ACTA PHYSICOCHIMICA U.R.S.S.

1946 Vol. XXI. No. 5

The Active Iron Electrode in Alkaline Solutions

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In a number of papers from the laboratory of Prof. Frumkin, in particular, in the investigations of Ershler there has recently been developed a method whereby a detailed study can be made of the structure of the surface layer of metallic electrodes and of the nature of the electrochemical processes taking place at the electrode surface.

The behaviour of the iron electrode in alkaline solutions has not been sufficiently studied. From the viewpoint of electrochemical theory the iron electrode is of special interest because it is typical of a whole group of metals with variable valency which, though easily passivated can yet, under certain conditions be active, *i. e.* can undergo sufficiently rapid phase transitions; the electrochemical behaviour of such metals is particularly complex.

An active iron electrode in alkaline solution can be obtained by pressing powdered iron reduced in an atmosphere of hydrogen. Such an electrode finds practical application in the Edison storage cell. Förster[1] and others studied the powdered iron electrode and advanced hypotheses concerning the nature of the electrochemical processes taking place on it, which we shall consider below.

Judging by the literature, no one has yet succeeded in obtaining a smooth iron electrode in alkaline solution at room temperature in the active state. Krassa[2] affirms that at room temperature even in comparatively concentrated alkaline solutions (20 %) smooth iron remains passive despite preliminary cathodic activation, and

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[1] **Förster**, Z. Elektrochem., **16**, 461 (1910); **Faust**, Z. Elektrochem., **13**, 161 (1907).

[2] **Krassa**, Z. Elektrochem., **15**, 490 (1909).

only the formation of a spongy layer on the surface, renders the electrode active.

The nature of the passivity of the iron group of metals has not been unambiguously explained as yet. Of the numerous theories proposed at different times, the most generally accepted is Faraday's theory according to which passivity is due to the formation of a protective surface film of the metal oxide or a similar compound.

The kinetics and mechanism of formation of oxide films on metals in contact with oxygen (for greater details see the paper by R. Burstein in this issue of Acta Phys. Chim.) have been studied sufficiently well. The crystalline structure of the films has also been proven and their thickness determined under various conditions.

A number of investigators, *e. g.* Müller[3], suggested that the protective action of oxide films is due to their electrical resistance. Kistiakowsky[4] justly pointed out that in the case of iron the resistance of the oxides is comparatively so small that it cannot explain passivity.

The mechanism of the anodic passivation of iron, free from air-formed oxides presents a considerably more complicated problem. The first question to be answered is: can passivity be due to the formation on the metal surface of an insulating layer of the primary product of the anodic process and to increased current density at the remaining uncovered points of the surface, which would raise the potential of the metal as a result of overvoltage of the anodic process, as was shown in the case of the passivation of lead in sulphuric acid[5], or is passivity due to an accessory process of oxidation of the metal surface, which takes place simultaneously with the primary anodic process, as Haber[6] suggested for the case of iron in alkaline solution and as was experimentally proved by Ershler[7] for platinum in hydrochloric acid. Ershler showed that when platinum is anodically dissolved in the presence of chlorine ions, passivity may be attributed to retardation of the ionization

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[3] W. Müller, Die Bedeckungstheorie der Passiwität der Metalle, Berlin, 1933.

[4] V. Kistiakowsky, Electrochemical Reactions and Electrode Potentials, Moscow, 1910 (diss.).

[5] B. Kabanov, C. R. Acad. Sci. URSS, **31**, 339 (1941).

[6] F. Haber u. G. Goldschmidt, Z. Elektrochem., **12**, 49 (1906).

[7] B. Ershler, J. Phys. Chem. (Russ.), **18**, 131 (1944); C. R. Acad. Sci. URSS, **37**, No. 7—8 (1942).

of the metal due to the chemisorption of oxygen on the platinum surface. This retarding action sets in upon the adsorption of extremely small quantities of oxygen, far too small even for the formation of a monomolecular layer. Passivity is probably due in this case to a change in the structure of the double electric layer upon adsorption of oxygen.

