Kinetics of Charge and Discharge of the Film on Superpassive Iron

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Dedicated to Professor Walter Feitknecht

Summary

In well-inhibited solutions, passivated iron acquires a small charge when anodically polarized some-what above the potential of incipient activation. The rates of charge and discharge have been determined potentiostatically, and have been found to follow a kinetic equation derived on the assumption of an activation-controlled process with an activation energy which varies with the extent of charge or discharge. The results are interpreted by application of the concept that the characteristics of the passive state derive from a small concentration of positive holes injected into the film. When the potential is suddenly lowered, the high mobility of electrons permits them to set up a space charge by which the activation energy for the slower influx of protons is initially diminished.

In the study of passivation and activation of iron in inhibiting solutions of the molybdate ion, it was observed that the transition between active and fully passive states proceeds in clearly defined steps.[1] The potentials at the inflections designated as X_1, X_2, and X_3 were shown to have a definite *p*H dependence. In addition, when anodic polarization was carried to 200 mv (or more) noble to the potential, X_3, of incipient activation, a state was produced which had the property of reacting with iron (II) ions in solution to produce a pseudo-equilibrium potential on open circuit. The value of this potential was shown to be a function of *p*H, $p\mathrm{Fe}^{++}$ and *p*Mo-VI, and its discharge to potentials only slightly noble to X_3 involved a charge which is very small in relation to the charge represented by formation of the passivating film itself.

When the "supercharge" was removed by lowering the polarizing potential, rather than by reaction of the film with iron (II) ions on open circuit, it was clearly seen that the rates of charge and discharge are much too slow to correspond merely to an electrostatic capacitance arising from displacement of electronic charge alone. Hence the kinetics of these processes has been investigat-

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[1] G. H. Cartledge, *Corrosion 24* (1968) 223.

ed. The results demonstrate that the superpassive state exhibits a kind of capacitance which depends upon the chemical properties of the film, as well as upon electronic displacement. Unlike the electrolytic capacitors, however, the passive film has a conductance which is predominantly electronic, so that it is unable to sustain high voltage drops because of evolution of oxygen. The kinetic results can be interpreted on the basis of the suggestion that the essential feature of the passive state is the presence in the film of electron holes, with the resultant electronic conductivity, increased ionic potential and low solubility characteristic of iron while it is passive.

Experimental

The Armco iron electrodes were similar to those used in previous work.[1] Polarization was effected by an electronic potentiostat (Fair Port Instruments, Inc., Model 610), to which was added a second reference-cell circuit in order to allow the polarizing potential to be switched quickly. The current recorders had a full-scale response of less than 0.5 sec (Moseley "Autograf", Model 680 and Hewlett-Packard, Model 7100B). In order to minimize the steady-state anodic currents, measurements were made in solutions of several inhibiting electrolytes in the *p*H range of 4.2 to 6.4 and 24°. The electrolytes were $KTcO_4$, $(Na, H)_2MoO_4$, and pertechnetate buffered by $10^{-2}f$ acetate, phthalate or phosphate, and freed of oxygen by a stream of helium. Polarizations were started by inserting the electrode immediately after its activation in 1-N HCl. The potential was set variously at a value 75 mv noble to the activation potential or, in other experiments, at the higher potential from which the rate of discharge was to be measured. Disturbance by iron ions in solution was avoided by draining and refilling the cell after the current fell into the passive range. In certain experiments, the potential was carried almost to the value for evolution of oxygen and then lowered in steps, in order to confirm the previous observation[1] that very little cathodic current can be detected until the potential has been lowered to within about 200 mv of the activation potential. This result was confirmed in both pertechnetate (phthalate and phosphate buffers) and molybdate solutions, hence charge and discharge were generally conducted over a 200-mv range, the lower potential being 75–100 mv noble to the activation potential (X_3 in molybdate solutions and the calculated Flade potential in the others). The reversible potential for reduction of the pertechnetate ion is so near the Flade potential at the *p*H chiefly used that formation of $Tc(OH)_4$ in the film was negligible under the chosen conditions.

