SHORT COMMUNICATIONS

AC HARMONIC METHOD OF MEASURING CORROSION RATE

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WHEN a sinusoidal perturbation of voltage or current is applied to an electrochemical system, the response contains a rectified component as well as harmonics. This arises essentially due to nonlinearity of current-voltage characteristic of metal/solution interface. When two or more frequency components are present in the applied signal, intermodulation effects are also observed. Prabhakar Rao et al[1] and Devay et al[2] have shown, by theory, that the measurement of harmonics provides a means of determining corrosion rate. However, there are some drawbacks in the proposed methods. Firstly, the methods that depend upon the measurement of total first harmonic current (sum of faradaic and non-faradaic currents) will not give the true corrosion current. Secondly, in the method suggested by Prabhakar Rao et al, the upper and lower bounds for the amplitude of a.c. input are difficult to be estimated without a knowledge Tafel constants whose magnitudes are in fact sought to be measured in the experiment. One of the methods suggested by Devay et al needs the polarisation of the electrode to the Tafel region. Such a polarisation will affect the morphology of electrode surface especially during anodic polarisation.

In this communication, we describe a new method of measuring corrosion rate. The experimental results obtained with a system of mild steel in 1N sulphuric acid are also presented and these are compared with the rates obtained with linear and logarithmic polarisation data.

Suppose a small amplitude sinusoidal voltage of the form $\varepsilon_p \cos \omega t$ is applied to the system, the total current comprising of both Faradaic and non-Faradaic components can be written as:

$$T + \tilde{I} = -C_{dl}\frac{d(\varepsilon_p \cos \omega t)}{dt} +$$
$$I_{corr}[\exp\{-\alpha(\eta + \varepsilon_p \cos \omega t)\} - \exp\{\beta(\eta + \varepsilon_p \cos \omega t)\}] \qquad (1)$$

where $\quad \alpha = \dfrac{\alpha_c ZF}{RT}\quad$ and $\quad \beta = \dfrac{\beta_a ZF}{RT}$.

T = Faradaic rectification current, $\tilde{I}$ = peak amplitude of all harmonics.

Expressions can be obtained from (1) for the first, second and third harmonic contents of the cell response. The higher order terms in all the cases are omitted as they are negligible.

For the Faradaic component of the first harmonic current,

$$\tilde{I}_1 = -I_{corr}\,\varepsilon_p\{(\alpha + \beta) + (\alpha^2 - \beta^2)\eta\}. \qquad (2)$$

For the second harmonic current,

$$\tilde{I}_2 = \frac{I_{corr}}{4}\varepsilon_p^2\{(\alpha^2 - \beta^2) - (\alpha^3 + \beta^3)\eta\}. \qquad (3)$$

Finally, for the third harmonic current at a d.c. polarisation $\eta = 0$,

$$\tilde{I}_3 = -\frac{I_{corr}}{24}\varepsilon_p^3\{(\alpha^3 + \beta^3)\}. \qquad (4)$$

It can be shown that it is possible to obtain α and β and hence I_{corr} by combining (2), (3) and (4). However, since the method of measuring first harmonic current free from non-Faradaic component is still in progress, it will be reported elsewhere.

When $\tilde{I}_2$ and $\tilde{I}_3$ measurements are combined with polarisation resistance $(\partial\eta/\partial I)_{\eta\to 0}$, it is possible to formulate three methods of measurement of I_{corr}.

Method (i) A plot of $\tilde{I}_2$ vs η is linear with

$$\frac{\text{Slope}}{\text{Intercept}} = -\frac{(\alpha - \beta)^2 + \alpha\beta}{(\alpha - \beta)}, \qquad (5)$$

From the linear polarisation curve,

$$\left(\frac{\partial I}{\partial \eta}\right)_{\eta\to 0} = -I_{corr}(\alpha + \beta). \qquad (6)$$

and also,

$$(\alpha - \beta) = \pm\frac{4}{\varepsilon_p^2}\left\{\frac{(\tilde{I}_2)_{\eta=0}}{(\partial I/\partial \eta)_{\eta\to 0}}\right\} \qquad (7)$$

Using (5) and (7) one gets α and β. Substitution in (6) leads to I_{corr}. When $\alpha > \beta$ RHS of (7) is positive and it is negative otherwise.

