MECHANISM OF THE ELECTRODEPOSITION OF CHROMIUM FROM TRIVALENT COMPOUNDS

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We studied the influence of complex strength and anion character on the reaction rates during electrodeposition of chromium and investigated the electrochemical behavior of a number of complex compounds of chromium (+3) with inorganic and organic ligands, using complexes with different strengths. It was shown that the principal factor affecting the chromium-deposition rate is the state of the electrode surface, which depends on the chemical nature of the ligands. Complex strength has no material effect on the rate of the process investigated.

We previously investigated the influence of complex structure and ligand chemical nature on the reaction rates during electrodeposition of chromium from solutions of its violet and green sulfates [1]. It was shown that the rates of the individual electrochemical reactions depend to a large extent on the state of the cathode surface, which is governed by the nature of the inorganic anions (OH^- and SO_4^{2-}) present in the complexes. The present work, a continuation of our prior research, was devoted to a study of different complex salts of chromium (nitrates, oxalates, and complexes with glycocoll and trylon B). We investigated the influence of complex strength and ligand nature on the rate of electrodeposition of chromium from its trivalent compounds.

The experimental method was described in detail in our previous report [1], It need only be noted that the experimental results were obtained by the potentiostatic method. The potentials are given with respect to a saturated calomel comparison electrode. Analytically pure salts were used. We studied freshly prepared blue-violet solutions of the appropriate salts with a constant chromium-ion (+3) concentration of 0.8 M at pH 2.3 and a temperature of 35°.

EXPERIMENTAL RESULTS AND DISCUSSION

The acid radicals with which Cr^{3+} forms complexes are arrayed in the following order of increasing affinity for complexing with chromium (+3) ions [2]: ClO_4^-... < NO_3^-... < Cl^-... < SO_4^{2-} < SO_3^{2-} < formate < acetate < oxalate < OH^- < glycocoll < trylon B. All the radicals following the SO_4^{2-} ion can completely

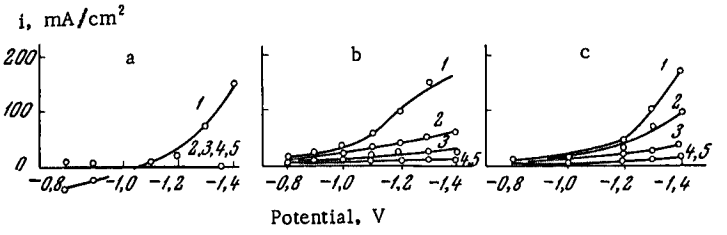

Fig. 1. Rates of electrochemical reactions involving precipitation of metal (a), $Cr^{3+} + \bar{e} \rightarrow Cr^{2+}$ (b), and $H_3O^+ + 2\bar{e} \rightarrow H_2 + H_2O$ (c) (the reaction designations are the same in Figs. 2-4) as a function of potential and of the nature of the anions and organic complexing agents; pH 2.3; $[Cr^{3+}] = 0.8$ M. Curves: 1) $Cr_2(SO_4)_3$; 2) $Cr(NO_3)_3$; 3) $Cr_2(C_2O_4)_3$; 4) glycocoll (saturated) + $Cr(NO_3)_3$; 5) trylon B (saturated) + $Cr_2(NO)_3$.

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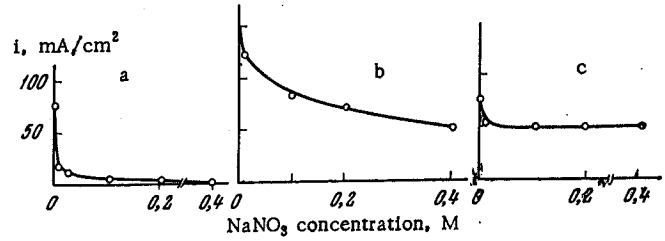

Fig. 2. Rates of electrochemical reactions a, b, and c as a function of $NaNO_3$ concentration in 0.4 M $Cr_2(SO_4)_3$ solution at pH 2.3; φ = const = −1.3 V.

