

VILNIUS UNIVERSITY

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THE KINETICS OF SILVER ELECTRODEPOSITION FROM SULFITE
SOLUTIONS

Summary of doctoral dissertation

Physical sciences, chemistry (03 P)

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The dissertation is available at the Library of Vilnius University and the Library of Institute of Chemistry.

VILNIAUS UNIVERSITETAS

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1. Introduction

Silver electrodeposition from sulfite electrolytes is considered to be one of the most promising processes to replace the extremely toxic traditional cyanide-based silver plating solutions with the additional advantage, that sulfite electrolytes can be successfully applied for silver deposition for micro-electro-mechanical systems (MEMSs). Mechanism of metal complexes electroreduction is an important result, especially when it may have a wide range of applications in the future. However, electrodeposition also has several shortcomings, including sulfite ion oxidation by oxygen in air and relatively negligible cathodic current densities, which are too low for qualitative galvanotechnique.

There are very few works dedicated to the chemistry and electrochemistry of silver sulfite complexes. Most publications related with this subject are concerned with the questions of applicability.

The main objective of this study was the investigation the electroreduction kinetics of the silver sulfite complexes. To achieve this goal, we studied the dependence of the exchange current density on the free sulfite ions concentration in a series of isopotential solutions. Our studies also allowed to determine the mechanism of this electrochemical charge transfer reaction.

The main aims of the work were as follows:

1. Study of kinetics and mechanism of silver discharge from sulfite complexes.
2. Assess potential for practical use of specific plating electrolytes.

The specific goals of the study were:

1. Determination of silver electrode potential change on time under different galvanostatic conditions, including extrapolation to $t = 0$.
2. Derivation of equations that describe the potential change.
3. Determination of diffusion overvoltage from experimental chronoamperometric and chronopotentiometric curves.

4. Analysis of silver ad-atom crystallization and charge transfer data.
5. Analysis of exchange current density dependence on the free sulfite ions concentration.
6. Determination of the reaction order and mechanism of the electrochemical reaction.
7. Determination of the silver coatings properties.
8. Analysis of the chemical compositions of the silver layer domains.

Statements for defence:

1. The electroreduction of silver sulfite leads to slow crystallization of metal ad-atoms. Mathematical analysis of the time dependence of the diffusion overvoltage was used to eliminate the impact of slow crystallization. By using this approach, we established that $AgSO_3^-$ species participate in the charge transfer reaction in this system.
2. Using sulfite plating electrolyte, we obtained silver coatings of high quality.

2. Experimental: Reagents, solutions, electrodes

The solutions were prepared based on distilled water applying p.a. qualification Na_2SO_3 and Ag_2SO_4 . The electrolytes were prepared freshly before every new experimental series, relating to quite rapid sulfite ion oxidation by air oxygen. All experiments were performed at 20°C temperature.

Chronoamperometric, chronopotentiometric and voltamperometric studies were performed using μ AUTOLAB (Type III) measurements system with an ordinary three-electrode cell. The working electrode was a silver wire of 0,5 mm in diameter. The counter electrode was made of an Ag spiral of 40 cm². The reference electrode was a saturated Ag/AgCl, KCl electrode, placed as close as possible to the working electrode by means of a Luggin capillary. In this work, all potentials are referred to the scale of the standard hydrogen electrode: $E_{(0)} = E_{Ag/AgCl} + 0,2 V$.

Deposition of silver was performed galvanostatically or with a pulse current at 5 mA·cm⁻² on copper and silver plates using the AUTOLAB 302 system and the control

device program for a computer GPS. Surface morphology was investigated with the scanning electron microscopes LEO 435VP and Philips XL 30 ft. 6.

The calculated thickness of the silver layer was close to $10 \mu\text{m}$.

3. Results and discussion

3.1 Kinetics of the electrochemical reaction

The chronoamperometry was chosen for j_0 experimental determination. It is known that in the cases when the process rate is determined by a charge-transfer step and slow diffusion of electroactive particles, experimentally determined $j-t$ dependences have to decrease consistently. In our investigated system the change of current density is different type (Fig. 1,2). Only in Fig. 2 curve 4, when polarization of electrode is 0.1 V , $j-t$ dependence is similar to classical.

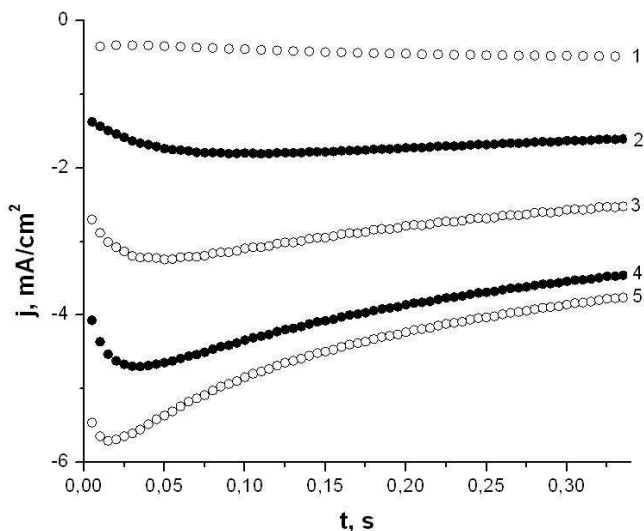


Fig. 1. Chronoamperograms of silver sulfite complexes. Solution composition (M): $\text{Ag(I)} - 0.05$; $\text{Na}_2\text{SO}_3 - 0.49$. Polarization of electrode (V): 1 - 0.02, 2 - 0.03, 3 - 0.04, 4 - 0.05, 5 - 0.06.

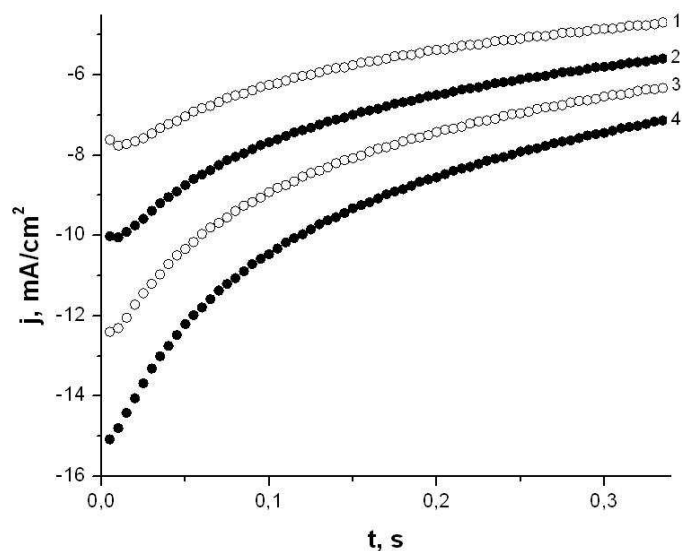


Fig. 2. Chronoamperograms of silver sulfite complexes. Solution composition (M): $Ag(I) - 0.05$; $Na_2SO_3 - 0.49$. Polarization of electrode (V): 1 – 0.07, 2 – 0.08, 3 – 0.09, 4 – 0.1.

