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Abstract

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THE MECHANISM OF ANODIC ACTIVATION OF IRON

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Earlier (^{1}) we showed that, under anodic polarization of passive iron in perchloric acid, its activation occurs and is caused by adsorption of ClO_4^- ions. This process is reversible. In sulfuric acid, activation does not occur; only upon reaching a certain anodic potential is the increase in the degree of passivity slowed. On potentiostatic polarization curves, anodic activation is expressed in a sharp increase in current upon reaching the activation potential; on chronoamperometric curves, activation is expressed in an increase of the polarizing current with time at unchanged potential.

To elucidate the mechanism of anodic dissolution of iron during anodic activation, we determined the influence of the composition of the solution on activation, as well as the valence of the iron entering the solution during anodic polarization of active and passive iron. During anodic polarization of iron in acidic sodium perchlorate solutions, activation occurs at a potential that decreases linearly with increasing logarithm of the concentration of the perchloric acid anion (Fig. 1). This agrees well with our view of the adsorption mechanism of anodic activation. Indeed, let us assume that activation occurs when one and the same value of the surface concentration of perchloric acid, Γ_{act}, is reached. If adsorption of ions under the given conditions obeys a logarithmic isotherm (average coverage on a heterogeneous surface), and, at a constant value of the anion concentration in solution C_i, the surface concentration of anions is proportional to the potential drop φ_a in the double layer (i.e., the double layer behaves like a capacitor), then the following theoretical expression may be written:

$$\Gamma_i = \varphi_a a - b \lg C_i + \text{const}_1,$$

where Γ_i is the surface concentration of anions, and a and b are positive constants.

Fig. 1. Dependence of the anodic activation potential on the change in the concentration of ClO_4^- ions at $[H^+] = 0.1\,N$

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Hence, under the condition that Γ_i is equal to the constant Γ_{act} and that φ_a differs from the electrode potential φ by a constant value, the following dependence is obtained:

$$-a\varphi_{\text{act}} = b\lg C + \text{const}_2$$

(where φ_{act} is the value of φ at $\Gamma_i = \Gamma_{\text{act}}$), which is in fact observed experimentally (Fig. 1).

It may be assumed that, in strongly acidic solutions, adsorption of ClO_4^- ions is determined by the reaction:

$$\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 6\text{ClO}_4^- = 3\text{H}_2\text{O} + [2\text{Fe} - (\text{ClO}_4)_3]_{\text{ads}},$$

i.e., dissolution of the oxide in acid and complex formation occur in one elementary act. Such displacement of oxygen atoms by ClO_4^- ions as the potential increases is possible owing to the greater polarizability of the ClO_4^- ion in comparison with oxygen atoms.*

* An exact comparison of the polarizability of ClO_4^- ions and oxygen atoms in solution is difficult because there are no data on the influence exerted on the polarization of oxygen atoms by cations and water molecules. Only an approximate comparison of the degree of polarizability of ClO_4^- ions in solution and of oxygen in the gas, based on refractive measurements (^{2}), is possible; it permits the assumption that ClO_4^- ions are capable of being polarized considerably more strongly than oxygen atoms.

However, we have shown that in not too acidic solutions φ_{act} does not depend on pH at a constant concentration of ClO_4^- (Fig. 2). Consequently, the reversible adsorption of ClO_4^- in weakly acidic solutions occurs independently of the possible reaction of dissolution of iron oxide in acid. Only in strongly acidic solutions (at a concentration of H^+ ions from 1 to $4.2\,N$) does φ_{act} shift in the negative direction with increasing H^+ concentration, which agrees with ideas about the passivating role of the oxide.

Fig. 1. Dependence of the anodic activation potential on the change in the concentration of ClO_4^- ions at $[H^+] = 0.1\,N$

Fig. 2. Dependence of the anodic activation potential on the change in H^+ concentration at $[ClO_4^-] = 4.2\,N$

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Figure 2: Fig. 2. Dependence of the anodic activation potential on the change in H^+ concentration at $[ClO_4^-] = 4.2\,N$

