# THE MECHANISM OF THE ANODIC ACTIVATION OF IRON

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We have shown earlier [1] that passive iron anodically polarized in perchloric acid will become activated as the result of $ClO_4^-$ ion adsorption. This process is reversible. Activation does not occur in sulfuric acid, but the rate of increase of the degree of passivation diminishes when a certain definite anodic potential is reached. Activation is accompanied by a sharp increase in the current at the point corresponding to the activation potential on the potentiostatic polarization curve and by an increase in the time rate of change of the polarization current on the chronoamperometric curve.

We have attempted to explain the mechanism of dissolution of iron in anodic activation by determining the effect of the solution composition on the activation and the valence of the iron which is thrown into solution in anodic polarization of the active and the passive metal. The activation potential for the polarization of iron in acidified solutions of sodium perchlorate diminishes linearly with an increase in the logarithm of the perchlorate ion concentration (Fig. 1). This fact is quite consistent with our own theory of the adsorption mechanism of anodic activation. In fact, we have assumed that activation sets in when the surface concentration of perchloric acid reaches a certain definite value, $\Gamma_{act}$. If ion adsorption under these conditions follows a logarithmic isotherm (moderate coverage for a nonuniform surface ) and the surface concentration of anions is proportional to the potential drop, $\varphi_a$, in the double layer (that is, the double layer functions as a condenser) at fixed anion concentration, $C_i$, in solution, it is possible to write the following theoretical equation

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

in which $\Gamma_i$ is the surface concentration of anions and a and b are positive constants.

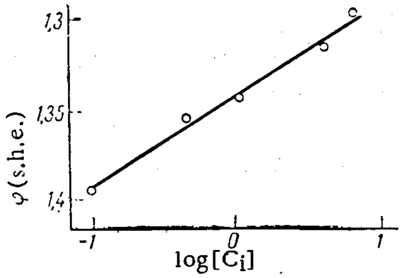

Fig. 1. Relation between the potential for anodic activation and the $ClO_4^-$ ion concentration at $[H^+] = 0.1$ N.

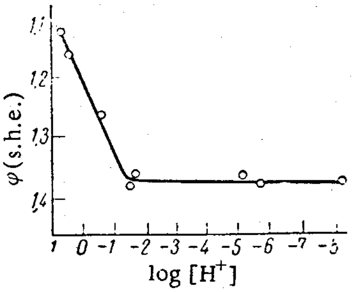

Fig. 2. Relation between the potential for anodic activation and the $H^+$ ion concentration at $[ClO_4^-] = 4.2$ N.

The experimentally observed relation $-a\varphi_{act} = b \log C + \text{const}_2$ (where $\varphi_{act}$ is the value of $\varphi$ when $\Gamma = \Gamma_{act}$) follows from this equation when the conditions are such that $\Gamma_i$ is equal to the constant $\Gamma_{act}$ and $\varphi_a$ differs from the electrode potential by a fixed amount (Figs. 1).

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

$$Fe_2O_3 + 6H^+ + 6ClO_4^- = 3H_2O + [2Fe - (ClO_4)_3]_{ads},$$

and therefore proceeds in a single elementary act involving acid dissolution of the oxide. Such displacement of the oxygen atoms by $ClO_4^-$ ions with increasing potential is possible because the polarizability of the ions is higher than that of the atoms.*

On the other hand, we have shown that $\varphi_{act}$ at fixed $ClO_4^-$ ion concentration is independent of the pH in solutions which are not too strongly acidic (Fig. 2). Thus, the reversible adsorption of $ClO_4^-$ ions in weakly acidic solutions is independent of the dissolution of the iron oxide in the acid. Only in strongly acidic solutions with $H^+$ ion concentrations ranging from 1 to 4.2 V is there a displacement of $\varphi_{act}$ in the negative direction with an increase in the concentration of the $H^+$ ions, a fact which is consistent with the theory of the passivating action of the oxide.

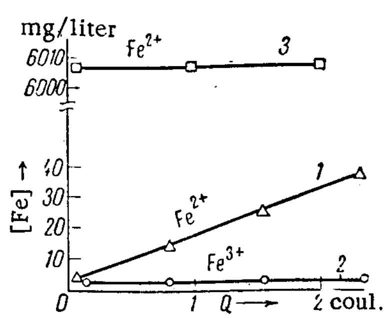

Fig. 3. Variation of the Fe content of a 1 N $HClO_4$ solution and its relation to the amount of current transmitted: 1) $Fe^{2+}$ from an anodically activated electrode; 2) $Fe^{3+}$ from an anodically activated electrode; 3) $Fe^{2+}$ on a passive electrode at a potential, $\varphi$, of 1.3 v, in the presence of added $Fe(ClO_4)_2$.

