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A hybrid method through faradaic rectification and a.c. impedance measurements for the corrosion rate determination of metal/oxide/electrolyte systems. I. Theory

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The interference of the oxide film in corrosion rate measurements of oxide covered metals is confirmed, and is found to limit the accuracy of measurements in all d.c. and a.c. polarization methods including impedance techniques.

A new method is proposed to measure the corrosion rate in metal/oxide/electrolyte systems. It involves the use of faradaic rectification measurements in the absence of concentration polarization. The contribution of the oxide film to the measured currents and potentials are appropriately compensated and this represents a unique feature of the proposed method. Alternating current impedance values of the oxide film measured at the same frequency as that of faradaic rectification are used for this purpose.

1. Introduction

A variety of electrochemical methods based on d.c. and a.c. polarization techniques are used for determination of the corrosion rate of metal/electrolyte systems. Among the d.c. techniques, the polarization plot and polarization resistance methods are most popular [1–6]. Several variations of them have been suggested in the literature [7–11]. The a.c. techniques may be classified under the impedance diagram method [12–18], methods based on harmonic analysis [19] and faradaic rectification [20–24]. Transient methods based on open-circuit voltage decay-curve [25], exponential current pulse [26] and galvanostatic charging [27, 28] have also been shown to be useful in this regard.

In the commonly accepted model, it is assumed that corrosion is due to the occurrence of an anodic metal dissolution reaction and a cathodic conjugate reaction, distributed uniformly on the surface of the metal according to the following reactions:

$$\mathrm{M} \rightarrow \mathrm{M}^{n+} + n\,\mathrm{e}^- \qquad (1)$$

$$\mathrm{O} + n\,\mathrm{e}^- \rightarrow \mathrm{R}. \qquad (2)$$

A general expression for the current at a surface sustaining the above two simultaneous reactions in the absence of concentration polarization is,

$$i = -C\frac{\mathrm{d}E}{\mathrm{d}t} + i_{\mathrm{cor}}\{\exp[-\alpha(E - E_{\mathrm{cor}})] - \exp[\beta(E - E_{\mathrm{cor}})]\} \qquad (3)$$

where i_{cor} is the corrosion current at the corrosion potential; i is the current (cathodic current positive) at the electrode potential E; C is the double layer capacitance; $\mathrm{d}E/\mathrm{d}t$ is the rate of change of potential with time (equal to zero in the case of d.c. polarization methods); $\alpha = 2.303/b_c$; $\beta = 2.303/b_m$; b_c and b_m are the experimental cathodic and anodic Tafel slopes respectively.

All the methods shown in the above references [1–28] are essentially explained on the basis of the above model.

Although these methods are useful in systems where the metal is directly in contact with the electrolyte, they often meet with difficulties in the case of metal/oxide/electrolyte systems, especially when the oxide is a poor conductor.

In the latter systems, the oxide is sandwiched between two interfaces, namely, the metal/oxide and the oxide/electrolyte. The conjugate reactions of the corrosion couple may occur at either or

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both of these interfaces. (In certain cases, they may also occur in the bulk of the oxide but, for the purpose of simplicity, such a situation is not considered in the present analysis). Irrespective of the site of the faradaic reactions, all the electrical currents are carried across the oxide phase (especially so when the oxide film is free from pores).

Vetter [29], Evans [30], Vermilyea [31] and many others have discussed the reaction schemes for such systems.

As has been inferred by Vetter [29, 32, 33] and others [34–36], the potential drop (E) across any metal/oxide/electrolyte system is comprised of drops across the bulk of the oxide (E^{Fl}) and across the two interfaces (E^{r_1} and E^{r_2}). Thus,

$$E = E^{\mathrm{r}_1} + E^{\mathrm{Fl}} + E^{\mathrm{r}_2} \qquad (4)$$

E^{Fl} depends upon the thickness of the oxide film, whereas E^{r_1} and E^{r_2} do not.

The kinetics of any faradaic reaction occurring in such systems depend upon the potential drop across the interface at which the process takes place. Equation 3 will therefore need to be modified appropriately to suit this situation. This aspect is very often ignored in practice, due perhaps to the difficulties associated with the measurement/calculation of the individual potential components in Equation 4.

This apart, determination of the anodic Tafel slopes of oxide covered electrodes is known to be difficult [20–22]. This again seriously limits the accuracy of corrosion rate measurements in all the methods described above, except in the transient methods and the a.c. impedance, harmonic analysis and faradaic rectification methods.

The transient methods [25–28], however, imply a knowledge of actual transfer functions of the system under investigation. Hence, the computed polarization resistance will largely depend upon the type of equivalent circuit adopted to get the best fit of the theoretical and experimental curves.

On the other hand, the presence of oxide films may have quite serious implications in the a.c. methods [12–24] because of the frequency dependence of a.c. impedance of such films [37, 38]. Notwithstanding the attempts by Epelboin *et al.* [16] to show that at very low frequencies (< 1 Hz) the measured impedance is due to polarization resistance of corrosion reactions, it is well established that the impedance of many oxide films are frequency dependent even at such low frequencies [38]. The non-interference of the oxide film impedance with the measured cell impedance will therefore need to be established first before equating the measured cell impedance with the polarization resistance.

2. Statement of the proposed technique

In the present study, a hybrid technique based on faradaic rectification and impedance measurements is proposed to measure the corrosion rates of oxide covered metal electrodes. It is shown that appropriate corrections for the impedance due to the oxide film can be made, following a technique developed by Srinivasan and Bose [37]. A faradaic rectification method [20–22], modified to suit this system, is used for the measurement of the electrochemical parameters. This technique specifically eliminates the need for measurements of the anodic Tafel slope, takes into account the presence of the oxide film even during cathodic Tafel slope determination, and is most suitable for metals covered with insulating and rectifying oxide films.

