INVESTIGATION OF THE FIRST ANODIC PROCESS OF SOLUTION OF IRON IN BASES BY THE IMPEDANCE MEASUREMENT METHOD

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The first anodic process of solution of an active iron electrode in bases which occurs at a potential of 0.86-0.88 volts with respect to a mercury oxide electrode in the same solution involves the conversion of metallic iron into ferrous hydroxide. The first product of iron oxidation passes into solution with the formation of the anion $HFeO_2^-$ in bases at concentrations up to 4-5 N [1] or of FeO_2^{-2} in more concentrated solutions [2] and hot solutions [3]. As a result of hydrolysis of these anions a porous residue of $Fe(OH)_2$ is formed. The process of anodic solution of iron in bases which leads to the formation of a complex of divalent iron, namely $HFeO_2^-$ occurs in two electrochemical stages: the first stage is the formation of an intermediate compound of monovalent iron by adsorption of the hydroxide and loss of the first electron, while the second stage consists in the formation of divalent iron from this intermediate compound by loss of the second electron [4]. The passivation process occurs simultaneously with the process of iron solution. Passivation is determined by the formation of oxides of valency exceeding two. These oxides have an adsorption character and can be assigned conditionally the formula $Fe\begin{matrix}=O\\ \diagdown OH\end{matrix}$, but passivation involves together with the solution of iron an overall first stage consisting in the electrochemical adsorption of hydroxyl [5].

In order to refine concepts on the mechanism of solution and passivation of iron in bases and to establish the velocity ratios of the various stages, the impedance of the iron/base solution boundary and the conditions obtained in the first anodic process were measured.

The frequency relations of the impedance in the process of solution of a small active iron electrode in a base at 20° were analyzed as in [6, 7], in the frequency range 0.21-10 kc/sec and resulted in the circuit A (Fig. 1)* as the

*All the circuits were drawn after subtracting the resistance of the solution.

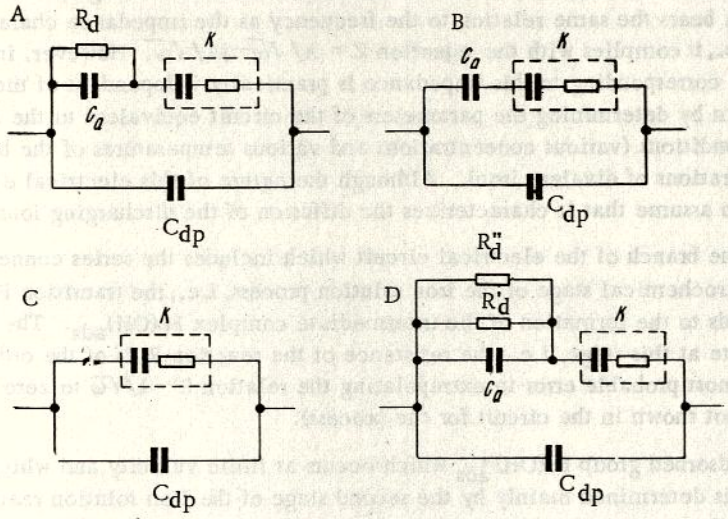

Fig. 1. Possible equivalent circuits for the anodic solution of iron in bases: C_{dp}) double layer capacity; K) electric elements with dispersion parameters; C_a) adsorption capacity; R_d) desorption resistance.

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TABLE 1. Parameters of Circuits A and B at 20°C

KOH conc., mole/liter	Equivalence region of circuit B, kc/sec	Constant A, $\Omega \cdot cm^2 \cdot sec^{-1/2}$ from the relation		C_a, from the relation $1/C'\omega^{1/2}$ $\mu F/cm^2$	Equivalence region of circuit A, kc/sec	C_a and R_d, calculated for a series of frequency pairs		
		$R'\omega^{-1/2}$	$1/C'\omega^{1/2}$			frequency pair, kc/sec	C_a $\mu F/cm^2$	R_d $\Omega \cdot cm^2$
2	From 10 To 0.8	180	170	74	From 0.8 To 0.21	0.8 and 0.41	79	53
						0.61 and 0.31	78	44
						0.41 and 0.21	78	50
						Mean	78	49
10	From 7 To 0.8	165	150	145	From 0.8 To 0.21	0.8 and 0.41	185	10.7
						0.61 and 0.31	186	11
						0.41 and 0.21	200	14
						Mean	190	12

TABLE 2. Parameters of Circuit C, 80°C

KOH conc., mole/liter	Equivalence region of circuit C, kc/sec	Constant A, $\Omega \cdot cm^2 \cdot sec^{-1/2}$	
		$R'-\omega^{-1/2}$	$1/C'-\omega^{1/2}$
2	From 10 to 0.21	136	137
10	From 10 to 0.41	83	87

