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Abstract

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STUDY OF THE KINETICS OF THE ELECTROCHEMICAL REDUCTION OF CHROMIC ACID ON A ROTATING DISK ELECTRODE

(Presented by Academician A. N. Frumkin, 7 X 1959)

Polarization curves for the electrochemical reduction of chromic acid show that the reduction process proceeds through several phases depending on the electrode potential. In the first phase of electrochemical reduction—the region of two maxima of the polarization curve—almost 100% of the chromic acid is reduced to trivalent chromium (^{1}). At a more negative potential at the cathode, three processes occur: a) reduction to trivalent chromium, b) reduction to metallic chromium, and c) hydrogen evolution.

The mechanism of the reduction of chromic acid is evidently complex. The first step in its study has been, especially recently, numerous investigations of the first phase ($^{2-5}$). The results of these investigations may be summarized as follows:

1. Chromic acid is reduced only in the presence of sulfuric acid or another foreign acid. In the absence of such an acid, only hydrogen is evolved.
2. The current strength i_{max} at the first maximum of the polarization curve is proportional to the concentration of sulfuric acid or another foreign acid (^{2,4,5}).
3. The value of i_{max} is greatly influenced by stirring conditions. Thus, Bagramyan found that, with a vertically moving electrode, the maximum current is proportional to the square root of the frequency of the electrode strokes per minute (^{2}).

These facts show that sulfate ions take some part in the electrode process of chromic-acid reduction and that the rate of this process depends on the rate of diffusion of sulfate ions to the electrode. The nature of the participation of sulfate ions is explained in different ways: Müller (^{6}) believed that, in the absence of sulfuric acid or another foreign acid, a thin nonconducting layer of basic salts of trivalent chromium is deposited on the electrode. Sulfuric acid dissolves this layer. In opposition to this view, Bagramyan (^{2}) assumes that chromic-acid ions cannot be reduced directly on the electrode. Reduction is possible only in the presence of sulfuric acid or another foreign acid, with which

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

the chromic-acid ions form complexes. An intermediate position between these extreme points of view is taken by Gerischer (^{7}) and Raikovskii and Knorr (^{8}), who believe that the layer of intermediate products of chromic-acid reduction blocking the electrode surface forms complexes with sulfuric acid, which are then further reduced to soluble complexes of trivalent chromium.

All three of these assumptions explain only the necessity of the presence of sulfate ions for current to flow, but not the limitation of the current by the rate of diffusion of sulfate ions. For such a limitation to arise, it is necessary that the sulfate ions be consumed in the overall electrode ···

in the process. Such consumption may occur, for example, as a result of the formation of complexes from the reduction products with sulfuric acid. In this case it is not required that this complex be very stable. It is sufficient that its mean lifetime be greater than the time during which it is located in the diffusion layer. Such an assumption is quite acceptable, since very stable complexes of sulfurous acid with trivalent chromium have recently been discovered (^{3,9}).

Fig. 1. Dependence of i_{max} (i in mA/cm^2) on $z^{1/2}$ (z in rpm) at 200 g/liter CrO_3 and 8.0 (1), 4.0 (2), 2.0 (3), 1.0 (4) g/liter H_2SO_4.
$t = 25$°C

Fig. 2. Dependence of $1/i_{\text{max}}$ (i in mA/cm^2) on $z^{-1/2}$ (z in rpm) at 200 g/liter CrO_3 and 8.0 (1), 4.0 (2), 2.0 (3), 1.0 (4), 0.48 (5) g/liter H_2SO_4. $t = 25$°C

In order to determine the mechanism and kinetics of the reduction of chromic acid, it is necessary to select, insofar as possible, strictly defined diffusion conditions for the course of this process. A rotating disk electrode provides such a possibility. The investigations with a rotating electrode carried out by Matulis and Mitskus (^{4}) apparently are the only ones meeting these requirements. However, these authors carried out electrolysis at a current of specified magnitude, which is not the most favorable condition for experiments of this kind. The results of our investigations were obtained in the reduction of CrO_3 on a gold rotating disk electrode at a specified potential. The solution contained 200 g/liter chromic acid and from 0.5 to 8 g/liter sulfuric acid. The temperature was maintained by a thermostat at three levels: 10, 25, and 45°.