The following assumptions have been made in evolving the theoretical basis for the proposed technique.

(a) The electrical field across the oxide film is uniform.

(b) The current–potential relationships for the transport of ions in the bulk of the oxide is exponential. Such a relation has a basis from elementary rate theory, as shown by Cabrera and Mott [39], and more extensively by Dignam [40] and others [32, 33, 41].

(c) A similar exponential relation is assumed for the conduction of electrons across the oxide film. Whether the mechanism of conduction in this case is by tunnelling or activation of electrons across any potential barrier, the above relation holds good because, in the former case, the probability of tunnelling is exponentially related to the applied field, and in the latter case, the energy levels of the potential barrier are distributed according to Boltzmann's law [42]. Its relevance to metal/oxide/electrolyte systems has been shown by Mayer [36] and Vijh [34, 35].

(d) The corrosion current (i_{cor}) is taken to be virtually independent of the thickness (x) of the oxide film over a small variation in x. Such variations are envisaged in the proposed technique so as to evaluate certain parameters associated with the properties of the oxide film (cf. Sections 3.2 and 3.3).[*] However, proper care should be taken during experimentation to avoid over-exploitation of this assumption.

(e) The impedances of the metal/oxide and oxide/electrolyte interfaces are independent of the thickness of the oxide phase; it is implicit here that the oxide film is free from pores. An experiment conducted on an oxide covered aluminium electrode supports this view [37].

3. Faradaic rectification method for metal/oxide/electrolyte system

In the case of metal/electrolyte systems, the corrosion reaction given by Equations 1 and 2, will occur at the metal–electrolyte interface. On the other hand, the present system offers various interesting possibilities regarding the plane of these reactions. For example, in this system, the final product of the metal dissolution reaction (Reaction 1) may be the hydrated metal ion or metal hydroxide or metal oxide. Depending upon the system under study, this reaction may take place either at the metal/oxide or oxide/electrolyte interface. This is true for the cathodic conjugate reaction (Reaction 2) also.

There are at least four possible combinations in this regard. Reactions 1 and 2 may occur either at (a) the metal/oxide interface (see 3.1.1.), or (b) the oxide/electrolyte interface (see 3.1.2.), or (c) reaction 1 at the metal/oxide interface and reaction 2 at the oxide/electrolyte interface (see 3.1.3.) or (d) reaction 1 at the oxide/electrolyte interface and reaction 2 at the metal/oxide interface (see 3.1.4.).

In all these four cases, under the influence of an a.c. signal, faradaic rectification will occur as long as the transfer coefficients of the two reactions are dissimilar. However, it is only the potential drop across the reaction plane (in case (a) and (b)) or reaction planes (in case (c) and (d)) that will be responsible for the magnitude of rectification.

Thus, faradaic rectification studies on oxide covered metal electrodes are different from oxide free metals. Besides, many metal oxides are themselves capable of rectification and can offer a finite impedance for the flow of both a.c. and rectified currents. Furthermore, many metal oxides are known to cause frequency dispersion (of impedance) at all frequency ranges, and hence may interfere with a.c. measurements in metal/oxide/electrolyte systems.

3.1. *Theory*

When an alternating voltage of amplitude V_p is applied across the electrochemical cell such that a small amplitude alternating potential $[E_p \cos(\omega t - \phi)]$ is incident across the metal/oxide/electrolyte system (Fig. 1), the current through the cell is given from Equation 3 as,

$$\begin{aligned} i &= \bar{i}+\tilde{i} \\ &= C'E_p \sin \omega t + i_{cor} \\ &\qquad \times (\exp\{-\alpha[E_1 + E_p\cos(\omega t-\phi) - E_{cor}]\} \\ &\qquad - \exp\{\beta[E_1 + E_p\cos(\omega t-\phi) - E_{cor}]\}) \qquad (5) \end{aligned}$$

where C' is the resultant of the double layer capacitances at the two interfaces as well as the capacitance due to the oxide film, and E_1 is the mean potential established spontaneously at the test electrode on the application of the alternating potential. The difference $|E_1 - E_{cor}|$ represents the 'on-load' faradaic rectification voltage developed at the test electrode, $\bar{i}$ the rectification current through the cell and $\tilde{i}$ the alternating current. Taking $E_1 - E_{cor} = \eta_1$, Equation 5 can be rewritten as

$$\begin{aligned} \bar{i}+\tilde{i} &= C'E_p \sin\omega t + i_{cor}(\exp\{-\alpha[\eta_1 \\ &\qquad + E_p\cos(\omega t - \phi)]\} \\ &\qquad - \exp\{\beta[\eta_1 + E_p \cos(\omega t - \phi)]\}). \qquad (6) \end{aligned}$$

Noting the identity with the Fourier expansion,

$$\exp(Z\cos\omega t) = I_0(Z) + 2\sum_{k=1}^{\infty} I_k(Z)\cos(k\omega t)$$

the d.c. components on both sides of Equation 6 may be equated to give

$$\bar{i} = i_{cor}[\alpha' \exp(-\alpha\eta_1) - \beta' \exp(\beta\eta_1)] \qquad (7)$$

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[*] Preliminary experiments conducted in our laboratory on aluminium/aluminium oxide electrodes show that a variation of 30% or less in x is acceptable for evaluation of these parameters.

where $\alpha' = I_0(\alpha E_p)$, $\beta' = I_0(\beta E_p)$ and $I_0(Z)$ is the modified Bessel function of the first kind and order zero in the argument Z.

