



The influence of the ion-exchange groups nature and the degree of chemical activation by silver on the process of copper electrodeposition into the ion exchanger

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Received 22 September 2006; received in revised form 19 March 2007; accepted 1 April 2007

Available online 5 April 2007

Abstract

The electrodeposition of copper into ion-exchange materials with different ionogenic groups is studied. We have worked out that the discharge of copper counterions in an ion-exchange matrix is characterized by a cathodic overvoltage that is higher than the overvoltage of the same process on a graphite substrate by 0.08 V, which is most probably connected with a limited mobility of counterions localized at ionogenic groups. It has been observed microscopically that the process of deposition begins at the graphite substrate/ion exchanger interface and passes into the volume of a polymeric matrix with the filling of nanodimensional pores by copper. Preliminary doping of the ion exchanger by silver leads to the jump of the deposition current of copper counterions that is caused by the appearance of sufficient electron conductivity of the doped polymeric matrix. The data of the local X-ray spectral microanalysis confirm the regular deposition of copper into the volume of an ion exchanger grain doped by silver. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Ion exchanger; Metal–polymer composite; Electrodeposition; Copper; Percolation

1. Introduction

Electrochemical intercalation of metals in different polymeric matrices is a perspective method of synthesis of materials with high catalytic and electrocatalytic activity [1]. A composite metal-ion exchanger (electron-ion exchanger) has good mechanical and thermal stability and high technological properties [2]; therefore the investigation of electrochemical synthesis of electron-ion exchanger is an actual scientific problem. The most common method of producing electron-ion exchangers is by chemical deposition. However, this procedure has some serious disadvantages such as high cost and toxicity of reducers [3]. The electrochemical method is more useful for synthesis of composite materials, as it has the opportunity of simple regulation of the amount and the particle size of deposited metals. But electrochemical deposition of metals into ion exchangers is complicated due to the absence of crystallization centers. Besides the absence of conjugated bond in the structure of polymeric results

in low electron conductivity, this hinders the metal electrochemical deposition even further. Furthermore, functional groups of different nature, which are in the ion exchangers, can influence the discharge of counterions by analogy with deposition of metals from complex electrolytes [4]. The most versatile method for the modification of non-conductive polymers is chemical doping by different metals (Pd, Ag, Cu) that causes the increasing of electron conductivity and the appearance of crystallization centers for the next electrochemical deposition of a target metal [5]. According to Ono et al. [6] an effective way of activation of dielectric and inactive surfaces is the treatment by tin(IV) chloride SnCl₂ for the next electrodeposition. However, the doping non-conducting matrices by metal nanoparticles do not always lead to an increase in the total conductivity. At the doping ion-exchange zeolites having ionic conductivity by small amount of silver nanoparticles (the size is about 5 nm) the type of conductivity does not change [7].

The application of electrochemical methods for the intercalation of high-dispersed copper into the ion exchanger will be strongly dependent on the ion-exchange group influence on the kinetic parameters of electrodeposition and the spatial localization of the process in the complex heterogeneous system such as

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graphite substrate – porous ion-exchange basic – solution inside ion exchanger.

Therefore, the main purpose of this work is the investigation of the influence of ion-exchange matrix and nature of ionogenic groups on the process of copper electrodeposition and spatial distribution of copper through the volume of a grain depending on the degree of doped silver.

2. Experimental

The voltammetric measurements were performed in a three-electrode electrochemical cell with separated cathodic and anodic spaces and a working electrode consisting of a paste graphite substrate and a cross-section of an ion-exchange grain. In contrast to the common procedure for the preparation of a paste electrode [8], the specimen was not mixed with powdered graphite. This particular substrate was chosen to create a reliable electric contact because of the low electron conductivity of the ion exchanger. The surface area of the graphite substrate was equal to 0.038 cm^2 . The electrode potential was measured relative to a saturated silver–silver chloride electrode. A platinum gauze electrode served as the auxiliary electrode. The potentials in the text are given in *V* versus SHE. Cyclic voltammograms were recorded with $0.005\text{--}0.100 \text{ V s}^{-1}$ sweep rate from $+0.8$ to -0.4 V . The electrochemical investigations were performed with the help of PI-50-1 potentiostat link to a computer data acquisition system. All experiments were performed at 25°C .

For the investigation of copper electrodeposition we chose macroporous strong-acid sulfonation exchanger CU-23 15/100S (Azot Ltd., Cherkassy, Ukraine) in the H^+ - and Cu^{2+} -forms, which possesses an ion-exchange capacity ε of $1.25 \text{ mg-equiv ml}^{-1}$. The grain size was 1 mm . For the comparative analysis we also used weak-acid carboxyl cation exchanger C-104 (Purolite Ltd., UK, Wales) and weak-base aminoanion exchanger Fuji PEI-CS-07 (Fuji Spinning Co. Ltd., Shizuoka, Japan), which have an ion-exchange capacity ε of 4.50 and $2.90 \text{ mg-equiv ml}^{-1}$, respectively.