The valence of the iron thrown into solution in polarization was determined colorimetrically. The relation between the $Fe^{2+}$ and $Fe^{3+}$ ion concentrations in a 1 N solution of perchloric acid, and the quantity of electricity passed through the solution is shown in Fig. 3. It is seen from this figure that more than 99% of the current involved in the dissolution of anodically activated iron in perchloric acid is expended in the formation of $Fe^{2+}$ and less than 1% consumed in the formation of $Fe^{3+}$. The $Fe \rightarrow Fe^{2+}$ reaction proceeds rapidly after anodic activation, the limiting rate being clearly related in a complex fashion to the $Fe^{2+}$ ion diffusion from the electrode. Thus, the dissolution of active iron in 1 N $HClO_4$ at a potential, $\varphi$, of 0.0 V and dissolution after anodic activation at a potential of 1.5 V both proceed with maximum velocity of ~1 amp/cm$^2$. Reducing the $ClO_4^-$ ion concentration also brings about a reduction in the maximum current.

Essentially only trivalent iron is obtained from the passive metal in perchloric acid, the situation in this respect being similar to that met in sulfuric acid where passivation does not occur at all [5]. In order to determine the extent to which the various stages of the oxidation of passive iron are independent of one another, ferrous perchlorate ($Fe(ClO_4)_2$) was added to a 1 N solution of perchloric acid to a concentration of 0.1 N, thereby increasing the concentration of this compound in the neighborhood of the passive iron electrode by a factor of 1000. Experiment showed that (Fig. 3, 3) there was almost no oxidation of the passive iron through the reaction $Fe^{2+} \rightarrow Fe^{3+}$ at a potential near 1.3 v [3], although the metal was oxidized to the trivalent condition rather than the divalent, just as had been the case prior to the addition of $Fe^{2+}$ to the solution.

This situation could be explained either by assuming that oxidation of the passive iron of the electrode (or an intermediate univalent surface compound of iron) to the trivalent state takes place in a single step which bypasses the free divalent state, or that oxidation proceeds in the solid phase [4] and without that considerable overvoltage which is responsible for the slowness of the reaction in solution. It is possible that the preferential adsorption of the $Fe^{3+}$ ions [3] prevents the approach of the $Fe^{2+}$ ions to the electrode surface and thereby increases the overvoltage.

Experiments in which $Fe^{2+}$ was added to sulfuric acid showed that there was just as little oxidation of the passive iron to the divalent state in this solution at potentials in the 1.3-1.4 V interval as in sulfuric acid itself. This indicates that the $ClO_4^-$ ions do not promote the oxidation of $Fe^{2+}$ on passive iron. Our work shows that anodic activation of passive iron does not increase the rate of formation of $Fe^{3+}$ in perchloric acid.

Reasoning in analogy with the case of platinum [6], it could be assumed that the rate of the $Fe^{2+} \rightarrow Fe^{3+}$ reaction on a free iron surface would be of the order of $10^{-3}$ amp/cm$^2$ at the standard potential of 0.77 V, and several orders higher still at a potential of 1.3 v. Experiment shows, however, that the current strength for oxidation of $Fe^{2+}$ on an anodically activated iron electrode is only $10^{-2}$ amp/cm$^2$. It must therefore be concluded either that the $ClO_4^-$ ions strongly retard the $Fe^{2+} \rightarrow Fe^{3+}$ reaction or that these ions regroup the oxygen on the surface rather than displacing it, so that the $Fe^{2+}$ oxidation proceeds on only a small portion of the surface. This last is the more probable.

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* An exact comparison of the polarizabilities of the $ClO_4^-$ ion and the oxygen atom in solution is made difficult by the lack of data on the effect of cations and water molecules on the oxygen polarizability. A crude comparison of the polarizabilities of $ClO_4^-$ ions in solution and of oxygen atoms in the gaseous phase can be had through refraction measurements [2],and suggests that the polarization of the $ClO_4^-$ ion is considerably greater than that of the oxygen atom.

The formation of pits, considered to be an indication of the dissolution of metal in anodic activation [7, 8], was observed only on those electrodes which had been prepared from rolled Fe. The pits were generally scattered at random over the electrode surface. As a rule, new pits were not formed in alternate passivation and anodic activation of such electrodes, but the pits already present continued to grow. The electrodes used in this work were prepared for the most part from wire; pitting was not observed on these, the surface of the wire dissolving uniformly. It is possible that this is due to the fact that the surface was smoothed and cold-hardened as the wire passed through the die.

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**All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.**