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SOME FEATURES OF THE CATHODIC REDUCTION OF CHROMIC ACID ON A CARBON ELECTRODE

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During cathodic polarization of a carbon or other inert electrode in solutions of chromic acid, phenomena are often observed in which the reduction reaction of the chromic-acid anion,

$$Cr_2O_7^{--} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O,$$

is suddenly inhibited; this is accompanied by an abrupt shift of the electrode potential in the negative direction.

Cathodic polarization at high current densities leads to a sharp shift of the potential by approximately 1 V in the negative direction, after which the hydrogen-evolution reaction begins (“complete passivation” of the electrode). Along with this phenomenon, in some cases at lower current densities potential shifts of several tenths of a volt are observed, while the hydrogen-evolution potential is not reached. This phenomenon will hereafter be called “partial passivation” of the electrode. Complete and partial passivation are observed both during a gradual increase in current density when polarization curves are recorded and with time during prolonged polarization of the electrode at a constant current density.

Complete passivation of inert electrodes in chromic-acid solutions has been the subject of investigations by numerous authors. Müller (1) put forward the widely accepted view that, in the course of cathodic reduction, a diaphragm is formed on the electrode surface from sparingly soluble compounds of trivalent and hexavalent chromium (the so-called chromichromate film), which does not allow chromic-acid ions to pass to the cathode and thus leads to inhibition or cessation of this electrochemical reaction. Partial passivation of inert electrodes has been studied to a far lesser extent. Individual observations on inert metallic electrodes pertaining to the region of partial passivation (i.e., to potentials more positive than the hydrogen-evolution potential) were also interpreted by Liebreich (2) on the basis of the assumption that a film of sparingly soluble trivalent chromium compounds forms on the electrode. Partial passivation of

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

the carbon electrode in chromic-acid solutions has not been studied in detail, although this phenomenon is of great importance for chemical current sources with chromic acid (elements of the Grenet type), since it leads to a stepped form of the discharge curve ([3]).

In the present work, the influence of a number of factors (solution composition, stirring, and cathode treatment) on the partial passivation of a carbon electrode was investigated. Curves of potential as a function of time were recorded at different current densities on a rotating electrode made of "spectral" uncalcined carbon. Figure 1 shows the influence of the concentration of bichromate ions; Fig. 2, the concentration of hydrogen ions; and Fig. 3, the concentration of salts on the partial passivation of the carbon electrode. It is evident from the figures that the potential of the upper and lower levels of the curve, corresponding to the active and partially passivated state of the elect-

of the electrode, as well as the duration of the active state, depend on the composition of the solution; the influence of the same solution components on the potential of the active electrode and on the potential of the partially passivated electrode is different. Especially notable is

Fig. 1. Effect of the concentration of bichromate ions: 1 –Cr_2O_3 –0.5 mol/l, H_2SO_4 –0.5 mol/l, $[H^+] = 1.5$ g-eq/l; 2 –CrO_3 –1.5 mol/l, H_2SO_4 absent, $[H^+] = 1.5$ g-eq/l; 3 –CrO_3 –1.0 mol/l, H_2SO_4 –0.5 mol/l, $[H^+] = 2$ g-eq/l; 4 –CrO_3 –3.0 mol/l, H_2SO_4 absent, $[H^+] = 2$ g-eq/l; 5 –CrO_3 –3.0 mol/l, H_2SO_4 –0.5 mol/l, $[H^+] = 8$ g-eq/l; 6 –CrO_3 –7.0 mol/l, H_2SO_4 –0.5 mol/l, $[H^+] = 8$ g-eq/l; $i = 20$ mA/cm^2, $t = 25°$, $w = 550$ rpm.

the effect of adding to the solution a high concentration of indifferent salt, which sharply shifts the potential of the partially passivated electrode in the negative direction and has almost no effect on the potential of the active electrode.

Fig. 2. Effect of the concentration of H^+ ions: 1 –1 g-eq/l, 2 –2 g-eq/l, 3 –3 g-eq/l, 4 –4 g-eq/l; 5 –6 g-eq/l, 6 –8 g-eq/l; $[CrO_3]$ everywhere 3 mol/l; $i = 20$ mA/cm^2, $t = 25°$, $w = 550$ rpm.

The introduction into the solution of the reduction product of chromic acid—trivalent chromium—in a concentration several times exceeding its stationary concentration at the surface of the rotating electrode has practically no effect on partial passivation. Such a result is obtained irrespective of whether the trivalent chromium is added in the form of a salt (chromium sulfate) or in the form of a previously electrolytically reduced solution of chromic acid (in the

Fig. 3. Influence of salt concentration: 1—CrO3—3 mol/l, H2SO4 0.5 mol/l; 2—the same, but 1 l and Cr2(SO4)3—4.5 g-eq/l; 3—the same, but 1 l and Na2SO4—4.0 g-eq/l; 4—the same, but 1 l and NaClO4—4.0 g-eq/l; i = 20 mA/cm2, t = 25°, w = 550 rpm

Figure 3: Fig. 3. Influence of salt concentration: 1—CrO3—3 mol/l, H2SO4 0.5 mol/l; 2—the same, but 1 l and Cr2(SO4)3—4.5 g-eq/l; 3—the same, but 1 l and Na2SO4—4.0 g-eq/l; 4—the same, but 1 l and NaClO4—4.0 g-eq/l; i = 20 mA/cm2, t = 25°, w = 550 rpm

latter case, along with the formation of trivalent chromium, there is a change in the acidity of the solution, analogous to that which occurs in the near-electrode layer of the solution during polarization of the electrode). In solutions with the addition of very high concentrations of chromium sulfate, a sharp shift of the potential is observed.

