Influence of some additives on Cu layer formation in underpotential and overpotential regions in acidic CuSO$_4$ solutions
9. Voltammetric and structural investigation of Cu UPD onto polycrystalline Pt in the presence of H$_2$SeO$_3$

Dijana Đimkûnaitë*,
Emilija Ivaðkeviè,
Vitalija Jasulaitienë,
Aleksandras Kalinièenko,
Ignas Valsiûnas,
Antanas Steponavièius

*Institute of Chemistry,
A. Goštauto 9,
LT-2600 Vilnius, Lithuania*

The underpotential deposition (UPD) of Cu onto polycrystalline Pt from acidic CuSO$_4$ solutions without or with H$_2$SeO$_3$ was monitored by electrochemical methods (cyclic voltammetry and potential pulse) in combination with structural investigations (XPS / AES, AFM). In all instances, the molar concentration ratio [Cu(II)] / [Se(IV)] was no less than $1\cdot10^3$. The dual action of H$_2$SeO$_3$ on the Cu UPD was revealed: Cu deposition was markedly suppressed at E more positive than approximately + 0.37 V due to a site-blocking effect and, on the contrary, at a more negative E somewhat enhanced deposition of Cu was observed, possibly due to the called CORC mechanism.

A transition from the monotonically decreasing current transients recorded in the absence of H$_2$SeO$_3$ in the E range + 0.70 to ~ + 0.40 V to the formation of a shoulder-like region in the transients at a more negative E was established. This feature of transients was suggested to imply that the dominant adsorption process at a more positive E transforms to a complex adsorption and nucleation / growth process with instantaneous nucleation at a less positive E. In the presence of H$_2$SeO$_3$, only monotonic current transients were recorded, suggesting the adsorption process to be dominant.

From the electrochemical and XPS measurements it follows that at + 0.35 V the co-existence of elemental Cu° and Se° species onto the Pt surface is possible in parallel with the simultaneous formation of Cu patches and Cu clusters, especially at E close to the reversible potential. The content of Se identified was *ca.* 9.5 at.%. The formation of Cu clusters proceeding predominantly at Pt surface defects was also monitored by AFM. Addition of H$_2$SeO$_3$ resulted in the formation of distinct chain-like structures composed of separate spherical particles and in an increase in the arithmetic roughness average R$_a$.

Key words: Cu UPD, Pt electrode, CuSO$_4$ solutions, H$_2$SeO$_3$, cyclic voltammetry, chronoamperometry, XPS, AFM

INTRODUCTION

Underpotential deposition (UPD) of metals (M) onto foreign substrates (S) is a well-established phenomenon observed with a great variety of M–S combinations in different experimental environments [1, 2]. This phenomenon is the key aspect in studying new metallic phase formation and electrocatalysis.

Many reports have been published, particularly on the most frequently studied systems such as the UPD of Cu on Pt from acidic CuSO$_4$ solutions. The UPD of Cu on Pt has been first observed with polycrystalline electrodes [3, 4]. More recently, investigations of this process have been performed with both polycrystalline and single crystal Pt electrodes [5–9].

Most of studies dealing with Cu UPD onto Pt has been made in the absence of any additive. However, it is known that the presence of other strongly adsorbed species can reduce the net binding energy

---
* Corresponding author.
E-mail address: nemezius@ktl.mii.lt

between the S surface and the M adlayer, allowing for easier surface diffusion of M adatoms. Consequently, formation of two-dimensional nuclei may be facilitated in such cases. Besides, the adsorption of such species has been shown to hinder or even inhibit the deposition of M adatoms, Cu onto Pt in particular [10–15].

An interesting class of systems under question is the UPD of Cu on Pt previously pretreated with halogen, particularly iodine [11, 12], and also with sulphur [13] or selenium [14]. It has been noted that the deposition of Cu on I-covered Pt (treatment with iodine vapour in vacuum) occurs by adsorption directly onto the Pt surface thereby causing a displacement of the iodine ad-lattice [11]. The formation of 2D Cu clusters in the UPD region onto I-covered Pt (immersion in an iodide solution) has also been suggested [12]. The specific voltammetric pattern of the Cu UPD process observed for a bare polycrystalline Pt electrode has been shown to disappear, and a new current peak at potentials much closer to the reversible potential for the Cu / Cu^{2+} couple has been established to manifest itself when using the sulphur- or selenium-precovered Pt electrodes [13–15]. A model of Cu deposition taking place onto free Pt sites at a more positive E or onto selenium-covered sites at a less positive E has been earlier suggested as one of the possible explanations of this effect [14].

The open questions, however, are how the additives can affect the kinetics of Cu UPD process when they are dissolved in a solution used for the measurements and what an interaction of the Cu adlayer may be expected with the adsorbed additives. In this context, Se(IV) compounds continue to be of considerable interest and are being explored for a variety of applications, including heterogeneous electrocatalysis (see, e.g., a review [16] and more recent publications [17, 18]) and electrodeposition of thin layers of copper selenides as semiconducting materials [19]. Besides, H_2SeO_3 has been shown to accelerate the discharge of Cu^{2+} ions at Cu electrodes in acidic $CuSO_4$ solutions [20].

The electrodeposition of II–IV compound semiconductors, including a Cu–Se system, has been reported in a large number of articles [19]. Like other metal selenides, copper selenides are electrodeposited from aqueous Cu(II) and Se(IV) solutions with comparable concentrations of the components. Regarding the effect of Se(IV) compounds on the formation of Cu layers on a foreign S or on the same S, that is, on the deposition of Cu adlayers, on the early stages of Cu electrocrystallization and on the kinetics of Cu^{2+} ions discharge, much less amounts of this additive, namely, those ranging from 10^{-6} to 10^{-4} M (this yields a ratio [Cu(II)] / [Se(IV)] from

$1.2 \cdot 10^4$ to $2.4 \cdot 10^5$ [20]) are typically used. Subsequently, the effect of Se(IV) compounds in the latter case is expected to be different as compared with the formation of thin overlayers of copper selenides.

The aim of the present work was to investigate the process of formation of Cu layers in the underpotential regime, Cu_{UPD}, on a polycrystalline platinum (Pt(poly)) electrode in the presence of H_2SeO_3 dissolved in acidic $CuSO_4$ solutions by means of electrochemical (cyclic voltammetry, chronoamperometry) and structural (XPS, AFM) measurements. It was also our objective to compare this information with the results obtained in the studies of Cu UPD onto a selenium-precovered Pt(poly) electrode in a pure acidic $CuSO_4$ solution.