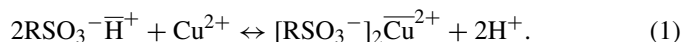
The experiments were carried out in the $0.1 \text{ M H}_2\text{SO}_4$ and $0.1 \text{ M H}_2\text{SO}_4 + x \text{ M CuSO}_4$ ($x = 0.01\text{--}0.1$) solutions (Dia M) aerated by argon. The micrographs of specimens were obtained with the help of the optical microscope MIM-7 at $100\times$ magnification. The measurements of electron conductivity of the doped sample by silver ion exchanger were carried out with pressed contacts in the form of polished silver disks at room temperature. The doped specimens were dried out under vacuum for water removal and exception of the ionic conductivity. Local X-ray spectrum microanalysis was carried out on MAR-2 instrument.

3. Results and discussion

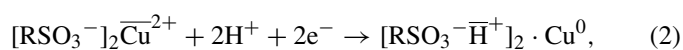
3.1. The influence of the ionogenic groups nature on the electrodeposition process

During copper electrodeposition into the ion-exchange matrix, the main source of discharging ions is the ionogenic groups $[\text{RSO}_3^-]_2\text{Cu}^{2+}$, because in an equivalent ion-exchange

reaction the sulfonation exchanger CU-23 15/100S in the H^+ -form absorbs Cu^{2+} ions from the external solution



where $\bar{\text{H}}^+$, $\bar{\text{Cu}}^{2+}$ are counterions inside the cation exchanger pores; H^+ , Cu^{2+} in the bulk solution; and R is a polymer matrix. Copper(II) ions are sorbed more preferably than univalent hydrogen ions [9]; therefore their content in ion-exchange resins is higher than in solutions. Because of macroporosity, a supraequivalently absorbed electrolyte is contained inside the grain of CU-23 15/100S. This fact leads to the absence of cathodic peaks (Fig. 1, curves 1–5), corresponding to the reduction of copper(II) counterions sorbed equivalently and supraequivalently by CU-23 15/100S in Cu^{2+} -form in a $0.1 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M CuSO}_4$ solution according to the reactions



It is connected with the absence of depletion of graphite substrate/cation exchanger interface by discharging ions because of high concentration of counterions $\bar{\text{Cu}}^{2+}$ which is maintained by the sorption from the outer solution.

At the same time, the cathodic current of copper deposition on a graphite substrate in $0.1 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M CuSO}_4$ solution, which is caused by the reaction



passes through a maximum as a result of intense depletion of a near-electrode layer by the discharging copper(II) counterions that is shown in Fig. 1, curve 6. Under these conditions the current maximum for the graphite substrate and the current of a plateau for sulfonation exchanger CU-23 15/100S are commensurable (at the same sweep rate), although the concentration of copper counterions in the ion exchanger exceeds a lot the concentration of copper ions in a solution. The rate of the copper electrodeposition reaction is probably determined by a limited

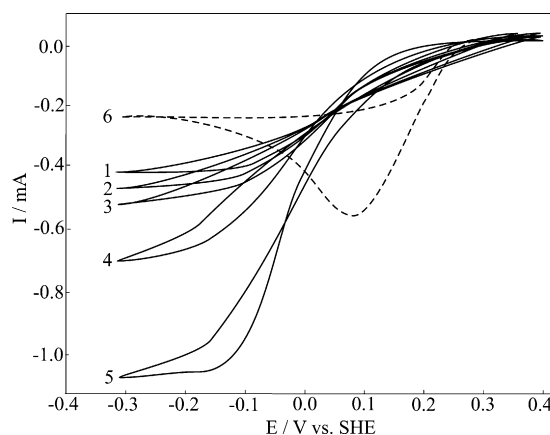
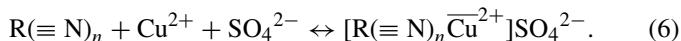


Fig. 1. Cyclic voltammograms of the sulfonation exchanger CU-23 15/100S (Cu^{2+} -form) in $0.1 \text{ M CuSO}_4 + 0.1 \text{ M H}_2\text{SO}_4$ with scan rate of 5 mV s^{-1} (1); 10 mV s^{-1} (2); 20 mV s^{-1} (3); 50 mV s^{-1} (4); 100 mV s^{-1} (5). (6) Electroreduction of copper(II) ions on a graphite substrate with scan rate of 10 mV s^{-1} .

mobility of the $\overline{\text{Cu}}^{2+}$ counterions inside the cation exchanger. At the increasing sweep rate the voltammogram shape does not change but the current of the cathodic process increases.

We have investigated the electroreduction of only equivalently sorbed counterions $\overline{\text{Cu}}^{2+}$ in a 0.1 M H_2SO_4 solution to elucidate the effect of ionogenic groups $[\text{RSO}_3^-]$ on the electrodeposition process. The ion exchanger was converted into a Cu^{2+} -form according to Eq. (1) and then the supraequivalently sorbed copper ions were washed away with an excess of distilled water. The initial absence of supraequivalently sorbed copper ions leads to a change in the shape of the voltammogram as a result of the reaction zone depletion by the depolarizer. Therefore, there is a current peak that is shown in Fig. 2, curve 1. The peak (C_1) of copper electrodeposition from counterions $\overline{\text{Cu}}^{2+}$ into the cation exchanger CU-23 15/100S is shifted by 0.08 V in the negative direction as compared with the peak of copper deposition on the graphite substrate from a solution with free copper(II) ions (Fig. 2, curve 6). The additional overvoltage is connected with the electroreduction of copper counterions from ionic pairs $[\text{RSO}_3^-]_2\overline{\text{Cu}}^{2+}$ according to Eq. (2) but not from a solution with free copper ions according to Eq. (4).