For the analysis of the data, the current and integrated charge were read from the chart. A chart speed of 0.1 to 0.2 in/sec permitted adequate accuracy after lapse of about 0.5 sec. In computing the charge passed during the charging step, the observed currents were corrected by subtraction of the approximately steady current ultimately reached: that is, in the charging curves the current density $j - j_\infty$ is plotted. In the discharge, however, no such correction was applied, the end point being taken when the cathodic current became immeasurably small.*

* In the beginning of the study, the discharge also was carried to the steady state on the anodic side. Annoying oscillations occur as j approaches zero, however, and since the correction at worst is very small it was later dropped. The kinetic analysis is unaffected by this procedure, only the numerical values derived from the data being slightly altered.

Results and Discussion

The molybdate system proved particularly advantageous for this study because it combines strong inhibitory action with a considerable buffering capacity at *p*H values 5.3 to 5.7. The pertechnetate ion leads to anodic passivation with passage of less charge, but has no buffer action in itself. Most measurements were therefore made in molybdate or buffered pertechnetate solutions; in the latter, some effectiveness of inhibition was sacrificed owing to competing adsorption of the buffering anions. The reversible potential of the Cr(VI–III) couple is so noble that reliable determinations in this medium cannot be made in the region of potential that is suitable with the other inhibitors. A few measurements at higher potentials, however, gave entirely similar results.

In the presentation of the results, j (or $j - j_\infty$) will be the current density in $\mu a/cm^2$, based on the projected area, q will be the integrated charge in $\mu C/cm^2$; the time, t, is in seconds. When a graph of q vs. log t was made, it became apparent that the discharge process follows a rate law very similar to that found for the ion-exchange of $^{51}Cr(VI)$ between the passivated film and electrolyte.[2]

The kinetic equation for that case was based on the assumption that the rate is controlled by an activation energy which increases linearly with the extent to which the process has occurred: that is,

$$\Delta H^{\neq} = \Delta H_0^{\neq} + rq. \qquad (1)$$

Such a relationship is well-known in certain measurements of the heat of adsorption.[3] In the former case, q represented the amount of ^{51}Cr removed from the film and it turned out that r remained constant throughout the process. If the same assumption is applied to the present experiment, the corresponding rate equation becomes:

$$j = j_0 \left[\frac{q_\infty - q}{q_\infty}\right]^n \exp\left[-\frac{rq}{RT}\right]. \qquad (2)$$

Here j_0 is the initial current density ($q = 0$) and q_∞ is the total integrated charge as $j \to 0$. The values of j_0 and q_∞ may be closely approximated from a graph of log j vs. q, hence the value of r is calculable. Provisionally, with q in $\mu C/cm^2$ and R in cal/mole-degree, r will be in the units cal-cm^2/mole-μC. The depletion factor $\left[\frac{q_\infty - q}{q_\infty}\right]$ with a possible order n is required to bring the rate ultimately to zero, in accordance with the experimental procedures.

From numerous experiments it became evident that Equation 2 is applicable if r is permitted to decrease

[2] G. H. Cartledge and Dieter H. Spahrbier, *J. Electrochem. Soc. 110* (1963) 644.

[3] See, e.g., J. J. F. Scholten and P. Zwietering, *Trans. Faraday Soc. 53* (1957) 1363.

during the process and $n = 1$. It developed that the decrease in r is accurately expressed by the relation:

$$r = r_0 \exp(-lq), \tag{3}$$

in which l is a determined constant in $cm^2/\mu C$. This exponential variation of r with q may be seen in Figures 3 and 4. The complete rate equation therefore becomes:

$$j = j_0 \left[\frac{q_\infty - q}{q_\infty}\right] \exp\left[-\frac{r_0 q}{RT} \exp(-lq)\right]. \tag{4}$$

The ratio j_0/q_∞ is the rate constant for a given set of conditions and would include the pH factor, if present.

