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# Kinetics and mechanism of chromium electrodeposition from formate and oxalate solutions of Cr(III) compounds

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#### ARTICLE INFO

### ABSTRACT

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Keywords: Chromium Electrodeposition Multistep electrode process Intermediates Kinetics Mechanism Kinetics of multistep reaction of Cr(III) ions discharge to metal was studied on a stationary electrode and on a rotating disk electrode from the solutions containing formic acid or oxalic acid. The electroreduction of Cr(III) complex ions in aqueous solutions is shown to proceed via the formation of relatively stable intermediates—Cr(II) compounds which are partially removed into bulk solution. The effect of pH, organic ligand concentration and disk rotation velocity on the partial current density of chromium electroplating was demonstrated. The kinetic equations of the studied process were derived and compared with the experimental data. Kinetic parameters for the discharge of Cr(II) ions were calculated. The mechanism of chromium electrodeposition reaction was proposed. The electrodeposition of chromium from formate bath is suggested to proceed with the participation of hydroxocomplexes of bivalent chromium. The oxalate complexes of bivalent chromium directly discharge in the electrolytes containing oxalic acid. The partial polarization curves of chromium electrodeposition exhibit a current peak which may be caused by blocking the electrode surface with poorly soluble Cr(III) hydroxide.

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#### 1. Introduction

Chromium electroplating is widely used in various branches of modern industry, the ordinary electrolytes containing extremely toxic chromic acid. The chromium deposition is known to be possible from solutions based on much less harmful Cr(III) compounds. Such electrolytes can be a real alternative to those containing chromic acid [1–18]. However, the electrochemical reactions taking place by chromium electroplating from solutions of Cr(III) salts are complicated and their comprehensive investigation is necessary in order to improve this process.

As far back as 1929, Demassieux, Heyrovsky and Prajzler [19] showed that the two well expressed waves were formed by the discharge of Cr(III) ions on a dropping mercury electrode. That means that the electrochemical process proceeds in steps with the formation of relatively stable intermediates-bivalent chromium compounds:

$$Cr(III) \xrightarrow{+e^{-}}_{I \text{ step}} Cr(II) \xrightarrow{+2e^{-}}_{I \text{ step}} Cr(0)$$
(I)  
$$E^{0} = -0.41 \text{ V} \qquad E^{0} = -0.91 \text{ V} \qquad (I)$$

where  $E^0$  is the standard equilibrium potential for the corresponding step.

Afterwards, the step-wise character of Cr(III)-electroreduction was confirmed in a number of publications [20–22].

The formation of Cr(II)—ions during the metal deposition from trivalent chromium baths was emphasized to be of great importance [2,11,13].

Some reaction schemes of chromium electrodeposition were proposed for baths containing compounds of Cr(III) [5,8,9,11,18].

For example, the electrochemical reduction of chromium(III) to metallic chromium in the presence of formic acids was stated to proceed via the formation of Cr(II) ions [11]. However, it is not quite clear from this work, what kind of Cr(II) complexes takes part in the discharge to the metal.

The electrodeposition reaction was studied from a trivalent chromium bath containing ammonium formate and sodium acetate [8]. The chromium electrodeposition process was suggested to involve two consecutive reduction steps. The first step was the reduction of a trivalent-Cr complex ion  $[Cr(H_2O)_5L]^{2+}$  to a bivalent-Cr complex ion  $[Cr(H_2O)_5L]^{2+}$  to a bivalent-Cr complex ion  $[Cr(H_2O)_5L]^{2+}$  to a bivalent-Cr complex in a cetate) ligand). Then the reduction of the bivalent-Cr complex ions to metallic Cr proceeds. The rate of chromium deposition process was controlled by the transport of the trivalent-Cr complex ions to the cathode surface.

The compositions of trivalent Cr complexes in electrolytes in the presence of formic acid and products of the electrochemical reduction process on cathode were investigated lately [17]. It was stated

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that the trivalent chromium exists in the form of  $[Cr(H_2O)_6]^{3+}$  in the solution.  $[Cr(H_2O)_6]^{3+}$  exhibits regular-octahedron structure which is a compact structure that does not make possible for the central  $Cr^{3+}$  ion to be involved in an electron transfer from the cathode. In the presence of formic acid, formate ions promote the formation of the reactive intermediate,  $[Cr(H_2O)_4CHOO]^{2+}$ , which possesses irregular-octahedron structure with  $Cr^{3+}$  ion as a vertex. Therefore,  $Cr^{3+}$  complex ion can immediately contact with the cathode and then obtain electrons easily.

A comprehensive analysis of literature data on the Cr-deposition process from trivalent baths was carried out recently [18]. It was emphasized that some oxide–hydroxide chromium compounds participate in the multistep electrochemical reaction of Cr(III) electroreduction.

Thus, even such a brief survey shows that there is no consensus on the mechanism of the electrochemical process concerned. The nature of the electroactive particles taking part in the electrodeposition reaction still needs to be determined.

