KINETICS OF ANODIC SOLUTION OF IRON IN SULFURIC ACID SOLUTIONS IN THE PRESENCE OF HYDROGEN PEROXIDE

F. M. Mikheeva, G. M. Florianovich, and Ya. M. Kolotyrkin

UDC 620.193.2

Previously [1], on the basis of indirect data we inferred that addition of sufficient amounts of hydrogen peroxide to 1 N sulfuric acid at 90°C retards anodic solution of iron. We failed to obtain direct data on the retarding influence of H_2O_2 on the anodic reaction, because under these conditions hydrogen peroxide simultaneously accelerated solution by a chemical mechanism, as a result of which the overall rate of solution over a wide range of potentials was independent of the potential and greatly exceeded the rate of the electrochemical process. It was also impossible to estimate the rate of the electrochemical reaction from the anodic current density, because it was masked by the cathodic current of H_2O_2 reduction.

In [1] we also established that at pH ≤ 2, chemical solution of iron is not accelerated by hydrogen peroxide. For this reason, to ascertain the laws of the influence of hydrogen peroxide on the rate of electrochemical solution of iron, in this investigation the measurements were performed in 0.01 N sulfuric acid. At various potentials more negative than the passivation potential of iron in sulfuric acid without additives we determined the rate of solution of iron at 90° in solutions containing different amounts of H_2O_2. The procedure was described in [1]. The rate of solution was determined analytically using radiometric [2] and atomic-adsorption [3] methods.

It will be seen from Fig. 1 that under the influence of hydrogen peroxide in concentrations of $5 \cdot 10^{-2}$ M or above, active electrochemical solution of iron in 0.01 N H_2SO_4 is retarded; this is expressed in a shift of the Tafel straight lines toward the positive side, the shift being greater the higher the H_2O_2 concentration. With a tenfold increase in the latter, at constant potential the rate of electrochemical solution is reduced by more than two orders of magnitude. This marked retardation may be due to adsorption of H_2O_2 molecules or the intermediate products of its reduction on the most active sectors of the surface. The theoretical possibility of such adsorption has been shown, in particular, in [4].

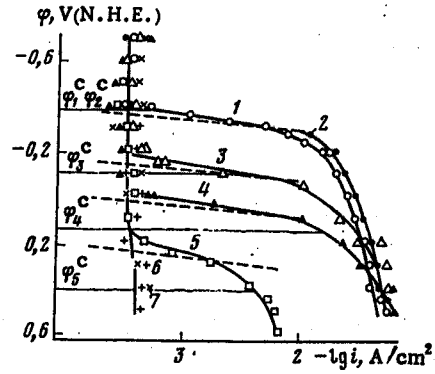

Fig. 1. Potential of overall rates of solution of iron, determined analytically, in a 10^{-2} M sulfuric acid solution with additions of hydrogen peroxide in the following concentrations (M): 1) 0; 2) $5 \cdot 10^{-3}$; 3) $5 \cdot 10^{-2}$; 4) $7.8 \cdot 10^{-2}$; 5) $1.0 \cdot 10^{-1}$; 6) $9.0 \cdot 10^{-1}$; 7) 6.56. The dashed lines are the same curves for electrochemical solution of iron; φ^c, corrosion potential.

L. Ya. Karpov Scientific-Research Physicochemical Institute. Translated from Zashchita Metallov, Vol. 15, No. 4, pp. 437-440, July-August, 1979. Original article submitted July 23, 1978.

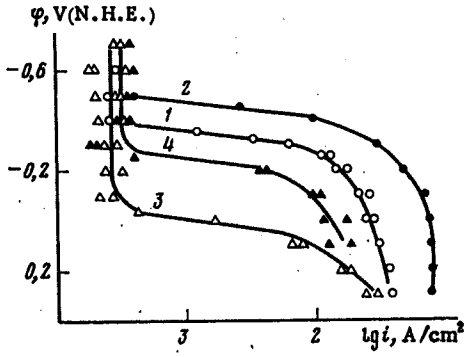

Fig. 2. Analytically determined rate of solution of iron vs potential in solutions: 1) 10^{-2} N H_2SO_4; 2) 10^{-2} N H_2SO_4 + $9 \cdot 10^{-2}$ N Na_2SO_4; 3) 10^{-2} N H_2SO_4 + $8.0 \cdot 10^{-2}$ M H_2O_2; 4) 10^{-2} N H_2SO_4 + $8.0 \cdot 10^{-2}$ M H_2O_2 + $9 \cdot 10^{-2}$ N Na_2SO_4.

The influence of potential and solution composition on the solution kinetics of iron in solutions with constant hydrogen peroxide content shows that the solution mechanism is similar to that observed in sulfate solutions without an oxidant. Thus, after a correction for solution by a chemical mechanism has been made (dashed lines in Fig. 1), when hydrogen peroxide is added the slope of the anodic Tafel straight lines remains practically the same (45 ± 5 mM) as for pure sulfate solutions [5].