The aim of our investigation was to obtain a smooth iron electrode in the active state, and to study its behaviour and the mechanism of passivation. The present paper sets forth in the main the results of the first part of our work.

Experimental part

Method[8]

The investigation of a smooth electrode presents several advantages over that of a porous electrode due to the greater accessibility of the surface. However, work with a smooth iron electrode entails certain difficulties connected, firstly, with the easy passivation of iron, secondly, with depolarization phenomena and thirdly, with the high overvoltage and small capacity of a number of processes which take place on the iron electrode. Most of the work on smooth electrodes reported in the literature was carried out at high current densities so that depolarization could be ignored (*e. g.* Miley and Evans[9]; more details will be given in a paper on passive iron, to appear shortly). However, in work with high current densities the accuracy of investigation of thin films and slow processes is insufficient.

In our investigation we used the apparatus schematically depicted in Fig. 1. The construction of the polarization cell was based on an idea due to Ershler[10]: the electrode takes up almost the entire vessel so that the volume left for the solution is very small. In our experiment the volume of the solution was about 0.02 cm^3 with an electrode surface of 3.5 cm^2. Thus the ratio of the volume of the solution to the electrode surface was approximately the same as in

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[8] The students Derjaguina und Stetsenko participated in the early stages of this work.

[9] Miley and Evans, J. Chem. Soc., **1937,** 1295.

[10] B. Ershler, Acta Phys. Chim., **7**, 327 (1937); J. Phys. Chem.,(Russ.), **14**, 708 (1940).

the usual measurements on porous electrodes; in this manner depolarization phenomena can also be avoided on a smooth electrode at small current densities.

The electrode in the form of a rod about 5 mm in diameter and 20 mm long is placed between two ground glass joints *A* and *B* (Fig. 1). These joints, like all the others, were not greased so that the electric current would pass through them, and were well ground to prevent the solution from the upper vessel leaking through the cell to the lower vessel. As simple computations show, a flow of a hydrogen-saturated solution at a rate of 0.01 cm^3 per hour is sufficient to keep up an anodic polarization current of 10^{-7} A/cm^2.

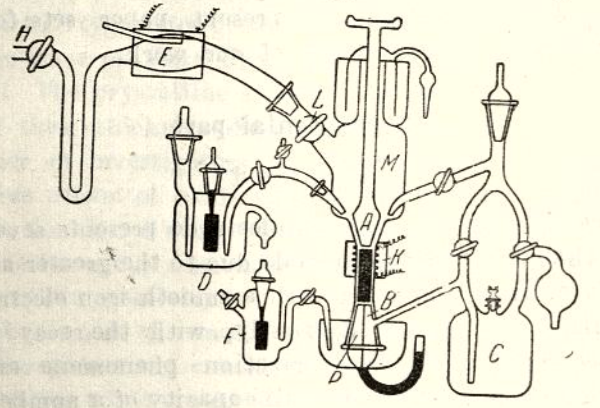

Fig. 1. Scheme of the apparatus.

The current enters the electrode through the platinum wire *P* sealed into the lower joint *B*. Polarization is effected through the lower joint by means of the auxiliary platinum electrode *F*.

The solution in which the measurements are carried out can be pre-saturated with hydrogen or nitrogen in the vessel *C* and then forced through the capillary into the measuring vessel. For this purpose the upper joint is slightly raised and the lower one turned so that the electrolyte can flow upwards along a scratch made on the upper part of the joint *B*.

The apparatus is connected by means of a ground glass joint with the quartz heater *E*, in which the surface of the electrode can be reduced in a current of hydrogen at 700—900°. After the heater has cooled off the stopcock *H* is closed, the heater is turned in the joint and the sample slides into the measuring vessel by way of the stopcock *L* with a wide bore without coming into contact with the air.