EXPERIMENTAL

The working solution 0.5 M H_2SO_4 + $CuSO_4$ + + H_2SeO_3 was prepared from doubly distilled water, copper sulphate (Fluka) preheated at 400 °C for 4 h, highest purity sulphuric acid (Russia) and selenious acid H_2SeO_3 (99.999% purity, Aldrich). The amounts of $CuSO_4$ and H_2SeO_3 were 0.01 or 0.1 M and from $1 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ mM, respectively. In all cases the molar ratio [Cu(II)] / [Se(IV)] was no less than $1 \cdot 10^3$. Prior to each experiment, the solutions were deaerated with Ar gas for 0.5 h.

All experiments were performed at a temperature of 20 ± 0.1 °C in a conventional three-electrode cell using a vertical Pt(poly) disc as the working electrode (0.85 cm²), a Pt sheet (4 cm²) as the counter electrode, and an Ag / AgCl / KCl(sat.) reference electrode. All potentials were recalculated with respect to the standard hydrogen electrode (SHE).

The pre-treatment and the estimation of the real surface area of the Pt electrode were described in detail elsewhere [14]. The roughness factor f was found to be 2.05 ± 0.05. The current densities are given with respect to the geometric surface area.

The electrochemical investigations were carried out using cyclic voltammetry (CV) and chronoamperometry. In all cases the Pt electrode was first allowed to stand at a starting potential (E_{start}) for 2 min. The potential sweeps were started with E_{start} = = +0.85 V, first toward more negative potentials. The potentiostatic current-time (I/t) transients were recorded starting with +0.80 V. This value was adopted here, because at this E no Cu UPD onto Pt has been observed [1, 3–9]. So, potential stepping from this E_{start} to potentials (E_{dep}) within the range of Cu underpotentials was thought to be performed with the Cu-uncovered Pt(poly) surface. The current transients were recorded over short periods of time (≤ 2 s) to minimize changes in the surface morphology.

Electrochemical 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). The experimental data acquisition was in a numerical form with a time resolution of 4 or 50 ms per point.

The XPS analysis was carried out for the Pt (poly) electrode treated in 0.5 M H_2SO_4 + 0.1 M $CuSO_4$ + + 0.05 mM H_2SeO_3 solution for 2 min at either + 0.80 or + 0.35 V. After preparation, the specimens were immediately stored in an analysis chamber, the exposure time to room atmosphere being no more than 2 min. The *ex situ* Pt $4f_{7/2}$, Cu $2p_{3/2}$, Se $3d_{5/2}$ and O *1s* spectra and the Cu $L_3M_{45}M_{45}$ Auger spectra were recorded on a VG ESCALAB MKII spectrometer (MgK$_\alpha$ 1253.6 eV) operated at 300 W, a band pass energy of 20 eV. Electron binding energies (E_B) for elements and their compounds used as the standard values of E_B are presented in Table. The following elemental sensitivity factors were used to determine the contents (in at.%) of Cu, Se, O and Pt: Cu $2p_{3/2}$ 4.2, Se $3d_{5/2}$ 0.67, O *1s* 0.66 and Pt $4f_{7/2}$ 4.4, [23].

Samples for *ex situ* AFM investigations were prepared treating the working Pt electrode with 0.5 M H_2SO_4 + 0.01 M $CuSO_4$ solution in the absence or in the presence of 0.05 mM H_2SeO_3 at E = + 0.35 V for 2 min. The AFM observation was performed using a TopoMetrix Explorer SPM with a Si_3N_4 tip operating in the contact mode. The top-view images are presented in the so-called "height mode" where the higher parts appear brighter. Cross-sectional analysis of the AFM images was also applied.

The reversible potential (E_r) for the Cu / Cu^{2+} couple was estimated measuring an open-circuit potential (OCP) of Cu under conditions of the zero net current in unstirred deaerated acidic $CuSO_4$ solutions at t = 2min and at 20 °C, and it was found to be equal to + 0.260 V for $1 \cdot 10^{-2}$ M Cu^{2+} and to + 0.282 V for $1 \cdot 10^{-1}$ M Cu^{2+} solutions.

RESULTS AND DISCUSSION

1. *Cyclic voltammetry.* A series of quasi-steady voltammetric profiles (the 20th cycles) for the Pt(poly) electrode in blank 0.5 M H_2SO_4 solution taken from the same cathodic limit $E_{s,c}$ = + 0.05 V successively to different anodic limits $E_{s,a}$ up to + 1.50 V in an increment of 0.1 V are shown in Fig. 1. The general shape of the CVs is quite close to that presented elsewhere [14, 27], and these curves are displayed for comparison.

Figure 2 shows a variation in the shape of the CVs in unstirred 0.5 M H_2SO_4 + 0.1 M $CuSO_4$ solution with a potential sweep rate (v) in the absence (Fig. 2a) or in the presence of 0.01 mM H_2SeO_3 (Fig. 2b). The CVs were recorded in the E range where the interference of the Cu UPD/stripping reactions and the electrochemical reactions involving the Pt oxidation or the reduction of surface platinum oxide might be ruled out. From the CVs the following information can be derived.

As one can see, the CVs exhibit certain chan-

Table. Electron binding energies (E_B) for elements and their compounds used as the standard values of E_B

Element	Oxidation state	Compound	Spectral lines				Refs.
			Pt $4f_{7/2}$	Cu $2p_{3/2}$	O *1s*	Se $3d_{5/2}$	
Pt	0	Pt metal	71.0				[21]
	2	PtO	72.2				[22]
	4	Pt(OH)$_2$	72.4				[21]
	4	PtO$_2$	74.4				[21]
	4	Pt(SO$_4$)$_2$ · zH$_2$O	74.4				[21]
	1	Oxide I*	73.6				[21]
Cu	0	Cu metal		932.6			[23]
	1	Cu$_2$O		932.5			[23]
	1	Cu$_2$Se		932.3			[24]
	2	CuO		933.7			[23]
	2	Cu(OH)$_2$		935.1			[23]
	2	CuSe		932.0			[25]
O**	–2	Cu$_2$O			530.3		[23]
	–2	CuO			529.6		[23]
	–2	Cu(OH)$_2$			531.2		[23]
Se	0	Se elemental				55.0	[24]
	–2	Cu$_2$Se				53.9	[24]
	4	SeO$_2$				*ca.* 60.9	[24]

