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*Characterization of electrolytic bubble evolution by spectral analysis. Application to a corroding electrode**

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The evolution regime of electrolytically generated hydrogen bubbles in acidic medium has been studied by means of spectral analysis. A stochastic model of the time series displayed by the electrolysis current during bubble evolution has been devised. The identification of the characteristic parameters of the evolution regime (nucleation rate, life time etc.) has been performed through the measured power spectral density. This analysis has been applied to the determination of the dissolution current of an iron electrode in sulphuric acid medium.

1. Introduction

At low anodic current density, for polarization close to the corrosion potential, the dissolution of iron in sulphuric acid medium takes place together with hydrogen formation. Hence the measured total current is the sum of an anodic current due to iron dissolution and a cathodic current due to hydrogen formation. The latter occurs through several interacting phemonena:

(a) electrochemical reactions leading to molecular hydrogen which dissolves into the solution
(b) nucleation and growth of bubbles from the dissolved hydrogen on some active sites on, or close to , the electrode surface
(c) detachment of the bubble after some time depending upon the physical conditions prevailing at the electrode–electrolyte interface such as surface tension and hydrodynamic conditions.

Under potentiostatic (galvanostatic) control, random fluctuations of the total current (potential) can be observed [1]. These are due to both the gas evolution and metal dissolution. As it can be shown [2] that dissolution processes alone generate fluctuations of a level four or five orders of magnitude lower than those observed, the observed fluctuations are due essentially to the hydrogen bubble growth and departure.

When the current density is high, the bubbles are so numerous that their occurrence cannot be counted and their individual effects cannot be separated on the recording of the current (or voltage) fluctuations. Hence no analysis is possible in the time domain.

In this paper, it will be shown that only a frequency (spectral) analysis of the observed fluctuations allows the parameters controlling the gas evolution regime to be determined. However, in order to demonstrate the validity of the approach, experimental conditions are selected so that the elementary current transients due to the bubbles can be separated, i.e. when the bubbles are not too numerous.

2. Theoretical model

A typical recording of the voltage fluctuations versus time under galvanostatic control is shown in Fig. 1. From optical observation of the electrode surface, it can be concluded that the steep jumps are related to the detachment of bubbles and that the slow linear voltage increase is due to the growth of bubbles.

From the recording given in Fig. 1, a quick qualitative analysis can be performed in order to obtain a first approximation of some parameters characteristic of the bubble evolution regime. In

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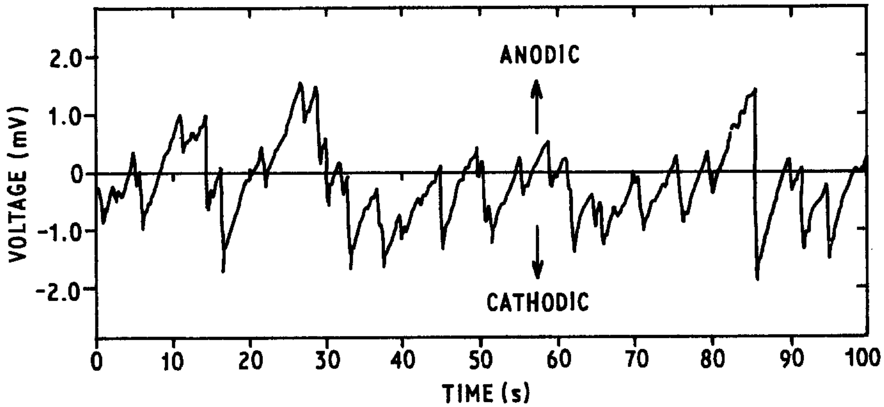

Fig. 1. Iron dissolution in 2N sulphuric acid medium. Voltage–time recording at a 3.7 mA cm^{-2} anodic current density in galvanostatic regime.

this 100 s recording, 47 jumps, whose amplitude is greater than 30 μV, can be counted. Due to the linear voltage–time relationship of the elementary transients, the size of the jumps is proportional to the life times of the bubbles. Hence a histogram of the jump sizes (Fig. 2) is equivalent to a histogram of the life times. The straight broken line modelling the distribution of the jump sizes (Fig. 2) corresponds to a mean life time of 0.9 s. Finally the slope of the voltage increase is 400 μV s^{-1} from Fig. 1.