If the d.c. bias (U) (Fig. 1) is now introduced in series with the cell so as to just nullify the current $\bar{i}$ in the circuit, the mean potential of the electrode will shift to a new value E_2. It is important to ensure that the amplitude of the alternating voltage cross the cell (V_p) is maintained at the same value as before. The spontaneous polarization ($E_2 - E_{cor}$) which may be termed as the 'off-load' (faradaic) rectification potential (denoted as η_2) is obtained by making $\bar{i} \to 0$, $\eta_1 \to \eta_2$ in Equation 8. Thus,

$$0 = i_{cor}[\alpha' \exp(-\alpha\eta_2) - \beta' \exp(\beta\eta_2)]. \quad (8)$$

Remembering that the above rectification current and potentials arise due both to the oxide film and the faradaic reactions, Equations 7 and 8 should be modified to get the corresponding terms due to the faradaic reactions alone.

The two interfaces and the oxide film between them, will give rise to drops in the rectification potentials (η_1 and η_2) as given by Equation 4.

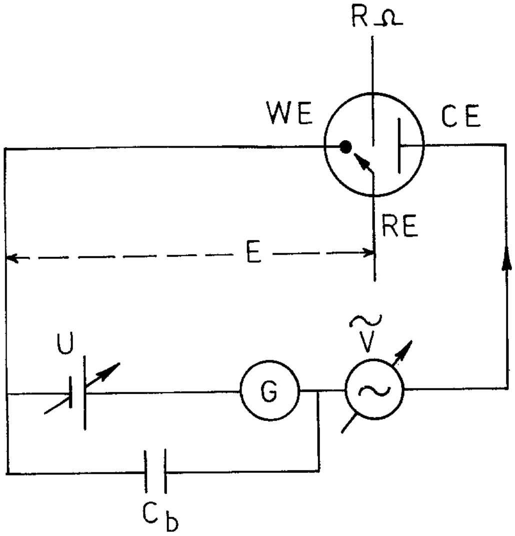

Fig. 1. Schematic diagram of faradaic rectification method for the determination of corrosion rate. G, d.c. galvanometer (to measure $\bar{i}$); C_b, by-pass capacitor providing a shunt path across U and G for a.c. current ($\tilde{i}$); U, low voltage variable d.c. power supply. WE, working electrode; CE, counter electrode; RE, reference electrode. $E = E_1 + E_p \cos(\omega t - \phi)$; $i = \bar{i} + \tilde{i}$; $\tilde{V} = V_p \cos(\omega t - \hat{\theta})$; $E_1 \to E_2$ if $\bar{i} \to 0$ at a given value of V_p.

Thus,

$$\eta_1 = f\eta_1^{\mathrm{r}} + \eta_1^{\mathrm{Fl}} + (1-f)\eta_1^{\mathrm{r}} \quad (9)$$

and

$$\eta_2 = f\eta_2^{\mathrm{r}} + \eta_2^{\mathrm{Fl}} + (1-f)\eta_2^{\mathrm{r}} \quad (10)$$

where, η_1^{r} $(= \eta_1^{\mathrm{r}_1} + \eta_1^{\mathrm{r}_2})$ and η_2^{r} $(= \eta_2^{\mathrm{r}_1} + \eta_2^{\mathrm{r}_2})$ are 'on-load' and 'off-load' rectification potentials across the two interfaces respectively; η_1^{Fl} and η_2^{Fl} are the corresponding terms across the oxide film, and f is the fraction.

A similar procedure should, in principle, be followed in the case of the alternating potential too. But in this case the addition should be vectorial, as the oxide film impedance can cause a phase shift between the current and the potential.

Thus, after correcting for the oxide film impedance, $[E_p \cos(\omega t - \phi)]$, the alternating potential across the metal/oxide and oxide/electrolyte interfaces may together be taken as $[E_p^{\mathrm{r}} \cos(\omega t - \theta)]$. (For details regarding determination of E_p^{r}, see Section 3.4.)

Under rigorous conditions, $[E_p^{\mathrm{r}} \cos(\omega t - \theta)]$ must also be vectorially separated between the two interfaces. This can be done if the individual impedances due to the two interfaces are known; however, this is not possible experimentally or otherwise. In the absence of such knowledge, $[E_p^{\mathrm{r}} \cos(\omega t - \theta)]$ is approximated to distribute between the two interfaces in the same way as described for the faradaic rectification potentials (Equations 9 and 10).* Thus

$$E_p^{\mathrm{r}} \cos(\omega t - \theta) = f[E_p^{\mathrm{r}} \cos(\omega t - \theta)] + (1-f)[E_p^{\mathrm{r}} \cos(\omega t - \theta)] \quad (11)$$

Thus, in the present system, Equations 7 and 8 should be modified depending on the assumption made regarding the site/sites where the conjugate reactions occur.

3.1.1. Reactions 1 and 2 at the metal/oxide interface. In this case the entire rectification due to the faradaic reactions will occur at the metal/oxide interface. In addition the oxide film may

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* Resort to this approximation results in an uncertainty of less than 20% in the calculated values of the alternating potential drops across each of these two interfaces. These calculations are based on typical values of phase shift = 20°, reaction impedances = 10 Ω, $E_p^{\mathrm{r}} = 5$ mV and $\bar{i} = 0.5$ mA.

also contribute to the process of rectification. The non-reacting interface (i.e., the oxide/electrolyte, in this case), may not have any contribution by way of rectification, but will have a part in the measured η_1 and η_2, due to the resistance of its junction. Thus, the total rectification potentials as measured using a reference electrode will be a sum of all the three potential drops, as described by Equations 9 and 10. Of these, only the first terms (in these equations), i.e., $f\eta_1^{\mathrm{r}}$ and $f\eta_2^{\mathrm{r}}$, should be considered for deriving the expression for corrosion current.

Similarly, the alternating potential across the metal/oxide interface given by the first term in Equation 11 i.e., $f[E_{\mathrm{p}}^{\mathrm{r}} \cos(\omega t - \theta)]$, should be considered for the above purpose.

