MECHANISM OF THE ELECTROREDUCTION OF CHROMIC ACID

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The rate of chromic acid reduction is usually related to the production and properties of a film formed on the cathode. The following characteristics are observed. In the presence of H_2SO_4 the rate of the electrochemical process in the first moment of electrolysis is very great but rapidly decreases to a small, definite value (Fig. 1). This sharp decrease of the reaction rate with time is not observed in the absence of H_2SO_4 (Fig. 2).

The sharp retardation with time of the electrochemical reaction in an electrolyte containing H_2SO_4 is most likely explained by the fact that in this case the reaction products form a film on the electrode surface and this hinders the electrochemical process. The formation of a film on the cathode surface during the electroprecipitation of chromium has been assumed by many investigators. However most of them consider that the introduction of H_2SO_4 into the solution promotes disintegration of the film, promoting the penetration of chromate ions to the cathode and their reduction to the metal. The curves in Figs. 1 and 2 show that this assumption is doubtflu as in the presence of H_2SO_4 the rate of the electrochemical process, on the contrary, decreases and this can only occur as a result of thickening,and not destruction,of the film. Figure 1 also shows that when the current is switched off, the film formed during electrolysis dissolves chemically in chromic acid as is indicated by the fact that when the current is reapplied the maximum value of the current density reaches the initial value. The formation of the film on the cathode leads to a displacement of the cathode potential in a negative direction [1] and makes the reduction of chromic acid to the metal and trivalent chromium possible in addition to the discharge of hydrogen ions. It can also be assumed that with the formation of the film the hydrogen overvoltage becomes considerably greater than on a pure chromium surface. In all probability this is explained by the fact that in the absence of H_2SO_4 when there is no film on the electrode surface the predominant process is the liberation of hydrogen.

In elucidation of the mechanism of the reduction of chromic acid ions to the metal the first problem that arises is whether this reduction proceeds directly or stepwise with the intermediate formation of trivalent chromium ions.

There is no single opinion on this [2-6]. The accuracy of this or that point of view can be checked by a tracer method. Ogburn and Brenner [7], who used the radioactive isotope of chromium Cr^{51} as a tracer, came to the conclusion that the hexavalent chromium ion is discharged directly to the metal without the stage of an intermediate valence. This conclusion was based on the fact that considerably less radioactive atoms of trivalent chromium passed into the electrodeposit than when hexavalent chromium was labeled. A number of objections were raised to the work of Ogburn and Brenner. Doubts were raised as to whether the trivalent chromium from the mass of the solution could penetrate to the cathode through the film, which had a different permeability to ions of different valence. In addition, the work of Ogburn and Brenner was carried out without considering the possibility of different states of trivalent chromium ions in solution, for these ions are known to exist in aqueous solution in the form of several modifications with different electrochemical behavior [8].

To solve the problem of the number of stages in the reduction of chromic acid to the metal,we also used radioactive tracers. Radioactive chromium was introduced into a chromium bath, containing 250 g/liter of Cr^{3+}, in the form of chromium sulfate or sodium bichromate, depending on the valence of the ion we wished to put into the solution. The radioactivity of the electrodeposit and a sample of the solution was measured with an end-window counter. For comparison of the separate results, all the radioactivity values of the deposits were corrected for layer thickness, allowing for self-absorption in the layer of chromium.

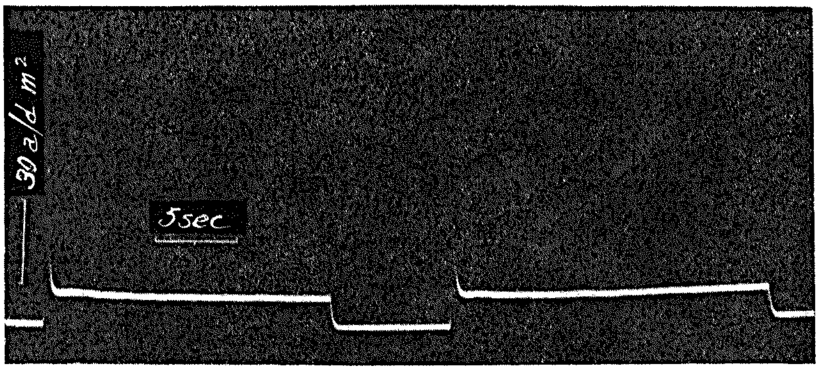

Fig. 1. Relation between current strength and duration of electrolysis obtained in a solution of 250 g/liter of CrO_3 and 2.5 g/liter of H_2SO_4 at a constant cathode potential of 1080 mv.

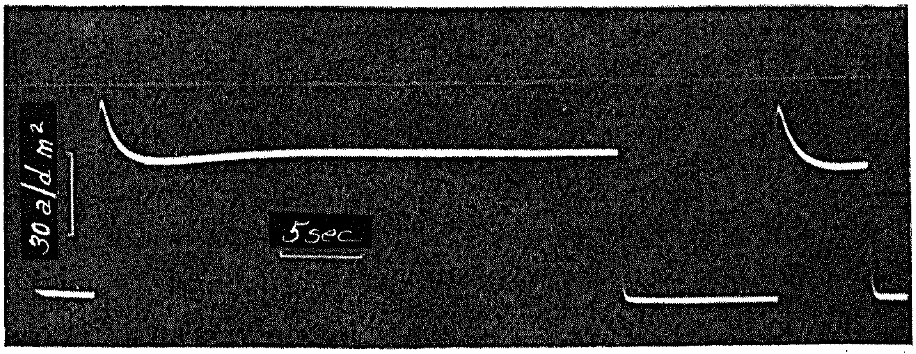

Fig. 2. Relation between current strength and duration of electrolysis obtained in a solution of 250 g/liter of CrO_3 at a constant cathode potential of 1080 mv.