An increase in the constant of complex formation during the transfer to ion-exchange materials with carboxyl and amino groups also leads to an increase in the overvoltage of the electroreduction of copper(II) counterions [4,10]. Copper ions form an acetate complex and a complex with amino groups



The stability constant $\log K_1$ for the complex $[\text{R}-\text{COO}^-]_2\overline{\text{Cu}}^{2+}$ is equal to 2.23, and the same constant for the complex

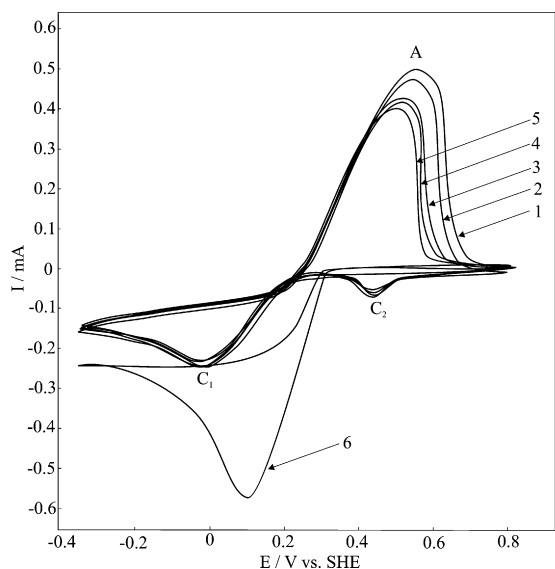


Fig. 2. Cyclic voltammograms (curves 1–5 are successive polarization cycles) of the sulfocation exchanger CU-23 15/100S (Cu^{2+} -form) in 0.1 M H_2SO_4 . Curve 6 refers to electroreduction of copper(II) ions on a graphite substrate in 0.1 M $\text{CuSO}_4 + 0.1$ M H_2SO_4 . Scan rate is 10 mV s^{-1} . C and A refer to cathodic and anodic peaks.

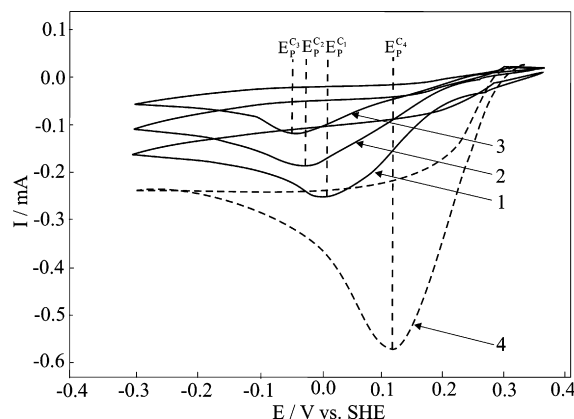
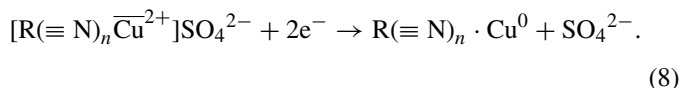
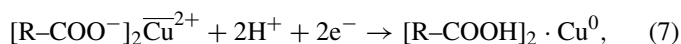


Fig. 3. Cyclic voltammograms of copper(II) counterions electrodeposition into the ion exchangers (Cu^{2+} -forms) in 0.1 M H_2SO_4 : 1, CU-23 15/100S; 2, Fuji PEI-CS-07; 3, C-104. Curve 4 refers to electroreduction of copper(II) ions on a graphite substrate in 0.1 M $\text{CuSO}_4 + 0.1$ M H_2SO_4 . Scan rate is 10 mV s^{-1} .

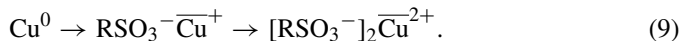
with amino groups $[\text{R}(\equiv \text{N})_n\overline{\text{Cu}}^{2+}]\text{SO}_4^{2-}$ is equal to 3.99 [11].

Cathodic voltammograms of copper(II) counterions electroreduction into weak-acid carboxyl cation exchanger C-104 and weak-base aminoanion exchanger Fuji PEI-CS-07 are shown in Fig. 3. During the potential scanning to the cathodic direction the reduction of copper counterions takes place according to Eqs. (7) and (8)



The overvoltage of the reduction of copper from the complexes increases by 0.13–0.14 V as compared to the overvoltage of the reduction of copper(II) on a graphite substrate (Fig. 3, curve 4).

