ROLE OF SALT DEPOSIT FORMATION IN THE ACTIVE DISSOLUTION OF IRON IN PHOSPHATE SOLUTIONS

A. N. Katrevich, G. M. Florianovich, and Ya. M. Kolotyrkin

UDC 620.193.01

The rate of dissolution of active iron electrodes in phosphate solutions at pH > 4 is found to depend simultaneously on the potential and the stirring conditions. This effect is explained by assuming that the electrode is partially coated during dissolution with a sparingly soluble salt, viz. iron phosphate. The grounds for this assumption are given and the mechanism of salt formation is considered.

When iron dissolves in neutral phosphate solutions, it is possible for sparingly soluble iron phosphate to form on its surface. This salt may be formed either at the stage of electrochemical oxidation of the iron or by the so-called volumetric mechanism (on account of the solubility product of the phosphate being reached in the part of the solution next to the electrode).

According to [1], the formation of a phosphate film on iron by an electrochemical mechanism takes place at potentials corresponding to the so-called primary passivation and leads to a retardation of dissolution. It was thought possible in [1] that the phosphate could also be formed by the volumetric mechanism in this potential region, but it was supposed that the phosphate deposited in this case does not have protective properties. The question of salt formation on an active iron electrode was not considered in [1].

We have examined the possibility and mechanism of the formation of phosphate films on iron at potentials more negative than the region of primary phosphate passivation, where iron electrodes are generally regarded as active, and also its role in the dissolution of the metal.

The dependence of the rate of dissolution of a rotating iron disk on the potential and the stirring conditions was determined by polarization measurements (using a P-5827 potentiostat) for solutions of different composition, primarily of different acidity. The data obtained were compared with the results of a photomicrographic investigation of the surface of a stationary electrode using an MBI-6 microscope and a special cell allowing the electrode to be observed and photographed in a deaerated solution through the wall of the cell.

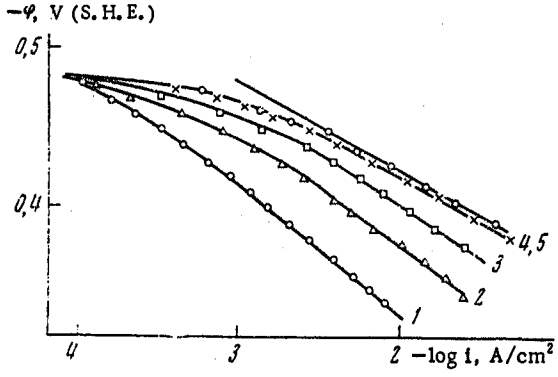

Fig. 1. Anodic polarization curves in 0.33 M phosphate solution at pH 5.2 at electrode rotation rates of: 1) 0; 2) 330; 3) 1460; 4) 2780; 5) 5000 rpm.

L. Ya. Karpov Physical Chemistry Scientific Research Institute. Translated from Zashchita Metallov, Vol. 10, No. 3, pp. 239-244, May-June, 1974. Original article submitted August 4, 1972.

