

Passive Behaviour of Iron in Alkaline Phosphate Solutions

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Polarization measurements confirm that iron in neutral and alkaline phosphate solutions exhibits an essentially potential- and pH-independent stationary passive current. The pH independence may suggest transfer of iron mostly as neutral complex species at the oxide/solution interface of the passive iron electrode. Potentiostatic transients yield initial polarization data which accord with the Cabrera-Mott equation and support $z = 2$ (rather than 3) for ions being transferred at the metal/oxide interface. Galvanostatic transients yield dc capacitance data which approach expectations from an exhausted semiconductor model and help to reveal both the mean dielectric constant of the passive film and the main charge distribution in the passive iron electrode under quasi-stationary conditions. Some differences to the behaviour of passive iron in acidic phosphate solutions are noted.

The passive behaviour of iron in acidic phosphate solutions has recently been studied in our laboratory by quasi-steady and transient polarization measurements.¹ The results of these studies call for an extension of the measurements to alkaline solutions, as do also some early observations on passive iron in such solutions.²⁻⁴ This is pursued in the present work.

Emphasis presently is on the initial polarization and the dc capacitance of well stabilized passive iron electrodes with various values of the passive film thickness. Through a Cabrera-Mott treatment,⁵ the initial polarization behaviour should reveal the charge number of the main ions transferred at the metal/oxide interface of the passive iron electrode. From an exhausted semiconductor model of the passive film,⁶ the capacitance data should elucidate both the main charge distribution in the passive iron electrode and the mean dielectric constant of its passive film. This may further elucidate the question of this passive film being a one-phase or a two-phase film. Moreover, studies on the quasi-stationary passive current should give some information on the metal-ion transfer process at the oxide/solution interface of the passive iron electrode.^{7,8}

Experimental

Experiments were performed mainly with materials, instruments and methods essentially as previously described.¹ Iron (99,6%, Goodfellow) sheet electrodes (4 cm²) were studied at 25°C in deoxygenated (N₂) solutions of the following compositions:

0.1 M NaH ₂ PO ₄ + 0.1 M Na ₂ HPO ₄	(pH 6.7)
0.002 M NaH ₂ PO ₄ + 0.1 M Na ₂ HPO ₄	(pH 8.0)
0.15 M Na ₂ HPO ₄	(pH 9.3)
0.15 M Na ₃ PO ₄	(pH 12.4)
0.15 M Na ₃ PO ₄ + 1 M NaOH	(pH 14)

Prior to use, the electrodes generally were mechanically polished and briefly etched (½ min in 20% HNO₃). Prepassivation (or two-step passivation) of test electrodes¹ were used only for studies in the solution of pH 6.7. In all other cases, one-step passivation was performed in the test solution prior to stabilizing the passive electrode potentiostatically for 20 h at a chosen stabilization potential. Thereafter, potentiostatic and galvanostatic transients were recorded on stepping the test electrode sharply and briefly (5–10 s) away from the quasi-steady state reached. Between such single pulses, regain of the originally stabilized state was waited for.

Finally, initial polarization data and dc capacitance data were determined by back extrapolation of the potentiostatic transients and from the initial slope of the galvanostatic ones, respectively.¹ These data accordingly apply to the quasi-stationary passive film thickness at the quasi-stationary passive state from which steps were made. This thickness is 20–40 Å, depending on the stabilization potential applied.⁹⁻¹⁷

Results

Fig. 1 exemplifies and illustrates the polarization data of the present work. In a Tafel diagram, it shows a quasi-stationary polarization point (E' , j') and initial polarization points (E , j) obtained on stepping away from $E = E'$ to various other values of E . The quasi-stationary point clearly lies on the anodic branch of the initial polarization

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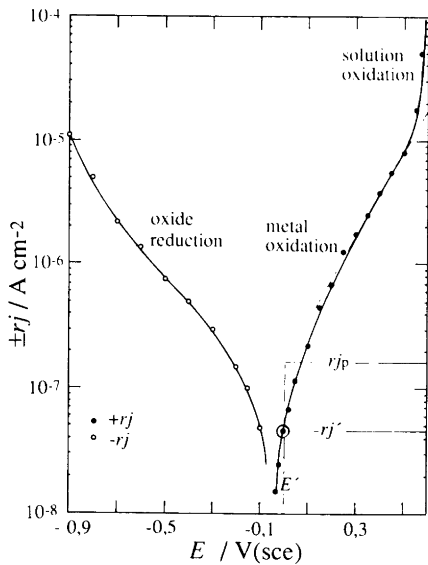


