HYDROGEN OVERVOLTAGE ON AN IRON CATHODE IN AN ALKALINE SOLUTION IN RELATION TO THE STATE OF THE SURFACE

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During the prolonged polarization of a cathode under certain conditions there is an increase in potential with time. This phenomenon has been explained by "poisoning" of the cathode surface by stray impurities (V. V. Stender) or concentration polarization and errors in the measurement of the potential at high polarizations [1].

Our systematic study of the cathode process showed, however, that the change in hydrogen overvoltage η with time is quite regularly connected with slow, but reversible, changes in the state of the cathode surface during polarization. The direction and nature of these changes depend on the nature of the metal, the initial potential of the cathode, the polarization region, the preliminary treatment of the cathode, and the electrolysis conditions.

Figure 1 gives curves showing the change in η_{H_2} with time at a constant current density i_c on three cathodes that had received different preliminary treatment. From a comparison of these curves it follows that preliminary removal of the passivating oxide film promotes a more rapid growth in η_{H_2} during electrolysis. Polarization curves plotted over a definite polarization range over different time intervals from the beginning of polarization did not coincide. Consequently, even with the same cathode it is possible to obtain a whole series of such curves. However, from the possible variety of overvoltage curves it is possible to pick out three stationary curves, which are quite readily reproducible under definite polarization conditions and correspond to three different, but relatively stationary physicochemical states of the cathode surface (Fig. 2).

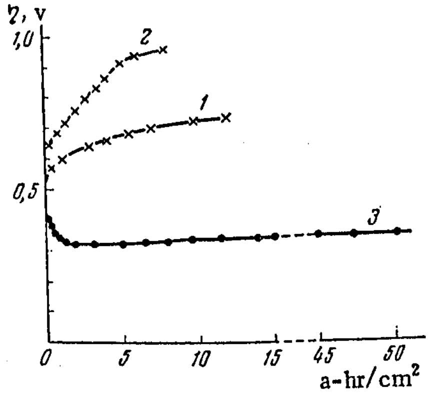

Fig. 1. Change in cathode potential of Fe in 5 N KOH at 25° under prolonged polarization in relation to the preparation of the Fe cathode. 1) Air-oxidized cathode; i_c=200 ma/cm²; 2) cathode thermally reduced in H_2 at 600°; i_c = 100 ma/cm²; 3) cathode thermally oxidized at 450°; i_c = 250 ma/cm².

We also used the alternating-current method for investigating the change in the state of the surface during polarization. The curves obtained in our experiments expressing the potential dependence of the hydrogen-liberation rate, the polarization capacity (C), and the ohmic component (r) are given in Fig. 3.

As Ya. M. Kolotyrkin, N. Ya. Bunĕ, and L. A. Medvedeva [2] showed, an analogous inflection on the curve of $\eta_{H_2} = f(\log i_c)$ in acid solutions on metals which do not adsorb hydrogen also appears at a surface overcharging potential more anodic than that at which adsorption of anions occurs. In our case the role of the anions is played by the hydrogen of hydroxyl or water.

From an analysis of our results and a comparison of them with literature data, the stationary states of the surface of an Fe electrode (Fig. 2) may be interpreted in the following way.

1. At low polarizations (without preliminary reduction of the cathode) the surface of the Fe electrode is covered with phase oxides, whose reduction occurs at η_{H_2} up to 0.27 v, lead-

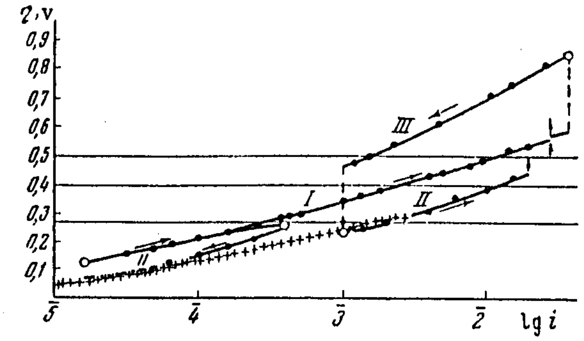

Fig. 2. Typical polarization curve on an Fe cathode in 5 N KOH at 25° with three branches of the curve $\eta_{H_2} = f(\log i_c)$, corresponding to the three different stationary states of the cathode surface. The crosses denote the curve of $\eta_{H_2} = f(\log i_c)$ constructed from the data of S. D. Levina and E. E. Kalmykova [7] for a smooth electrode, whose surface the authors considered to be completely reduced. This curve corresponds to that we obtained for state II of the surface.