Figure 1 gives the dependence of the maximum current on the rotation rate z of the electrode. It is seen from the graph that the dependence of i_{max} on $z^{1/2}$ is considerably more complex than that which might be expected for purely diffusion-limited currents. At high rotation rates, a decrease in the current strength is observed in comparison with that which would correspond to a linear dependence; this can be explained by the appearance of an additional limitation of the current strength. Such a limitation may be caused by some process

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

preceding the electrode process proper (for example, dissolution of a surface film, formation of electroactive complexes, etc.). Provided that the rate of this process is first order with respect to the concentration of sulfate ions, for calculating the current strength one can

but use the equation

$$\frac{1}{i} = \frac{1}{i_d} + \frac{1}{i_k}, \tag{1}$$

where i_d is the value of the limiting current determined only by the rate of diffusion, and i_k is the value of the limiting current determined only by the kinetics of the preceding reaction [10].

Bearing in mind that the diffusion current i_d is proportional to $z^{1/2}$ according to the Levich equation [11], while i_k (the so-called kinetic current) does not depend on the rotation rate, we obtain, according to equation (1), that $1/i$ must be a linear function of $z^{-1/2}$. From Fig. 2 it is evident that this dependence is well obeyed, at any rate at high electrode rotation rates. The slope of this curve makes it possible to determine i_d at $z = 1$, and the ordinate intercept gives the value i_k^*. Figure 3 gives the dependence of the kinetic current (calculated in this way) on the concentration of sulfuric acid. The same graph also gives the dependence of the diffusion current at $z = 1$ on the concentration of sulfate ions. As can be seen, both the kinetic and diffusion currents are proportional to the concentration of sulfate ions in the electrolyte. It is interesting to note that if, in the Levich equation, values from 1 to $3 \cdot 10^{-5}$ cm^2/sec are used for D, then for n (the number of exchanged electrons per one molecule of sulfuric acid) values from 12 to 24 are obtained. In the reduction process, however, only CrO_3 participates, and three electrons are consumed per one molecule of CrO_3 ($Cr^{6+} \rightarrow Cr^{3+}$). Consequently, on average, from 8 to 4 molecules of chromic acid are reduced in the interaction of one molecule of sulfuric acid with the blocking layer.

Fig. 3. Dependence of $i_d(z = 1)$ and i_k on the concentration of H_2SO_4

Fig. 4. Dependence of $1/i_{\max}$ (i in ma/cm^2) on $z^{-1/2}$ (z in rpm) at 200 g/l CrO_3 and 4.0 g/l H_2SO_4. $t = 10°$ (1), $25°$ (2), $40°$ (3)

The temperature dependence of the maximum current was also investigated. Figure 4 gives the values obtained at 10, 25, and 40°C. The coordinates

* A similar analysis of the dependence of current on the number of revolutions was carried out by A. N. Frumkin et al. in studying the kinetics of ionization of H_2 and Cl_2 on a platinum electrode [12,13].

of the plot: $1/i$ and $z^{-1/2}$. As was noted above, the intercept cut off on the ordinate axis is equal to the reciprocal of the kinetic current. It is seen from the figure that the changes in the kinetic current lie within the limits of the measurement accuracy and that the kinetic current does not depend substantially on temperature. The dependence of the diffusion current on temperature, obtained from the slope of the straight lines in Fig. 4, corresponds to the temperature coefficient $\frac{1}{i}\frac{di}{dt} = 0.019$. This value agrees well with the value that may be expected on the basis of Levich' s equation for convective diffusion.

The diffusion limitation of the current shows that sulfate ions are consumed at the electrode surface. This may occur through the formation of complexes of the reaction products with sulfate ions. The stability of these complexes must be sufficient that, during their residence in the diffusion layer, they do not decompose. In this case the sulfate ions will leave it in the form of complexes. At low rotation rates, however, the diffusion processes are strongly slowed down, and the complexes formed may decompose before leaving the diffusion layer. The sulfate ions thus liberated will, of course, again take part in the diffusion process, and the current will be greater than corresponds to the normal diffusion current. Thus, at low numbers of revolutions, some catalytic current should be observed, which in the i–$z^{1/2}$ plot will give a curvature analogous to the curvature observed experimentally (Fig. 1).

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