

---

# Voltammetric investigation of the codeposition and anodic stripping of copper and silver from platinum in sulphate solution

---

V. Kapočius,  
V. Karpavičienė and  
A. Steponavičius

*Institute of Chemistry,  
Gostauto 9,  
Vilnius, LT 2600, Lithuania*

The codeposition of copper and silver from acidic sulphate solutions containing  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  ions onto a polycrystalline smooth platinum electrode has been investigated by potentiodynamic and potentiostatic techniques. The composition of an overlayer deposited has been preliminarily estimated from the anodic stripping data. It has been demonstrated that two current peaks related to the bulk silver and bulk copper deposition appear on the cathodic scan, whereas on the reverse scan three anodic peaks which can be attributed to the dissolution of copper and silver and also likely of alloy  $\text{Cu}_x\text{Ag}_y$  become visible. The composition of an overlayer deposited by a potential pulse carried out from the starting potential  $E_{\text{st}}$  of 1.0 V to various values of deposition potential was shown to depend on not only the  $E_{\text{d}}$ , but also on the time it was taken for deposition. From the differences between the cathodic and anodic charges it has been supposed that a certain part of deposited silver passes into the solution as the uncharged species when the subsequent anodic scan has been applied.

**Key words:** copper, silver, codeposition, stripping, platinum electrode, linear potential sweep, potential step

---

## INTRODUCTION

The number of papers dealing with the mechanism and kinetics of electrodeposition of single metal is very high. The codeposition of some different metals is less understood [1, 2]. In particular, relatively little has been reported about the deposition of thin and ultrathin metal films consisting of different components. It is known that in recent years such films have been of increasing importance, e.g. in the electrodeposition of compositionally modulated layers, in the preparation of electrodes of higher catalytic activity toward various redox reactions, etc. In this regard, the codeposition of copper with other metals onto various substrates has received more attention recently [1, 2]. Among metals whose codeposition with copper appears to have considerable fundamental or industrial applications nickel [2–7], cadmium [2, 3], silver [6, 8] and bismuth [2, 9] can be mentioned.

Despite the reported benefits of controlling the electrical properties of Ag/Cu multilayers [6], the main regularities of copper codeposition with silver, from the theoretical point of view, remain to be

investigated. In particular, while the codeposition of copper and silver in the submono- or monolayer amounts has already been studied by cyclic voltammetry in a thin layer twin electrode cell [8], there is a great many of unsolved questions as to the deposition of the same metals over a wider range of potentials covering both underpotential and overpotential regions. In particular, not much is known so far about the dependencies of the composition of such thin films deposited onto inert substrates, on the deposition potential and the thickness of film. Among other factors, both of the listed ones have a marked influence on the properties of thin films obtained, as reported in [1, 2]. Besides, it is believed that such an investigation may be of importance not only for itself, but also for a deeper insight in the formation of thin metal layers in general.

The aim of the present work was thus to study the codeposition of copper and silver from sulphate solution on polycrystalline smooth platinum in both the underpotential and overpotential regions and to characterize preliminarily the obtained thin deposit by its anodic stripping followed by potentiodynamic and potentiostatic techniques.

## EXPERIMENTAL

### 2.1. Apparatus

A computer-controlled PI 50–1 potentiostat was used to apply potentiodynamic or potentiostatic techniques and to collect the data. All voltammetric experiments were carried out at 298 K in a conventional three-electrode cell using the working electrode, the Pt foil counter electrode (area 4 cm<sup>2</sup>) and a Hg|Hg<sub>2</sub>SO<sub>4</sub>|K<sub>2</sub>SO<sub>4</sub> (1M) reference electrode (+0.682 V vs. SHE). All potentials were reported relative to SHE. High purity argon gas was used to deoxygenate a solution.

### 2.2. Working electrode

The working electrode was a vertical platinum disc sealed in glass (exposed geometrical area 1 cm<sup>2</sup>). The electrode was polished mechanically with 0.1 μm diamond paste to a mirror finish. After polishing, the electrode was cleaned in hot (80 °C) concentrated nitric acid for 10–15 min, rinsed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and then, without any additional rinsing, transferred into the electrochemical cell with the supporting 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. In this cell, the Pt electrode was conditioned electrochemically by cycling the potential from +1.50 to +0.05 V at the scan rate ( $\nu$ ) of 20 mV s<sup>-1</sup> until the reproducible background  $i/E$  curve characteristic of polycrystalline Pt in this solution [10, 11] was obtained. Such a procedure of pre-treatment, except mechanical polishing, was carried out prior to each series of experiments.

