

# Polarization and DC Capacitance of Passive Iron in Acid Phosphate Solution

C. Simon and T. Hurlen\*

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway

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Quasi-stationary (20 h stabilization) polarization measurements confirm that iron exhibits an essentially potential-independent passive current ( $j_p$ ) which at pH below about 5 obeys  $d \log j_p/d \text{pH} \approx -0.8$  and at higher pH approaches pH independence. Potentiostatic transients yield initial polarization data which accord with the Cabrera-Mott equation and suggest  $z=2$  (rather than 3) for the charge number of metal ions being transferred at the metal/oxide interface. Galvanostatic transients yield dc capacitance data which largely satisfy an insulator (or exhausted semi-conductor) model, reveal the main charge distribution in the passive iron electrode, and combine with film thickness data to give the mean dielectric constant of the quasi-stationary passive film at various pH. The results favour a one-phase description of the passive film.

The passive behaviour of iron has been the subject of numerous investigations, most of which are well surveyed.<sup>1–6</sup> However, studies based on potentiostatic and galvanostatic transients following single square pulses on well stabilized passive electrodes are largely lacking (but see Discussion). Such studies have been found quite informative in recent work at our laboratory on a number of other passive metals (Al,<sup>7</sup> Ti,<sup>8</sup> Zr,<sup>9</sup> Hf,<sup>10</sup> Nb<sup>11</sup> and Ta<sup>12</sup>). Main findings are that the transient polarization and the dc capacitance of passive metal electrodes generally accord with the Cabrera-Mott equation<sup>13</sup> for metal-ion transfer at metal/oxide interfaces and with an insulator (or exhausted semi-conductor) model<sup>7,8</sup> for passive films on metals, respectively. This is presently pursued to the important case of passive iron in acid solution.

## Experimental

Quasi-stationary and transient polarization measurements have been made on pre-passivated iron (99.6%, Goodfellow) sheet electrodes (2 cm<sup>2</sup>) after 20 h potentiostatic stabilization at some

chosen potential within the passive range for iron in the test solution concerned. Test solutions were 0.2 M NaH<sub>2</sub>PO<sub>4</sub> with additions of H<sub>3</sub>PO<sub>4</sub> or Na<sub>2</sub>HPO<sub>4</sub> to give pH values of 2.0, 3.5, 5.3 or 6.0. They were mostly oxygenated and used under a pure oxygen atmosphere, but some measurements were also made in deoxygenated solutions under an atmosphere of purified nitrogen. The deoxygenation was generally found to have little effect on the present measurements, however. All experiments were performed at 25°C in a fully thermostatted three-compartment Pyrex cell with a platinum auxiliary electrode and a saturated mercurous sulphate reference electrode. For reasons of comparison, however, all potentials are presently referred to the saturated calomel electrode (sce).

All solutions were prepared from A.R. quality chemicals and twice-distilled water. Prior to use or to re-use, the iron electrodes were mechanically polished (1200 mesh SiC), degreased with chloroform and acetone, etched for 30 s in 20% HNO<sub>3</sub>, thoroughly rinsed with twice-distilled water and pre-passivated<sup>14</sup> by immersion for 20 h in aerated phosphate solution of pH 11.3 [where a passive corrosion potential around  $-0.28$  V (sce) generally was reached]. Finally, they were once

\*To whom correspondence should be addressed.

more rinsed with twice-distilled water, transferred to the test cell and immediately brought to a chosen potential for 20 h potentiostatic stabilization before transient studies were made. The importance of pre-passivation (or two-step passivation) has previously been demonstrated and discussed.<sup>14,15</sup>

Sometimes, an electrode stabilized and studied at one potential was afterwards brought directly to another and higher stabilization potential for further studies after a new stabilization period of 20 h. This could even be repeated several times, covering successively higher and higher stabilization potentials, but with a progressive accumulation of stabilization periods for the electrode.