Thus Equations 7 and 8 should be modified for the present case and more precisely represented as

$$\bar{i} = i_{\mathrm{cor}}[\alpha_{\mathrm{r}}' \exp(-\alpha^{\mathrm{r}} f\eta_1^{\mathrm{r}}) - \beta_{\mathrm{r}}' \exp(\beta^{\mathrm{r}} f\eta_1^{\mathrm{r}})] \tag{12}$$

and

$$0 = i_{\mathrm{cor}}[\alpha_{\mathrm{r}}' \exp(-\alpha^{\mathrm{r}} f\eta_2^{\mathrm{r}}) - \beta_{\mathrm{r}}' \exp(\beta^{\mathrm{r}} f\eta_2^{\mathrm{r}})] \tag{13}$$

where $\alpha_{\mathrm{r}}' = I_0(\alpha^{\mathrm{r}} fE_{\mathrm{p}}^{\mathrm{r}})$, $\beta_{\mathrm{r}}' = I_0(\beta^{\mathrm{r}} fE_{\mathrm{p}}^{\mathrm{r}})$, $\alpha^{\mathrm{r}} = 2.303/b_{\mathrm{c}}^{\mathrm{r}}$, $\beta^{\mathrm{r}} = 2.303/b_{\mathrm{m}}^{\mathrm{r}}$; $b_{\mathrm{c}}^{\mathrm{r}}$ and $b_{\mathrm{m}}^{\mathrm{r}}$ are the cathodic and anodic Tafel slopes determined appropriately after accounting for the oxide film. (For more details regarding α^{r}, see Appendix 1).

If the amplitude of $E_{\mathrm{p}}^{\mathrm{r}}$ is restricted such that

$$E_{\mathrm{p}}^{\mathrm{r}} \ll \frac{1}{\alpha^{\mathrm{r}}}, \ \frac{1}{\beta^{\mathrm{r}}},$$

then

$$\alpha_{\mathrm{r}}' = 1 + \frac{(\alpha^{\mathrm{r}} fE_{\mathrm{p}}^{\mathrm{r}})^2}{4} \tag{14}$$

and

$$\beta_{\mathrm{r}}' = 1 + \frac{(\beta^{\mathrm{r}} fE_{\mathrm{p}}^{\mathrm{r}})^2}{4}. \tag{15}$$

With these approximations Equations 12 and 13 give after simplification

$$\bar{i} = i_{\mathrm{cor}}\left\{-f(\alpha^{\mathrm{r}} + \beta^{\mathrm{r}})\eta_1^{\mathrm{r}} + \frac{[(\alpha^{\mathrm{r}})^2 - (\beta^{\mathrm{r}})^2](fE_{\mathrm{p}}^{\mathrm{r}})^2}{4}\right\} \tag{16}$$

and

$$0 = i_{\mathrm{cor}}\left\{-f(\alpha^{\mathrm{r}} + \beta^{\mathrm{r}})\eta_2^{\mathrm{r}} + \frac{[(\alpha^{\mathrm{r}})^2 - (\beta^{\mathrm{r}})^2](fE_{\mathrm{p}}^{\mathrm{r}})^2}{4}\right\} \tag{17}$$

From Equations 16 and 17, after eliminating β^{r},

$$\bar{i} = 2\,i_{\mathrm{cor}}(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})\left[f\alpha^{\mathrm{r}} - \frac{2\eta_2^{\mathrm{r}}}{(E_{\mathrm{p}}^{\mathrm{r}})^2}\right]. \tag{18}$$

3.1.2. Reactions 1 and 2 at the oxide/electrolyte interface. This is very similar to 3.1.1., except that the fraction $(1 - f)$ of the faradaic rectification potentials (η_1^{r} and η_2^{r}) and the alternating potential $[E_{\mathrm{p}}^{\mathrm{r}} \cos(\omega t - \theta)]$ across the oxide/electrolyte interface, only, should be considered for the current–potential relation. Thus, modifying Equations 7 and 8 by substituting for η_1, η_2 and $[E_{\mathrm{p}} \cos(\omega t - \phi)]$ in them through the fractions represented by $(1 - f)$ in Equations 9–11, it can be shown that,

$$\bar{i} = 2\,i_{\mathrm{cor}}(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})\left[(1 - f)\alpha^{\mathrm{r}} - \frac{2\eta_2^{\mathrm{r}}}{(E_{\mathrm{p}}^{\mathrm{r}})^2}\right]. \tag{19}$$

3.1.3. Reaction 1 at the metal/oxide interface, and reaction 2 at the oxide/electrolyte interface. In this case, with regard to the reaction of the metal/oxide interface, the fraction f of η_1^{r}, η_2^{r} and $E_{\mathrm{p}}^{\mathrm{r}}$ should be taken into account. Similarly, the fraction $(1 - f)$ of the corresponding potentials should be considered for the reaction at the oxide/electrolyte interface.

Thus, Equations 7 and 8 should be modified as,

$$\bar{i} = i_{\mathrm{cor}}[\alpha_{\mathrm{r}}'' \exp(-\alpha^{\mathrm{r}}(1 - f)\eta_1^{\mathrm{r}}) - \beta_{\mathrm{r}}' \exp(\beta^{\mathrm{r}} f\eta_1^{\mathrm{r}})] \tag{20}$$

and

$$0 = i_{\mathrm{cor}}\{\alpha_{\mathrm{r}}'' \exp[-\alpha^{\mathrm{r}}(1 - f)\eta_2^{\mathrm{r}}) - \beta_{\mathrm{r}}' \exp(\beta^{\mathrm{r}} f\eta_2^{\mathrm{r}})\} \tag{21}$$

where $\alpha_{\mathrm{r}}'' = I_0[\alpha^{\mathrm{r}}(1 - f)E_{\mathrm{p}}^{\mathrm{r}}]$ and $\beta_{\mathrm{r}}' = I_0(\beta^{\mathrm{r}} fE_{\mathrm{p}}^{\mathrm{r}})$.