We chose formate and oxalate trivalent chromium baths [5,7–9,11–13] for our study.

The stability constants for oxalate complexes of Cr(II) and Cr(III) are known to be substantially higher than those for formate complexes [2]. It is of interest to compare the kinetics and mechanism of electrochemical reactions which proceed in electrolytes containing formate or oxalate complexes of Cr(III).

The purpose of this investigation is to obtain and analyze the quantitative data on chromium electrodeposition from formate and oxalate baths as well as to propose the mechanism of electroreduction of Cr(III)-Cr(0).

#### 2. Experimental

For the chromium deposition the following stock solutions were used:  $0.2 \text{ M KCr}(SO_4)_2$ ,  $1.0 \text{ M Na}_2SO_4$ ,  $0.5 \text{ M H}_3BO_3$ , and 0.4 M HCOOH or  $0.4 \text{ M H}_2C_2O_4$  as complexing agents. The pH of these solutions was adjusted to a required value by addition of H<sub>2</sub>SO<sub>4</sub> or NaOH.

Chromium electrodeposition was carried out in a threeelectrode cell in a potentiostatic mode (PI-50-1.1 potentiostat). The solutions were deaerated by blowing with electrolytic hydrogen. A stationary copper-foil plate  $(S=1 \text{ cm}^2)$  as well as a gold disk (Ø 5 mm) served as the working electrodes. In some cases, the same gold disk pressed into Teflon was used as a rotating electrode. Prior to each experiment, the working electrode was polished with magnesium oxide and then washed with bidistillate water. The counter electrode was made of titanium-manganese dioxide [23] and separated by a glass porous diaphragm. A saturated Ag/AgCl electrode was used as a reference electrode. The potentials were recalculated to a standard hydrogen electrode scale. The ohmic potential drop was measured using the potential decay curves in a pulsed electrolysis and automatically compensated by means of the IR-compensator of the potentiostat. The electrochemical cell was thermostated at  $25 \pm 0.1 \,^{\circ}\text{C}$ 

The total current density through the electrochemical cell was determined by a copper coulometer. The partial current density of chromium deposition was calculated from the cathode's gain in weight for deposition time 20 min. The weight of chromium deposits obtained on a gold disk electrode (deposition time 5 s) was determined from the charge consumed in their electrochemical dissolving in 1.0 M NaOH. Preliminary experiments showed that chromium dissolved in 1.0 M NaOH on the gold electrode via reaction  $Cr(0) \rightarrow Cr(VI) + 6e^-$ , with a virtually 100% current efficiency. The partial current density of hydrogen evolution was found from the hydrogen volume evolved.

#### 3. Results and discussion

#### 3.1. Cathodic polarization curves

The standard potential of chromium is highly negative (see above); therefore, the electrodeposition reaction in aqueous solution is always accompanied by hydrogen evolution. Hence, the following three reactions proceed at the cathode during the electroplating of chromium from aqueous solutions of its trivalent compounds:

$$Cr(III) + e^{-} \rightarrow Cr(II)$$
 (1)

$$Cr(II) + 2e^{-} \rightarrow Cr(0)$$
 (2)

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

It should be mentioned that the chromium deposits prepared from electrolytes containing formic acid, oxalic acid as well as and some other organic compounds are known to contain carbon (mainly in the form of chromium carbides) [13,15,24–26]. The electrore-duction of organic substances are realized at the cathode together with the metal deposition. As a first approximation, let us assume that the multi-electron process of chromium(III) electroreduction takes place at the cathode independently of reduction of the organic compounds. Such an assumption simplifies analysis of the problem concerned.

In view of a substantial difference between the standard potentials of individual stages in the reaction scheme (I), the deposition of chromium should begin upon reaching the limiting current of Cr(III) electroreduction to Cr(II), which is confirmed by the partial polarization curves shown in Fig. 1 for oxalate bath. The results obtained for formate bath look very much alike.

By plotting of the above-mentioned partial voltammetric curves, the current density corresponding to reaction (1)  $i_1$  was calculated as the difference:

$$i_1 = i_{\Sigma} - i_{H_2} - i_2 \tag{4}$$

were  $i_{\Sigma}$  is the total current density through the electrochemical cell,  $i_{H_2}$  is the partial current density of hydrogen evolution reaction,  $i_2$  is the partial current density of metal electrodeposition.

As one can see, the partial polarization curve of chromium deposition  $i_2$  vs. *E* looks like wave with a current peak.

With an increase in the concentration of formic or oxalic acid in the electrolyte, the initial (ascending) segment of the  $i_2$  vs. *E* curve shifts towards more negative potentials (Fig. 2), which points to the decrease in the metal deposition rate.