Potentiostatic and galvanostatic transients were produced by superimposing single square pulses of various amplitudes on the stabilization potential or on the quasi-steady current. After a pulse of a few seconds duration, several minutes could elapse before the pre-pulse state of the electrode was well restored. Full restitution was required in the present case before a new pulse was applied. For this reason, 2–3 h were generally needed for a suitable programme of transient studies on a stabilized electrode to be accomplished.

Instruments used were mainly a PAR-173/176 potentiostat/galvanostat, a Tektronix-564B storage oscilloscope (with 3A9 differential amplifier and 3B4 time base) and a Goerz-SE-120 recorder.

## Results

In the present work, a passive iron electrode was generally brought from a lower to a higher potential for potentiostatic stabilization. The anodic current through the electrode then rapidly rose to an early value from which it fell with time at a decreasing rate. After 20 h stabilization it was generally still falling, but slowly enough to change negligibly over the time period needed for transient studies (2–3 h) and to be regarded as quasi-stationary passive current. This all accords with previous observations (e.g. Refs. 16, 17).

*Quasi-stationary data.* In all the test solutions employed, the iron electrode exhibited an essentially potential-independent quasi-stationary passive current (defined above). Values presently obtained for this passive current ( $j_p$  or rather  $rj_p$

Table 1. Properties of the passive iron electrode in acidic phosphate solution at 25 °C (see text).

pH	2.0	3.5	5.3	6.0
$rj_p/\mu\text{A cm}^{-2}$	9.5	0.7	0.05	0.04
$k_b$	0.20	0.20	0.22	0.24
$a/\text{\AA V}^{-1a}$	16	18	20	20
$zfg$	3.2	3.5	3.6	3.3
$r\sigma_p'/\mu\text{C cm}^{-2}$	84	50	28	28
$r\sigma_{ox}'/\mu\text{C cm}^{-2}$	-89	-57	-37	-38
$r\epsilon$	152	100	63	63

<sup>a</sup>From Fig. 3 of Ref. 18.

where  $r$  is the roughness factor applying) at various pH are listed in Table 1 below. Approach is found to  $d \log j_p/d \text{pH} = -0.8$  at low pH (below about 5) and to pH independence for  $j_p$  at higher pH. This all agrees with previous results.<sup>17,18</sup>

*Potentiostatic transients.* The potentiostatic transients presently obtained mainly show a continuous fall in current with time and no distinct sign of any superpolarization (which should have exhibited itself by an early minimum and subse-

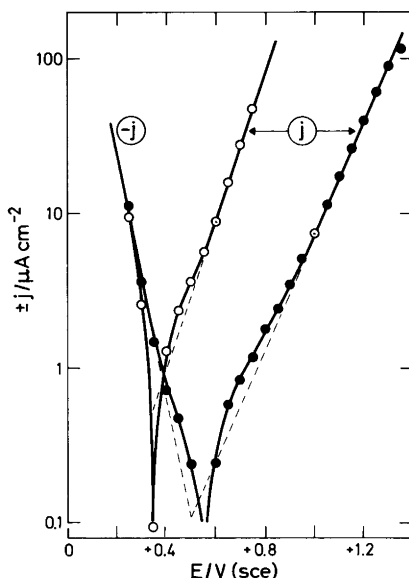


Fig. 1. Initial polarization data from potentiostatic transients after steps from one or the other of two different quasi-steady states (○) for passive iron electrodes in phosphate solution of pH 2.0 at 25 °C.

quent maximum or a related inflection in potentiostatic transients<sup>7,8</sup>). Examples of initial polarization data determined from such transients by back extrapolation<sup>8</sup> are given in the Tafel diagram of Fig. 1. The examples are data obtained in a given solution on stepping from one or the other of two different quasi-steady passive states (centred circles in Fig. 1). The data mostly apply to the anodic metal conversion process, but a cathodic process enters and takes over at sufficiently low potentials (highly negative potential pulses). Initially, the metal conversion process clearly follows the Tafel law with slope depending on the quasi-steady state (or stabilization potential) from which potential steps are made.