To remove the gas bubbles formed on the electrode during polarization the upper joint is raised and the electrode brought into motion by means of the electromagnet *K*.

A hydrogen electrode *D* in the same solution serves as reference electrode.

The sodium hydroxide solutions were prepared by the action of water (twice distilled) on sodium amalgam obtained by the electrolysis of pure alkali. The iron electrode was prepared in the following manner. A rod of spectroscopically pure Hilger iron (HS brand) was ground with crushed glass powder (fraction not sedimenting in water during 7 min); the iron was then boiled for 1 min in a 10 per cent sodium hydroxide solution to remove grease, was etched for 10 sec with 5 per cent sulphuric acid, quickly washed with water and dried on filter-paper. It was then heated at 700—900° in a current of electrolytic hydrogen purified as usual and dried by passing through a liquid air-trap.

Results of the experiments

1. Active and passive iron

The iron thus prepared was transferred without exposure to air to the polarization vessel which contained a 2 *N* NaOH solution saturated with hydrogen, and anodic polarization was immediately started at constant current density. The resulting polarization curves have the form given in Fig. 2: at a steady current density

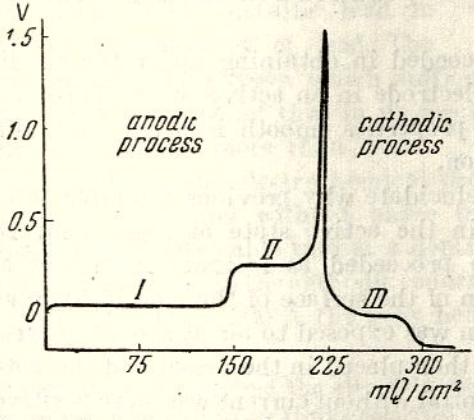

Fig. 2. Polarization curve of an active smooth iron electrode. *I* and *II*—anodic polarization, *III*—cathodic polarization.

of 2.4×10^{-5} A/cm^2 the potential rises making two long arrests at $+0.04$ V and $+0.27$ V as referred to the hydrogen electrode in the same solution and increases up to a maximum value of 1.6 V. In general form these curves are not different from the discharge curves of an electrode of pure iron powder in an alkaline solution obtained by Förster[11] and the polarization curves of porous iron obtained by Faust[1]. At 18° the length of the first arrest corresponds to 150 millicoulombs per cm^2 of apparent surface (according to R. Burstein, the true surface of smooth iron heat-treated in hydrogen is 2—3.5 times greater than the apparent surface). For a comparison of the capacity of the smooth and powder electrodes we utilize unpublished data obtained in our laboratory by S. Rosenzweig, who investigated electrodes prepared from spectroscopically pure powder iron[12]. According to these data upon the anodic discharge of powder iron in 5 *N* alkaline solution, the capacity corresponding to the first arrest of the potential equals 1.4×10^3 coulombs per g of iron powder. Burstein gives for the true surface of a powdered iron electrode prepared in the same manner 5×10^3 cm^2 per g of iron powder. Thus the capacity of the powder electrode per cm^2 equals 280 millicoulombs; in other words, the capacity of the smooth iron electrode prepared as described was of the same order of magnitude as that of the powdered iron electrode computed for the true surface[13].

We thus succeeded in obtaining under the conditions described a smooth iron electrode in an active state. This proves that by its electrochemical properties smooth iron does not differ in principle from porous iron.

In order to elucidate why previous attempts to obtain a smooth iron electrode in the active state at room temperature had been unsuccessful we proceeded as follows. After the above described careful reduction of the surface of the iron in hydrogen at high temperature the iron was exposed to air at room temperature for several minutes; it was then placed in the vessel and the potential was measured. The potential without current was more positive than that cor-

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[11] Förster, Elektrochemie wässriger Lösungen, Leipzig, 1923.

[12] Unpublished data.