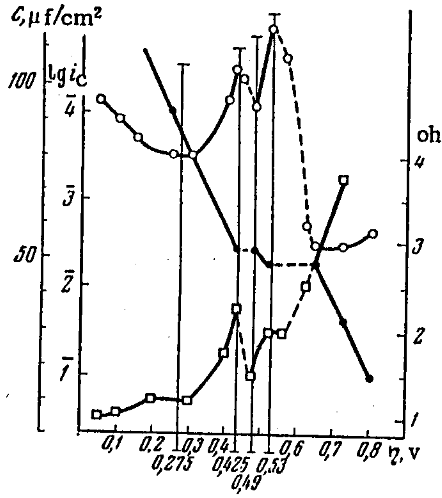

Fig. 3. Comparison of potential values at points on the inflection on the curve of $\eta_{H_2} = f(\log i_c)$ and curves for the cathode characteristics (C and r) obtained by the alternating-current method. •–• $\eta = f(\log i_c)$, transition II → III □–□ $r = f(\eta)$ at a frequency of 500 cps; –○–○– $C = f(\eta)$ at a frequency of 500 cps; – – – – constant current density.

ing, in particular, to development of the cathode surface. The maximum on the curve of $C = f(\eta_{H_2})$ at $\eta_{H_2} \sim 0.2$ v (this curve is not given in Fig. 3) corresponds to this process.

2. There is then established a new state (II) of the cathode in which its surface is free from volume layers of oxygen and hydrogen. However, on it there is present surface-adsorbed oxygen with a stronger Fe–O bond, which is removed only at $\eta_{H_2} \sim 0.5$ v, and also hydrogen atoms adsorbed on the oxides or on the surface partially freed from them. This state is characterized by the lowest value of η_{H_2} ($\eta_I - \eta_{II} = 100 - 150$ mv). At $\eta_{H_2} > 0.4$ v, the adsorption of hydrogen increases, and there is elimination of the more strongly bound oxygen. This process corresponds to the maximum on C at $\eta_{H_2} = 0.4 - 0.5$ v (Fig. 3).

3. At $\eta_{H_2} > 0.5$ v, the cathode surface is completely free from oxygen; a further displacement of the potential in a negative direction is accompanied by the accumulation of atomic hydrogen on the surface and in the volume of the cathode. This surface state is attained slowly and the highest values of η_{H_2} correspond to it ($\eta_{III} - \eta_{II} = 0.25 - 0.30$ v at 25°).

The presence of different forms of the Fe – O bond on the cathode surface is confirmed by the data of R. Kh. Burshtein et al. [3] and other investigators. In contrast to previous authors [4], however, we consider that the cathode surface is completely free from oxygen at more cathodic potentials than follows from published data.

The form of polarization curves depends considerably on the method of measurement. With rapid measurement, the stationary curves may be extended in both directions, extending the range of i_c for them. With an extension of curve I in this way up to $\eta_{H_2} \geq 0.5$ v, it is possible to observe the direct transition I → III (Fig. 2). Depending on the conditions of preliminary polarization of the cathode and the rate of the measurements, a sharp transition from one surface state to another may not be observed. The adsorption processes occurring thereupon on the cathode are manifested by the position of the polarization curve on the graph of η_{H_2} against log i_c and a decrease (transition I → II) or increase (transition II → III) in its slope.

In plotting curves of $\eta_{H_2} = f(\log i_c)$ on Fe (5 N NaOH, 50°) with the same holding times at different values of i_c, G. A. Tsyganov and N. I. Tugov [5] observed an increase in the slope of the curve at $i_c \sim 100$ ma/cm² ($\eta_{H_2} \sim 0.4$ v) and also associated this with the effect of adsorbed hydrogen. The effect of the latter on the cathode potential has now been reported by I. A. Bagotskaya [6].

