Electrochemical Noise - Guidance for Improving Measurements and Data Analysis

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ABSTRACT

From the results of the three Round-Robin tests on electrochemical noise (EN) measurements with dummy cells performed between 2014 and 2017 by the European Cooperative Group on Corrosion Monitoring of Nuclear Materials, it was concluded that achieving valid EN measurements is jeopardized by a lack of theoretical knowledge as well as by software and hardware issues. This paper is aimed at guiding users of the EN technique by providing the minimum knowledge for EN measurements, including the necessary validation of the signals measured at different sampling frequencies by calculation of their power spectral densities. Two practical works performed with a commercial potentiostat are proposed. The first one is devoted to the measurement of the thermal noise of three resistors of equal value connected in a ‘star’ arrangement and used in the conventional three-electrode EN measurement setup using a zero-resistance ammeter. This allows the instrumental noise of the equipment to be determined. The second practical work concerns pitting corrosion of two identical aluminum electrodes in potassium chloride to show that the noise impedance is equal to the modulus of the impedance of the electrodes, which is another way to validate the EN measurements. A bias voltage is then applied between the electrodes to obtain one anode and one cathode, which shows the difficulty of analyzing the measured EN in asymmetric systems.

KEY WORDS: electrochemical noise, guideline, dummy cell, pitting corrosion

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INTRODUCTION

In order to evaluate the reliability of electrochemical noise (EN) measurements performed by commercial general-purpose potentiostats, Round-Robin (RR) tests have been performed by different groups.^{1,2} Recently, three new RR tests on EN measurements with dummy cells have been performed by the European Cooperative Group on Corrosion Monitoring of Nuclear Materials (ECG-COMON).³ Using dummy cells, composed of three resistors of equal value connected in a ‘star’ arrangement, with a potentiostat working in a zero-resistance ammeter (ZRA) mode, gives the possibility of measuring voltage and current noise signals of reproducible amplitude, in contrast to corrosion processes that often evolve with time.

As shown in Figure 1(a), the power spectral densities (PSDs) of the potential fluctuations due to the thermal noise of 1 M Ω dummy cells measured by all participants are extremely different, some of them being 8 decades higher than the theoretical value of $6kTR$, where k is Boltzmann’s constant, T is the temperature in Kelvin and R is the resistance in Ohm.⁴ An important cause of the large discrepancy in the results comes from aliasing of high to low frequencies during the analog-to-digital conversion in potentiostats that are not equipped with analog low-pass anti-aliasing filters that eliminate frequencies above half the sampling frequency to respect the Shannon theorem.⁵ Consequently, for such measuring devices, signals measured at different sampling frequencies have PSDs that do not overlap in common frequency ranges, as shown for example by the non-overlapping PSDs in turquoise and peach colors (amplitude between 10^{-6} and 10^{-7} V²/Hz) on the top of Figure 1(a) (see also Figure 5 in Reference 3). From this work, it was concluded that only very few commercial potentiostats are actually able to perform valid EN measurements. Working with a potentiostat equipped with an anti-aliasing filter gives better results, as illustrated in Figure 1(b) in which all curves are in a range of only 5 decades above $6kTR$. Nevertheless, this figure exhibits some errors in the measurements and different levels in the PSDs at low frequencies, which was unexpected since only the gain of the voltage amplifier had to be fixed adequately. The results are even worse for the current fluctuations according to the much larger scatter observed in the PSDs observed during the

RR tests.³ It is then important to train people to learn how to perform valid EN measurements, which is the aim of this paper that presents two practical works, one using dummy cells and the other a corrosion system. It is not intended in these works to perform complete EN studies on new systems: pitting corrosion of aluminum in 1M potassium chloride solution was chosen for its rapidity to generate pits and, as a consequence, an EN signal of high level easy to measure. However, it is not possible for a beginner in the EN technique to start working directly with a corrosion system since the EN results vary from one user to another according to the experimental conditions, while the level of the thermal noise generated by dummy cells is well known. It is then necessary to start EN measurements with dummy cells to try measuring the expected level of noise and, for that, to learn how to use the software controlling the potentiostat. The thermal noise of dummy cells is a signal of low level, so the measurement is difficult, but it should be noticed that the EN generated by a passive electrode is as low. It is then important to succeed in achieving such measures. In a second step, pitting corrosion was investigated first using identical electrodes to show how to valid the EN measurements using the noise impedance, and then asymmetric electrodes to raise awareness of the difficulty of analyzing the noise measured in such conditions.