**Fig. 1.** Partial polarization curves for reactions (1)–(3) obtained on a stationary electrode in the electrolyte containing  $0.2 \text{ M KCr}(SO_4)_2$ ,  $0.4 \text{ M H}_2C_2O_4$ ,  $0.5 \text{ M H}_3BO_3$ , 1.0 M Na<sub>2</sub>SO<sub>4</sub>. pH 2.5; deposition time 20 min.



**Fig. 2.** Partial polarization curves of chromium electrodeposition from (a) formate bath and (b) oxalate bath on the gold electrode at different concentrations of organic acid, mol/dm<sup>3</sup>: (1) 0.2 HCOOH; (2) 0.4 HCOOH; (3) 0.2 H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; (4) 0.4 H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; (5) 0.8 H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, pH 2.5; deposition time 5 s.

In the initial segment of polarization curve, the rate of electrochemical reaction of metal deposition increases with an increase in pH for formate bath (Fig. 3). On the contrary, with increasing pH for oxalate bath, the metal deposition rate slightly diminishes.

The value of the maximum current density  $(i_{2,max})$  was found to rise with increasing HCOOH concentration. Quite the opposite, at higher concentration of  $H_2C_2O_4$ , the current density of the peak decreases.

When pH being diminished, the maximum achievable chromium deposition rate  $i_{2,max}$  grows both for oxalate electrolyte and for formate one.

All other factors being equal, the maximum current density of the chromium electrodeposition in the formate bath is achieved at much higher values than in oxalate electrolyte (the corresponding values differ approximately by an order of magnitude).

Presumably, some difference between the values of  $i_2$  in Figs. 1–3, respectively, results from the diversity of experimental conditions (different nature of copper and gold substrates and different deposition time).

In accordance with experimental data (Fig. 4), an increase in the electrode rotation rate decelerates the chromium electrodeposition process in the ascending section of polarization curve for formate bath. In solutions containing  $H_2C_2O_4$ , the rate of the chromium electrodeposition reaction remains virtually unchanged with increasing the disk rotation velocity (in ascending section of  $i_2$  vs. *E* curve).



**Fig. 3.** Partial polarization curves of chromium electrodeposition from (a) formate bath and (b) oxalate bath on the gold electrode at different pH: (1) 2.5; (2) 3.0; (3) 3.6. Deposition time 5 s.

In all cases, the increase in the electrode rotation rate results in the increase in the maximum values of electrodeposition current density  $i_{2,max}$ .

#### 3.2. Theoretical model

Turning back to the above-mentioned question about the multistep mechanism of chromium deposition process, it should be emphasized that the possibility of the simultaneous transfer of three electrons by the discharge of Cr(III) ions was examined in literature along with the stepwise mechanism of chromium(III) ions reduction. For example, the direct transfer of three electrons was discussed for the process of chromium electrodeposition from acetate complexes of Cr(III) without formation of intermediates [27].

However, similar assertions are relatively not numerous and there is no convincing theoretical argumentation of the assumption about the simultaneous transfer of three electrons in the reaction of chromium deposition. It is necessary also to take into account that the extraordinarily small probability of simultaneous transfer of several electrons in an elementary act is generally accepted in modern electrochemistry [28,29]. Therefore, there is good reason to believe that multistep reaction scheme of Cr(III) electroreduction is generally accepted among most researchers of this process.

As indicated above, the rate of chromium deposition reaction depends on the concentration of reactants which do not participate immediately in the total reaction (2); then one can suppose that the electrochemical process concerned is complicated and involves some different chemical and electrochemical steps. Thus,



**Fig. 4.** Partial polarization curves of chromium electrodeposition from (a) formate bath and (b) oxalate bath on the gold rotating disk electrode. pH 2.5; deposition time 5 s.

the expressions described the chromium deposition process have to be derived.

As it follows from Fig. 1, the current density of incomplete reduction of Cr(III) ions to Cr(II) is greater than the current density of metal deposition. It means that only a part of the total amount of Cr(II) ions formed at the first stage of Cr(III) discharge is reduced further to the metal. The excess of bivalent chromium ions are accumulated in the bulk electrolyte. Hence, the electroreduction of Cr(II) compounds is the limiting stage of electrochemical transformations in Eq. (I).

In accordance with the aforesaid, the rates of individual steps of the Cr(III) electroreduction should satisfy the relationship:

$$\frac{l_1}{F} = \frac{l_2}{2F} + \nu \tag{5}$$

where v is the rate of the convective–diffusion removal of Cr(II) ions into bulk solution.

We suppose that charge transfer stage (2) follows a fast chemical reaction where electroactive complexes (EAC) are formed from ions Cr(II)<sub>init</sub> generated in reaction (1):

$$\operatorname{Cr}(\mathrm{II})_{\mathrm{init}} + \sum_{i} \nu_{i} X_{i} \rightleftharpoons \operatorname{Cr}(\mathrm{II})_{\mathrm{EAC}} + \sum_{j} \nu_{j} X_{j}$$
(6)

where  $X_{i,(j)}$  are possible participants in the EAC formation (organic ligands, H<sup>+</sup> and OH<sup>-</sup> ions, solvent molecules, etc.), and  $v_{i,j}$  are corresponding stoichiometric coefficients.

