LISTENING TO
CORROSION

by François Huet, Asunción Bautista, and Ugo Bertocci

About 30 years ago, one of the authors had a colleague, a microbiologist interested in biocorrosion, who, in the spirit of free inquiry, had constructed a contraption with two electrodes connected through capacitors and a little microphone in between. The present author was invited to see the apparatus and to listen to corrosion. Sure enough, he could hear the deep groans, louder or fainter, depending on the rate of corrosion, varied by changing the aggressivity of the electrolyte.

The system was very simple: no filters, no spectrum analyzers, above all no first or second order statistics, maximum entropy or Fourier transforms. The present author, who at the time thought only in terms of deterministic electrode kinetics, had difficulties appreciating what a stochastic approach could bring. Warren Iverson, the distinguished microbiologist, did not care much for the rather heavy mathematical apparatus later brought to bear on electrochemical noise, and pursued other areas of research. Nevertheless, he published a short article in the *Journal of The Electrochemical Society* that many still quote as the first paper on electrochemical noise in corrosion.[1] Incidentally, this journal should be congratulated for its foresight in publishing the article, which could easily have been rejected, unusual as it was.

Many semi-macroscopic phenomena related to corrosion, either localized or uniform, are stochastic by nature, so that the analysis of the spontaneous fluctuations of the electrical quantities of a galvanic system, known as electrochemical noise (EN), is the method of choice for their study and has a number of attracting features for corrosion research and engineering.

The analysis of EN, begun a few decades ago, only recently has been introduced as a method for assessing and monitoring corrosion. The pioneering work of Eden *et al.*,[2] has been instrumental in introducing the idea of a corrosion cell with two working electrodes (WE), where both current and voltage fluctuations can be measured. The question remained of putting the interpretation of the data on a firm basis. This is now possible, so that both the working of symmetrical or asymmetrical cells can be analyzed with confidence. An intuitive description of the functioning of such a corrosion cell is that the noise generated by one of the electrodes acts as a source signal for the measurement of the impedance of the other electrode. The measurement of the impedance by means of an external broadband excitation is certainly not new, but in the EN case the source is internal, which simplifies considerably the instrumentation necessary, and makes its application attractive for on-line corrosion monitoring.

Because EN measurements on a single corroding electrode do not permit obtaining the corrosion rate, most applications in the field are based on the use of cells with two identical electrodes (same material, same size, same surface preparation), connected through a zero-resistance ammeter (ZRA) so as to have both WEs at the corrosion potential.[2]

There are two principal uses of EN. One is based on the analysis of current transients, and is directed to detecting localized corrosion. The second application consists of determining the corrosion rate from the measurement of both current and voltage fluctuations, with the help of a third electrode, used as the reference electrode (RE). The first application has great potential as a diagnostic tool to distinguish, possibly in real time, between various kinds of localized corrosion, on the basis of shape and amplitude of current transients, but the results are still rather controversial. In this article we will discuss only the second use, whose theoretical basis is now well established.

NOISE RESISTANCE AND NOISE IMPEDANCE

The noise resistance R_n is defined as the ratio of the standard deviations of the voltage and current fluctuations. Historically, this is the first quantity derived from measurements with the two-electrode cell. In many situations the values of R_n are found to be close to the polarization resistance R_p of the WEs, so that the corrosion rate can be deduced by means of the Stern-Geary relationship.[3] A more detailed analysis can be carried out in the frequency domain, by calculating the power spectral density (PSD) of the fluctuations, so as to determine the frequency distribution of the signal power, and obtaining data like those discussed later in Fig. 4. The noise impedance Z_n, defined as the square root of the ratio of the PSDs of the voltage and current noises, Ψ_V and Ψ_I respectively, is experimentally found to be equal to the modulus of the WE impedance, under readily realizable conditions, such as low-noise RE and negligible solution resistance.[4-6]

In short, this can be explained by considering that the phenomena caused by corrosion on the WEs, such as bubble formation and detachment, metastable or stable pitting or crack advance, that give rise to voltage and current fluctuations, can be modeled by current noise sources, i_1 and i_2, in parallel with the impedances, Z_1 and Z_2 of the WEs.[4] These noise sources are not directly measurable. Only the fluctuations ΔI of the current flowing between the two electrodes and ΔV of the coupled WE potential are accessible to measure. The noise impedance $Z_n(f)$ can be derived by applying Ohm's law in the frequency domain to the cell equivalent circuit.[4]