The change in η_{H_2} with time depends very strongly on temperature. An increase in the latter accelerates the increase in η_{H_2} by facilitating the removal of oxygen and the hydrogenation of the cathode. Thereupon there is some loosening of its surface. As a result of preliminary polarization at 80°, the difference in overvoltage for curves II and III increased to 0.45 – 0.50 v (Fig. 4). The connection between the increase in η_{H_2} and the hydrogenation of the cathode is confirmed by the form of the upper branch of the curve (Fig. 5). If this curve was plotted rapidly to low values of i_c without a delay at the inflection potential η_{H_2} = 0.48 v, then it consisted of semilogarithmic and horizontal sections. The curve could be reproduced in forward and backward directions. The horizontal section on the curve (Fig. 5) and the delays corresponding to it in potential on the fall curves (Fig. 6) are connected with the removal of large amounts of atomic hydrogen, adsorbed in a nonequilibrium state on the surface and absorbed in the volume of the metal, which may proceed by recombination, electrochemical desorption, or ionization of H atoms. As the surface is freed, oxygen is again adsorbed on the metal and the transition III → II occurs. The more cathodic the final potential under current and the longer the cathode operates in the region of high polarization and temperature, the greater is the delay on the fall curve, i.e., the greater the saturation of the cathode with hydrogen. Despite the absence of polarization, gas bubbles were evolved vigorously from the surface with a gradual decrease in them as the potential fell. The appearance of macroscopic bulges on the smooth surface of a rolled electrode after electrolysis at 80° or prolonged polarization at high cathodic potentials at 25° indicated a considerable hydrogen pressure in the volume of the metal. It should be pointed out that the presence in the electrolyte of dissolved oxygen, which hinders the adsorption of hydrogen, retards the increase in overvoltage associated with the transition from state II to state III. The solution of hydrogen in iron may be retarded by the use of $i_c \geq 1$ a/cm^2. The latter is evidently associated with a change in the character of gas evolution: coarser bubbles are formed on the cathode and the gas emulsion in the catholyte disappears.

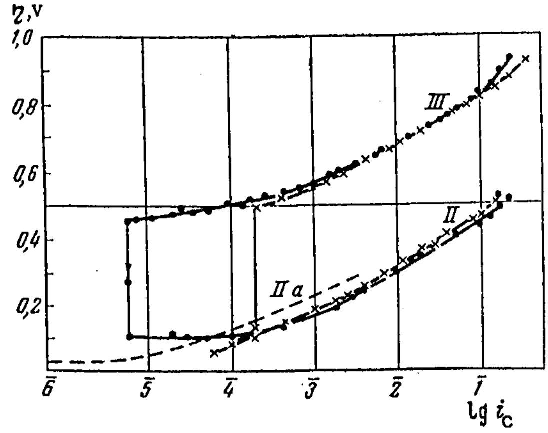

Fig. 4. Overvoltage curves for two different (●, x) iron electrodes in 5 N KOH at 25° after their cathode polarization at 80° (surface states II and III). The broken curve (IIa) was obtained from the data of E. E. Kalmykova and S. D. Levina.

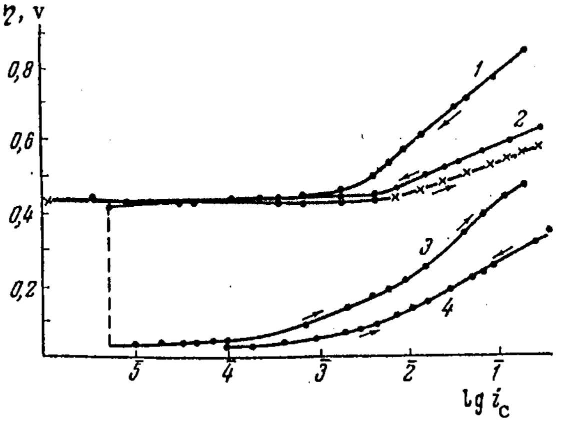

Fig. 5. Comparison of two branches of overvoltage curves with a horizontal plateau on the upper branches for smooth (air-oxidized) and thermally oxidized iron cathodes in 5 N KOH at 25° after preliminary polarization at 80°. 1) Smooth after heating; 2) thermally oxidized after heating; 3) smooth after heating; 4) thermally oxidized before heating.

The main rules of the cathode process observed on an Fe cathode are also true for other metals. We present as an example only one of the fall curves for a Ni cathode (Fig. 6).

The experimental material we obtained for a series of metals shows that the kinetics of hydrogen liberation over a wide range of potentials cannot be described on the basis of the idea of the slowness of one of the possible stages of the over-all process. The mechanism of overvoltage on metals which adsorb hydrogen, especially in alkaline solutions, is more complex. For a complete description of it, it is necessary to consider two and possibly more states which occur at commensurate rates in definite polarization regions. The relative role of these individual stages in the over-all process changes not only for different metals but also for the same metal (and electrode), depending on the polarization region, the nature and state of the cathode surface, and other conditions [1]. On solid metals the cathode process is also determined by the nature of surface compounds formed on the electrode [8].