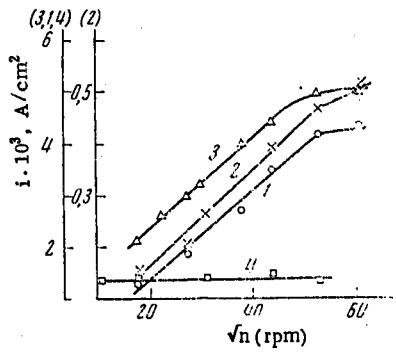

Fig. 2

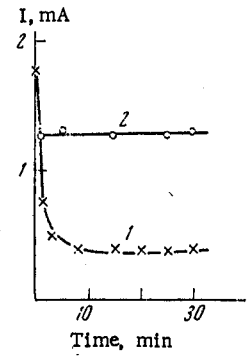

Fig. 3

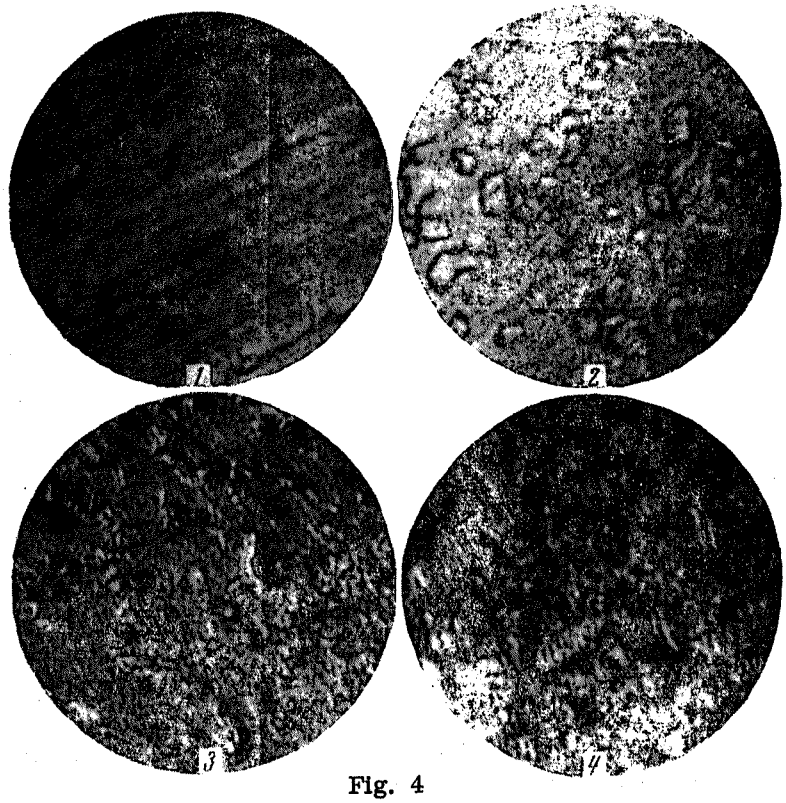

Fig. 4

Fig. 2. Dependence of the anodic current at constant potential on the square root of the rotation rate of the disk: 1) 0.33 M, pH = 5.2, φ = −0.44 V; 2) 0.033 M, pH 5.3, φ = −0.44 V; 3) 0.33 M, pH 4.5, φ = −0.41 V; 4) 1 M, pH 1.7, φ = −0.3 V.

Fig. 3. Variation of current with time at φ = −0.43 V in a 0.165 M phosphate solution, pH 5.9, on a stationary electrode (1) and an electrode rotating at a rate of 2780 rpm (2).

Fig. 4. Appearance of the electrode surface after polarization at α = −0.43 V for: 1) 0; 2) 5; 3) 15; 4) 30 min.

The steady-state polarization curves were obtained at between −0.48 and −0.34 V (S. H. E.), the potential being varied by 5 mV every 3 min. The electrodes were made of vacuum-smelted iron containing 0.005% C, 0.04% Si and 0.002% S. The working surface of the electrode was 0.2 cm^2, and the rate of rotation was varied from 300 to 5000 rpm. Before the experiment, the electrode was cleaned with fine emery paper, washed with doubly distilled water, alcohol and then doubly distilled water again, and transferred to a cell containing a solution deaerated by flushing with argon. The phosphate solutions were prepared by mixing equimolar solutions of H_3PO_4 and KH_2PO_4 (pH 0.75-4.5) or of KH_2PO_4 and Na_2HPO_4 (pH 4.5-7.0). The total phosphate concentration was between 0.01 and 4 M.

The steady-state curves of the dissolution current (i) of the iron disk versus the potential in a 0.33 M solution with a pH of 5.2 (Fig. 1) are observed to have a Tafel section, the position of which depends on the number of revolutions n of the disk. When n is increased from 0 to 2700 rpm, the slope of the Tafel lines decreases somewhat (from 70-80 to 60 mV) and the lines are shifted to more negative potentials. At constant potential, i increases linearly with $\sqrt{n}$ (Fig. 2, curve 1). Above some limiting rotation rate ($n_{lim} \approx 2700$ rpm), the rate of dissolution ceases to depend on n.

This type of i-n dependence is retained at other phosphate concentrations in solution (Fig. 2, curve 2), and also when the pH of the solution varies between 4.0 and 7.0.

In more acidic solutions (pH between 0.75 and 4.00), the dissolution rate is independent of the rate of rotation of the electrode (Fig. 2, curve 4).

Visual observation showed that after polarization in solutions with pH > 4.0 and $n < n_{lim}$, the surface of the electrode is covered with a finely crystalline deposit, the rate of formation of which decreases with increasing n. No deposits are formed at pH < 4.0. According to x-ray analysis data, the composition of a deposit taken from the electrode surface after polarization for 5 h in a stirred 0.33 M phosphate solution with a pH of 5.2 at a potential of −0.40 V, corresponds to $Fe_3(PO_4)_2 \cdot 8H_2O$.

