} on the S-modified Pt(poly) electrode may be as follows. In acidic sulphate solutions, electrochemical deposition of Cu takes place via a two-step mechanism [50]:

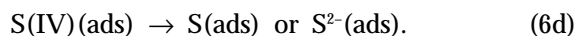
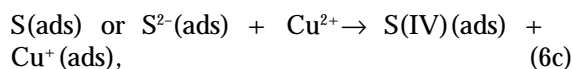


When the current is passed, cupric ions first reduce to cuprous ions. Using an S-modified Pt electrode, cuprous ions can be formed not only through reaction (6a) but by the so-called catalytic ox/red cycle (CORC) mechanism [51] as well. This mechanism involves a fast partial reduction of Cu^{2+} to an intermediate Cu^+ through a chemical route:

Table. Analysis of Cu nucleation process on clean Pt(poly) and S-modified Pt(poly) electrodes (modification in $0.5 \text{ M H}_2\text{SO}_4 + 3 \text{ mM Na}_2\text{SO}_3$ solution, a potential scan from $+0.65$ to 0.05 V) in $0.5 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M CuSO}_4$ solution from chronoamperometric data according to the Scharifker and Hills model [41]

$E_{\text{start}} = +0.35 \text{ V}$

Electrode	$E_{\text{dep}}, \text{ V}$	$t_{\text{max}}, \text{ s}$	$I_{\text{max}}, \text{ A}$	$10^{-6} \cdot N_t, \text{ cm}^{-2}$	$r_{\text{av}}, \mu\text{m}$	$10^6 D, \text{ cm}^2 \text{ s}^{-1}$
Clean Pt(poly)	+ 0.26	12.4	0.00172	0.04	0.20	2.91
	+ 0.255	3.5	0.00209	0.15	0.21	
	+ 0.25	1.85	0.00302	0.29	0.24	
	+ 0.24	1.15	0.00352	0.46	0.26	
	+ 0.23	0.65	0.00468	0.82	0.28	
	+ 0.22	0.45	0.00571	1.18	0.30	
	+ 0.21	0.25	0.00854	2.13	0.34	
	+ 0.20	0.15	0.01008	3.45	0.36	
	+ 0.19	0.12	0.01245	4.27	0.39	
	+ 0.18	0.1	0.0129	5.33	0.40	
S-modified Pt(poly)	+ 0.19	1.72	0.01311	0.31	0.39	
	+ 0.18	1.01	0.01648	0.53	0.43	
	+ 0.17	0.65	0.0244	0.83	0.49	
	+ 0.16	0.44	0.0284	1.21	0.51	
	+ 0.15	0.34	0.03384	1.57	0.54	



Then, if the concentration of Cu^+ ions increases at the interface of the working electrode, N_i is expected to be smaller and, in contrast, r_{av} is larger. The sulphur species adsorbed at Pt(poly) clearly play a similar role as the selenium species whose effect on the Cu electrodeposition has been discussed earlier [20, 21, 47].

CONCLUDING REMARKS

In this study, the early stages of Cu electrodeposition onto clean Pt(poly) and S-modified Pt(poly) were investigated in 0.5 M H_2SO_4 + 0.1 M CuSO_4 solution by a chronoamperometry technique. The analysis of chronoamperometric data indicated that the Cu electrodeposition onto clean or S-modified Pt(poly) electrodes precovered with underpotentially deposited Cu adlayer in an amount not exceeding one monolayer agrees rather well with the limiting model of instantaneous 3D nucleation and diffusion-controlled growth proposed by Scharifker and Hills. The values of the diffusion coefficient (D) for Cu^{2+} ion, the number of nuclei (N) being of the order of 10^5 to 10^6 cm^{-2} , and the average radius (r_{av}) of Cu nuclei were estimated. It was obtained that N_i decreased and r_{av} slightly increased with a change of the clean Pt(poly) electrode to the S-modified one. The possible explanations for these findings are presented.

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KAI KURIŲ PRIEDŲ ĄTAKA CU SLUOKSNIŲ FORMAVIMUISI POTENCIALŲ ZONOSE, TEIGIAMESNĖSE IR NEIGIAMESNĖSE UÞ PUSIAUSVYRINĖ SISTEMOS Cu^{2+}/Cu^0 POTENCIALO REIKĖMĖ, RŪGĖIUOSE $CuSO_4$ TIRPALUOSE

11. CU ELEKTROKRISTALIZACIJOS PIRMINIŲ STADIJŲ TYRIMAS ANT S-MODIFIKUOTO Pt(POLI) ELEKTRODO

Santrauka

Vario elektrocheminis nusodinimas ant ėvaraus Pt(poli) ir ant S-modifikuoto Pt(poli) elektrodŲ buvo tiriamas taikant potencialo ėjungimo metodą 0,5 M H_2SO_4 +0,1 M $CuSO_4$ tirpale. ChronoamperometriniŲ rezultatŲ analizė parodė, kad vario nusodinimas ant ėio substratŲ prasideda pagal Scharifkerio ir Hillso pasiūlytą momentinės 3D nukleacijos ir difuzijos kontroliuojamo augimo mechanizmą. Parodyta, kad susidariusiŲ branduoliŲ tankis (N) mažėja ir, priešingai, branduoliŲ vidutinis radiusas (r_{av}) ėiek tiek didėja, kai ėvaraus Pt(poli) elektrodas pakeičiamas S-modifikuotu Pt(poli) elektrodu. Aptartos ėio reiĖkinio galimos prieþastys.