EXPERIMENTAL PROCEDURES

Dummy cells

Figure 2 shows two dummy cells composed of three identical resistors of 1 and 10 M Ω in a 'star' arrangement, the latter being installed on a printed circuit board. The resistors were connected to the counter electrode (CE), working electrode (WE), and reference electrode (RE) inputs of the potentiostat that imposed a zero potential difference between the CE and the WE (ZRA mode).²⁻⁴ Therefore, no current was flowing through the resistors that were at thermodynamic equilibrium. A simple Faraday cage made of aluminum paper surrounding the dummy cell and connected to the floating ground cable of the potentiostat, or to the ground of the mains supply, was used to eliminate as much as possible 50/60 Hz electrical interference. The dummy cell must first be wrapped in

insulation paper to avoid any contact with the aluminum foil. In practice, it is advised to use a Faraday cage for investigating systems with high impedance at high frequency, as for the dummy cell, since this drastically reduces the amplitude of the signal components at 50/60 Hz and harmonics that hinder the measurement of the EN at low frequencies.

Electrochemical system

As mentioned above, pitting corrosion of aluminum (Al) electrodes in 1 M potassium chloride was chosen as a real electrochemical system to start EN measurements. Two identical Al electrodes consisting of disks of 25 mm in diameter (surface area of about 4.9 cm²) polished on 1200 emery paper were used as WE and CE. The electrodes faced each other at a distance of about 1 cm in a vertical position by a retaining ring. A saturated calomel electrode (SCE) was used as RE. As for the dummy cells, a zero potential difference was imposed between the Al electrodes by the potentiostat in ZRA mode so that both electrodes were at corrosion potential (symmetric system). In another experiment, an asymmetric system was obtained by imposing a bias potential of 800 mV between the WE and the CE so that one electrode could be considered as an anode, the other one as a cathode. No Faraday cage was used since the external noise sources in the laboratory environment were insignificant. When the EN signals are corrupted by 50/60 Hz electrical interference, it is necessary to use a Faraday cage, for example as that described above.

Procedure for EN measurement and validation

A Gamry Reference 600[†] potentiostat with software ESA410[†] was used in this work for measuring the fluctuations of the potential difference between the WE and the RE, and the fluctuations of current flowing between the WE and the CE. The measurement procedure in ZRA mode for this particular measuring device is given in Appendix A. For potential measurements, only

[†] Trade name

the range of the potential channel (V_{ch} range) has to be set by the user, which fixes the amplification gain of the potential difference between the WE and the RE (see Table 1) in the potentiostat. In contrast, measuring the current fluctuations is more complex since the user must set the values of two parameters, the I-E range, which fixes the value of the current-measuring resistance (R_m), and the I_{ch} range, which fixes the gain of the amplifier (see Table 1) installed at the output of the I-E converter. Table 2 gives the values of R_m and the effective gain in V/A of the I-E converter as a function of the I-E range. It also indicates the upper value of the frequency bandwidth of the measurement channels as a function of the I-E Stability parameter. Depending on the corrosion system, the I-E range and the I_{ch} parameter must be fixed according to the amplitude of the current fluctuations at the sampling frequency f_s employed (see the procedure in Appendix A) with a special attention to the fact that the upper limit of the frequency bandwidth might not be half of the sampling frequency when low I-E ranges are selected (see Table 2). Extremely low frequencies can be analyzed, the lowest being f_s/N where N is the number of data points recorded as long as desired but, in practice, the EN is not stationary enough to investigate frequencies well below 1 mHz.