It should be stressed that the complexes of Cr(II) are labile, so the exchange of ligands in their inner-sphere occurs with very high rate. Indeed, the rate constant of H<sub>2</sub>O-ligand exchange for Cr(II)-ion was estimated to be greater than ca.  $10^9 \, \text{s}^{-1}$  [30]. This

fact justifies the assumption that the reaction (6) can be always in equilibrium.

The concentration of EAC of bivalent chromium near the electrode surface ( $C_S$ ) is related to the concentration of Cr(II)<sub>init</sub> by the formula:

$$C_{\rm S} = K_{\rm eq} C_{\rm S,init} \cdot \frac{\prod_i C_{X_i}^{\nu_i}}{\prod_j C_{X_j}^{\nu_j}} = K_{\rm eq} C_{\rm S,init} \cdot \prod C_{i,j}^{\nu_{i,j}}$$
(7)

where  $K_{eq}$  is the equilibrium constant of reaction (6);  $C_{S,init}$  is the concentration of Cr(II)<sub>init</sub>;  $\prod C_{i,j}^{\nu_{i,j}} = \prod_i C_{X_i}^{\nu_i} / \prod_j C_{X_j}^{\nu_j}$  is a co-factor that takes into account the product of equilibrium concentrations of reactants  $X_{i(i)}$ .

We assume that the activity factors of participants of reaction (6) are included into equilibrium constant  $K_{eq}$ .

For reaction (2), the following equation is valid:

$$i_2 = 2Fk_2C_{\rm S}\exp\left[-\frac{\alpha_2F}{RT}E\right] \tag{8}$$

where  $k_2$  is the rate constant of the electrode reaction (2);  $\alpha_2$  is the apparent transfer coefficient; *E* is the electrode potential.

From (7) and (8), we obtain the equation:

$$i_2 = 2Fk'_2C_S \prod C_{i,j}^{\nu_{i,j}} \exp\left[-\frac{\alpha_2 F}{RT}E\right]$$
(9)

where  $k'_2 = k_2 k_{eq}$  is an effective rate constant.

The rate of the diffusion flow of Cr(II) ions from the electrode surface to the electrolyte volume can be estimated from the equation:

$$\nu = \frac{D}{\delta}(C_{\rm S} + C_{\rm S,init}) = k_{\rm D}C_{\rm S,init} \left(1 + K_{\rm eq} \cdot \prod C_{i,j}^{\nu_{i,j}}\right)$$
(10)

where *D* is the diffusion coefficient for Cr(II) complex ions, which we assume the same for both Cr(II)<sub>init</sub> and Cr(II)<sub>EAC</sub>;  $\delta$  is the effective diffusion layer thickness;  $k_D = D/\delta$  is a diffusion mass transfer coefficient. Assume now that  $K_{eq} \cdot \prod C_{i,j}^{v_{i,j}} \ll 1$ , which means  $C_S \ll C_{S,init}$ . Then Eq. (10) takes the form:

$$v = k_{\rm D} C_{\rm S,init} \tag{11}$$

From (5), (9), and (11), we obtain:

$$i_{2} = \frac{2i_{1}k'_{2}\prod C_{i,j}^{\nu_{i,j}} \exp\left[-(\alpha_{2}F/RT)E\right]}{k'_{2}\prod C_{i,j}^{\nu_{i,j}} \exp\left[-(\alpha_{2}F/RT)E\right] + k_{\mathrm{D}}}$$
(12)

This equation contains no  $C_{S,init}$ , whose experimental determination is very difficult. Eq. (12) can be put in the linear form:

$$\ln \frac{i_2}{2i_1 - i_2} = \ln \frac{k'_2 \prod C_{i,j}^{\nu_{i,j}}}{k_D} - \frac{\alpha_2 F}{RT} E$$
(13)

In accordance with Eq. (13), the lines plotted on the coordinates  $\ln(i_2/(2i_1 - i_2))$  vs. E can be used in order to calculate kinetic parameters of reaction (2). Such a method of determination of kinetic parameters is applicable to any form of the  $i_1$  vs. *E* curve.

It seems reasonable to obtain an equation for an  $i_2$  vs. *E* curve which does not contain  $i_1$ . For mixed kinetics of reaction (1), the formula is valid:

$$i_1 = \frac{i_{1,\lim} \cdot i_{1,k}}{i_{1,\lim} + i_{1,k}}$$
(14)

where  $i_{1,\text{lim}}$  is the limiting diffusion current density of reaction (1), and  $i_{1,k}$  is the current density of the discharge stage in reaction (1).

