Electrolysis with Flow-Through Carbon Electrodes in the Process of Electrolytic Processing of Ammine Rinsing Solutions of Cadmium Plating

V. I. VARENTSOVA[1] and V. K. VARENTSOV[1,2]

[1]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 6300128 (Russia)*

[2]*Novosibirsk State Technological University, Pr. K. Marksa 20, Novosibirsk 630092 (Russia)*

E-mail: vvk@ngs.ru

Abstract

Regeneration of cadmium deposited by electrolysis on carbon fibrous electrodes during processing ammine rinsing solutions from cadmium plating due to the performance of the short-circuited electrochemical system or anodic dissolution is investigated. Changes of the properties of carbon fibrous electrodes during their cyclic use in the processes of cadmium electrodeposition–dissolution and the possibility of their repeated use were examined.

Key words: cadmium, deposition, dissolution, carbon fibrous electrode, short-circuited electrochemical system

INTRODUCTION

Because of specific properties, cadmium coatings are used to protect hardware against aggressive environment (increased humidity, tropical conditions) [1–3]. At the same time, cadmium is a rare expensive metal; its compounds are highly toxic. In this connection, it is necessary not only to neutralize rinsing solutions formed during cadmium plating but also to bring cadmium in the form of the metal or as a salt back into production. One of the methods allowing one to solve these questions is electrolysis with flow cathodes made of carbon fibrous materials (CFM). This method is used for electroextraction of precious, rare and nonferrous metals from the solutions in various branches of industry, in particular from rinsing solutions and worked out electrolytes of electroplating [4, 5]. We demonstrated previously that carbon fibrous electrodes (CFE) can be efficiently used for cadmium deposition from ammine rinsing solutions of cadmium plating [6].

The use of CFE for electrolytic extraction of nonferrous metals from rinsing solutions of electroplating is connected with the necessity to regenerate carbon electrodes and return the metal to the main process. However, systematic investigations of the changes of CFE properties during their cyclic use in electrodeposition–dissolution processes and their effect on the parameters of both processes have not been carried out yet. On the basis of previous investigations [7–10] it may be assumed that the use of CFE in cyclic processes will affect their properties to a substantial extent. However, due to a small amount of data available, it is difficult to make an unambiguous conclusion about the positive or negative effect of these changes on the main process of metal electrodeposition.

The goal of the present work is to study the possibility of regeneration of cadmium extracted from ammine rinsing solutions of cadmium plating using CFE, due to the operation of a short-circuited electrochemical system (SCES) or anodic dissolution; evaluation of the

properties of CFM and the parameters of the process in electrodeposition−dissolution cycle.

EXPERIMENTAL

In the investigation, we used the industrial ammine electrolytes of cadmium plating having the following composition, g/L: 1) $CdSO_4$ 50, $(NH_4)_2SO_4$ 150, H_3BO_3 25, pH 5; 2) $CdSO_4$ 50, $(NH_4)_2SO_4$ 250, urotropine 20, dispersant NF 75 mL/L, pH 6 [2, 3]. Background solutions contained the same components except cadmium salt. The electrode polarization of CFM was performed from the direct-current power supply TES-14 under the galvanostatic conditions with the solution circulating at a flow rate of 0.2 mL/($cm^2 \cdot s$) through the volume of the carbon fibrous electrode and an intermediate vessel with the help of a peristaltic pump of pmp-304 type using the set-up and procedure described in [10]. The circuit with the rear (with respect to the counter electrode) delivery of the solution into the electrode with rear current feeder was used. The material of the carbon fibrous electrode was carbonized graphitized carbon NT-1 2 mm thick, with the overall area of 2 cm^2, and the current contact was a perforated plate made of titanium or platinum; counter electrode was made of platinum wire. Cadmium electrodeposition was performed using the same set-up with dilution of the background electrolyte 5 times (No. 2) and 20 times (No. 1). Cadmium concentration in solution was determined by means of atomic absorption. The efficiency of electroextraction of cadmium was estimated as the degree of extraction (α):

$$\alpha = (c_0 - c_\tau)/c_0$$

where c_0 and c_τ are the initial and final concentrations of cadmium in solution, respectively, g/L.