Equation 1 shows that Z_n depends on the impedances of the two WEs, as well as their noise levels, represented by the PSDs Ψ_{i1} and Ψ_{i2}. It is easy to see that if the WEs have the same impedance ($Z_1 = Z_2$, denoted Z), as often for identical WEs at the same potential, the noise impedance is equal to the modulus of the electrode impedance $|Z(f)|$. This result is valid whatever the origin of the noises (localized or uniform corrosion, bubble evolution) and the shape of the impedance plot, even if the noise levels of the two electrodes are different. In that case,

$$Z_n(f) = \sqrt{\frac{\Psi_V(f)}{\Psi_I(f)}} = \left|Z_1(f)Z_2(f)\right| \sqrt{\frac{\Psi_{i_1}(f) + \Psi_{i_2}(f)}{\left|Z_1(f)\right|^2 \Psi_{i_1}(f) + \left|Z_2(f)\right|^2 \Psi_{i_2}(f)}}$$
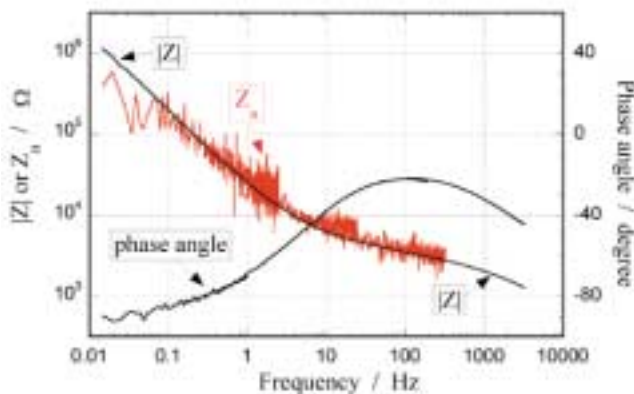
Equation 1

FIG. 1. Impedance, Z, of two identical sealed Al electrodes (surface area: 12.6 cm^2) with coating thickness of 22 μm, and noise impedance, Z_n, measured after one day in 0.5 M NaOH + 0.27 M NaCl solution (pH = 11).[7]
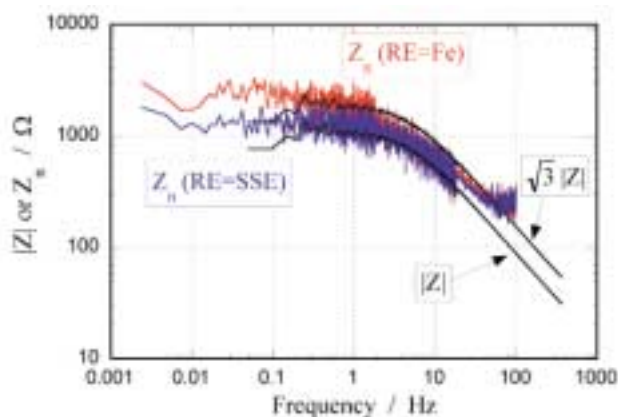

FIG. 2. Z_n and |Z| for Fe WEs (surface area = 0.2 cm^2) in 1 M Na$_2$SO$_4$ at pH = 3. Z_n obtained from measurements with two REs, Fe, and SSE. Impedance measurements performed with a 3-electrode cell.[5]

noise measurements are equivalent to impedance measurements, in which the external signal perturbation has been replaced by the internal noise sources due to corrosion processes. Figure 1 shows an example, for Al in a chloride-containing solution.

There are many cases, particularly in field applications, such as corrosion monitoring in pipes or tanks, where the use of a low-noise RE, like the saturated calomel electrode or the saturated sulphate electrode (SSE) so common in electrochemistry laboratories, would be impractical. In these cases, one can employ as RE a third electrode, identical to the other two WEs. Obviously, such a RE would contribute to the noise of the system. It turns out, however, that in such an arrangement the noise impedance Z_n is equal to √3|Z|, so that a simple numerical correction is sufficient.[4] A more serious problem is that this result depends on the three electrodes having the same impedance and contributing the same noise PSD. As every corrosion worker knows, initially identical elec-

trodes tend to diverge in behavior with time. Experience has shown that this is particularly troublesome in case of localized corrosion, and could introduce significant errors. Nevertheless, this experimental setup is often good enough for corrosion monitoring. As an example, Fig. 2 presents Z_n curves measured with a true RE (SSE) and a third identical corroding electrode, in the case of Fe in Na$_2$SO$_4$ at pH = 3 where the EN was generated by hydrogen bubble evolution, which, being localized, differed on the three electrodes. Z_n measured with three Fe electrodes was not equal to √3|Z| in the whole frequency range, while, on the contrary, Z_n measured with a SSE was equal to |Z|.