[13] There might be a difference due to the different concentrations of alkali and different true current density in the experiments with the smooth and powdered electrodes.

responding to the first or second processes. The polarization curves show no cathodic or anodic arrests corresponding to the processes on an active electrode. The brief action of air thus causes complete passivation of iron.

During anodic polarization the potential of the passive electrode rises from 0.0 V to 0.5 V upon the passage of only 0.1 millicoulombs (Fig. 3)[14] whereas the same change in the potential of the active electrode is brought about by approximately 200 millicoulombs, *i. e.* by a quantity of electricity 2000 times as great.

Judging by the literature[15] upon short exposure of pure iron to the air a thin oxide film (thickness about 20—40 Å) forms on its surface. Hence such a thin oxide film is sufficient to make an iron electrode completely passive.

A thin film of oxides or adsorbed oxygen can hardly offer noticeable resistance to electric current. Passivity in this case cannot, therefore, be explained as, for example, the passivity of lead in sulphuric acid[5], by the insulating action of the lead sulphate film in the first stage of passivity. Neither can it be explained by the formation of a new quasi-metallic oxide which plays the role of a new metal completely covering the original surface like lead peroxide on metallic lead in the second stage of the passivity of lead. The smallness of the quantity of oxygen which suffices to make iron passive gives grounds for the belief that in its mechanism of passivity iron resembles platinum[7] more than lead.

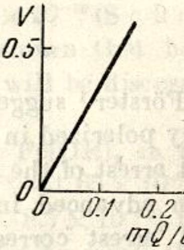

Fig. 3. Anodic polarization curve of an air-passivated smooth iron electrode.

Under certain conditions the electrochemical process on an iron electrode oxidized in air occurs without phase transitions. Such a process can proceed at a noticeable rate at a depth of one or more molecular layers of oxide. Thus, in the cathodic reduction of α—Fe_2O_3, obtained in the form of a layer 500 Å thick by heating iron in air

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[14] Before the capacity was measured the electrode was subjected to the following treatment. After exposure to air it was polarized anodically to 1.0 V then cathodically to 0.0 V. Such treatment did not essentially affect the quantity of oxygen on the electrode surface.

[15] Winterbottom, Disc. Trans. Electrochem. Soc., **76**, 303 (1939); Nature, **140**, 364 (1937); Gulbransen, Trans. Elektrochem. Soc., **81**, 327 (1942).

at 300°, the polarization curve is almost linear without any arrests from the potential 0.7 V up to 0.0 V with a capacity of 300—500 μF; this corresponds to the reduction of three layers of the Fe_2O_3 lattice to Fe_3O_4 or of one layer to FeO. A similar situation is observed upon the anodic oxidation of γ—Fe_2O_3.

In order to investigate the process on an active iron electrode in alkaline solutions we measured the cathodic and anodic potentials corresponding to the respective processes at different current densities.

The overvoltage of the two processes was found to be comparatively large. At high densities of the cathodic current the curves showed bends evidently related to concentration polarization with respect to iron-containing anions.

2. The first process

Förster[1] suggested that when a porous iron electrode is anodically polarized in alkaline solutions the only reaction product at the first arrest of the potential is $Fe(OH)_2$. Other hypotheses have also been advanced in the literature. Thus Faust[1] presumed that the first arrest corresponds to ionization of the hydrogen dissolved in the iron, but Förster proved this assumption to be false.

Extrapolation of the anodic and cathodic overvoltage curves to intersection in the direction of low current densities gives the value of the «mean potentials» whose magnitude does not differ noticeably from that of the equilibrium or steady potentials of the processes studied. Thus, for the first process we found a value of about —0.05 V and for the second of about +0.13 V (referred to the hydrogen electrode in the same solution).

According to the best measurements in the literature, the equilibrium potential of the system $Fe/Fe(OH)_2$ equals —0.046 V[16]. Since the equilibrium potential of iron is more negative than that of hydrogen these measurements actually give the value of the steady potential displaced in the positive direction with respect to the equilibrium value[17]. However, this shift of the experimentally

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[16] Rendall u. Frandsen, J. Am. Chem. Soc., **54**, 40, 47 (1932).