The complexing properties of ionogenic groups cause the stabilization of intermediate counterions $\overline{\text{Cu}}^+$, which appear during the anodic dissolution of copper (Fig. 2, peak A) that was deposited in the first cycle of cathodic polarization according to scheme (9)



As a consequence, there is an additional cathodic peak at potential +0.42 V in the voltammogram (C_2) during repeated cycling of potential (Fig. 2, curves 2–5). The cathodic peak is connected with the reduction of copper(I) counterions at +0.42 V according to Eq. (10)



The parameters of the process of electroreduction of copper(II) counterions into the ion exchanger were determined by the analysis of the voltammograms shown in Fig. 2. For comparison, the same analysis was performed for the process of electroreduction of copper(II) ions on the graphite substrate. The copper electrodeposition into the ion exchanger and on the surface of a graphite substrate is an irreversible process as the

difference of the peak potential E_P and the half-peak potential $E_{P/2}$ in the voltammogram (Fig. 2) does not correspond with the theoretical value for a reversible process [12] according to the equation

$$E_{P/2} - E_P = 2.20 \frac{RT}{zF}, \quad (11)$$

where z is the number of electrons participating in the reactions (2) and (3).

For the irreversible process the value of the product of the charge transfer coefficient and the corresponding number of electrons in the step of charge transfer (αz_α) may be calculated with the help of the equation that connects potentials E_P and $E_{P/2}$:

$$E_{P/2} - E_P = 1.86 \frac{RT}{\alpha z_\alpha F}, \quad (12)$$

The potential of the cathodic peak in the voltammogram for copper electrodeposition into the ion exchanger and on the surface of a graphite substrate depends on the sweep rate. Therefore, the value of αz_α may be calculated on the basis of the equation for the peak potential of an irreversible electrode process

$$E_P = E^0 + \frac{RT}{\alpha z_\alpha F} \cdot 0.78 + \frac{2.3RT}{\alpha z_\alpha F} \cdot \log K_\alpha^0 - \frac{2.3RT}{\alpha z_\alpha F} \cdot \log \left(D \frac{\alpha z_\alpha F}{RT} \nu \right), \quad (13)$$

where K_α^0 is the rate constant for the charge transfer process, D the diffusion coefficient, and ν is the sweep rate. The values of αz_α , which were calculated with Eqs. (12) and (13) are presented in Table 1.

The diffusion coefficients for copper(II) ions in reactions (2) and (4) were calculated with the help of the Eq. (14) for the peak current (Table 1)

$$I_P = 3 \times 10^5 z(\alpha z_\alpha)^{1/2} D^{1/2} S C_{Ox}^0 \nu^{1/2}. \quad (14)$$

This equation is valid for an irreversible process at 25 °C. Here, S is the surface area of an electrode. The value of the diffusion coefficient for copper(II) ions in the bulk solution conforms to the data reported in [13]. The diffusion coefficient for counterions \overline{Cu}^{2+} in a grain of the sulfocation exchanger CU-23 15/100S has the same power of the value as the diffusion coefficient for these counterions by sulfogroups, which was determined by the method of electron spin resonance [14]. The decrease of the diffusion coefficient for counterions \overline{Cu}^{2+} in the

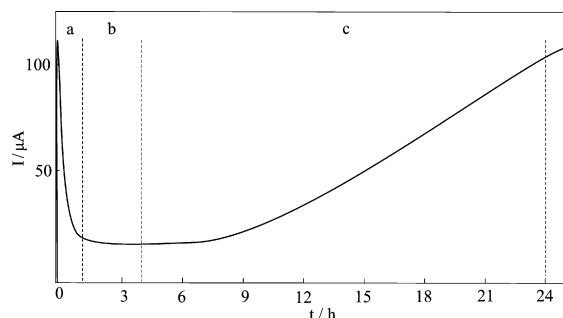


Fig. 4. Copper deposition current transient using the cation exchanger CU-23 15/100S (Cu²⁺-form) in 0.1 M CuSO₄ + 0.1 M H₂SO₄. The deposition potential is –0.01 V.

cation exchanger CU-23 15/100S as compared with the value of D in the bulk solution is probably connected with the limited mobility of counterions which are localized near ionogenic groups.

3.2. Direct electrodeposition of copper into ion exchanger

The ion exchanger CU-23 15/100S has no sufficient electron conductivity (because of absence of π -conjugate bonds in the main chain of a polymer) therefore the formation of electrodeposited copper particles begins from the graphite substrate and takes place in pores of the ion exchanger “from particle to particle” with saving the contact between particles, which is called template synthesis in membranes [15–17]. During the cathodic polarization the diffusion flows of copper counterions \overline{Cu}^{2+} are directed to the polymeric matrix/graphite substrate interface. The reduction of copper(II) ions sorbed equivalently and supraequivalently according to reactions (2) and (3) in the solution 0.1 M CuSO₄ + 0.1 M H₂SO₄ at the polymer/graphite interface is limited by the internal diffusion of copper counterions in pores of the ion exchanger. Therefore, there is a limited current of copper(II) counterions electrodeposition in the voltammogram in the range from 2 to 5 h (Fig. 4). It is possible to mark two stages of the deposition process: (1) the nucleation and grow of copper crystals on the graphite substrate (Fig. 4, section a of the curve); (2) the filling of nanodimensional pores of the ion exchanger by deposited metal (Fig. 4, sections b and c of the curve). With the increase of deposited time there is a gradual filling of the ion exchanger pores by copper and the front of the metal moving into the volume of a polymer, that is confirmed by the micrographs of the grain slices after electrodeposition (Fig. 5).