Notes: *) Assignment of oxide I has been made in reference to an intermediate surface oxidation state after completion of a PtOH monolayer structure [21].
**) It is common knowledge that in the general case the O *1s* spectra can be considered under an assumption of some distinct oxygen species being at a Pt surface, *i.e.* in terms of O *1s* signals of Pt–OH, Pt–OH$_2$ (adsorbed species of hydroxyl and water), Pt–O–Pt (oxygen in metal–metal bond) and also of adsorbed molecular oxygen. No plausible data on the O *1s* spectra characteristics for the Pt–O systems were found. We can mention the assignment of the O *1s* signal at 531.8 eV to chemisorbed oxygen (PtO$_{ads}$) [26].
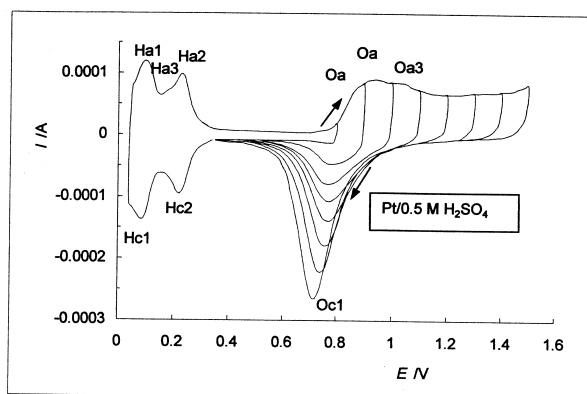
Fig. 1. Potentiodynamic profiles for Pt(poly) electrode in 0.5 M H$_2$SO$_4$ solution recorded at 50 mV s^{-1} from the cathodic limit $E_{s,c}$ = +0.05 V successively to increasing anodic limits $E_{s,a}$ in 0.1 V increments
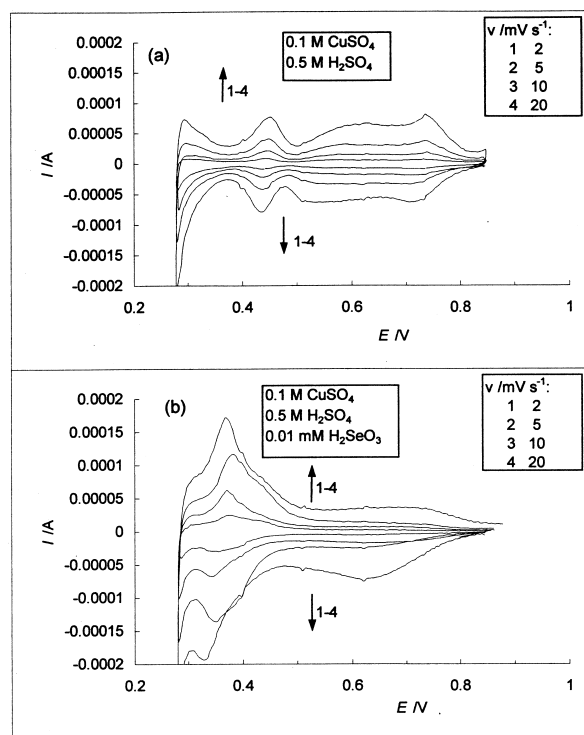

Fig. 2. Cyclic voltammograms (1st sweep) for Cu deposition/stripping at Pt(poly) electrode at different potential scan rate v in acidic 0.1 M CuSO$_4$ solution without (a) or with H$_2$SeO$_3$ (b)

ges in their profiles under the influence of H$_2$SeO$_3$. The specific pattern of the Cu UPD onto Pt(poly) [6, 8, 14] was somewhat changed, and a new current peak was revealed at E much closer to the bulk Cu deposition, namely, a current peak at about +0.35 V (Fig. 2b, curve 4). It should be remarked that a rather good parallelism is observed between the voltammetric data recorded in our work and

those obtained earlier for selenium- [14] and sulphur-modified [28] Pt(poly) electrodes in pure acidic CuSO$_4$ solution and also for a bare Pt(poly) electrode in the acidic CuSO$_4$ solutions containing various sulphur compounds, such as thiourea [15] or 4,7-dithiadecyl-1,10-disodiumsulphate [15]. Therefore, it can be suggested that in both cases, i.e. with a Se-precovered and with a bare Pt(poly) electrodes but in the presence of Se(IV) substance as a solution constituent, the Cu UPD process takes place at Pt substrates of rather similar properties.

The effect of the concentration (c) of H$_2$SeO$_3$ is shown in Fig. 3. Even at a very low c of this additive the typical Cu UPD current peak is reduced in size, while the new current peak mentioned above increases. In contrast to a pure electrolyte, a hysteresis between this new cathodic peak and the stripping peak is observed (Fig. 3). A similar overall pattern was also found with increasing v (Fig. 2b). So, the hysteresis just mentioned tends to increase with increasing c of H$_2$SeO$_3$ and v (Figs. 2, 3).

The above results suggest that, in the presence of even very small c of H$_2$SeO$_3$, e.g., at molar bulk concentration ratios [Cu(II)] / [Se(IV)] from 10^5 to 10^4, the Cu UPD reaction onto the Pt(poly) surface can be affected by an inhibition process, possibly due to adsorption of certain Se(IV) or Se(0) species. The adsorption of selenium at Pt has been found to be irreversible [17, 29, 30]. Now, the question to be considered is how the Cu adlayer builds up with an inhibiting layer of Se species during a single potential sweep cycle. Some insight into this problem has already been gained from the voltammetric and structural results reported earlier [14, 31]. First of all, it is worth noting that a model involving the Cu deposition onto free Pt sites in the region of higher underpotentials and that onto partially Se-covered Pt sites as well, as E was moved toward lower values, i.e. closer to E_r, has been
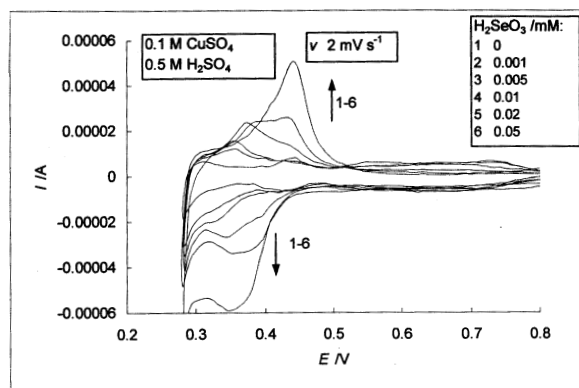

Fig. 3. Cyclic voltammograms (1st sweep) for Cu deposition/stripping at Pt(poly) electrode in acidic 0.1 M CuSO$_4$ solution containing different amounts of H$_2$SeO$_3$

proposed as one of the possible explanations for this phenomenon. This problem will be additionally considered below, using new experimental results.