Expressions for the values of  $i_{1,\text{lim}}$  and  $i_{1,k}$  can be written as follows:

$$i_{1,\text{lim}} = \frac{FDC_{\text{Cr(III)}}}{\delta} = k_{\text{D}}FC_{\text{Cr(III)}}$$
(15)

$$i_{1,k} = Fk_1 C_{Cr(III)} \exp\left[-\frac{\alpha_1 F}{RT} E\right]$$
(16)

where  $C_{Cr(III)}$  is the Cr(III) concentration in bulk electrolyte; *D* is the diffusion coefficient for Cr(III) complex ions (to simplify mathematical expressions, we assumed the same diffusion coefficients for Cr(III) and Cr(II) ions);  $k_1$  is the rate constant of reaction (1);  $i\alpha_1$  is the transfer coefficient of reaction (1).

In the general case, some equilibrium chemical reactions can precede the discharge of Cr(III) ions. To simplify expression (16), we included into  $k_1$  a co-factor that allows for the product of equilibrium concentrations of reactants.

From (12) and (14)–(16), we have

TT .....

$$i_{2} = \frac{2F\kappa_{1}\kappa_{2}^{\prime}\kappa_{D}C_{Cr(III)}\prod C_{i,j}^{\prime\prime,ij} \exp[-(\alpha_{1}F/RI)E]\exp[-(\alpha_{2}F/RI)E]}{\left(k_{D}+k_{1}\exp[-(\alpha_{1}F/RI)E]\right)\cdot\left(k_{2}^{\prime}\prod C_{i,j}^{\nu_{i,j}}\exp[-(\alpha_{2}F/RI)E]+k_{D}\right)}$$
(17)

As follows from data presented in Fig. 1, the current density of reaction (1) is close to the limiting diffusion value at the potentials of chromium electrodeposition. Hence, the rate of the reaction (1) is determined primarily by transport restrictions, i.e.,  $k_D \ll k_1 \exp[(-\alpha_1 F/RT)E]$ ; then, the expression (17) can be written as follows:

$$i_{2} = \frac{2Fk_{2}'k_{D}C_{Cr(III)}\prod C_{i,j}^{\nu_{i,j}} \exp[-(\alpha_{2}F/RT)E]}{k_{2}'\prod C_{i,j}^{\nu_{i,j}} \exp[-(\alpha_{2}F/RT)E] + k_{D}}$$
(18)

The final expression (18) describes the kinetics of chromium electrodeposition. Based on kinetic equations obtained, it is possible to explain some peculiarities of the step-wise discharge of Cr(III) ions to the metal.

It is clearly from Eq. (18) that the  $i_2$  vs.  $k_D$  dependence is nonlinear and is determined by the balance between the terms in the denominator of Eq. (18). If  $k'_2 \prod C_{i,j}^{v_{i,j}} \exp[-(\alpha_2 F/RT)E] \ll k_D$ , then we obtain:

$$i_{2} = 2Fk_{2}^{\prime}C_{Cr(III)}\prod C_{i,j}^{\nu_{i,j}} \exp\left[-\frac{\alpha_{2}F}{RT}E\right]$$
(19)

In this case,  $i_2$  is independent of the solution stirring, because an increased generation of Cr(II) ions in reaction (1) with a more intensive stirring accelerates the diffusion removal of Cr(II) ions from the electrode surface. Hence, the values of  $C_{\text{S,init}}$  and  $i_2$  do not depend on the electrolyte stirring conditions in the initial segment of an  $i_2$  vs. *E* curve. However, intensifying the mass transfer by increasing convection can alter surface concentrations of reactants  $X_{i(j)}$  involved in reaction (6), which affects  $i_2$ . An analysis of these relations can provide valuable information on the formation of Cr(II) electroactive complexes.

At a sufficiently negative electrode potentials, we have  $k'_2 \prod C_{i'i'}^{\nu_i} \exp[-(\alpha_2 F/RT)E] \gg k_D$ , and as follows from Eq. (18):

$$i_2 \to i_{2,\text{lim}} = 2k_{\text{D}}FC_{\text{Cr(III)}} = 2i_{1,\text{lim}}$$
 (20)

where  $i_{2,\text{lim}}$  is the limiting current density of reaction (2) determined by convection–diffusion limitations of reaction (1). At this conditions, the value of  $i_{2,\text{lim}}$  depends on the same factors as  $i_{1,\text{lim}}$ , in particular, on solution stirring intensity. As follows from Eqs. (5) and (20), v = 0, i.e. no intermediates are accumulated in the bulk electrolyte.

One can observe a chromium deposition at the limiting diffusion current, as a rule, on a dropping mercury electrode [18–22]. On a solid electrode, the limiting *diffusion* current of chromium electrodeposition appears in some cases in electrolytes of certain composition [8,31].