As mentioned before, another widely used quantity in the analysis of EN is R_n, attractive because it is calculated in the time domain and requires simpler instrumentation. However, its relationship with R_p, the polarization resistance that corrosion workers employ to calculate corrosion rates, is not so obvious. One can take advantage of the theorem

that shows that the standard deviation is the square root of the integral of the PSD over the frequency range used in the measurement. In this way it is possible to understand when $R_n \approx R_p$ and when this is not true. Roughly speaking, if the Bode plot of |Z| reaches the low frequency asymptote R_p in the measurement frequency bandwidth, as in Fig. 2, R_n will be very close to R_p. On the contrary, if R_p is very large, as for passive electrodes or coated electrodes (Fig. 1), R_n may be substantially lower than Rp.[4,8]

ASYMMETRIC CELLS

Interest in studying the behavior of asymmetric cells is easy to understand, because asymmetry is often unavoidable. Cases may be envisaged where identical electrodes cannot be used, as in stress corrosion cracking investigations where only one electrode is under stress, or in crevice corrosion studies where crevice attack occurs on one electrode only.[9] It is encouraging, therefore, that recent work has shown that such cells can be analyzed and their behavior understood.[7,10] Instead of trying to prevent asymmetry, some authors have purposely employed it, in order to limit corrosion to one electrode, but still derive the noise resistance by measuring both current and voltage signals. In one case a Pt microcathode was utilized as one of the electrodes,[11] in another asymmetry was produced by applying a bias potential between the two electrodes.[12] The technique of biasing the cell, so as to separate physically the anodic from the cathodic processes, is interesting and might be exploited with success in many electrochemical systems.

The analysis of asymmetric cells can be carried out on the basis of Eq. 1. For example, if hydrogen bubbles are evolving on the cathode while the anode undergoes generalized corrosion, the noise of the cathode is orders of magnitude larger than that of the anode, so that Z_n becomes equal to the impedance modulus of the anode, $|Z_a|$. In these conditions, while the time records appear to show only the cathodic processes, the impedance measured is that of the anode, using the noise of the cathode as input signal. An opposite case is provided by a cell where the anode is undergoing pitting, while the cathodic reaction is the reduction of oxygen dissolved in the solution. Since the anodic noise is preponderant, Eq. 1 shows that Z_n is equal to the impedance modulus of the cath-

ode, $|Z_c|$. The anodic noise is the internal signal source utilized for the measurement of the impedance of the cathode. In intermediate cases the results of the measurement of Z_n are difficult to interpret.[10] For the noise resistance R_n, analysis shows that, if the impedances Z_a, Z_c are equal to the polarization resistances R_{pa}, R_{pc} in the frequency range measured, R_n is equal to the polarization resistance of the anode, R_{pa}, for a noisy cathode, and to the polarization resistance of the cathode, R_{pc}, for a noisy anode.[10]

An informative example is given by aluminum coupled to a Pt microcathode in 1 M KCl. Because of the very small surface area of the cathode, coupling has a negligible influence on the potential of the anode, where pitting generates large transients of the order of one mV. As shown in Fig. 3, since the noise generated by the reduction of dissolved oxygen on the Pt is small, there is excellent correlation between the voltage and the current transients. The current spikes flow from the anode to the Pt, which is the positive direction in the plot, while the potential of the coupled electrodes becomes more negative with respect to the RE. Interestingly, the decay rates of the voltage and the current transients are about the same.

The voltage and current PSDs (Fig. 4) may provide information on the shapes of the transients. For instance, the slope of the PSDs has been proposed as a critical parameter for the identification of specific forms of localized attack. In the case of asymmetric systems, however, the interpretation is difficult because both shape and amplitude of the current transients measured by the ZRA are affected by the asymmetry in the impedances. This is the reason why, in Fig. 4, the PSDs Ψ_{i_a} and Ψ_I differ.

To test the characteristics of this kind of asymmetrical cell, the impedance of the two electrodes was measured separately, and compared with Z_n, as shown in Fig. 5. As it could be expected from Eq. 1, the noisy anode works as the signal source, so that Z_n is equal to the impedance of the Pt microcathode. While examination of the time records and possibly of certain features of the individual PSDs might lead to useful information on the corrosion of the anode, employing a microelectrode does not allow to obtain the impedance of the corroding electrode.

