The Anodic Dissolution of Iron

II.   The Passivation of Iron in Neutral Acetic Acid-Sodium Acetate Solutions

H. NORD, C. E. FOVERSKOV and G. BECH NIELSEN

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

A new potentiostatic circuit is described. Under the conditions of the experiments of this study the kinetics of the anodic dissolution reaction (a.d.r.) is, in the active potential range, reasonably well represented by Tafel lines. These are extrapolated into the range of passivation, and on this basis a degree of passivation is defined. The formal equilibrium

$$A \rightleftharpoons P + nH^+$$

is examined. It is shown that two hydrogen ions are involved in the passivation process. The results are discussed on the basis of competitive chemisorption of water molecules and acetate ions.

In a previous paper [1] it was suggested that the anodic dissolution of iron, including the passivation, is largely explained by assuming a potential and pH controlled protolytic dissociation of chemisorbed water molecules. This dissociation leads to three potential ranges, a negative range where the water is undissociated (cathodic protection), a positive range where the two hydrogen ions are fully expelled from the surface, so that an oxide layer is formed (passivation), and an intermediate range where the catalytic influence of chemisorbed hydroxyl ion is important [2-4]. Fig. 4 illustrates the anodic behaviour of the iron electrode.

It was shown that, for hydrochloric acid-sodium chloride media, plots of reciprocal rate against hydrogen ion concentration at constant potential are linear in agreement with the above mechanism. Similar plots for acetic acid-sodium acetate media are nearly linear at very low acetic acid concentrations, but flatten out at higher concentrations, *i.e.* the dissolution velocities are higher than would be predicted from the suggested mechanism, apparently revealing an alternative reaction path, not inhibited by acid.

In the experiments reported in this paper, the experimental conditions are somewhat changed from those of our earlier studies. Thus we have used another iron sample, our media did not contain *ortho*-phenanthroline and we used another technique to obtain the data.

It has turned out that for the conditions prevailing in the present study the over-all dissolution velocity for the most negative part of the potential range, where corrosion is appreciable, is in reasonable accordance with the Tafel equation (see Fig. 5)

$$E = a + b \log i \qquad (1)$$

E is the potential (in this study referred to the normal hydrogen electrode), i is the anodic current (in this study in mA/cm^2). As a result we are able to report determinations of a "passivation degree", Θ, defined by the equation

$$i = (1-\Theta) \cdot I \qquad (2)$$

i is the actually measured anodic current as a function of potential and of solution composition, I is the current with which the electrode would have corroded, were the electrode completely active. I is defined by extrapolation beyond the active region of eqn. (1). This procedure is preliminary and empirical, but is justified partly by impedance measurements to be reported in a subsequent paper, partly by the consistency of the results of the present paper.

CIRCUIT

It is well known that simple DC operational amplifiers as used in analogue computers make quite good potentiostats. Such potentiostats are stable, accurate, and extremely simple to operate. Although they are useful for many purposes it was necessary for us to develop a more advanced instrument deviating from the simple potentiostat in several ways:

(a) In the new instrument the required potential as a function of time is introduced single ended, *i.e.* referred to ground potential. This assures versatility in the choice of generators for potential programs.

(b) The current is measured as the potential drop over a resistor, one end of which is ground connected. This potential drop is also available as two amplifier outputs with different polarities. These features assure flexibility in the choice of current measuring and recording devices.
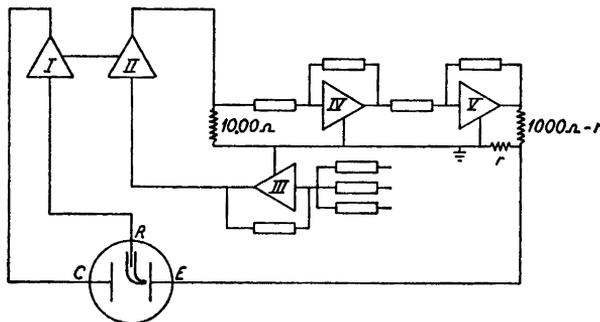

Fig. 1. The potentiostat. E, R and C are experimental electrode (iron electrode), reference electrode (silver/silver chloride in saturated potassium chloride) and counter electrode (platinum), respectively.

