EFFECT OF A GROWING $Fe(OH)_2$ FILM ON ANODIC IRON IONIZATION IN KOH SOLUTIONS

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During the anodic polarization of iron in alkali solutions, the Fe^{2+} ions emerging from the metal react with OH^- ions and settle on the electrode as an $Fe(OH)_2$ film. The further progress of the reaction is limited by the rate of Fe^{2+} ion transport in the film to the film/solution interface. At first the $Fe(OH)_2$ film is thin and the dissolution current is high, but then, as it grows thicker, the rate of ion transport and the limiting reaction current will decrease. The Fe^{2+} ions move under the effect of concentration and potential gradients, which become smaller as the film grows thicker. The reaction rate is dropping accordingly.

For the analogous reaction where an anodic $Cd(OH)_2$ film is formed in alkaline solution on Cd, Croft [1] derived equations for the current as function of time in the case where the driving force is an ionic concentration gradient:

$$i = \left(\frac{kT}{e}\frac{\sigma}{2\Omega}\right)^{1/2}\left[1-\exp\left(-\frac{e\varphi}{kT}\right)\right]^{1/2} t^{-1/2} \quad (1)$$

and where it is a potential gradient:

$$i = \left(\frac{\sigma}{2\Omega}\right)^{1/2} \varphi^{1/2} t^{-1/2}, \quad (2)$$

where σ is the ionic conductivity, Ω is the volume of oxide produced per coulomb of electric current, φ is the overpotential, e is the elementary charge, T is the absolute temperature, k is the Boltzmann constant, and t is time.

Rozovskii and Solov'eva [2, 3] studied the effect of additives and impurities in the material of iron powder electrodes on the limiting currents of cathodic film reduction. They suggested that metals having a more negative reduction potential than Fe (e.g., Ca, Mn, Ti, V, and Cr) are capable of producing solid solutions and isomorphous mixtures [4] which reduce the ionic conductivity when they form a sort of clots in the film's micropores.

In the present work we studied the limiting currents of anodic iron ionization at constant potential (E) as functions of time with a potentiostat using a smooth electrode made of pure, zone-melted iron preheated to 700°C. The experiments were conducted in argon atmosphere in purified KOH solutions at 20 ± 1°C. Prior to experiment, the electrodes were polished with fine glass powder, etched in 1 N H_2SO_4, and cathodically polarized with a current of 10^{-2} A/cm^2. The potentials were measured relative to a mercury–mercuric oxide reference electrode in alkali solution of the same concentration.

Plots of i against $t^{-1/2}$ calculated from the experimental i vs. t curves for a number of KOH solution concentrations are reported in Fig. 1. These plots are straight lines approaching the coordinate origin for $t \to \infty$. The slopes of the straight lines, $\Delta i/\Delta t^{-1/2}$, which are 10, 36, 53, and 60 μA/cm$^2 \cdot$ min$^{-1/2}$, increase with the KOH concentration (c = 1, 5, 7, and 10 N); to a certain approximation they are proportional to the logarithm of KOH concentration.*

An increase in anodic potential also leads to an increase in the slope of the i vs. $t^{-1/2}$ straight lines, which approach the coordinate origin (Table 1). The substantial effect of potential on the ionic conductivity and on the rate of film formation evidently must be attributed chiefly to the effect of an electrostatic field gradient on these reactions. This follows from the observation that the current density increase, in harmony with Eq. (2), is proportional to $\sqrt{E}$ (Fig. 2).

*The slope, $\Delta i\, \Delta t^{-1/2}$, of the straight lines characterizes the ionic conductivity of the film, and determines the current density at t = 1 min.

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TABLE 1. Values of $\Delta i/\Delta t^{-1/2}$, in $\mu A/cm^2$ $min^{-1/2}$, at Different Electrode Potentials

−E, V	KOH, N		−E, V	KOH, N	
	1	5		1	5
0,81	37,5	–	0,86	10,7	36,0
0,83	28,0	77,0	0,87	–	27,0
0,85	18,1	52,0			

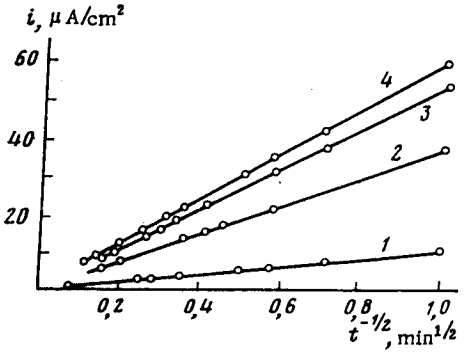

Fig. 1

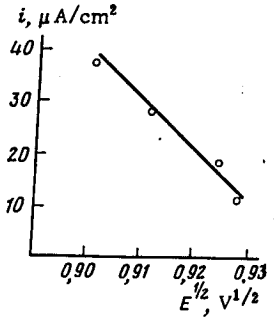

Fig. 2

Fig. 1. The anodic current, i, as function of $t^{-1/2}$ in 1.0 (1), 5.0 (2), 7.0 (3), and 10.0 N KOH (4) at E = −0.86 V.