The real surface area of the working electrode was estimated from the hydrogen adsorption region in the voltammogram recorded at 50 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>, as reported in [12]. The roughness factor ( $f$ ) was obtained to be  $2.2 \pm 0.2$ .

### 2.3. Measurements

For the Pt working electrode, cyclic voltammetry (CV) was used with the scan rates of 10, 20, 50, 100 and 200 mV s<sup>-1</sup>. The potential window for this technique was 1.0 to -0.1 V. Background subtractions were made using data from a cell containing only the supporting 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

Potential step measurements were carried out from a starting potential  $E_{st} = 1.0$  V to different values of the deposition potential ( $E_d$ ), corresponding to different underpotentials or overpotentials ( $\eta$ ) with reference to the equilibrium potentials for the couples Cu/Cu<sup>2+</sup> ( $E_{eq,Cu}$ ) or Ag/Ag<sup>+</sup> ( $E_{eq,Ag}$ ), which were estimated by separate experiments. The duration of potential step ( $\tau$ ) was mainly varied from 2 to 100 s.

The metal layer deposited freshly onto platinum by a selected potential pulse was subsequently stripped by an anodic-going potential scan.

### 2.4. Solutions

The working solutions were prepared from doubly distilled water, highest purity H<sub>2</sub>SO<sub>4</sub> and analytical grade CuSO<sub>4</sub>·5H<sub>2</sub>O; the latter reagent was purified additionally by recrystallization. Ag<sup>+</sup> ions were introduced into the solution through the anodic dissolution of required amount of metallic Ag (99.98% purity) at current density of 0.05 mA cm<sup>-2</sup>, with stirring by Ar gas. The amount of Ag<sup>+</sup> was determined by potentiometric titration with 0.01 M NH<sub>4</sub>SCN solution.

## RESULTS AND DISCUSSION

### 3.1. Voltammetric studies

Figure 1 shows the voltammetric profiles recorded for Pt electrode in a 0.5M H<sub>2</sub>SO<sub>4</sub> solution containing Cu<sup>2+</sup> and Ag<sup>+</sup> ions at various potential scan rates. The potential sweeps were performed in the range 1.0 to -0.1 V. On the negative-going sweep, two separate current peaks are observed – at 0.55–0.60 V (peak I) and at 0.05–0.2 V (peak II). The first peak was associated with the discharge of Ag<sup>+</sup> ions and the second one with the discharge of Cu<sup>2+</sup> ions.

On reversing the direction of scan at a potential being in the range of the ascending branch of peak I, appearance of a hysteresis loop was observed. Such a feature of cyclic voltammogram was shown to indicate, at least in a qualitative way, an occurrence of a nucleation and growth process [13]. A voltammogram displaying the similar characteristic feature has been recorded, in particular, for the silver deposition onto a vitreous carbon electrode from a

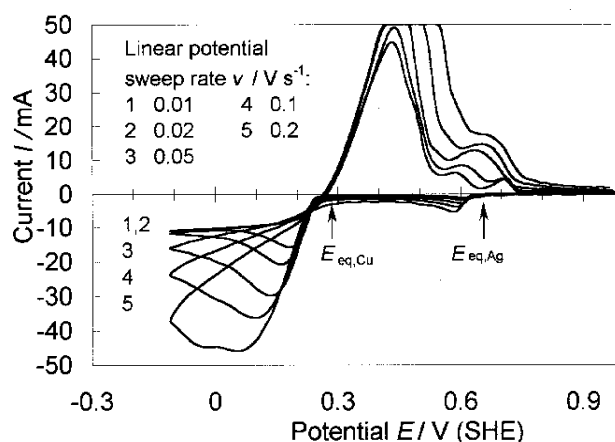


Fig. 1. Cyclic voltammograms at Pt electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.1 M CuSO<sub>4</sub> + 4.8·10<sup>-3</sup> M Ag<sub>2</sub>SO<sub>4</sub> solution; temperature 25 °C

perchlorate [14] or nitrate [15] solution or for other systems [16]. The analogous response obtained here for copper deposition was markedly weaker and, in addition, was observable only in the event when the reverse potential was more positive than the value of half-peak potential for peak II.

