

Fluctuation analysis in electrochemical engineering processes with two phase flows

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Fluctuation analysis in electrochemical systems appears to be a suitable method for obtaining information on the system dynamic behaviour, especially when the voltage or current fluctuations are due to elementary events on the electrode at a semi-macroscopic scale, for example growth and detachment of bubbles on a gas-evolving electrode or contacts between charged particles in a fluidized or circulating bed reactor, or pits in localized corrosion. Therefore this situation is largely encountered in electrochemical engineering processes with two phase flows. By analysing the current (voltage) fluctuations at constant potential (current) and/or the electrolyte resistance fluctuations, this technique provides quantitative parameters which are often inaccessible by traditional deterministic techniques, steady state or not, which deal with time-averaged signals. The technique also leads to a better understanding of the elementary processes on the electrode. Two examples are given: the first concerning a gas-evolving electrode and the second a circulating bed electrode.

1. Introduction

The kinetics of an electrochemical system can be generally investigated in three steps. First, the current–voltage curve analysis gives information on the rate–determining process at the metal–electrolyte interface. Secondly, the system dynamic behaviour can be investigated by measuring the electrochemical impedance of the electrode: this technique allows the relaxations of the elementary processes (charge transfer, species adsorption, mass transport, etc.) to be separated. These two techniques deal with the deterministic responses of the electrode, i.e. the random behaviour of the electrode is completely ignored. In other words, elementary events, such as growth and detachment of bubbles in a gas-evolving electrode, or contacts between metallic particles and the current collector in a circulating bed reactor, or pits in localized corrosion, which occur randomly in time and on the electrode surface, cannot be analysed by either of these deterministic techniques.

The next step of the investigation of the electrode kinetics therefore deals with the random behaviour which can be investigated through an analysis of the noise generated by the electrochemical system, i.e. electrode potential fluctuations when the system is galvanostatically controlled, or current fluctuations when the system is potentiostatically controlled and/or via fluctuations of the electrolyte resistance. The aim of the noise analysis is to obtain information on the random elementary events occurring on the electrode surface, i.e. to provide a more

precise description of the electrode phenomena. In addition, it is often difficult to use deterministic techniques with two-phase flow processes as they are generally related to large random fluctuations of the current compared to its average steady-state value.

Electrochemical noise has been investigated since the early 1970s. The pioneering works of Tyagai [1] have been followed by many other studies, mainly devoted to noise generated by metal electrocrystallization [2, 3], localized corrosion [4, 5], electrochemical reaction [6, 7] or gas evolution [8–10].

The first question which arises in the stochastic behaviour analysis of an electrochemical system is the determination of the possible origin(s) of the voltage or current fluctuations. This problem, quite simple in some cases (e.g. pitting corrosion), becomes difficult for many practical situations (e.g. gas-evolving electrode, electrocrystallization). Various causes can lead to voltage or current fluctuations. The concentration of the reacting species fluctuates first because these species are produced and/or consumed by the chemical or electrochemical reactions taking place at the electrode, and secondly because of the electrolyte motion (forced or natural convection). In a two-phase flow process bubbles or particles may screen a part of the electrode active surface which fluctuates owing to the continuous change of the current distribution on the electrode. Localized corrosion shows electrode activity fluctuations: the electrode is active in the pits and passive outside them. In a fluidized bed electrode, the electrode conductivity fluctuates because of the intermittent contacts between charged metallic particles. Many other examples could be given.

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In this paper the stochastic behaviour of two electrochemical systems involving two-phase flows, i.e. a gas-evolving electrode and a circulating bed electrode, is investigated to show the kind of information that can be obtained.

2. Experimental details

The electrochemical noise depends on how the system is maintained at the polarization point (I, V). Under constant current ($\Delta I(t) = 0$) the electrode potential may be written as

$$V(t) = V + \Delta V(t) \quad (1)$$

where $\Delta V(t)$ is the voltage electrochemical noise, and under constant potential ($\Delta V(t) = 0$) the current may be written as

$$I(t) = I + \Delta I(t) \quad (2)$$

where $\Delta I(t)$ is the current electrochemical noise. Obviously these noises $\Delta V(t)$ and $\Delta I(t)$ give the same information because both are induced by fluctuations of the same physical quantities. As the stationarity of $\Delta V(t)$ and $\Delta I(t)$ is assumed, their power spectral densities (PSD) $\Psi_v(f)$ and $\Psi_i(f)$, i.e. the distribution of the $\Delta V(t)$ and $\Delta I(t)$ powers in the frequency domain can be defined; these PSDs are related by the following equation:

$$\Psi_v(f) = \Psi_i(f) \cdot |Z(f)|^2 \quad (3)$$

for low-amplitude fluctuations, where $Z(f)$ is the electrode electrochemical impedance, which takes into account the electrode reactions and the double layer charging current.

For simplification, only the voltage electrochemical noise will be studied in this paper. The fluctuations, ΔV , of the electrode total potential can be written under current control [8]:

$$\Delta V(t) = \Delta V_{\text{ohm}}(t) + \Delta V_a(t) + \Delta V_c(t) \quad (4)$$

where ΔV_{ohm} , ΔV_a , ΔV_c represent the fluctuations of the spatial averages over the electrode surface necessary to take into account the nonuniform current distribution, of the ohmic drop, the activation overpotential and the concentration overpotential, respectively.