The effect of increasing c of H_2SeO_3 on the Cu UPD in solution with lower c of $CuSO_4$ is presented in Fig. 4. The overall picture is quite similar to that shown in Fig. 3.

2. *Chronoamperometry.* Cathodic current transients were obtained by using a Pt(poly) electrode
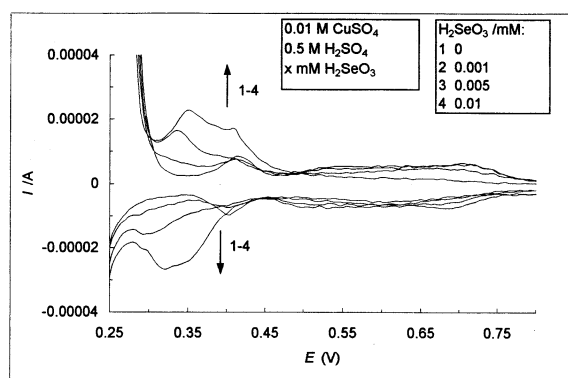

Fig. 4. The same as in Fig. 3 but in 0.01 M $CuSO_4$ solution

Fig. 5. Potentiostatic current transients for Cu UPD at Pt(poly) in acidic 0.01 M $CuSO_4$ solution without (*a*) or with H_2SeO_3 (*b*) recorded at various values of deposition potential E_{dep}. E_r for a couple Cu / Cu^{2+} is 0.282 V

which was first held at E_{start} = + 0.80 V for 2 min, as mentioned above, and then E was stepped to E_{dep} in the range + 0.27 ≤ E_{dep} ≤ + 0.70 V to record the current transients. As also mentioned above, such potential pulses were thought to be performed with a Cu-uncovered Pt(poly) electrode. Besides, taking into account the voltammetric behaviour of Pt(poly) in the blank 0.5 M H_2SO_4 solution depending on the value of $E_{s,a}$ (Fig. 1) and also the fact that the current transients were recorded here with E_{start} = + 0.80 V, these transients can, in principle, be related to the deposition of the Cu adlayer with a negligible contribution of adsorbed O species.

Stepping to various E_{dep} within the Cu UPD region resulted in a series of current transients as shown in Fig.5. Monotonically decreasing current transients are observed in H_2SeO_3-free $CuSO_4$ solution in the region from + 0.70 V to about + 0.40 V (part of the typical transients is presented in Fig. 5a), implying the adsorption process to be dominant [32]. At lower E_{dep}, the initial current decrease is followed by a shoulder-like region which may be typical of the adsorption and nucleation/growth model with instantaneous nucleation [32]. So, in the latter case, the coexistence of Cu adatoms and Cu clusters produced through the nucleation/growth process seems to be possible, in agreement with the earlier observations [6]. In the presence of H_2SeO_3, only monotonic current transients were recorded
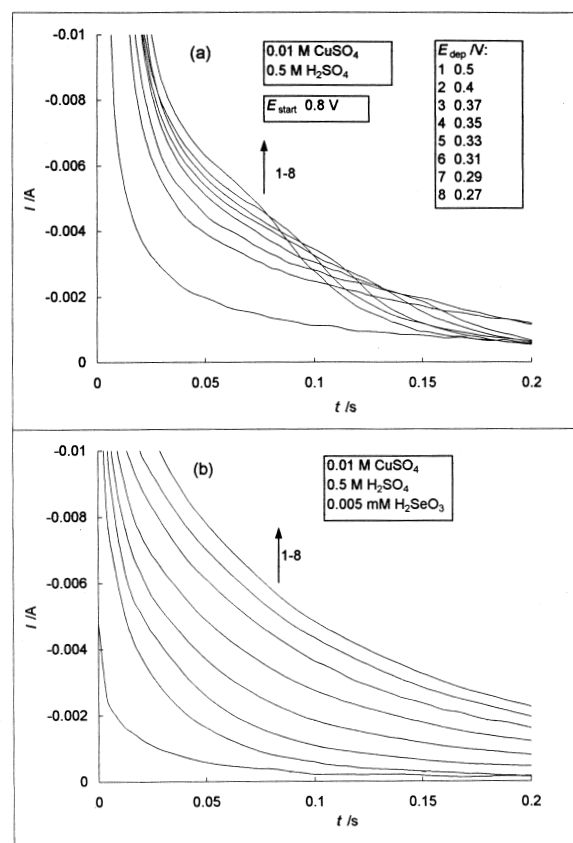
(Fig. 5b), suggesting, as noted above, the dominant role of adsorption.

Integration of an area in the current transient shows a strong inhibition of the Cu deposition process over a wide region of E_{dep} (up to about + 0.37 V) under the action of H_2SeO_3 (Fig. 6). As one can see, the integration of the current transient recorded by a potential pulse to a certain E_{dep}, say, to + 0.35 V, yielded the Q_c charge densities of about 440 and 400 $\mu C \ cm^{-2}$ in the absence and in the presence of H_2SeO_3, respectively. Then, taking the charge of 450 $\mu C \ cm^{-2}$ involved in the formation of a complete Cu monolayer onto Pt(poly), these values of Q_c resulted in Cu_{UPD} in amounts of about 1 or 0.9 monolayers, respectively (the deposition of a Cu overlayer alone was assumed to occur in the latter case). The overestimated values of Q_c at E_{dep} < + 0.35 V in the absence of H_2SeO_3 (Fig. 6) are possibly associated with the formation of thin Cu patches which do not possess the bulk properties of thick Cu patches, and also with the coexistence of Cu adatoms and bulk Cu clusters, especially at E_{dep} close to E_r, as has been supposed earlier [6]. The point to emphasize is also that Q_c depends strongly

on the applied value of E_{dep}, *i.e.* on the value of the underpotential, both in the absence and presence of an additive (Fig. 6).
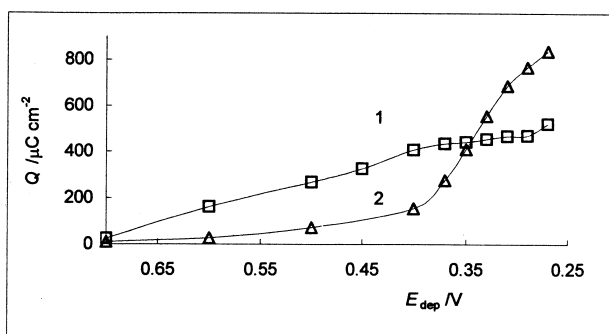