Validation of EN measurements is not possible in the time domain since the amplitude of the noise depends on the sampling frequency, as shown below (Figure 3(a)). Validation can only be performed in the frequency domain by calculating the PSDs of signals sampled at least at two different frequencies.⁴ The two main calculation methods usually employed are the maximum entropy method and the periodogram method based on the fast Fourier transform. After comparison, the latter was preferred to obtain a good overlap of the PSDs of wide-band random signals requiring to be sampled at various frequencies.⁶ In this work, the PSD of each time record was calculated using the program `psd-detrend_ECG-COMON.exe` that can be downloaded for free from the ECG-COMON website (www.ecg-comon.org) with its configuration file `config_psd-detrend_ECG-COMON.txt`, after having exported the raw time data (extension `.esa`) to an ASCII file consisting of three columns (time in s, potential noise in V, and current noise in A), separated by tabs. Following the instructions given by the user in the configuration file, the program calculates the potential PSD, the current PSD, and

the noise impedance (Z_n), which is defined as the square root of the ratio PSD V/PSD I, by dividing the ASCII file in several (at least 10 is recommended) sections of N data points to get averaged PSDs in the frequency bandwidth $[f_s/N, f_s/2]$ that are accurate enough to control the overlap of the PSDs.³

To limit the measurement time in a practical training work, it is possible to successively sample the signals at frequencies $f_s = 1$ kHz during 30 s, 100 Hz during 4 min, 10 Hz during 4 min 30 s, and 2 Hz during 5 min 30 s. In that case, the PSDs are calculated with 14, 11, 10, and 10 sections of $N = 2048, 2048, 256$, and 64 data points, respectively. Obviously, the analyzed frequency bandwidth is limited at low frequency ($f_s/N = 0.5$ Hz, 0.05 Hz, 0.04 Hz, and 0.03 Hz, respectively) in this exercise. In practice, for a complete study of a given electrochemical process, it is necessary to analyze lower frequencies by selecting a lower sampling rate and/or a higher number N of data points per section. In the literature, in most studies using the EN technique, the analyzed frequency bandwidth is roughly $[1 \text{ mHz} - 1 \text{ Hz}]$ when the measurements are performed in ZRA mode since the corrosion processes at the open circuit potential (OCP) are slow. Higher sampling rates have to be used when the measurements are carried out in potentiostatic mode in the passivation domain to investigate pitting corrosion since the passive layer breakdown and pit repassivation are fast processes.

RESULTS AND DISCUSSION

Measurement of the thermal noise of resistors

The aim of this practical work is to learn how to perform and validate EN measurements on a stationary system giving reproducible results on the one hand, and to determine the noise level of the potentiostat on the other hand. According to the Fluctuation-Dissipation theorem (Nyquist law),⁷ the PSD of the thermal noise voltage generated by a resistor at thermodynamic equilibrium is equal to $4kTR$. For the dummy cell considered in this work, it has been shown that the PSDs of the potential and current noise is equal to $6kTR$ and $2kT/R$, respectively.⁴ The thermal noise level is low, as low as that generated by a passive electrode, and it is important to carry out the EN measurements at

different I-E ranges to identify in the measured EN the contribution due to electrochemical processes and that due to the potentiostat.

Validating EN measurements is not possible in the time domain since the peak-to-peak amplitude of the time records varies according to the sampling frequency selected, as shown in Figure 3(a) for the dummy cell but this could be shown for any electrochemical system. This is due to the presence of the anti-aliasing low-pass filter required in the measurement channel before the analog-to-digital conversion: the lower f_s , the lower the cut-off frequency of the filter, the higher the number of filtered frequencies, and therefore, the lower the amplitude of the signal. In contrast, validation of the EN measurements is possible in the frequency domain by checking the overlap of the PSDs. As an example, Figure 3(b) shows the good overlap of the PSDs of the time records presented in Figure 3(a). Moreover, the PSD level is equal to $6kTR$ at frequencies above 5 Hz, indicating that the voltage thermal noise of the dummy cell was actually measured. A pure $1/f$ behavior, typical of noise generated by semiconductors and originating from the instrumentation, can be observed at lower frequencies. In this range, an electrochemical potential noise of lower amplitude cannot be measured in the operating conditions employed.