Table 1

Values of αz_α and diffusion coefficient D for copper(II) ions for the process of electroreduction of copper on a graphite substrate ($S = 0.038 \text{ cm}^2$) in 0.1 M CuSO₄ + 0.1 M H₂SO₄ solution and for the process of electrodeposition of counterions into the sulfocation exchanger CU-23 15/100S in 0.1 M H₂SO₄ solution with scan rate of 10 mV s^{-1}

Material for deposition	E_P (V)	$E_{P/2}$ (V)	αz_α		$I_P \times 10^3$ (A)	$D \times 10^{10}$ (m ² s ⁻¹)	$D \times 10^{10}$ (m ² s ⁻¹)
			Eq. (12)	Eq. (13)			
Graphite substrate	0.098	0.215	0.41	0.39	0.56	9.7 ± 0.6	7.5 [13]
CU-23 (Cu ²⁺ -form)	0.014	0.163	0.27	0.26	0.22	0.09 ± 0.01	0.15 [14]

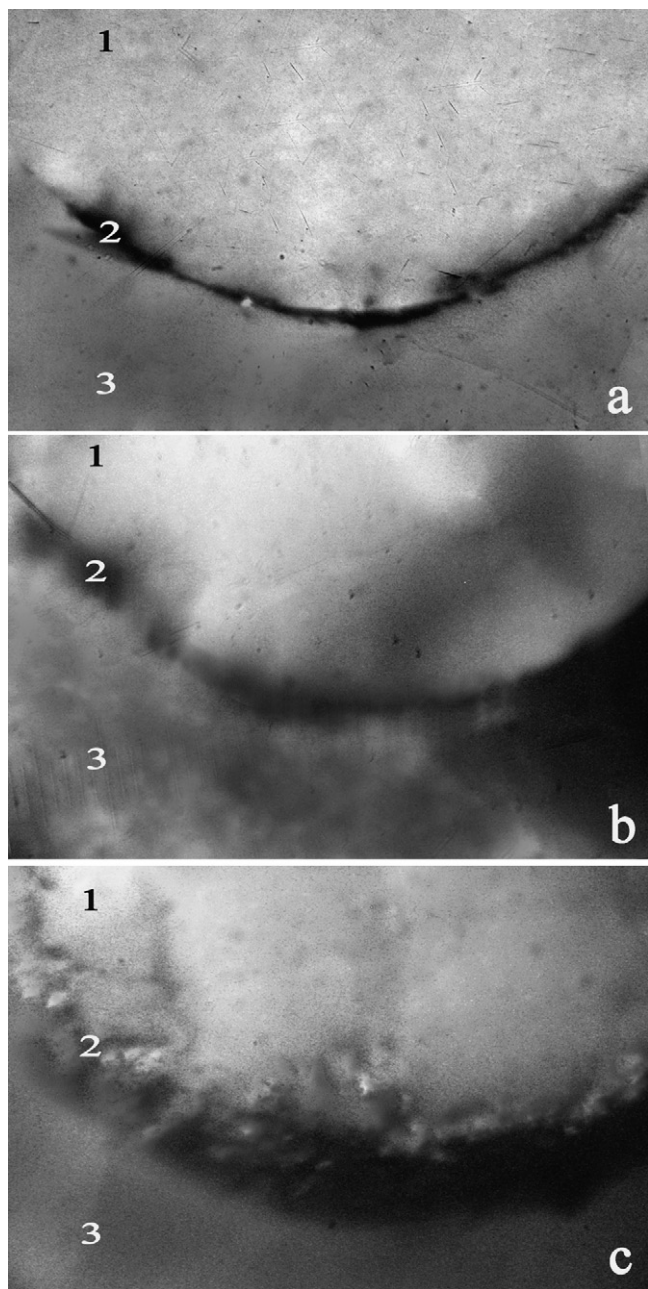


Fig. 5. Micrographs of cross-section of CU-23 15/100S after copper deposition. 1, polymeric matrix; 2, front of deposited copper; 3, graphite substrate. The time of deposition: (a) 1 h; (b) 4 h; (c) 20 h. The magnification is 100×.

3.3. Electrodeposition of copper into doped ion exchanger

Thus, the low electron conductivity of the ion-exchange matrix does not allow to synthesize a composite with an evenly distributed metal. The gradual filling of the ion exchanger pores by copper is a very slow process. One of the effective methods to increase the electron conductivity of the polymeric basis is a preliminary doping by chemically deposited metals [5,6]. As the doped ion exchanger is a composite which has ionogenic groups and a metal in pores, the conductivity of such material is mixed. It is provided by counterions (ionic conductivity) and

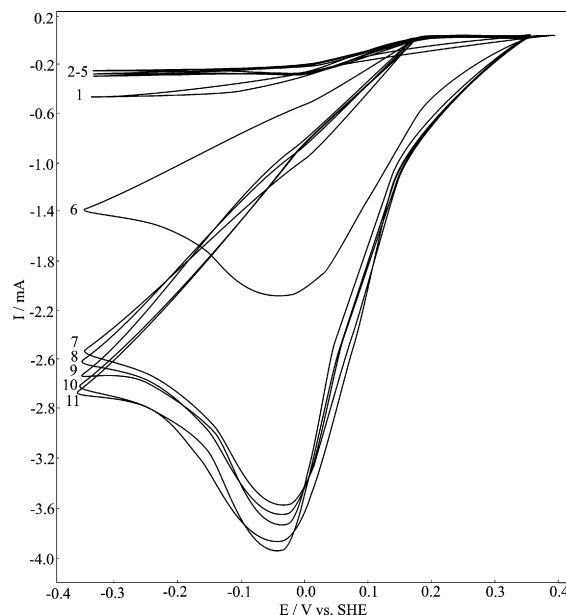
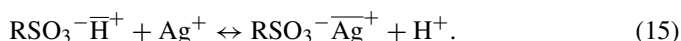


