DIFFERENTIAL CAPACITY OF THE IRON ELECTRODE IN ALKALINE SOLUTION

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Measurements of the differential capacity [1-3] and of the potential decay [4, 5] in alkaline solutions have revealed significant quantities of adsorbed hydrogen on the surface of iron electrodes. In the cathodic region the $C-\varphi$ curves exhibit two flat maxima which correspond to the ionization of adsorbed hydrogen, one type more and one type less strongly bound to the metal. At low ac frequencies these maxima attain 320 to 400 $\mu F/cm^2$. At high frequencies the capacity decreases to 35 $\mu F/cm^2$ and said maxima disappear [3]. The high dispersion with ac frequency evidently is due to slow ionization and discharge of the adsorbed hydrogen.

In acidic solutions (1 N H_2SO_4), the differential capacity on the electropolished iron electrode is significantly smaller (25 $\mu F/cm^2$ at 800 Hz), and is almost independent of potential until the iron starts to ionize when the stationary potential is approached. At high ac frequencies the capacity decreases to 18 $\mu F/cm^2$, and hence is determined chiefly by double-layer capacity [3].

In the present work we have studied the impedance of iron electrodes in the cathodic and anodic potential range in pure KOH solution and in KOH solution containing certain additives which serve to raise or lower the discharge capacity of the iron electrodes in alkaline storage batteries.

The measurements were made on electrodes of pure, zone-melted iron having a surface area of about 0.03 cm^2 which for the release of stresses [6, 7] were thoroughly heated for 4 h to 750°C in hydrogen atmosphere under reduced pressure. The electrodes were ground, electrolytically polished, and washed with alcohol and water. The idle parts of the electrodes were covered with a lacquer of polystyrene dissolved in distilled toluene. Just prior to the tests the electrodes were etched for 1 min in 1 N H_2SO_4 to remove oxide films, then placed into the cell, and cathodically polarized for 2 h at $\varphi = -1.4$ V vs the Hg/HgO electrode in 1 N KOH. The electrolyte was 1 N KOH prepurified by prolonged cathodic polarization at a Pt screen while hydrogen was passed through. The $C-\varphi$ curves were recorded with the aid of an R-568 ac bridge, and the results obtained were recalculated in terms of a parallel-connection network of capacitance and resistance [3, 8]. The chief measurements were performed at 800 Hz. Results obtained in the forward (φ from -1.4 to -1.0 V) and reverse direction coincided, but when the measurements were extended to $\varphi = -0.75$ V, then the curve obtained in the reverse direction was not the same, and polarization to $\varphi = -1.4$ V did not restore agreement between the curves. Etching of the electrode in 1 N H_2SO_4 followed by cathodic polarization completely eliminated the oxide film, and led to agreement between the curves in the following cycle. Curves were recorded shown to $\varphi = -0.3$ to -0.5 V vs Hg/HgO in order to examine the impedance in the anodic potential range.

The $C-\varphi$ curves in 1 N KOH exhibited two cathodic and two anodic maxima (Fig. 1, curve 1). Their average values: 320 ($\varphi = -1.3$ V), 375 ($\varphi = -1.05$ V), 475 ($\varphi = -0.8$ V), and 400 $\mu F/cm^2$ ($\varphi = -0.65$ V). Of the two anodic maxima just mentioned, the first is due to adsorption of OH^- ions and the passage of a faradaic current of iron ionization, the second is due to the oxidation of divalent to trivalent iron compounds.

When $Ca(OH)_2$, $Mg(OH)_2$, or $Ba(OH)_2$ are added to saturation to the 1 N KOH (Table 1), the capacity in the maxima decreases relative to the values in pure KOH solution, but the two cathodic maxima are preserved, while the second anodic maximum disappears (Fig. 1, curve 2).

Considering the strong decrease in the solubilities of the hydroxides in the series $Ba(OH)_2 > Ca(OH)_2 > Mg(OH)_2$ and the close values of ΔC one can conclude that the adsorption of their cations from alkaline solution onto iron increases strongly in the series from Ba to Mg.

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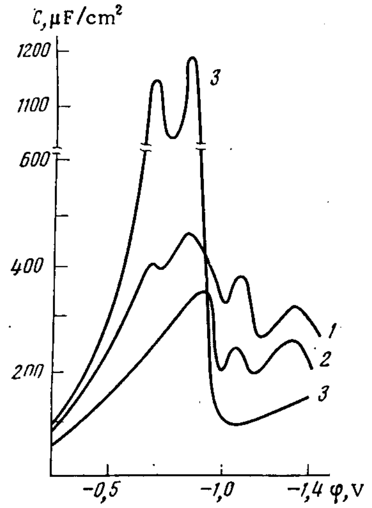