From many measurements in the molybdate system over the narrow range of suitable pH values of 2.5 units it has been found that any variation in j_0/q_∞ associated with pH is too small to be isolated from other variables. Most measurements have been made, therefore, between 5.4 and 5.7, and the applicability of Equation 4 to the discharge process has been fully confirmed. The same equation holds also for the charging process after the film has been once formed. While the electrode is being initially passivated, however, the charge associated with this process predominates so overwhelmingly over the supercharge that the value of l is either abnormally small or even zero. For the latter case, the so-called "logarithmic rate law"

$$q = m \log(nt + 1) \tag{5}$$

describes the behavior until the steady-state current density is approached and the depletion becomes dominant. These relationships may be illustrated by considering a series of measurements of both charge and discharge in a buffered pertechnetate solution.

Table I. Kinetic Parameters for Calculation of Filled Circles in Figures 2 and 3

	j_0	q_∞	r_0	l	j_0/q_∞
a_1	119	3500	0.655	0	0.034 0
a_2	4.9	900	0.58	0	0.005 44
a_3	0.420	3.90	360	0.256	0.107 7
b_1	0.55	61.7	90	0.0431	0.089 1
b_2	0.424	4.24	600	0.419	0.100
c	23.0	1852	0.824	0	0.012 4

Figure 1 shows the sequence of successive charge and discharge processes. The chosen range of potentials satisfies the condition that the lower value is safely above the Flade potential and the potential for a significant rate of reduction of the pertechnetate ion. The 200-mv span is sufficient to cover essentially the complete cathodic process, as shown in several reductions from higher potentials in 50-mv steps. Figures 2 and 3 represent the curves for the charging and discharging processes, respectively, and Table I gives the values of j_0 and q_∞ upon which the calculated values of r_0 and l are based. The filled circles in all curves represent values of j calculated from Equation 4 by use of the numbers in the Tables. The agreement is all that could be desired. It is seen, also that the value of l is zero in steps a_1, a_2, and c, in all of which new film was being formed, whereas a normal value of l is found for step b_1, in which the film was being merely recharged to the higher potential. Further, the rate constants for the two discharge steps a_3 and b_2 are similar very. The values of q_∞ for a_1, and a_2 are seen to be far greater than those for the subsequent discharge and recharge processes.

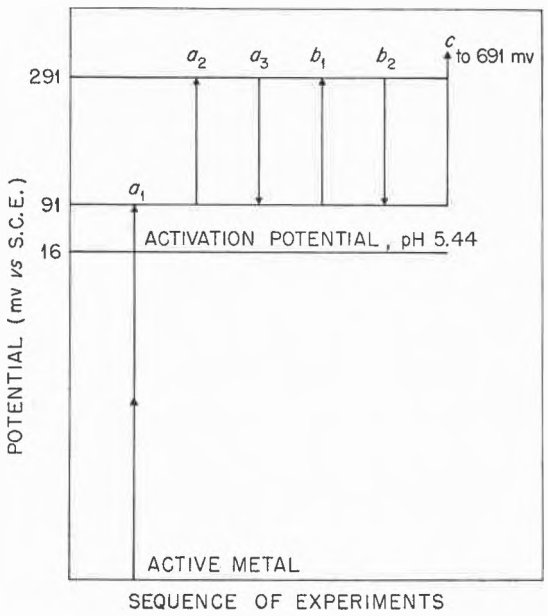

Fig. 1. Sequence of polarizations in $2.5 \times 10^{-3} f$ $KTcO_4$ in $10^{-2} f$ phthalate at pH 5.44: formation of film and charging in a_1 and a_2. Discharge or recharge in a_3, b_1, and b_2; charge to 691 mv in c

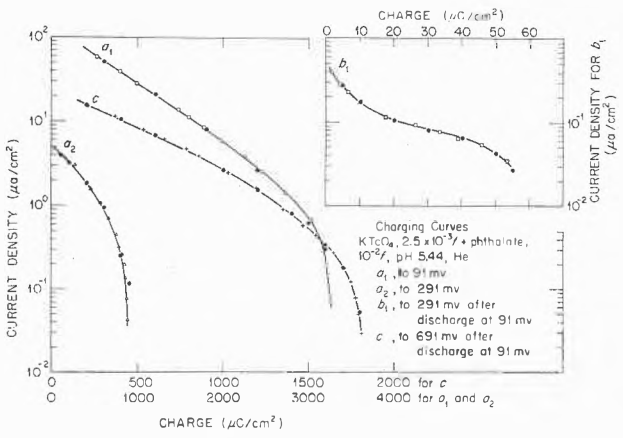

Fig. 2. Charging curves for a_1, a_2, b_1, and c. Filled circles (●) represent current densities calculated from the values of j_0, q_∞, r_0 and l shown in Table I