#### 3.3. Calculation of kinetic parameters

Kinetic parameters of the reaction (2) were determined by linearizing the experimental data in the coordinates of Eq. (13) (some



**Fig. 5.** Partial polarization curves, plotted in coordinates of Eq. (13), for chromium electrodeposition on a stationary electrode in electrolytes containing 0.2 M KCr(SO<sub>4</sub>)<sub>2</sub>, 0.5 M H<sub>3</sub>BO<sub>3</sub>, 1.0 M Na<sub>2</sub>SO<sub>4</sub>, and (1) 0.2 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (pH 2.5) or (2) 0.4 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (pH 3.0).

lines are shown in Fig. 5). The slope of the lines and the intersections in the ordinate were calculated by the least squares method. The diffusion mass transfer coefficient  $k_D$  was calculated with Eq. (15) on the basis of experimentally determined  $i_{1,lim}$  values.

It should be stressed that it is impossible to determine accurately the value of co-factor  $\prod C_{i,j}^{\nu_{i,j}}$ , because there is no sufficient information on the composition of the near-electrode layer. Therefore, the obtained data enable us to calculate only the coefficient  $\tilde{k}_2 = k'_2 \prod C_{i,j}^{\nu_{i,j}}$  (Table 1).

As one can see in the table, the coefficient  $\tilde{k}_2$  increases with a decrease in the H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> concentration and pH in an oxalatecontaining electrolyte. In a formate-containing electrolyte, the coefficient  $\tilde{k}_2$  increases with a decrease in the HCOOH concentration and with an increase in the pH.

The calculated apparent transfer coefficients  $\alpha_2$  lie in the range from 0 to 1. It seems that from this we could have assumed that the transfer of the first electron is the limiting stage at the discharge of Cr(II) ions. However, one must compare apparent transfer coefficients both for cathodic reaction and for anodic one in order to determine the limiting stage of the multi-electron process [28]. Therefore, it must be stressed that the available kinetic data are insufficient for a reliable determination of slow stage in the twoelectron reaction (2).

#### 3.4. Mechanism of the chromium electrodeposition

When generalizing the results of the analysis of kinetic data obtained, we conclude that despite many common features, the

#### Table 1

Kinetic parameters of the Cr(II) discharge at 298 K.

Organic ligand concentration (M)	pН	Parameters	
		$\alpha_2$	$\tilde{k}_2 \ ( imes 10^6 \ { m cm/s^a})$
$H_2C_2O_4$			
0.2	2.5	0.32	0.55
0.4	2.5	0.28	0.38
0.4	3.0	0.37	0.09
нсоон			
0.2	2.5	0.28	20.06
0.4	2.5	0.23	11.90
0.4	3.0	0.38	38.16

<sup>a</sup> Coefficient  $\tilde{k}_2$  is given for standard potential  $E^0 = -0.91 \text{ V}$  of the reaction  $\operatorname{Cr}^{2+} + 2e^- \Leftrightarrow \operatorname{Cr}^0$ . We assume here that the co-factor  $\prod C_{i,j}^{\nu_i}$  is dimensionless.

kinetics and mechanism of chromium electrodeposition from the oxalate and formate baths are different. These distinctions are likely to be caused by the different nature of the electroactive complexes participating in the discharge that yields the metal.

We believe that the electroactive complexes in the formate bath are hydroxocomplexes of bivalent chromium formed at the electrode surface as the products of the dissociation of inner-sphere-coordinated water molecules, which precedes the discharge. Then the mechanism of the chromium electrodeposition can be conditionally presented by the following approximate reaction scheme<sup>2</sup>:

$$[Cr(II)(HCOO)_m(H_2O)_n]_{ads}^{(2-m)}$$
  

$$\leftrightarrow [Cr(II)(HCOO)_{m-k}(H_2O)_{n-1}(OH)]_{ads}^{(1-m+k)} + kHCOO^- + H^+ \quad (21)$$

$$[Cr(II)(HCOO)_{m-k}(H_2O)_{n-1}(OH)]_{ads}^{(1-m+k)} + 2e^{-}$$
  

$$\rightarrow Cr^0 + (m-k)HCOO^{-} + (n-1)H_2O + OH^{-}$$
(22)

where m = 1, 2; k = 0, 1, 2; n = 1, 2, ...

According to this mechanism, an increase in pH and a decrease in the formic acid concentration in the bath must result in the shift of the equilibrium (21) to the right, thus contributing to the increase in the electrochemically active complex concentration. Hence, the co-factor  $\prod C_{i,j}^{v_{i,j}}$  and the rate constant  $\tilde{k}_2$  increase. This agrees well with the experimental data obtained.

We note that the composition of chromium complexes is shown in the scheme provisionally. It is possible that certain other adsorbed complexes different from those shown above or several Cr(II) hydroxocomplexes of different composition concurrently can also be electroactive.