In a two-phase flow, the total potential fluctuations have three main origins: the electrode active surface fluctuations (leading to ΔV_{ohm} and ΔV_a), the charge exchanges during collisions of metallic particles on the electrode (leading to ΔV_a), and the concentration overpotential fluctuations (leading to ΔV_c) when the electrolyte motion due to bubbles or particles provokes a change in the concentration gradients of the dissolved reacting ions in the vicinity of the electrode.

Equation 4 allows separation of the total potential fluctuation $\Delta V(t)$ into two terms: the ohmic drop fluctuation $\Delta V_{\text{ohm}}(t) = \Delta R_e(t)I$, where $\Delta R_e(t)$ is the electrolyte resistance fluctuation and I the mean electrolysis current, and the faradaic potential fluctuation $\Delta E(t)$, including activation and concentration

overpotential fluctuations, $\Delta V_a(t)$ and $\Delta V_c(t)$. Hence,

$$\Delta V(t) = \Delta R_e(t)I + \Delta E(t) \quad (5)$$

This equation may be derived by linearization of the general equation giving the electrode potential:

$$V(t) = R_e(t)I + E(t) \quad (6)$$

where the mean electrolysis current, I , is constant under galvanostatic control ($\Delta I(t) = 0$).

To separate these two components, it is necessary to simultaneously measure the electrolyte resistance fluctuations $\Delta R_e(t)$ and the total potential fluctuations $\Delta V(t)$ [11]. The experimental arrangement is depicted in Fig. 1. A 100 kHz sinusoidal current i_{100} is superimposed to the direct electrolysis current I , so that the voltage difference between the reference electrode and the working electrode is

$$V + \Delta V(t) + v_{100}(t)$$

where V is the mean voltage, $\Delta V(t)$ the potential fluctuations and v_{100} the sinusoidal voltage response whose amplitude is proportional to the electrolyte resistance R_e , as the impedance is reduced to the electrolyte resistance at 100 kHz for the electrochemical systems studied in this paper. Hence the amplitude of the v_{100} voltage is modulated by the fluctuations of the electrolyte resistance.

The potential fluctuations are classically measured on one channel whereas in the second one the electrolyte resistance fluctuations are demodulated with a diode and a low-pass filter. Therefore the voltage fluctuations Δv_{R_e} at point B are proportional to the electrolyte resistance fluctuations:

$$\Delta v_{R_e}(t) = a\Delta R_e(t) \quad (7)$$

where a is a constant factor, which can be calibrated. The phase shift between the voltages at points A and B is less than 1° at 1 kHz. The Fourier analyser samples the two signals and calculates the PSD $\Psi_v(f)$, $\Psi_{R_e}(f)$, $\Psi_{R_e I}(f)$ and $\Psi_e(f)$ of the potential fluctuations $\Delta V(t)$, the electrolyte resistance fluctuations $\Delta R_e(t)$, the ohmic drop fluctuations $\Delta R_e(t)I$ and the faradaic potential fluctuations $\Delta E(t)$ in the frequency bandwidth (d.c. – 5 kHz), respectively.

3. Examples

3.1. Stochastic behaviour of a gas-evolving electrode

Gas evolution is a common process arising in electrochemical engineering. Gas bubbles induce parasitic overpotential increments, and therefore power loss, because first the electrodes are partially screened by the attached bubbles, and secondly in the bulk of the electrolyte the bubbles reduce the electrolyte conductivity. In contrast gas evolution is favoured in some reactors to enhance mass transfer. To date, almost all the investigations have been made by deterministic techniques. The few preliminary analysis of the gas evolution stochastic behaviour [8–10, 12] have shown that they can lead to a better understanding of the elementary phenomena

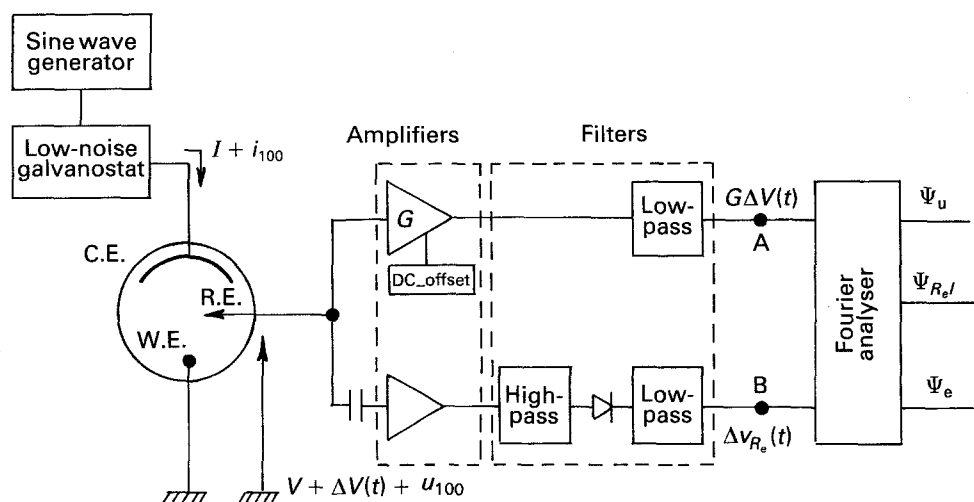


Fig. 1. Experimental arrangement used for measuring the power spectral density of the potential and electrolyte resistance fluctuations.

occurring on the electrode (nucleation, growth, coalescence, detachment of bubbles, influence of the bubbles on the electrochemical reactions etc.), and to an estimation of the parameters which characterize the gas evolution such as the number of bubbles evolved per unit time, the average bubble detachment radius and the gas evolution efficiency.