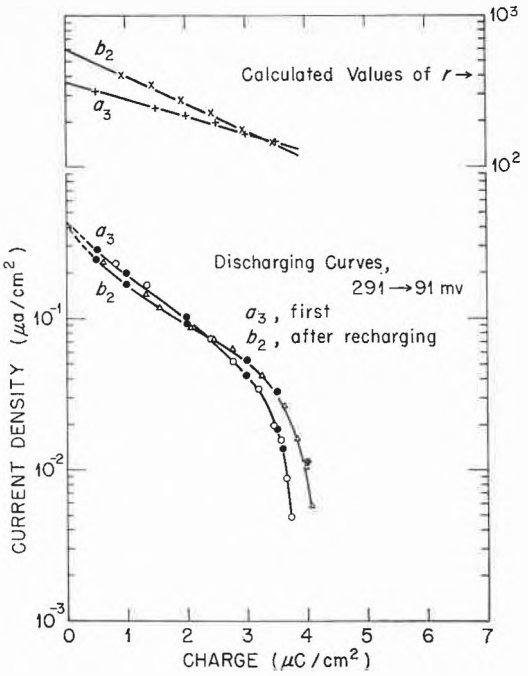

Fig. 3. Discharging curves, 291 to 91 mv for a_3 and b_2. Upper curves, values of r calculated from Equation 4

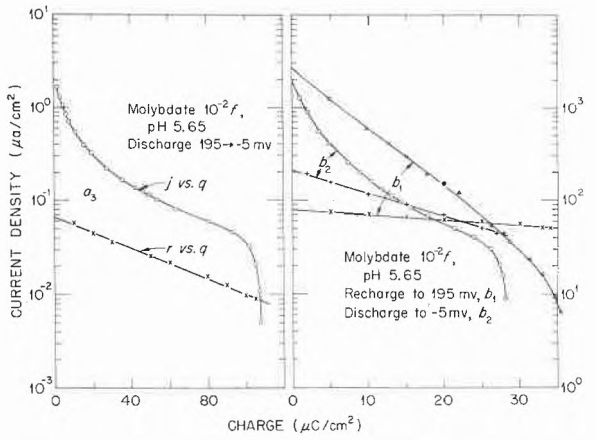

Fig. 4. Charge and discharge in $(Na,H)_2MoO_4$, 10^{-2} f at pH 5.65

Figure 4 illustrates a measurement in a molybdate solution in which the electrode was passivated at +195 mv overnight and then taken to +550 mv in order to determine, for this system, the charge associated with reduction of the potential in steps. It was again found that no more than 1 to 3 μC/cm² was required to bring the potential back to 195 mv. As shown previously,[1] anodic passivation in this inhibitor proceeds through formation of a film containing an Fe(II) molybdate species in the film, which becomes oxidized at higher potentials. For this reason, steps a_1 and a_2 (not shown) involve passage of a considerably larger charge than is sufficient in the more efficient pertechnetate inhibitor. Nevertheless, the curves in Figure 4 show that the kinetics of supercharge from −5 to +195 mv (b_1) and discharge (a_3, b_2) follows the same equation as suffices for the much thinner film in the buffered pertechnetate solution.

