USE OF THE ROTATING DISK ELECTRODE TO STUDY THE REACTIONS ON AN IRON ELECTRODE IN ALKALINE SOLUTION

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There have already been numerous studies of the behavior of the iron electrode in alkaline solutions [1-4]. It is a well-known fact that the passivity of the powdered iron electrode is the limiting factor in fixing the ampere-hour discharge capacity of alkaline storage batteries. It has been suggested [2] that this passivity results from the formation of ad adsorbed oxide containing iron with a valence in excess of 2. X-ray analyses [4] have identified the final products of the first and second anode reactions as $Fe(OH)_2$ and δ-FeOOH. In part, these products pass into the alkaline solution in the form of $HFeO_2^-$ and FeO_2^- ions. The reduction of FeO_2^- on a rotating iron disk electrode in concentrated KOH solutions has been studied in [5].

The present paper reports the results obtained in a study of the anodic reaction and cathodic iron oxide reduction on a rotating iron disk electrode. This electrode was carried in a Teflon jacket and had a surface area of 0.283 cm^2; it was set in motion by a synchronous motor mounted so as to eliminate the possibility of vibrations. Prior to use, the electrode was cleaned and polished in a stream of moist finely pulverized powdered glass, washed with alcohol and water, etched for 40-50 sec in 2N H_2SO_4, and then cathodically polarized in an alkaline electrolyte for 1-2 h under a current of $2 \cdot 10^{-4}$ A. The KOH solution was given a preliminary purification by being subjected to cathodic polarization on a Pt/Pt gauze while being aerated with argon. Potentials were measured with respect to a HgO electrode in the solution, each measurement being made at 20°C. Potential measurements at fixed current strength were made at 20-30 sec intervals.

It is clear from Fig. 1a (curves 1-3) that each of the I vs φ curves showed two regions over which the current was strongly dependent on the applied potential and two over which sharp increases in the potential brought about only minute alteration in the current. The strong I vs φ interrelation was characteristic of the region over which the first and second anodic reactions were proceeding at low overvoltage. The sharp displacement in potential was associated with so-called limiting currents (I_{lim}) under which the electrode was passivated and the potential carried over to the value corresponding to the next anodic reaction. It can be seen that alteration in the rate of electrode rotation had no appreciable effect on the rate of the first anodic reaction. The slight increase in the I_{lim} value for the second anodic reaction may possibly be traced back to the formation of $HFeO_2^-$ in the first anodic reaction, these ions diffusing to the electrode to undergo oxidation. Similar I vs φ curves were also obtained in experiments with 10 N KOH, but there the passivation of the first anodic reaction began at higher currents (at $2 \cdot 10^{-4}$ instead of the $1.5 \cdot 10^{-4}$ A as in the experiments with 1.0 N KOH).

Experiments on iron electrode discharge were also carried out with KOH solutions which had been saturated with hydrogen.* Ionization of the dissolved hydrogen led to an increase in the value of I_{lim} (Fig. 1a, curves 4, 5). This increase in the value of I_{lim} proved to be in direct proportion to the square root of the rotation rate (Fig. 1b). The I_{lim} vs $\sqrt{m}$ line cut the axis of ordinates (m = 0) at an I_{lim} value

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*The alkaline electrolyte of the storage battery is saturated with hydrogen during recharging and at the end of the charging process; it also becomes saturated with hydrogen on standing, as a result of self-discharge. Hydrogen ionization proceeds during discharge.

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TABLE 1

$I\cdot10^6$	t	$I^2\cdot10^{12}$	$A=I^2\cdot t\cdot10^{10}$	$I\cdot10^6$	t	$I^2\cdot10^{12}$	$A=I^2\cdot t\cdot10^{10}$
12	5,5	144	7,9	8	12	64	7,7
11	6,4	121	7,7	6	22	36	7,9
9	9,5	81	7,6	5	40	25	10

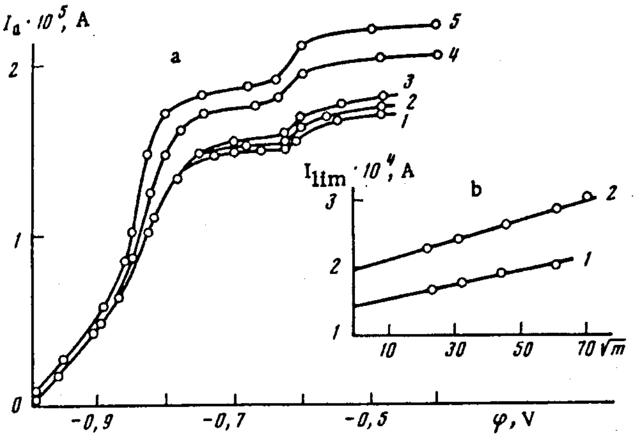

Fig. 1. a) I vs φ curves for the anodic oxidation of iron in 1 N KOH and under an atmosphere of argon: 1-3) at m = 510, 1060, and 2150 rpm and in an atmosphere of hydrogen; 4) 2150; 5) 3730 rpm. b) The I_{lim} vs $\sqrt{m}$ relation for the first anodic reaction in an atmosphere of hydrogen: 1) 1 N KOH, 2) 10 N KOH.