Distinctive ionization waves can be observed on the return sweep – the high copper stripping peak and another peak situated at  $E > E_{\text{eq,Ag}}$  and associated with silver dissolution. It should be noted that a rather distinct prewave can be also resolved at  $E$  being slightly more negative than  $E_{\text{eq,Ag}}$ . This prewave is likely due to an ionization process of alloy  $\text{Cu}_x\text{Ag}_y$ , as supposed by Bruckenstein and Tindall [17].

Integration of both entire cathodic and anodic parts of cyclic voltammogram gave a charge ratio  $Q_c/Q_a > 1$ . Besides, the difference  $Q_c - Q_a$  was obtained to decrease with increasing a potential scan rate (Table 1). When the difference  $Q_c - Q_a$  was correlated with the time consumed for silver deposition onto the electrode covered with bulk copper, *i.e.* under conditions of both the cathodic-going scan from  $E_{\text{eq,Cu}}$  to a reverse  $E$  and the anodic-going scan from this reverse  $E$  to  $E_{\text{eq,Ag}}$ , it was obtained that such a time-dependence of this difference can be satisfactorily approximated by a straight line with a slope of 0.21 mA (Fig. 2). The latter quantity is rather close to a limiting diffusion current for  $\text{Ag}^+$  ions  $I_{\text{diff}} = nFcD/\delta$  calculated taking the bulk concentration of  $\text{Ag}^+(c)$  of  $9.6 \cdot 10^{-6} \text{ mol cm}^{-3}$ , the diffusion coefficient for this ion ( $D$ )  $7.5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [15] and the thickness of diffusion layer ( $\delta$ ) of 0.03 cm. This finding can suggest that, in our opinion, a codeposition of copper and silver occurs in the way that a certain part of discharged silver forms separate crystallites or clusters which pass into a solution as uncharged species when the anodic-going sweep is subsequently applied. As is evident from the cyclic voltammograms presented in Fig. 1, the potentiodynamic conditions of electrolysis, however, restrict the possibility to change the ratio of amounts of codepositing metals.

Table 1. Variation of the cathodic and anodic charges with a potential scan rate. Solution: 0.5 M  $\text{H}_2\text{SO}_4$  + 0.1 M  $\text{CuSO}_4$  +  $4.8 \cdot 10^{-3}$  M  $\text{Ag}_2\text{SO}_4$ ; temperature 25 °C. Charges calculated by integrating the respective half-cycles of cyclic voltammograms

$v/\text{V s}^{-1}$	$Q_c/\text{mC}$	$Q_a/\text{mC}$	$(Q_c - Q_a)/\text{mC}$
0.01	$773 \pm 5$	$720 \pm 5$	53
0.02	$441 \pm 5$	$400 \pm 5$	41
0.05	$235 \pm 2$	$202 \pm 2$	33
0.1	$154 \pm 2$	$123 \pm 2$	31
0.2	$104 \pm 1$	$74 \pm 1$	30

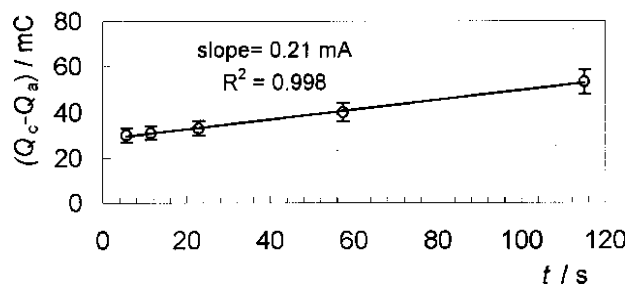


Fig. 2. Variation of the difference between cathodic and anodic charges with the length of time of silver deposition onto the copper-covered Pt electrode