The observed current change on time is possible due to a slow crystallization of metal ad-atoms.

For further study chronopotentiometry was used. Using this method more accurate data can be obtained.

The chronopotentiometry can be chosen for j_0 experimental determination as well. In many cases, the measured electrode polarization consisted of charge transfer and diffusion overvoltage sum. Since the diffusion overvoltage depends on time, its input in the total electrode polarization should be eliminated using coordinates $\Delta E - t^{1/2}$. Investigating systems without complex ions, the extrapolation of straights obtained in these coordinates towards $t^{1/2} = 0$, enabled us to determine the exact values of the charge transfer overvoltage.

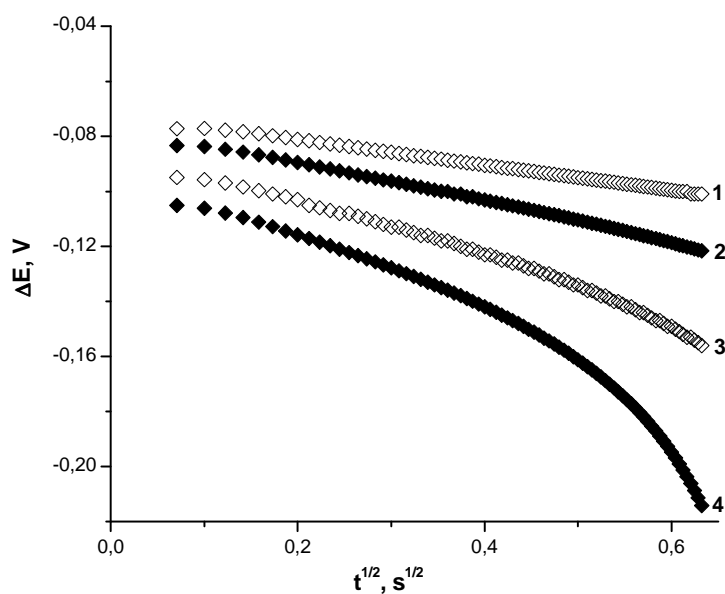


Fig. 3. Dependences of the silver electrode polarization on time. Solution composition (M): $Ag(I) - 0.1$; $Na_2SO_3 - 0.77$. Cathodic current densities used ($mA \cdot cm^{-2}$): 1 – 10; 2 – 14; 3 – 18; 4 – 22.

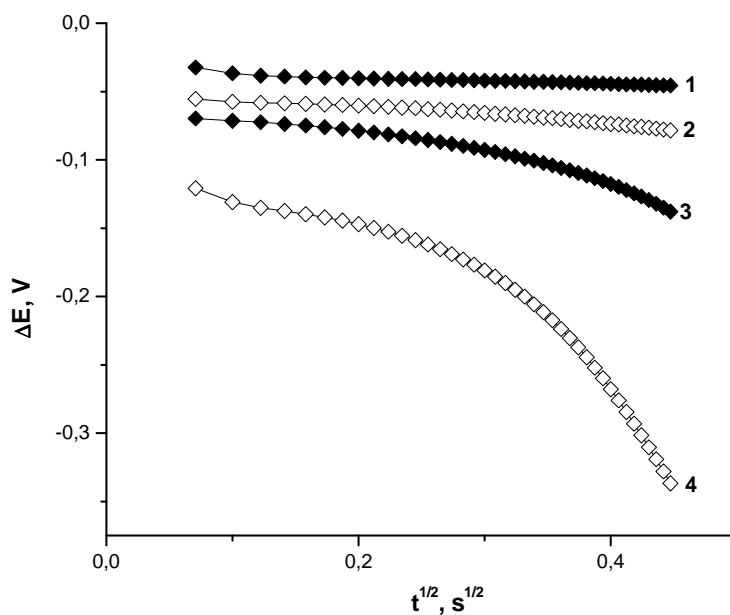


Fig. 4. Dependences of the silver electrode polarization on time. Solution composition (M): $Ag(I) - 0.01$; $Na_2SO_3 - 0.2$. Cathodic current densities used ($mA \cdot cm^{-2}$): 1 – 10; 2 – 14; 3 – 18; 4 – 20.

From Fig. 3 and Fig. 4, it is seen that in our investigated system (even when solution composition is different) the experimentally determined $\Delta E - t^{1/2}$ dependences are not linear, so the elimination of diffusion impact becomes problematical. Herewith, the determination of the charge transfer overvoltage becomes complicated. Whereas our investigated electrochemical reaction proceeds in the presence of complex ions, we attempted to determine the influence of diffusion on the total electrode polarization by derivating an equation, which estimated not only metal complexes, but also free ligand ion impact on the diffusion overvoltage change in time. In this case, one can use the Nernst equation, written for the system metal/metal ions:

$$E = E_0 + (RT / zF) \ln[Ag^+] \quad (1).$$

We can express the value of ion concentration from dissociation constant by equation:

$$[Ag^+] = K([Ag(SO_3)_x]^{1-2x} / [SO_3^{2-}]^x) \quad (2).$$

In this electrochemical system $z=1$ for silver. Introducing this into the Nernst equation we obtain:

$$E = E_0 + (RT / F) \ln K + (RT / F) \ln[Ag(SO_3)_x^{1-2x}] - (xRT / F) \ln[SO_3^{2-}] \quad (3).$$

When a galvanostatic impulse is used the potential of silver electrode is determined by surface concentrations of silver sulfite complexes and free sulfite ions (marked by index "s"):

$$E_{(j,t)} = E_0 + (RT / F) \ln K + (RT / F) \ln[Ag(SO_3)_x^{1-2x}]^s - (xRT / F) \ln[SO_3^{2-}]^s \quad (4).$$

From literature data it is known that total change of silver electrode polarization assigned to diffusion overvoltage:

$$\Delta E_{dif} = (RT / F) \ln[Ag(SO_3)_x^{1-2x}]^s - (xRT / F) \ln[SO_3^{2-}]^s - (RT / F) \ln[Ag(SO_3)_x^{1-2x}]^o + (xRT / F) \ln[SO_3^{2-}]^o \quad (5).$$

We can rearrange (5) equation as follows:

$$\Delta E_{dif} = (RT / F) \ln([Ag(SO_3)_x^{1-2x}]^s / [Ag(SO_3)_x^{1-2x}]^o) - (xRT / F) \ln([SO_3^{2-}]^s / [SO_3^{2-}]^o) \quad (6).$$