The model presented in this paper is only phenomenological in the sense that only the shape of the elementary transient is considered, without taking into account the cause of such a shape. However, such a linear increase of the overvoltage could be explained by the screening effect due to the bubble. As the growth of the bubble is diffusion controlled, it has been shown that the radius of the bubble increases proportionally to the square root of the time [3]. Hence the screening effect, proportional to the surface of the disc which is the projection of the bubble, could explain the linear variation of the overvoltage with time.

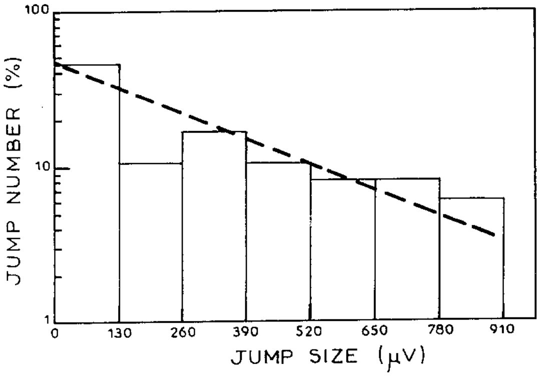

Fig. 2. Histogram of the jump sizes of Fig. 1.

From the time series recorded in Fig. 1, the observed fluctuations of the voltage is the sum of elementary voltage transients which are a linear function of time (Fig. 3). For each elementary transient, the following model can be used:

$$v(t-s,u) = W(t-s,u)Z(t-s) \quad (u,\, t-s>0) \tag{1}$$

where s is the nucleation time of the bubble, u its life time; $W(t,u)$ is defined by

$$\begin{aligned} W(t-s,u) &= 1 \quad \text{if} \quad t-s<u \\ &= 0 \quad \text{if} \quad t-s\geqslant u \end{aligned} \tag{2}$$

and $Z(t)$ defines the shape of the elementary transient, i.e. in this case

$$\begin{aligned} Z(t) &= kt \quad \text{if} \quad t\geqslant 0 \\ &= 0 \quad \text{if} \quad t<0 \end{aligned} \tag{3}$$

where k is a proportionality constant.

The total voltage fluctuation related to the hydrogen evolution is then given by

$$V(t) = \sum_{i=1}^{N(t)} v(t-s_i,u_i) \tag{4}$$

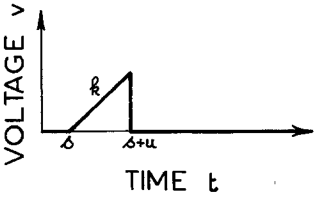

Fig. 3. Shape of the elementary transient used in the model.

where s_i, and u_i are the nucleation time and the life time of the ith bubble respectively, and $N(t)$ is the total number of nucleations at time t. s_i and u_i are two random quantities whose probability laws have to be defined. In the conditions where the number of bubbles is not too high, the elementary events can be considered as independent. Hence the distribution of the nucleation time s_i of the ith bubble can be assumed to follow a homogeneous Poisson law of intensity λ. The life times u_i can also be supposed to be independent and to have the same exponential probability distribution with parameter α (i.e. $1/\alpha$ represents the mean life time), such as

$$P(u > x) = \exp(-\alpha x) \quad x > 0 \tag{5}$$

as supported by the histogram given in Fig. 2, which shows that there are many more small bubbles than larger ones.

The mean and the power spectral density (p.s.d.) of the total voltage fluctuations can be calculated using the generalized shot noise (or filtered Poisson process) theory [4]

$$< V(t) > = \lambda \int_{-\infty}^{+\infty} < v(t-s,u) >_u \, \mathrm{d}s \tag{6}$$

and

$$\psi_V(f) = \lambda < |\tilde{V}(f,u)|^2 >_u \tag{7}$$

where

$$< X(u) >_u = \int_0^{\infty} X(u)\, f(u)\, \mathrm{d}u \tag{8}$$

where $f(u)$ is the distribution density of the u's, which is from $P(u > x)$

$$f(u) = \alpha \exp(-\alpha u) \tag{9}$$

and $\tilde{V}(f,u)$ is the Fourier transform of $v(t,u)$

$$\tilde{V}(f,u) = \int_{-\infty}^{+\infty} \exp(-2\pi j f s)\, v(s,u)\, \mathrm{d}s \tag{10}$$

In the case of the model considered in this paper

$$< V(t) > = \frac{\lambda k}{\alpha^2} \tag{11}$$

and

$$\psi_V(f) = \frac{2\lambda k^2}{\alpha^2} \frac{3\alpha^2 + 4\pi^2 f^2}{(\alpha^2 + 4\pi^2 f^2)^2} \tag{12}$$

The theoretical power spectral density has been plotted in Fig. 4.