A typical time recording of the potential fluctuations is given in Fig. 2(a) for a hydrogen-evolving platinum disc electrode facing upwards in 1M sulphuric acid. This recording shows steep potential increases and, from optical observation at a lower electrolysis current, it has been shown that each increase is related to a bubble detachment. The jump amplitude is a random parameter which depends on the evolved bubble diameter. For this time recording, the number of bubbles evolved per time unit can be estimated by counting the potential jumps, and a statistical analysis of the jump amplitude, ΔV , gives, for example, the moments of the jump amplitude distribution, such as $\langle \Delta V \rangle$, $\langle \Delta V^2 \rangle$. In more complicated situations, no potential transient can be seen on the time recordings and the only way to analyse the potential fluctuations is to perform a spectral analysis.

Figure 2(b) shows the PSD corresponding to the time recording in Fig. 2(a). This PSD was obtained by ensemble averaging of N elementary spectra $(2/T)|\mathcal{F}[\Delta V(t)]|^2$ (where \mathcal{F} is the Fourier transform) calculated from N voltage-time recordings sampled over an observation time, T [7]. Three observation times were used in this case, 20 s, 2 s, 0.2 s, giving a PSD in the frequency range [50 mHz – 5 kHz]. In Fig. 2(b) the PSD was plotted for frequencies higher than 0.5 Hz, because at lower frequencies it showed only the low-frequency plateau. The good reproducibility of the PSD measured at various times confirms the stationarity of the voltage fluctuations. Moreover for time periods corresponding to the measurement time the stationarity is corroborated by the good quality of the measured spectrum, i.e. the relative measurement error is found to be inversely proportional to the square root \sqrt{N}

of the number of averaged elementary spectra, as predicted by theory. In Fig. 2(b), the low frequency plateau is followed by a peak at 10 Hz and a decrease at first in f^{-2} , then in $f^{-5/2}$ in the high frequency range. The great variety of the measured PSD must be related to the complexity of the phenomena involved on a gas evolving electrode, and further study is needed to completely interpret these PSD.

As shown previously [8], two parameters can be derived from the PSD; first the mean number, λ , of bubbles evolved per time unit, secondly the average $\langle \Delta V^2 \rangle$ of the square of the voltage jump amplitude due to a bubble detachment. At a high electrolysis current, the jump amplitude, ΔV , involved in bubble detachment can be written $\Delta V = \Delta R_e I$. This was confirmed later [11] by simultaneously measuring the potential and electrolyte resistance fluctuations generated during hydrogen evolution on an iron disc electrode in 1M sulphuric acid at a current density 400 mA cm^{-2} . Figure 2 in [11] shows that at any time t

$$\Delta V(t) = \Delta R_e(t)I \quad (8)$$

As explained previously [8], the jump amplitude $\Delta R_e I$ can be related to the radius of the evolved bubble. Hence the mean radius $\langle r_d \rangle$ of the evolved bubbles can be calculated from the value of $\langle \Delta V^2 \rangle$. As an example, in Fig. 3(a), the mean radius $\langle r_d \rangle$ of the evolved bubbles is plotted against the electrolysis current density for hydrogen evolution in 1M NaOH. When the current density increases, the radius $\langle r_d \rangle$ increases, which is in agreement with the optical observation. The $\langle r_d \rangle$ values obtained in the experiments from the voltage fluctuations PSD are also in agreement with other optical observations: the hydrogen bubbles are smaller than oxygen bubbles in alkaline medium, but bigger than oxygen bubbles in acidic medium.

Knowing the parameters λ and $\langle r_d \rangle$, the gas evolution efficiency e , i.e. the amount of produced molecular gas which evolves under gaseous form, can be calculated [8]. In Fig. 3(b), the efficiency e is