As explained above, measuring the thermal noise in current (current noise) is more difficult since two parameters, the I-E range and the I_{ch} range, have to be set by the user. For the $10\text{ M}\Omega$ dummy cell, various PSD levels can be viewed in Figure 4 for the current noise measured at different I-E ranges with the I-E Stability parameter “Fast”. This parameter is usually selected because it allows the highest upper limit of the frequency bandwidth to be measured for a given I-E range (see Table 2) without playing any role on the lowest frequency that can be analyzed. To explain the magnitude of each PSD and select the proper I-E range, it is necessary to model the different noise sources influencing the measurement of the electrochemical current noise.⁸ Figure 5 presents the schematic circuit of the potentiostat used in ZRA mode (Z_1 , Z_2 , and Z_3 are the electrochemical impedances of the WE, CE, and RE, respectively) with the main noise sources due to the electrochemical processes and to the instrumentation:

- i_1 , i_2 , and i_3 are the current noise sources due to the electrochemical processes, here the thermal noise of the resistors,
- i_{nm} is the current thermal noise source of the current-measuring resistor R_m ,
- e_{n1} is the voltage noise source of the operational amplifier controlling the potential in the potentiostat,
- e_{n2} is the voltage noise source of the amplifier (gain G equal to 1) measuring the potential difference between the CE and WE,
- $e_{n,v}$ is the voltage noise source of the potential amplifier of gain G_v ,
- $e_{n,i}$ is the voltage noise source of the current amplifier of gain G_i .

Writing the generalized Ohm's law at point A and across the resistor R_m gives in the frequency domain (j is the square root of -1), respectively:

$$e_{n1} = G [e_{n2} + Z_2(i - i_2) + Z_1(i + i_1)] \quad (1)$$

and:
$$\frac{1}{Cj\omega} i_C = R_m(i - i_C - i_{nm}) \quad (2)$$

where C is the capacitance in parallel with R_m , which depends on the I-E Stability parameter selected. Equations 3 and 5 are then straightly derived:

$$i = \frac{1}{Z_1 + Z_2} [e_n - Z_1 i_1 + Z_2 i_2] \quad (3)$$

with:
$$e_n = e_{n1} - G e_{n2} \quad (4)$$

and:
$$i_C = \frac{R_m Cj\omega}{1 + R_m Cj\omega} \frac{1}{Z_1 + Z_2} (e_n + Z_2 i_2 - Z_1 i_1 - (Z_1 + Z_2) i_{nm}) \quad (5)$$

which gives the expressions of the potential and current measured by the potentiostat:

$$V_{meas} = \frac{V_{out}}{G_v} = e_{n,v} + Z_3 i_3 + Z_1(i + i_1) = \frac{Z_1 Z_2}{Z_1 + Z_2} (i_1 + i_2) + Z_3 i_3 + e_{n,v} + \frac{Z_1}{Z_1 + Z_2} e_n \quad (6)$$

and:
$$I_{meas} = \frac{I_{out}}{G_i R_m} = \frac{e_{n,i}}{R_m} + \frac{1}{Cj\omega R_m} i_C = \frac{1}{1 + R_m Cj\omega} \left[\frac{Z_2 i_2 - Z_1 i_1}{Z_1 + Z_2} + \frac{e_n}{Z_1 + Z_2} - i_{nm} \right] + \frac{e_{n,i}}{R_m} \quad (7)$$