Furthermore, the rate of electrochemical solution of iron in the presence of hydrogen peroxide at constant pH increases with the sulfate ion concentration in the solution (curves 3 and 4, Fig. 2). Admittedly, the order of the reaction of solution of iron with respect to sulfate ions in the presence of H_2O_2 ions is appreciably higher than in pure sulfuric acid solutions, in which, according to previous measurements [6, 7] and repeat measurements at 90°C (curves 1 and 2 in Fig. 2), it is equal to unity. This is possibly due to partial desorption of the oxidant from the metal surface as a result of competing adsorption of sulfate.

Finally, the fact that the laws of solution of iron in sulfuric acid with and without hydrogen peroxide are the same is manifested also in the dependence of the process rate on the solution acidity. It is known that in sulfuric acid media the electrochemical solution rate increases with the solution pH by a first-order law [5]. At constant H_2O_2 concentration, for the pH range from 1.15 to 2.2.* The magnitude of the reaction of OH^- ions is equal to 1.2.

Our results agree closely with the ideas developed by one of the authors [8, 9]. According to these, adsorption of the solution components on the metal surface retards its solution if the strength of the bond between the metal and adsorbate is much higher than that between the particles being adsorbed and the solution.

It can be expected that such adsorption will be observed primarily on the most active centers of the metal surface and in a particular case may retard the process, all the signs of solution of the metal in the active state being retained. Like the results in [10], the above data can be regarded as experimental confirmation of the ideas developed in [8, 9]. From these data it follows that with passivating adsorption of certain added components on the metal, solution of the latter may continue by the same mechanism by which the metal dissolved in the pure initial solution. In this connection, however, solution does not take place over the whole surface but only on centers of relatively low activity not occupied by adsorbed components acting as retarders of the process.

These laws of the influence of hydrogen peroxide on the solution kinetics of iron differ from those established for chromium [11]. In the latter case, addition of hydrogen peroxide to a sulfuric acid solution shifts the metal passivation potential toward the negative side. This difference in the behavior of iron and chromium is readily understandable if we take account of the different oxygen affinities of these metals.

*It is difficult to obtain data for a wider pH range, because at pH ≤ 1 iron dissolves predominantly by a chemical mechanism [1], and at pH ≥ 2.5, in the presence of H_2O_2, a film of sparingly soluble products is formed on the electrode during cathodic polarization.

In the case of iron, which is less inclined to react with oxygen, according to the foregoing, the oxygen of the hydrogen peroxide molecules blocks only part of the surface atoms of the metal. It seems that there is attained the potential at which the strength of the bond between the metal and oxygen is sufficiently high for such blocking to lead to retardation of solution on part of the surface. The kinetics of transfer of the atoms of the metal not covered by oxidant to the solution remain unchanged. As the H_2O_2 concentration in the solution increases, new centers are included in the process of passivation adsorption of oxygen, with a resultant regular increase in the degree of surface coverage. There is a corresponding decrease in the proportion of atoms dissolving according to the laws of the kinetics of active solution of iron.

A different picture is observed in the case of chromium. At its contact with the H_2O_2-containing solution, owing to their high affinity for oxygen practically all the metal atoms are blocked by the oxygen of the oxidant. It is only when we observe attainment of a potential ensuring a bond strength sufficient for a retarding effect to be manifested by the adsorbed oxygen that active electrochemical solution virtually ceases. Chromium begins to dissolve by the laws typical of solution of metals in the passive state.

LITERATURE CITED

1. F. M. Mikheeva, G. M. Florianovich, and V. V. Mikhalitsyn, Zashch. Met., 12, 369 (1976).
2. M. A. Dembrovskii and G. M. Florianovich, Zashch. Met., 1, 115 (1965).
3. W. Slavin, Atomic Absorption Spectroscopy [Russian translation], Khimiya, Leningrad (1972).
4. V. M. Berenblit, V. A. Gus'kov, and V. A. Abramov, in: Passivity and Corrosion of Metals [in Russian], Khimiya, Leningrad (1971), p. 105.
5. G. M. Florianovich, L. A. Sokolova, and Ya. M. Kolotyrkin, Elektrokhimiya, 3, 1027 (1967).
6. G. M. Florianovich, L. A. Sokolova, and Ya. M. Kolotyrkin, Elektrokhimiya, 3, 1359 (1967).
7. G. M. Florianovich, L. A. Sokolova, and F. M. Mikheeva, Abstracts of Reports to the All-Union Electrochemistry Conferences [in Russian], Tbilisi (1969), p. 671.
8. Ya. M. Kolotyrkin, in: Corrosion of Chemical Apparatus [in Russian], MIKhM, Moscow (1975), p. 5.
9. Ya. M. Kolotyrkin, ZhVKhO im. Mendeleeva, 20, 59 (1975).
10. V. V. Gorodetskii, Ya. M. Kolotyrkin, A. P. Bukin, and V. V. Losev, Dokl. Akad. Nauk SSSR, 225, No. 4, 858 (1975).
11. V. A. Goryachkin, G. M. Florianovich, and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 218, 604 (1974).