Method (ii)

When the cell is polarised such that $\tilde{I}_2 = 0$, then,

$$\frac{1}{(\eta)_{\tilde{I}_2=0}} = \frac{(\alpha - \beta)^2 + \alpha\beta}{(\alpha - \beta)}. \qquad (8)$$

Equation (8) combined with (7) gives α and β. I_{corr} can be evaluated from α and β using (6).

Method (iii)

$\tilde{I}_2$ and $\tilde{I}_3$ are measured at $\eta = 0$, then

$$\frac{6(\tilde{I}_3)_{\eta=0}}{\varepsilon_p(\tilde{I}_2)_{\eta=0}} = -\frac{(\alpha-\beta)^2+\alpha\beta}{(\alpha-\beta)}. \qquad (9)$$

Using (7) and (9) one can get α and β hence I_{corr}.

The system chosen for evaluating the method is mild steel in IN sulphuric acid. The cell design is according to ASTM G-72. The sample used as a working electrode is a rectangular strip which is masked off with araldite everywhere except at the bottom to expose a fixed area. Platinum strips are used as a counter electrode and SCE as a reference electrode.

A sinusoidal signal of 10 mV RMS and a frequency of 42 Hz is derived from a low distortion (0·05 %) Aplab (Type AG 3) oscillator. This is applied to the system through a high stability potentiostat designed for this purpose. The cell response is passed through tuned amplifiers to separate second and third harmonic components.

Figure 1 shows the plot of $\tilde{I}_2$ against η_a and η_c. Since $\tilde{I}_2$ decreases with increasing η_c and the reverse is the case with η_a, it is concluded that $\alpha < \beta$.
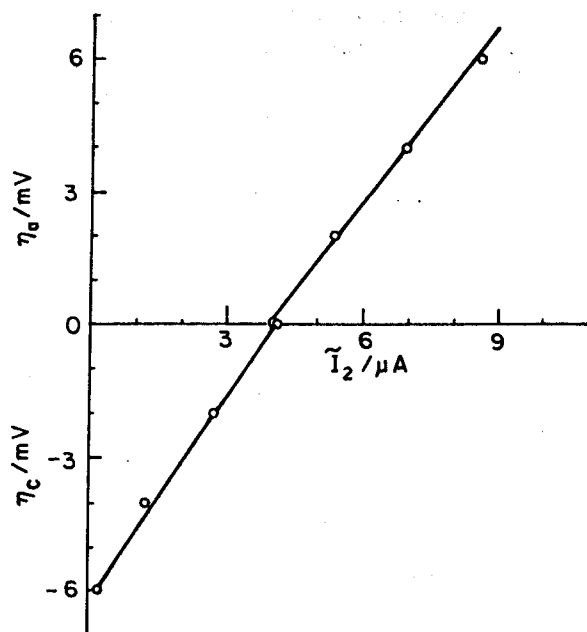
The results obtained by various methods are shown

Figure 1. I_2 vs η_a (upper) and I_2 vs η_c (lower) curves for mildsteel in IN sulphuric acid. $E_p = 14$ mV, Electrode area $= 1.2$ cm^2.

Table 1 *Comparison of Corrosion rate for Mild steel in 1 N sulphuric acid obtained by different methods.*

Method	I_{corr} $\mu A/cm^2$
$\tilde{I}_2$ vs η_c and polarisation resistance	361
$\tilde{I}_2$ vs η_a and polarisation resistance	398
$(\eta)\tilde{I}_2 = 0$ and polarisation resistance	390
$\tilde{I}_2$ and $\tilde{I}_3$ and polarisation resistance	389
Logarithmic polarisation	358
Linear polarisation (using α and β from logarithmic polarisation)	340

in table 1. These values are in good agreement with the corrosion rate obtained by classical polarisation methods.

Following are the advantages of the proposed method:

(i) Since d.c. polarisation involved is around 10 mV, surface morphology is not affected.

(ii) α and β are obtained close to corrosion potential which is an advantage over logarithmic polarisation method.

(iii) The method is quite fast and measurements can be done in approximately 10 minutes.

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1. Prabhakar Rao, G. and Mishra, A. K., *J. Electroanal-Chem.*, 1977, **77**, 121.
2. Devay, J. and MesZaros, I., *Acta Chim. Acad. Sci. Hung.*, 1979, **84**, 100.

LATTICE THERMAL CONDUCTIVITY OF GERMANIUM AT LOW TEMPERATURES

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LATTICE thermal conductivity of germanium and other non-metallic solids has been widely studied by many workers[1-3] in the past, using Callaway's model[4] and modifications thereof. In all these studies, it has been implicitly assumed that the relaxation rates due to