[17] This problem is more fully investigated in papers on powdered iron electrodes by Rosenzweig and by Levina and Platonova, to be published soon.

measured steady potential with respect to the equilibrium value is not very great, and for our purpose we can take the value of the equilibrium potential given in the literature as being approximately correct.

The fact that the values of our mean potential and the equilibrium potential coincide lends support to Förster's hypothesis that the first anodic process consists in the formation of $Fe(OH)_2$ from metallic iron.

To elucidate the mechanism of this process let us consider the data in the literature on the solubility of $Fe(OH)_2$.

The older computations of the solubility of $Fe(OH)_2$ were based mainly on the values of the solubility product determined from the electromotive force measurements. These values varied over a very wide range in the papers of different authors, from 7×10^{-13} (Schrager[18]) to 4.5×10^{-21} (Britton[19]). It can be shown that both these extreme values are undoubtedly wrong. This will be discussed in another paper.

The other values of the solubility product of $Fe(OH)_2$ in the literature lie within the narrower limits: $8.7 \times 10^{-14} - 1.65 \times 10^{-15}$. If one accepts even the largest of these values (*i. e.* 8.7×10^{-14}) the concentration of $Fe^{\cdot\cdot}$ in alkaline solution comes out so small that the $Fe^{\cdot\cdot}$ ion cannot be potential-determining and it should be concluded that the process $Fe \rightleftarrows Fe(OH)_2$ cannot take place in the solution but must proceed entirely in the solid phase. However, the stability of the transition potential indicates that the reaction takes place between two solid phases, while if one assumes a one-phase transition the great depth of the transformation in the metal could be explained only by making highly improbable special assumptions, for example, an exceedingly high surface mobility of $Fe(OH)_2$. Indeed, before becoming passive, active smooth iron is oxidized upon anodic polarization to a very great depth of the order 0.05 μ—while the oxidation product is transported to an even greater distance corresponding to the greater apparent molecular volume of the deposit of $Fe(OH)_2$ compared to Fe.

This contradiction is easily resolved if one recalls to mind that in alkaline solutions of even comparatively small concentrations

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[18] Schrager, Chem. News, **138**, 354 (1929).

[19] Britton, J. Chem. Soc., **127**, 2110 (1925).

divalent iron is present mainly in the form of anions. Indeed, as far back as 1929 Schrager showed by means of polarographic analysis that the solubility of $Fe(OH)_2$ in alkali is comparatively great (5×10^{-5} mol/l in 2 N solution) and increases in direct proportion to the concentration of the alkali. The latter fact shows that in alkaline solutions at least of concentrations 0.5—4 N iron is present mainly in the form of the univalent ions $HFeO_2'$:

$$\frac{[HFeO_2']}{[OH']} = 2.5 \times 10^{-5} \text{ mol/l}.$$

Such a solubility is without doubt great enough for the $HFeO_2'$ ion in solution to be the intermediate state of the process $Fe \rightleftarrows Fe(OH)_2$. It may be recalled that in the case of a lead electrode in sulphuric acid it was proven quantitatively that the intermediate stage of the electrode process is the dissolution and deposition of lead sulphate, the solubility of which is 3.5×10^{-6} mol/l.

A computation of the regime of the diffusion of $HFeO_2'$ which is formed in the anodic process shows that in 2 N alkali at a current density, *e. g.* of 3×10^{-5} A/cm² already after one second an almost tenfold supersaturation of the solution with respect to $HFeO_2'$ sets in at the surface of the iron electrode bringing to the deposition of $Fe(OH)_2$. As can easily be computed, at this moment supersaturation can also set in at a considerable distance from the electrode, *e. g.* fivefold supersaturation at a distance of 0.3 μ. At a current density of 3×10^{-6} A/cm² it takes about 100 sec for a tenfold supersaturation to set in at the surface. The shift of the potential corresponding to the passage of a definite amount of electricity at the beginning of the anodic polarization curve, as shown by our measurements, is considerably greater than it could be expected if the potential of the electrode were an equilibrium potential and the shift would be due to supersaturation of the solution by $HFeO_2'$ ions. Hence the potential of anodically polarized iron is not the equilibrium potential with respect to the $HFeO_2'$ ions, but is determined by the overvoltage, *viz.*, by the kinetics of the ionization of iron: $Fe \rightarrow HFeO_2'$.