The distribution of cadmium over electrode thickness was studied during cadmium electrodeposition on CFE composed of two CFM layers. Each CFE layer after electrodeposition and rinsing was dried in the air to the constant mass and weighed. On the basis of the difference of CFE layer masses before and after electrolysis we calculated the amount of deposited cadmium. The fraction (M) of cadmium deposited on the rear (M_r) and front (M_f) sides of the electrode with respect to the counter electrode was determined using equation

$$M = m_{r(f)}/(m_r + m_f) \cdot 100\%$$

where m_r and m_f are cadmium masses on the rear and front sides of the electrode, respectively, g.

To study the changes of the mass and specific conductance of CFE, we washed it with distilled water and dried at 80−100 °C. The stationary electrode potential of cadmium plate and CFE in electrolytes Nos. 1 and 2 was measured with respect to saturated silver chloride electrode and calculated for the hydrogen scale. The electric conductance of CFE was measured using the set-up and procedure described in [4], using the ac-bridge VM-509; the stationary electrode potential was measured with a GDM-8135 voltmeter. Polarization curves were recorded under potentiodynamic conditions on a graphite microelectrode 2 mm in diameter with the surface renewed in solution using the procedure described in [11], with the help of a PA-2 polarograph at the potential sweep rate of 50 mV/s.

The results of experiments on modelling the process of electrolytic extraction of cadmium from the recovery bath in application to the automatic cadmium-plating line are presented in Fig. 1. Portions of cadmium-plating electrolyte modelling a single rinsing procedure were introduced into the solution circulating between the electrolytic tank and intermediate vessel (recovery bath). A corresponding increase in cadmium concentration in solution was 25 mg/L. Cadmium electroextraction was performed at the current density of 750 A/m^2. One can see that under the selected conditions the whole amount of cadmium introduced during rinsing is extracted through electrolysis between two subsequent rinsing procedures.

Depending on the composition of electrolyte, the amount of cadmium deposited on 1 g of CFE differs; it is due to the structure of the deposit and to cadmium localization in the CFE volume. These factors are determined by the features of cadmium electrodeposition in the electrolytes under consideration. The factor which is important for metal distribution over the electrode volume during electrodeposition of metals on the cathodes made of CFM is overvoltage of hydrogen evolution on CFE and the depositing metal [4]. The over-voltage of hydrogen evolution on cadmium is 1.1 V, on graphite 0.8 V [1, 12], so the electrode is over-
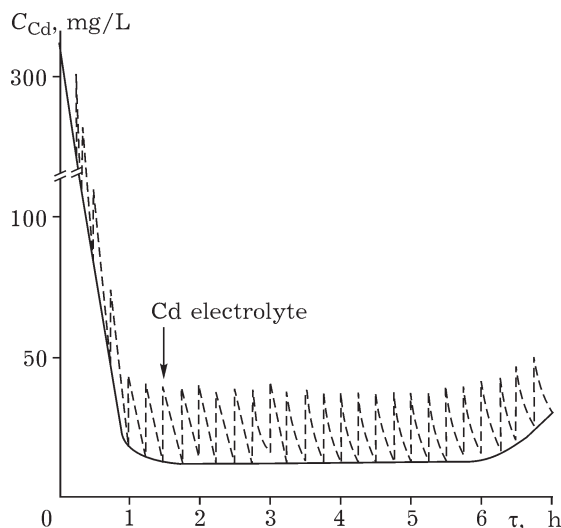
C_{Cd}, mg/L

Fig. 1. Dependence of the change of cadmium concentration in the rinsing ammine solution on rinsing time during modeling cadmium electroextraction from recovery bath. Process conditions: electrolyte No. 1, initial concentration of cadmium 330 mg/L, $n = 20$, periodicity of rinsing 15 min, increase in cadmium concentration after single rinsing 25 mg/L.

grown with cadmium mainly on the metal deposited during the initial period of electrolysis. Rather important factor is pH of solution, which determines the stability of ammine complexes of cadmium. For instance, at pH > 5 the complexes prevailing in solution are $Cd(NH_3)_2^{2+}$ ($K_{ins} = 1.8 \cdot 10^{-5}$) [2, 13]. In addition, electrolyte No. 2 contains the complexes of cadmium with urotropine and a surfactant additive, so cadmium electrodeposition from this electrolyte should be characterized by higher polarizability [2, 3].