(c) The electrolyte resistance between probe (reference electrode with Luggin capillary) and experimental electrode is cancelled out.

The circuit is shown in Fig. 1. It consists of five DC amplifiers out of which I and II must be floating whereas III—V are used with ground connected zeros. I and II have common zero and thus form a kind of differential amplifier. The input potential of II and hence of I (*i.e.* the potential of the reference electrode) is governed by the output of a summing amplifier, III, which we call the program amplifier. The inputs of this amplifier are various terms, the sum of which form the potential program.

The current is primarily measured as the potential drop over the resistor R, which we usually select as 10.00 Ω. This potential drop is amplified exactly — 10 times by amplifier IV and further exactly — 20 times by amplifier V, *i.e.* totally + 200 times. The output of V is connected to the experimental electrode through a 1000 Ω resistance and a small, variable resistance, r, is inserted between experimental electrode and ground. A current twice the electrolysis current flows through the 1000 Ω resistance and divides at the experimental electrode. This arrangement provides a positive feed-back to the potentiostat proper (amplifiers I and II) and, when r is set at the appropriate value the electrolyte resistance mentioned above, r_{Ω}, is cancelled out. The corrected potential difference between reference electrode and experimental electrode, *i.e.* the potential difference, were the distance between the electrodes zero, is then the output of the program amplifier. It is actually impossible to set r exactly at r_{Ω} as the setup is then unstable so the potentiostat oscillates. This was also noticed in an earlier attempt to compensate r_{Ω}.[5]

The oscillations are in our setup efficiently quenched when a small fraction of 1 Ω is left uncompensated.

The potentiostat seems to be nearly completely characterized as an EMF source equal to the output of the program amplifier in series with a self-inductance and a negative resistance (150 μH and $-r$, respectively) operating between the probe and the experimental electrode. The frequency and the damping of the oscillations mentioned are quantitatively accounted for as being generated by an EMF source of this character and by the electrode capacity. As the zero point stability and the amplification of the amplifiers used (KINTEL 111 BFO and Solartron A.A. 900) is extremely good, the DC and low frequency accuracy of the total setup is virtually determined by the care with which other circuit elements (potential sources, resistances and measuring instruments) are selected and adjusted. The instrument works satisfactorily up to a few hundred c/sec.

EXPERIMENTAL PROCEDURE

The iron electrode has a rather complicated pattern of behaviour. To assure reproducibility, strict methods for selection of initial conditions must be adhered to.

The solutions used in the present study were all 1.00 M in sodium acetate. They were made up from reagent grade chemicals and from doubly distilled water. The concentrations of acetic acid varied between 1.4 × 10⁻³ M and 10⁻² M, corresponding to the pH range 7.57 — 6.72. The iron electrodes were rotating discs (1800 r.p.m., 0.200 cm²). The rate of rotation was uncritical for the experiments quoted here. The iron electrodes were