Fig. 6. Variation of cathodic charge densities Q_c with deposition potential E_{dep} (from transients in Fig. 5)

The above data show that the presence of H_2SeO_3 manifests itself in a dual effect on Cu UPD. First of all, this additive suppresses the Cu UPD process at higher underpotentials (at E_{dep} more positive than ca. $+0.35$ V) and, secondly, enhances it at lower values of the underpotential. This effect was found to be more distinct with increasing c of H_2SeO_3 (not shown here). Provided Cu is not capable of displacing Se species from the Pt(poly) surface in the E_{dep} range of interest, the randomly coadsorbed Cu and Se species might be assumed to coexist, as already considered above.

A question can arise whether it is possible to exclude the contributions of the reduction of adsorbed O- and Se-containing species. As for the first question, from the comparison of the current transients (Fig. 5) with the voltammetric behaviour of bare Pt(poly) in the blank 0.5 M H_2SO_4 solution (Fig. 1), it is believed that these transients and consequently the calculated values of Q_c (Fig. 6) are in principle related to deposition of Cu overlayer with only a negligible contribution of O-adsorbed spe-
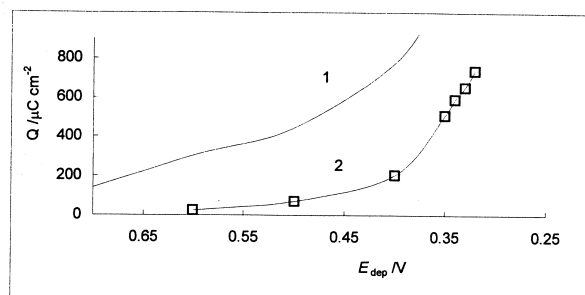

Fig. 7. Variation of voltammetric (*1*) (from CV at 2 mV s^{-1}) and chronoamperometric (*2*) (from Fig. 6) charge densities Q_c with deposition potential E_{dep} in 0.01 M $CuSO_4$ solution containing 0.01 mM H_2SeO_3

cies. A consideration on the possible contribution of Se will be presented below.

Under conditions of our experiments, the cumulative voltammetric Q_c are higher than the chronoamperometric Q_c (Fig. 7). Such a difference seems to be due to the different techniques applied in these experiments or, more strictly, due to the different state of the Pt(poly) electrode surface at a certain value of E_{dep}.

3. *X-ray photoelectron and Auger electron spectroscopic analysis.* Two types of specimens were used in the XPS/AES analysis. Firstly, the Pt(poly) electrode was held at $E_{start} = +0.80$ V for 2 min in $CuSO_4$ solution containing 0.05 mM H_2SeO_3. Secondly, this holding was performed at $E_{dep} = +0.35$ V. As mentioned above, these values of E were chosen to obtain either a Cu-uncovered Pt substrate or a Pt substrate with a certain amount of Cu_{UPD}.

The results of XPS / AES analysis were as follows. We found Pt, Se and O on the surface of both specimens. As expected, a certain amount of Cu_{UPD} was actually identified from the specimen which was held at $+0.35$ V.

The Pt $4f_{7/2}$ peak at 70.9 eV is in good agreement with the standard E_B for metallic Pt (Table). Besides, this E_B is markedly lower than E_B for Pt $4f_{7/2}$ spectra from oxygenated Pt(II) and Pt(IV) compounds. Therefore, in either case the top layer of Pt(poly) is believed to remain non-oxidized, *i.e.* as Pt°. The contents of Pt were found to be equal to 83.20 at.% at $+0.80$ V and 56.09 at.% at $+0.35$ V.

The Se $3d_{5/2}$ spectrum has two peaks at 54.9 and 54.3 eV (at $+0.80$ V) and a single peak at 54.3 eV (at $+0.35$ V). The peak with the higher E_B is undoubtedly due to elemental selenium, Se°. The peak with the lower E_B can formally be explained at least by a double effect. On the one hand, such a value of E_B can also be assigned to Se° provided that a negative shift of 0.7 eV observed here with respect to the standard E_B for bulk Se corresponds to the amount of Se° much less than a monolayer (2.55 and 9.45 at.% at $+0.80$ and $+0.35$ V, respectively), as it has previously been found, for example, for Cu deposited underpotentially onto Pt [33]. On the other hand, by analogy with XPS data concerning various metal selenides of MSe type, a negative chemical shift might be caused by a formation of a surface compound like PtSe. In this connection it should be noted that PtSe as a surface compound has previously been assumed to be formed in perchlorate [34] and sulphate [30] solutions of H_2SeO_3. However, the absence of XPS signal typical of oxidized Pt leads us to a conclusion that no evidences for the formation of PtSe as a sur-

face compound were obtained. So, both Se $3d_{5/2}$ peaks are taken here to be due to adsorbed Se° species.

The O $1s$ spectrum has two peaks at 532.2 and 530.6 eV (at +0.80 V) and a single peak at 531.6 eV (at +0.35 V). The XPS data relating the O $1s$ signal obtained here from the first specimen are rather difficult to analyze. Firstly, the E_B value of 532.2 eV is larger than that of chemisorbed oxygen, PtO_{ads} (531.8 eV [26]). Then, it can be tentatively suggested that this O $1s$ peak corresponds to oxygen in M-OH (adsorbed hydroxide, OH_{ads}, derived from H_2O in acidic solution) or $M-OH_2$ bonds (M is a noble substrate, *e.g.*, Rh [22] or likely Pt), or to adsorbed molecular oxygen. Secondly, the O $1s$ peak at 530.6 eV is also impossible to assign with certainty to a specified O-containing species. Perhaps one can assume that the O $1s$ peak at 530.6 eV might arise from oxygen in M-O-M bond, *i.e.* from the lattice oxygen as proposed in [22]. Quite apparently, taking into account the consequences of the exposure of the Pt specimen to atmosphere prior to the XPS investigations, such XPS results are not unexpected. The O $1s$ peak at 531.6 eV recorded from the second specimen is rather close to that of chemisorbed oxygen PtO_{ads}. In our opinion, an additional support for these considerations should be required.