Under the hypothesis of independent noise sources, the expressions of the PSDs of the measured potential and current can be derived:

$$\Psi_{V_{\text{meas}}} = \left| \frac{Z_1 Z_2}{Z_1 + Z_2} \right|^2 (\Psi_{i_1} + \Psi_{i_2}) + |Z_3|^2 \Psi_{i_3} + \Psi_{e_{n,v}} + \left| \frac{Z_1}{Z_1 + Z_2} \right|^2 \Psi_{e_n} \quad (8)$$

$$\Psi_{I_{\text{meas}}} = \frac{1}{1 + R_m^2 C^2 4\pi^2 f^2} \left[\frac{|Z_1|^2 \Psi_{i_1} + |Z_2|^2 \Psi_{i_2} + \Psi_{e_n}}{|Z_1 + Z_2|^2} + \Psi_{i_{nm}} \right] + \frac{1}{R_m^2} \Psi_{e_{n,i}} \quad (9)$$

For the dummy cell, $Z_1 = Z_2 = Z_3 = R$. The PSD of the current thermal noise of a resistor R being equal to $4kT/R$, Equations 8 and 9 become:

$$\Psi_{V_{\text{meas}}} = 6kTR + \Psi_{e_{n,v}} + \frac{1}{4} \Psi_{e_n} \quad (10)$$

and:
$$\Psi_{I_{\text{meas}}} = \frac{1}{1 + R_m^2 C^2 4\pi^2 f^2} \left[\frac{2kT}{R} + \frac{1}{4R^2} \Psi_{e_n} + \frac{4kT}{R_m} \right] + \frac{1}{R_m^2} \Psi_{e_{n,i}} \quad (11)$$

The last two terms in Equation 10 correspond to the voltage noise of the instrument, which is preponderant at frequencies lower than 5 Hz in Figure 3, as mentioned above. The expression of the PSD of the measured current noise is more involved but Equation 11 allows the results of Figure 4 to be explained. For the lowest values of R_m (2 k Ω to 2 M Ω), the PSD varies in $1/R_m^2$ at low frequency. According to Equation 11, the main source of noise below 5 Hz is then the differential amplifier of gain G_I . At high frequency, $\Psi_{I_{\text{meas}}}$ is inversely proportional to R_m so the measured noise may be attributed to the thermal noise of R_m .

For $R_m = 20$ M Ω and 200 M Ω , the spectra $\Psi_{I_{\text{meas}}}$ are identical at low frequency, indicating that the current noise below 5 Hz can be attributed to the noise of the amplifiers in the potentiostat, Ψ_{e_n}/R^2 . At high frequency, it must be noted that the presence of the capacitance C (close to 150 pF for “Fast” I-E Stability) in parallel with the resistor R_m introduces a low-pass filtering with a cut-off frequency of $1/(2\pi R_m C)$, which plays a significant role when high values of R_m are selected. For example, for $R_m = 20$ M Ω (I-E range = 6 nA), the PSD starts decreasing at a frequency close to 50

Hz, as expected from Table 2 for the I-E Stability parameter “Fast”. The PSD decrease would have appeared at a lower frequency if another value of the I-E Stability parameter had been used. Around 10 Hz, the PSD value is equal to the sum of the PSD values of the current thermal noise of the dummy cell and resistor R_m , $2kT/R + 4kT/R_m$. If a higher value of R_m is selected ($R_m = 200\text{ M}\Omega$, i.e. I-E range = 600 pA) to eliminate the influence of $4kT/R_m$ and measure the thermal noise of the dummy cell, the cut-off frequency decreases, which explains the shift on the left of the high frequency part of the PSD of the current noise.

In conclusion, according to Figure 4, for $R = 10\text{ M}\Omega$ the best value of R_m to obtain a PSD plateau close to the expected amplitude of $2kT/R$ was $20\text{ M}\Omega$, which is a value of the same order of magnitude as R . In practice, for stationary systems showing a low EN level, as for dummy cells or for passive electrodes, it is important to select the highest value of R_m that does not overload the current amplifier. For electrochemical systems, when the noise level is expected to increase with time, it is advised to select a lower value of R_m (see Appendix A).

