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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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THE INFLUENCE OF THE STATE OF THE CATHODE SURFACE ON THE CHARACTER OF AN ELECTROCHEMICAL REACTION

(Presented by Academician V. I. Spitsyn, 13 IX 1963)

The state of the surface of a solid electrode has a substantial influence on the rate of discharge of ions and on the character of the reaction taking place. The discharge of silver ions, for example, proceeds at a high rate on an active surface and is sharply slowed on a passive one (*1*). Ions of other metals, such as nickel or manganese, on a passive surface cease to be reduced altogether (*2*). Electroreduction of chromic acid may serve as a striking example of how, when the state of the cathode surface changes, not only the rate but also the character of the principal electrode reaction changes. At low current densities, corresponding to the region of incomplete reduction of chromic acid on a chromium cathode, the reaction $2H^+ \rightarrow H_2$ or $Cr^{6+} \rightarrow Cr^{3+}$ may occur, depending on the state of its surface.

Fig. 1

In a standard chromic-acid electrolyte solution containing 2.5 M chromic anhydride and 0.025 M sulfuric acid, at a temperature of 40° and a current density of 20 mA/cm^2 on a chromium cathode just coated with an electrolytic layer of chromium and immersed in the electrolyte under current (or when the current is switched on very rapidly), almost all the current is consumed in the reaction of incomplete reduction of chromic acid,

$$Cr^{6+} \rightarrow Cr^{3+}.$$

The cathode potential in this case corresponds to a value of $-0.51--0.52$ V (curve 1, Fig. 1), and visually one can observe the products of the reaction

Fig. 2

Figure 2: Fig. 2

$Cr^{6+} \rightarrow Cr^{3+}$ flowing down from the cathode in the form of a dark stream. The discharge of hydrogen ions occurs in this case to a very small extent. Under the same experimental conditions, on a cathode left in the solution before the current is switched on for $\tau = 15$ sec, the reaction of hydrogen evolution,

$$2H^+ \rightarrow H_2,$$

proceeds predominantly. The cathode potential then increases to −0.9−−0.88 V (curve 2, Fig. 1). No matter how long electrolysis is continued, the cathode potential does not decrease, and the principal reaction on such a cathode remains the discharge of hydrogen ions. Thus, only as a result of keeping the chromium cathode in the chromic-acid solution without current is the reaction $Cr^{6+} \rightarrow Cr^{3+}$ sharply impeded.

It is evident that, when the chromium cathode is kept in a chromic-acid solution without current, passivation of its surface occurs, since chromic acid possesses a strong oxidizing action and is used specially for the formation of passive films on various metals (*3*). It is possible that on an oxidized surface the adsorption of chromic-acid anions is greatly hindered and the reaction $Cr^{6+} \rightarrow Cr^{3+}$ is sharply inhibited. It is true that complete cessation of this reaction does not occur. Analysis of the electrolysis products showed that on passive chromium approximately 75% of the current is consumed in the reaction

$$2H^+ \rightarrow H_2,$$

and the remaining current goes to the reac-

of $Cr^{6+} \rightarrow Cr^{3+}$.* This shows that not the entire surface of the cathode is equally passive. In all probability, incomplete reduction of chromate ions occurs on active or less passive areas.

It is interesting to note that, when in the above-mentioned standard chromium electrolyte the amount of trivalent chromium appearing as a result of the reaction $Cr^{6+} \rightarrow Cr^{3+}$ reaches a certain limit, the passivation process manifests itself differently. If a chromium cathode is left in such a solution for the same period of time $\tau = 15$ sec (at 40°),

Fig. 2

one can visually observe that in the first seconds of electrolysis hydrogen is vigorously evolved at the cathode. Then the hydrogen bubbles disappear and the products of the reaction $Cr^{6+} \rightarrow Cr^{3+}$ begin to appear. On the oscillograms (Fig. 2), the first period—the hydrogen-evolution reaction—corresponds to a more negative value of the cathode potential. After several seconds the potential drops abruptly, which corresponds to the second period—the reaction of incomplete reduction of chromic acid. Thus, in the present case one can observe a spontaneous change of reactions $Cr^{6+} \rightarrow Cr^{3+}$ and $2H^+ \rightarrow H_2$.** Apparently, this occurs as a result of reduction of the passive film over the course of electrolysis by the hydrogen being evolved. It is possible that, as a result of adsorption of trivalent chromium ions, the strength of the bond between oxygen and the metal becomes lower, and therefore the oxides can be reduced.

