JOURNAL OF APPLIED ELECTROCHEMISTRY 20 (1990) 26–31

Mechanism of enhancement of the corrosion of steel by alternating currents and electrocatalytic properties of cycled steel surfaces

M. L. MATEO, T. FERNANDEZ OTERO

Departmento de Ciencia y Tecnologia de Polimeros, Facultad de Quimica, Universidad del Pais Vasco,
Apdo 1072, 20080 San Sebastian, Spain

D. J. SCHIFFRIN

Wolfson Centre for Electrochemical Science, Chemistry Department, The University,
Southampton SO9 5NH, UK

Received 8 February 1989; revised 7 April 1989

The effect of potential cycling on the growth of oxide layers on steel is analysed. It is shown that the redox reactions in the oxide layers formed are diffusion controlled and it is proposed that the transport of OH^- is the limiting step of growth. The relationship of these results to ac corrosion is discussed and it is shown that alternating currents flowing through structures can accelerate the corrosion rate if the potential excursion encompasses the reduction of an 'inner' oxide layer, not only by the growth of hydrated oxide layers, but also by the observed enhancement of the electrocatalytic properties towards oxygen reduction of the oxide layers formed on cycling.

1. Introduction

It was considered that alternating currents flowing through structures have little influence on their rates of corrosion unless a significant degree of rectifiction occurs [1]. The origin of this commonly held belief is the need to have a net transfer of charge between cathodic and anodic sites for corrosion to occur. Unfortunately, not much work has been carried out to study these problems. Chin *et al.* [2, 3] have studied the acceleration of the corrosion of steel by alternating currents and have proposed that these effects are due both to the breakdown of passivity and to the shift of the average potential of the sample during the ac cycle. The acceleration of the corrosion of underground electrical distribution systems has been considered to be caused by alternating currents [4], although a systematic treatment of the electrochemical aspects of these effects is still lacking. The previous literature on corrosion has been reviewed [5].

The practical situations where the understanding of these problems is of importance is in the corrosion behaviour of pressure tubes of hydroelectric utilities and in transmission lines. In the former case, it is almost impossible to isolate the ground of the generators from the pressure tubes and, therefore, the ground connection of the whole plant will inevitably involve the latter. This is a consequence of the usually very large area of contact of the pressure tube with ground, even when the pipe is encased in cement, because the impregnation of the whole structure with water can readily occur. Thus, any imbalance in the phases of the generators will lead to large ac currents to ground and a significant part of these currents can be dispersed through the water-bearing pressure tube.

The purpose of the present work is to analyse the influence of cyclic polarisation on corroding metals. This is of importance for two reasons: (a) to find out under what conditions the presence of superimposed ac currents can affect the corrosion rates by altering the protective nature of the corrosion products, and (b) to relate the information available on the electrochemical properties of the hydrous oxide layers extensively studied by Burke and coworkers [6–12] to the electrocatalytic properties of oxidized iron surfaces towards oxygen reduction, which is the usual cathodic depolarization reaction in natural waters.

2. Experimental

Cyclic voltammetry has been used as the technique for establishing the formation and growth of oxide layers. This technique is useful since a pseudo-capacitative peak is observed when a layer undergoes a redox transition, and a peak in the corresponding linear sweep voltammogram is indicative of both the nature of the oxide present and of its thickness.

A conventional three-electrode cell was employed. All the potentials were referred to the saturated calomel electrode, which was connected to the cell via a salt bridge containing the same solution under study, in order to avoid chloride contamination. The counter-electrode was a platinum flag immersed in the solution under study. The working electrode consisted of a