made from iron cylinders * inserted into centrally drilled, closely fitting holes in 1 cm diameter Perspex rods, and cemented with Araldite. They were abraded with emery paper and polished with diamond powder.** Fig. 2 shows the reaction vessel. The nitrogen
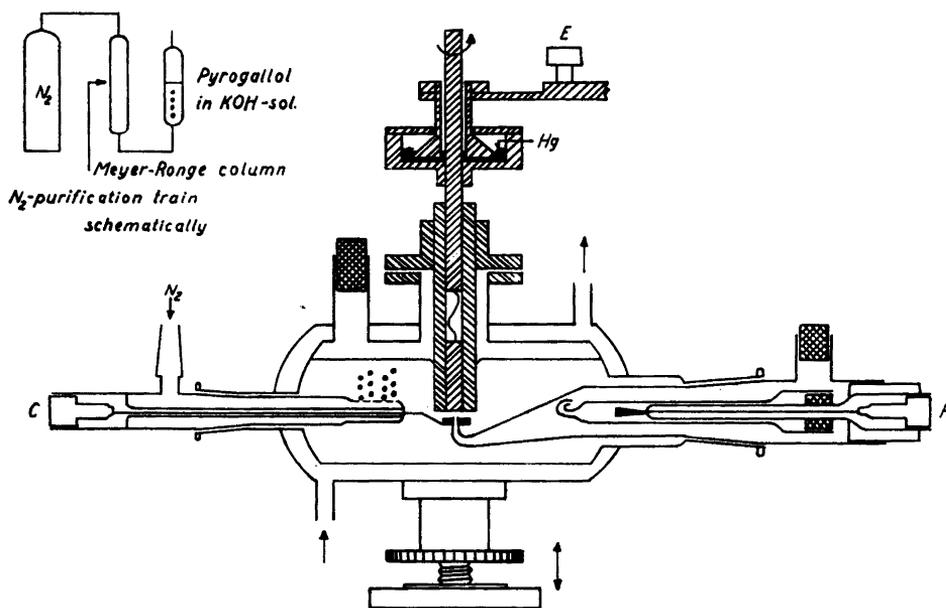

Fig. 2. Electrolysis cell with rotating disc experimental electrode. The distance between this and the Luggin capillary of the reference electrode is adjustable as indicated. The vessel has a constant temperature water jacket.

was deoxygenated with activated copper in a Meyer-Ronge apparatus.[6] No coloration was observed in the washing flask with pyrogallol. The reaction vessel was thermostated at 25°C.

Each experiment was preceded by an initial run which ensured that the setting of the apparatus was correct, and that the initial conditions of the electrode were as required. The standard medium for our studies in neutral acetic acid is 10^{-2} M in acetic acid and 1.00 M in sodium acetate, pH 6.72, and the "running in" experiment a series of potential sweeps, up and down, between $E_h = -400$ mV and $E_h = +100$ mV with rate of change of potential: 10 mV/sec. After three periods (5 min) the electrodes were generally completely reproducible. Subsequent sweeps gave identical $i - E_h$ diagrams as seen on Fig. 3. The difference between one electrode and another was generally quite small (less than 10 %). If not typical the electrode was discarded. This, however, only happens very rarely. It is seen from Fig. 3 that there is hardly any hysteresis on the ascending part of the diagram, but quite an appreciable one in the potential range where the electrode is more or less passive.

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* Matthey Spectrographically Standardized Iron Rods; produced from sponge by powder metallurgy. Impurities: C: 0.03 %, O_2: 0.01 %, N_2: 0.01 %; Mn: 2 p.p.m., Si: 1 p.p.m., Mg, Cu < 1 p.p.m.
** First with 7μ grade diamond paste, then with B-paste (approximately 1 μ grade), both from Struers Scientific Instruments, Copenhagen, Denmark.
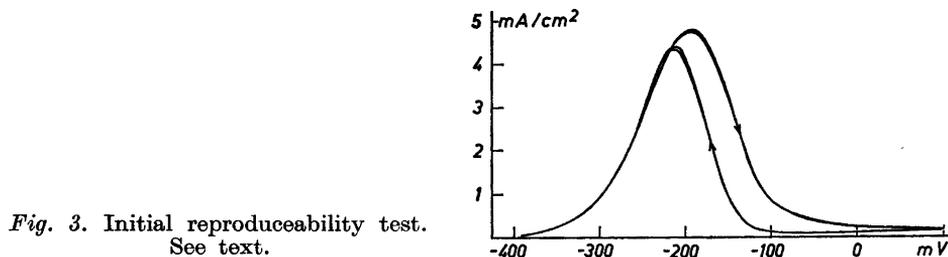
Fig. 3. Initial reproduceability test. See text.