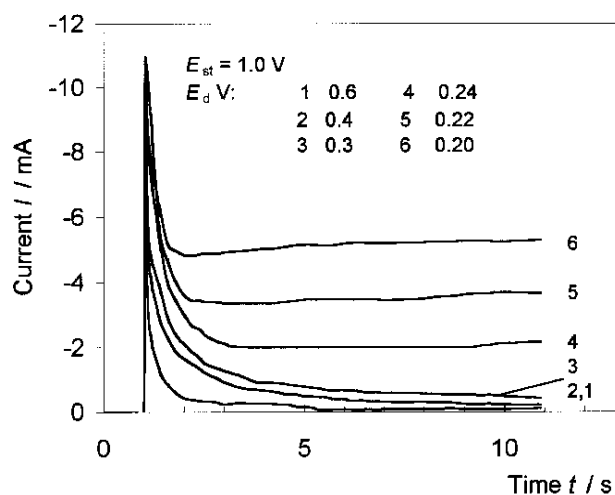


Fig. 3. Current–time transients at Pt electrode in 0.5 M  $\text{H}_2\text{SO}_4$  + 0.1 M  $\text{CuSO}_4$  +  $4.8 \cdot 10^{-3}$  M  $\text{Ag}_2\text{SO}_4$  solution for the potential step from  $E_{\text{st}} = 1.0$  V to various values of deposition potential  $E_d$

### 3.2. Chronoamperometric studies

When using the potential step technique, the current–time transients of several types were recorded depending on the values of the deposition potential ( $E_d$ ) or, respectively, overpotential ( $\eta$ ) with respect to  $E_{\text{eq,Ag}}$  or to  $E_{\text{eq,Cu}}$ . If  $E_{\text{eq,Ag}} > E_d > E_{\text{eq,Cu}}$ , the shape of these transients (Fig. 3, curves 1–3) can be explained according to the Cottrell's equation for silver deposition. In addition, within the rather narrow interval of potentials ( $E_d = 0.56$ – $0.59$  V) the run of  $i/t$  curves is characteristic of the cathodic process involving the nucleation and growth under diffusion control [18].

When  $E_d < E_{\text{eq,Cu}}$ , the shape of  $i/t$  transients was obtained to be significantly changed (Fig. 3, curves 4–6). However, on the further negative shift of  $E_d$ , in particular, at  $E_d < 0.1$  V, the shape of  $i/t$  transients again approaches that described by the Cottrell's equation, but with higher values of the current. Besides, it should be stressed that, under the latter conditions, there is no  $E_d$  range within which

the  $i/t$  transients would be indicative of the nucleation-growth process mentioned above, whereas such transients have been easily registered for  $\text{Ag}^+$ -free acid  $\text{CuSO}_4$  solutions [19, 20].

### 3.3. Stripping of deposits

Anodic polarization curves for the overlayers freshly deposited at various  $E_d$  are presented in Fig. 4. As is seen from the diagram, two separate current peaks are observed. The height of the current peak located at more positive potentials and related to the ionization of bulk silver increases, as  $E_d$  is made progressively more negative up to the commencement of bulk copper deposition (Fig. 4, curves 1–4). The further negative shift of deposition potential resulted only in an increase in the height of another current peak related to the copper dissolution, whereas the former peak and, respectively, the amount of silver to be stripped in this potential region remained essentially unchanged.

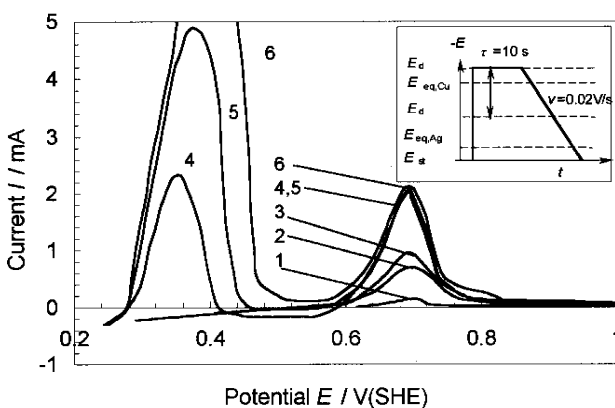


Fig. 4. Anodic stripping voltammetric curves at Pt electrode covered with an overlayer freshly deposited from 0.5 M  $\text{H}_2\text{SO}_4$  + 0.1 M  $\text{CuSO}_4$  +  $4.8 \cdot 10^{-3}$  M  $\text{Ag}_2\text{SO}_4$  solution by the potential step at the pulse length of 10 s from  $E_{st} = 1.0$  V to the values of deposition potential  $E_d$ : 1 – 0.6, 2 – 0.4, 3 – 0.3, 4 – 0.24, 5 – 0.22 and 6 – 0.2 V. The inset shows the time course of potential