If the current passing through the electrochemical system is low enough or the duration of the process is short enough: $2j / zFC^0 \sqrt{t / \pi D} \ll 1$, the concentration

dependence on time and the current density of the cathodic process can be expressed by a simplified Sand equation:

$$\begin{aligned} [Ag(SO_3)_x]^{1-2x}]^s &= [Ag(SO_3)_x]^{1-2x}]^o - (2j/F)\sqrt{t/\pi D_o} \\ [SO_3^{2-}]^s &= [SO_3^{2-}]^o + (x2j/F)\sqrt{t/\pi D_o} \end{aligned} \quad (7),$$

where D_o is the diffusion coefficient of an oxidized form. Then (7) equation can be rewritten as follows:

$$\begin{aligned} [Ag(SO_3)_x]^{1-2x}]^s / [Ag(SO_3)_x]^{1-2x}]^o &= 1 - (2j/F[Ag(SO_3)_x]^{1-2x}]^o) \\ [SO_3^{2-}]^s / [SO_3^{2-}]^o &= 1 + (x2j/F[SO_3^{2-}]^o)\sqrt{t/\pi D_o} \end{aligned} \quad (8).$$

Introducing the obtained expressions into (6) equation, we find that the electrode polarization for the cathodic and anodic processes respectively is equal:

$$\Delta E_{dif} = RT/zF \left[\begin{aligned} &\ln \left(1 \pm \frac{2jF[Ag(SO_3)_x]^{1-2x}]^o}{\sqrt{t/\pi D_o}} \right) - \\ &- x \ln \left(1 \pm \frac{2jF[SO_3^{2-}]^o}{\sqrt{t/\pi D_o}} \right) \end{aligned} \right] \quad (9).$$

Performing calculations, it is convenient to use a notation: $a = 2/(nF\sqrt{\pi D_o})$. Then (9) equation can be rewritten as follows:

$$\Delta E_{dif} = RT/F \left[\begin{aligned} &\ln \left(1 \pm \frac{aj/[Ag(SO_3)_x]^{1-2x}]^o}{\sqrt{t}} \right) - \\ &- x \ln \left(1 \pm \frac{axj/[SO_3^{2-}]^o}{\sqrt{t}} \right) \end{aligned} \right] \quad (10).$$

By calculating the diffusion overvoltage of the cathodic process of the electrochemical reaction under study, the „ – “ sign has to be written in the first term under the logarithm, because the total concentration of free sulfite ions increases during the cathodic process. The signs in the terms under the logarithms should be opposite for the case of an anodic process.

In order to use the obtained equation (10), it is necessary to determine the silver complexation degree x and the complex diffusion coefficient D_o . Both these parameters depend on the solution composition.

In a system of silver-silver sulfite complexes the complexity degree could vary from 2 to 3. Thus, we can write:

$$x = 2 + [Ag(SO_3)_3^{5-}] / A = 2 + [SO_3^{2-}] / [SO_3^{2-}] + K \quad (11).$$

Under boundary conditions, if $[Ag(SO_3)_3^{5-}]$ is not composed, i.e. when $[Ag(SO_3)_3^{5-}] = 0$, thus $x = 2$, and if $[Ag(SO_3)_3^{5-}]$ is present in a maximum amount, we get $[Ag(SO_3)_3^{5-}] = A$ and $x = 3$.

Concentration of free sulfite ions can be calculate from material balance equations:

$$\begin{aligned} K \cdot [Ag(SO_3)_3^{5-}] &= [Ag(SO_3)_2^{3-}] \cdot [SO_3^{2-}] \\ [Ag(SO_3)_3^{5-}] + [Ag(SO_3)_2^{3-}] &= A \\ [SO_3^{2-}] + 2[Ag(SO_3)_2^{3-}] + 3[Ag(SO_3)_3^{5-}] &= L \end{aligned} \quad (12).$$

When constant of complex formation is large, we can calculate the concentration of free sulfite ions using equation:

$$[SO_3^{2-}] = (L - K_1 - 3A) / 2 + \sqrt{(L - K_1 - 3A)^2 / 2 + K_1(L - 2A)} \quad (13).$$

In this case concentration of free silver ions can be calculated from equation:

$$[Ag^+] = (AK_1K_2) / K_1[SO_3^{2-}]^2 + [SO_3^{2-}]^3 \quad (14).$$

By using equation (11), it is simple to calculate the degree of complexation of silver–silver sulfite complexes in the all isopotential solutions under consideration (Table 1). Since the layer composition near electrode changes during the experiments, the degree of complexation depends on time as well. We have derived the corresponding equations, but the calculations corresponding showed that a change of x on time has a negligible influence on the calculated values of ΔE_{dif} . Therefore, we do not present these equations here.

Table 1. Composition of isopotential solutions ($E_{(0)} = 0.300$ V) and parameters of electrochemical system.

No.	Solution composition, M		System parameters				
	$Ag(I)$	Na_2SO_3	$[SO_3^{2-}]$, M	$[Ag(SO_3)_2^{3-}]$, M	$[Ag(SO_3)_3^{5-}]$, M	$D_o \cdot 10^6$, cm^2s^{-1}	x
1.	0.003	0.115	0.108	0.002	0.0009	5.54	2.31
2.	0.01	0.2	0.176	0.006	0.004	5.45	2.41
3.	0.03	0.33	0.255	0.015	0.015	4.97	2.51
4.	0.05	0.49	0.359	0.02	0.029	4.33	2.59
5.	0.1	0.77	0.499	0.033	0.067	3.36	2.67

The diffusion overvoltage of silver sulfite complexes could be simply evaluated knowing all values presented in equation (9) or equation (10). Furthermore, following these equations, even before performing detailed calculations, a conclusion suggested itself that in the case of complex solutions, the dependences $\Delta E_{dif} - t^{1/2}$ should not be necessary linear. As seen from the data presented in Fig. 5, the dependences of the electrode polarization on time are linear only at small current densities and only in short time regions.

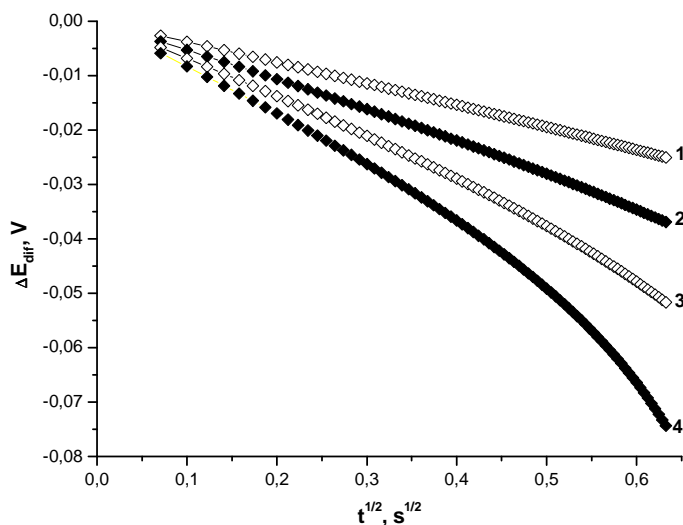


Fig. 5. Dependences of the diffusion overvoltage calculated via Eq. (9) or Eq. (13) on the time. Solution composition and used cathodic current densities as in Fig. 3.