It was shown experimentally that cadmium deposited on CFE during electroextraction from electrolyte No. 1 is localized on the front (closer to the anode) side of the electrode. In this case the deposit is friable; its adhesion to carbon fibres is weak. The amount of cadmium deposited on 1 g of CFC does not exceed 4.0 g; the deposit grows on filaments to the depth of the electrolyte and shatters into the solution. Cadmium obtained by electroextraction from electrolyte No. 2 is localized on the rear (closer to the current contact) size of the electrode. The deposit is denser, coats each filament of the CFE, grows to the depth of the electrode; the amount of deposited cadmium is 6.0−6.2 g per 1 g of CFE.

Previously [14] it was shown for copper electrodeposition from sulphuric solution that preliminary electrode treatment of CFM causes substantial changes in the parameters of the metal deposition process. It may be assumed that preliminary electrode polarization of CFM in electrolyte No. 2 containing surfactant components will affect subsequent electrodeposition of cadmium also from electrolyte No. 1.

It was established that after both cathode and anode polarization in background electrolyte No. 2 the mass of CFE increases; subsequent electrodeposition of cadmium reaches 80 and 46 %, respectively. Only the effect of the cathode polarization was studied later on.

It follows from the data presented in Table 1 that after cathode polarization in the background solution of electrolyte No. 1 the mass of CFM remained almost unchanged, after treatment in the background solution of electrolyte No. 2 the mass of CFE increases by 4.9−5 %. Specific electric conductance of NT-1 changes only slightly.

Let us consider the effect of these changes in CFE properties on subsequent electrodeposition of cadmium on these electrodes. One can see (Table 2) that preliminary treatment of CFE in the background solution of electrolyte No. 2 causes an increase in the degree of cadmium

TABLE 1

Changes of mass (Δm) and specific electric conductance (χ) of CFM after cathode polarization in background solution of electrolyte No. 2 at different values of current density (i). $\chi_{init} = 0.024$ S/cm, duration of cathode polarization: 0.5 h

Solution composition, g/L	i, A/m^2	Δm,%	χ_{fin}, S/cm
(NH$_4$)SO$_4$ 150, H$_3$BO$_3$ 25	500	−0.15	0.024
(NH$_4$)SO$_4$ 250, urotropine 20, NF dispersant 75 ml/L	0	+5.0	0.024
	250	+4.9	0.023
	500	+4.9	0.025
	750	+5.0	0.027

TABLE 2

Effect of the conditions of preliminary treatment of NT-1 in background electrolyte No. 2 on cadmium distribution over electrode thickness during cadmium electrodeposition from electrolyte No. 1. $\tau = 0.5$ h, $i = 500$ A/m^2, $C_{Cd} = 300$ mg/L, rear supply of solution into the electrode

Treatment conditions		α_{Cd}, %	M_r, %	M_f, %
i, A/m^2	τ, h			
0	0	66.7	100	0
0	0.5	72.8	15	85
250	0.5	74.7	14	86
500	0.5	78.5	26	74
750	0.5	74.7	24	76

electroextraction by 6−12 % and change of the ratio between the amounts of cadmium deposited on the rear and front sides of the electrode.

This fact is due to the improvement of current distribution and thus the distribution of cadmium deposit over the electrode thickness. It is possible to deposit 4.2−4.4 g of cadmium on 1 g of this CFM.

During the electrolytic deposition of metals on the flow CFE, the process efficiency depends on current density and the direction of solution supply into the electrode (rear or front). For thick electrodes this effect must be the most substantial due to the non-uniformity of the distribution of electrochemical process over the electrode thickness.

One can see (Table 3) that the change of the direction of solution supply from the rear to the front one causes improvement of cadmium distribution over electrode thickness but the degree of cadmium electroextraction decreases by a factor of 1.6−2.5. This fact is connected with a decrease in the mass of cadmium electrodeposited on the front side of the electrode. To analyze the reasons of this phe-

nomenon, we carried out the process of cadmium electrodeposition in two stages.