When normal behaviour was ensured that triangular sweep was switched off at $E_h =$ -400 mV. We generally used a sweep of 1 mV/sec. for experiments designed to give virtually steady state conditions. With this rate of change of potential the hysteresis in the potential range of passivation was not more than about 3 mV.
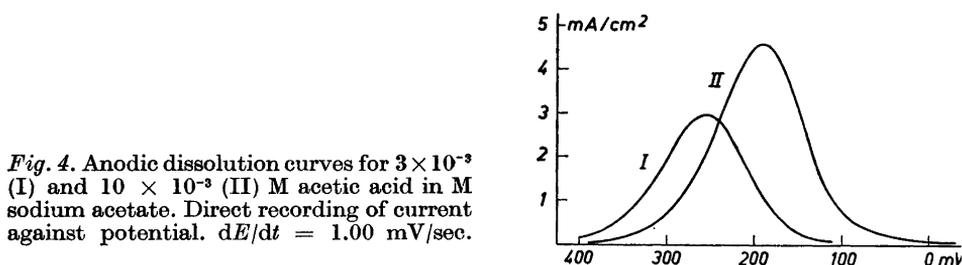

Fig. 4. Anodic dissolution curves for 3×10^{-3} (I) and 10×10^{-3} (II) M acetic acid in M sodium acetate. Direct recording of current against potential. $dE/dt = 1.00$ mV/sec.

Fig. 4 shows $i-E_h$ curves for two solutions containing 3×10^{-3} and 10×10^{-3} mole/liter acetic acid in 1.00 molar sodium acetate. The acid inhibition of a.d.r. described in Ref.[1] is apparent. Similar experiments were performed with 1.4×10^{-3}, 2×10^{-3}, 5×10^{-3} and 7×10^{-3} mole/liter acetic acid.

RESULTS

Fig. 5 shows a $\log i - E_h$ diagram for the experiments of Fig. 4. It is apparent that quite good Tafel lines can be drawn for the ascending branches of the
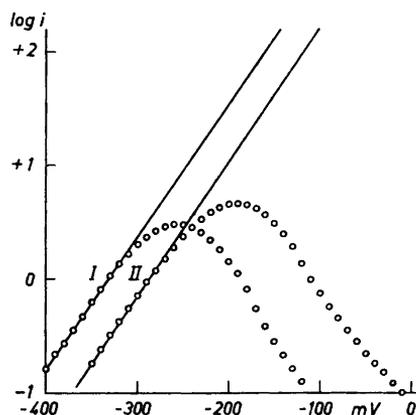

Fig. 5. Logarithmic curves for the experiments of Fig. 4.

curves. It was decided, for the purpose of this study, preliminarily to let the extrapolations of these lines represent the rate of the a.d.r. from yet active surface elements of the partly passive electrode. Values of actual and of extrapolated current were inserted in eqn. 2, and the family of passivation curves
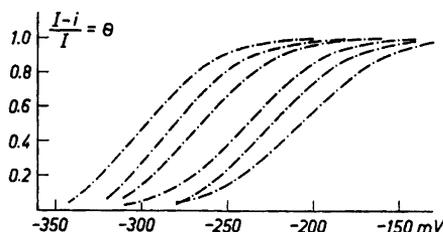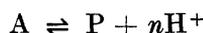

Fig. 6. Formation curves for the passive layer. The pH values are from left to right: 7.58, 7.42, 7.24, 7.02, 6.88, and 6.72.

shown in Fig. 6 were calculated. Their relative position shows that, in accordance with experience, passivation is inhibited by acid.