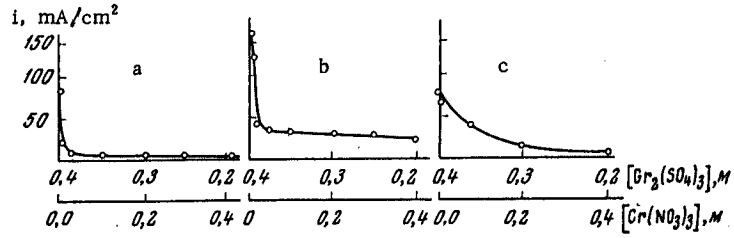

Fig. 3. Influence of $[Cr_2(SO_4)_3]$:$[Cr(NO_3)_3]$ ratio at constant chromium (3+) concentration of 0.8 M on rates of electrochemical reactions a, b, and c at pH 2.3; φ = const = −1.3 V.

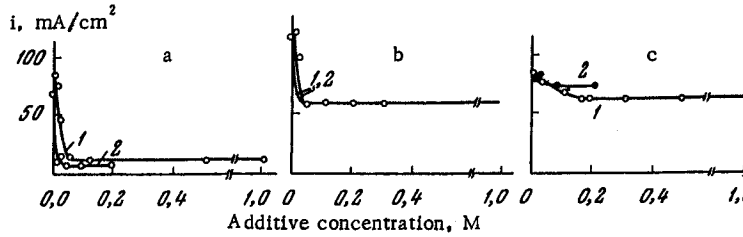

Fig. 4. Influence of organic additives in sulfate solutions on rates of electrochemical reactions a, b, and c. 1) Glycocoll; 2) trylon B, pH 2.3; φ = −1.3 V.

displace the latter from complexes with chromium. We studied the individual members of this series of different complexing strengths.

If complex strength were the limiting factor in the electroreduction process, it would be expected that, in accordance with this sequence, the nitrate complex, which is the weakest in the series, would be reduced at the highest rate. However, as can be seen from the experimental data (Fig. 1a, curve 2), * chromium ions in nitrate solution were not reduced to the metal and the chromium did not dissolve; the rates of incomplete reduction of the chromium ions and of hydrogen evolution were substantially lower than in sulfate solution (compare curves 1 and 2 in Fig. 1b and c). Thus, the rate of incomplete reduction of the

* The conditions under consideration (a high chromium-ion concentration and evolution of hydrogen, which causes alkalization of the layer near the electrode and disrupts the stability of the diffusion layer) virtually exclude the possibility of reduction of nitrate ions at the cathode [3].

TABLE 1. Influence of Electrolyte Composition on Steady-State Potentials of Chromium

Electrolyte composition	Modification	pH	Cathodic-polarization potential $-\varphi$, V	Steady-state potential $-\varphi$, V
0,4 *M* $Cr_2(SO_4)_3$	Violet	1,5—2,3	1,0—1,3	0,70—0,78
0,4 *M* $Cr_2(SO_4)_3$	Green	1,5—2,3	1,0—1,3	0,7—0,84
0,4 *M* $Cr_2(SO_4)_3$+ +0,002 *M* $Cr(NO_3)_3$	Violet	1,8	0,8—1,3	0,60
0,4 *M* $Cr_2(SO_4)_3$+ +0,02 *M* $Cr_2(NO_3)_3$	"	1,8	0,8—1,3	0,52
0,35 *M* $Cr_2(SO_4)_3$+ +0,1 *M* $Cr(NO_3)_3$	"	1,8	0,8—1,3	0,45
0,3 *M* $Cr_2(SO_4)_3$+ +0,2 *M* $Cr(NO_3)_3$	"	1,8	0,8—1,3	0,43—0,27
0,8 *M* $Cr(NO_3)_3$	"	2,0—2,3	0,8—1,3	0,30—0,28
0,8 *M* $Cr(NO_3)_3$+ +0,2 *M* K_2SO_4	"	1,8	0,8—1,3	0,30—0,31
0,4 *M* $Cr_2(C_2O_4)_3$	"	2,3—2,8	1,1—1,4	0,5—0,45
0,8 *M* $Cr(NO_3)_3$+ + 1,0 glycocoll (saturated)	"	2-3	1,0—1,5	0,37—0,30
0,8 *M* $Cr(NO_3)_3$+ +0,1 *M* trylon B (saturated)	"	2-3	1,0—1,4	0,50--0,45
0,4 *M* $Cr_2(SO_4)_3$+ +0,01 *M* trylon B	"	1,8—1,9	1,3	0,77
0,4 *M* $Cr_2(SO_4)_3$+ +0,1 *M* trylon B (saturated)	"	2,3	1,3	0,60
0,4 *M* $Cr_2(SO_4)_3$+ +0,01 *M* glycocoll	"	2,3	1,3	0,53
0,4 *M* $Cr_2(SO_4)_3$+ + glycocoll (saturated)	"	2,3	1,3	0,51

chromium ions at a potential of −1.3 V reached 150 mA/cm^2 in the sulfate solution but only 50 mA/cm^2 in the nitrate solution.