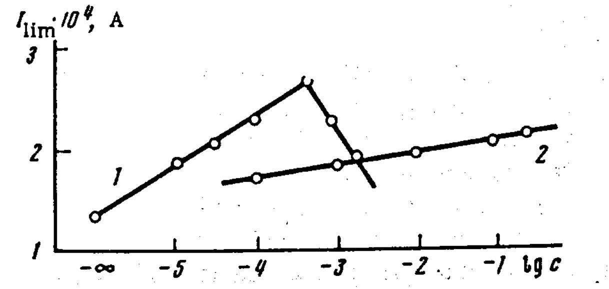

Fig. 2. Relation between I_{lim} in 1 N KOH and the logarithm of concentration: 1) Na_2S; 2) KCNS in an atmosphere of argon.

close to that corresponding to measurements on the hydrogen-free electrolyte. It is seen from Fig. 1a that iron and hydrogen underwent simultaneous ionization at φ = −0.86 V.

Study was made of the effect of activators on the anodic reaction. The activators investigated were Na_2S, KCNS, $KNaC_4H_4O_6$ and $(NH_2)CS$. The limiting passivation current was found to increase in direct proportion to the concentration of added passivator. In the case of Na_2S, however, this increase in the value of I_{lim} continued only up to a concentration of $5\cdot10^{-4}$ N, decreasing as the activator concentration was carried beyond this point (Fig. 2, curve 1). At these same concentrations, the activational effect of KCNS was much less pronounced, the relation, remaining linear up to a concentration of 0.5 N in the KCNS (Fig. 2, curve 2). The presence of the Na_2S caused the iron electrode to become covered with a film which became blacker and blacker as the concentration of the activator was increased. It is clear that an FeS phase film was formed at Na_2S concentrations in excess of $5\cdot10^{-4}$ N. A dark electrode film was also formed at the higher KCNS concentrations. Rochelle salt weakly activated the anodic reaction, but without forming a film on the electrode. The Na_2S adsorbed very rapidly, the KCNS and Rochelle salt more slowly. It should be emphasized that the compounds in question here activated only the first anodic reaction, having no appreciable effect on the second reaction. The effect of the sulfur-containing activators was probably through retardation of the formation of a passivating oxide film of iron with a valence in excess of 2, the bonding of S^{2-} ions to iron being stronger than that of the OH ions and oxygen which participate in formation of the passive adsorptional film.

Cathodic reduction of the iron oxide also retards the reaction, thereby reducing the degree of utilization of the current. The amount of $Fe(OH)_2$ reduced diminishes as the current density rises.

The I vs φ $Fe(OH)_2$ reduction curves of Fig. 3 (curve 2) were obtained from anodic oxidation of iron under a current of $6\cdot10^{-6}$ A, allowing the reaction to proceed for 80 min, at which time φ = −0.800 V. It is seen that the cathodic potential increased sharply at $I = 0.7\cdot10^{-5}$ A, the oxidation curve merging at this point with the I vs φ curve for hydrogen evolution from a completely reduced iron electrode in this same solution (curve 1). A second reduction curve (curve 3), obtained after the electrode had been allowed to stand for some time, fell in the immediate neighborhood of the first.*

The φ vs t curves of Fig. 4 were obtained at fixed values of I; from them it is seen that the time required for reaching the hydrogen evolution potential (as read from curve 1 of Fig. 3) could be diminished

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*Since the I vs φ curve was developed over 5-7 min, no more than 0.1 of $Fe(OH)_2$ resulting from the earlier anodic oxidation could have been reduced.