We have analysed the curves on the basis of the formal equilibrium

$$A \rightleftharpoons P + nH^+$$

A represents active surface molecules, P passive molecules. The relative concentrations are $1-\Theta$ and Θ, respectively. The mass action law in logarithmic form is therefore:

$$\log \frac{\Theta}{1-\Theta} = \log K + n\mathrm{pH} \qquad (4)$$

where K is a function of potential.

Fig. 7 shows the relation at constant potential ($E_h = -250$ mV) of $\log[\Theta/(1-\Theta)]$ against pH. The $n = 2$ line drawn is seen to be close to the experimental points, so n must be very nearly 2.

According to the general mechanism given by us[1] the active state should comprise surface iron atoms with chemisorbed water and hydroxyl ions, the atoms with hydroxyl ions being partly oxidized:

$$LOH_2 \rightleftharpoons LOH^- + H^+$$
$$LOH^- \rightleftharpoons FeOH^+ + 2\,e^-$$

L means surface iron atoms belonging to the lattice, Fe iron atoms oxidized, but belonging to the surface. These three forms together comprise, according to the general mechanism, the active part of the surface. The passive form suggested is FeO:

$$FeOH^+ \rightleftharpoons FeO + H^+$$
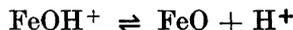
According to Fig. 7 the two forms with chemisorbed hydroxyl ion must be rare under the experimental conditions of this study.

Fig. 8 shows the dependence of $\log K$ on potential at constant pH. It is seen that K does not change with potential as expected for an electrode equilibrium comprising two charges (two hydrogen ions). This would involve $dE/d \log K = 29$ mV. The actual dependence of $\log K$ on potential would suggest an equilibrium comprising much nearer one charge.
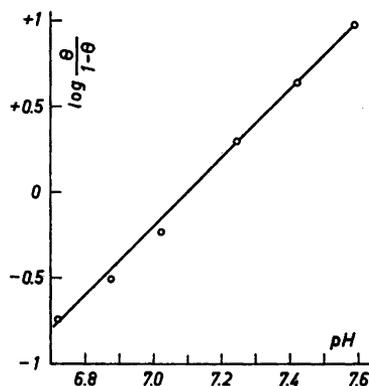
Fig. 7. pH dependence of $\log[\Theta/(1-\Theta)]$ at constant potential $(E_h = -250 \text{ mV})$.
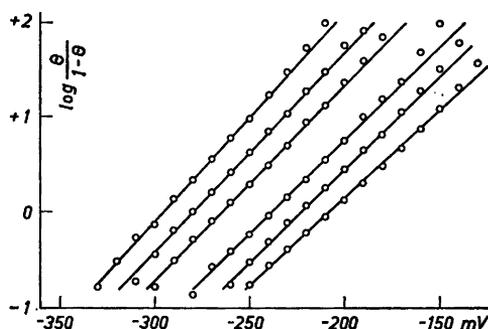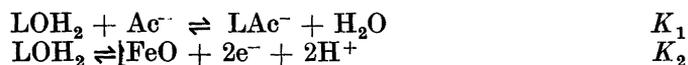

Fig. 8. Potential dependence of $\log[\Theta/(1-\Theta)]$ for the data of Fig. 6.

Acetate ion has a pronounced influence on the a.d.r. The anodic current is rather higher, at equal pH, in media containing apparently less strongly adsorbed ions: hydrogen carbonate ion or formate ion. Thus we must regard chemisorbed acetate ion as another component of the active surface, and the equilibrium.

$$\text{LOH}_2 + \text{Ac}^- \rightleftharpoons \text{LAc}^- + \text{H}_2\text{O}$$
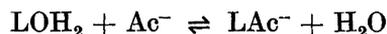
should be added to the steps given above.