The valence of the iron passing into solution under anodic polarization was determined colorimetrically. Figure 3 shows the dependence of the concentrations of Fe^{2+} and Fe^{3+} in a $1\,N$ hydrochloric acid solution on the amount of electricity passed. As is evident from Fig. 3, in hydrochloric acid solution, during the dissolution of anodically activated iron, more than 99% of the current is consumed in the formation of Fe^{2+}, and only less than 1% in Fe^{3+}. The reaction $Fe \to Fe^{2+}$ after anodic activation proceeds rapidly, and its limiting rate is apparently connected in a complex way with the diffusion of the Fe^{2+} ion from the electrode. Thus, active iron in $1\,N\,HClO_4$ (at potential $\varphi = 0.0$ V) dissolves with a maximum rate equivalent to $\sim 1\,A/cm^2$, and after anodic activation (at potential $\varphi = 1.5$ V) also with a rate of $\sim 1\,A/cm^2$. As the concentration of ClO_4^- decreases, the maximum current also decreases.

In hydrochloric acid, as in sulfuric acid (^{5}), in which activation does not occur, in the passive state of iron practically only trivalent iron is formed. To determine the degree of independence of the individual stages of oxidation of passive iron, ferrous perchlorate $Fe(ClO_4)_2$ was added to a $1\,N$ hydrochloric acid solution to a concentration of $0.1\,N$, i.e., its concentration near the passive iron electrode was increased approximately 1000-fold. It turned out (Fig. 3, 3) that on passive iron at a potential close to 1.3 V, the oxidation reaction $Fe^{2+} \to Fe^{3+}$ practically does not proceed (^{3}), whereas the metal itself at the same time is oxidized not to the divalent but to the trivalent state, as without the addition of Fe^{2+} to the solution.

This could be explained either by the fact that the anodic oxidation of iron (or of an intermediate surface monovalent iron compound) to the trivalent ion on a passive electrode occurs in one stage, bypassing the free divalent state, or by the fact that oxidation takes place in the solid phase (^{4}) and that divalent iron inside the solid phase is oxidized to the trivalent state without hindrance, whereas in solution it is oxidized very slowly because of the considerable overvoltage. It is possible that specifically adsorbed Fe^{3+} ions (^{3}) hinder Fe^{2+} ions from approaching the electrode surface, which increases the overvoltage.

The addition of Fe^{2+} to a sulfuric acid solution showed that, in this solution on passive iron at a potential of 1.3–1.4 V, ferrous iron is oxidized just as little as in perchloric acid. This shows that ClO_4^- ions do not accelerate the oxidation of Fe^{2+} on passive iron. Our experiments showed that the rate of formation of Fe^{3+} in perchloric acid during anodic activation of passive iron does not increase.

By analogy with platinum (6), it may be assumed that, on the free surface of iron, the reaction $Fe^{2+} \to Fe^{3+}$ should occur at the standard potential (equal to

Fig. 3

Figure 3: Fig. 3

0.77 V) at a rate of the order of 10^{-3} A/cm^2, and at a potential of 1.3 V the rate should be higher by several orders of magnitude. However, experiment shows that the current density of anodic oxidation of Fe^{2+} on anodically activated iron is only 10^{-2} A/cm^2. Hence it must be concluded that ClO_4^- ions are either capable of strongly inhibiting the reaction $Fe^{2+} \rightarrow Fe^{3+}$, or, what is more probable, they practically do not displace oxygen from the surface, but only rearrange it, and the anodic oxidation of Fe^{2+} proceeds on a small part of the surface.

Fig. 3. Change in the Fe content in a $1N$ $HClO_4$ solution as a function of the amount of electricity passed:
1 –Fe^{2+} of the anodically activated electrode,
2 –Fe^{3+} of the anodically activated electrode,
3 –Fe^{2+} on a passive electrode at potential $\varphi = 1.3$ V in the presence of added $Fe(ClO_4)_2$

The formation of pittings, considered a characteristic sign of metal dissolution during anodic activation (7, 8), was observed by us only on electrodes made of rolled Fe. Usually the pittings were distributed irregularly over the electrode surface. With alternate passivation and anodic activation of such electrodes, the formation of new pittings was, as a rule, not observed, while the already existing ones continued to grow. In the present work, however, we used electrodes made mainly from wire; on these, no pitting formation was observed in an acid medium, and the surface of the wire was etched uniformly. This can probably be explained by the fact that, when the wire is drawn through dies, its surface is smoothed and work-hardened, which brings about more uniform dissolution.

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Note: Figure translations are in progress. See original paper for figures.