0021-891X/90 $03.00 + .12

Table 1. Percent composition of the steel used

C	*Si*	*S*	*P*	*Mn*	*Cr*	*Ni*	*Mo*
0.033	<0.1	0.015	0.018	0.25	<0.02	<0.02	<0.05

steel bar which was included in a cold mounting epoxy-resin support (Struers, Denmark). Electrical contact was established by soldering a copper wire to the sample. The sides of the sample were abraded with 600 grade abrasive paper before inclusion and the exposed surface was abraded with several grades of silicon carbide paper, finishing with 1000 grit. With this sample preparation technique no significant crevice corrosion effects were observed. Merck KOH (AR grade) was employed to make the solutions and the water was distilled from alkaline $KMnO_4$. The composition of the steel studied is shown in Table 1. The potentiostat used was a Wenking ST72 and the signal generator was a Wenking VSG 72. The voltammograms were recorded using a PL4 J.J. Lloyce Instrument (England) X–Y recorder.

3. Results

Alkaline solutions were chosen to minimise the effects of iron species dissolving in the solution and thus allow for the use of a simple electroanalytical technique to study the elementary steps of iron incorporation in surface layers of corrosion products and their effect on the reduction of oxygen. Figure 1 shows the influence of cycling on the voltammetric response of a steel electrode in alkaline solution. The growth of layers of corrosion products by alternating potentials results in new redox reactions which are characteristic of the film of corrosion products formed. Although for simplicity the experiments have been carried out in alkaline solutions, the results are easily extrapolated to neutral solutions (see below).

Four main oxidation and reduction peaks (E_1, E_2, E_3 and E_4) can be observed. Peaks E_1 and E_4 are seen to remain constant, whereas the oxidation and reduction waves E_2 and E_3 increase with cycling. This behaviour has already been observed by Burke and coworkers for a variety of metals (Ir, Pt, Mn) [6–9] and is also reported to occur on iron [10–12]. A significant characteristic of the influence of cycling is the visual observation of the growth of an oxide layer, termed a hydrous oxide layer by Burke and coworkers [6–12]. This layer displays electrochromic properties related to the processes occurring at E_2 and E_3. If the electrode is left cycling for a long period of time (several hours), the hydrous oxide layer becomes too thick and easily detaches itself from the metal and a new layer replaces it, continuing the growth and the corrosion of the material. Thus, although the ferric oxides/hydroxides are very insoluble in alkaline solutions, corrosion can proceed by virtue of the mechanism described above.

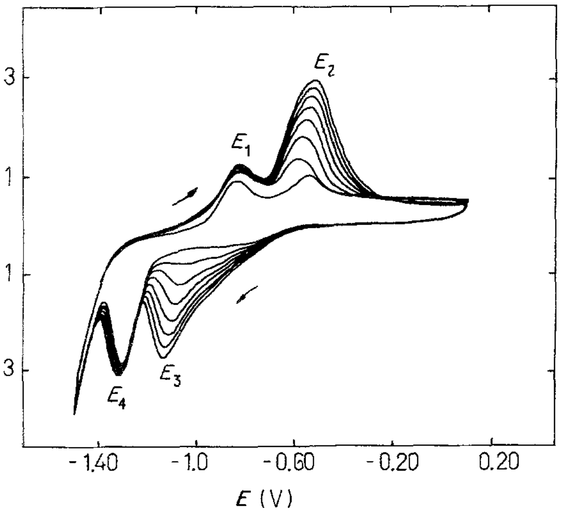

Fig. 1. Repetitive cyclic voltammetry for a steel electrode in 0.05 M KOH between the potential limits of −1500/100 mV; sweep rate is $0.05\,V\,s^{-1}$.

The rate of growth of the hydrous oxide layer is dependent on the rate of change of the applied potential, as is shown in Fig. 2. Faster sweep rates result in a lower growth per cycle; qualitatively, this is what should be expected since the time spent per cycle at the growth potentials decreases with an increase in sweep rate. The peak heights of the hydrous oxide layer processes (E_2 and E_3) do not increase linearly with sweep rate as would be expected for a surface layer transformation [13]. At low sweep rates, the peak current, i_p, is linearly dependent on $v^{1/2}$ (v is the sweep rate), as shown in Fig. 3, whereas i_p becomes proportional to v at high sweep rates.