For the further analysis, the charge transfer overvoltage (E_{ct}) was found from the experimentally measured total electrode polarization by eliminating the calculated diffusion overvoltage.

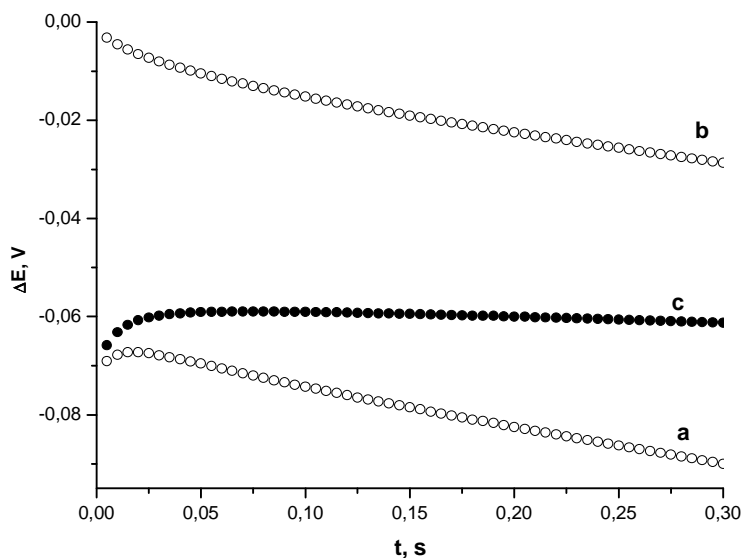


Fig. 6. Chronopotentiograms of silver sulfite complexes: *a* – experimentally determined, *b* – calculated via Eq. (9) or Eq. (10), *c* – difference between *a* and *b*. Solution composition (*M*): $Ag(I) - 0.05$; $Na_2SO_3 - 0.49$. Cathodic current density: $8 \text{ mA}\cdot\text{cm}^{-2}$.

As seen from Fig. 6, curve **c** was obtained practically as time-independent polarization value, which attributed to the charge transfer overvoltage. Thus, there appears a possibility to avoid a fairly problematical non-linear data extrapolation.

To show the impact of silver ad-atom crystallization overvoltage, we chose the solution with relatively negligible sodium sulfite amount (solution composition $Ag(I) - 0.05 \text{ M}$, $Na_2SO_3 - 0.49 \text{ M}$). As shown in Fig. 7, the deviation from the charge transfer and diffusion overvoltage gained maximum when cathodic current density is $8 \text{ mA}\cdot\text{cm}^{-2}$ (curve 1). When cathodic current is 10 (curve 2) and $12 \text{ mA}\cdot\text{cm}^{-2}$ (curve 3), the deviation is smaller. As charge transfer overvoltage must be independent of time, all deviation is attributed to the crystallization overvoltage.

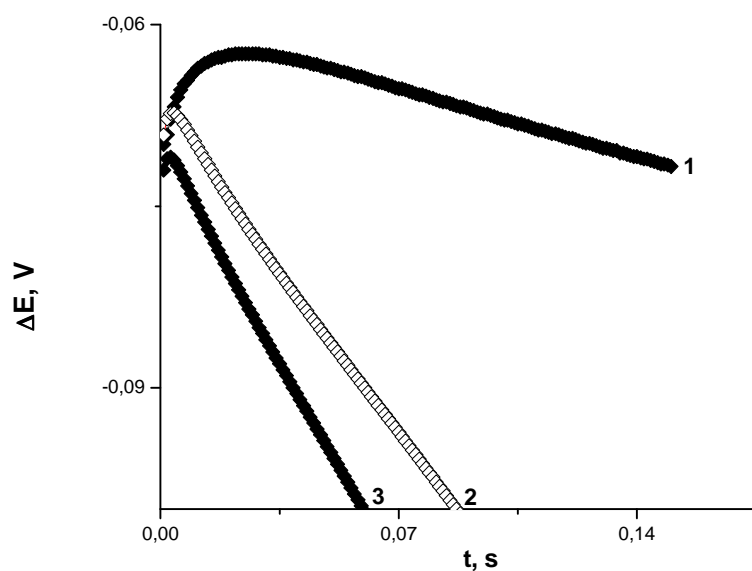


Fig. 7. Polarization of silver electrode in time. Solution composition (M): $Ag(I) - 0.05$; $Na_2SO_3 - 0.49$. Cathodic current densities used ($mA \cdot cm^{-2}$): 1 – 8, 2 – 10, 3 – 12.

Changing the cathodic current densities for all isopotential solutions, the charge transfer overvoltages varying from -60 mV to -160 mV were determined. Since in the obtained overvoltage region Tafel dependences ($\ln j - \Delta E_{ct}$) are not entirely valid, the Allen-Hickling coordinates ($\ln Y - \Delta E_{ct}$) were used.

Fig. 8 shows that these dependences are linear. The extrapolation of these dependences towards $\Delta E = 0$ allows to calculate the exchange current densities of the electrochemical reaction. The determined values vary from $0.9 \text{ mA} \cdot \text{cm}^{-2}$ (when the solution is prepared with $0.003 \text{ M } Ag(I)$ and $0.115 \text{ M } Na_2SO_3$) to $2.46 \text{ mA} \cdot \text{cm}^{-2}$ (when the solution is prepared with $0.1 \text{ M } Ag(I)$ and $0.77 \text{ M } Na_2SO_3$).

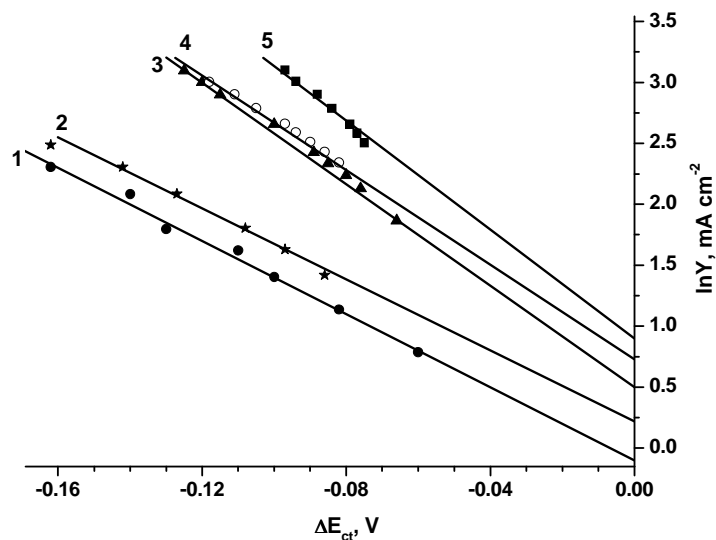


Fig. 8. Dependences of cathodic current density on the polarization of the silver electrode in coordinates of Allen-Hickling. Numbers on the lines correspond to solution numbers presented in the Table 1.

In order to identify the composition of the complex particle, which directly participates in the charge transfer stage, the dependence of the determined exchange current densities on free sulfite ions concentration was plotted in coordinates $\ln|j_0| - \ln[SO_3^{2-}]$ (Fig. 9).