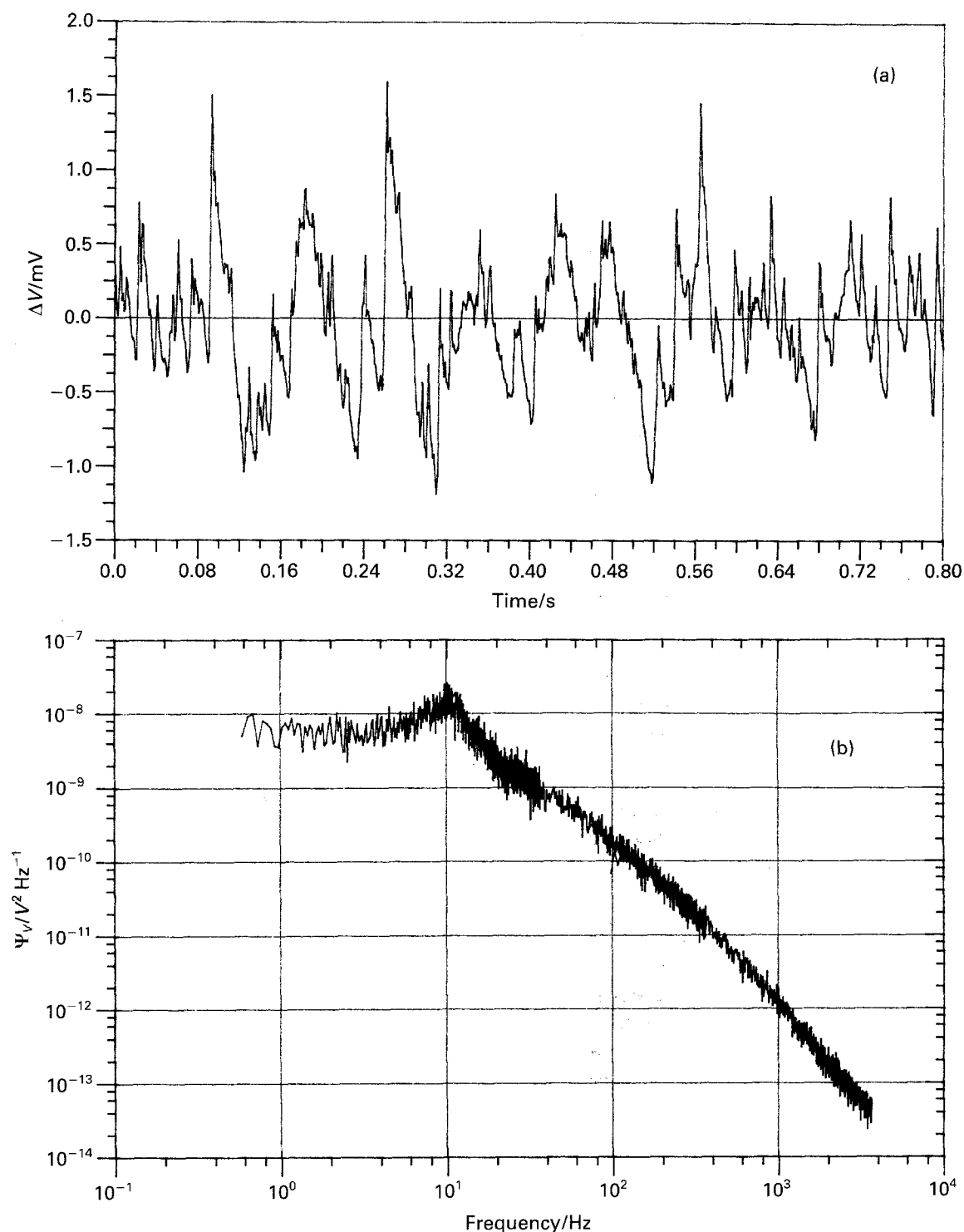


Fig. 2. (a) Time recording, (b) PSD of the potential fluctuations induced by hydrogen evolution on a platinum disc electrode (diameter 0.5 mm) facing upwards in 1 M H_2SO_4 at a current density 380 mA cm^{-2} .

plotted against the electrolysis current density for the same experimental conditions as in Fig. 3(a). Figure 3(b) shows low values of efficiency (10–30%), far from the often supposed value 100%. This low efficiency can be explained by the fact that on a small disc electrode diameter (0.5 mm), the bubble growth is essentially controlled by bubble coalescence which is known to be difficult for hydrogen bubbles in alkaline medium [13].

This derivation of the parameters $\langle r_d \rangle$ and e is not valid at low electrolysis current, as the potential fluctuations cannot be explained by ohmic drop

fluctuations. Figure 4 shows the $\Delta V(t)$ and $\Delta R_e(t)I$ time recordings for hydrogen evolution in 1 M NaOH on a platinum disc electrode at a current density of 28 mA cm^{-2} . For the two curves, the fluctuations are very similar, indicating they are both due to gas evolution. But the potential fluctuations are in this case mainly due to activation overpotential fluctuations or concentration overpotential fluctuations of dissolved hydrogen in the electrolyte. The derivation of the gas evolution parameters must be made from the PSD Ψ_{R_e} instead of the PSD Ψ_v in low-current electrolysis conditions.

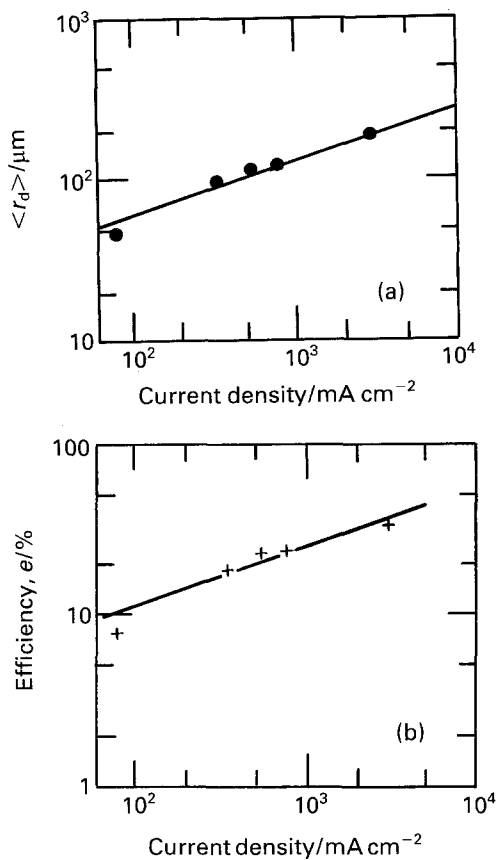


Fig. 3. (a) Average bubble detachment radius $\langle r_d \rangle$ and (b) gas evolution efficiency e for hydrogen evolution on a platinum disc electrode (diameter 0.5 mm) facing upwards in 1 M NaOH.