Table II. Kinetic Parameters for Curves in Figure 4

	j_0	q_∞	r_0	l	j_0/q_∞
a_3	1.70	112	66	0.0189	0.0152
b_1	2.59	37	80	0.0135	0.0700
b_2	1.80	30	208	0.0550	0.0600

The results of a more extensive experiment in the molybdate solution (10^{-2} f at pH 5.70) are given in Table III. In this case the active iron electrode was polarized initially at −5 mv and a surge of current passed during 1.4 minutes while the film was forming; at this time the current density had fallen to 6.5 μa/cm² and ca. 32 mC/cm² of charge had passed. The solution was renewed and this point was taken as the zero of time for the remainder of step a_1. From Table III it may be seen that the four discharge steps require only 10–20 μC/cm², the corresponding rate constants varying only between 0.113 and 0.144. Again, $l = 0$ for the film-building step a_2, and the recharging steps b_1, c_1, and d_1 require only slightly more charge than was required for discharge (24–41 μC/cm²). Further, comparison of Tables I and III shows that the values of j_0/q_∞ in the pertechnetate and molybdate systems are closely the same.

Table III. Kinetic Parameters for 10^{-2} f Molybdate at pH 5.70

Potential, mv		j_0	q_∞	r_0	l	j_0/q_∞
a_1	−5	4.80	780	1.18	0.00113	0.00616
a_2	195	5.3	800	1.21	0	0.00663
a_3	−5	3.0	20.8	151	0.0613	0.144
b_1	195	1.25	41	78	0.0299	0.0305
b_2	−5	1.70	12.6	170	0.0847	0.135
c_1	195	1.05	38.0	108	0.0303	0.0277
c_2	−5	1.20	10.6	150	0.0993	0.113
d_1	195	1.66	24.5	170	0.0473	0.0653
d_2	−5	1.41	10.2	220	0.107	0.138

The results of over fifty measurements show relations among the values of r_0, l, and q_∞ such that, after the discharge process is perhaps half complete, the complex exponential factor in Equation 4 becomes nearly constant. Thereafter the rate and integrated charge data follow rather closely a first-order course. The relation is not precise, however, since r_0, in particular, is very sensitive to errors in determining j_0 and q during the first second or two of an experiment.

Sato[4] has reported a study of the charging and discharging of the superpassive film on iron in an alkaline

[4] Norio Sato, *Electrochim. Acta 1967*, 1135.

borate medium and his curves show the same log j vs. q behavior as is here observed for the first part of the discharge. Unfortunately, however, his graphs seem to indicate that his measurements were not taken to sufficiently low current densities to bring out the complex behavior represented by Equation 4. Hence the interpretation based on "proton sorption-desorption" is not entirely adequate. He does show, however, the significance of the very small charge for the superpassive state.

The present results are capable of being interpreted on the basis of the model of the superpassive state postulated in the work on passivation and activation in the molybdate system.[1] It was proposed that, at potentials above that for completion of the oxidation of the film, a few electrons are drawn from the film, leaving positive holes, ⊡. This raises the average charge of the cations and, correspondingly, their average ionic potential (ionic charge over radius). Also, since there is good evidence for assuming the film to contain protons in some form (FeO · OH, for example), the effect of the polarization will be to displace protons toward the aqueous phase. The particular form in which the protons are present is not necessarily FeO · OH, but, for simplicity, this compound may be used to illustrate the assumptions. On this basis, the processes of charge and discharge may be represented as follows:

$$\text{(Discharged) FeO·OH} \rightleftarrows \text{FeO·O} \boxdot + e^- + H^+ \text{ (Charged)}$$

Such a charging process is seen to be equivalent to that which Professor FEITKNECHT and his associates have shown to occur in the oxidation of certain of the lower hydrous oxides.

The essential feature of the hypothesis here proposed rests on the presumably large difference in the mobility of electrons and protons in the electronically conducting film. When the potential of the charged film is suddenly lowered, as in these experiments, the film itself is not destroyed nor is the electrode activated. At the first moment, however, electrons move into some of the holes, only a few being required to establish a space charge that has two effects: firstly, the access of more electrons is hindered by the field and, secondly, the activation energy for return of protons to the film is decreased. If the overall rate is then determined by the slower migration of protons, the activation energy will start with a minimum value and will increase as the field is progressively neutralized. The potentiostat controls the potential at the metal, but the change in the activation energy is determined by another varying potential, Φ, which is set up in the film so long as the discharge is incomplete.