As expected, a certain amount of Cu_{UPD} (17.75 at.%) was identified from the second specimen. As regards the oxidation state of Cu and the composition of its compounds, it should be borne in mind that the Cu $2p_{3/2}$ peaks and in some instances the Cu $L_3M_{45}M_{45}$ peaks can be uninformative due to the closeness of the values of E_B or E_K obtained from different Cu compounds (see, *e.g.*, [23–25] and Table). Nevertheless, if to compare the experimental E_B (932.3 eV) and E_K (918.1 eV) for Cu with E_B for the O $1s$ and Se $3d_{5/2}$ signals from Cu oxides and Cu selenides, respectively, it can be suggested that such stoichiometric Cu compounds as Cu_2O, CuO, Cu_2Se and CuSe could practically be ruled out. Then, the negative shift in the value of E_K (918.1 eV obtained here *vs.* 918.6 eV for bulk Cu [23]) might specifically be related with a small amount of Cu_{UPD} being less than a Cu° monolayer, as argued earlier [33].

The main points that can be extracted from the XPS results seem to be as follows: (*i*) a relatively "free" part of the Pt(poly) substrate surface was markedly decreased with the shift of *E* to a negative direction, namely, Pt ~56.1 at.%. at +0.35 V *vs.* 83.2 at.% at +0.80 V; (*ii*) the Se species adsorbed onto Pt(poly) are presumed to correspond to $Se°_{ads}$ (this adsorption has been known to be irreversible on active surface sites [29, 30]); (*iii*) taking into account the features of the Cu UPD onto a bare Pt(poly) substrate (see, *e.g.*, [4, 6, 14]) and those onto a Se-precovered Pt(poly) substrate [14], the coexistence of the elemental Cu° and Se° species adsorbed onto the Pt surface is believed to take place over the whole *E* range under study, with the irreversibly adsorbed Se° species showing a site-blocking effect and the Cu° species in essence reversibly depositing at the non-blocked surface Pt sites. The Se° species are produced and adsorbed at *E* which are more positive than the onset of the formation of the Cu_{UPD} layer. Because of the low values of both the bulk *c* of H_2SeO_2 and the content of Se identified on the Pt(poly) surface, it seems that Cu deposition at the remaining Se-covered Pt(poly) sites can be possible only at a much more negative *E* or at a significantly higher Se coverage, similarly as in the case of Cd UPD at Te-precovered electrodes [35, 36]. In addition, even at a low Se coverage, the presence of adsorbed Se° species results in significant alterations in the Cu UPD features (Fig. 2).

4. *Ex-situ AFM morphological examination.* AFM images (Fig. 8) show that at E_{dep} = +0.35 V the Cu UPD proceeds via the formation of the clusters mainly at the Pt(poly) substrate surface defects prior to the complete Cu monolayer formation (the surface defects such as scratches were likely generated
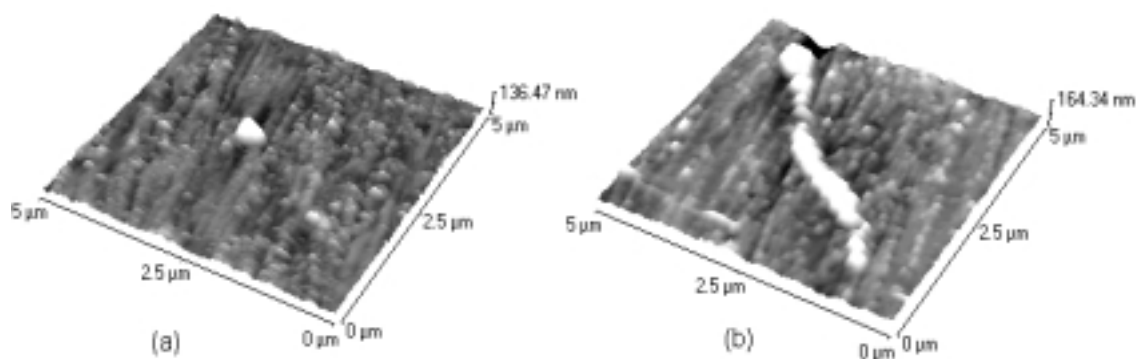

Fig. 8. *Ex situ* AFM images of Pt(poly) surface after Cu deposition at +0.35 V for 2 min from acidic 0.01 M $CuSO_4$ solution without (*a*) or with 0.005 mM H_2SeO_3 (*b*)

during mechanical polishing of Pt). In H_2SeO_3-free $CuSO_4$ solution the individual clusters are of a comparatively uniform size and are distributed preferentially along these scratches acting as the most active sites for Cu deposition. Moreover, Cu deposition seems to be uneven along them, because some rather rough protrusions are also well-observed. So, in some instances, the clusters grow not only laterally, but rather intensively in a normal direction to the surface as well giving a ratio $x/z \approx 5$.

Although in the presence of H_2SeO_3 a similar morphology of the specimen was obtained (Fig. 8b), distinct chain-like structures (not observed in the absence of H_2SeO_3) are clearly seen. These structures were found to be composed of numerous separate spherical particles.

From the cross-sectional profiles (Figs. 9, 10) along the lines positioned in the AFM images (as in Fig. 8 but displayed as top-views), one can see that in the presence of H_2SeO_3 a rougher surface of the specimen was obtained as reflected in its arithmetic roughness average R_a with respect to that in the absence of this additive.