This first attempt to derive some parameters characteristic of a gas evolution from the electrochemical noise PSD is promising, but further studies are necessary to validate the parameter derivation. The

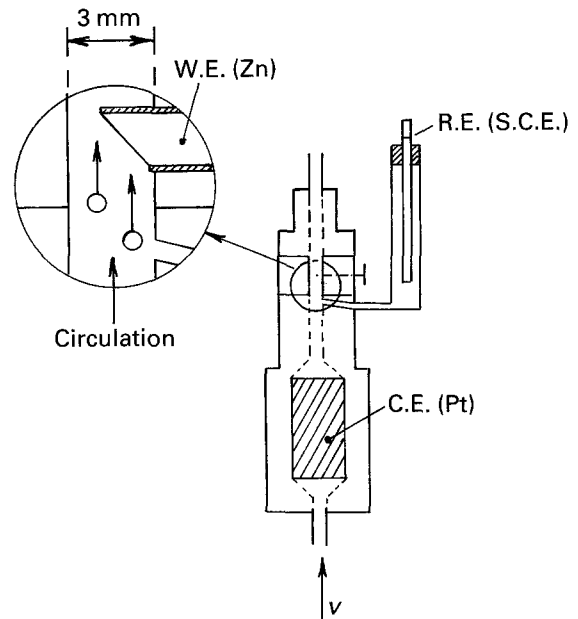


Fig. 5. Circulating electrolyte and particles electrolyser. W.E.: working electrode (zinc rod); R.E.: reference electrode (saturated calomel electrode); C.E.: counter electrode (platinum grid).

analysis of the potential fluctuations to estimate the gas evolution parameters will then be a technique which, on the one hand, is easier to employ than the classical use of a high-speed film camera, and, on the other hand, allows the gas evolution efficiency to be estimated at the electrode surface and not at a few millimetres above, as is usually done [13, 14]. If pictures of the bubbles while they were still attached to the electrode, i.e. while they were still growing, were taken, it would have been impossible to determine their mean detachment radius.

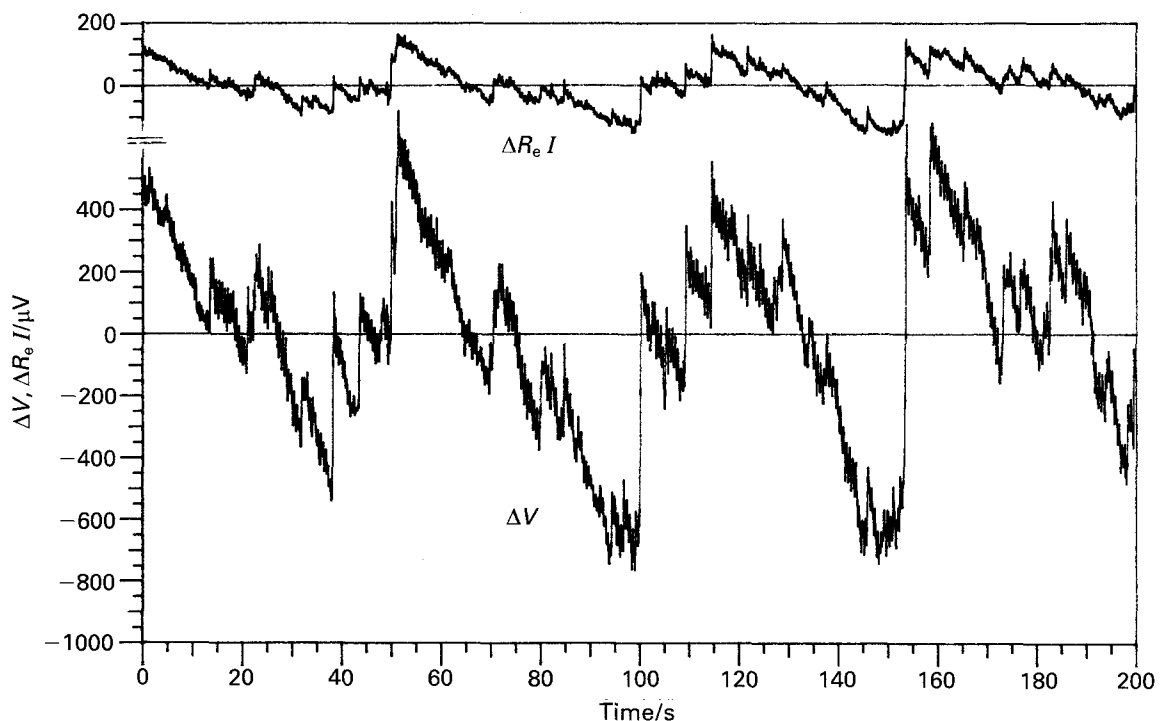


Fig. 4. Time recordings of potential $\Delta V(t)$ and ohmic drop $\Delta R_e(t)I$ fluctuations measured under galvanostatic control ($J = 28 \text{ mA cm}^{-2}$) for hydrogen evolution on a platinum disc electrode (diameter 5 mm) in 1 M NaOH.