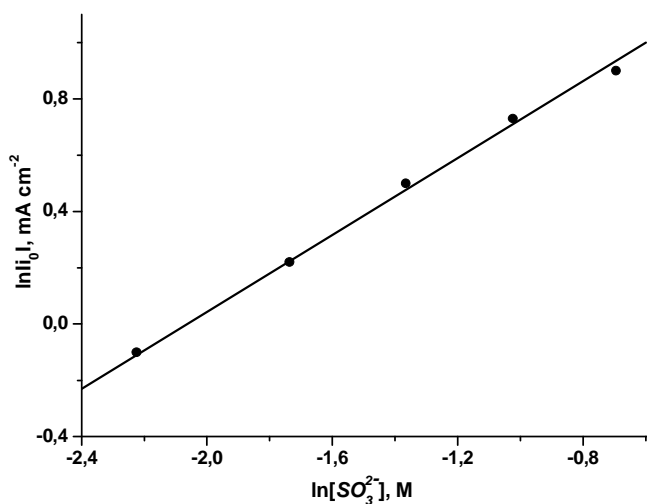
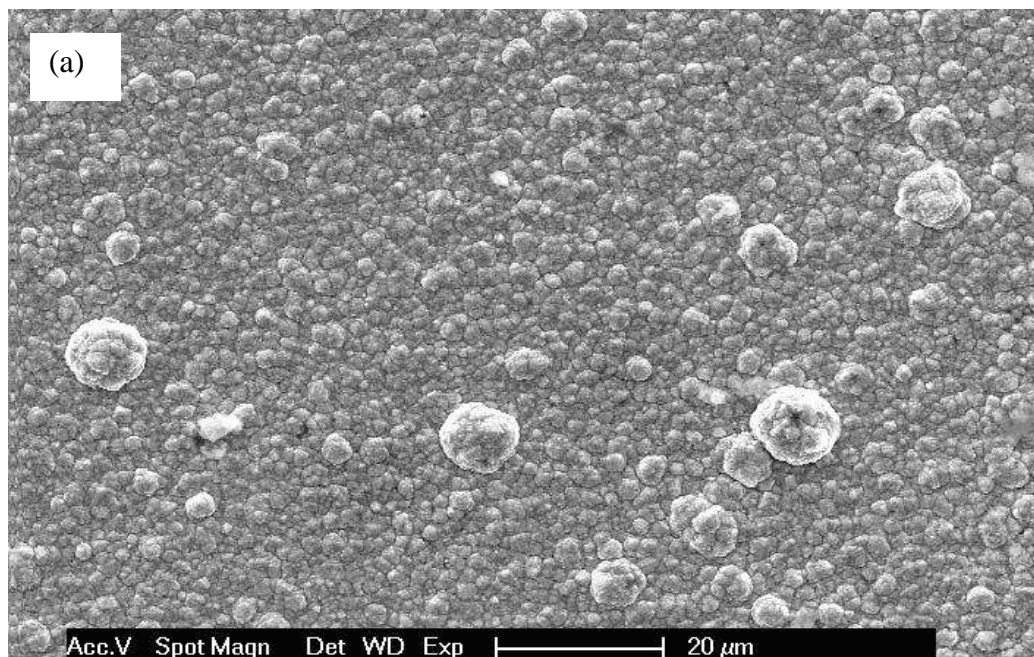


Fig. 9. Dependence of the exchange current density on the free sulfite ions concentration.

In this figure, one can easily find the reaction order to be equal to 0.67. This result suggests that an unambiguous conclusion concerning the investigated electrochemical system mechanism is impossible to explain. Probably, the particle $AgSO_3^-$ participates in the charge transfer reaction and distortions are caused by the adsorption of sulfite ions or slow electrocrystallization of Ag, which was not taken into account here.

3.2 Study of silver electroplating coatings deposited from sulfite solutions

We studied galvanic silver layers deposited from aqueous sulfite solutions. We investigated such layers using scanning electron microscopy (SEM). Fig. 10 shows the representative SEM images of morphology of silver layers electrodeposited at a constant current ($5 \text{ mA} \cdot \text{cm}^{-2}$) (a) or using a pulse current (b). As can be seen, when a current pulse was used, the linear dimensions of crystals were obtained to be smaller. In particular, the dimensions of silver crystals range from 0.7 to 5 μm (a) and from 0.1 to 0.5 μm (b).



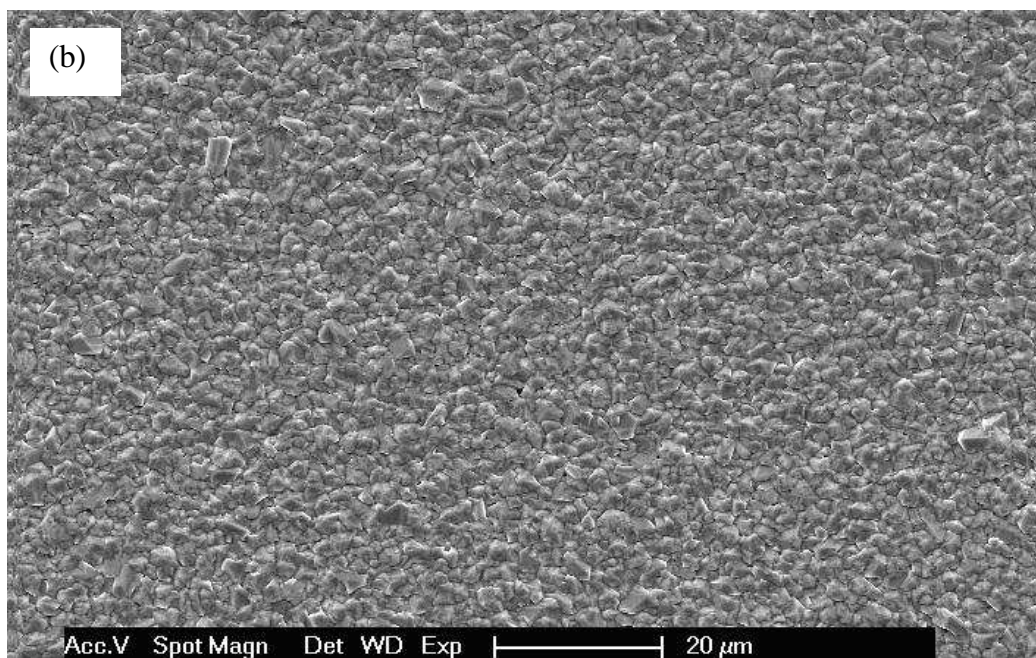


Fig. 10. The SEM images of morphology of silver coatings. Solution composition (M): $\text{Ag}_2\text{SO}_4 - 0.3$, $\text{Na}_2\text{SO}_3 - 2$. Cathodic current density $-5 \text{ mA} \cdot \text{cm}^{-2}$. The current mode – constant (a) or pulse (b).