Figure 4 shows the voltammetric response of the steel electrode in the presence of oxygen. The reduction potential for oxygen is seen to shift in the positive direction when the hydrous layer is grown. For comparison, Fig. 5 shows the voltammetric response in the absence

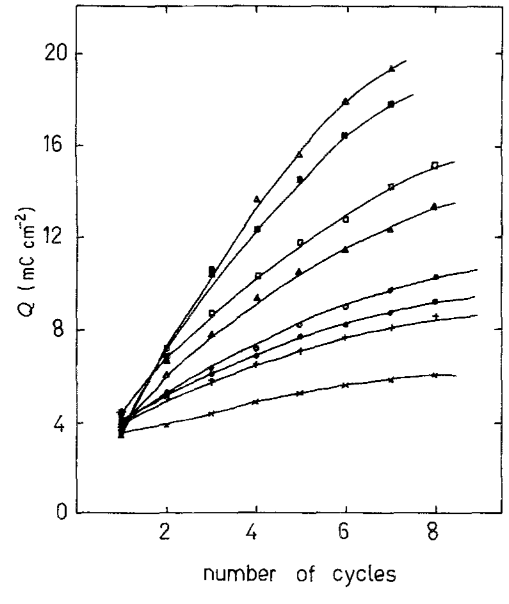

Fig. 2. Dependence of the charge accumulated in the hydrous layer during the oxidation cycle on the number of cycles for a steel electrode in 0.1 M KOH; potential limits of −1500/100 mV. Sweep rates: △ 3, ■ 5, □ 10, ▲ 20, ○ 50, ● 100, + 200 and × 500 $mV\,s^{-1}$.

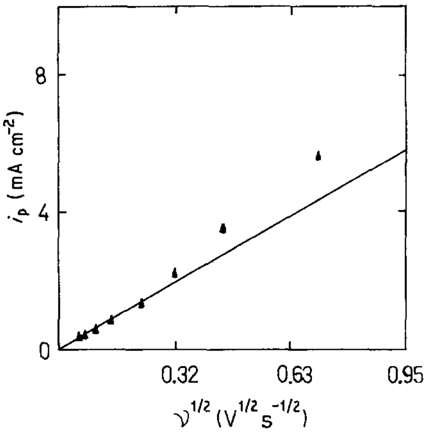

Fig. 3. Sweep rate dependence of the peak curent at E_2. The measurements were taken for an electrode cycled four times and the conditions were the same as for Fig. 2.

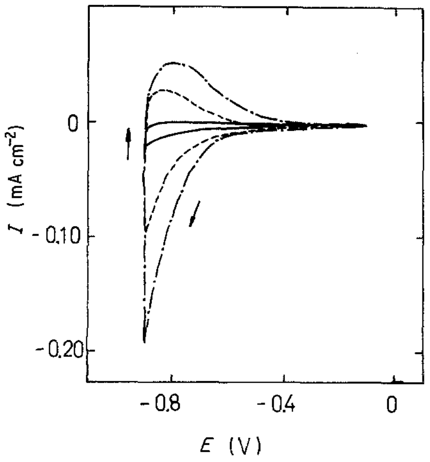

Fig. 5. Same conditions as in Fig. 5, but in a deaereated solution.

of O_2 and Fig. 6 shows the oxygen reduction currents corrected for capacitative oxide contributions.

Figure 7 shows the dependence of the peak currents for O_2 reduction, corrected for the oxide reduction currents, as a function of the square root of sweep rate. The uncycled electrode follows the classical prediction for cyclic voltammetry, but the electrodes with hydrous layers grown show significant deviations from this behaviour.