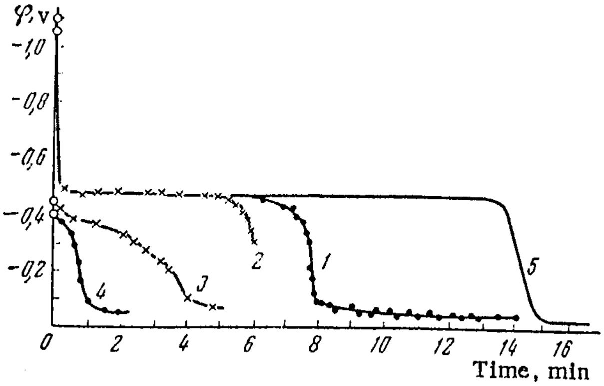

Fig. 6. Curves of the potential fall of an iron cathode in 5 N KOH at 25° after preliminary polarization at 80°. 1) Polarization current(i_c=250 ma/cm^2) switched off at η_{H_2}= 1.05 v; 2) current switches off at η_{H_2} = = 0.50 v after plotting of the linear part of the upper branch of the curve over the range η_{H_2} = 1.10– 0.50 v; 3) curve obtained after plotting of the upper branch of the overvoltage curve completely (including the horizontal plateau). Current switched off at η_{H_2} = 0.44 v; 4) the same, current switched off at η_{H_2} = 0.40 v; 5) fall curve on Ni cathode. Polarization current (i_c = 200 ma/cm^2) switched off at η_{H_2} = 1.0 v.

From the data presented it follows that the curve of η_{H_2} = f (log i_c) cannot be described by the normal Tafel equation. It must be supplemented by at least one more term (Δv), allowing for adsorption changes on the cathode:

$$\eta_{\mathrm{H}_2} = a + b \lg i_{\text{к}} + \Delta v,$$

which was also pointed out in the work of Ya. M. Kolotyrkin [2] and L. I. Antropov [7]. In cases where there is no accumulation of discharged H atoms on the cathode surface and they immediately recombine to molecules (a mercury cathode in acid and solid metals at low polarizations), the rate of the over-all process may be determined only by the discharge of H$^+$ ion in acid or H_2O in alkali:

$$\mathrm{Me} + \mathrm{H_2O} + e \rightarrow \mathrm{MeH} + \mathrm{OH^-}.$$

We showed that on metals like iron in a definite polarization region there is a considerable accumulation of hydrogen adsorbed on the surface and even in the volume of the cathode. In this case it is necessary to recognize the determining effect on the process rate of the molecule-formation stage, which may proceed by two routes that are difficult to distinguish experimentally:

Recombination:

$$\mathrm{MeH} + \mathrm{MeH} \rightarrow 2\mathrm{Me} + \mathrm{H_2};$$

Electrochemical desorption:

$$\mathrm{Me} + \mathrm{H_2O} + e \rightarrow \mathrm{Me} + \mathrm{H} + \mathrm{OH^-}.$$

In the region of technical current densities (10 – 300 ma/cm^2), when the whole of the cathode surface is covered with adsorbed hydrogen the discharge of H$^+$ ions or H_2O proceeds by an electrochemical mechanism on which a catalytic mechanism may be superposed.

A comparison of the upper and lower branches of an overvoltage curve with horizontal sections in the region of low current densities (Fig. 5) shows that they are approximately the same, but clearly refer to qualitatively different states of the cathode surface. The upper branch of the curve evidently characterizes the kinetics of H_2 liberation not on iron, but on its hydride. The horizontal section of the curve will then correspond to the decomposition potential of this hydride (η_{H_2} ~ 0.48 v). For this case we may write:

$$(\mathrm{FeH})\,\mathrm{H} + \mathrm{H_2O} + e \rightarrow (\mathrm{FeH}) + \mathrm{H_2} + \mathrm{OH^-}.$$

For industrial electrolysis it is important that surface state II, which is characterized by the minimal overvoltage, is retained for a long period. At relatively high values of i_c (50 – 250 ma/cm^2) this may be achieved by development of the cathode surface, in particular, by preliminary thermal oxidation of the electrode under the optimal conditions we found or by introduction of soluble iron salts or oxidants into the electrolyte. In the light of the data obtained it is necessary to raise again the problem of evaluating the efficiency of various recommendations for reducing overvoltage by comparing their effect with the completely determined curve of H_2 overvoltage (for surface state II) on the cathode. It should also be pointed out that under the conditions of industrial electrolysis the cathode has a developed surface as a result of deposition of sponge Fe (during the electrolysis of water) or the action of anode products (in chlorine electrolysis).

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