Fig. 2. The anodic current, i, as a function of $\sqrt{E}$ in 1 N KOH solution at t = 1 min.

At potentials more positive than −0.81 V, the i vs. $t^{-1/2}$ straight lines do not approach the coordinate origin, obviously because of passivation. Sometimes a break occurs in the straight lines, and when extrapolated they intersect the y axis at negative values of current.

We have investigated the effect of additives to the electrolyte on the current−time relations and on the ionic conductivity of the $Fe(OH)_2$ layer. Saturation of the 1 N KOH with $Ca(OH)_2$ or $Mg(OH)_2$ produced a decrease in $\Delta i/\Delta t^{-1/2}$, and hence caused inhibition of current flow in the $Fe(OH)_2$ layer (E = −0.86 V) as shown below:

	$\Delta i/\Delta t^{-\frac{1}{2}}$
1 N KOH	10.0
1 N KOH+$Ca(OH)_2$(sat)	7.3
1 N KOH+$Mg(OH)_2$(sat)	5.3

To the contrary, low concentrations of anionic additives, as a rule, increase i_a and $\Delta i/\Delta t^{-1/2}$ (Fig. 3); hence they raise the ionic conductivity of $Fe(OH)_2$. The straight lines of i against $t^{-1/2}$ for certain anions (SiO_3^{2-}, CrO_4^{2-}, $S_2O_3^{2-}$) do not approach the coordinate origin upon extrapolation, and obey the equation

$$i = a + bt^{-1/2}, \tag{3}$$

where a is the current density of a side reaction not depending on t.

As indicated, the $Fe(OH)_2$ film is growing further at its outer surface after the ions have passed through its entire thickness; this follows from the linear dependence of i on $t^{-1/2}$ observed in the experiments. But partial film growth is possible when the Fe^{2+} ions are interacting with OH^- ions directly at the electrode. In this case the process obeys Eq. (3), where a corresponds to the current density consumed for $Fe(OH)_2$ formation at the inner surface, which does not depend on t but changes with potential and solution composition.

The above linear dependence of i on $t^{-1/2}$ is an expression for the classical parabolic law of anodic-film growth as a function of time. In fact, the thickness of the anodic film (δ) is proportional to the product it, whence

$$\delta = \int bt^{-\frac{1}{2}}\,dt = 2b\sqrt{t} + \text{const.} \tag{4}$$

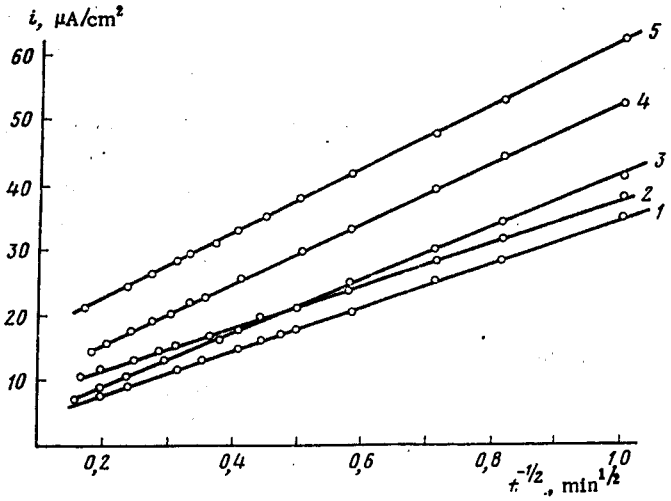

Fig. 3. Plots of i against $t^{-1/2}$ at E = −0.86 V in 5 N KOH without (1) and with additives: 2) 10^{-3} M Na_2SiO_3; 3) 10^{-2} M KVO_3; 4) 10^{-3} M K_2CrO_4; 5) 10^{-3} M $Na_2S_2O_3$.

To prove this law with respect to the process studied, i.e., anodic-film growth on iron in KOH solution, we did a calculation for 5 N KOH and E = −0.86 V using the equation

$$\delta = (Q - Q_d)\frac{M}{\rho F z f}, \tag{5}$$

where M is the molecular weight of $Fe(OH)_2$; ρ is its density (3.4); z is the charge; f is electrode roughness (2.5); F is the Faraday constant; Q is the amount of charge consumed for film formation up to the time t, which was found by graphical integration of the i vs. t curve; and Q_d is the amount of $Fe(OH)_2$ that has dissolved up to the time t (in coulombs). The curve of Fig. 4 confirms the parabolic growth law for the $Fe(OH)_2$ film arising on iron when it is anodically polarized in alkali. The anodic $Fe(OH)_2$ film on iron is microporous, and lacks electronic conductivity and valve properties.