After simplification and readjustment of Equations 20 and 21,

$$\bar{i} = 2i_{\mathrm{cor}}(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})\left[(1 - f)\alpha^{\mathrm{r}} - \frac{2\eta_2^{\mathrm{r}}}{(E_{\mathrm{p}}^{\mathrm{r}})^2}\right] \tag{22}$$

3.1.4. Reaction 1 at the oxide/electrolyte interface and reaction 2 at the metal/oxide interface. This is the reverse of 3.1.3. The final expression for the corrosion current in this case can be shown to be

$$\bar{i} = 2i_{\mathrm{cor}}(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})\left[f\alpha^{\mathrm{r}} - \frac{2\eta_2^{\mathrm{r}}}{(E_{\mathrm{p}}^{\mathrm{r}})^2}\right]. \tag{23}$$

The expression for the corrosion current for all the four cases given by Equations 18, 19, 22 and 23 may be recast into the general form

$$\bar{i} = 2i_{\mathrm{cor}}(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})\left[K\alpha^{\mathrm{r}} - \frac{2\eta_2^{\mathrm{r}}}{(E_{\mathrm{p}}^{\mathrm{r}})^2}\right] \tag{24}$$

where $K = f$ or $(1 - f)$ as the case may be.[*] The implication of Equation 24 is described in Section 4.

Thus, an appropriate method of corrosion rate measurement in metal/oxide/electrolyte systems reduces to one of evaluating η_1^{r}, η_2^{r} and $E_{\mathrm{p}}^{\mathrm{r}}$ from the experimentally measured parameters, namely, η_1, η_2 and V_{p}. This is done following a modified approach over the conventional faradaic rectification and impedance measurements. Furthermore, $K\alpha^{\mathrm{r}}$, the term corresponding to the cathodic Tafel slope, will need to be independently determined, as shown in Appendix 1.

3.2. *Determination of* $(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})$

This is obtained by faradaic rectification measurements. In the presence of an electric field across the oxide film, a current will flow through it due to the transport of ions and/or electrons. The relation between such a current and the field may be taken as exponential (see assumptions under Section 2) and represented in a form analogous to Equation 3 (see also [33]). Thus,

$$i = -C^{\mathrm{Fl}}\frac{\mathrm{d}E^{\mathrm{Fl}}}{\mathrm{d}t} + i_{\mathrm{cor}}\left\{\exp\left[-k\frac{(E^{\mathrm{Fl}} - E_{\mathrm{cor}}^{\mathrm{Fl}})}{x}\right] - \exp\left[l\frac{(E^{\mathrm{Fl}} - E_{\mathrm{cor}}^{\mathrm{Fl}})}{x}\right]\right\} \tag{25}$$

where C^{Fl} is the oxide film capacitance: $(E^{\mathrm{Fl}} - E_{\mathrm{cor}}^{\mathrm{Fl}})$, the polarization of the film from its rest potential $(E_{\mathrm{cor}}^{\mathrm{Fl}})$; x, the thickness of the oxide film; k and l are constants which include the tunnelling probability of electrons, forward and reverse transfer coefficients for ions, the number of charges on ions/electrons, jump or hopping distance (characteristic of every oxide film) and the other usual constants R, T and F.

In the presence of an alternating voltage of amplitude V_{p} across a cell containing an oxide covered working electrode, which corresponds to a small amplitude alternating potential $[E_{\mathrm{p}}^{\mathrm{Fl}} \cos(\omega t - \hat{\phi})]$ incident across the oxide film, it is possible to arrive (from Equation 25) at relations similar to Equations 16 and 17. Thus,

$$\bar{i} = i_{\mathrm{cor}}\left[-(k + l)\frac{\eta_1^{\mathrm{Fl}}}{x} + (k^2 - l^2)\frac{(E_{\mathrm{p}}^{\mathrm{Fl}})^2}{4x^2}\right] \tag{26}$$

and

$$0 = i_{\mathrm{cor}}\left[-(k + l)\frac{\eta_2^{\mathrm{Fl}}}{x} + (k^2 - l^2)\frac{(E_{\mathrm{p}}^{\mathrm{Fl}})^2}{4x^2}\right] \tag{27}$$

where η_1^{Fl} and η_2^{Fl} are the 'on-load' and 'off-load' rectification potentials due to the oxide film. On subtracting Equation 27 from 26,

$$\bar{i} = i_{\mathrm{cor}}\left[(k + l)\frac{(\eta_2^{\mathrm{Fl}} - \eta_1^{\mathrm{Fl}})}{x}\right]. \tag{28}$$

Between Equations 9, 10 and 28, they give

$$x = i_{\mathrm{cor}}\left[\frac{(k + l)}{\bar{i}}[(\eta_2 - \eta_1) - (\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})]\right] \tag{29}$$

In Equation 29, the quantities x, $\bar{i}$, η_1 and η_2 are experimentally accessible.

At various values of the film thickness (x), but at a constant rectification current ($\bar{i}$) which can be achieved by applying a suitable alternating potential, V_{p} across the cell), a set of η_1 and η_2 values can be experimentally determined.[†] A plot

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[*] The term corresponding to the anodic Tafel slope (β^{r}) has been eliminated in all the four cases. The site of the cathodic conjugate reaction (reaction 2) is the same for cases 3.1.1. and 3.1.4. Hence the expression for i_{cor} for these two cases (i.e., Equations 18 and 23) are identical. A similar identity may be found between cases 3.1.2. and 3.1.3 (Equations 19 and 22) also.