Closer examination of the SEM images obtained from the surface of silver sample deposited with a pulse current shows that, even in this case, the surface of electrode has some regions where the deposits seems to be of rather inhomogeneous nature (Fig. 11). It is quite possible that the coating consists of pure silver and this inhomogeneity is due to the different orientation of Ag crystals. For more detailed analysis, the different magnifications of SEM images were applied. The part of the obtained results is presented in Fig. 11a and Fig. 11b. It should be mentioned, that in these cases, silver was electrodeposited on the copper substrate.

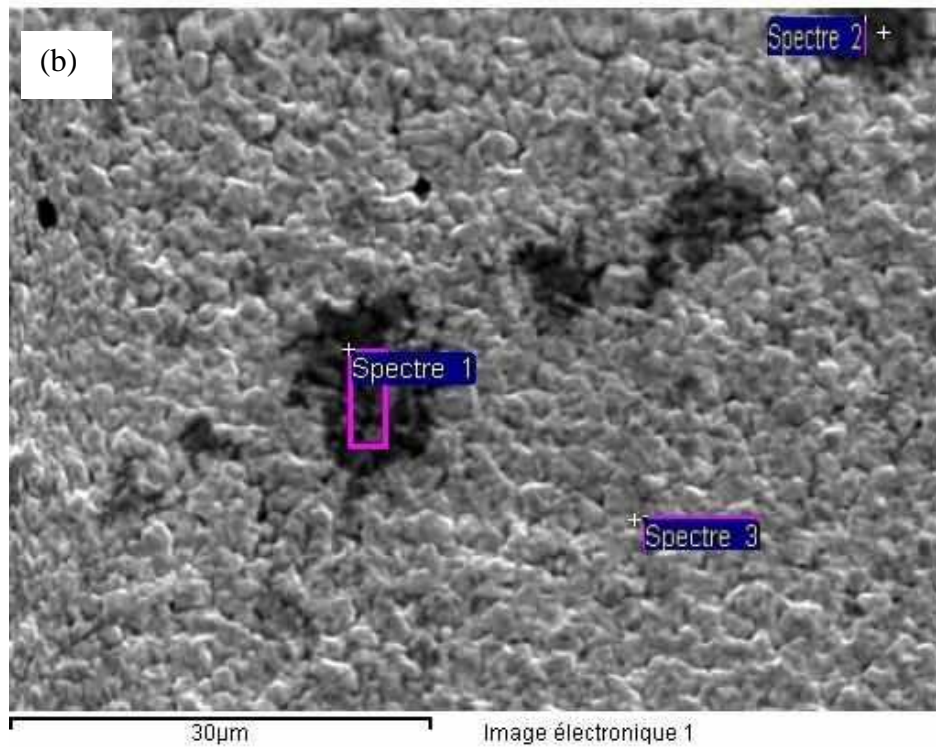
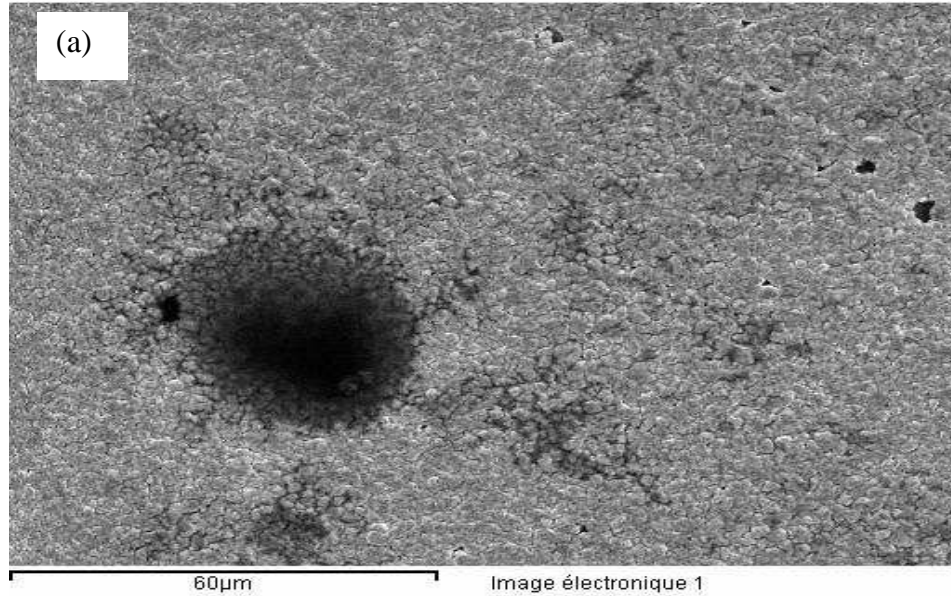
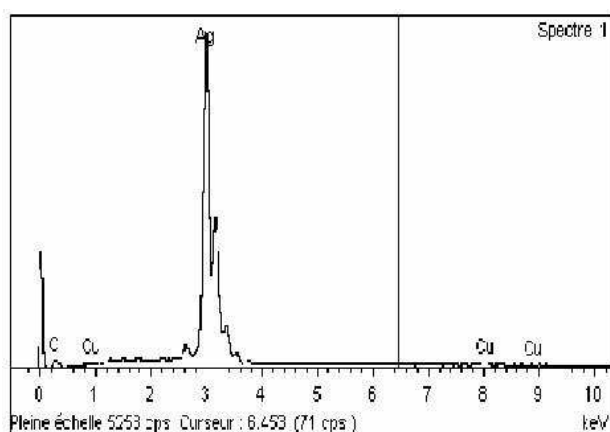
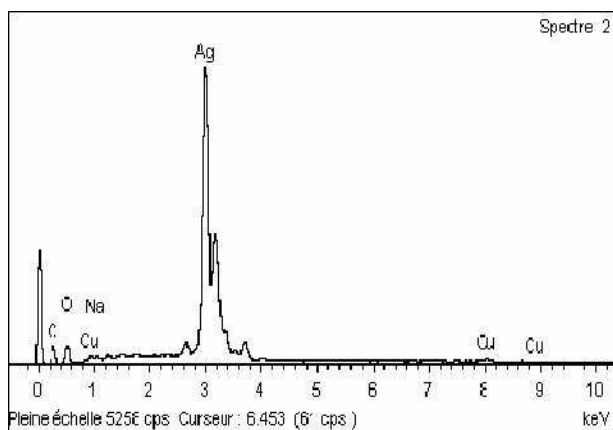


Fig. 11. The SEM images of morphology of silver coating obtained with pulse current at different magnification (copper substrate). Solution composition (M): $\text{Ag}_2\text{SO}_4 - 0.3$, $\text{Na}_2\text{SO}_3 - 2$. Cathodic current density $- 5 \text{ mA} \cdot \text{cm}^{-2}$.