4. Discusion

4.1. *The growth of the hydrous oxide layer*

The mechanism of growth of the unusual peaks E_2 and E_3 has been discussed in the literature [4, 6] and understanding them is essential in order to predict the long term corrosion effects of ac currents on steel. Figure 1 clearly shows that a steel structure which has ac potentials imposed on it runs the risk of very rapid deterioration. Note that the peaks E_2 and E_3 do not grow if the potential is cycled up to a potential less negative than that corresponding to wave E_4, that is, the growth of the hydrous oxide layer occurs as a result of the electrochemical reactions at potentials more negative than -1.25 V against the SCE. There has been some discussion regarding the nature of the reduction process at E_4 [10–12]. As mentioned above, the occurrence of this process appears to be essential for the growth of the hydrous oxide layers. Burke and Murphy [10] proposed that this process corresponds to the partial reduction of Fe_3O_4 according to the reaction

$$Fe_3O_4 + 2H^+ + 2e^- \longrightarrow 3FeO + H_2O \quad (1)$$

which has a standard potential of $E^0 = -0.197$ V. It was proposed that the FeO formed is incorporated in the hydrous layer in the subsequent oxidation. However, the reaction at E_4 has the characteristics of a nucleation process [14] which is most probably related to the reduction of a mixed oxide layer close to the metal surface (the compact oxide layer in Burke's terminology). Since the density of iron oxides is much lower than that of metallic iron, the full reduction of an oxide will necessarily result in the nucleation of 'voids', that is, regions where the reduction has started and left sections of the lattice void of O^{2-} ions. At the end of this reduction process, a completely distorted and consequently highly reactive Fe surface lattice will remain.

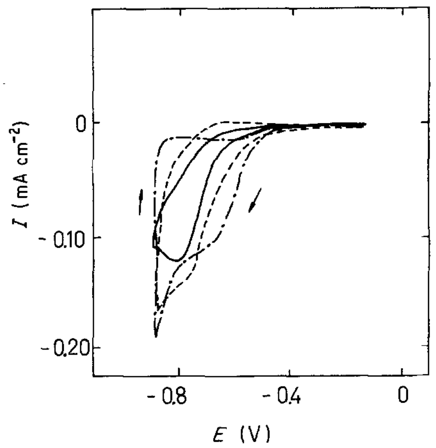

Fig. 4. Cyclic voltammetry for a steel electrode in O_2 saturated 0.1 M KOH between $-900/-100$ mV at a sweep rate of 0.01 V s^{-1} for different thicknesses of the hydrous oxide layer grown by electrode cycling between $-1500/100$ mV: (———) uncycled electrode; (– – –) 12.8; (–·–·–) 14.6 mC cm^{-2}. The negative limit was chosen sufficiently positive to avoid further growth during the experiment.

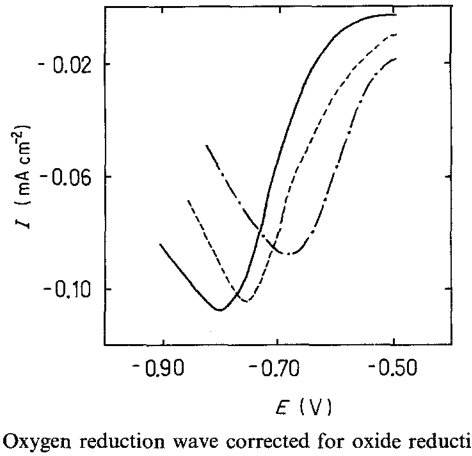

Fig. 6. Oxygen reduction wave corrected for oxide reduction currents for different thicknesses of the oxide layer. Conditions as in Fig. 4.

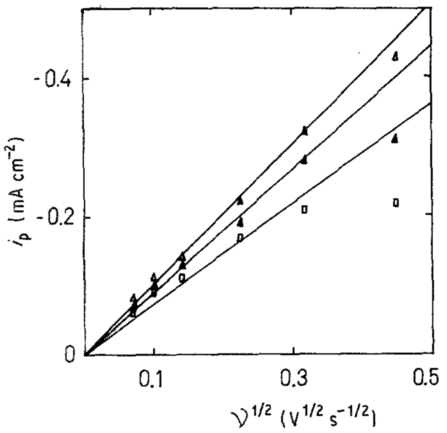

Fig. 7. Sweep rate dependence of the oxygen reduction peak current for the results corrected for the oxide reduction currents (Figs 4 to 6); △ 0, ▲ 12.8 and □ 14.6 mC cm^{-2}.