After the first stage, the electrolysis was stopped, the electrodes were dried, and then the second stage was carried out: cadmium electrodeposition with the front supply of solution to the electrode. It follows from the data shown in Table 4 that this causes cadmium «etching» from the front side of the electrode. Due to this, cadmium distribution over electrode thickness is improved, and the degree of cadmium extraction decreases substantially.

Such an unusual change of cadmium distribution over the electrode thickness depending on the direction of solution supply to the electrode can have the following explanation. First of all, according to the cell design, the current contact to the electrode is rear, so the most negative potential characterizes the rear size of the electrode; second, during the electrolytic extraction of cadmium in the circulation mode with constant flow of the electrolyte through the electrode volume it gets saturated with oxygen and depleted of cadmium. Polarization curves characterizing the cathode process of cadmium reduction (Fig. 2) provide evidence that the process of cadmium reduction (region II) is preceded by the reduction of dissolved oxygen (region I), and a decrease in cadmium concentration in solution (curves *3, 4*) causes the shift of the potential of the start of evolution to the negative side. This phenomenon was described in more detail in [15]. As a result, at the front side of the CFE with the front supply of solution, the major cathode process is the reduction of oxygen, while the potential necessary for cadmium reduction may be not reached. So, with respect to cadmium electroreduction, this part of the electrode is the an-

TABLE 3

Effect of the direction of solution supply into electrode (A) during cadmium electrodeposition on NT-1 from electrolyte No. 1 on cadmium distribution over electrode thickness. Preliminary cathode treatment: $i = 500$ A/m^2, $\tau = 0.5$ h

Cathode	A	α_{Cd}, %	M_r, %	M_f, %
Initial	Rear	71.2	8	92
	Front	28.8	37	63
Treated	Rear	78.5	26	74
	Front	46.9	58	42

Note. Conditions of electrodeposition: see Table 2.

TABLE 4

Effect of the change of the direction of solution supply to electrode (A) on the distribution of cadmium over NT-1 electrode thickness during cadmium electrodeposition from electrolyte No. 1. Process conditions for each stage: $\tau = 0.5$ h, $i = 500$ A/m^2, initial concentration of cadmium 300 mg/L

Cathodes	I stage						II stage			ΣM_r %	ΣM_f, %	$\Sigma\alpha$, %
	A	α, %	m, mg		M_r, %	M_f, %	A	m, mg				
			R	F				R	F			
Initial	R	70.4	4.6	48.2	8.7	91.3	R	7.5	44.9	11.4	88.6	70.5
Treated	R	78.5	15.2	43.6	25.8	74.2	R	16.8	45.5	26.4	73.6	80.7
Initial	R	71.2	4.4	49.0	8.0	92.0	F	5.0	−14	21.0	79.0	29.0
Treated	R	76.7	14.5	43.0	25.2	74.8	F	11.0	−22	55.0	45.0	30.9

ode. Third, cadmium deposited on the CFE can get dissolved due to the work of the short-circuited electrochemical system (SCES) [6]. Thus, the rear supply of solution into the electrode is more efficient.

It is necessary to regenerate cadmium deposited on the CFE and to return in into the galvanic process. For this purpose, it is promising to use the electrochemical method − anode dissolution.