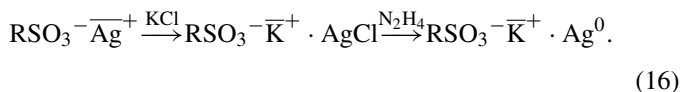
Fig. 6. Cyclic voltammograms of copper(II) counterions electrodeposition at the doped CU-23 15/100S (Cu²⁺-form) by silver in 0.1 M CuSO₄ + 0.1 M H₂SO₄. The quantity of silver: 1, 0 mmol ml⁻¹; 2, 0.20 mmol ml⁻¹; 3, 0.65 mmol ml⁻¹; 4, 1.14 mmol ml⁻¹; 5, 1.47 mmol ml⁻¹; 6, 1.87 mmol ml⁻¹; 7, 2.21 mmol ml⁻¹; 8, 2.65 mmol ml⁻¹; 9, 2.92 mmol ml⁻¹; 10, 3.29 mmol ml⁻¹; 11, 3.70 mmol ml⁻¹. Scan rate is 10 mV s⁻¹.

particles of the metal (electron conductivity). Electron conductivity allows to deposit copper(II) counterions throughout the ion exchanger grain.

The doping of the ion exchanger CU-23 15/100S was carried out by chemically deposited silver for increasing electron conductivity. Firstly, the cation exchanger was transformed into Ag⁺-form

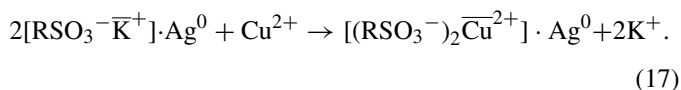


Then the Ag⁺ counterions were reduced to metal Ag⁰



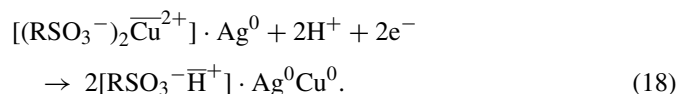
The presence of the intermediate stage (the forming of AgCl) is connected with a more complete reduction of silver ions Ag⁺ by hydrazine from salt than from the free ions. Repeating the necessary number of operations of ion-exchange and chemical reduction gives the gradual increase of silver amount in the ion exchanger.

The ion exchanger was transformed into Cu²⁺-form after the doping by the necessary quantity of silver according to Eq. (17)



The gradual increase of the doped silver amount in the cation exchanger till $\varepsilon_{\text{Ag}} = 2.21 \text{ mmol ml}^{-1}$ leads to the decrease of the current peak I_{P}^{C} in the voltammogram (Fig. 6, curves 2–5) of

copper(II) counterions electroreduction according to Eq. (18) in comparison with the non-doped cation exchanger (Fig. 6, curves 1).



For amounts of silver up to $2.21 \text{ mmol ml}^{-1}$ the metal particles do not take part in the current transport. They occupy part of the pores' volume of the cation exchanger and prevent the diffusion of copper counterions to the boundary with graphite substrate. In this case, the conductivity of the doped ion exchanger is only ionic as the direct contact between silver particles is limited. However, for silver quantities higher than $2.21 \text{ mmol ml}^{-1}$ a sudden change of the current peak takes place; that is probably caused by the beginning of electron conductivity of the doped ion exchanger (Fig. 6). To find out the reasons of the sudden change of the current peak I_p^C the measuring of electron conductivity of the doped ion exchanger was carried out depending on the amount of silver.

The analysis of voltage–current characteristics of the doped ion exchanger shows a divergence from linear dependence of current from voltage. It is known from literature [18,19] that this fact indicates the transition of electrons through isolated partitions by the tunnel mechanism. The experimental data show that all specimens of the doped ion exchanger with amount of silver less than $1.87 \text{ mmol ml}^{-1}$ are almost non-conductive (Table 2). This fact indicates the isolation of metal particles and the absence of significant electron exchange between them. The sharp increase of electron conductivity (up to five times) for $[\text{Ag}]$ of $1.87 \text{ mmol ml}^{-1}$ corresponds to the formation of a conjugate metal system with a good contact between silver particles. The dependence of electron conductivity on the quantity of the doped metal has a percolation character. When changing the silver amount from 1.14 to $1.87 \text{ mmol ml}^{-1}$ the percolation threshold of electron conductivity is observed. Electron conductivity of the doped ion exchanger by silver appears at the metal volume fraction equal to about 0.15 (Table 2). This result is in good agreement with the theory of percolation that conductivity of heterogeneous medium appears at a metal volume fraction

Table 2

The dependence of electron conductivity of doped ion exchanger CU-23 15/100S by silver on the quantity of metal

