KINETICS AND MECHANISM OF ELECTROREDUCTION OF THE ANODIC PRECIPITATE OF FERROUS HYDROXIDE IN ALKALINE SOLUTIONS

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The cathodic reduction of an $Fe(OH)_2$ precipitate as well as its formation on iron in KOH solutions is characterized by the appearance of limiting currents, caused by a low diffusion rate of iron ions to the electrode as a result of insufficient ionic conductivity of the $Fe(OH)_2$ layer [1-5]. In the present study we have investigated the influence of the potential and the KOH concentration on the rate of reduction of the ferrous hydroxide. It proceeds mainly in the solid phase: $Fe(OH)_2 + 2e \rightarrow Fe + 2OH^-$, and at a certain rate through the iron ions formed after dissolution of the precipitate in the electrolyte: $Fe(OH)_2 + OH^- \rightarrow HFeO_2^- + H_2O$, and reduction: $HFeO_2^- + 2e + H_2O \rightarrow Fe + 3OH^-$.

The experiments were carried out with an electrode made of pure iron prepared by zone melting, and polished with a fine glass powder slurry. After rinsing, the electrode was etched in 2 N H_2SO_4 for 40-50 sec, subjected to cathodic polarization with a current of 10^{-2} A/cm² for one hour, and placed in a KOH solution, purified by cathodic polarization on a platinized platinum gauze. A $Fe(OH)_2$ precipitate was then applied in an argon atmosphere, using an anodic polarization with a current of 3×10^{-5} A/cm² to E = −0.75 V, and the quantity of electricity measured which was spent for its formation. The precipitate was then reduced by measuring the current at a constant potential, set by means of an electronic potentiostat. The potentials are given against a HgO electrode in KOH solution of the same concentration. The temperature of the tests was 20 ± 1°C.

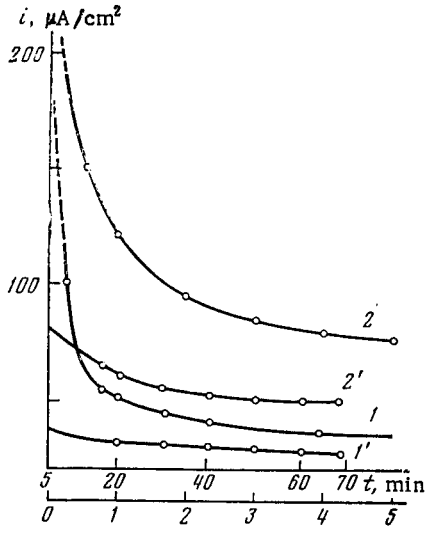

Fig. 1

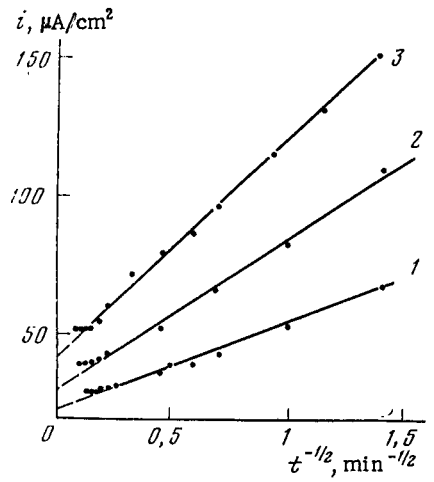

Fig. 2

Fig. 1. Density of the limiting cathodic reduction current of the anodic film of $Fe(OH)_2$ on iron as function of time in 4.8 N KOH at E: 1) −0.99 V, 2) −1.10 V; curves 1 and 2 from start of the test to 5 min, curves 1' and 2' from 5 to 70 min.

Fig. 2. Limiting reduction current as function of the reciprocal value of the square root of time in 4.8 N KOH at E: 1) −0.99 V, 2) −1.05 V, 3) −1.10 V.

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TABLE 1. Influence of the Potential on the Parameters of the Reduction of the Anodic Precipitate $Fe(OH)_2$ in 4.8 N KOH

$-E$, V	0,99	1,00	1,05	1,10	1,15
$\partial i/\partial t^{-1/2}$, $t^{-1/2}$	30	40	56	79	100
i_{H_2}, $\mu A/cm$	18	19	23	41	60
Q_{Fe}, mC/cm^2	13	23	42	60	85
Q_{side}, mC/cm^2	90	100	126	214	310

TABLE 2. Influence of the KOH Concentration of the Solution on the Reduction Parameters of the Anodic $Fe(OH)_2$ Precipitate at E = —1.02 V

KOH concentration, N	1,3	4,8	7,0	10
$\partial i/\partial t^{-1/2}$, $t^{-1/2}$	32	41	56	65
i_{H_2}, $\mu A/cm^2$	9	18	20	28
Q_{Fe}, mC/cm^2	20	30	38	49
Q_{side}, mC/cm^2	48	81	100	185