The anode polarization curves depicting cadmium dissolution (see Fig. 2) provide evidence that the process of cadmium dissolution occurs without complications. Cadmium is well dissolved in the background solutions of electrolytes Nos. 1, 2 under different values of the anode current density (Fig. 3). Anode dissolution of cadmium deposited on the CFE in the electrolytic tank without the separation of electrode spaces allows one to obtain electrolytic cadmium powder on the cathode. If electrode spaces are separated with an ion exchange membrane and the anode dissolution is carried out in the
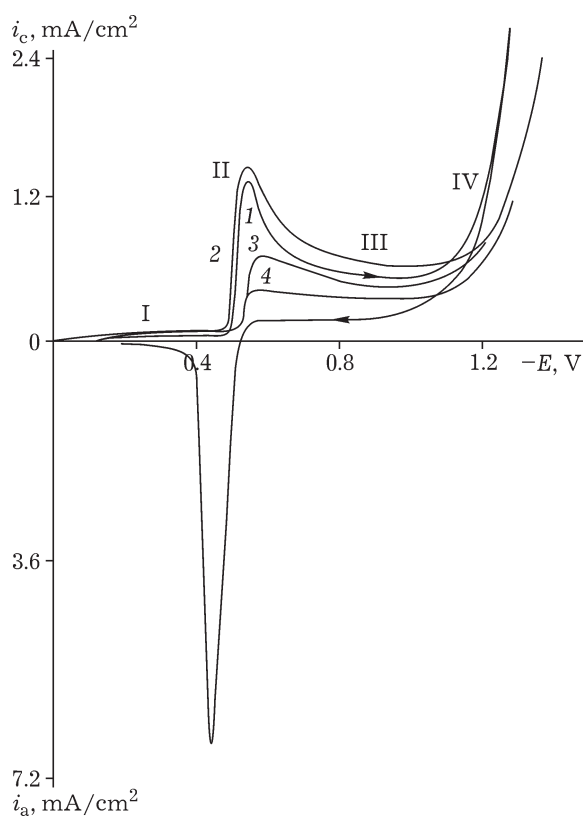

Fig. 2. Polarization curves characterizing electrode processes on graphite microelectrode in electrolyte No. 1. Cadmium concentration, mg/L: 300 (1, 2), 150 (3), 50 (4); dilution of background electrolyte: 0 (1), 50 (2), 20 (3, 4).
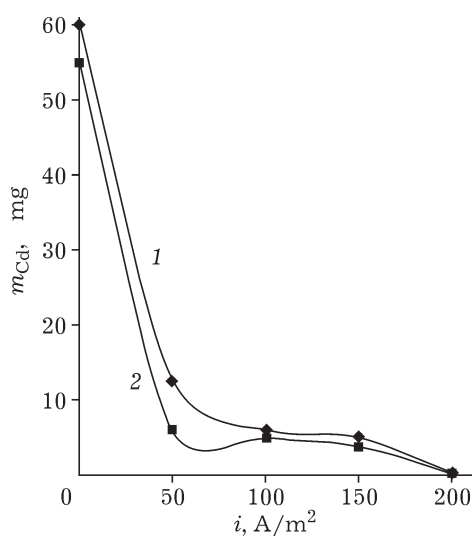

Fig. 3. Decrease in the mass of cadmium deposited on CFE during anode dissolution in background solution of electrolytes Nos. 1 (1) and 2 (2) at different values of anode current. $\tau = 30$ min, solution volume: 100 mL.

background solution of the corresponding electrolyte, it is possible to obtain the solution of cadmium-plating electrolyte. This method of the regeneration of cadmium deposited on CFE can be carried out in the same electrolytic tank. Cadmium dissolution proceeds with the high current efficiency; in some cases the yield as a function of current exceeds 100 %. This is the evidence of a parallel reaction accompanied by cadmium dissolution. As we have already mentioned, this reaction may be cadmium dissolution due to the operation of the SCES: CFE−cadmium−electrolyte solution.

The values of the standard electrode potentials of cadmium and CFE in the solutions of electrolytes are −0.48 and +0.41 V, respectively (electrolyte No. 1), −0.53 and +0.42 V, respectively (electrolyte No. 2) for cadmium concentration 100 mg/L. The difference between the stationary potentials of cadmium and CFE for both electrolytes is high (890−950 mV), so cadmium deposited on CFE must dissolve in the background ammine solution due to the operation of the SCES. Investigation showed that the dissolution of cadmium due to the SCES proceeds with the cathode control; dissolved oxygen is reduced on the cathode regions; the degree of cathode control is 94 %.

According to the literature data, oxygen reduction from acid solutions on different carbon electrodes including porous coal proceeds through the formation of hydrogen peroxide according to reaction

$$O_2 + 2H^+ + 2\bar{e} \leftrightarrow H_2O_2$$
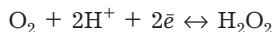
hydrogen peroxide is rather stable in the vicinity of the stationary potential [18, 19].

