THE USE OF NON-LINEAR TECHNIQUES FOR THE ASSESSMENT OF CORROSION RATES

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ABSTRACT

The paper involves corrosion on mild steel in 0.1M HCl solution, using harmonic analysis and faradaic rectification techniques.

In the harmonic analysis a sweep of the three first harmonics of a Taylors Series expansion is carried out. The measurement of the sinusoidal currents produced allow the determination of the corrosion rate and the Tafel coefficients.

In the faradaic rectification method the corrosion rate is determined by measuring the d.c. current at the potential for which the second harmonic of a sinusoidal perturbation shows a minimum. This current is related to the corrosion rate by the equation $i_{corr} = 0.6\ i_{d.c.}$.

Values of the corrosion rate obtained for the system under study by both methods are presented which agree with the value obtained by electrochemical impedance.

Key-words: Corrosion rate, harmonic analysis, faradaic rectification.

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INTRODUCTION

Until recently, the use of electrochemical techniques for the determination of corrosion rates was restricted to d.c. techniques, such as the polarization resistance and the extrapolation of the Tafel lines. However, in the past 15 years the a.c. impedance technique has been used in an increasing scale, at least in laboratory studies. This technique has allowed to overcome many problems found with the d.c. techniques, namely in what concerns the non-stationary state.

Two other electrochemical techniques - harmonic analysis and faradaic rectification - whose theoretical treatment was presented by Meszaros (1-3) have reached less popularity, although they seem very promissing in some studies, since they allow the separation of the anodic and cathodic contribution for the overall process of corrosion. In the first of these techniques the amplitude of the currents of the 1st, 2nd and 3rd harmonics are determined and from these values the corrosion rates and the Tafel coefficients are estimated. In the faradaic rectification the corrosion rate can be estimated, measuring the d.c. current at the potential for which the second harmonic of a sinusoidal perturbation presents a minimum. In many cases this current is related to the corrosion current through the relationship $i_{corr} = 0.6\ i_{d.c.}$ (3,4).

EXPERIMENTAL

The present study was performed using specimens of carbon steel, with an area of 1 cm^2 and immersed in 0.1M HCl.

The harmonic analysis was carried out using a Solartron 1250 frequency response analyser. This equipment allows, through its generator to produce a sinusoidal wave of amplitude 10 mV (r.m.s) which was applied to the system by a Thompson 251 Ministat, used in a three electrode comfiguration. The frequency of the 1st harmonic used was 50 mHz, this value being near the frequency corresponding to the intersection of the impedance plot with the real axis, in the low frequencies region, obtained for the same system.

The current corresponding to the three harmonics was also measured with the frequency response analyser.

In the faradaic rectification, the minimum (inflexion point) of the current for the 2nd harmonic was determined measuring the variation of current corresponding to this harmonic with the d.c. potential.

Simultaneously the d.c. current flowing in the cell, for the different potentials, was measured by the ohmic drop through a counter resistor placed in series with the cell.

The impedance plot was carried out using the frequency response analyser and sweeping the frequency between 10 KHz and 10 mHz.

RESULTS

The corrosion rate has been determined by (1-3):

$$i_{corr} = \frac{i^2_1}{\sqrt{48}\ .\ \sqrt{2i_1i_3-i_2^2}}$$

where i_1, i_2 and i_3 are the amplitudes of the currents corresponding to the 1st, 2nd and 3rd harmonics, respectively. The anodic and cathodic Tafel coefficients $ß_a$ and $ß_c$, can be estimated by the following relationships:

$$\frac{1}{ß_a} = \frac{1}{2U_0}\left(\frac{i_2}{i_{corr}} + 4\frac{i_2}{i_1}\right)$$

$$\frac{1}{ß_c} = \frac{1}{2U_0}\left(\frac{i_1}{i_{corr}} - 4\frac{i_2}{i_1}\right),$$

if $ß_a < ß_c$, or

$$\frac{1}{\beta_a} = \frac{1}{2U_0} \left(\frac{i_1}{i_{corr}} - 4 \frac{i_2}{i_1} \right)$$

$$\frac{1}{\beta_c} = \frac{1}{2U_0} \left(\frac{i_1}{i_{corr}} + 4 \frac{i_2}{i_1} \right)$$

if $\beta_a > \beta_c$. U_0 is the amplitude of the applied potential.

The results obtained for i_1, i_2 and i_3 allow to estimate a corrosion rate of $i_{corr} \approx 52\ \mu A.cm^{-2}$. The estimated anodic and cathodic coefficients show respectively values of 35 mV/decade and 37 mV/decade.

The faradaic rectification, whose results are presented in Fig. 1, allow to obtain for the minimum of the 2nd harmonic the value of the current $i_{d.c.} = 90\ \mu A.cm^{-2}$, which gives for the corrosion rate:

$$i_{corr} = 0.6\ i_{d.c.} = 54\ \mu A.cm^{-2}$$

The impedance plot obtained for the same system is shown in Fig. 2 and, using the Stern-Geary equation and the values of β_a and β_c determined by the harmonic analysis, it is possible to estimate a corrosion rate of $51\ \mu A.cm^{-2}$.

The values of the corrosion rate obtained by the three methods are presented in Table I.