As follows from Fig. 4, the rate of the chromium deposition decreases with an increase in the disk rotation velocity  $\omega$  (for ascending section of  $i_2$  vs. *E* curve). Due to a parallel discharge of hydrogen ions, chromium electrodeposition from aqueous solutions is always accompanied by an increase in pH<sub>S</sub> in the nearelectrode solution layer [32]. An increase in the disk electrode rotation velocity favors the lowering of pH<sub>S</sub>. This naturally leads to the lowering of the electroactive complexes concentration; thus, the rate of the chromium deposition reaction diminishes.

A thermodynamic stability of the Cr(II) oxalate complexes exceeds that of the corresponding formate complexes by several orders of magnitude [2]; therefore, the formation of a significant amount of the hydroxocomplexes is questionable; we may assume that it is the oxalate complexes of bivalent chromium that directly discharge (involving hydrogen ions):

$$[Cr(II)(C_2O_4)(H_2O)_n]_{ads} + 2H^+ + 2e^- \rightarrow Cr^0 + H_2C_2O_4 + nH_2O$$
(23)

The suggested reaction scheme (23) agrees with the data obtained: in particular, the rate of chromium deposition from oxalate bath increases with an increase in the solution acidity and a decrease in the  $H_2C_2O_4$  concentration.

Due to a high buffer capacity of the oxalate-containing electrolyte, the pH<sub>S</sub> deviation from the solution pH is probably small and, therefore, hardly changes with an increase in the disk electrode rotation velocity  $\omega$ . Hence, the chromium electrodeposition rate is independent of  $\omega$  in the electrolytes containing oxalic acid (see Fig. 4).



**Fig. 6.** The value of  $i_{2,max}$  as a function of disk rotation velocity for (1) formate bath and (2) oxalate bath.

It should be stressed that the presence of a peak in the  $i_2$  vs. *E* curves does not follow from the above equations, thus indicating that the adopted kinetic model fails to account for all the features of the chromium electrodeposition process.

The dependence of  $i_{2,max}$  on the disk electrode rotation velocity  $\omega$  cannot be described by the Levich equation [33] (see Fig. 6). Hence, the formation of a current peak in the partial polarization curves is not related with the convection–diffusion limitations of the transport of some chromium-containing ions.

We believe that a decrease in the partial current density of chromium electrodeposition is probably caused by blocking the electrode surface with poorly soluble adsorbed hydroxide compounds of Cr(III) [14]. This phenomenon is due to the abovementioned local increase in pH<sub>S</sub> near the electrode layer. At the electrode potential range corresponding to the descendent segments in the  $i_2$  vs. *E* curves, we observed the deterioration of the deposit appearance. The particles of the Cr(III) hydroxide sol cover the electrode surface and are incorporated into coating structure, which causes cracking and darkening of deposits.

With an increase in the acidity and the concentration of bufferligand (HCOOH or  $H_2C_2O_4$ ) in the electrolyte, the amount of Cr(III) hydroxide adsorbed on the cathode decreases. That is the reason for the corresponding increase in the value of peak current density  $i_{2,max}$ . Obviously, such effects must be highly sensitive to changes in the convective mass transfer, which agrees well with our data. Indeed, the pH<sub>S</sub> value and the cathode blocking by adsorbed Cr(III) hydroxide evidently decrease with increasing  $\omega$ .

The phenomenon involved is rather complex and can be described quantitatively by introducing additional terms into above kinetic equations, which would take into account the blocked electrode surface and a decreased Cr(III) concentration in the nearelectrode layer caused by the Cr(III) hydroxide formation. This problem must be considered in detail in a separate communications.

#### 4. Conclusions

(1) The electroreduction of Cr(III) complex ions in aqueous solutions is demonstrated to proceed step-wise, via the formation of relatively stable intermediates—Cr(II) compounds. Only a part of the total amount of Cr(II) complexes formed at the first stage of Cr(III) discharge is reduced further to the metal. Hence, the rate of the chromium deposition is determined by the current density of Cr(II) ions electroreduction. The corresponding kinetic equations were derived and compared with the experimental data obtained on a stationery and rotating disk electrode. Kinetic parameters for the Cr(II) ions discharge were calculated.

<sup>&</sup>lt;sup>2</sup> A similar reaction scheme has been proposed by us for the electrodeposition process in trivalent chromium baths containing aminoacetic acid [14].

- (2) The kinetics and mechanism of chromium deposition from oxalate and formate baths proved to be different. In case of formate electrolyte, the metal chromium deposits probably via the discharge of electroactive hydroxocomplexes of bivalent chromium which are formed in the near-cathode layer due to the dissociation of inner-sphere-coordinated water molecules. In case of oxalate electrolyte, the formation of a significant amount of the hydroxocomplexes is questionable. Therefore, the reaction of chromium deposition from oxalate bath is assumed to proceed with the participation of oxalate complexes of Cr(II). The reaction schemes proposed agree well with the experimental data obtained.
- (3) The partial polarization curves of chromium electrodeposition exhibit a current peak. A decrease in the partial current density may be caused by blocking the electrode surface with poorly soluble hydroxide compounds of Cr(III).