Evidently, hydrogen peroxide that is formed on the cathode regions of the SCES can interact with the surface of CFM fibres. The results of our investigations published previously
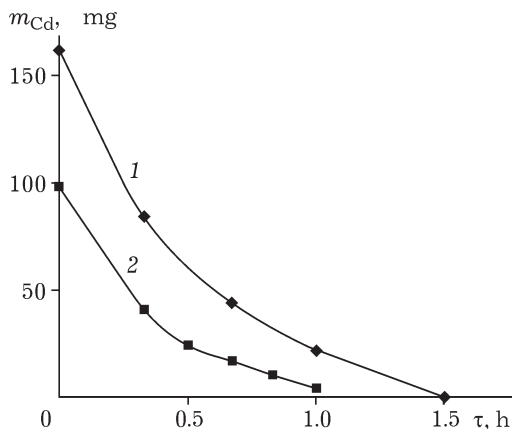

Fig. 4. Decrease in the mass of cadmium deposited on CFE during cadmium dissolution due to SCES in background solution of electrolyte Nos. 1 (2) and 2 (1). Solution volume: 100 mL.

showed that carbonized CFM including NT-1 used in the present work are prone to the strongest oxidation [6, 7, 9].

The process of cadmium dissolution due to SCES can be used separately for cadmium regeneration. This is a simpler method efficiently used by us for the regeneration of zinc and palladium deposited on CFE [16, 17]. Investigation showed that cadmium deposited on CFE is dissolved in the background solution of the corresponding electrolyte with a substantial rate (Fig. 4). The solutions containing $CdSO_4$ 35−40 g/L were thus obtained; they may be used to prepare cadmium-plating electrolytes.

During deposition and subsequent dissolution of cadmium, the CFE is subjected to cyclic cathode and anode polarization. It was demonstrated previously that the properties of the CFE can vary substantially [6−9]. In this connection, it was necessary to study the change of CFE properties after several cycles of electrodeposition−dissolution of cadmium.

It follows from the analysis of the data shown in Table 5 that after five cycles of elec-

TABLE 5

Change of mass (Δm) and specific electric conductance (χ) of CFE after five cycles of electrodeposition−dissolution of cadmium (χ_{init} = 0.024 S/cm)

Dissolution methods	Electrolytes			
	No. 1		No. 2	
	Δm, %	χ, S/cm	Δm, %	χ, S/cm
Dissolution due to SCES	−6.2	0.012	−3.0	0.014
Anode dissolution	+8.2	0.002	+7.0	0.004

TABLE 6

Change of the degree of cadmium electrodeposition (α) and the maximal amount of cadmium deposited per unit mass of CFE (m_{Cd}/m_{CFE}) after five cycles of electrodeposition–dissolution of cadmium ($i = 750$ A/m^2, $C_{Cd} = 250$ and 300 mg/L for electrolytes Nos. 1 and 2, respectively)

Electrolytes	α, %					m_{Cd}/m_{CFE}
	Time of electrolysis, min					
	10	20	30	60	90	
	Initial CFE					
No. 1			66.2	94.4	99.1	4.0
No. 2	28.2	57.8	96.4			6.2
	Electrodeposition–dissolution due to SCES					
No. 1			52.9	87.6	96.4	4.0
No. 2	48.0	84	99.9			8.3
	Electrodeposition–anode dissolution					
No. 1			36.3	83.9	93.6	3.5
No. 2	61.6	92	99.9			7.2

trodeposition–dissolution due to SCES we observe a decrease in the mass of CFE and its specific electric conductance. The changes observed in the properties of NT-1 can be connected with the interaction of hydrogen peroxide with the surface of fibres; however, these changes are weakened by the cathode polarization of the CFM.

More substantial changes of the CFM properties were detected after five systems of electrodeposition–anode dissolution: the mass of CFE increases, specific electric conductance of the samples decreases 6–12 times depending on the composition of the electrolyte. This is due to the formation of surface oxide groups on the surface of carbon fibres during the anode cycle, and also due to possible adsorption of the organic components of electrolyte on the surface of CFM fibres [8, 9].