The effect of the film on the possibility of trivalent chromium penetrating to the cathode was determined by interrupting the current during the electrodeposition of chromium for, as has already been mentioned above, the film was dissolved after the current had been switched off. Electrolysis with an intermittent current was accompanied by formation and destruction of the film which made it possible for ions to reach the cathode surface to a large extent. The conditions of deposition with an intermittent current were as follows: current density – 20 a/dm^2, temperature – +20°, electrolysis time – 1.25 sec. and interruption time – 9 sec. By comparing the data obtained with the results of depositing chromium with a continuous current it was established that the specific activity of the deposits was identical for the two cases. This showed that the presence of the film had no effect on the experimental results.

To determine the effect of the modification of the trivalent chromium salt on its electrochemical behavior, the radioactive atoms of trivalent chromium were introduced into the bath in the form of green or violet sulfates, i.e., the usual modifications of these salts for aqueous solutions. The violet sulfate was obtained by solution of chromium hydroxide in H_2SO_4 in the cold and the green one by prolonged boiling of the violet solution with subsequent rapid cooling. The two modifications were prepared immediately before introduction into the chromium bath.

The results of the experiments are presented in the table. For comparison the table also gives the specific activity of a deposit obtained from a bath with radioactive hexavalent chromium. The table shows that the behavior of the violet and green modifications were analogous and that the electrodeposit of chromium obtained in both cases in their presence had a radioactivity that was two orders less than in the case when radioactive hexavalent chromium was introduced into the electrolyte.

The data presented indicate that trivalent chromium is not an intermediate stage in the reduction of chromic acid to the metal and that this reduction proceeds without the formation of stable trivalent ions.

Results of Experiments with a Radioactive Tracer

Valence of radioactive tracer	Modification of radioactive chromium sulfate	Specific activity of starting solution, counts/min • ml	Specific activity of electrodeposit	Corrected specific activity of electrodeposit
			counts/min • g	
			4.3	
III	Violet	$5.3 \cdot 10^4$	$4.3 \cdot 10^3$	$1.1 \cdot 10^3$
III	Green	$4.4 \cdot 10^4$	$5.6 \cdot 10^3$	$1.6 \cdot 10^3$
VI	–	$1.3 \cdot 10^4$	$1.9 \cdot 10^5$	$1.9 \cdot 10^5$

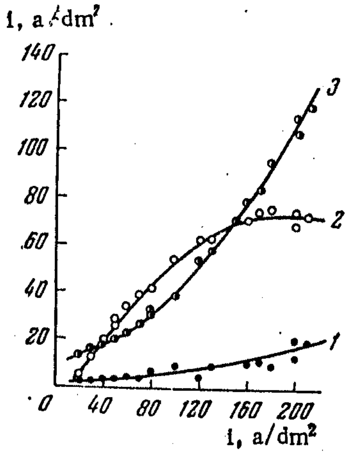

Fig. 3. Relation between the rates of the separate reactions and the over-all current density in the electrodeposition of chromium. 1) $Cr_2O_7^{2-} + 14 H^+ 6 e \rightleftharpoons 2Cr^{3+} 7H_2O$; 2) $Cr_2O_7^{2-} + 14 H^+ + 12 e \rightleftharpoons 2 Cr + 7 H_2O$; 3) $2 H^+ + 2 e \rightarrow H_2$.

The problem naturally arises as to why one part of the chromate ions are reduced directly to the metal and the other only to the trivalent state under the same conditions. The most probable answer is that the reactions proceed by different routes. If such a hypothesis is correct, then the rate of each reaction must obey its own laws and the limiting current will be reached by them independently.

To test this hypothesis, we studied the rate of each reaction under different electrolysis conditions. Obviously, it is possible to observe the limiting current for the separate reactions at a comparatively low total current density with low chromic anhydride concentrations in the bath and at comparatively low temperatures.

Figure 3 shows curves of the relation between the rates of each separate reaction and the over-all rate of the process, obtained in a solution with the composition of 40 g/liter of CrO_3 and 0.8 g/liter of H_2SO_4 at 20°.

As can be seen from the curves, in the case of the reaction $Cr^6 \rightarrow Cr$ the current reaches a limiting value even at a total current density of 150-160 a/dm², while the rate of the reaction $Cr^{6+} \rightarrow Cr^{3+}$ under these conditions continues to increase smoothly similarly to the rate of hydrogen evolution. At first glance, this difference may seem strange as the starting ion that is reduced is the same in both cases. With a decrease in its concentration at the cathode surface to zero, the current must reach a limiting value not only for the deposition of the metal, but also for the formation of trivalent chromium. This indicated that in this region of potentials where metallic chromium is liberated, the reduction of chromate ion proceeds differently: in the case of metal deposition the reduction proceeds directly on the electrode by an electrochemical method, but in the reduction to Cr^{3+} it probably occurs at some distance from the electrode by a chemical route by means of atomic hydrogen. The latter hypothesis seems all the more plausible as it has already been shown in a series of works [6] that the reduction of chromic acid to the trivalent state by atomic hydrogen is possible in principle.

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