The difference in the behavior of the iron electrode in the two different pH ranges also shows up in the character of the current versus time curves obtained under potentiostatic conditions. In acidic solutions (pH < 4.0), the rate of dissolution at constant potential is constant with time, irrespective of the stirring conditions. At pH > 4.0, the character of the variation in the anodic current with time is determined by the rate of rotation of the disk. At $n < n_{lim}$, the current first decreases with time and then reaches a steady value (Fig. 3, curve 1). The time required to reach the constant current does not exceed 5-10 min for any of the conditions investigated. At $n > n_{lim}$, the current is constant with time (Fig. 3, curve 2).

The kinetic features of the process cannot be explained by the retarded diffusion of phosphate to the electrode on the basis of the simultaneous dependence of the rate of iron dissolution (at pH > 4.0) on the potential and the stirring conditions. The increase in i with increasing n at pH > 4 could also be connected with a change in the pH of the layer of solution next to the electrode during dissolution. In fact, the solution would generally be expected to become acidified in the vicinity of the iron anode (on account of hydrolysis of the iron ions being formed), which could lead to the retardation of dissolution since the dissolution of active iron is accelerated with increasing pH in many media [2]. As we have shown, however, the rate of anodic iron dissolution in phosphate solutions at pH > 4 is practically independent of the pH, which means that the dependence of i on n cannot be explained by a change in pH in the vicinity of the electrode.

The same conclusion also follows from the results which we obtained by measuring the pH of the layer next to the electrode. Using a glass microelectrode, prepared by the method of [3], we measured the pH in the vicinity of the electrode. By determining the pH at different distances from the electrode and with different polarization circuit breaking times, it was established that the measured pH could be identified with the pH of the layer next to the electrode (pH_S) if the microelectrode was brought up close to the electrode and the circuit broken for 3-5 sec.

Acidification of the layer next to the electrode was observed only when the pH was >3.0 and the current density was higher than some value which decreases with increasing pH of the solution. * This effect was relatively slight† and, as shown by calculation, cannot explain the shift in the polarization curves with stirring, even if the ionization of iron were a first order reaction with respect to OH^- ions.

The dependence of the dissolution rate simultaneously on the hydrodynamic conditions and on the potential can also be observed when the process proceeds with the participation of components of the solution under mixed kinetic conditions, as realized, for example, in the dissolution of titanium in fluoride solutions [4], or when the discharge-ionization of the metal takes place reversibly with retarded removal of the metal ions [5]. However, the behavior that follows from the theory of mixed kinetics [6] and from the theory of reversible

*A 10% decrease in pH from the initial value for pH values of 3.1, 4.5, and 5.0 occurred at currents of 4.60, 3.95, and 2.65 mA/cm^2 respectively.

†When i = 3.9 mA/cm^2, a pH_0 in the bulk of the solution of 4.5 corresponded to a pH_S of 4.05, and a pH_0 of 5.0 corresponded to a pH_S of 4.3.

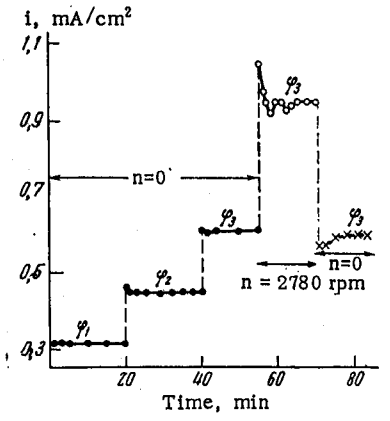

Fig. 5. Variation of current with time on a disk in a 0.085 M phosphate solution with a pH of 6.1.

reactions with retarded removal of reaction products, is not in accord with the experimental results. *

With certain provisos, the simultaneous dependence of the rate of dissolution on the potential and on the stirring conditions can be explained by assuming that these factors affect the degree of surface coverage of the metal by dissolution products, which, in turn, determines the rate of the process. This hypothesis is in good agreement with the parallelism observed in our experiments between the time variation of the anodic current at constant potential on the one hand, and the rate of deposit build-up on the electrode surface on the other. It was established that in sufficiently acidic solutions, the electrode is not coated with a deposit even in prolonged experiments (2 h). At pH > 4, the appearance of salt crystals on the electrode surface can be observed after only 5 min. The amount of deposit on the surface increases with the duration of the experiment (Fig. 4).

From a comparison of these results with the current versus time curve (Fig. 4), it follows that the moment at which a constant current is established does not coincide with the moment at which constant surface coverage of the electrode is reached. The deposit continues to be formed after the current has ceased to change. This result can be understood if it is assumed that the first layers of deposit connected directly to the electrode surface affect the current.