Such oscillograms with maxima were observed by Yu. Yu. Matulis and A. Yu. Mitskene ([4]) in studying the electroreduction of chromic acid in the region of very low current densities on chromium, nickel, and iron cathodes. Owing to the very small current densities (less than 1 mA/cm^2), observation of the nature of the reaction occurring at the cathode was very difficult. Nevertheless, the authors cited correctly noted in that work that on a passive cathode surface the reduction of chromic acid is sharply hindered and is replaced by the reduction of hydrogen ions. However, according to the data given above on determination of the products of the cathodic reaction, complete cessation of the reduction of chromic acid on a passive cathode in the presence of sulfate ions does not occur; consequently, some part of the surface remains active. In all probability, the preservation of some fraction of the surface in an active state is a consequence of the dynamic character of the process of formation and destruction of the passive film, or of adsorption of other particles on the metal surface that do not cause its oxidation.

As is evident from the results presented, reduction of the passive film by the hydrogen evolved at the cathode and the sharp decrease in cathode potential corresponding to the transition from the reaction $2H^+ \rightarrow H_2$ as the principal one to the reaction $Cr^{6+} \rightarrow Cr^{3+}$, in the case of a chromium cathode, does not always occur. Such reduction, leading to activation of the cathode, takes place in the presence of trivalent chromium ions, and also when the concentration of chromic acid or in increasing the sulfuric acid content in comparison with the concentrations corresponding to the standard solution.

It is interesting to note here that in solutions with an increased concentration of sulfuric acid (for example, up to 5 g/l), activation of the surface occurs so rapidly that it is no longer possible to observe hydrogen evolution at the cathode at the moment the current is switched on: after several seconds the appearance of trivalent chromium is visible. Only on the oscillograms is there preserved a

* The distribution of current between the reactions $Cr^{6+} \rightarrow Cr^{3+}$ and $2H^+ \rightarrow H_2$ strongly depends on the content of trivalent chromium in the electrolyte. An increase in the concentration of Cr^{3+} promotes an increase in the fraction of current going to the reaction $Cr^{6+} \rightarrow Cr^{3+}$.

** At a certain concentration of Cr^{3+}, such a change of reactions occurs very rapidly, so that hydrogen at the electrode cannot be noticed.

Fig. 3

Figure 3: Fig. 3

sharp potential peak when the current is switched on, apparently corresponding to the initial reduction of H ions.

Fig. 3

It is evident that the ability of the passive film to be reduced depends on its composition and on the presence at the surface of other adsorbed ions, such as, for example, Cr^{3+} or SO_4^{2-} ions. Since, with an increase in the concentration of sulfuric acid in the solution, passive films on chromium are reduced more rapidly, it may be assumed that in the absence of sulfuric acid in the solution the passive film forming at the cathode is not reduced by hydrogen. It is possible that this is precisely why the reduction of chromic acid at a chromium cathode does not occur in the absence of sulfate ions.

The fact that the change in the character of the principal electrode reaction is caused only by a change in the state of the cathode surface can be clearly confirmed in the following way. Scraping the surface of a chromium cathode, on which a stable passive film has formed (not reducible by hydrogen), with the point of a glass rod causes a sharp decrease in the cathodic potential by 0.4 V and replacement of the principal reaction $2H^+ \rightarrow H_2$ by the reaction $Cr^{6+} \rightarrow Cr^{3+}$. Figure 3 shows the corresponding oscillographic record of the cathodic potential (curve *a*—before scraping, curve *b*—after scraping).

When the current is switched off and the cathode that has been scraped is left in the chromium electrolyte for $\tau = 1$ min, the passive film forms again, since when the current is switched on again after $\tau = 1$ min the cathode potential once more has a high negative value (-0.9 V) (Fig. 3b). This shows that the cause of the change in the character of the principal electrode reaction upon scraping the cathode surface is precisely the destruction or removal of the passive film, and not crystallographic changes of the electrode surface.

The results presented show that the state of the electrode surface substantially affects the character of the electrode reaction taking place. It may be assumed that the simultaneous occurrence of several reactions at the cathode is caused mainly by the inhomogeneity of the electrode surface. In this case, different reactions probably proceed on different portions of the surface. A change in the degree of inhomogeneity of the electrode, depending on the electrolysis conditions, in all likelihood affects the rates of the individual reactions and, consequently, the current efficiency in electrodeposition of metals.

In conclusion, the following should be noted. The mechanism of electrode processes is often studied by means of short current pulses, and the conclusions obtained are extended to stationary electrolysis conditions. In doing so, it is usually not taken into account that the initial state of the surface as a rule, never corresponds to the stable conditions of electrolysis. Therefore, at the initial moment of electrolysis, the electrochemical reaction taking place at the electrode may not be the one that occurs under conditions of steady-state electrolysis on an active electrode. Interpreting the results without taking into account the influence of the state of the surface on the character of the electrochemical reaction may lead to erroneous conclusions.

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Note: Figure translations are in progress. See original paper for figures.