Note that the AFM examination described above is preliminary. More systematic studies are in progress.
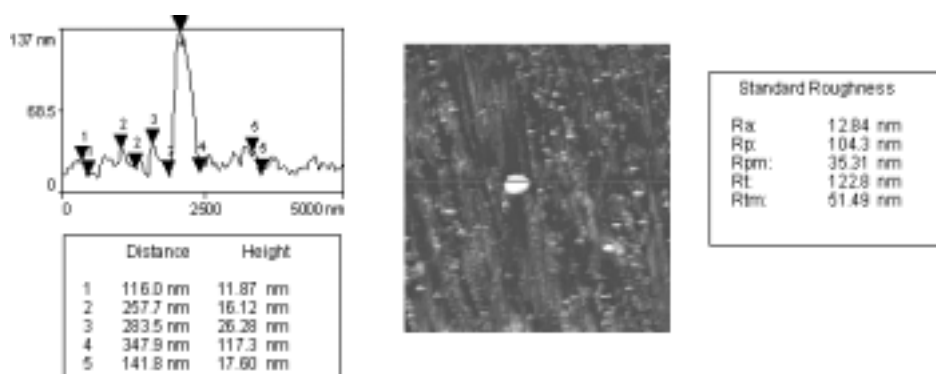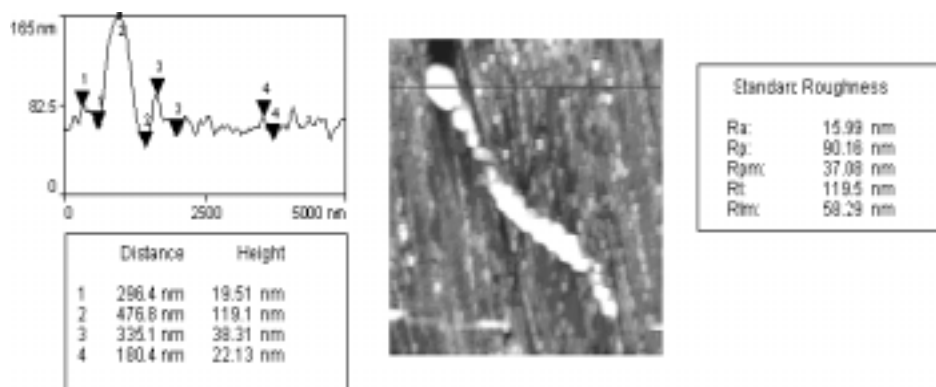
CONCLUDING REMARKS

In this study, Cu UPD on Pt(poly) was investigated in acidic $CuSO_4$ solution containing H_2SeO_3 when the molar concentration ratio [Cu(II)] / [Se(IV)] was no less than $1 \cdot 10^3$. The presence of H_2SeO_3 in working solutions manifested itself in a dual action on the Cu UPD onto Pt(poly): firstly, Cu deposition was markedly suppressed at potentials more positive than ~ $+0.37$ V due to a site-blocking effect and, secondly, the Cu deposition was somewhat enhanced below this E likely due to the so-called CORC mechanism involving partial reduction of Cu^{2+} ions to the intermediate Cu^+ and consequently an increase in c of Cu^+ at the surface of the working electrode. As a result, the typical pattern of the cyclic voltammetric curve for Cu UPD onto a bare Pt(poly) electrode was changed, namely, a new cathodic current peak at potentials much closer to the E_r was formed.

Using chronoamperometry, transition from monotonically decreasing potentiostatic current transients in the E range $+0.70$ to ~ $+0.40$ V to the formation of a shoulder-like region in these transients at more negative E values was established in the absence of H_2SeO_3. This can imply that the dominant adsorption process transforms to the adsorption and nucleation / growth model with instantaneous nucleation. In the presence of H_2SeO_3, only monotonic current transients were recorded.

From the results of voltammetric and chronoamperometric measurements, it was supposed that the coexistence of elemental Cu and Se particles on Pt(poly) surface is possible with simultaneous formation of both Cu patches, which do not possess the bulk properties, and Cu clusters. Formation of Cu clusters seems to be more intensive at potentials close to E_r.

XPS investigation confirms the presence of elemental Se° species on Pt(poly). The content of selenium identified at

Fig. 9. Cross-sectional profile along a selected line (from Fig. 8a)

Fig. 10. Cross-sectional profile along a selected line (from Fig. 8b)

+0.35 V was found to be *ca.* 9.5 at.%. No plausible evidence for the formation of PtSe as a surface compound and such stoichiometric Cu compounds as Cu_2Se and CuSe were obtained in our work.

AFM images showed that in the absence of H_2SeO_3 the Cu UPD at +0.35 V proceeded via the clusters formation predominantly at the Pt(poly) substrate surface defects, *e.g.*, scratches, prior to complete monolayer formation. In some instances, they grew not only laterally but also vertically up to the ratio $x/z \approx 5$. A similar pattern was obtained for $CuSO_4$ solution containing H_2SeO_3, but in this case the formation of distinct chain-like structures composed of separate spherical particles and the increase in the value of the arithmetic roughness average R_a with respect to that in the absence of the additive were revealed as well.