If we disregard the two intermediates with hydroxyl ions, which as indicated above seem rare under the conditions used here, we may write the passivation process as two competing equilibria:

$$\text{LOH}_2 + \text{Ac}^- \rightleftharpoons \text{LAc}^- + \text{H}_2\text{O} \qquad\qquad K_1$$
$$\text{LOH}_2 \rightleftharpoons \text{FeO} + 2\text{e}^- + 2\text{H}^+ \qquad\qquad K_2$$

The active form now comprises the two surface species LOH_2 and LAc^-, the passive form, as before, is FeO.

The mass action law for this system reads

$$\frac{\Theta}{1-\Theta} = \frac{K_2}{[\text{H}^+]^2 \, (1 + K_1[\text{Ac}^-])} \tag{5}$$

where K_1 should obey a 58 mV law and K_2 a 29 mV law, being equilibrium constants for reactions comprising one and two charges, respectively.

Eqn. 5, and hence the reactions on which it is based, seems to explain the results of the experiments. It has been observed that reduction of acetate concentration makes passivation easier whereas addition of sodium benzoate, which seems to be more strongly adsorbed, makes passivation more difficult. The method of this paper cannot be used to treat such experiments quantitatively as good Tafel lines are not obtained for ascending branches of the $i-E_h$ curves.

Table 1. Comparison of d log i/dE (descending branches) calculated from (6) and determined directly from the experiments.

$[HE] \times 10^{-3}$	1.4	2	3	5	7	10
$\dfrac{dE}{d \log I}$ mV	88.5	88	86	89.5	97.5	84.5
$\dfrac{dE}{d \log K}$ mV	45.5	48	49	51	51	54.5
$-\dfrac{dE}{d \log i}$ exptl.	71	75.5	71	72.5	73.5	89
$-\dfrac{dE}{d \log i}$ calc.	93	106	114	119	108	151

We wish at this point to stress the preliminary character of the quantitative results of this paper. The extrapolation of Tafel lines is an uncertain method for obtaining the kinetics at the active part of the incompletely passivated surface. Table 1 illustrates this uncertainty. The two first rows show for the experiments of this study the (reciprocal) slopes of the Tafel lines of the ascending branches of the a.d.r. and the potential dependences of log K from Fig. 8. It is in principle possible to calculate the Tafel slopes of the descending branches of the a.d.r. for $\Theta \to 1$:

$$i = (1-\Theta) I \tag{2}$$

$$\frac{d \log i}{dE} = \frac{d \log (1-\Theta)}{dE} + \frac{d \log I}{dE} \tag{6}$$

The unsatisfactory agreement between third and fourth row can be explained, if the active kinetics at more noble potentials in Fig. 5 should have been represented by a function bending somewhat down towards the abcissa rather than by the extrapolated Tafel line. This, for an overall reaction involving a sequence of steps with different potential dependences, would be in accordance with a statement regarding the analogous case of the temperature dependence of complicated reactions given by Christiansen.[7]

The discrepancy revealed makes it unrealistic to attempt a calculation of relative affinities to the iron surface of water molecules and acetate ions from the data given in the present work. Nevertheless, some results seem to be quite certain:

(1) The formation of the passive state is a continuous function of potential and of solution compositions, not a sharp transition.

(2) Two hydrogen ions per surface molecule are involved.

It is not certain that the experiments of this study are best described by assuming a Langmuir type adsorption isotherm. The accuracy with which low Θ values are determined is poor, as they are very sensitive to the choice of the Tafel line defining I. It is seen from Fig. 8 that the linear relationship between $\log[\Theta/(1-\Theta)]$ and E does not hold at high Θ values. Maybe the discrepancy revealed in Table 1 indicates that calculations based on the assumption that all sites on the electrode are equivalent are too approximate. Our experiences do, however, make it possible to select definitely active conditions for a more detailed study of the mechanism of the a.d.r. of the iron electrode in similar media. It is likely that a precise knowledge of the kinetics of the active electrode thus obtained will furnish a more satisfactory basis for the extrapolation into the pH—potential range of passivation. This again might provide more reliable data, from which we hope conclusive information regarding the nature of passivity can be drawn.

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