The process examined can be visualized as follows. The Fe^{2+} ions appearing during anodic current flow settle in sites of the $Fe(OH)_2$ lattice (the $Fe(OH)_2$ film is amorphous, but its structure can be regarded as intermediate between a crystal lattice and glasses while one uses the same laws as in the case of crystal structures [5]). Under the effect of the potential and concentration gradients being set up, these ions acquire additional energy – activation energy – which is sufficient to lift them from the lattice sites and transfer them to interstitial sites, where under the effect of said gradients they will move via vacancies or defects to the

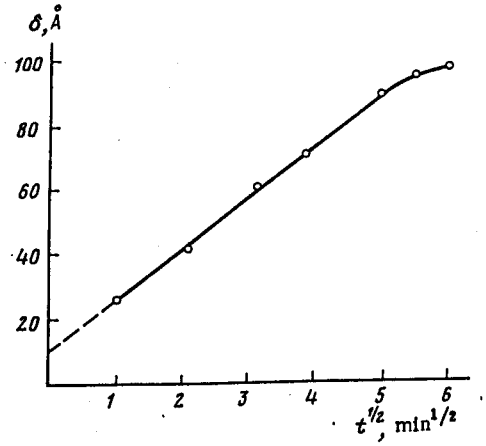

Fig. 4. Thickness of the anodic $Fe(OH)_2$ film as a function of time ($\sqrt{t}$) in 5 N KOH at E = −0.86 V.

film/solution interface. Film growth at this interface takes place by interaction of Fe^{2+} and OH^- ions.

The higher ionic conductivity and limiting reaction current found in KOH solutions when anions have been added and also when the OH^- ion concentration has been increased probably are due to the adsorption of these ions in the lattice sites. This gives rise to additional negative charge surrounding the Fe^{2+} ions and facilitates their transfer to interstitial sites; this leads to a higher Fe^{2+} ion concentration in the interstitial sites and to higher ionic conductivity of the film. Cationic additives have the opposite effect. The positive charge created by them inhibits the transfer of Fe^{2+} ions to interstitial sites, and thus lowers the ionic conductivity of the film.

LITERATURE CITED

1. G. Croft, J. Electrochem. Soc., 106, 279 (1959).
2. V. M. Rozovskii, N. A. Solov'eva, and L. A. Maklyarskaya, Studies in the Field of Chemical Power Sources [in Russian], Intercollegiate Scientific Collection of Saratov University, No. 4, 95 (1976).
3. V. M. Rozovskii and N. A. Solov'eva, in: Fifth All-Union Conference on Electrochemistry [in Russian], Part 2, VINITI, Moscow (1974), p. 480.
4. V. S. Lyzlov, Tr. Leningr. Technol. Inst., No. 10, 76 (1941).
5. L. Young, Anodic Oxide Films, Academic Press, New York (1961).

CURRENT DENSITY DISTRIBUTION ALONG A RESISTIVE ELECTRODE

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The effect of component geometry of electrochemical cells on the current distribution along the electrodes has been described by a number of authors [1-4]. Consistent solutions have been obtained in [3, 4] for the condition of linear polarization. But this assumption is an approximation, and will be unjustified at large deviations from equilibrium, i.e., at relatively high current densities where the Tafel equation is valid. In addition, following the above work one cannot solve the problem for electrodes of arbitrary shape.

A resistive electrode 1 which has a profile determined by the curve $x_0(y)$ is separated from electrode 2 by electrolyte 3 (Fig. 1). Relative to electrode 1, electrode 2 is an infinitely good conductor. The terminals to which the voltage powering the cell is connected are shown in Fig. 1.

The present problem is first solved for steady-state conditions, i.e., disregarding the dynamics of a changing profile of electrode 1 on account of its dissolution; secondly, it is assumed that transient processes associated with charging the electric double-layer capacity have been completed; and thirdly, that the current density is independent of coordinate z.

If electrode 1 is cut up into n current ducts (Fig. 1), then $\Delta y = y_1/n$, $\Delta x = x_0(0)/n$, and $\Delta y/\Delta x = y_1/x_0(0)$. The shape of the current ducts is changing with the shape of function $x_0(y)$. But for the ratio between the duct cross section, ΔS_2, at the electrode/electrolyte boundary $x_0(y)$, ($l = l_k$) and the normal duct cross section, ΔS_1, at the duct's beginning, $l = 0$, one has

$$\frac{\Delta S_2}{\Delta S_1} = \frac{\Delta y}{\Delta x}\sqrt{1+\left(\frac{dx_0(y)}{dy}\right)^2} = \frac{y_1}{x_0(0)}\sqrt{1+\left(\frac{dx_0(y)}{dy}\right)^2} = \frac{y_1\varepsilon}{x_0(0)}. \quad (1)$$

The field strength vector in electrode 1, which is an isotropic medium, coincides everywhere with the duct direction $\vec{dl}$. Therefore, by assuming the potential of the terminal of resistive electrode 1 to be zero and using Ohm's law in differential form we can write an expression for the potential of electrode 1 at the electrode electrolyte interface $x_0(y)$ for $y = y_k$:

$$U_- = -\frac{1}{\sigma_0}\int_0^{l_k}\frac{\Delta I}{\Delta S(l)}\,dl = -\frac{j}{\sigma_0}\int_0^{l_k}\frac{dl}{L(l)}; \quad (2)$$

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