Changes of CFE properties may affect cadmium electrodeposition. According to the data shown in Table 6, after 5 cycles of electrodeposition–dissolution on CFE samples the parameters characterizing cadmium electroextraction from electrolyte No, 1 did not worsen substantially, while the mass of cadmium deposited per unit mass of CFE decreased by 12 % in comparison with the initial material.

The parameters of cadmium electrodeposition on these electrodes from electrolyte No. 2 improved substantially. As a result of the improvement of deposit structure and its more uniform distribution over electrode thickness, the amount of cadmium deposited per 1 g of CFM increased by 15–33 %. This is connected with the fact that the efficiency of electrochemical process in a three-dimensional flow electrode is characterized by the distribution of potential, polarization, local current densities over the electrode thickness. Change of this distribution causing a change of the efficiency of cadmium electrodeposition in cyclic deposition–dissolution process can be connected with the presence of such components as urotropine and NF dispersant in electrolyte No. 2. The positive effect of these components on cadmium electroextraction from amine solutions is likely
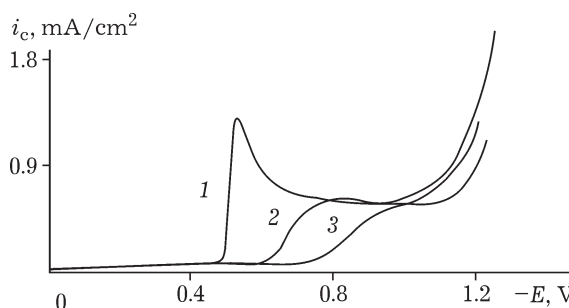

Fig. 5. Polarization curves characterizing electrode processes of cadmium electroreduction on graphite renewable microelectrode during its cyclic cathode-anode polarization in electrolytes Nos. 1 (*1*) and 2 (*2, 3*). Cadmium concentration: 300 mg/L; dilution of background electrolyte: 20 (*1, 2*) and 5 (*3*) times; cycles: 1–5 (*1*), 1 (*2*), 2–5 (*3*).

to be connected with the interaction of these components with the surface of CFE fibres during the cyclic polarization of the electrode. To test this assumption, we carried out special polarization studies. Graphite electrode was preliminarily subjected to cathode-anode polarization up to five cycles in electrolytes Nos. 1 and 2 containing 300 mg/L cadmium.

It follows from the analysis of the data shown in Fig. 5 that the cyclic treatment of CFE in the solution containing no urotropine and NF dispersant (electrolyte No. 1) has almost no effect on the appearance of polarization curve (curve *1*). In the solution containing these components, even after the first cycle of cadmium deposition−dissolution we observe a shift of the polarization curve to the electronegative potential, the slope of the second region of polarization curve increases substantially (curve *3*), therefore, polarizability increases. Renewal of the electrode surface by cutting off in solution brings the polarization curve back to its initial state, that is, the appearance of the curve is similar to that recorded with the initial surface (curve *2*).

CONCLUSION

Thus, CFE can be efficiently used for cadmium electrodeposition from rinsing solutions formed during the deposition of cadmium coatings from ammine electrolytes. The character of polarization curves recorded with graphite microelectrode renewed in solution is determined by the concentration of cadmium ions in solution and by the concentration of the components of background solution. The anode process takes place without complications. The structure of the electrolytic cadmium deposit and its distribution over CFE thickness depend on the composition of solution; 4.5−6.5 g of cadmium gets deposited per 1 g of CFE.

Cadmium deposited on CFE can be regenerated due to SCES operation or by anode dissolution. Solutions containing 35−40 g/L $CdSO_4$ or cadmium powder can be obtained. Changes of the mass and specific electric conductance of CFE during its cyclic use in cadmium electroreduction−regeneration processes were studied.

The largest changes were recorded for cadmium regeneration by anode dissolution: the mass of CFE increased by 7−8 %, specific electric conductance decreased 6−12 times. The parameters of cadmium electroreduction on CFE after its cyclic use (five times) did not worsen. An increase in the degree of cadmium extraction was observed in solutions containing organic components. The amount of cadmium deposited per 1 g of the carbon fibrous cathode increased by 15−30 %.

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