Quantity of silver, ε_{Ag} (mmol ml^{-1})	Mass part of silver, γ_{Ag}	Volume part of silver, α_{Ag}	Conductivity σ ($\text{Ohm}^{-1} \text{cm}^{-1}$)
0.20	0.63	0.02	2.80×10^{-7}
0.66	0.85	0.05	3.10×10^{-7}
1.14	0.90	0.09	3.10×10^{-7}
1.48	0.93	0.12	0.30×10^{-2}
1.87	0.94	0.15	2.80×10^{-2}
2.21	0.95	0.18	2.96×10^{-2}
2.65	0.96	0.21	2.99×10^{-2}
2.92	0.96	0.23	3.17×10^{-2}
3.29	0.96	0.26	3.36×10^{-2}
3.70	0.97	0.30	3.37×10^{-2}

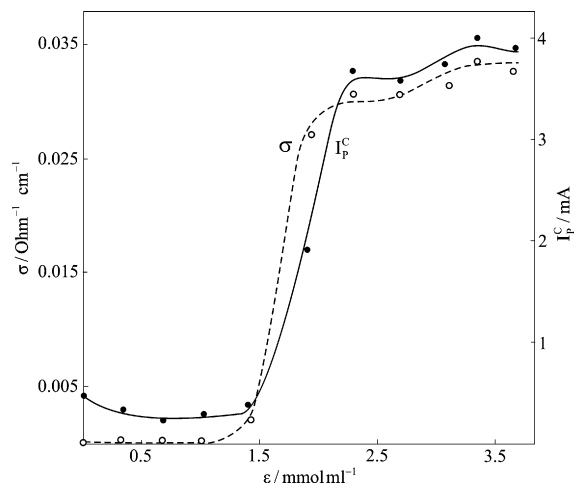


Fig. 7. Dependence of current peak of copper(II) counterions deposition and electron conductivity of doped ion exchanger CU-23 15/100S on the quantity of silver.

equal to 0.16 . It corresponds to the formation of a united cluster of conductive particles [20].

The sudden change of the current peak I_p^C and electron conductivity takes place approximately at the same amount of chemically deposited silver ($\varepsilon_{\text{Ag}} = 2.21$ and $1.87 \text{ mmol ml}^{-1}$, respectively) (Fig. 7). Some difference in the amount of the metal is connected with the change of the ion-exchange matrix volume during its dehydration under vacuum (this operation is necessary for measuring only electron conductivity). The sudden change of the current of reaction (18) is connected with the appearance of additional crystallization centers as a united cluster of Ag^0 -particles. Therefore, the process of electrodeposition becomes regularly distributed on the volume of the ion exchanger grain.

Thus the conditions found when the reaction of deposition (18) becomes regularly distributed enable to perform the electrochemical synthesis of the copper-containing composite on the basis of the doped ion exchanger. Such synthesis is possible when we alternate the operations of ion-exchange (17) with electrochemical reduction (18). The operation of ion-exchange was carried out in $0.1 \text{ M CuSO}_4 + 0.1 \text{ M Na}_2\text{SO}_4$ solution and the process of electrodeposition in $0.1 \text{ M Na}_2\text{SO}_4$ solution to exclude the filling of the surface of the doped ion exchanger by copper at the potential -0.010 V . During the increase of number of the ion-exchange–electroreduction operations there is gradual growth of maximum current that is connected with reduction of copper(II) counterions on the new Cu^0 crystallization centers but not only at Ag^0 centers.

The data of the local X-ray spectral microanalysis of the distribution of deposited copper throughout the ion exchanger grain is shown in Fig. 8. Uneven deposition of copper for silver quantities up to $\varepsilon_{\text{Ag}} = 1.87 \text{ mmol ml}^{-1}$ (Fig. 8a) is connected with the glow of copper counterions to the crystallization centers that causes the enrichment of one part and the impoverishment of the other part of the grain by copper. The electron conductivity of the doped ion exchanger is insufficient and at the same time the ion-exchange takes place with the outer solution according

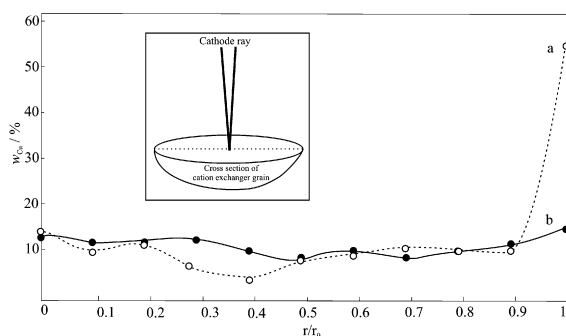
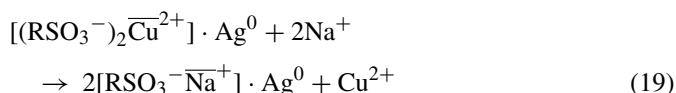


Fig. 8. Distribution of copper throughout the doped ion exchanger grain: dotted line (a) $1.87 \text{ mmol ml}^{-1}$ of silver; firm line (b) $2.21 \text{ mmol ml}^{-1}$ of silver. r_0 is the radius of ion exchanger grain. (a) The scheme of local X-ray spectrum microanalysis of the cross-section of grain. w_{Cu} is the relative content of copper into the ion exchanger grain.

to Eq. (19), that decreases the quantity of copper counterions $\overline{\text{Cu}}^{2+}$.