When strong complexing agents (glycocoll or trylon B) were added to the nitrate solution, the metal was not precipitated and the rates of the other two reactions were reduced by a factor of 2 or more (Fig. 1a, b, and c, curves 4 and 5). Nitrate ions obviously promote passivation of the chromium surface [5] and cause kinetic inhibition of the electrode chromium-dissolution and chromium-precipitation reactions, while the other two reactions (incomplete reduction of the chromium ions and hydrogen evolution), which have a lower activation energy, can also occur at passive sections of the electrode surface. The observed decrease in the rates of these reactions in the presence of organic additives (glycocoll and trylon B) can be attributed to additional screening of the electrode surface and partial displacement of the chromium ions being reduced.

As in solutions of the weakest nitrate complexes, neither precipitation nor dissolution of metallic chromium occurred in solutions of strong oxalate complexes in the potential region investigated (−0.8 to −1.3 V; Fig. 1a, curve 3). The rates of incomplete chromium-ion reduction and hydrogen evolution (Fig. 1b and c, curves 3) were also lower in the oxalate solution than in the sulfate solution.

Thus, when the complexes are compared with respect to strength (nitrate, sulfate, and oxalate complexes), it can be seen that there was no direct correlation between complex strength and the rate of chromium electrodeposition. The SO_4^{2-} anion, which occupies an intermediate position in the complex-strength series, promoted higher rates for all the electrochemical reactions, while the weakest nitrate complexes and the oxalate complexes, which are stronger than SO_4^{2-}, caused kinetic retardation of these reactions. The observed phenomena can be attributed to the influence of the anions in the chromium complexes on the state of the cathode surface and hence on the rates of the electrochemical reactions. Complex strength is obviously of secondary importance in the electrodeposition of chromium.

Actually, as is well known, the passivity or activity of a metal depends to a large extent on the electrolyte composition, particularly on its pH and the anions present. The specific influence of acid anions lies in their effect on the state of the surface: they act to passivate the metal or to dissolve the passivating layer. Adsorption of passivating NO_3^- ions [5] leads to development of a passivation barrier on the metal surface, which reduces its adsorptive capacity [6] and consequently prevents electrodeposition of chromium.

Activating SO_4^{2-} anions, which are rapidly and stably adsorbed, prevent adsorption of or even repel chemisorbed oxygen and increase the hydrogen-evolution overvoltage [7]. As a result of dissolution of the passivating layer, both precipitation (between −1.1 and −1.3 V) and dissolution (between −0.8 and −1.0 V) of chromium are possible in definite cathodic-potential regions; we observed this phenomenon in the presence of SO_4^{2-} ions.

Oxalate anions, glycocoll, and trylon B, which exhibit no marked tendency toward passivation of chromium, nevertheless inhibited the electrochemical reactions. This can be explained in the following manner. Competition between two phenomena occurs at the surface of the growing crystal during electrodeposition: precipitation of the metal tends to enlarge the active surface, while adsorption of foreign particles ($C_2O_4^{2-}$ anions and organic radicals) tends to reduce it. When the conditions are unfavorable for electrodeposition of chromium (adsorption of inactivating additives, such as $C_2O_4^{2-}$ or organic complexing agents), formation of an adsorbed layer prevents the continuous renewal of the surface that occurs during deposition of the metal [8]. The influence of $C_2O_4^{2-}$ anions, glycocoll, and trylon B can therefore be attributed to the inhibitory effect resulting from blocking of the surface and their influence on the energy mechanism: the latter involves poisoning of the active centers and inhibition of the electrochemical reactions by the dipole potential jump [9].

Investigation of the behavior of numerous complexes has shown that the nature of the coordinated groups and the thermodynamic stability of the complex ions has a definite influence on the quality of the platings produced [10]. Complexes that are too readily or too difficultly reduced and complexes containing large coordination groups (organic radicals of the aromatic type) yield poor platings; complexes with intermediate strength (such as sulfate complexes) give good platings.