Fig. 1. Initial polarization points (E, j) for passive iron electrodes after stepping from a given stabilized state (E'/j') in phosphate solution of pH 14 at 25°C (r is the roughness factor).

curve, but not on the initial Tafel line for metal oxidation. It hence does not represent the metal oxidation process alone, but seems codetermined by some interfering reduction process. The stationary passive current for metal oxidation (j_p) is then obtained by extrapolating the Tafel line for metal oxidation back to the stabilization potential applied (E'), as exemplified in Fig. 1. This yields $j_p > j'$.

Analogous observations were made for all the solutions of the present work and at all the stabilization potentials applied. It hence appears that the cathodic interference in a

stabilized state is "dragged" along with this state when it is changed. These observations in alkaline solutions differ from corresponding ones in acidic solutions. In acidic solutions the relation $j_p = j'$ appears (or negligible interference in quasi-steady passive states).¹ It also is noteworthy that the waiting time needed after a pulse for the prepulse state to be regained generally is much longer in alkaline solutions (15–30 min) than in acidic ones¹ (1–2 min).

Passive current. In any of the solutions of the present work, the quasi-stationary passive current j_p (determined as described above) shows little or no dependence on the stabilization potential. Nor does it vary much with the pH over the alkaline range. The latter is illustrated in Fig. 2, where the mean value of rj_p in a test solution (averaged over values at various stabilization potentials) is plotted against the solution pH together with previous values¹ for acidic phosphate solutions. At a pH slightly below 5, a transition appears from a rather strong pH dependence ($d \log j_p / d \text{pH} = -0.8$) at lower pH to essential independence at higher pH. This agrees with previous results.^{8,10,11}

Initial polarization. In Fig. 3, values presently obtained for the initial Tafel slope (b) for metal oxidation (Fig. 1) in two of the solutions used (pH 6.7 and 14) are plotted against the stabilization potential (E') to which they apply. Except at too high potentials, where solution oxidation may also play a rôle, such data of the present work mostly obey:

$$b / \text{decade}^{-1} = 0.27 (E' - E_b) \tag{1a}$$

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

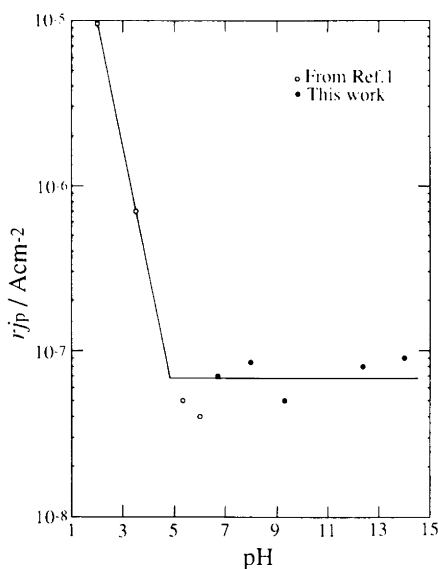


Fig. 2. Quasi-stationary passive current (j_p) for iron in phosphate solutions of various pH at 25°C (r is the roughness factor).

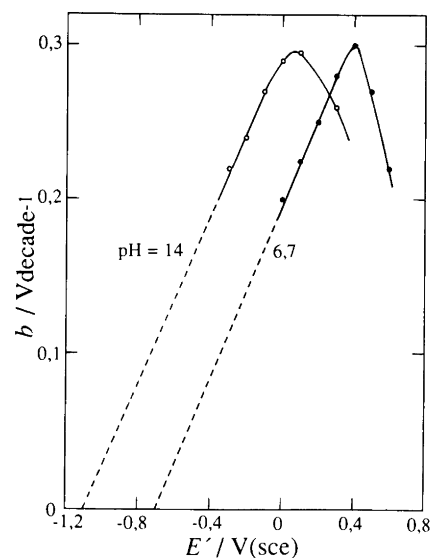


Fig. 3. Initial Tafel slope (b) of metal oxidation (Fig. 1) for passive iron after stabilization (20 h) at various electrode potentials (E') in phosphate solutions of pH 6.7 or 14 at 25°C.

where E_b is the extrapolated potential of zero Tafel slope. Empirically, the latter potential comes close to the reversible Fe_2O_3 , $6\text{H}^+/2\text{Fe}$, $3\text{H}_2\text{O}$ potential.¹⁸ This all accords with previous findings for acidic phosphate solutions.¹

The initial polarization of oxide reduction in alkaline solution is remarkable (Fig. 1), but has not yet been studied thoroughly enough. It is hoped to treat this matter separately in a future contribution.