The hydrogen evolution reaction is observed at more cathodic potentials and it is expected that the incorporaton of atomic hydrogen in the metal will also aid the distortion of the surface layers of the metal. During the oxidation cycle, the process occurring at E_1 is nearly independent of the number of cycles and of the thickness of the hydrous oxide layer and, therefore, must represent the growth of an inner layer of oxide whose charactristics are independent of the outside layers. It is reasonable to consider that in this potential region, the reduction products of the previous cycle (a dispersed form of Fe on a distorted surface lattice) are reoxidized.

Peaks E_4 and E_1 are related to each other, but cycling between these two potential regions is insufficient to bring about further growth of the hydrous oxide layer, which only occurs when the anodic potential is more positive than ~0.7 V. Therefore, the growth of the new inner oxide layer occurs during the further oxidation of the metal. In each cycle, new charge is incorporated into the hydrous oxide layer since the reduction of the compact inner oxide film does not reproduce the original iron lattice, but rather leaves the reduced Fe atoms mismatched with respect to the metal lattice. It is not possible at present to decide whether the Fe resulting from the reduction of the inner oxide layer is chemically oxidized by water, or whether its oxidation, initially to $Fe(OH)_2$, is electrochemical. Either mechanism will lead to the same result, that is, new layers of atoms from the metal lattice will be incorporated into the hydrous layer during each anodic/cathodic cycle.

4.2. *Diffusional processes in the film*

The sweep rate dependence of the peak currents in E_2 and E_3 is characteristic of a diffusion controlled reaction [15]. It has been proposed that the diffusion of OH^- in the hydrous oxide layer is the slow process [7]. Since electroneutrality must be preserved, the oxidation of Fe(II) centres must occur simultaneously with OH^- incorporation, as is well known for the redox electrochemistry of conducting polymers and of thin layer electrochromic electrodes [16]. For sufficiently fast sweep rates, that is, for characteristic oxidation times sufficiently small to allow the film to be treated as a classical semi-infinite diffusional field, the classical diffusion equations for cyclic voltammetry should be approximately applicable. This is justified later on. For a reversible charge transfer reaction at 25° C, the peak current is given by [15]

$$i_p = 2.69 \times 10^5 n^{3/2} D^{1/2} C v^{1/2} \qquad (2)$$

where i_p is the peak current (in A cm^{-2}), n is the number of electrons involved in the charge transfer reaction, D the diffusion coefficient of the species responsible for the charge transfer (in cm^2 s^{-1}), C its concentration (in mole cm^{-3}) and v the sweep rate (in V s^{-1}). From the results in Fig. 3, and using $C_{KOH} = 0.1$ M, a value of $D = 6.5 \times 10^{-8}$ cm^2 s^{-1} is obtained. This is an interesting result, since the value calculated is several orders of magnitude greater than the values expected for solids, but less than two orders of magnitude smaller than the corresponding ionic diffusion coefficient in aqueous solutions. The value obtained is in agreement with the notion that the hydrous layer has a very open structure and the material is heavily hydrated.

Although it is not possible at present to decide whether the Fe(III) growth is initiated at the metal–oxide or the oxide–solution interface, both mechanisms will lead to the same i–t behaviour.

The characteristic time of the cyclic voltammetry experiments (that is, the time required for carrying out the diffusion controlled oxidation of the hydrous layer) is a few seconds at the lowest sweep rates studied. For a diffusion controlled reaction, the characteristic diffusion time is given by

$$\tau_D = x_D/D \qquad (3)$$

where τ_D is the characteristic diffusion time, and x_D is the distance over which we are computing τ_D. For the value of D previously calculated, $x_D \sim 2 \times 10^{-4}$ cm. In the present case the characteristic diffusion length will be the thickness of the film and the value obtained is reasonable considering the heavily hydrated nature of the outer layers formed.