[†] For the reactions at the interfaces, a relation similar to Equation 28 can be derived as

$$\bar{i} = i_{\mathrm{cor}}[(\alpha^{\mathrm{r}} + \beta^{\mathrm{r}})(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})]K.$$

From this it is clear that $(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})$ will be a constant at any fixed value of $\bar{i}$ and independent of x, or E_{p}, the potential across the metal/oxide/electrolyte system. Furthermore, once the values of $\bar{i}$ and $(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})$ are fixed, $E_{\mathrm{p}}^{\mathrm{r}}$ will also be fixed at a constant value (cf. Equation 24) and will be independent of x.

of x versus $(\eta_2 - \eta_1)$ should now give a straight line and $(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})$ can be computed from it as the ratio of its intercept and slope.

3.3. *Determination of* $E_{\mathrm{p}}^{\mathrm{r}}$

The amplitude of the alternating potential, $E_{\mathrm{p}}^{\mathrm{r}}$, incident across the plane of the reaction zone has to be evaluated from the total drop V_{p} across the cell. This is done following impedance measurements. (For a simple equivalent circuit representation of the metal/oxide/electrolyte system, see Fig. 2 in [37].) The operation is in two steps: (a) the alternating potential E_{p} across the test electrode should be first evaluated after a suitable correction for the drop across the electrolyte resistance ($R\Omega$). (b) $E_{\mathrm{p}}^{\mathrm{r}}$ should then be calculated from E_{p} after suitably correcting for $E_{\mathrm{p}}^{\mathrm{Fl}}$, the drop across the film. $E_{\mathrm{p}}^{\mathrm{r}}$, should however be evaluated, for each value of x (at which i_{cor} is desired to be known) from the corresponding value of V_{p}.

Assuming that the impedance of the large area counterelectrode is negligible, E_{p} is given by the relation [20–24, 43]:

$$E_{\mathrm{p}}^2 = V_{\mathrm{p}}^2 + (i_{\mathrm{p}} R\Omega)^2 - 2V_{\mathrm{p}} R\Omega\, i_{\mathrm{p}} \cos\hat{\theta} \quad (30)$$

where $\hat{\theta}$ is the phase shift between V_{p} and i_{p}, i_{p} is the peak value of the a.c. current $(\tilde{i})$ through the cell and $R\Omega$ is the resistance due to the electrolyte between the test electrode and the counter electrode (and equal to the cell impedance measured at infinite frequency). The value of $\hat{\theta}$ can be measured in practice, for example, with a phase meter or an oscilloscope.

In a similar manner, it is possible to obtain the value of $E_{\mathrm{p}}^{\mathrm{r}}$ from the relation

$$(E_{\mathrm{p}}^{\mathrm{r}})^2 = E_{\mathrm{p}}^2 + [i_{\mathrm{p}}|Z_{\mathrm{Fl}}|]^2 - 2E_{\mathrm{p}}\, i_{\mathrm{p}}|Z_{\mathrm{Fl}}| \cos(\hat{\phi} - \phi) \quad (31)$$

where $|Z_{\mathrm{Fl}}|^2 = (R_{\mathrm{s}}^{\mathrm{Fl}})^2 + 1/(\omega C_{\mathrm{s}}^{\mathrm{Fl}})^2$, $|Z_{\mathrm{Fl}}|$ being the absolute value of the impedance due to the film measured at any angular frequency ω in terms of the series equivalent resistance ($R_{\mathrm{s}}^{\mathrm{Fl}}$) and capacitance ($C_{\mathrm{s}}^{\mathrm{Fl}}$) of the film. $\hat{\phi}$ is the phase shift between $E_{\mathrm{p}}^{\mathrm{Fl}}$ and i_{p} and is calculated from the relation $\tan\hat{\phi} = (\omega R_{\mathrm{s}}^{\mathrm{Fl}} C_{\mathrm{s}}^{\mathrm{Fl}})^{-1}$.

The values of $|Z_{\mathrm{Fl}}|$ and $\hat{\phi}$ can be determined at any required angular frequency ω, following the film impedance measurements described in [37].*

Thus the correction due to the oxide film impedance can be made at the frequency at which the faradaic rectification measurements are made. This will also eliminate any ambiguity, which may otherwise be introduced, due to the frequency dependence of the oxide film impedance.

3.4. *Determination of* η_2^{r}

This is evaluated from the data generated in Section 3.2 and 3.3.

From Equation 9

$$\eta_1 = \eta_1^{\mathrm{r}} + \eta_1^{\mathrm{Fl}}.$$

In this, η_1 is an experimentally accessible parameter. η_1^{r} can be determined provided η_1^{Fl}, the potential drop across the oxide film in presence of the rectification current, $\bar{i}$, is known.

By Kirchoff's law for direct current, with due regard to sign (cathodic current positive) [22],

$$\eta_1^{\mathrm{Fl}} = -\bar{i}\,|Z_{\mathrm{Fl}}| \quad (32)$$

where $|Z_{\mathrm{Fl}}|$ is the absolute value of the impedance† due to the oxide film, as determined at the frequency at which $\bar{i}$ is measured (cf. Section 3.3).

Following Equation 29, $(\eta_2^{\mathrm{r}} - \eta_1^{\mathrm{r}})$ can be determined from faradaic rectification measurements. Taking this value as η^1, and from Equations 9, 10 and 32

$$\begin{aligned} \eta_2^{\mathrm{r}} &= \eta^1 + \eta_1^{\mathrm{r}} \\ &= \eta^1 + \eta_1 + \bar{i}\,|Z_{\mathrm{Fl}}|. \quad (33) \end{aligned}$$

Thus, η_2^{r} can be determined at any value of the oxide film thickness (x) and the applied alternating potential V_{p}, knowing the corresponding rectification current $\bar{i}$. The values of x and V_{p} should however correspond to the same as those used for the calculation of $E_{\mathrm{p}}^{\mathrm{r}}$ in Section 3.3.

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* Reference [37] describes a procedure to compute the impedance of the oxide film from the measured cell impedance, with the cell having the oxide covered metal at the test electrode.