of a partially passivated electrode; however, this effect is apparently associated not with the presence of trivalent chromium, but with an increase in the total concentration of the electrolyte, since the same displacement of the curve also occurs when an equivalent concentration of sodium sulfate or perchlorate is added to the solution (Fig. 3). A sharp shift in the potential of a partially passivated electrode is also observed in solutions with a high concentration of sulfuric or chromic acid (Fig. 1, curves 5 and 6; Fig. 2, curve 6). Changing the number of revolutions of the rotating electrode, which also leads to a change in the stationary concentration of the reaction components (in particular, trivalent chromium) in the near-electrode layer of the solution, has practically no effect on the potentials of the upper and lower portions of the polarization curve or on the duration of the active state of the electrode.

Fig. 3. Influence of salt concentration: 1—CrO_3—3 mol/l, H_2SO_4 0.5 mol/l; 2—the same, but 1 l and $Cr_2(SO_4)_3$—4.5 g-eq/l; 3—the same, but 1 l and Na_2SO_4—4.0 g-eq/l; 4—the same, but 1 l and $NaClO_4$—4.0 g-eq/l; $i = 20$ mA/cm^2, $t = 25°$, $w = 550$ rpm

The phenomena described should be regarded as inhibition of the electrochemical reaction, and not as a change in its nature, since at potentials of both the upper and lower levels of the curve, for thermodynamic reasons, the only stationary electrode reaction under these conditions is the reduction of hexavalent chromium to trivalent chromium.

The experimental data obtained in the present work contradict the assumption that the cause of the inhibition of the reaction is the formation at the cathode of a diaphragm composed of sparingly soluble compounds of trivalent chromium. This follows from the independence of the phenomenon of partial passivation from additions of trivalent chromium to the solution and from the rate of stirring.

It appears probable that the phenomenon of partial passivation is associated with a change in the state of the oxide layers on the surface of the electrode, occurring simultaneously with the reaction of reduction of chromic acid. This follows, in particular, from experimental data according to which all factors that shift the potential of the active electrode in the positive direction simultaneously also lead to an increase in the duration of the active state of the electrode. Experiments studying the influence of preliminary treatment of the electrode also support this view. Preliminary cathodic polarization of the electrode in a solution of chromic acid leads to the disappearance of the active portion of the curve or, in any case, to a sharp shortening of it upon repeated polarization after a brief interruption of the current. With a prolonged interruption, the electrode "rests" and, when the polarization is switched on again, shows a normal form of

curve with "active" and "semi-passivated" regions. Depassivation of the electrode is not accelerated if the electrolyte solution is changed during the interruption. However, under the action of weak anodic polarization, the electrode very rapidly (in 1-1.5 min) reaches its normal active state. The electrode behaves somewhat differently after prior strong anodic polarization, both in a chromic-acid solution and, for example, in a sulfuric-acid solution. In this case, during subsequent cathodic polarization of the electrode in a chromic-acid solution, the upper portion of the curve disappears completely and the electrode operates only in a partially passivated state. The change in the state of the electrode is irreversible—the electrode does not "rest" and does not return to the active state.

In considering the data presented above on the influence of a high concentration of dissolved substances, it is necessary to take into account that, at high ionic concentrations, aggregation of chromic-acid ions into ions of polychromic acids, Cr_3O_{10} and Cr_4O_{13}, is possible. The change in the reduction potential of chromic acid in such solutions is therefore naturally explained by a change in the nature of the particles containing hexavalent chromium. It is interesting to note that, in the active state of the electrode, no such effect of the nature of the particles on the reduction rate is observed.

The data presented above indicate that the active state of the electrode corresponds to certain forms of surface oxides, which gradually disappear in the course of cathodic polarization and are formed again during mild anodic polarization of carbon. These oxides either themselves participate in the process or promote the appearance of active sites on the electrode surface, on which the reduction process of Cr_2O_7 proceeds more readily than on the rest of the surface. The acceleration of the reduction process at these sites is possibly connected with the fact that, on them, reduction proceeds through the formation of intermediate surface compounds, whereas on the inactive surface direct reduction of chromic-acid ions takes place. With sufficient adsorption energy of the intermediate compounds, a considerable portion of the active sites may be filled regardless of the form in which hexavalent chromium is present in solution. This, in particular, could explain why the nature of the chromic-acid ions affects only the reduction potential on a partially passivated electrode, on which intermediate surface compounds are not formed.

The phenomenon of partial passivation of the carbon electrode may thus be regarded as a change in the electrochemical mechanism of the reaction of reduction of hexavalent chromium ions to trivalent chromium, occurring as a consequence of a change in the state of the oxide layers on the electrode surface.

Qualitatively analogous phenomena are observed on inert electrodes of platinum and gold.

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CITED LITERATURE

1. E. Müller, *Zs. Elektrochem.*, **32**, 400 (1926).
2. E. Libreich, *Zs. Elektrochem.*, **27**, 94, 453 (1921); **40**, 73 (1934).
3. H. A. Barbiand, McNulty, *Trans. Electrochem. Soc.*, **91**, 387 (1947).

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