Figure 1 shows the curves representing the current as function of time in 4.8 N KOH at E = —0.99 and —1.1 V. It can be seen from the graph that the passing current is initially very high and that it decreases then to values which are practically independent of time. This current which establishes itself near the end of the test is evidently related to the current of side reactions which are not related to the diffusion in the $Fe(OH)_2$ film. The experimental data for the relationship between i and t give straight lines in the coordinates i, $t^{-1/2}$ (Fig. 2). Extrapolation of the lines gives segments on the ordinate which determine the current of discharge of the water molecules. Consequently, in the equation of the straight line $i = A + kt^{-1/2}$ A is the current of hydrogen evolution, k is the slope of the straight line $(\partial i/\partial t^{-1/2})$ which characterizes the ionic conductivity of the $Fe(OH)_2$ layer and depends on the potential and composition of the solution. The currents, cut on the ordinate by extrapolation of the straight lines $i, t^{1/2}$ are somewhat lower than the currents near the end of the test according to the curves in Figs. 1 and 2. This excess current corresponds probably to the reduction current of $HFeO_2^-$ ions. In the calculations we have assumed that these side reactions at a constant potential during the whole test proceed at a constant rate. Integration of the area under the curves i,t in Fig. 1, after deduction of the quantity of electricity consumed during the same time (70 min) for the side reactions (Q_{side}) gave the amount of electricity Q_{Fe} used to reduce the $Fe(OH)_2$ precipitate. Some of the results obtained in 4.8 N KOH by calculation are shown in Table 1.

Table 1 shows that the ionic conductivity of the $Fe(OH)_2$ layer increases with an increasing cathodic potential, as well as the limiting current density of reduction of this layer. The latter increases proportionately to the square root of the potential as in the case of anodic ionization of iron [4, 5]. Naturally, the hydrogen evolution current also increases, as well as the amount of electricity consumed for the reduction of the precipitate Q_{Fe}. As the cathodic potential increases, the amount of electricity consumed for the side reactions (hydrogen evolution and reduction of $HFeO_2^-$ ions) also increases. As a result of this, after 70 min of test the amount of electricity consumed is higher by a factor of 3-4 than the amount required for the reduction of the precipitate of $Fe(OH)_2$ itself. At all potentials the amount of electricity consumed for the latter reaction is significantly smaller than that required for the anodic formation of this precipitate (approximately 110 mC/cm^2).

An increase in the KOH concentration also leads to an increase in the ionic conductivity and the limiting density of the reduction current of the $Fe(OH)_2$ layer. Some results obtained in the calculations of the tests carried out at E = —1.02 V are shown in Table 2.

The existence of a linear relationship between the limiting current of cathodic reduction of the $Fe(OH)_2$ precipitate and the reciprocal value of the square root of time

indicates that the process studied proceeds according to a parabolic law of decreasing thickness of the oxide film with time. The mechanism of current transfer within the $Fe(OH)_2$ film, analogously to the mechanism of current limitation during the growth of such a film in the anodic oxidation of iron [5, 6], can be explained as follows. Initially the concentration of Fe^{2+} ions in the film near the electrode is very high. When the current is switched on, their concentration at the electrode surface becomes equal to zero and a concentration gradient is formed. The further course of the reaction depends on the influx of Fe^{2+} ions to the electrode. As the diffusion front moves and the thickness of the diffusion layer increases, the concentration gradient decreases, since the current passing through also decreases. This leads to the establishment of the relationship between current and time shown in Fig. 1. The iron ions are located in the nodes of the $Fe(OH)_2$ lattice. Under the action of the potential applied, they acquire additional energy, overcome the energy barrier and pass into the internodal spaces, moving over the vacancies and defects under the effect of the established concentration and potential gradients towards the electrode where they are reduced and deposited in the form of the metal. The liberated OH^- ions accumulate at the electrode, form a reverse concentration gradient, and move under its influence and the action of the electrical field towards the boundary between film and solution.

Due to the large difference between the densities of the metal being deposited and the disappearing oxide, a vacuum can form between the electrode and the oxide film, which can result in peeling off of the film. However, the film is retained on the electrode due to this vacuum and the adhesion forces; it does not break down nor does it peel off in spite of the evolution of hydrogen. This is confirmed by the absence of inflections on the curves representing the relationship between current and time.

LITERATURE CITED

1. A. P. P'yankova and Z. A. Iofa, Élektrokhimiya, 10, 1334 (1974).
2. V. M. Rozovskii and N. A. Solov'eva, Abstracts of Papers presented at the Fifth All-Union Conference on Electrochemistry [in Russian], Izd. Tartusk. Univ. (1974), p. 480.
3. V. M. Rozovskii, N. A. Solov'eva and A. A. Maklyarskaya, Sb. Rabot Saratovsk. Gos. Universiteta, No. 4, 95 (1976).
4. T. G. Stepina, Materials of the Second Georgian Republican Conference of Young Chemists [in Russian], Metsniereba, Tbilisi (1978), p. 114.
5. T. G. Stepina and Z. A. Iofa, Élektrokhimiya, 15, 151 (1979).
6. L. Young, Anodic Oxide Films [Russian translation], Nauka, Leningrad (1967).