We observed a decrease in the rates of all three reactions under consideration when a very small nitrate-ion concentration (0.002 M) was added to a 0.4 M chromium sulfate solution (Fig. 2). This effect demonstrated that the passivating action of NO_3^- anions is stronger than the activating action of SO_4^{2-} ions. Similar data were obtained for a solution with different NO_3^- and SO_4^{2-} concentrations and the same Cr^{3+} concentration (Fig. 3). Thus, the rate at which Cr^{3+} was reduced to Cr^0 and Cr^{2+} was severely reduced at a ratio $[NO_3^-]:[SO_4^{2-}] = 1:240$ (0.005 M $Cr[NO_3]_3$ and 0.4 M $Cr_2[SO_4]_3$) (Fig. 3a and b); the hydrogen-evolution rate was also reduced, but more smoothly. Precipitation of metallic chromium completely ceased at a ratio $[NO_3^-]:[SO_4^{2-}] = 1:2$.

The results presented above indicate that the state of the electrode surface, which depends on the chemical nature of the anions in solution (whether they have a passivating or activating effect), is of greater importance than the strength of the complexes containing these anions. If the chromium surface is sufficiently active, i.e., ready for electrocrystallization, the strength of the complexes is obviously not too great an energetic obstacle to electroreduction of the ions to metallic chromium, although it affects the rates of the electrochemical reactions.

The influence of very small concentrations of strong complexing agents (glycocoll and trylon B) in chromium sulfate solution is interesting in this respect (Fig. 4). The metal-deposition rate, although reduced by a factor of 6, did not drop to zero at concentrations of 0.002 M glycocoll and 0.01 M trylon B, while the rate of the $Cr^{+3} + \bar{e} \rightarrow Cr^{2+}$ reaction decreased by a factor of 2. It can thus be seen that organic additives have a greater effect on electrocrystallization of the metal [11] than on incomplete reduction of the chromium ions or hydrogen evolution.

Complex strength is apparently also of secondary importance in this case, since it is difficult to imagine that complete complexing of the chromium ions could have occurred at concentrations of 0.01 M organic additive and 0.8 M Cr^{3+} and a coordination number of six. The patterns observed can probably be attributed to screening of the electrode surface by the large, well-adsorbed organic molecules of glycocoll and trylon B.

It is important to note that the rates of the electrochemical reactions at $\varphi = \text{const} = 1.3$ V in the presence of glycocoll or trylon B (in saturation concentrations) were an order of magnitude higher in the sulfate solution than in the nitrate solution (Fig. 1b and c, curves 4 and 5). Despite the complexing of the chromium (3+) ions by the organic radicals, the specific influence of anion character on the state of the electrode surface is obviously stronger than that of complex strength. Adsorption of anions can alter the chemical and electrochemical reactivity of the metal surface [12] and thus affect the rates of the reactions under consideration.

Another important characteristic of the state of the chromium surface is the steady-state potential, which is measured 1-2 min after the polarizing current is switched off.

It can be seen from the data in Table 1 that the steady-state potential was virtually independent of the modification and amounted to from −0.7 to −0.8 V (n.c.e.) for the sulfate, depending on the pH. When NO_3^- anions were added to the same sulfate solution and their concentration was increased, the potential shifted in the positive direction, reaching −0.3 V in 0.8 M nitrate solution. This indicates considerable passivation of the surface by NO_3^-. Conversely, when SO_4^{2-} anions were added to the nitrate solution, the steady-state potential held constant at −0.3 V. The steady-state potential was 300 mV more positive in the oxalate solution than in the sulfate solution.

CONCLUSIONS

1. We have shown that there is no direct correlation between the strength of the complex chromium ions and the rate at which they are reduced.

2. The NO_3^- anion, which forms very weak complexes, causes substantial passivation of the metal surface, which prevents precipitation and dissolution of the chromium and inhibits incomplete reduction of the chromium ions and hydrogen evolution. The rates of these reactions are maximal in the presence of the SO_4^{2-} anion, which occupies an intermediate position in the complex-strength series. In mixtures of NO_3^- and SO_4^{2-}, the passivating effect of the former is stronger than the activating effect of the latter.

3. The state of the cathode surface, i.e., its activity, depends on the chemical nature of the anions present in the complex (the ligands) and is a more important and decisive factor in the electroreduction of chromium ions than in complex strength. The state and activity of the surface can be evaluated by studying the kinetics of the cathodic reactions and measuring the steady-state potentials.

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