The first anodic process on an active iron electrode $Fe \rightarrow Fe(OH)_2$ terminates, as is known, due to passivation after the passage of a certain amount of electricity (Fig. 2). $Fe(OH)_2$ like other similar strongly hydrated oxides, has a large specific resistance. However, the linearity in the semi-logarithmic scale of the anodic polarization (overvoltage) curves of the process $Fe \rightarrow Fe(OH)_2$, and especially of the second process $Fe(OH)_2 \rightarrow Fe_2O_3\ n\ H_2O$ shows that no noticeable electrical resistance arises on the electrode surface as a result of passivation [20]. Hence $Fe(OH)_2$ separates out in the form of a porous deposit and does not form a continuous electrically insulating layer on the surface of the passivated electrode. Neither can $Fe(OH)_2$ mechanically separate the passive electrode from the solution, as does Fe_2O_3 or Fe_3O_4, since it does not possess the high electrical conductivity of the latter, and mechanical insulation would entail electrical insulation.

It might be thought that the potential shift in passivation is due to increase in the true current density resulting from a gradual covering of the iron surface by a ferrous hydroxide deposit, as takes place in the passivation of lead in sulphuric acid solution. However, the variety of forms of the polarization curves of the process $Fe \rightarrow Fe(OH)_2$ depending on the degree of activity of the electrode makes this assumption highly improbable: one would have to assume that the surface of an active electrode begins to be covered only at the end of the arrest of the potential, whereas with a semi-active electrode almost the entire surface becomes covered at the beginning of the arrest and the total cross-section of the pores then remains constant for some time. In addition, such an assumption makes it difficult to explain the form of that section of the curve which corresponds to the second process.

Neither can anodic passivation be attributed to some form of aging of the ferrous hydroxide (*e. g.* to partial loss of water). Special experiments have shown that an interruption of the current for two days did not hinder continuation of the transition $Fe(OH)_2 \rightarrow Fe_2O_3$ n H_2O and the reverse process.

In view of all this we are inclined to accept Haber's hypothesis[6] (formulated without sufficient experimental grounds) that the anodic passivation of iron in alkali results from the accumulation of a by-product of the anodic process. Several considerations induce us to believe that this by-product is an absorption oxide which does not form a separate phase. The results of experimental verification

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[20] This conclusion can also be confirmed by measuring the capacity of the electrode with alternating current of various frequencies.

and a detailed disoussion of this hypothesis will be communicated in another papar.

As was experimentally shown in our laboratory by Rosenzweig[21] the irreversibility of the electrode system Fe/Fe(OH)$_2$ can be attributed as well to retardation of the cathodic, as of the anodic process. The investigation was carried out on a pure iron powder electrode. The electrode was discharged to the first arrest of the polarization curve and then cathodically reduced at constant current density. The current used in reducing the Fe(OH)$_2$ was controlled by measuring the rate of the accompanying evolution of hydrogen. It appeared that approximately one-half the total amount of ferrous hydroxide is reduced easily (*e. g.* at -0.16 V by a current density of 10^{-5} A/cm^2 true surface); whereas the second part is reduced only at a potential approximately 0.1 V more negative than the first half. Finally, a certain amount of ferrous hydroxide cannot be reduced either at this potential nor at a potential 0.1 V more negative.

This difficulty of reducing Fe(OH)$_2$ to Fe is evidently connected with some subtile changes in the structure or composition of the metal surface.