Electrode capacitance. In Fig. 4, values presently obtained for the inverse dc capacitance (C^{-1}) of stationary passive iron electrodes in two of the solutions used (pH 6.7 and 14) are plotted as $(rC)^{-1}$ against the stabilization potential (E') to which they apply. Except at too high potentials, where solution oxidation may also occur, such data of the present work generally exhibit a linear C^{-1}/E' relationship with slope showing little systematic variation with the pH over the alkaline range covered. By use of an insulator or exhausted semiconductor model for the passive film,⁶ this may be written:

$$C^{-1} = (E' - E_c) / \sigma'_m \quad (2)$$

where E_c is the extrapolated potential of zero inverse capacitance, and σ'_m is the surface charge density on the metal at the metal/oxide interface under stationary passive conditions.

In Fig. 5, E_c values presently and previously¹ obtained for passive iron in various phosphate solutions are plotted against the solution pH to which they apply. This shows how E_c changes from approaching the zero-charge flatband potential (E_{fb}^0) of Fe_2O_3 at low pH to approaching the reversible Fe_2O_3 , $6\text{H}^+/2\text{Fe}$, $3\text{H}_2\text{O}$ potential at high pH. The

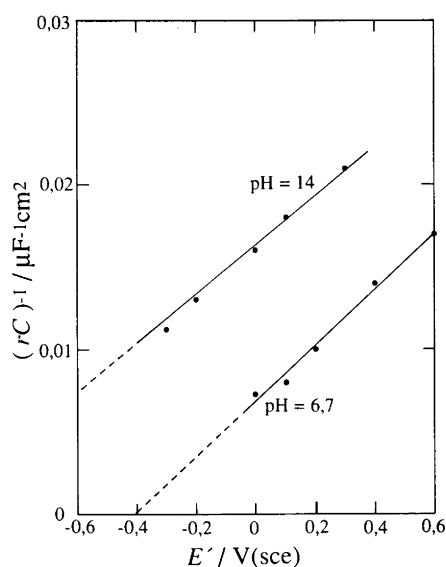


Fig. 4. Inverse dc capacitance (C^{-1}) of passive iron electrodes after stabilization (20 h) at various potentials (E') in phosphate solutions of pH 6.7 or 14 at 25°C (r is the roughness factor).

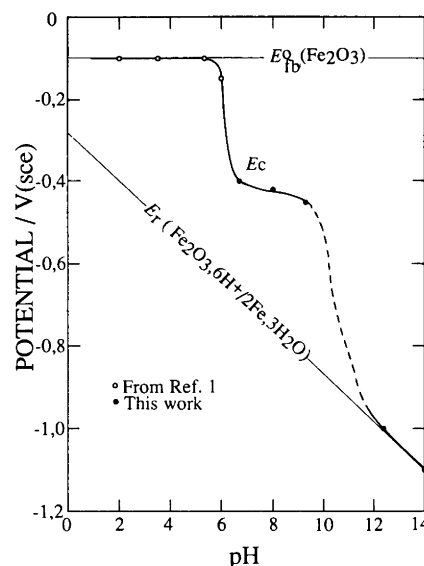


Fig. 5. the extrapolated potential (E_c) of zero inverse capacitance for passive iron electrodes in phosphate solutions of various pH at 25°C.

change may seem to occur in two partial steps at pH values slightly above 6 and 10, respectively. A corresponding change appears for passive titanium, but is not fully accomplished over the normal alkaline range.^{19,20}

Surface charges. The values presently obtained for σ'_m (or $r\sigma'_m$) from capacitance data and use of eqn. (2) roughly average to $r\sigma'_m/\mu\text{C cm}^{-2} = 40 \pm 20$. This compares reasonably with previous results for acidic phosphate solutions.¹ The determination is rather unprecise, however, and needs to be improved.