Data presently obtained for the initial Tafel slope ( $b$ ) as a function of the stabilization potential ( $E'$ ) in the various solutions employed are presented in Fig. 2. The lines in Fig. 2 for pH below 6 obey:

$$b/\text{decade}^{-1} = k_b(E' - E_b) \quad (1a)$$

$$E_b/V(\text{sce}) = -0.28 - 0.06 \text{ pH} \quad (1b)$$

where the extrapolated potential of zero Tafel slope ( $E_b$ ) comes close to the reversible  $\text{Fe}_2\text{O}_3, 6\text{H}^+/2\text{Fe}, 3\text{H}_2\text{O}$  potential,<sup>19</sup> and  $k_b$  has val-

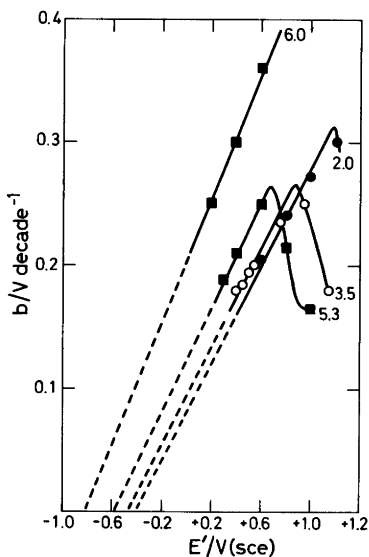


Fig. 2. Anodic  $b/E'$  data for passive iron electrodes in phosphate solutions of various pH at 25°C. Values of pH are given on the curves.

ues as given in Table 1 at various pH. Deviations occur at high potentials where also solution oxidation may begin to play a role. At pH 6.0, a higher lying and steeper line with lower (more negative)  $E_b$  appears. Analogous results have previously been obtained for a number of other passive metals.<sup>7-12</sup>

**Galvanostatic transients.** The galvanostatic transients presently obtained largely support the above initial polarization data. From their initial slope ( $dE/dt$ ) and the capacitance equation  $C = \Delta j/(dE/dT)$ , where  $\Delta j = j - j'$  is the amplitude of the current density pulse applied, they moreover yield data for the dc differential capacitance ( $C$ ) of the passive iron electrode at various quasi-steady states ( $E', j'$ ). Such data are presented as  $C^{-1}$  vs.  $E'$  at various pH in Fig. 3.

At pH below 6, the dependence appears largely to fit a linear relationship:

$$C^{-1} = k_c^{-1}(E' - E_c) \quad (2a)$$

$$E_c/V(\text{sce}) = -0.10 \quad (2b)$$

with pH-dependent slope ( $k_c^{-1}$ ) but with pH-independent extrapolated potential of zero inverse capacitance ( $E_c$ ). Values obtained for  $k_c$  are tabulated as  $\sigma'_m (= k_c)$  in Table 1 (see below). The value obtained for  $E_c$  comes close to the zero-charge flatband potential ( $E_{fb}^0$ ) for  $\text{Fe}_2\text{O}_3$ .<sup>20</sup> At pH 6.0, eqn. (2a) still applies, but with a lower (more negative) value for  $E_c$  than given by eqn. (2b). Deviations appear at high potentials, where solution oxidation also may occur. Analogous results have previously been obtained for a number

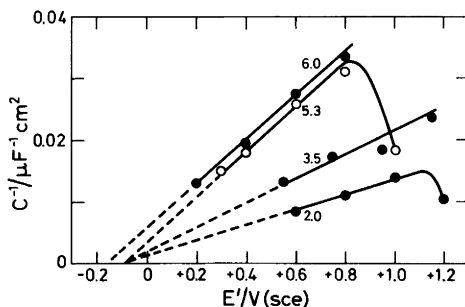


Fig. 3.  $C^{-1}/E'$  data for passive iron electrodes in phosphate solutions at four different pH values as indicated on the curves (25°C).

of other passive metals.<sup>7-12</sup> The closest relationship is found to passive titanium.<sup>8</sup>

## Discussion

The quasi-stationary data of the present work mainly confirm previous observations<sup>17,18</sup> and will not be discussed any further. The transient data, however, are largely novel and deserve some attention. Of special importance is that the transients originate from well stabilized passive states (20 h potentiostatic stabilization).