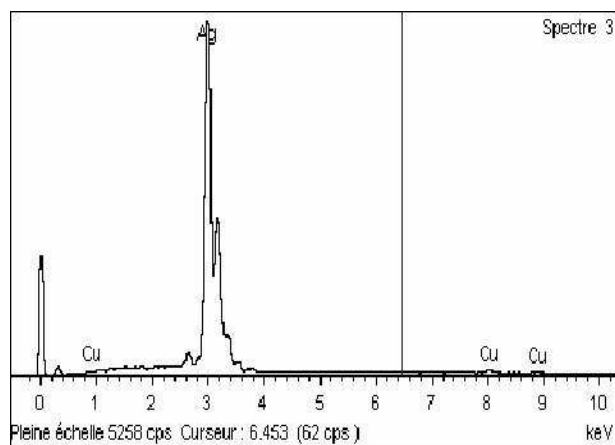
Then, using SEM with X-ray microanalyzer it was found that in the sampled regions, particularly, as shown in Fig. 11b, the indications of the presence of copper were revealed (Fig. 12). Bearing in mind, that copper ions are absent in the working solution and that the deposition of copper from sulphite solutions is rather difficult, it can be concluded that the X-ray microanalyzer fixed the copper phase from the copper substrate. In some cases, the signal indicating the presence of Na in the pore was identified (Fig. 11b). On the basis of our experimental data, this fact can not be reasonable explained.



Elements	Mass. %	Atom. %
Cu	1.64	3.27
Ag	98.36	96.73
Total:	100.00	



Elements	Mass. %	Atom. %
Na	1.55	6.8
Cu	1.97	3.1
Ag	96.48	90.1
Total:	100.00	



Elements	Mass. %	Atom. %
Cu	1.25	2.11
Ag	98.75	97.89
Total:	100.00	

Fig. 12. The elemental compositions of silver deposits determined by SEM with X-ray microanalyzer. These spectra were obtained from the sampled separate regions in Fig. 11b.

Considering the contents of copper in silver coating pores, it can be rather roughly supposed that their values can be approximately correlated with the total area of these pores.

To check additionally whether the determination of Cu signals in the pores of Ag deposits was not caused by the contamination of reagents with the Cu salts the separate experiments were carried out with the pure silver substrate. It was found that, in this case, electrolytical silver was also porous (Fig. 13).

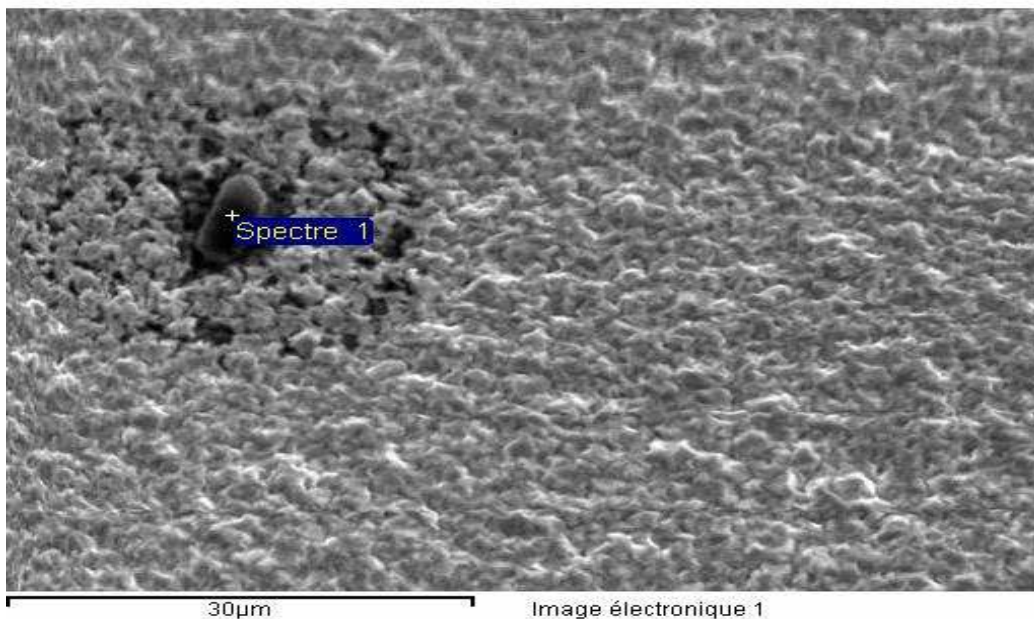


Fig. 13. The SEM images of morphology of silver coating obtained with pulse current at different magnification (silver substrate). Solution composition (M): Ag_2SO_4 – 0.3, Na_2SO_3 – 2. Cathodic current density – $5\text{ mA}\cdot\text{cm}^{-2}$.

However, with the use of the X-ray microanalyzer, it was shown that the elemental composition of the incorporated particles in the pores differs from data for the Ag coatings on the Cu substrate. As can be seen Fig. 14, the signal characteristic of sulphur was revealed in this case. Such a finding is supposed can be due to Na_2SO_3 or its degradation compounds. It is obvious, that such a supposition should be strongly verified in future. The possibility of formation of surface silver sulphide can not be ruled out as well.

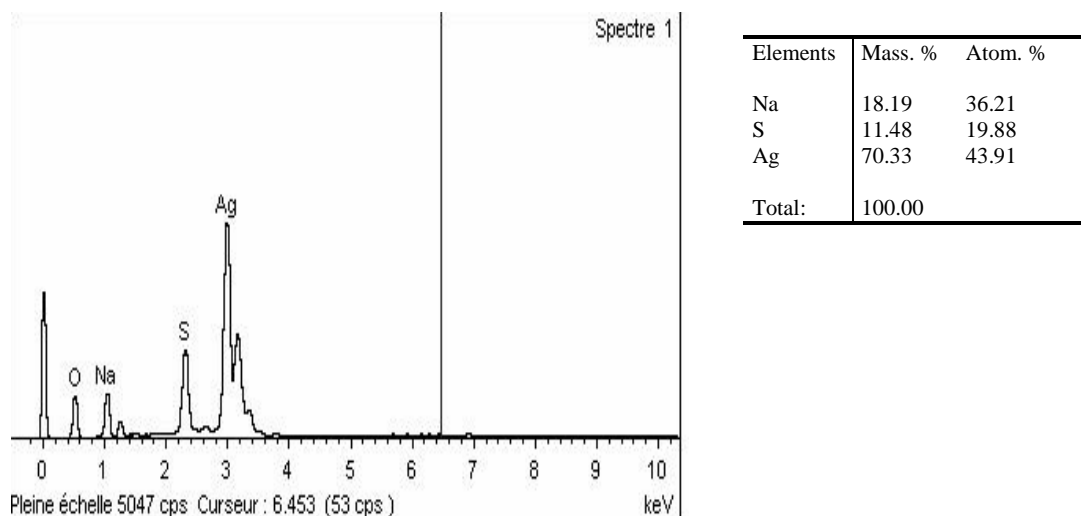


Fig. 14. The elemental compositions of silver deposits determined by SEM with X-ray microanalyzer. These spectra were obtained from the sampled separate region in Fig. 13.