For the surface charge density on the oxide at the oxide/solution interface of a passive metal electrode under stationary conditions (σ'_s), the insulator model yields:^{19,20}

$$\sigma'_s = -\sigma'_m + C_H(E_b - E_{fb}^0) \quad (3)$$

where C_H is the Helmholtz capacitance of the electrode. Using $18 \mu\text{F cm}^{-2}$ for C_H ,¹ eqn. (1b) for E_b , -0.1 V(sce) for E_{fb}^0 (Fig. 5) and the above noted result for σ'_m , one obtains $r\sigma'_s/\mu\text{C cm}^{-2} = -40 - (3 + 1.1 \text{ pH})r \pm 20$.

Dielectric constant. The effective dielectric constant or relative permittivity of a stationary passive film should be given by:^{1,19,20}

$$\epsilon = a \sigma'_m / \epsilon_0 \quad (4)$$

where a is the anodization ratio of the passive metal electrode under stationary conditions, and ϵ_0 is the permittivity of free space. With a previously determined average value of 25 \AA V^{-1} for a over the alkaline range,¹⁴ and with the above determined value for σ'_m , eqn. (4) yields $r\epsilon = 114 \pm 57$. For iron oxide crystals, ϵ increases strongly with

their Fe(II) content, viz. from about 10 for Fe₂O₃ to about 250 for Fe₃O₄.²¹ Hence, the passive film on iron may appear to have an appreciable Fe(II) content. This agrees with results of surface analytical studies.^{16,17}

Discussion

The passive iron electrode is complicated. One difficulty is that the preparation of a test electrode may affect its subsequent behaviour.^{16,17} In the present work, this has been sought overcome both by a standardized pretreatment and by a long stabilization period (20 h) prior to the measurements. However, from comparisons especially with previous capacitance data,^{3,11,14,16,17,22} the roughness factor may seem to be rather high (perhaps 2–3) for our electrodes. This must be considered in extracting values for j_p , C , σ'_m , σ'_s and ϵ from our data. The way in which this factor enters is described in the presentation of results above.

Most capacitance data on stationary passive iron electrodes show a linear C^{-1}/E' relationship. In acidic phosphate solutions,¹ the C^{-1}/E' lines have a pH-dependent slope and extrapolate to a pH-independent potential of zero inverse capacitance (E_c) close to the zero-charge flat-band potential (E_{fb}^0) of Fe₂O₃. In alkaline phosphate solutions, however, E_c falls with increasing pH and approaches the reversible Fe₂O₃, 6H⁺/2Fe, 3H₂O potential at high pH (Fig. 5). An understanding of this behaviour, which to some extent is shared with passive titanium electrodes,^{19,20} has recently been sought in model studies.⁶ More clarification is needed, however, and this is a challenge for future work.

For passive iron in acidic phosphate solutions, a slightly modified Cabrera-Mott treatment of the initial polarization of metal oxidation yields values from 3.2 to 3.6 for the triple product zfg of charge-transfer valence, field factor and site factor, respectively.¹ With 25 Å V⁻¹ as an average for the stationary anodization ratio over the alkaline range,¹⁴ the same treatment yields about 3.7 for this triple product from the initial polarization data of the present work. As previously discussed,¹ this may suggest $z = 2$ (rather than 3) for ions being transferred at the metal/oxide interface of the passive iron electrode. The question arises, however, as to whether the simple Cabrera-Mott treatment is sufficiently valid for such a complex case as the passive iron electrode (where ϵ may vary with distance or depth in the passive film, and the anodic Faraday current may be shared between the metal-iron transfer and various other oxidation processes in or on this film^{2,16,17,22,23}).

From the general theory of passive metal behaviour by Vetter^{7,8} (see also the Appendix of Ref. 19), it appears that the pH-independence observed for the stationary passive

current of iron dissolution in alkaline solution (Fig. 2) most likely reflects rate control by transfer of some uncharged iron species at the oxide/solution interface of the passive iron electrode. This may be species such as FeO(OH), FePO₄ or similar species. The pH-dependence observed at low pH has correspondingly been ascribed to control by transfer of some uni-positive species.⁸

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