CONCLUSION

Through this analysis it is possible to compare the usefulness of the two main

FIG. 3. Time records of the voltage and current fluctuations generated during pitting corrosion of an Al disk (diameter 2.5 cm) connected to a platinum disk (diameter 1 mm) through a ZRA in 1 M KCl. Zeros of scales are arbitrary.[10]
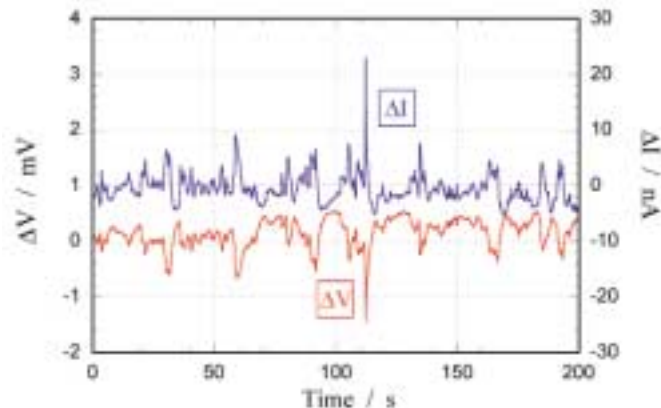

FIG. 4. PSDs Ψ_V, Ψ_I, of the voltage and current fluctuations shown in Fig. 3; and PSD Ψ_{i_a} of the current fluctuations on the anode.[10]
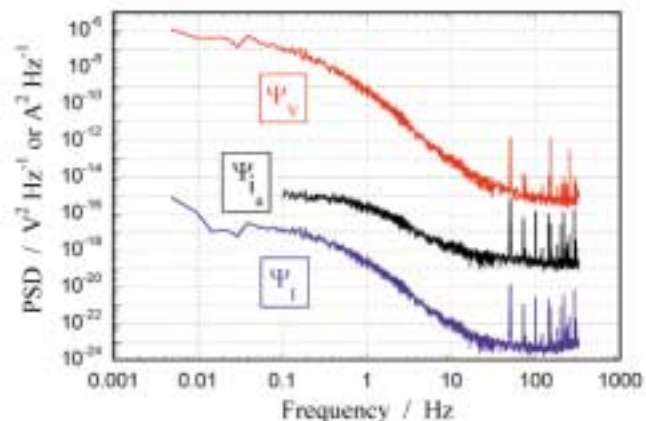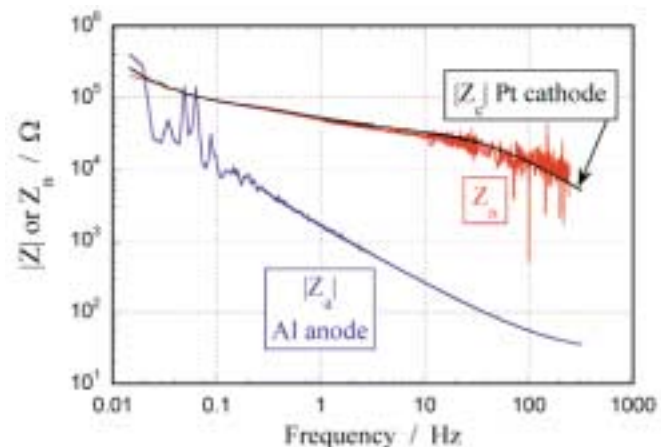

FIG. 5. Impedance moduli of the platinum disk, the Al disk, and noise impedance measured under the conditions of Fig. 3.[10]

quantities, R_n and Z_n, derived from this kind of noise measurements. While for identical electrodes at the same potential Z_n corresponds to the modulus of the electrode impedance in the frequency range studied, the noise resistance R_n is simply a number, which may or may not be equal to the polarization resistance of the electrodes under investigation, even for symmetric systems.[5-7] For asymmetric cells, Z_n often gives the impedance modulus of the less noisy of the two electrodes, and R_n its polarization resistance.

Beside the derivation of the electrode impedance (therefore estimating the corrosion rate), there are other issues of interest in EN measurements, on which recent papers have contributed to a better understanding of what is being measured, and what are the experimental practices to be preferred. These include, from the experimental point of view, examinations of the contribution of instrumental noise, always a very important subject, since EN is often measured at the lower limits of detectability,[13] the issue of the importance and methods of drift removal, and of which processing algorithms are most suited for obtaining second order statistics. For the purpose of a better understanding of the noise generating processes, there is also the

issue of the repartition of the current between the two electrodes kept at the same potential, the effects of resistance fluctuations during gas evolution at electrodes, as well as the influence of the shape of the voltage and current transients on the slope of the PSDs. However, much work is still needed to relate EN data to corrosion processes, for example to identify the specific forms of localized attack. In particular, the interpretation of the PSDs remains a hot topic, especially when no transient are observable on the voltage and time records.

As shown in the regular technical symposia on field applications of EN at the annual NACE Corrosion meetings, EN is already used in the field, as a complementary technique to traditional on-line monitoring methods that do not give information on localized corrosion events. Attempts have even been made to automate the interpretation of the huge amount of EN data provided by real-time monitoring by using neural networks. ∎

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