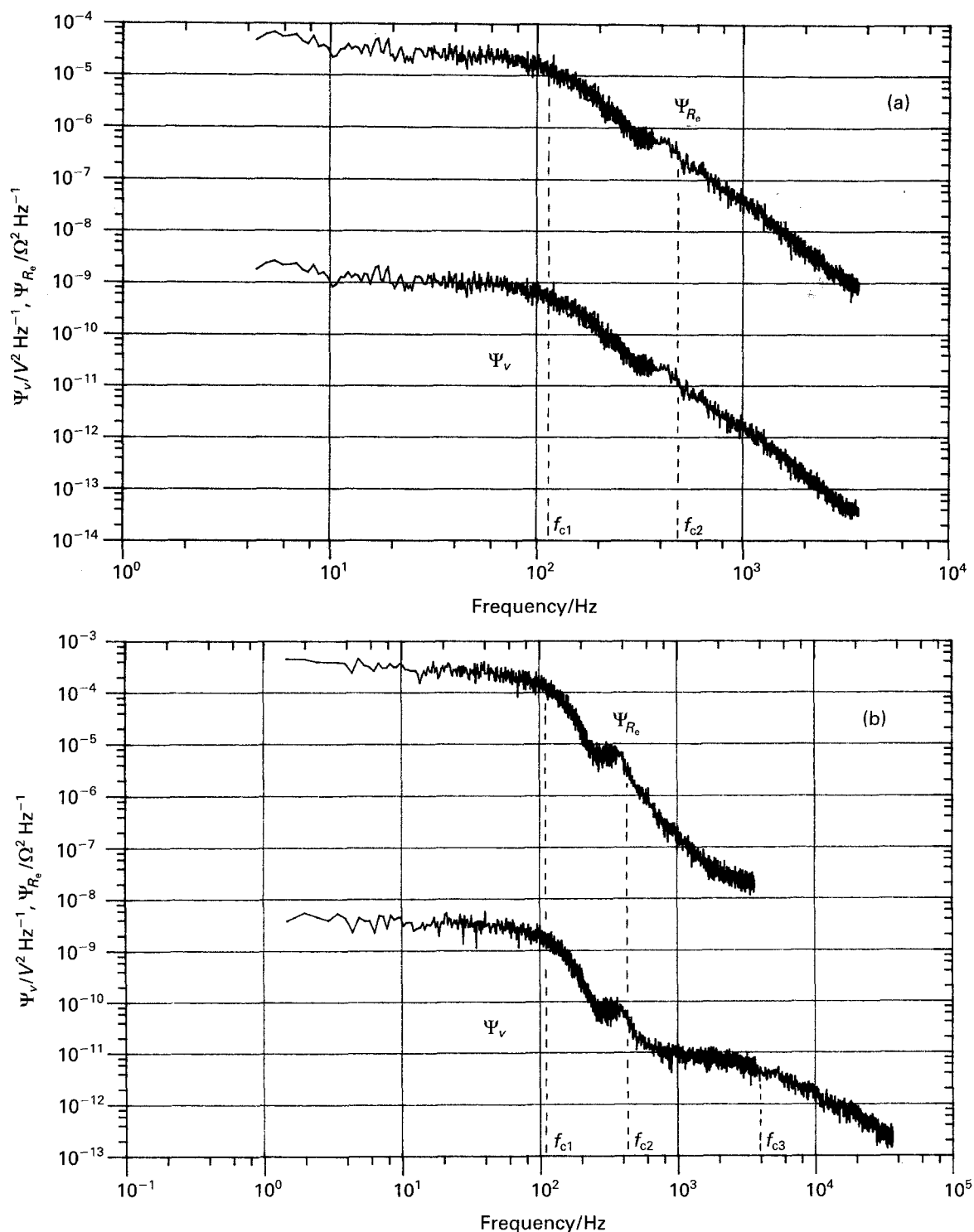


Fig. 6. PSDs Ψ_v and Ψ_{R_e} of the potential and electrolyte resistance fluctuations in the presence of particles (2%) at a 120 cm s^{-1} circulation velocity and a 120 mA cm^{-2} cathodic current density (f_{c_i} are cutoff frequencies): (a) glass beads and (b) zinc beads.

3.2. Electrolyser with circulating electrode and particles

Circulating electrolyte and particle electrolysers are used in some electrochemical engineering processes such as batteries. An example is in the electrocrystallization of zinc using zinc particles [15–17]. Interest in such an electrolyser is first the continuous removal of the active surface of the particles and, secondly, that electrode-particle collisions eliminate the dendritic growth of zinc

which otherwise leads to short circuits between the battery plates.