The results of the estimation of charges corresponding to the deposition and dissolution of the overlayer (corrected for double-layer charging in the supporting 0.5 M  $\text{H}_2\text{SO}_4$  solution) showed the values of  $Q_c$  and  $Q_a$  to coincide very closely when  $E_d > E_{eq,Cu}$ . However, at  $E_d < E_{eq,Cu}$  a rather significant difference between these quantities was observed, as in the case of voltammetric measurements (Table 2). If such a difference is assumed to be due to the co-deposition of copper and silver and to the dissolution of a certain part of silver without charge transfer as mentioned above, the calculated amount of silver in the deposit should change from 41 at.% at  $E_d = 0.24$  V to 25 at.% at  $E_d = 0.2$  V. In the  $E_d$  range 0.15 to

Table 2. Variation of the cathodic total charge, the difference between cathodic and anodic total charges and the anodic total charges for dissolution of copper and silver with the potential of overlayer deposition onto Pt electrode. Solution: 0.5 M  $\text{H}_2\text{SO}_4$  + 0.1 M  $\text{CuSO}_4$  +  $4.8 \cdot 10^{-3}$  M  $\text{AgSO}_4$ . Cathodic charges calculated from potentiostatic current-time transients, anodic ones from the subsequent anodic stripping curves

$E_d/\text{V}$	$Q_c/\text{mC}$	$Q_{a,Cu}/\text{mC}$	$Q_{a,Ag}/\text{mC}$	$(Q_c - Q_a)/\text{mC}$
0.60	$0.5 \pm 0.1$	0	$0.5 \pm 0.1$	0
0.40	$3.5 \pm 0.2$	0	$3.5 \pm 0.2$	0
0.30	$5.2 \pm 0.2$	0	$5.2 \pm 0.2$	0
0.24	$20.5 \pm 0.3$	$8.5 \pm 0.3$	$9.0 \pm 0.3$	3
0.22	$40.5 \pm 0.5$	$24 \pm 0.5$	$9.5 \pm 0.3$	7
0.20	$73 \pm 0.5$	$54 \pm 0.5$	$10 \pm 0.3$	9

0.1 V, when  $Q_c$  was almost constant and equal to  $170 \pm 0.5$  mC, the difference  $Q_c - Q_a$  also became constant and equal to  $8 \pm 0.5$  mC. The calculated amount of silver in this instance would run to 8–9 at.%.

When cathodic polarization was carried out at a rather low  $\eta_c$  with respect to  $E_{eq,Cu}$  (e.g. at  $\eta_c = 0.04$  V or, respectively, at  $E_d = 0.252$  V), the shape of  $i/t$  transient recorded was analogous to that presented by curve 3 in Fig. 3, with the only difference that the current began to increase after a certain time lapse, in particular, from 0.27 mA at  $t = 10$  s to 0.54 mA at  $t = 100$  s. The current was obtained to be unchanged with further extending the experiment time, at least up to 10 min.

To investigate a relationship between the duration of overlayer deposition ( $\tau$ ) and the subsequent run of overlayer stripping curve, the overlayer was deposited at  $E_d < E_{eq,Cu}$  applying various  $\tau$ . It was obtained that no copper stripping peak could be revealed for  $\tau < 5$  s (Fig. 5, curves 1, 2), whereas such a peak appeared for  $\tau = 10$  s. The height of this peak was found to increase with further increasing  $\tau$  (Fig. 5, curves 3–6). Furthermore, the height of the current peak attributed to silver dissolution somewhat diminished when  $\tau$  was extended from 2 to 10 s and, thereafter, it remained almost constant irrespective of further increase in  $\tau$ .

As in the previous case, a dissimilarity between  $Q_c$  and  $Q_a$  and, in addition, an increase in the magnitude of  $Q_c - Q_a$  with increasing  $\tau$  were observed (Table 3). Besides, a calculation analogous to the above described showed that the deposit subjected to the stripping in the potential range corresponding to copper ionization may contain from  $85 \pm 2$  at.% of silver when  $\tau = 10$  s to approximately 67 at.% when  $\tau = 100$  s. The quantitative composition of the overlayer remained unchanged with further increasing  $\tau$  up to 500 s.