We can conclude from the observed stirring effect that the protective layer is formed by the volumetric mechanism. It is natural to assume that the deposit forms, in general, not on the whole surface, but at separate sites which are most favorable either for accelerated dissolution or for crystallization of the salt (i.e. for reaching supersaturation). In time, the deposit also forms on other sections of the surface. While this is happening, however, the deposit formed earlier may be completely dissolved. It is natural to suppose that under steady-state conditions, the rates of formation and dissolution of the salt layer will be equal and there will be some constant degree of coverage (shielding) of the electrode. The latter will increase as the potential is shifted in the positive direction and will decrease as the rate of rotation of the disk is increased (to practically zero in the limit, when $n > n_{lim}$). It is this that may determine the simultaneous dependence of the anodic iron-dissolution current on the potential and the stirring conditions. †

The reversibility of the observed dependences of i on φ and n is in complete accord with this scheme: the forward and reverse steady-state polarization curves coincide, and the anodic current at φ = const is determined only by the value of n, irrespective of what stirring conditions precede its establishment (Fig. 5). The experimental data for acidic solutions, in which the phosphate is soluble and stirring is not found to have any effect on the iron-dissolution current, are also in good agreement with this scheme. It is also confirmed by experiments with solutions saturated with iron phosphate. ‡ It is to be expected that a state of complete salt passivation will arise under these conditions and that the rate of iron dissolution will cease to

*In particular, the linear relations between $1/i_\varphi$ (i_φ is the current density at constant potential) and $1/\sqrt{n}$ and between i and φ required by the theory of mixed kinetics are not confirmed. It follows from the theory of reversible reactions that the dependence of the potential in the absence of current on log n should be linear, whereas experiment shows that this potential is independent of n. The slopes of the Tafel curves differ from the theoretical slope (29 mV for a two-electron ionization-discharge reaction).

†This possibility is proved theoretically in [9].

‡The saturated solutions were prepared by prolonged anodic dissolution of an iron electrode with a large surface area in a phosphate solution at pH = 5.2.

depend on the stirring conditions (as in the case of the dissolution of zinc in zincate-saturated alkaline solutions [7]). Experiment confirmed this supposition by showing the simultaneously strong retardation of dissolution when the solution was saturated.

The works known to us in which the possibility of metal dissolution being retarded by the deposition of sparingly soluble salts of the metals has been considered [8] have all been restricted to conclusions concerning the fact that this effect leads to the appearance of limiting currents (or current maxima) on the anodic polarization curves, and to considering the theory of this phenomenon. There is practically no information in the literature about the effect of salt formation on the process at potentials at which the limiting current has not yet been reached (or the current has still not started to drop). This investigation of the dissolution of iron in phosphate solutions shows that it is possible in principle for dissolution to be retarded by salt layers formed by the volumetric mechanism, in which the dependence of the steady-state dissolution rate on potential remains close to a Tafel dependence, i.e. when the electrode can be regarded as active.

LITERATURE CITED

1. Ya. M. Kolotyrkin, Yu. A. Popov, Yu. V. Alekseev, G. M. Florianovich, K. A. Mishenina, and G. M. Ostrovskii, Élektrokhimiya, 8, 3 (1972).
2. G. M. Florianovich, L. A. Sokolova, and Ya. M. Kolotyrkin, Élektrokhimiya, 3, 1027 (1967).
3. T. M. Ovchinnikova, Candidate's Dissertation, Leningrad (1962).
4. A. Caprani and J. Epelboin, C. R. Acad. Sci., C-269, No. 19, 1087 (1969).
5. V. V. Losev, A. I. Molodov, and V. V. Gorodetskii, Élektrokhimiya, 1, 572 (1965).
6. A. N. Frumkin and G. A. Tedoradze, Dokl. Akad. Nauk SSSR, 118, 530 (1958); Z. Elektrochem., 62, 251 (1958).
7. Z. Ya. Nikitina, Zh. Prikl. Khim., 36, 218 (1962); T. I. Popova, V. S. Bagotskii, and B. N. Kabanov, Zh. Fiz. Khim., 36, 1439 (1962).
8. E. Müller and K. Schwabe, Z. Elektrochem., 38, 407 (1932); 39, 414, 791 (1933); M. N. Hull, J. E. Ellison, and J. E. Toni, J. Electrochem. Soc., 117, 192 (1970); A. D. Davydov, V. D. Kashcheev, and B. N. Kabanov, Élektrokhimiya, 5, 221 (1969); M. Froment, M. Keddam, and P. Morrel, C. R. Acad. Sci., 253, 2529 (1961); M. Melendez and J. Brenet, Electrochim. Acta, 16, 61 (1971).
9. Ya. M. Kolotyrkin, Yu. A. Popov, A. A. Vasil'ev, G. M. Florianovich, and A. N. Katrevich, Élektrokhimiya, 9, 192 (1973).