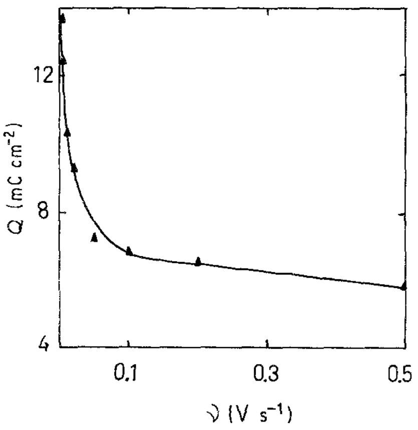

Fig. 8. Dependence of the charge accumulated in the hydrous layer during the oxidation cycle on sweep rate. The steel electrode was cycled four times between −1500/100 mV in 0.1 M KOH.

Understanding the effect of sweep rate on the redox reactions of the hydrous layer is essential in order to be able to extrapolate these results to the ac case. As discussed above, the rate of growth will be proportional to the time the system is present at the growth potential. The results in Fig. 2 clearly show that the growth of the hydrous layer is strongly dependent on the sweep rate. Figure 8 illustrates this effect: since the process is diffusion controlled, the total charge accumulated, Q, will depend on the distance the diffusion front travels within the film in the time of growth.

From this analysis, $Q \propto x_D \propto v^{-1/2}$ and a plot of Q against $v^{-1/2}$ should be linear. This is indeed the case as can be seen in Fig. 9. However, for a purely diffusion controlled reaction, the value of Q should extrapolate to zero at infiite frequency, whereas it is very clear that a limiting value of Q is observed for fast sweep rates. The data in Fig. 9 correspond to a fixed number of cycles (six in this case) and it was found that the limiting value increases with the number of cycles. This is a very interesting result since it shows two important features: (a) superimposed on a diffusion controlled process is a charge transfer reaction, the kinetics of which only become apparent at high sweep rates; (b) the limiting thickness is a function of the sweep rate and does not become negligible at fast sweep rates.

These aspects are the most important in relation to ac corrosion since the observed growth kinetics will result in long term film growths which, by themselves, are sufficient to cause rapid material deterioration by spalling of the poorly adherent layers formed. As is shown later, the growth of these layers results in a substantial enhancement of the cathodic depolarizing reaction with the subsequent increase in corrosion susceptibility. This analysis assumes uniform film growth. In practice, non-uniform effects will occur, enhancing corrosion rates.

According to the model discussed, the rate of growth of the hydrous layer will be mainly determined by the diffusion and migration of the OH^- ions through it. Thus, the amount of charge accumulated will be related to the time the system stays in the growth region, provided the potential excursions are sufficiently large to encompass the reduction of the inner oxide layer.

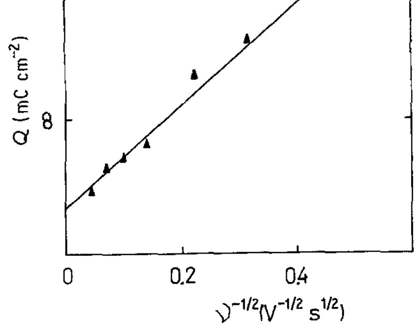

Fig. 9. Dependence of the charge accumulated after cycling on $v^{-1/2}$, to test the diffusion controlled model of film growth. The data are from Fig. 8.