A process entirely similar to the anodic polarization of active iron takes place when dissolved oxygen reacts with active iron in the absence of a current.

A 2 *n* NaOH solution saturated with air was passed through the reservoir *C* (Fig. 1) and came in contact with an electrode which had been reduced in an atmosphere of hydrogen and transferred to the measuring vessel without exposure to air. For some time (depending on the rate of flow of the solution) the potential of the electrode remained within the limits of the first anodic arrest of the polarization curve, then passed over into the region of the second arrest when the electrode became rapidly covered with a dark red layer of ferric hydroxide (the colourless Fe(OH)$_2$ which covered the electrode prior to this was faintly visible). If the electrode after reduction with hydrogen was exposed for a few minutes to the action of atmospheric oxygen, the dissolved oxygen was without any apparent action and the electrode acquired in the solution a positive potential of about 0.8 V.

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[21] To be published shortly.

3. The second process

Various theories have been proposed to explain the stoichiometry of the second stage of the anodic oxidation of the alkaline iron electrode. Förster [11] suggests that the process consists in the oxidation of $Fe(OH)_2$ to the anhydrous ferric oxide Fe_2O_3.

We carried out experiments on the cathodic reduction of films of anhydrous oxides, such as α—Fe_2O_3 obtained by heating iron in air at 250° or 300° and γ—Fe_2O_3 obtained at room temperature or at 150° [22]. In all cases the polarization curves (Fig. 4) differed from the curves obtained in the cathodic reduction of the products of the second process with an active electrode (Fig. 2, branch *III*). These experiments and some general considerations lead us to believe that anhydrous Fe_2O_3 in aqueous solution cannot be the primary product of the electrochemical reaction on an active electrode. The formation of anhydrous Fe_2O_3 postulated by Förster cannot, therefore, be regarded as the basis of the second process.

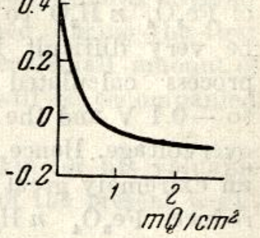

Fig. 4. Cathodic polarization curve of an air-passivated electrode.

Another of Förster's hypothesis regarding the second process is that the protective film of $Fe(OH)_2$ is torn and a short circuit $Fe-Fe_2O_3$ arises which brings to the formation of $Fe(OH)_2$ more quickly than the direct anodic oxidation of iron. This assumption is unfounded. If in the second process short circuitings of the ferric oxide and metallic iron did bring to the additional formation of $Fe(OH)_2$ which could again oxidize to the ferric form, there should be no special relation between the lengths of the first and second arrests of the anodic polarization curve; the second arrest could even be longer than the first. As a matter of fact it is evident from the experimental data that in anodic polarization the arrest of the second process in the first cycle is a little less than one-half as long as the arrest of the first process.

From the fact that the second arrest is one-half the length of the first we are led to conclude that the second process consists mainly in the oxidation of ferrous iron to the ferric form. The slight devia-

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[22] **Iimori**, Nature, **140**, 278 (1937); **Miley** and **Evans**, J. Chem. Soc., **1937**, 1295.

tion from this relation observed experimentally may denote either that a small amount of $Fe(OH)_2$ (about 5%) remains unoxidized or that the first process is accompanied by a secondary process in which in addition to $Fe(OH)_2$ a small amount of some other substance is formed. We shall return to this question later. At present it suffices to state that formation of $Fe_3O_4\ n\ H_2O$ from the metal as a by-product of the first process is not in contradiction with the laws of thermodynamics. According to calculations based on thermodynamical data the equilibrium value of the potential at which $Fe_3O_4\ n\ H_2O$ can be oxidized to Fe_2O_3 should equal approximately 1 V as measured against the hydrogen electrode in the same solution, hence the $Fe_3O_4\ n\ H_2O$ formed during the first arrest could not be oxidized further at the potential of the second arrest. The reduction of $Fe_3O_4\ n\ H_2O$ to the metal through cathodic polarization should be very difficult inasmuch as the equilibrium potential of this process calculated thermodynamically, is equal approximately to —0.1 V and the process can probably take place only at a high overvoltage. Hence, due to the small overvoltage of hydrogen on iron an extremely great current density will evidently be necessary to reduce $Fe_3O_4\ n\ H_2O$ cathodically.