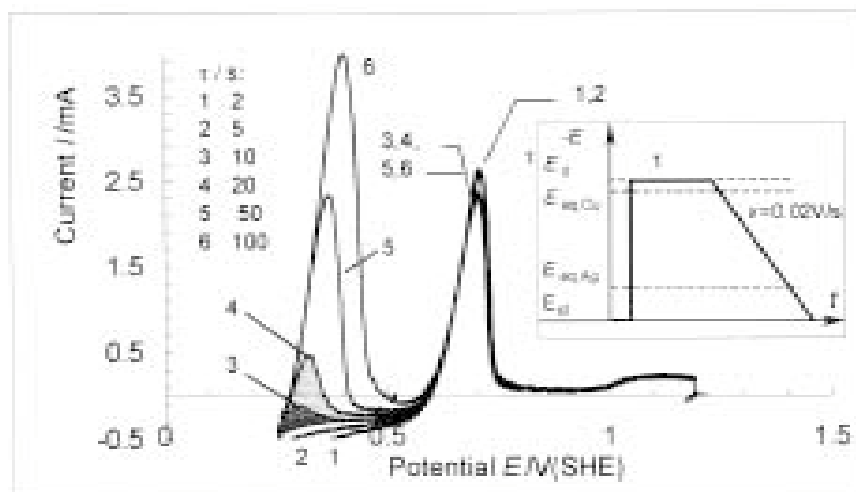


Fig. 5. Anodic stripping voltammetric curves at Pt electrode covered with an overlayer freshly deposited from 0.5 M  $\text{H}_2\text{SO}_4$  + 0.1 M  $\text{CuSO}_4$  +  $4.8 \cdot 10^{-3}$  M  $\text{Ag}_2\text{SO}_4$  solution by the potential step of different duration from  $E_{st} = 1.0$  V to the deposition potential  $E_d = 0.252$  V corresponding to the copper overpotential  $\eta_c = 0.04$  V

Table 3. Variation of the cathodic total charge, the difference between cathodic and anodic total charges and the anodic partial charges for dissolution of silver and copper with the duration of overlayer deposition onto Pt electrode. Solution: 0.5 M  $\text{H}_2\text{SO}_4$  + 0.1 M  $\text{CuSO}_4$  +  $4.8 \cdot 10^{-3}$  M  $\text{Ag}_2\text{SO}_4$ . Calculation of charges as in Table 2

$\tau/s$	$Q_c/mC$	$(Q_c - Q_a)/mC$	$Q_{a,Ag}/mC$	$Q_{a,Cu}/mC$
2	11	0.5	$10.5 \pm 0.2$	0
5	11.6	0.8	$10.3 \pm 0.2$	0
10	12.4	1.7	$9.0 \pm 0.2$	$0.6 \pm 0.1$
20	17.4	4.2	$9.0 \pm 0.2$	$2.0 \pm 0.2$
50	34.4	12.7	$9.0 \pm 0.2$	$11 \pm 0.5$
100	55	23	$9.0 \pm 0.2$	$22 \pm 0.5$