References

1. D. M. Kolb, in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 11 (Eds. H. Gerischer and Ch. W. Tobias), pp. 125–271, Wiley-Interscience, New York–Chishester–Brisbane–Toronto (1978).
2. E. Budevski, G. Staikov and W. J. Lorenz, *Electrochim. Acta*, **45**, 2559 (2000).
3. M. Breiter, C. A. Knorr, W. Völkl, *Z. Elektrochem., Ber. Bunsenges. Physik. Chem.*, **59**, 681 (1955).
4. M. W. Breiter, *J. Electrochem. Soc.*, **114**, 1125 (1967).
5. B. Bittins-Cattaneo, E. Santos and W. Vielstich, *Electrochim. Acta*, **31**, 1495 (1986).
6. D. Margheritis, R. C. Salvarezza, M. C. Giordano and A. J. Arvia, *J. Electroanal. Chem.*, **229**, 327 (1987).
7. M. Watanabe, H. Uchida and N. Ikeda, *J. Electroanal. Chem.*, **380**, 255 (1995).
8. A. I. Danilov, E. B. Molodkina and Yu. M. Polukarov, *Rus. J. Electrochem.*, **36**, 976 (2000).
9. A. I. Danilov, E. B. Molodkina, Yu. M. Polukarov, V. Climent and J. M. Feliu, *Electrochim Acta*, **46**, 3137 (2001).
10. C. Alonso, M. J. Pascual and H. D. Abru¹a, *Electrochim. Acta*, **42**, 1739 (1997).
11. J. L. Stickney, S. D. Rosasco and A. T. Hubbard, *J. Electrochem. Soc.*, **131**, 260 (1984).
12. J. H. White and H. D. Abru¹a, *J. Electroanal. Chem.*, **274**, 185 (1989).
13. A. Steponavièius, S. Lichuðina and D. Đimkûnaitë, *Chemija* (*Vilnius*), **11**, 197 (2000).
14. A. Steponavièius and D. Đimkûnaitë, *Rus. J. Electrochem.*, **38**, 488 (2002).
15. D. P. Bhatt, T. Twomey, W. Plieth, R. Schumacher and H. Meyer, *J. Electroanal. Chem.*, **322**, 279 (1992).
16. G. Kokkinidis, *J. Electroanal. Chem.*, **201**, 217 (1986).
17. E. Herrero, A. Rodes, J. M. Pérez, J. M. Feliu and A. Aldaz, *J. Electroanal. Chem.*, **412**, 165 (1996).
18. D. Lippkow and H.-H. Strehblow, *Electrochim. Acta*, **43**, 2131 (1998).
19. R. K. Pandey, S. N. Sahu and S. Chandra, *Handbook of Semiconductor Electrodeposition*, Ch 7, Marcel Dekker, Inc., New York–Basel–Hong Kong (1996).
20. M. R. H. Hill and G. T. Rogers, *J. Electroanal. Chem.*, **68**, 149 (1976).
21. J. S. Hammond and N. Winograd, *J. Electroanal. Chem.*, **78**, 55 (1977).
22. M. Hara, K. Asami, K. Hashimoto and T. Masumoto, *Electrochim. Acta*, **28**, 1073 (1983).
23. *Handbook of X-Ray Photoelectron Spectroscopy* (Ed. G. E. Muilenberg), Perkin-Elmer Corp. (1979).
24. D. Cahen, P. J. Ireland, L. L. Kazmerski and F. A. Thiel, *J. Appl. Phys.*, **57**, 4761 (1985).
25. R. Romand, M. Roubin and J. P. Deloume, *J. Electron Spectrosc. Relat. Phenom.*, **13**, 229 (1978).
26. K. S. Kim, N. Winograd and R. E. Davis, *J. Amer. Chem. Soc.*, **93**, 6296 (1971).
27. H. Angerstein-Kozlowska, B. E. Conway, B. Barnett and J. Mozota, *J. Electroanal. Chem.*, **100**, 417 (1979).
28. A. Steponavièius and S. Lichuðina, *Chemija (Vilnius)*, Nr. 1, 36 (1999).
29. J. M. Feliu, R. Gómez, M. J. Llorca and A. Aldaz, *Surf. Sci.*, **289**, 152 (1993).
30. P. Carbonnelle and L. Lamberts, *J. Electroanal. Chem.*, **340**, 53 (1992).
31. A. Steponavièius and D. Đimkûnaitë, *Chemija* (*Vilnius*), Nr. 4, 297 (1998).
32. E. Bosco and S. K. Rangarajan, *J. Chem. Soc., Faraday Trans. 1*, **77**, 1673 (1981).
33. J. S. Hammond and N. Winograd, *J. Electroanal. Chem.*, **80**, 123 (1977).
34. R. Modolo, M. Traore and D. Vittory, *Electrochim. Acta*, **31**, 859 (1986).
35. F. Forni, M. Innocenti, G. Pezzatini and M. L. Foresti, *Electrochim Acta*, **45**, 3225 (2000).
36. Th. Pauporté and D. Lincot, *Electrochim. Acta*, **45**, 3345 (2000).

**D. Đimkûnaitë, E. Ivaðkeviè, V. Jasulaitienë,
A. Kalinièenko, I. Valsiûnas, A. Steponavièius**

KAI KURIØ PRIEDØ ÁTAKA Cu SLUOKSNIØ FORMAVIMUISI POTENCIALØ ZONOSE, TEIGIAMESNĖSE IR NEIGIAMESNĖSE UÞ PUSIAUSVYRINÆ SISTEMOS $Cu^{2+}/Cu°$ POTENCIALO REIKÐMÆ, RÛGÐÈIUOSE $CuSO_4$ TIRPALUOSE 9. Cu IKIÁTAMPINIO NUSODINIMO ANT POLIKRISTALINĖS Pt ESANT H_2SeO_3 VOLTAMPEROMETRINIS IR STRUKTÛRINIS TYRIMAS

S a n t r a u k a

Ikiátampinis Cu nusodinimas (IÁN) ant polikristalinës Pt (Pt(poli)) ið rûgðèiø $CuSO_4$ tirpalø be H_2SeO_3 priedo ir su juo buvo tiriamas elektrocheminiais metodais (ciklinë voltamperometrija, potenciostatinis ájungimas) kartu su

RFES/AES, atominës jëgos mikroskopija AJM. Visais atvejais moliniø koncentracijø santykis [Cu(II)]/[Se(IV)] buvo ne maþesnis kaip $1 \cdot 10^3$. Nustatytas dvigubas H_2SeO_3 poveikis Cu IÁN – Cu nusodinimas buvo apsunkinamas esant teigiamesniems kaip maþdaug $+0,37$ V potencialams dël kristalizacijos centrø blokavimo ir, prieðingai, buvo palengvinamas esant neigiamesniems E, matomai, dël vadinamojo katalitinio oks/red ciklo.

Nustatyta, kad $CuSO_4$ tirpaluose be H_2SeO_3 priedo srovës transientai yra dvejopi – potencialø intervale nuo $+0,70$ V iki maþdaug $+0,40$ V jie monotoniðkai þemëja, o esant neigiamesniems potencialams transientuose pastebima papildoma banga. Literatûros duomenimis, tokia transientø eiga pirmuoju atveju gali bûti bûdinga vyraujan-

èiai adsorbcijai, o antruoju – kompleksiniam adsorbcijos ir kristalizacijos bei augimo procesui esant momentinei kristalizacijai. Tirpaluose su H_2SeO_3 priedu visame potencialø intervale transientø þemëjimas buvo monotoniðkas.

Remiantis elektrocheminiais ir RFES/AES matavimø rezultatais, manoma, kad $E = +0,35$ V atveju ant Pt(poli) pavirðiaus vienu metu gali egzistuoti elementiniø Cu ir Se dalelës, Cu° ir Se°, kartu su Cu lopais ir Cu klasteriais, ypaè arèiau Cu / Cu^{2+} pusiausvyriojo potencialo E_r. Ant elektrodo paviršiaus nustatytas Se kiekis buvo maþdaug 9,5 at.%. AJM metodu parodyta, kad Cu klasteriai susiformuoja daugiausia Pt(poli) pavirðiaus defektø vietose. Dël H_2SeO_3 priedo susidaro ryðkios grandininës struktûros ir padidëja aritmetinis ðiurkðtumo vidurkis R_a.