Fig. 1

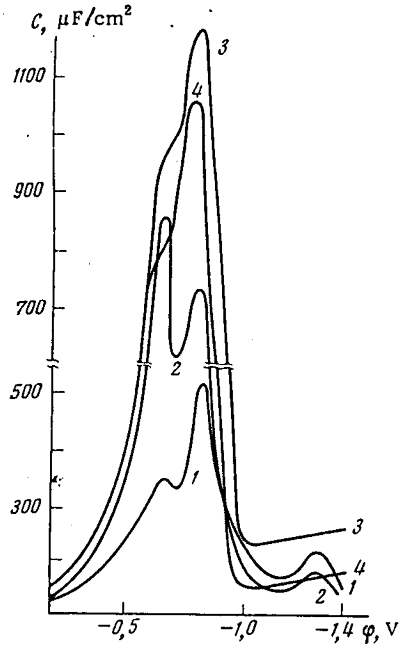

Fig. 2

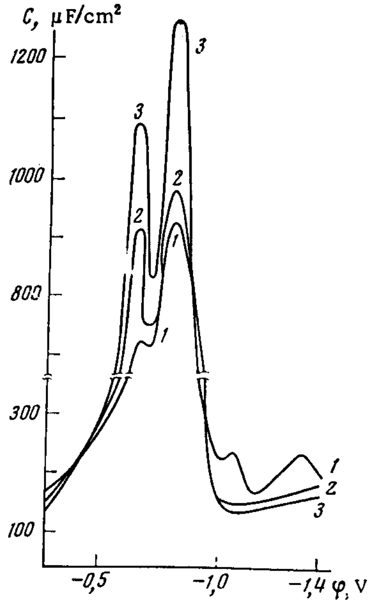

Fig. 3

Fig. 1. Differential capacity curves of iron in 1 N KOH (1), and in 1 N KOH containing $Ca(OH)_2$ to saturation (2) or sat. $Ca(OH)_2 + 10^{-4}$ M Na_2S (3); 800 Hz.

Fig. 2. Differential capacity curves of iron in 1 N KOH containing Na_2S: 1) 10^{-6} M, 2) 10^{-5} M, 3) 10^{-4} M, and 4) 10^{-3} M.

Fig. 3. Differential capacity curves of iron in 1 N KOH containing $Na_2S_2O_3$: 1) 10^{-6} M, 2) 10^{-5} M, and 3) 10^{-4} M; 800 Hz.

TABLE 1. Lowering of the Maxima (ΔC), in μF/cm²

Solution	φ, V		
	−1,3	−1,05	−0,85
1 N $KOH + Ca(OH)_2$	50	40	180
1 N $KOH + Mg(OH)_2$	35	45	200
1 N $KOH + Ba(OH)_2$	50	35	200

It is interesting to note that the adsorption of said cations on iron from 1 N KOH produces a decrease in hydrogen overvoltage $\Delta\eta$ which increases in the same series: nil for Ba, −35 mV for Ca, and −65 mV for Mg.

Figures 2 and 3 show C−φ curves recorded in 1 N KOH containing Na_2S and $Na_2S_2O_3$. It can be seen from the figures that these compounds depress the differential capacity in the cathodic potential range. At low concentrations (10^{-6} to 10^{-5} M), the cathodic maxima are preserved, but at higher concentrations they disappear due to poisoning of the active sites by adsorption of atomic hydrogen.

There is a strong increase of capacity in the anodic potential range: In 10^{-4} M solutions of Na_2S or $Na_2S_2O_3$ the maxima attain 1200 μF/cm² at $\varphi = -0.8$ V, and 800 to 900 μF/cm² at $\varphi = -0.65$ V, but the maxima decrease noticeably when the concentrations of these additives are made smaller or higher.

In 10^{-3} M and 10^{-4} M Na_2S (Fig. 2), the second anodic maximum disappears, probably because a phase layer of iron sulfide is formed at $\varphi = -0.8$ V.

The increase in differential capacity and the observed stimulation of the anodic process during discharge of iron electrodes in the presence of sulfides are due to negative potential shift of the electrode which occurs under the effect of the adsorbed S^{2-} ions. This accelerates the anodic reaction when observed at constant potential, and retards the accumulation of trivalent passivating oxides on the electrode surface while the first stage of the anodic process is taking place.

The adsorbed cations of Ca, Mg, and Ba displace the electrode potential toward positive values, which retards the anodic ionization of iron but accelerates the accumulation of passivating oxides while the first stage of the anodic reaction is taking place, and accelerates its passivation.

The above results are in harmony with the conclusions which can be drawn from the $I-\varphi$ curves recorded potentiostatically. The $I-\varphi$ curves exhibit anodic maxima of the current at the same potentials where maxima of differential capacity had been observed on the $C-\varphi$ curves [9, 10]. The first current maximum on the $I-\varphi$ curves increases strongly in the presence of sulfides, but decreases when calcium or magnesium hydroxide is added.

The addition of sulfide ions to a KOH solution containing $Ca(OH)_2$ to saturation serves to prevent the passivating effect of the $Ca(OH)_2$, as can be seen from the fact that the height of the anodic maxima of differential capacity returns to the values observed in these solutions when $Ca(OH)_2$ is absent (Fig. 1, curve 3).

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EFFECT OF THE BASE METAL ON HYDROGEN PERMEATION DURING CHROMIUM ELECTRODEPOSITION

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By examining, with the electrochemical technique [1], the diffusion of hydrogen into the base material during the electrodeposition of metals one can, in the opinion of a number of authors [2-4], characterize the barrier properties of the coatings being produced, i.e., their ability to retard hydrogen permeation into the base metal. As an indicator of the barrier properties one usually uses the dependence on electrolysis time (t) of the maximum of ionization current (I_H) of the hydrogen diffusing across the membrane, i.e., the values t_m and I_m, or the rate of decay (slope of the $I-t$ curve) after the maximum ($\Delta I/\Delta t$).

Our examination [5, 6] of hydrogen diffusion into iron and steels during chromium electrodeposition showed a large difference between the barrier properties of matte and bright chromium. But these differences vary with the base metal. The present work is concerned with a more detailed examination of this question.*

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*V. M. Alekseev, student at the D. I. Mendeleev Chemical Engineering Institute, Moscow, took part in the experimental work.

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