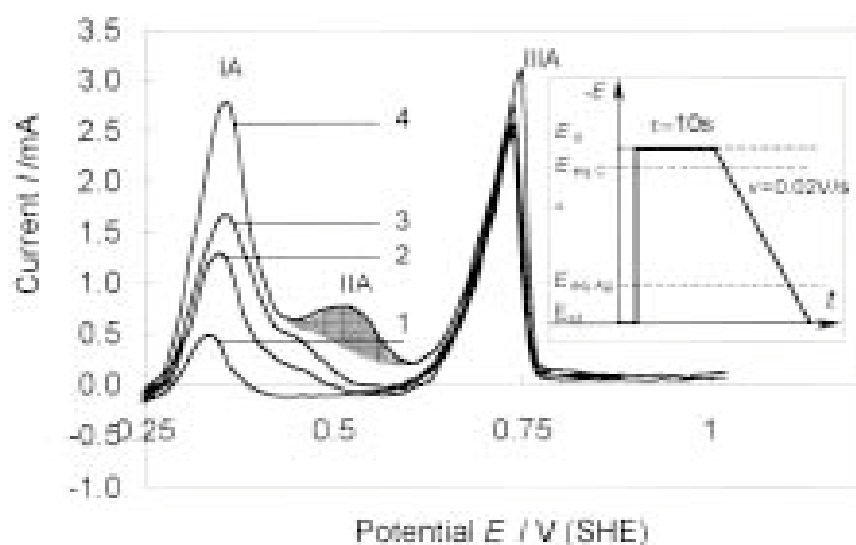


Fig. 6. Anodic stripping voltammetric curves at Pt electrode covered with an overlayer freshly deposited from 0.5 M  $\text{H}_2\text{SO}_4$  + 0.01 M  $\text{CuSO}_4$  +  $4.8 \cdot 10^{-3}$  M  $\text{Ag}_2\text{SO}_4$  solution by the potential step at the pulse length of 10 s from  $E_{st} = 1.0$  V to  $E_d$ : 1 - 0.225, 2 - 0.205, 3 - 0.185 and 4 - 0.065 V

A separate experiment was conducted in an effort to confirm a possibility of the deposition of a compact overlayer with a high content of silver and also to prove the assumption as to the dissolution of the part of silver in the form of uncharged species. The electrode was first covered with a metal overlayer at  $E_d = 0.252$  V for 500 s, further it was rinsed thoroughly with doubly distilled water and, finally, was transferred into an electrochemical cell of small volume (of the order of 10 cm<sup>3</sup>) with the supporting 0.5 M  $\text{H}_2\text{SO}_4$  solution and immediately subjected to a linear potential sweep at 10 mV s<sup>-1</sup> from 0.23 to 0.5 V. After such

a procedure, no  $\text{Ag}^+$  ions were detected by an addition of some drops of a HCl solution. What is more, addition of 2 ml of concentrated  $\text{HNO}_3$  under stirring caused this solution to become turbid after 1–2 min, thus indicating the  $\text{Ag}^+$  ions to be already formed.

The anodic stripping curves displayed in Figs. 4 and 5 showed that in no case there was an additional current peak which could be likely related to the dissolution of alloy  $\text{Cu}_x\text{Ag}_y$ , as was obtained when the overlayer deposited freshly under the potentiodynamic conditions was subjected to stripping (Fig. 1). So, deposition of the overlayer at a constant potential (Figs. 4, 5) somewhat contrasted with that performed using potential sweeps as to the subsequent stripping of the respective layers. At the same time such a current peak was found to become revealable, if the working solution containing a smaller amount of  $\text{Cu}^{2+}$  ions was applied for the experiment (Fig. 6).

## CONCLUSIONS

In this preliminary work, it has been demonstrated that two current peaks related to silver and copper deposition from acidic sulphate solutions containing  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  ions onto a platinum electrode are observed on the cathodic-going potential scan. The anodic scan shows

the occurrence of three peaks which can be attributed to the dissolution of copper and silver and likely of alloy  $Cu_xAg_y$ .

When the deposition of the overlayer is carried out at a constant potential, the composition of this overlayer, in particular the copper and silver contents ratio, was found to depend on both the values of deposition potential and the duration of deposition. The dependence of the cathodic and anodic charge ratio on some factors, including the deposition potential and duration of deposition, was interpreted in terms of dissolution of a certain part of deposited silver in the form of uncharged species.