The investigation of the charge exchange between a circulating particle and the zinc electrode is of interest as it controls the whole behaviour of the electrolyser. However, the observed potential under current control is random, as each collision between the electrode and a particle generates an elementary potential transient; hence the electrode potential can be seen as the superposition of many elementary transients when many particles circulate in the

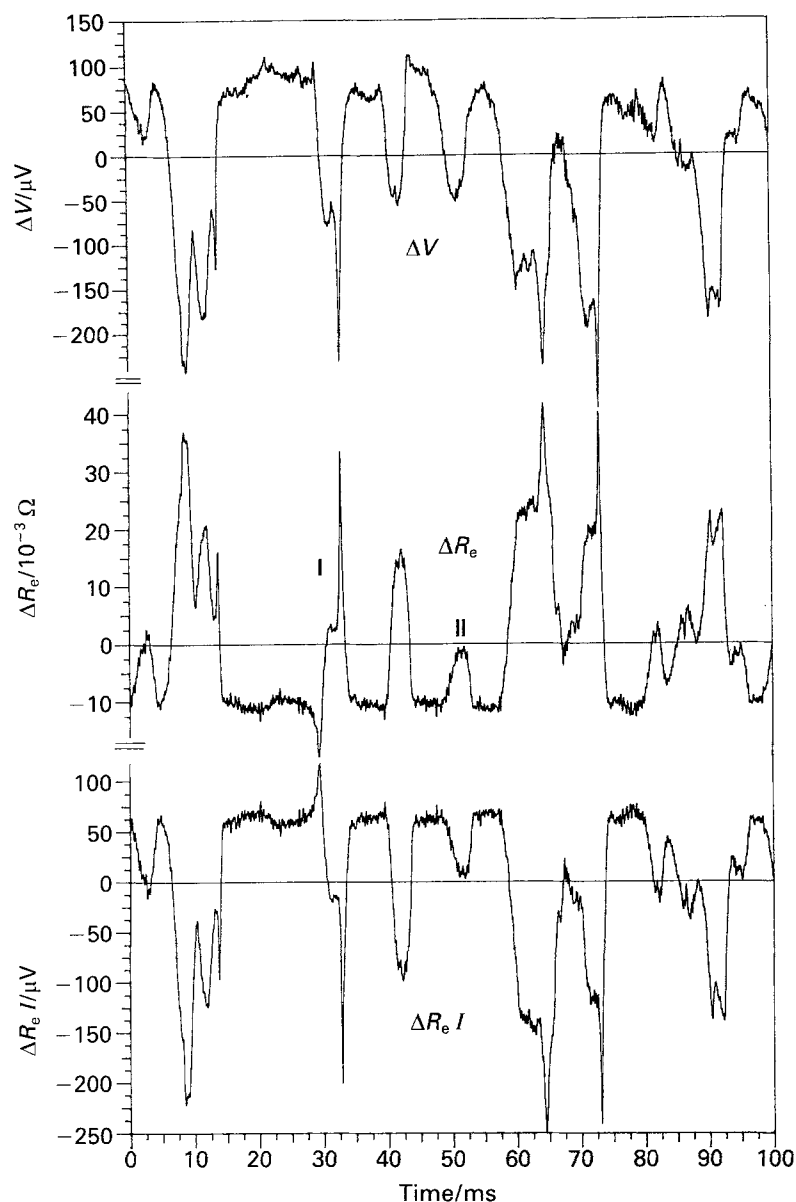


Fig. 7. Time recordings of the potential $\Delta V(t)$, electrolyte resistance $\Delta R_e(t)$ and ohmic drop $\Delta R_e(t)I$ fluctuations for glass beads (0.08%) at a 120 mA cm^{-2} cathodic current density and a 120 cm s^{-1} circulation velocity.

electrolyte. In this case, the measurement of the fluctuations of the electrolyte resistance is very useful for understanding the process involved in the charge exchange.

The scheme of the electrolyser is given in Fig. 5. The particles are zinc coated polystyrene beads ($300\text{--}500 \mu\text{m}$ in diameter) and glass beads ($290\text{--}320 \mu\text{m}$ in diameter) for comparison. The current collector (working electrode) is a 0.05 cm^2 ellipse (cross section of a 2 mm zinc rod) 45° inclined with respect to the electrolyte flux.

The PSDs of the potential and electrolyte resistance fluctuations are plotted in Fig. 6 for glass and zinc beads. For the glass beads, two cut-off frequencies f_{c1} and f_{c2} can be observed and for the zinc beads a third one (f_{c3}) is detected.

In the case of glass beads, the PSDs Ψ_v and Ψ_{R_e} shown in Fig. 6(a) lead to

$$\Psi_v(f) = \Psi_{R_e}(f)I^2 = \Psi_{R_e I}(f) \quad (9)$$

Hence Equation 8 is verified. It may be concluded that all the potential fluctuations derive from the ohmic

drop perturbations generated by the glass beads passing close to the electrode. On the other hand, in the case of zinc beads (Fig. 6(b)), although there are some similarities in the low frequency range of the PSDs, Equation 8 is not verified. In addition, a further feature occurs in the high frequency range. Therefore, it is concluded that other processes than ohmic drop generate potential fluctuations in the case of metallic beads.

To thoroughly investigate these processes, the fluctuations were recorded with respect to time for a low bead concentration in order to have the elementary transients well separated. Figures 7 and 8 give the elementary transients recorded for glass and zinc beads, respectively. For glass beads (Fig. 7), $\Delta V(t)$ and $\Delta R_e(t)$ transients are in the opposite direction. Furthermore, the recordings $\Delta V(t)$ and $\Delta R_e(t)I$ (with $I < 0$ for a cathodic current) fit very well. This means that the potential fluctuations are generated by the ohmic drop fluctuations related to the passage of the beads close to the electrode (Equation 8). This is a confirmation of the result obtained from the PSD (Fig. 6(a)).