4.3. *Influence of the hydrous oxide layer on the reduction of oxygen*

The reduction of oxygen is the cathodic depolarization reaction in natural waters. As shown above, when ac currents are imposed on steel the structure and nature of the layers of corrosion products are significantly altered. Previous work [17] has shown that the mechanism of O_2 reduction on an oxidized Fe surface is determined by a surface redox catalytic cycle involving the formation of [Fe(II)] sites, which are responsible for the electron transfer reactions to an O_2 molecule to give adsorbed peroxide according to

$$2[\mathrm{Fe(III)}]\mathrm{OH}^- + 2\mathrm{e}^- \rightleftharpoons 2[\mathrm{Fe(II)}] + 2\mathrm{OH}^- \tag{4}$$

$$2[\mathrm{Fe(II)}] + \mathrm{O}_2 \rightleftharpoons [\mathrm{Fe(III)}]_2\mathrm{O}_2^{2-} \tag{5}$$

$[\mathrm{Fe(III)}]_2\mathrm{OH}^-$ represents an Fe(III) centre which has a coordinated OH^- ion. OH^- coordination is required to account for the observed reaction order of the rate of O_2 reduction with respect to OH^-, which is -1. The rate determining step is the reduction of the adsorbed peroxide

$$[\mathrm{Fe(III)}]_2\mathrm{O}_2^{2-} + 2\mathrm{H_2O} + 2\mathrm{e}^- \longrightarrow 2[\mathrm{Fe(III)}] + 4\mathrm{OH}^- \tag{6}$$

and the overall value of the standard rate constant will depend on a combination of the rate constants of Reaction 6 and the equilibrium constant describing the electrochemical pre-equilibrium Reactions 4 and 5. The latter will determine the number of [Fe(II)] sites available for reaction. It is easy to see that, if for any reason the surface concentration of these sites is larger at a given potential, this should increase the rate constant for O_2 reduction and, hence, shift the polarization curve to more positive potentials. Since the hydrous oxide layer has a charge capacity much greater than the compact inner oxide layer and the Fe(III) oxide reduction occurs at more positive potentials, the reduction of oxygen should also shift to more positive potentials. The peak potential of O_2 reduction can be used as a simple comparison between the rate constants in the presence and absence of the hydrous oxide layer, since this is sensitive to the value of the overall standard rate constant according to [15]

$$E_p = E^0 - \frac{RT}{\alpha n_a F}\left[0.780 + \ln\left(\frac{D}{k}\right)^{1/2} + \ln\left(\frac{\alpha n_a F v}{RT}\right)^{1/2}\right] \tag{7}$$

where α is the transfer coefficient, n_a is the number of electrons involved in the rate determining step, k is the rate constant and n is the total number of electrons per mole of reactant. The product αn_a can be calculated from the Tafel slope for O_2 reduction and has a value of 0.42 for passive iron [17]. E'^0 is the normal potential.

Comparison of the results in Figs 4 to 6 clearly shows that, for cycled electrodes, the shift in the reduction potential of the Fe(III) oxide to give Fe(II) centres also results in a marked shift in the oxygen reduction wave. Thus, the formation of hydrous oxide layers, in this case, produces a catalytic effect on the reduction of O_2, which is bound to have a profound effect on the rate of corrosion of steel.

These effects can be readily quantified using the theory of irreversible sweep voltammetry [15]. From Equation 7, we can estimate the change in the rate constant for O_2 reduction when a hydrous layer is grown on passive iron. The shift in peak potential is related to the change in the value of k by

$$\Delta E_\mathrm{p} = -\frac{2.3RT}{\alpha n_\mathrm{a} F} \log (k^0/k') \qquad (8)$$

where ΔE_p is the change in peak potential and k^0 and k' are the rate constant for oxygen reduction for cycled and uncycled electrodes, respectively. From the results in Fig.6, $\Delta E_\mathrm{p} = 0.13\,\mathrm{V}$, which corresponds to an increase of one order of magnitude in k^0 on cycling the electrode.