Neither do the laws of thermodynamics exclude the possibility of $Fe_3O_4\ n\ H_2O$ forming from $Fe(OH)_2$; the equilibrium potential of this process has been calculated to be approximately —0.2 V. However, probably for kinetic reasons, $Fe_3O_4\ n\ H_2O$ cannot be formed in appreciable amounts at the potentials of the first and second arrests. It is probable that under certain conditions Fe_3O_4 can be formed only when nuclei of this phase are present. The conditions under which Fe_3O_4 is reduced to $Fe(OH)_2$ are at present being studied.

Förster assumes further that when the second process is reverted, Fe_2O_3 is directly reduced to metallic iron.

It can be shown, however, that for thermodynamic reasons the direct reduction of ferric oxide, anhydrous or hydrated to metal cannot take place at the potentials at which the second process can proceed cathodically. Moreover, the cathodic arrest of the polarization curve for the second process on active iron (Fig. 2, *III*) is almost as long as or slightly shorter than the anodic arrest (Fig. 2, *II*) whereas if the process went deeper during cathodic than during anodic polarization the cathodic curve would be the longer one.

The second process like the first, evidently proceeds by way of solution with formation of the intermediate compound $NaFeO^2_2$ in the solution, the solubility of which probably approaches that of $NaHFeO_2$.

As was observed above, the second anodic arrest of the polarization curve of active iron in the first cycle is almost one-half the length of the first arrest. This denotes that the anodic phase of the second process comes to an end due to exhaustion of the supply of $Fe(OH)_2$ which was on the electrode before the second process began. The mechanism of the passivation of iron with respect to the second process thus evidently consists in the solution adjacent to the electrode being depleted of $HFeO_2'$ ions, as a result of the expenditure of $Fe(OH)_2$, while the surface of the metallic iron remains covered with a passivating oxide layer which was formed during the first arrest. During further anodic polarization a very small amount of oxygen may penetrate into this oxide and this will be accompanied by a continual rise in potential.

We are greatly indebted to Prof. A. Frumkin for his valuable suggestions which facilitated the carrying out of the present work.

Summary

1. The electrochemical behaviour of an iron electrode in alkaline solution was investigated. The experiments were performed in an apparatus which permitted after heating the electrode at a high temperature in an atmosphere of hydrogen, to transfer it to the polarization vessel, without coming into contact with the air, and carry out polarization measurements over a range of current densities from 10^{-8} to 10^{-3} A/cm² in the absence of foreign depolarizing agents. The apparatus also permitted of sending past the electrode a continuous flow of a solution pre-saturated with the desired gas.

2. By heating rods of pure iron in hydrogen at 800° a smooth iron electrode was obtained which was active in dilute solutions of sodium hydroxide at room temperature. A short exposure to the air of such iron heat-treated in hydrogen results in complete passivity of the iron. The passivity of iron can thus be due to the formation on it in air of a thin film of the oxide γ—Fe_2O_3 or of an adsorbed layer of oxygen.

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[23] G. Grube u. H. Gmelin, Z. Elektrochem., **26**, 459 (1920).

3. The stoichiometry and mechanism of the electrode processes on active iron are discussed.

The electrode processes in dilute alkaline solutions take place by way of the solution with formation of the intermediate compounds $NaHFeO_2$ and $NaFeO_2$; these have a solubility of the order of 10^{-4} mol/l sufficient for diffusion and for deposition of the corresponding ydroxide in the form of a porous deposit, which explains the possibility of anodic oxidation of smooth active iron to a considerable depth.

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Received
January 20, 1946.