The nucleation rate λ and the mean life time $1/\alpha$ of the bubbles can then be determined from the asymptotic values of the p.s.d.

$$\psi_V(0) = \frac{6\lambda k^2}{\alpha^4} \quad \text{when } f \to 0 \tag{13}$$

$$\psi_V(f) \sim \frac{\lambda k^2}{2\alpha^2 \pi^2 f^2} \quad \text{when } f \to \infty \tag{14}$$

Hence

$$\alpha^2 = 12\pi^2 f^2 \frac{\psi_V(f)}{\psi_V(0)} \quad \text{for } f \gg \frac{\alpha}{2\pi} \tag{15}$$

and

$$\lambda = \frac{\alpha^4 \psi_V(0)}{6k^2} \tag{16}$$

In a similar manner, under potentiostatic conditions, the current transient, mean current due

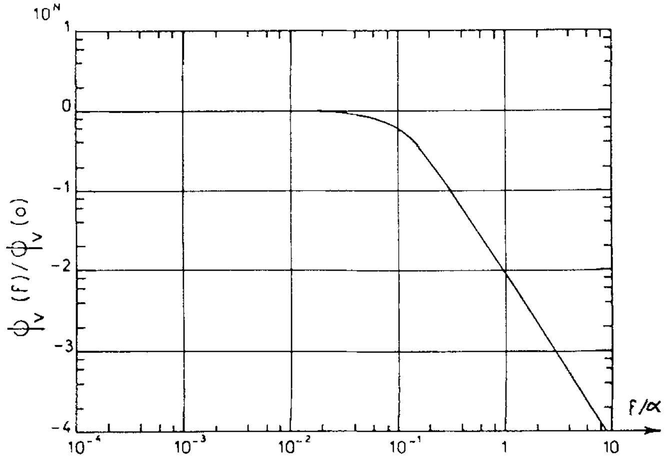

Fig. 4. Theoretical power spectral density (p.s.d.) of the voltage fluctuations corresponding to the recording of Fig. 1.

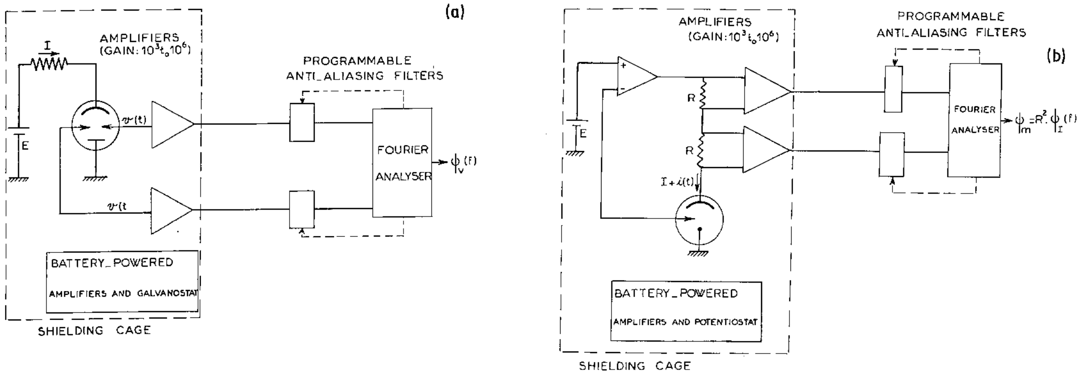

Fig. 5. Experimental arrangements used for measuring the p.s.d. in galvanostatic (a) and potentiostatic (b) control.

to the hydrogen bubble evolution and the p.s.d. of the current fluctuations can be written as

$$i(t-s,u) = k(t-s)\,W(t-s,u) \tag{17}$$

$$I(t) = \sum_{j=1}^{N(t)} i(t-s_j,u_j) \tag{18}$$

$$<I(t)> = \frac{\lambda k}{\alpha^2} \tag{19}$$

$$\psi_I(f) = \frac{2\lambda k^2}{\alpha^2}\,\frac{3\alpha^2+4\pi^2 f^2}{(\alpha^2+4\pi^2 f^2)^2} \tag{20}$$

In the same way one gets

$$\alpha^2 = 12\pi^2 f^2\,\frac{\psi_I(f)}{\psi_I(0)} \quad \text{for}\, f \gg \frac{\alpha}{2\pi} \tag{21}$$

and

$$\lambda = \frac{\alpha^4\,\psi_I(0)}{6k^2} \tag{22}$$

where the units of k are A s^{-1}.