These considerations make it plausible to correlate the changing activation energy, as empirically determined and expressed in Equations (1) and (4), with its equivalent in the terms of electrochemical kinetics. Thus, in Equation (1), $\Delta H_0^{\neq}$ is the activation energy at the first moment after the potentiostat is switched to the lower potential. This value increases as discharge proceeds, and

$$\frac{d(\Delta H)}{dq} = r. \tag{6}$$

For a cathodic process under activation control, the corresponding expression is

$$\frac{d(\Delta H)}{dq} = -\alpha z F \frac{d\Phi}{dq}. \tag{7}$$

$\frac{d\Phi}{dq}$ being a negative quantity. Hence we have

$$r = r_0 \exp(-lq) = -\alpha z F \frac{d\Phi}{dq} \tag{8}$$

and, for the initial point ($q = 0$),

$$r_0 = -\alpha z F \left(\frac{d\Phi}{dq}\right)_0. \tag{9}$$

Since $dq/d\Phi$ is in the form of a capacitance associated with the charge within the film, the result shows that r_0 is related reciprocally to this capacitance, and the decrease in r during discharge represents a corresponding increase in the capacitance as the charge is progressively neutralized. (For numerical calculations the values of r or of r_0 previously given in cal-cm²/mole-μC have to be multiplied by the joule-calorie equivalent, 4.18.)

We may estimate the magnitude of the initial capacitance for the experiments summarized in Table III from the average value of r_0 for the discharge steps. Multiplication by 4.18 gives 7.23×10^8 microjoules-cm²/mole-μC. If αz is taken as 0.5 and F as 10^5, we obtain $70\,\mu F/\text{cm}^2$. Furthermore, Equation (8) may be integrated between limits corresponding to the initial and final states ($q = 0, \Phi = \Phi_0$ and $q = q_\infty, \Phi = \Phi_\infty = 0$). One obtains

$$\frac{r_0}{l}\left\{1 - \exp(-lq_\infty)\right\} = \alpha z F \Phi_0. \tag{10}$$

For the discharge steps in Table III, the average values of r_0/l and lq_∞ are 8360 joules/mole and 1.13, respectively. With $\alpha z F = 5 \times 10^4$, we thus find $\Phi_0 \simeq 0.11$ v, which may be compared with the 0.2 v by which the potential of the electrode was lowered.

It may be suggested tentatively that the observed decrease in r during discharge arises from the influence of the induced field on the optical polarizability of the film. The increase in the average cationic potential and expulsion of protons during the charging process lead to both a "tightening" of the lattice and a loss of the polarizability associated with the OH dipoles. Both effects cause a lowering of the polarizability, to which the dielectric constant is related. These changes are

reversed during the process of discharge. It may be significant that REDDY, RAO, and BOCKRIS[5] reported the refractive index of the film on passive nickel to decrease rather abruptly when the potential was raised beyond the passivating potential. Since the values of j_0/q_∞ for different conditions gave no indication of any significant dependence on *p*H, it may be concluded that the aqueous side of the film is so amply saturated with the source of protons that their concentration is not a limiting factor in the rate. The source could be either $(H_3O)^+$ or H_2O adsorbed on the film.

The experiments may be taken to support the view that the peculiarities of the superpassive condition of iron are, in fact, associated with the small amount of charge maintained by the high applied potential or by a vigorous electron acceptor like HNO_3 or OsO_4. Once this supercharge has been neutralized, further addition of electrons reduces the cations to the Fe(II) state and passivity is lost. The Flade potential, or X_3 in the molybdate system, would then represent the potential at which this occurs. In contrast to some other views, the suggested picture of the passive iron electrode is not one of equilibrium, but of tension—a condition that involves both the electrical and chemical properties of the film. That such metals as aluminum, titanium, and zirconium are naturally passive under atmospheric conditions may similarly be due to the fact that their oxide lattices already have a high interionic field strength and consequent low solubility, without withdrawal of extra electrons beyond those corresponding to a normal, stable valence.

[5] A.K.N. REDDY, M.G.B. RAO and J.O'M. BOCKRIS, *J. Chem. Physics 42* (1965) 2246.

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