**Superpolarization.** No clear sign of superpolarization (overshoot or undershoot in galvanostatic or potentiostatic transients, respectively) was seen in the quite slow transients recorded in the present work. In previous work on passive iron, however, a weak superpolarization has been observed in galvanostatic transients<sup>21-23</sup> and a more strong one in the ms time range of potentiostatic transients (Fig. 6 of Ref. 24). This indicates that relative changes of kink density in the reacting metal surface (held responsible for the superpolarization<sup>7,8,25</sup>) are mostly accomplished too early to show up clearly in the shape of the transients presently recorded. Such early changes should affect the initial polarization data extracted from the slow transients, however. The corresponding situation for some other passive metals has recently been discussed.<sup>11</sup>

**Initial polarization.** The initial faradaic polarization of potentiostatically well stabilized passive iron electrodes is found in the present case to obey the Tafel law, with slope ( $b$ ) increasing linearly with the stabilization potential ( $E'$ ) and extrapolating to a pH-dependent zero-point potential ( $E_b$ ) close to the reversible  $\text{Fe}_2\text{O}_3, 6\text{H}^+/2\text{Fe}, 3\text{H}_2\text{O}$  potential. Previous ellipsometric studies<sup>3,14,18</sup> have shown that the quasi-stationary passive film thickness ( $\delta$ ) also increases linearly with the stabilization potential and extrapolates to about the same zero-point potential as above. This means that  $\delta = a(E' - E_b)$ , where  $a$  is the quasi-stationary anodization ratio. The Cabrera-Mott expression for the initial Tafel slope then becomes:

$$b = 2.303(RT/F)(E' - E_b)al(z\lambda fg) \quad (3)$$

where  $z$  is the charge number for ions being transferred at the metal/oxide interface,  $\lambda$  is their activation (half-jump) distance, and  $f$  and  $g$  are a transient field and site factor, respectively.<sup>7-12</sup>

Using 1.5 Å for  $\lambda$ <sup>7-12, 25</sup> and the values of Table 1 for  $a$  and  $k_b$  in matching the theoretical eqn. (3) with the empirical eqn. (1a), one obtains the co-tabulated values for the triple product  $zfg$ . These values average to  $zfg = 3.4$ . On its own, this could further be taken to imply that  $z = 3$  and  $fg = 1.1$ , but a value near unity for  $fg$  disagrees with the superpolarization observations above. A more acceptable possibility is  $z = 2$  and  $fg = 1.7$ . Some justification for this conclusion is provided by a previous discussion of superpolarization and  $fg$  values.<sup>11</sup> Under stationary conditions, furthermore, a number of occurrences of the ion transfer step  $\text{Fe}(\text{metal}) \rightarrow \text{Fe}^{2+}(\text{oxide}) + 2e^-(\text{metal})$  must be followed by the same number of occurrences of the electron transfer step  $\text{Fe}^{2+}(\text{oxide}) \rightarrow \text{Fe}^{3+}(\text{oxide}) + e^-(\text{metal})$ , since only Fe(III) species are found to enter the solution from the passive film.<sup>3,4,17,23</sup>

Eqn. (3) implies that the electric field ( $\vec{E}$ ) affecting metal-ion transfer at the metal/oxide interface is the same as the average field in the oxide film [i.e.  $\vec{E}' = (E' - E_b)/\delta = 1/a$  under quasi-steady conditions], and its applicability supports the validity of this implication. This hardly allows the quasi-steady passive film on iron to be divided into an inner electronically conducting part and an outer dielectric part (as often proposed<sup>1-6,26,27</sup>). The film must rather be a dielectric throughout for eqn. (3) to apply. This supports some recent conclusions on this matter.<sup>28-32</sup>