3. Experimental results

The power spectral density was measured by using a Fourier Analyser (Hewlett-Packard 5451C) based on a F.F.T. algorithm. The experimental arrangements are depicted in Fig. 5 for galvanostatic and potentiostatic control measurements. The p.s.d. determination is based on a cross-spectrum technique which allows the parasitic noises of the measurement channels (amplifiers, filters, reference electrodes in the galvanostatic mode, and standard resistances in the potentiostatic mode) to be eliminated.

The measurements were made on a pure iron electrode (Johnson Matthey), which was a 1 mm diameter disc facing upwards, in a sulphuric acid medium (pH = 0) close to the corrosion potential (low current density). The reference electrodes were of the saturated mercurous sulphate type. Two different measurements were carried out, the first one under galvanostatic control (see Fig. 1) for recording of voltage fluctuations, and the second one under potentiostatic control (Fig. 6). The power spectral density of the fluctuations generated by hydrogen bubble evolution during the two experiments are depicted in Fig. 7.

From the asymptotic values of the p.s.d. and the factors k determined from the time-recording, the values of the mean life time $1/\alpha$, the nucleation rate λ and the mean of the fluctuations ($<V>$ or $<I>$ depending on the mode of control used) can be calculated. Their values are given in Table 1.

As the total d.c. current I_t flowing through the electrode, which is the only measurable current, is the sum of an anodic current I_a due to the metal dissolution and of a cathodic current I_c due to hydrogen formation, one has

$$I_t = I_a - I_c \tag{23}$$

If the efficiency of gas evolution is assumed to be 100%, i.e. if all the dissolved hydrogen evolves outside the electrochemical interface through bubbles [5], the cathodic current I_c due to the molecular hydrogen formation is equal to the mean $<I>$ of the current fluctuations due to gaseous bubble evolution. In these conditions, the anodic current I_a can be calculated simply from the measured cur-

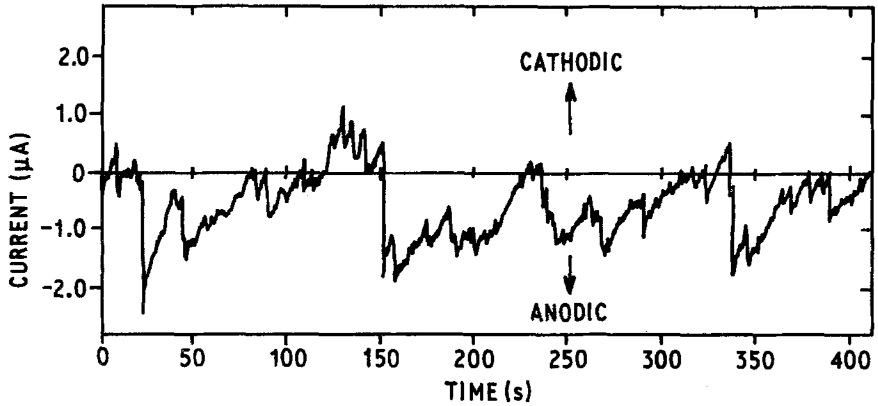

Fig. 6. Current–time recording at a 3 mA cm^{-2} anodic current density in potentiostatic regime.

rent I_t and the mean current $<I>$ of the fluctuations deduced from the p.s.d. measurements:

$$I_a = I_t + <I> \tag{24}$$

In the galvanostatic control case, the mean voltage fluctuation was 0.5 mV and as the polarization resistance, measured by an a.c. technique or by the slope of the $I-V$ curve, was $R_p = 1.2\ \mathrm{K}\Omega$, the mean hydrogen current was $<I> = 0.42\ \mu\mathrm{A}$. Hence, as $I_t = 29\ \mu\mathrm{A}$, the anodic current due to the dissolution of iron was $I_a = 29.4\ \mu\mathrm{A}$. In the second case, when $I_t = 23\ \mu\mathrm{A}$, $<I> = 0.39\ \mu\mathrm{A}$, the iron dissolution current was $I_a = 23.4\ \mu\mathrm{A}$.