It is interesting to notice that the diffusion coefficient of O_2 calculated from the dependence of the peak current on sweep rate, decreases when the electrode is cycled. For the results shown in Fig. 7, values of the diffusion coefficient for O_2 of $2.3 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ can be calculated for the uncycled electrode. For this calculation, the solubility of oxygen in 0.1 M KOH was taken from Landolt–Bornstein tables [18]. This value compares favourably with literature data of 1.95, 1.90 and $2.12 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ [17, 19, 20]. For the cycled electrode, a value of $D = 1.2 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ is obtained at low sweep rates. The decrease in D for cycled electrodes results from the lower diffusion coefficient of O_2 in the hydrous layer as compared with the diffusion in the bulk of the solution. It should be noted, however, that significant deviations from the behaviour expected for an irreversible reaction occur at high sweep rates, as can be clearly seen in Fig. 7. This is probably due either to diffusion limitations in the thick hydrous film or to the onset of a chemical limiting step, such as Reaction 5. Further work is in progress to elucidate the details of the mechanism.

From these experimental observations, it is clear that the mechanism of the reduction reaction remains the same for a cycled as for an uncycled electrode and the only change observed corresponds to the shift of the Fe(III)/Fe(II) passive film redox potential. This also explains the observed decrease in D on cycling, since the O_2 molecules must partially diffuse through the hydrous oxide before reaction, although Reaction 5 occurs throughout the film. In terms of corrosion rates, the observed increase of the value of the rate constant for the cathodic corrosion reaction will shift the corrosion potential to more positive values, and hence, increase also the corrosion rate.

5. Conclusions

The main effect of ac currents applied to steel is the formation of hydrous oxide layers that give rise to an increase in the corrosion rate due to their mechanical detachment and to the enhancement of the rate of the oxygen reduction reaction.

Acknowledgements

Miss M. L. Mateo had a studentship from the Basque Government and a visiting studentship from the British Council; T.F.O. and D.J.S. gratefully acknowledge support by the British Council and the Basque Government for exchange visits.

References

[1] U. R. Evans, 'The Corrosion and Oxidation of Metals, Scientific Principles and Practical Applications', Edward Arnold, London (1960) p.266.

[2] D. -T. Chin and T. W. Fu, *Corrosion* (NACE) **35** (1979) 514.

[3] D. -T. Chin and S. Venkatesh, *J. Electrochem. Soc.*, **126**, (1979) 1908.

[4] H. C. Robinson and J. W. Rog, *Mater. Perform.* **13** (1974) 27.

[5] S. Venkatachalam and S. G. Mehendale, *J. Electrochem. Soc. India* **30** (1981) 231.

[6] L. D. Burke and D. P. Whelan, *J. Electroanal. Chem.* **162** (1984) 121.

[7] L. D. Burke and R. A. Scannell, *ibid.* **175** (1984) 119.

[8] L. D. Burke and C. M. B. Roche, *ibid.* **129** (1982) 2641.

[9] L. D. Burke and M. J. G. Ahern, *ibid.* **183** (1985) 183.

[10] L. D. Burke and O. J. Murphy, *ibid.* **109** (1980) 379.

[11] M. E. G. Lyons and L. D. Burke, *ibid.* **170** (1984) 377.

[12] L. D. Burke and M. E. G. Lyons, *ibid.* **198** (1986) 347.

[13] S. Srinivasan and E. Gileadi, *Electrochim. Acta.* **11** (1966) 321.

[14] C. V. D'Alkaine, R. Pereiro and D. J. Schiffrin, 'The Passive Iron Electrode', Extended abstracts, 25th ISE Meeting, Brighton (1974).

[15] A. J. Bard and L. R. Faulkner, 'Electrochemical Methods', Wiley, New York (1980).

[16] G. C. S. Collins and D. J. Schiffrin, *J. Electroanal. Chem.* **139** (1982) 335.

[17] E. J. Calvo and D. J. Schiffrin, *ibid.* **243** (1988) 171.

[18] Landolt–Bornstein, Losungsgleichgewichte I, II Teil, Bandteil b, Springer, Heilderberg (1962).

[19] K. E. Gubbins and R. D. Walker, *J. Electrochem. Soc.* **112** (1965) 469.

[20] J. Jordan, E. Ackerman and R. L. Berger, *J. Am. Chem. Soc.* **78** (1956) 2979.