**Capacitance.** For potentiostatically well stabilized (20 h) passive iron electrodes, the inverse differential dc capacitance ( $C^{-1}$ ) at the stabilization potential is found in the present case to increase linearly with this potential (when below the oxygen evolution range). At pH below 6, the  $C^{-1}/E'$  lines have a pH-dependent slope and extrapolate to a pH-independent zero-point potential ( $E_c$ ) close to the zero-charge flatband potential ( $E_{fb}^0$ ) for  $\text{Fe}_2\text{O}_3$  (Fig. 3). This type of behaviour is shared fully with titanium<sup>8</sup> and partly with zirconium<sup>9</sup> and hafnium.<sup>10</sup> Somewhat different behaviour is observed for aluminium,<sup>7</sup> niobium<sup>11</sup> and tantalum.<sup>12</sup>

Provided space charge effects in the passive film and in the Gouy layer on the solution side may be ignored, the insulator model yields:

$$C^{-1} = [(E' - E_{fb}^0)/\sigma'_m] + [((d\sigma_{ox}/d\sigma_m) - (\sigma'_{ox}/\sigma'_m))/C_H] \quad (4)$$

for the above inverse capacitance.<sup>8</sup> In this equation,  $\sigma_m$  and  $\sigma_{ox}$  are the surface charge densities on the metal at the metal/oxide interface and on the oxide at the oxide/solution interface, respectively,  $C_H$  is the Helmholtz capacitance, and the prime ties a parameter to its quasi-steady state value.

If, in the initial part of galvanostatic transients,  $d\sigma_{ox}/d\sigma_m$  should become equal to (or approach)  $\sigma'_{ox}/\sigma'_m$ , the theoretical eqn. (4) matches directly the empirical eqn. (2a) and gives expectations of  $E_c = E_{fb}^0$  (as observed) and  $k_c = \sigma'_m$  (already used to obtain the values listed for  $\sigma'_m$  in Table 1). This matter has been discussed to some extent for the case of passive titanium,<sup>8</sup> but it still needs further theoretical clarification.

Eqn. (4) clearly allows the zero-potential for a  $C^{-1}/E'$  line to differ from that for a corresponding  $\delta/E'$  (or  $b/E'$ ) line on a metal with a one-phase passive film. This invalidates the sometimes assumed necessity of introducing the concept of a two-phase film with an inner conducting part to explain such zero-point differences.<sup>26</sup>

*Surface charges.* For the sum of the surface charge densities introduced above, the insulator model yields:<sup>7,8</sup>

$$\sigma'_m + \sigma'_{ox} = C_H(E_b - E_{fb}^0) \quad (5)$$

which allows  $\sigma'_{ox}$  to be estimated from data for the other parameters involved. The separate determination of  $\sigma'_m$  is described above, and values obtained are listed in Table 1. For  $C_H$ , the situation is unclear, but a value of  $18 \mu\text{F cm}^{-2}$  (as for negatively charged mercury<sup>33</sup>) is presently adopted. Using also the values from eqns. (1b) and (2b) for  $E_b$  and  $E_{fb}^0 (= E_c)$ , respectively, the values listed for  $\sigma'_{ox}$  in Table 1 are obtained. The surface charge density sum ( $\sigma'_m + \sigma'_{ox}$ ) appears negative over the entire pH region covered, and increasingly so with increasing pH.

*Dielectric constant.* According to the insulator model, the electric field in the passive film under

quasi-steady conditions is given both by  $1/a$  and by  $\sigma'_m/\epsilon\epsilon_0$ . From the equality of these two expressions, the dielectric constant ( $\epsilon$ ) of the passive film should be given by:

$$\epsilon = a \sigma'_m/\epsilon_0 \quad (6)$$

where  $\epsilon_0$  is the permittivity of free space. Values thus obtained for  $\epsilon$  are listed in Table 1. Considering also the roughness factor ( $r$ ) presently involved, these values may be compared to values of  $\epsilon$  for iron oxide crystals. The latter values increase strongly with the Fe(II) content of the crystals, viz. from 10 for  $\gamma\text{-Fe}_2\text{O}_3$  to 250 for  $\text{Fe}_3\text{O}_4$ .<sup>34</sup> The comparison may then indicate that the relative Fe(II) content of the quasi-stationary passive film increases with decreasing pH of the solution used for final growth and stabilization of the film.

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