Received  
15 May 2000  
Accepted  
10 July 2000

#### References

1. A. R. Despic, in *Comprehensive Treatise of Electrochemistry*, Vol. 7 (Eds. B. E. Conway, J. O'M. Bockris, E. Yeager, S. U. M. Khan, and R. E. White), Chapt. 7 (Part B), Plenum Press, New York–London (1983).
2. Yu. D. Gamburg, *Electrochemical Crystallization of Metals and Alloys*, Janus-K, Moscow (1997) (in Russian).
3. S. S. Kruglikov, V. I. Kharlamov and T. A. Vagramyan, *Trans. Inst. Metal Finish.*, **74**, 18 (1996).
4. Q. Xue and W. Zhang, *J. Phys. D: Appl. Phys.*, **30**, 3301 (1997).
5. T. A. Green, A. E. Russel and S. Roy, *J. Electrochem. Soc.*, **145**, 875 (1998).
6. J.-P. Celis, P. Cavallotti, J. Machado Da Silva and A. Zielonka, *Trans. Inst. Metal Finish.*, **76**, 163 (1998).
7. S. Cere, M. Vasquez, S. R. de Sanchez and D. J. Schiffrin, *J. Electroanal. Chem.*, **470**, 31 (1999).
8. S. Stucki, *J. Electroanal. Chem.*, **78**, 31 (1977).
9. V. V. Povetkin, Y. V. Ratz and Y. I. Ustinovshchikov, *Elektrokhimiya*, **30**, 26 (1994).
10. H. Angerstein-Kozłowska, B. E. Conway and W. B. A. Sharp, *J. Electroanal. Chem.*, **43**, 9 (1973).
11. B. E. Conway, H. Angerstein-Kozłowska and W. B. A. Sharp, *Analyt. Chem.*, **45**, 1331 (1973).
12. T. Biegler, D. A. J. Rand and R. Woods, *J. Electroanal. Chem.*, **29**, 269 (1971).
13. S. Fletcher, *Electrochim. Acta*, **28**, 917 (1983).
14. G. Gunawardena, G. Hills and I. Montenegro, *J. Electroanal. Chem.*, **138**, 241 (1982).
15. J. P. Sousa, *J. Electroanal. Chem.*, **372**, 151 (1994).
16. D. R. Salinas, E. O. Cobo, S. G. Garcia and J. B. Bessone, *J. Electroanal. Chem.*, **470**, 120 (1999).
17. G. W. Tindall and S. Bruckenstein, *J. Electroanal. Chem.*, **22**, 367 (1969).
18. B. Scharifker and G. Hills, *Electrochim. Acta*, **28**, 879 (1983).
19. L. Heerman and A. Tarallo, *J. Electroanal. Chem.*, **470**, 70 (1999).
20. V. Karpavičienė and V. Kapočius, *Chemija (Vilnius)*, Nr. 2, 56 (1997).

V. Kapočius, V. Karpavičienė ir A. Steponavičius

#### VOLTAMPERMETRINIAI VARIO IR SIDABRO ELEKTRONUSODINIMO ANT Pt ELEKTRODO IR ANODINIO TIRPINIMO DĖSNINGUMAI SULFATINIULOSE TIRPALUOSE

S a n t r a u k a

Linijinio potencialo skleidimo ir potenciostatinio įjungimo metodais tirtas bendras vario ir sidabro elektronusodinimas ant glotnaus Pt elektrodo iš rūgščių sulfatinių tirpalų. Nusodintų sluoksnių apytikrė sudėtis buvo nustatoma anodiškai juos tirpinant. Parodyta, kad katodiniame cikle stebimi du srovės maksimumai, sąlygojami tūrinio sidabro ir vario elektronusodinimo. Anodinio ciklo metu stebimi trys srovės maksimumai, kurie susiję su vario, sidabro ir, matomai,  $Cu_xAg_y$  tirpimu. Nustatyta, kad potenciostatinio įjungimo metodu nusodintų sluoksnių sudėtis priklauso ne tik nuo poliarizacijos dydžio, bet ir nuo elektronusodinimo laiko trukmės. Spėjama, kad neatitikimas tarp krūvių katodinio ir anodinio ciklo metu gali būti susijęs su tuo, kad dalis nusodinto sidabro anodinio ciklo metu pervedama į tirpalą nejonizuotoje būklėje.

В. Капочюс, В. Карпавичене и А. Степонавичюс

#### ВОЛЬТАМПЕРОМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ СОВМЕСТНОГО РАЗРЯДА И АНОДНОГО РАСТВОРЕНИЯ МЕДИ И СЕРЕБРА НА Pt ЭЛЕКТРОДЕ В СЕРНОКИСЛЫХ РАСТВОРАХ

Р е з ю м е

Методами вольтамперометрии и хроноамперометрии исследовано совместное электроосаждение серебра и меди на гладком Pt электроде в сернокислых растворах. Предварительная оценка состава гальваноосадков определена по анодным поляризационным кривым. Показано, что в катодном полуцикле наблюдаются два максимума тока, связанные с электроосаждением меди и серебра, а во время анодного полуцикла наблюдается три максимума тока, вызванные растворением меди, серебра и, предположительно, сплава  $Cu_xAg_y$ . Состав электроосадков, полученных методом потенциостатического замыкания цепи, зависит не только от величины поляризации, но и от продолжительности процесса электроосаждения. Предполагается, что несоответствие между зарядами в катодном и анодном полуциклах связано с тем, что некоторая часть серебра во время анодного растворения переходит в раствор в нейонизированном состоянии.