4. Discussion

The gas evolution regime at a given polarization potential depends very much on the state of the electrode surface, which is linked not only to the polishing technique (emery paper or alumina) but also to the history of the electrode (time at the corrosion potential favours hydrogen penetration into the metal and thus changes the properties of the surface) which leads to a certain irreproducibility of the experiment. However, the shape of the elementary transient which is related to single bubble nucleation and growth is always the same. For example, the two reported experiments show two different gas evolution regimes at almost the same polarization potential. This fact demonstrates that the gas evolution process is not, in these experimental conditions, the rate limiting step in the overall proton reduction process.

The phenomenological model reported in this paper does not take into account all the complexities of bubble evolution such as coalescence

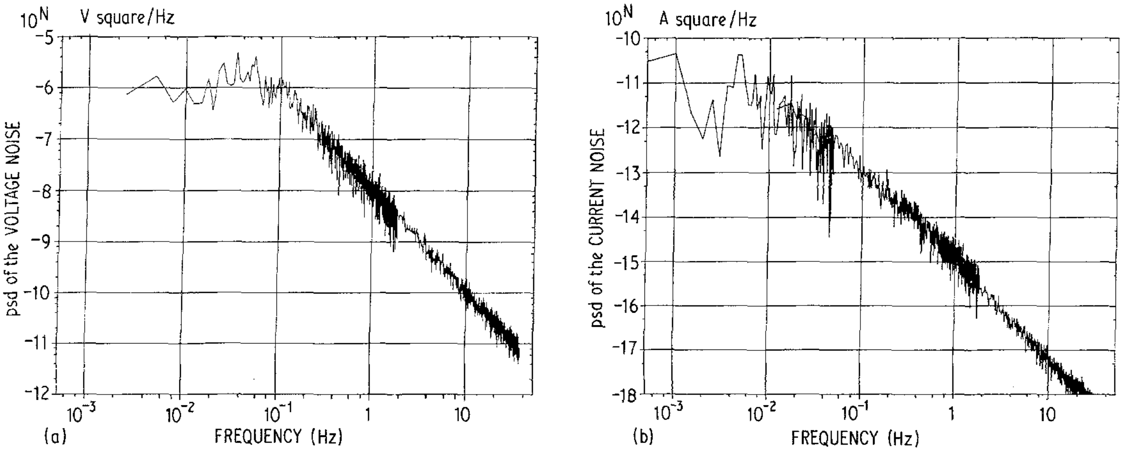

Fig. 7. Power spectral density of the fluctuations related to hydrogen evolution. (a) measurement in galvanostatic regime corresponding to Fig. 1. (b) measurement in potentiostatic regime corresponding to Fig. 6.

Table 1. Determination of the characteristic parameters of bubble evolution

	ψ (0)	ψ ($f = 10$ Hz)	k	$1/\alpha$ (s)	λ (s^{-1})	< >
Galvanostatic control	$\psi_V(0) = 10^{-6}$ V^2 Hz^{-1}	$\psi_V(f) = 10^{-10}$ V^2 Hz^{-1}	400 μV s^{-1}	0.9	1.5	$<V> = 0.5$ mV
Potentiostatic control	$\psi_I(0) = 2 \times 10^{-12}$ A^2 Hz^{-1}	$\psi_I(f) = 1.4\ 10^{-15}$ A^2 Hz^{-1}	70 nA s^{-1}	3.5	0.5	$<I> = 0.39$ μA

of bubbles. However, it allows the characteristic parameters of the bubble evolution regime to be obtained. These results are difficult to obtain from the time-recording in the case of low nucleation rate of bubbles as in the reported experiments, and impossible to obtain in the case of high nucleation rate of bubbles, which is manageable by spectral analysis. The slight discrepancy between the qualitative determination of the interesting parameters from the time-recording and the quantitative one from the p.s.d. is due to the fact that the determination from the time-recording is based on only one recording and the measurement of the p.s.d. is averaged over an ensemble of 10 or 20 recordings.

As the p.s.d. of the fluctuations generated by an iron electrode at the corrosion potential is very similar to those depicted above, such a technique could be appropriate for measuring the corrosion rate. In this case, as $I_t = 0$, the dissolution current is being obtained $I_a = <I>$. This technique would have the advantages of not being destructive like weight loss measurements and not using an exciting signal like d.c. or a.c. techniques. Simply 'listening' to the potential noise without any external pertubation would, in principle, allow the corrosion rate to be determined.

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