When the sampled region was chosen in the area of homogeneous Ag coating, the same analysis showed 100% pure silver surface.

From the foregoing experimental data we can conclude that when the silver deposition proceeds via the discharge of silver sulphite complexes this coating is of rather good quality. The application of cathodic current pulses was found to increase a degree of microcrystallinity of Ag layers. This fact can be illustrated, particularly, by the decrease of the dimensions of Ag crystals from $0.7 \div 5 \mu\text{m}$ at constant current to $0.1 \div 0.5 \mu\text{m}$ at the pulse current, i.e. approximately 10 times. Unfortunately, it should be stressed that the problem of porosity of Ag coatings electrodeposited from sulphite solutions remains to be unsolved. The porosity of these coatings forms 1 – 3 % of their surface.

CONCLUSIONS

1. Our investigations confirmed published results that electrocrystallization of silver from sulfite solutions mostly depends on slow adsorption of silver atoms at the surface of the galvanic layer. This result is especially clear when potential is in the equilibrium range.

2. The most reliable results in charge-transfer studies were obtained far from the equilibrium potential.

3. The most reliable results in studies of exchange current dependence on concentration isopotentials were obtained when concentrations of silver complexes and sulfite ions ranged from $0.003 < Ag(I) < 0.1$ and $0.108 < [SO_3^{2-}] < 0.499$.

4. Charge transfer overvoltages varying from -60 mV to -160 mV were determined from the cathodic current density. The reaction order was calculated to be equal to 0.67.

5. The calculated reaction order 0.67, enables us to explain the mechanism of electrochemical reaction, i.e. permits to make a suggestion that $AgSO_3^-$ participates in the charge transfer reaction.

6. We successfully obtained microcrystalline galvanic layers by reducing silver sulfite complexes. Such layers have higher quality when pulse current is used.

7. However, even for the best layers, some porosity (ranging between 1 – 3 % in the different regions of the layer) is still present.

The list of Original Publications by the Author

Articles in journals

1. **G. Viselgienė**, G. Baltrūnas, H. Cesiulis, D. Šimkūnaitė. Structural study of Ag layers deposited from the solution of silver sulphite complexes//*Chemija*, **1** (2010) 13 – 16.

2. G. Baltrūnas, A. Valiūnienė, Ž. Margarian, **G. Viselgienė**, G. Popkurov. The electroreduction kinetics of silver sulfite complexes//*Electrochimica Acta*. **53** (2008) 6513 – 6520.

3. G. Baltrūnas, A. Valiūnienė, A. Andruškevič, **G. Viselgienė**. Electroreduction of silver sulphite complexes//*Chemija*, **18** (2007) 7 – 11.

4. A. Valiūnienė, **G. Viselgienė**, Ž. Margarian, G. Baltrūnas, Lėta sidabro elektrokristalizacija iš sulfitinų tirpalų//*Cheminė technologija*, **2** (2007) 29 – 34.

Published contributions to academic conferences

1. G. Baltrūnas, A. Valiūnienė, G. Viselgienė. *Sidabro elektrokristalizacija iš sulfitinių tirpalų*//Neorganinių junginių chemija ir technologija – Kaunas: Technologija, 2007, 61 – 65.
2. G. Baltrūnas, A. Valiūnienė, G. Viselgienė. *Electroreduction of silver sulfite complexes*//Lietuvos 8-oji chemikų konferencija – Vilnius: Chemija, 2007, 61.

CURRICULUM VITAE

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1998 – 2002 Bachelor Studies at Vilnius University – Bachelor Degree in Chemistry.

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SIDABRO ELEKTRONUSODINIMO IŠ SULFITINIŲ TIRPALŲ KINETIKOS TYRIMAS

SANTRAUKA

Naudojant chronopotenciometrijos metodą buvo tirta sidabro elektronusodinio iš sulfitinų tirpalų kinetika. Eksperimentiniai tyrimai patvirtino negausius žinomus literatūrinius duomenis, kad sidabro elektrokristalizacija iš sulfitinų elektrolitų yra apsprendžiama lėta sidabro ad-atomų kristalizacija galvaninės dangos paviršiuje. Tai ypač akivaizdu pusiausvyrinio potencialo srityje. Nustatyta, kad patikimiausi rezultatai, tiriant krūvio pernešimo stadiją, gaunami maksimaliai nutolus nuo pusiausvyros potencialo. Tai lengviausia ir tiksliausia realizuoti chronopotenciometrijos sąlygomis, o nustatytas mainų srovės tankis svyruoja tarp $0,9 \text{ mA/cm}^2$ (kai tirpalo sudėtis $0,003 \text{ M Ag(I)}$ ir $0,115 \text{ M Na}_2\text{SO}_3$) iki $2,46 \text{ mA/cm}^2$ (kai tirpalo sudėtis $0,1 \text{ M Ag(I)}$ ir $0,77 \text{ M Na}_2\text{SO}_3$). Patikimiausi rezultatai buvo gauti matuojant mainų srovės tankių priklausomybes nuo laisvų sulfito jonų koncentracijos izopotencialių ($E_H = 0,300 \text{ V}$) tirpalų serijoje. Visuose izopotencialiuose tirpaluose buvo nustatyti krūvio pernašos viršįtampiai $-60 - -160 \text{ mV}$ intervale. Naudojantis $(\partial \ln j_0 / \partial \ln C_L)_{E_0} = R_L$ lygtimi ir mainų srovės tankio priklausomybės nuo laisvų sulfito jonų koncentracijos grafiku, iš eksperimentinių duomenų nuolinkio kampo apskaičiuotas reakcijos laipsnis $R_L = 0,67$. Atsižvelgiant į galimas paklaidas, tikėtina, kad jis yra lygus 1. Gauti rezultatai rodo, kad artimas vienetai reakcijos laipsnis sulfito jonų atžvilgiu atitinka teiginį, jog betarpiškai fazių sąlyčio riboje redukuojasi kompleksinė dalelė AgSO_3^- . Atsiradusios paklaidos greičiausiai yra susiję su tirpalo komponentų adsorbcijos bei sidabro paviršiaus rekristalizacijos reiškiniais.

Redukuojant sidabro sulfitinius kompleksus, katodo paviršiuje formuojasi gana kokybiška sidabro galvaninė danga. Naudojant impulsinę srovę, sidabro dangos kokybė (smulkiakristališkumas) žymiai pagerėja. Naudojant nuolatinę elektros srovę, atskirų sidabro kristalų matmenys svyruoja nuo $0,7$ iki $5 \mu\text{m}$, o panaudojus impulsinę – Ag kristalų matmenys sumažėja beveik 10 kartų ($0,1 \div 0,5 \mu\text{m}$). Deja, reikėtų pabrėžti, kad

iš sulfitinių kompleksų nusodinant sidabro galvanines dangas porėtumo problemos lieka neišspręstos. Šių dangų akytumas skirtingose paviršiaus vietose svyruoja tarp 1 ir 3 %.