For silver quantities larger than $\varepsilon_{\text{Ag}} = 2.21 \text{ mmol ml}^{-1}$ the process of electrodeposition occurs evenly in the grain volume (Fig. 8b). In this case, every crystallization center is equal because of good electron conductivity of the doped ion exchanger. This fact is connected to the presence of a united percolation cluster of conductive Ag^0 -particles [21].

4. Conclusions

During the crystallization of copper into the ion exchanger electron conductivity of the polymer matrix exerts basic influence on the place of forming nuclei. As the consequence of insufficient electron conductivity of the polymer matrix of the ion exchanger CU-23 15/100S, the transport of equivalently adsorbed counterions $\overline{\text{Cu}}^{2+}$ occurs over ionogenic groups in the direction of the boundary of reaction on a graphite substrate. In the presence of supraequivalently adsorbed electrolyte, counterions $\overline{\text{Cu}}^{2+}$ move both over ionogenic groups and via the porous space in the direction of the boundary of the reaction. The discharge of copper counterions in the ion-exchange matrix is characterized by the cathodic overpotential that increases on 0.08–0.13 V in comparison with the overpotential of free ions reduction from the solution on the graphite substrate. It

is most likely connected with the restricted mobility of copper counterions localized at the ionogenic groups. The value of the overpotential of copper counterions electroreduction depends on the ionogenic groups nature and grows at the transition from sulfogroup $-\text{SO}_3\text{H}$ to carboxy group $-\text{COOH}$ and amine group $-\text{NH}_2$, that have the ability to form stable complexes with copper counterions $\overline{\text{Cu}}^{2+}$. The doping of the ion exchanger by chemically deposited silver gives the percolating dependence of the rate of copper electrodeposition on the amount of the incorporated metal. After the percolation threshold of electron conductivity the process of copper deposition becomes regularly distributed through the volume of the doped ion exchanger.

References

- [1] S.T. Farrell, C.B. Breslin, *Electrochim. Acta* 49 (2004) 4497.
- [2] T.A. Kravchenko, I.V. Aristov, in: D. Muraviev, V. Gorshkov, A. Warsawsky (Eds.), *Kinetics and Dynamics of Redox Sorption*, vol. 1, Marcel Dekker, New York, Basel, 2000, p. 691.
- [3] A.V. Kozhevnikov, *Electron-ion Exchangers*, Khimiya, Leningrad, 1972.
- [4] Y.D. Gamburg, *Electrocrystallization of Metals and Alloys*, Yanus-K, Moscow, 1997.
- [5] L. Chien-Liang, W. Chi-Chao, W. Yun-Yung, *J. Electrochem. Soc.* 150 (2003) C125.
- [6] S. Ono, K. Naitoh, T. Osaka, *Electrochim. Acta* 44 (1999) 3697.
- [7] G.D. Bagratishvili, Z.I. Badzhadze, D.E. Demetrashvili, *Kinet. Catal.* 12 (1971) 1341.
- [8] E.P. Medvedeva, Z.B. Rozhdestvenskaya, *Vestn. Akad. Nauk Kaz. SSR* N3 (1976) 61.
- [9] T.A. Kravchenko, E.V. Zolotukhina, V.A. Krysanov, *Russ. J. Phys. Chem.* 76 (2002) 1812.
- [10] J.C. Moutet, A. Zouaoui, *Electrochim. Acta* 46 (2001) 4035.
- [11] Yu.Yu. Lur'e, *Handbook of Analytical Chemistry*, Khimiya, Moscow, 1989.
- [12] Z. Galus, *Fundamentals of Electrochemical Analysis*, Ellis Horwood, Chichester, 1976.
- [13] A.M. Sukhotin (Ed.), *A Reference Book on Electrochemistry*, Khimiya, Leningrad, 1981.
- [14] N.I. Nikolaev, V.I. Muromtsev, G.G. Chuvileva, *High-Molecular-Weight Redox Compounds*, Khimiya, Leningrad, 1967, p. 47.
- [15] B.I. Podlovchenko, V.N. Andreev, *Russ. Chem. Rev.* 71 (N10) (2002) 950.
- [16] P. Forrer, F. Schlottig, H. Siegenthaler, M. Textor, *J. Appl. Electrochem.* 30 (2000) 533.
- [17] M. Platt, R.A.W. Dryfe, E.P.L. Roberts, *Electrochim. Acta* 48 (2003) 3037.
- [18] V.E. Gul, L.Z. Shenfil, *Conductive Polymeric Composites*, Khimiya, Moscow, 1984.
- [19] V.V. Vysotskii, V.I. Roldugin, *Colloid J.* 61 (1999) 90.
- [20] B.I. Shklovskii, A.L. Efros, *Electronic Properties of Doped Semiconductors*, Nauka, Moscow, 1979.
- [21] R.L. Verezhinskaia, T.M. Burkat, V.N. Pak, *Russ. J. Gen. Chem.* 70 (N3) (2000) 403.