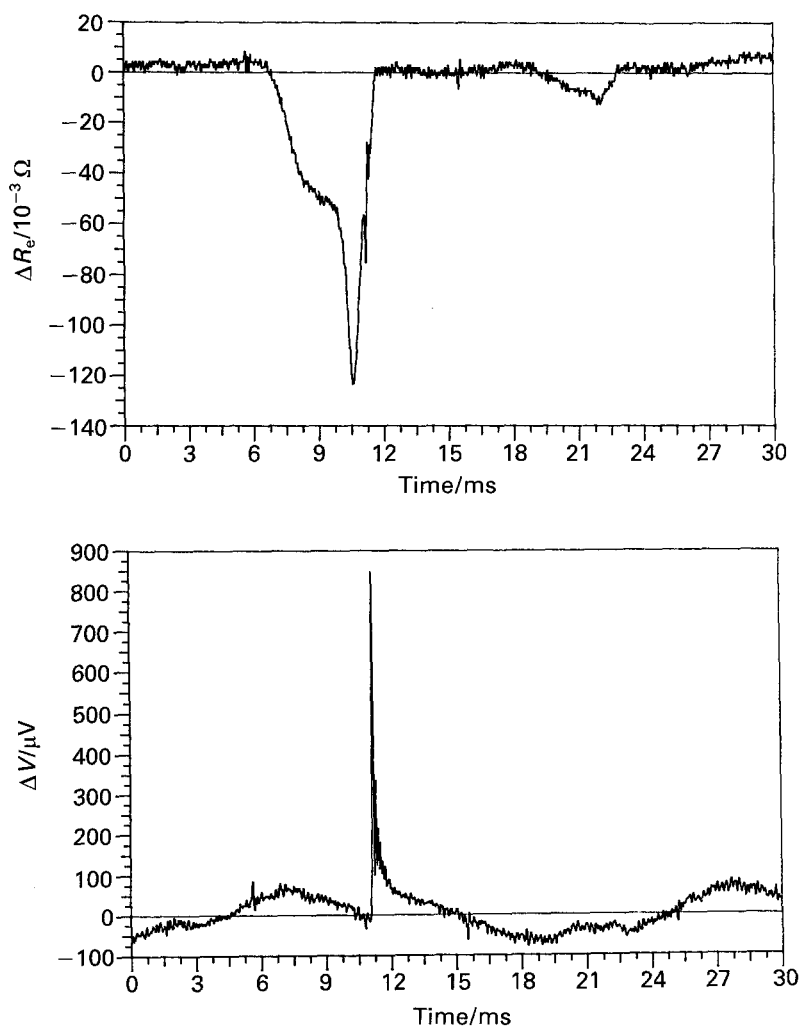


Fig. 8. Time recordings of the potential $\Delta V(t)$ and electrolyte resistance $\Delta R_e(t)$ fluctuations for zinc beads (0.04%) at a 10 mA cm^{-2} cathodic current density and a 120 cm s^{-1} circulation velocity.

Two types of electrolyte resistance transients can be observed in Fig. 7, the type II transient related to the passage of the glass beads between the working electrode and the reference electrode in the electrolyte channel, and the type I transient, similar to the first one, but with a steep increase showing the passage of the glass bead in the vicinity of the electrode. It can be shown [15–17] that the common part of type I and type II transients gives the low frequency part (f_{c1}) of the fluctuations PSDs whereas the peak gives the medium frequency contribution (f_{c2}).

Concerning the elementary transients related to the zinc beads (Fig. 8), the electrolyte resistance fluctuations are very similar to those of the glass beads, although they are in the opposite direction (the high frequency electrolyte resistance decreases when conductive beads are mixed with the electrolyte). However, the potential fluctuations show a steep peak related to the exchange of charge during collision between a zinc bead and the electrode, in addition to ohmic drop fluctuations similar to those found for glass beads. This transient shape corroborates the measured PSD (Fig. 6(b)) where a third time constant (f_{c3}) is found in the potential fluctuations PSD.

The concomitant use of the PSD and of the $V(t)$ recordings allows the ratio λ_c/λ_p which represents the fraction of beads which are charged on the

collector to be evaluated [15, 17] (Table 1). The number of beads λ_p which pass in front of the electrode per unit time can be estimated from the low frequency plateau of the Ψ_{R_e} PSD, and the $V(t)$ recordings allow the number of beads, λ_c , which are charged on the collector per unit time, to be estimated by statistical counting.

Table 1 shows that the ratio decreases when the bead concentration increases and that there is a critical concentration beyond which the ratio becomes constant.

4. Conclusion

The classical deterministic methods to analyse the kinetics of an electrochemical system (current–voltage curve, cyclic voltammetry, impedance etc.) only give an average (in time and over the electrode surface) of the elementary events randomly occurring

Table 1. Ratio λ_c/λ_p for different zinc bead concentrations

% beads	λ_c/λ_p
0.08	0.8
0.4	0.3
2	0.23
4	0.23

on the electrode, such as the birth, growth and detachment of bubbles for a gas-evolving electrode, or the collisions between particles and the current collector for a circulating bed electrode.

The analysis of the fluctuations of potential, current and electrolyte resistance gives a better understanding of these elementary events and a quantification of some parameters usually inaccessible by the deterministic techniques especially in two-phase flow systems. The number of bubbles evolved per time unit, the bubble detachment mean radius or the gas evolution efficiency for a gas-evolving electrode, or the number of particles per time unit passing in front of or touching the metallic probe for a circulating bed reactor, are attainable by this way.

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