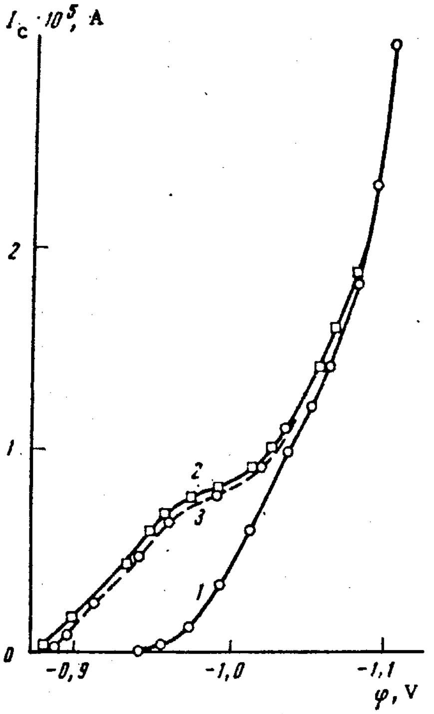

Fig. 3

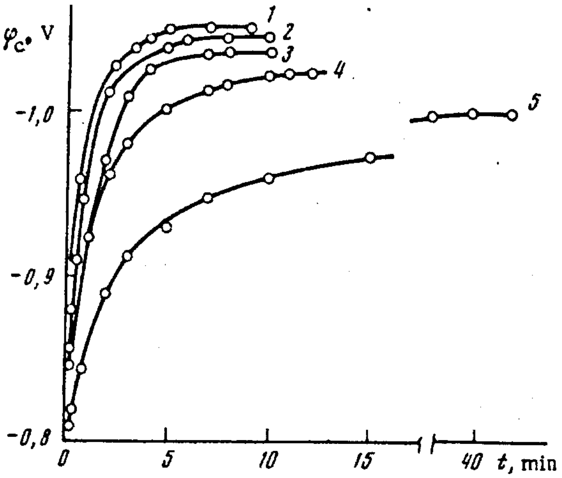

Fig. 4

Fig. 3. Cathodic I vs φ curves in 5 N KOH: 1) Hydrogen evolution on reduced iron; 2) reduction of iron oxide; 3) the same, repeated (circles) at m = 460 rpm in an atmosphere of argon.

Fig. 4. Cathodic I vs φ curves in 5 N KOH at various values of the current strength, I_c: 1) $1.2 \cdot 10^{-5}$; 2) $1.1 \cdot 10^{-5}$; 3) $9 \cdot 10^{-6}$; 4) $8 \cdot 10^{-6}$; 5) $5 \cdot 10^{-6}$ A, in an atmosphere of argon.

by increasing the strength of the reducing current. This, of course, also entailed a reduction in the amount of $Fe(OH)_2$ reduced. Table 1 shows the time (t, min) required for reaching a rate of hydrogen evolution equal to that observed on pure iron at various values of the cathodic current I_c. Variation of the rate of disk rotation from 0 to 460 rpm had essentially no effect on either the potential or the time. There was no time effect even at 1000 rpm, but the hydrogen evolution potential was displaced toward more negative values by 10-15 mV. The factors responsible for this displacement are not as yet understood. The results of these experiments made it clear that the $Fe(OH)_2$ reduction is a solid phase reaction which proceeds independently of the solution ions. The fact that the oxide reduction was an inhibiting reaction accompanied by the appearance of a limiting current and displacement of the potential for $Fe(OH)_2$ reduction to the hydrogen evolution potential for an electrode carrying a large amount of $Fe(OH)_2$ made it clear that the rate of diffusion of the iron ions to the solid phase surface had been too low to maintain the reduction to the metal [6]. This was a case of nonstationary diffusion, the driving concentration gradient in the immediate neighborhood of the electrode being given by the expression

$$\left(\frac{dc}{dx}\right)_{x=0} = \frac{c_0}{\sqrt{\pi D t}},$$

in which t is the time elapsed from the initiation of polarization and c_0 the bulk solid phase ion concentration. The diffusion front moves away from the surface of the electrode with the passage of time and the concentration gradient diminishes. The diffusion current is thereby diminished, being now given by the expression

$$I_d = nFD\frac{c_0}{\sqrt{\pi D t}} \quad \text{or} \quad I \sim 1/\sqrt{t}; \quad t = A\frac{1}{I^2},$$

in which A is a factor of proportionality. It is clear that essentially all of the oxide on the electrode surface can undergo reduction when the current density is equal to, or less than, that critical value at which the rate of ion diffusion out of the solid phase into the reaction zone becomes identical with the rate of reduction. Tabulated data indicate that A is constant at current densities in excess of critical. This observation tends to confirm the belief that iron oxide reduction ceases, and hydrogen evolution at the rate corresponding to that observed on the pure iron electrode begins, when the rate of iron ion diffusion to the surface oxide falls below a certain critical value.

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