† It is appropriate to use the impedance of the oxide film rather than its d.c. resistance for the purpose of '*iR* drop' calculations. This is because, the process of rectification by many of the oxides (attributed to p–i–n or p–n junction) has a non-linear current–potential characteristic [44–46]. Though the thickness of the barrier (between the metal and the oxide), responsible for rectification, might be very small, the space charge layer might extend over its entire bulk. This is particularly true with oxides of valve metals at very small thicknesses ($x \simeq 1000$ nm) [44].

3.5. *Determination of* i_{cor} *and verification of the assumptions*

With all the required parameters in Equation 24 being evaluated i_{cor} can be calculated.

Two internal cross checks are possible to verify the validity of the assumptions involved in the proposed theory.

(a) From Equation 29, a plot of x versus $(\eta_2 - \eta_1)$ at any given value of $\bar{i}$ should be linear. This will be so only when the exponential relation between the current and potential is applicable uniformly all over the oxide film.

(b) i_{cor} can be calculated at different values of the thickness of the oxide film (x) (over which x is varied as in Sections 3.3 and 3.4), using the above procedure. The limits within which these values agree, will indicate the validity of the assumption of the independence of i_{cor} with respect to variations of x.

4. Implications of the theory

It is therefore possible to obtain the corrosion rate for oxide covered metal electrodes by coupling faradaic rectification and impedance measurements. The expression for corrosion current is described in Equation 24 in terms of faradaic rectification potentials (η_1^r, η_2^r) and current ($\bar{i}$) at an alternating potential E_p^r, taken as occurring together across both the reaction interfaces, i.e., the metal/oxide and oxide/electrolyte. It implies that the corresponding rectification and alternating potential drops across the oxide film should be accurately accounted for. The theory following Equation 24 (Section 3.2–3.5) describes how this could be done, by making use of the fundamental laws that govern the mechanism of conduction and rectification by oxide films.

Equation 24 also has the interesting feature of being independent of any assumption in regard to the mechanism of the corrosion reactions. The two conditions under which the rectification potentials are measured (as described in Fig. 1 as well as by Equations 7 and 8, i.e., η_1 at $\bar{i} > 0$ and η_2 as $\bar{i} \to 0$; both at a given value of V_p), are utilized to eliminate all the contributions due to the anodic reaction in the final expression (Equation 24). It has contributions only from the cathodic reaction in terms of $K\alpha^r$. The product $K\alpha^r$ will need to be determined independently, but with no need of any knowledge of the mechanism of the cathodic reaction (see Appendix 1).

It may also be seen from the theory described between Sections 3.2 and 3.5 that the above procedure amounts to an estimate of the rectification and impedance parameters of the oxide film present on the metal electrode. Further, such estimations should be done using an electrolyte which would react with the oxide or corrode the metal least. (For example, aluminium/aluminium oxide/sulphate, pH $\approx$ 2–7.) These parameters are intrinsic to the given oxide film of thickness x and are independent of the electrolyte with which they might come into contact.*

Having determined the rectification potentials (η_1^{Fl}, η_2^{Fl}) and the impedance (Z_{Fl}) due to the oxide film of thickness x, the corrosion current of the metal may be evaluated in any other electrolyte by a single point measurement. Thus, the method may be used for instantaneous (accelerated and non-destructive) measurement of corrosion rate.

Besides this, the proposed method may also be used to determine the 'transfer coefficients' k and l associated with the oxide film conduction (in Equations 25–29). This might help in obtaining an insight into the mechanism of conduction and rectification by the oxide film.

The proposed method has certain important advantages over the other methods proposed and employed so far [1–28].

(a) The only auxilliary information needed is the value of the apparent cathodic Tafel slope. (This, however, should be determined following the procedure described in Appendix 1).

(b) The need for an independent knowledge of the resistive and/or reactive part of the interfaces and of the oxide film, is completely eliminated. There is no need to resort to any electrical equivalent circuits and assume values for individual components to compute the corrosion current.

(c) The interference of the frequency dependent oxide film impedance (Z_{Fl}) with the measured faradaic rectification parameters is eliminated. As

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* This, of course, does not hold good in electrolytes containing dissolved gases such as oxygen, which may diffuse into the oxide film rapidly and change its electrical conductivity.

a result it is possible to independently evaluate the frequency dependence, if any, of the corrosion current, as claimed by some workers [16].

However, the method is applicable only in such cases where the oxide film impedance is comparable in magnitude to that of the faradaic impedance. It may not be possible to use it if the oxide film is a relatively good conductor, because the effects due to the potential drop across the oxide layer (cf. Equations 28 and 29) cannot be fully exploited in such cases.

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Appendix 1

Evaluation of $K\alpha^r$: Under a large cathodic d.c. polarization, Equation 25 may be simplified to give

$$-\frac{k}{y}(E^{\mathrm{Fl}} - E^{\mathrm{Fl}}_{\mathrm{cor}}) = x \qquad \text{(A1)}$$

where $y = \ln i/i_{\mathrm{cor}}$.

Between Equations 4 and A1

$$-\frac{k}{y}[(E - E_{\mathrm{cor}}) - (E^r - E^r_{\mathrm{cor}})] = x \quad \text{(A2)}$$

where $E^r = E^{r_1} + E^{r_2}$ and $E^r_{\mathrm{cor}} = E^{r_1}_{\mathrm{cor}} + E^{r_2}_{\mathrm{cor}}$. Under the assumption that $(E^r - E^r_{\mathrm{cor}})$ is independent of the thickness (x) of the oxide film (over which x is varied), the former can be determined in the same manner as $(\eta^r_2 - \eta^r_1)$ in Equation 29. Thus, a set of values $(E^r - E^r_{\mathrm{cor}})$ can be generated at various values of i.