Table I - Values of i_{corr} estimated by different techniques

Harmonic analysis	Faradaic rectification	Impedance
$52\ \mu A.cm^{-2}$	$54\ \mu A.cm^{-2}$	$51\ \mu A.cm^{-2}$

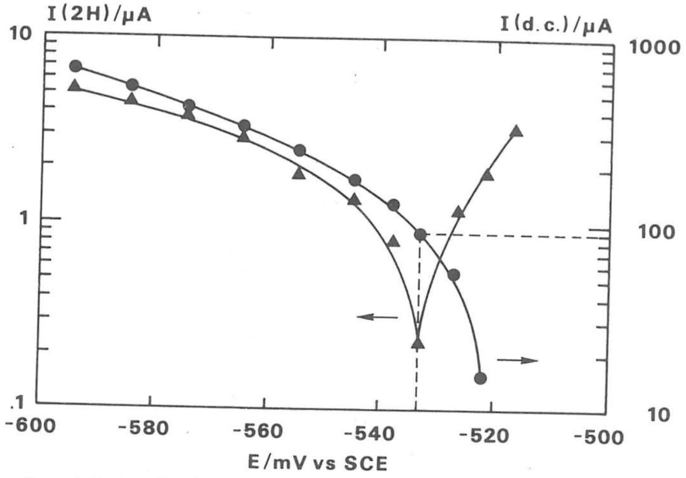

Fig. 1 - Plot of the current amplitude (2nd harmonic) and of the d.c. current as a function of the d.c. applied potential. (Main frequency: 100 mHz)

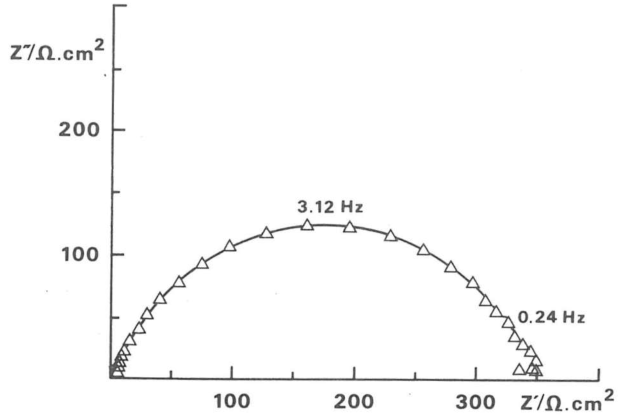

Fig. 2 - Impedance plot for mild steel in 0.1M HCl, obtained at the free corrosion potential (-516 mV Vs SCE). Amplitude of the applied signal: 10 mV.

The values are very similar which shows the good applicability of the three methods to the system under study.

CONCLUSIONS

1. The harmonic analysis and faradaic rectification methods confirm the conclusions both of the theoretical work (1-3) and the experimental work carried out by other authors for other systems (4).

2. Both techniques have over the a.c. impedance or the polarization resistance the advantage of allowing the determination of the corrosion rate without the knowledge of the Tafel coefficients which are very often difficult to estimate.

3. For the system studied, since it is activation controlled, both methods gave very similar results for the corrosion rate, which are self checked through the use of the Stern-Geary equation.

Similar agreement of results was obtained by Gill et al. (4) for carbon steel in NaCl solution, although as stated by those authors, for more complex systems there is no guarantee of identical success.

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OXYGEN REDUCTION ON PLATINUM ELECTRODES COATED WITH NAFION

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ABSTRACTS: *The electroreduction of O_2 in 0.5 M H_2SO_4 on platinum finely dispersed on pyrolytic graphite and coated with Nafion films ranging in thickness from 0.5 to 18 μ was studied. It was found that i) the film does not alter the mechanism of the reduction reaction; ii) the film does not prevent sintering of the catalyst; iii) the film concentrates O_2 from the solution but, nevertheless, the current measured for the filmed electrodes only increases relatively to the uncoated electrodes near the onset of the reduction when electron transfer controls; once diffusion becomes important the current decreases because, whatever the thickness, the transport of O_2 inside the film is slowed down; iv) thick films behave like recast films whereas thin films behave like membranes.*

1. INTRODUCTION

In gas phase and at low temperatures O_2 adsorbs dissociatively on platinum so that at 150 ^{0}K there are O atoms on the surface *[1]*. In solution, however, O_2 has to compete with water or with specifically adsorbed ions (electrolyte anions for example) for the Pt surface and therefore its interaction with this surface is only favoured at the pzc. On the other hand, Pt is used finely dispersed in practical porous electrodes in order to obtain high current densities; however, due to the gradual sintering of the Pt particles these practical electrodes cannot sustain such high currents for a long time.

In this context, there has been considerable interest in the incorporation of perfluorosulphonic acids like Nafion into O_2 cathodes. With the use of these ionomers it is hoped: a) to take advantage of the lower dielectric constant in the ionomer phase to favour O_2 adsorption on catalytic sites thus decreasing the reduction overpotential; b) to take advantage of increased O_2 concentration inside the ionomer phase next to the electrode to increase the current at a given overpotential; c) to decrease the loss of the surface area of the catalyst by slowing down processes possibly responsible for that loss, such as surface detachment of the catalyst particles from the carbon suport and classical "Ostwald ripening"; d) to take advantage of the cation permselectivity of the ionomer to prevent the blocking of the catalyst surface by the electrolyte anions.

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