#### References

- [1] N.T. Kudryavtsev, I.I. Potapov, N.G. Sorokina, Zashch. Met. 1 (1965) 304.
- [2] J. Datta, Galvanotechnik 73 (1982) 106.
- [3] D. Smart, T.E. Such, S.J. Wake, Trans. Inst. Metal. Finish 61 (1983) 105.
- [4] I. Roubal, Galvanotechnik 69 (1978) 301.
- [5] M.N. Ben-Ali, F.I. Danilov, M.M. Mandryka, Elektrokhimiya 27 (1991) 532.
- [6] Ya.M. Kolotyrkin, E.A. Larchenko, G.M. Florianovich, Elektrokhimiya 32 (1996) 431.
- [7] I. Drela, J. Szynkarczuk, J. Kubicki, J. Appl. Electrochem. 19 (1989) 933.
- [8] Y.B. Song, D.-T. Chin, Electrochim. Acta 48 (2002) 349.
- [9] S. Survilene, O. Nivinskiene, A. Cesuniene, A. Selskis, J. Appl. Electrochem. 36 (2006) 649.

- [10] J. McDougall, M. El-Sharif, S. Ma, J. Appl. Electrochem. 28 (1998) 929.
- [11] J. Szynkarczuk, I. Drela, J. Kubicki, Electrochim. Acta 34 (1989) 399.
- [12] A.A. Edigaryan, Yu.M. Polukarov, Zashch. Met. 32 (1996) 504.
- [13] A.A. Edigaryan, Yu.M. Polukarov, Zashch. Met. 34 (1998) 117.
- [14] F.I. Danilov, V.S. Protsenko, Zashch. Met. 37 (2001) 251.
- [15] L.N. Vykhodtseva, A.A. Edigaryan, E.N. Lubnin, Yu.M. Polukarov, V.A. Safonov, Elektrokhimiya 40 (2004) 435.
- [16] G. Hong, K.S. Siow, G. Zhiqiang, A.K. Hsieh, Plat. Surf. Finish 88 (2001) 69.
- [17] Z. Zeng, Y. Sun, J. Zhang, Electrochem. Commun. 11 (2009) 331.
- [18] V.N. Korshunov, V.A. Safonov, L.N. Vykhodtseva, Elektrokhimiya 44 (2008) 275.
- [19] I.M. Kolthoff, J.J. Lingane, Polarography, Interscience, New York, 1941.
- [20] A.V. Pamfilov, A.I. Lopushanska, A.M. Balter, J. Phys. Chem. USSR 36 (1962) 2481.
- [21] A.V. Pamfilov, A.I. Lopushanska, A.M. Balter, J. Phys. Chem. USSR 37 (1963) 615.
- [22] A.V. Pamfilov, A.I. Lopushanska, S.A. Pohmelkina, Elektrokhimiya 4 (1968) 780.
   [23] F.I. Danilov, A.B. Velichenko, S.M. Loboda, S.E. Kalinovskaya, Elektrokhimiya 23 (1987) 988.
- [24] Yu.M. Polukarov, V.A. Safonov, A.A. Edigaryan, L.N. Vyhodtseva, Zashch. Met. 37 (2001) 499.
- [25] S.C. Kwon, M. Kim, S.U. Park, D.Y. Kim, D. Kim, K.S. Nam, Y. Choi, Surf. Coat. Technol. 183 (2004) 151.
- [26] V.A. Safonov, L.N. Vykhodtseva, Yu.M. Polukarov, O.V. Safonova, G. Smolentsev, M. Sikora, S.G. Eeckhout, P. Glatzel, J. Phys. Chem. B 110 (2006) 23192.
- [27] I. Drela, J. Szynkarczuk, J. Kubicki, Electrochim. Acta 33 (1988) 589.
- [28] V.V. Losev, Itogi Nauki Tekh., Ser.: Elektrokhimiya (VINITI, Moscow) 6 (1971) 65.
   [29] A.J. Bards, L.R. Faulkner, Electrochemical Methods—Fundamentals and Applications, second ed., Wiley, New York, 2001, p. 108.
- [30] V.I. Kravtsov, Ravnovesie i Kinetika Elektrodnyh Reaktsiy Kompleksov Metallov, Khimia, Leningrad, 1985, p. 153.
- [31] V.V. Kuznetsov, E.G. Vinokurov, V.N. Kudryavtsev, Elektrokhimiya 36 (2000) 756.
- [32] V.S. Kublanovskii, A.V. Gorodysky, V.N. Belinskii, T.S. Glushchak, Concentration Variations in the Near-electrode Layers during Electrolyses, Naukova Dumka, Kiev, 1978.
- [33] V.G. Levich, Physicochemical Hydrodynamics, Prentice-Hall, Englewood Cliffs, NJ, 1962.