TABLE 3. Measurement of Parameters of Circuit A as Passivation Proceeds

$-\varphi$ mer. ox.el.	A, $\Omega \cdot cm^2 \cdot sec^{-1/2}$	C_a, $\mu F/cm^2$	R_d, Ω/cm^2
0,875—0,872	175	78	49
0,847—0,81	145	139	28

equivalent electrical circuit at low frequencies (0.21-0.81 kc/sec), which at higher frequencies (1-10 kc/sec) simplifies to circuit B. In hot base solutions ($t° = 80°$) this circuit can be simplified still further to give circuit C. The parameters of the equivalent circuit A and B are recorded in Table 1 and those for circuit C in Table 2. Moreover, the parameters of the equivalent circuit A corresponding to passivation of the iron electrode were determined on the basis of the frequency relation, i.e., at the middle and at the end of the first plateau after the passage of 68 $\mu C/cm^2$ (at a potential of 0.872-0.875 V) and 107 $\mu C/cm^2$ (at a potential of 0.81-0.847 V) of electricity. The values of these parameters are recorded in Table 3. Circuit A contains the element K ringed in the figures by a broken line, the impedance of which bears the same relation to the frequency as the impedance characterizing the process of diffusion in solution, i.e., it complies with the equation $Z = A/\sqrt{\omega} - jA/\sqrt{\omega}$. However, in contrast to diffusion in solution the coefficient A corresponding to this impedance is practically independent of the ionic concentration in the solution. This was shown by determining the parameters of the circuit equivalent to the first anodic process under various experimental conditions (various concentrations and various temperatures of the base solutions, and consequently various concentrations of divalent iron). Although the nature of this electrical element is at present not clear, it is reasonable to assume that it characterizes the diffusion of the discharging ions at the surface.

We suggest that the branch of the electrical circuit which includes the series connected elements C_a and K simulates the first electrochemical stage of the iron solution process, i.e., the transition Fe → Fe (I) with the loss of one electron, which leads to the formation of the intermediate complex $Fe(OH)_{ads}$. The electrochemical reaction itself has a very high rate at this stage, i.e., the resistance of the reaction R is of the order of 4×10^{-2} $\Omega \cdot cm^2$ (it was determined as the most probable error in extrapolating the relation $R' - 1/\sqrt{\omega}$ to zero assuming an infinitely high frequency, and is not shown in the circuit for the process).

The drift of the adsorbed group $Fe(OH)^*_{ads}$ which occurs at finite velocity and which determines the resistance R_d in circuit A (Fig. 1) is determined mainly by the second stage of the iron solution reaction Fe (I) → Fe (II) (this is indicated by the fact that R_d is inversely proportional to the base concentration) and partly by the formation of a passivating oxide. In fact, R_d increases and C_a increases as passivation proceeds. At the beginning and in the middle of the first anodic process $1/R_d$ evidently reflects the reaction rate for the reaction

$$Fe(OH)^*_{ads} + OH^- \rightarrow HFeO_2^- + H^+ + e^-, \quad (1)$$

which is here greater than the rate of formation of the passivating oxide, and at the end of the first anodic arrest, when the displacement of the potential in the positive direction accelerates the passivation process to a greater degree than the solution process [5]; while R_d to a great extent reflects the rate of formation of the passivating oxide. Instead of a single resistance R_d it is possible to visualize two resistances R'_d and R''_d (circuit D) connected in parallel, where R'_d is the resistance of reaction (1), and R''_d is that of the reaction corresponding to the formation of the passivating oxide. However, in practice the impedance method is used to measure only their total resistance.

According to this interpretation of the results of impedance measurements on an iron electrode during the first anodic process it is possible to represent this process as taking place in accordance with the scheme [5]:

$$Fe + OH^- \xrightarrow{-e^-} Fe(OH)_{ads.} \rightarrow Fe(OH)^{\bullet}_{ads.} \begin{cases} \xrightarrow{+OH^-} HFeO_2^- + H^+ + e^- \\ \xrightarrow{+OH^-} Fe\begin{matrix} O \\ \diagup\!\!\diagup \\ OH \end{matrix} + H^+ + 2e^- \end{cases}$$

On comparing the resistance of the electrochemical process occurring in the first state ($R_r < 4 \times 10^{-2}\ \Omega \cdot cm^2$) with that of the second stage ($R_d \sim 10\text{-}50\ \Omega \cdot cm^2$) it is reasonable to conclude that the rate of the process Fe (I)→Fe (II) is two orders of magnitude less that the rate of the process Fe ⇌ Fe (I). Consequently, in alkaline solution the rate determining stage for anodic oxidation of metallic iron to the divalent state is the second stage, a result which is in agreement with those obtained in [8-10], although these results referred to metals of a different type.

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