These values of $(E^r - E_{\mathrm{cor}})$ represent the total potential drop across the two interfaces (metal/oxide and oxide/electrolyte), in the presence of the current i. But, only a fraction of this drop will be due to the reaction resistance. This fraction will depend upon the interface at which the cathodic reaction (Reaction 2) actually takes place. Thus in cases 3.1.1. and 3.1.4. described under Section 3.1, the fraction of the drop will be $f(E^r - E^r_{\mathrm{cor}})$ (Reaction 2 at the metal/oxide interface), and in cases 3.1.2. and 3.1.3., it will be $(1 - f)(E^r - E^r_{\mathrm{cor}})$ (Reaction 2 at the oxide/electrolyte interface).

In general, the drop due to the (cathodic) reaction resistance may be represented as $K(E^r - E^r_{\mathrm{cor}})$.

Following the laws of electrochemical kinetics, under large cathodic polarization conditions the current i through the system may be represented as

$$i = i_{\mathrm{cor}} \exp[-K\alpha^r(E^r - E^r_{\mathrm{cor}})]. \qquad \text{(A3)}$$

The values of $(E^r - E^r_{\mathrm{cor}})$ evaluated at various values of i (following Equation A2) may now be utilized to determine $K\alpha^r$ through a usual Tafel plot.

Appendix 2

Nomenclature and constants used in the calculations:

b_c	experimental cathodic Tafel slope defined as $b_c = 2.303/\alpha$
b_m	experimental anodic Tafel slope defined as $b_m = 2.303/\beta$
b^r_c	cathodic Tafel slope as described by Equations 12 and 13 and in the Appendix, defined as $b^r_c = 2.303/\alpha^r$
b^r_m	anodic Tafel slope as described by Equations 12 and 13 and defined as $b^r_m = 2.303/\beta^r$
C	double layer capacitance of metal/electrolyte interface
C^{Fl}	capacitance of oxide film
C'	resultant capacitance of the double layer at the metal/oxide and oxide/electrolyte interfaces and C^{Fl}
C^{Fl}_s	series equivalent capacitance of the oxide film
E	potential of the test electrode
E_{cor}	corrosion potential of the test electrode
$E^{\mathrm{Fl}}, E^{r_1}, E^{r_2}$	as defined by Equation 4
E_1, E_2	mean potential of the test electrode under a steady state a.c. polarization of constant ampli-

	tude. E_1 is the value when the current $\bar{i}$ is non-zero; E_2 is the value when $\bar{i}$ is zero
E_p	peak value of the alternating potential at the test electrode/electrolyte interface
$E_\mathrm{p}^\mathrm{Fl}, E_\mathrm{p}^{\mathrm{r}_1}, E_\mathrm{p}^{\mathrm{r}_2}$	peak values of the alternating potential incident across the oxide film, metal/oxide interface and oxide/electrolyte interface respectively
E_p^r	amplitude of the alternating potential incident across both the reaction interfaces (also defined by Equation 31)
e^-	an electron
f	$\eta_1^{\mathrm{r}_1}/\eta_1^\mathrm{r}\,;\ \eta_2^{\mathrm{r}_1}/\eta_2^\mathrm{r}$
$(1-f)$	$\eta_1^{\mathrm{r}_2}/\eta_1^\mathrm{r};\ \eta_2^{\mathrm{r}_2}/\eta_2^\mathrm{r}$
i	current at the test electrode; cathodic current positive
$\bar{i}$	faradaic rectification current
$\tilde{i}$	alternating current
i_p	peak value of the alternating current $\tilde{i}$
i_cor	corrosion current at the test electrode
I_0, I_k	modified Bessel function of the first kind of order zero and order K respectively
K	f in case 3.1.1. and 3.1.4. and $(1-f)$ in case 3.1.2. and 3.1.3. in Section 3.1.
M	metal of the test electrode
M^{n+}	metal ion with a positive charge n
n	number of equivalents involved in a given electrode reaction
O	oxidant (reaction 2)
R	reductant (reaction 1)
R_s^Fl	series equivalent resistance of the oxide film
$R\Omega$	resistance of the electrolyte in the cell
t	time coordinate
V_p	peak value of the alternating potential applied across the cell
x	thickness of the oxide film
Z_Fl	impedance of the oxide film
α	$2.303/b_\mathrm{c}$
β	$2.303/b_\mathrm{m}$
α^r	$2.303/b_\mathrm{c}^\mathrm{r}$
β^r	$2.303/b_\mathrm{m}^\mathrm{r}$
α'	$I_0(\alpha E_\mathrm{p})$
α_r'	$I_0(\alpha^\mathrm{r} f E_\mathrm{p}^\mathrm{r})$
α_r''	$I_0(\alpha^\mathrm{r}(1-f)E_\mathrm{p}^\mathrm{r})$
β'	$I_0(\beta E_\mathrm{p})$
β_r'	$I_0(\beta^\mathrm{r} f E_\mathrm{p}^\mathrm{r})$
η_1	on-load faradaic rectification potential $(E_1 - E_\mathrm{cor})$
η_2	off-load faradaic rectification potential $(E_2 - E_\mathrm{cor})$
$\eta_1^\mathrm{Fl}, \eta_1^{\mathrm{r}_1}, \eta_1^{\mathrm{r}_2}$	as defined by Equation 9
$\eta_2^\mathrm{Fl}, \eta_2^{\mathrm{r}_1}, \eta_2^{\mathrm{r}_2}$	as defined by Equation 10
η_1^r	$\eta_1^{\mathrm{r}_1} + \eta_1^{\mathrm{r}_2}$
η_2^r	$\eta_2^{\mathrm{r}_1} + \eta_2^{\mathrm{r}_2}$
$\hat{\theta}$	phase shift between V_p and i_p
ϕ	phase shift between E_p and i_p
$\hat{\phi}$	phase shift between E_p^Fl and i_p
θ	phase shift between E_p^r and i_p
ω	angular frequency.

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