Measurement of the EN generated by pitting corrosion of aluminum electrodes

Symmetric system

Figure 6 shows time records of the potential and current fluctuations generated by pitting of Al electrodes in potassium chloride, and their corresponding PSDs, together with the noise impedance Z_n and the modulus of the impedance of the electrodes that was measured from 100 kHz to 0.1 Hz in potentiostatic mode at OCP using an excitation signal of $10\text{ mV}_{\text{rms}}$ amplitude. As for the dummy cells, validation of the noise measurements is given by the satisfying overlap of the PSDs measured at different sampling frequencies, as shown in Figure 6(b). Furthermore, the noise impedance derived from the potential and current PSDs fits well with the modulus of the impedance in Figure 6(c), which is another argument for noise validation. Indeed, this result has been demonstrated theoretically⁹ and experimentally¹⁰ when the RE is a true reference electrode (such as calomel, sulfate, silver/silver chloride reference electrodes). It must be noticed that such result is obtained as long as the noise of the instrumentation can be neglected⁸, as in the present experiment in which the high pitting activity

was due to many individual pitting transients that overlapped so that they cannot be observed separately in Figure 6(a). The amplitude of the resulting noise is large, a few mV for the potential and a few μA for the current. Of course, such result could not be obtained with the dummy cell since the noise of the RE had the same amplitude as the noises of the CE and WE. It cannot be obtained either in the field when a third identical electrode is used as a pseudo RE since the noise generated by corrosion processes on this electrode has a great influence on the noise impedance.^{9,10}

Asymmetric system

Asymmetry in the electrodes has sometimes been purposely employed, so as to limit corrosion on one electrode, the anode, the other electrode acting as a cathode.¹¹ In other cases, 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. As an easy exercise to appreciate the difficulty of the EN analysis for asymmetric systems, a bias potential of 800 mV was applied between the two identical aluminum electrodes and the potential and current noises were measured in ZRA mode. Then, the impedance of each electrode was measured. It must be noted that the anode potential varied significantly with time so that it was difficult to perform the impedance measurement in potentiostatic mode at the electrode potentials measured when the bias potential was applied. Therefore, the impedance measurements were carried out in galvanostatic mode by imposing a DC current of +4.3 mA for the anode, which gave a potential of -0.74 V/SCE, and -4.3 mA for the cathode, which gave a potential of -1.54 V/SCE (see Figure 7(a)). The amplitude of the current excitation was 0.7 mA_{rms}.

Figures 7(b) and 7(c) show the time records and PSDs of the potential and current fluctuations, respectively. A relatively high mean current (4.3 mA) and current fluctuations of 100 μA amplitude can be observed, indicating a more intense pitting activity than in the absence of bias potential ~~because of the more noble potential of the anodic electrode~~. While the time records and PSDs of the current fluctuations have an amplitude much higher than that at OCP in Figure 6 and do reflect pitting corrosion, the noise impedance derived from the PSDs is equal to the impedance modulus of the

cathode, according to Figure 7(d), which is an a priori surprising result. This can be explained using Equations 8 and 9, in which all noise sources due to the instrumentation have been neglected in front of the EN caused by pitting corrosion. The PSDs of the measured current and potential fluctuations can be written:

$$\Psi_{V_{\text{meas}}} = \left| \frac{Z_a Z_c}{Z_a + Z_c} \right|^2 (\Psi_{i_a} + \Psi_{i_c}) \quad \text{and} \quad \Psi_{I_{\text{meas}}} = \frac{|Z_a|^2 \Psi_{i_a} + |Z_c|^2 \Psi_{i_c}}{|Z_a + Z_c|^2} \quad (12)$$

where Z_a and Ψ_{I_a} (resp. Z_c and Ψ_{I_c}) are the impedance and the current noise source of the anode (resp. cathode). For the present system, the impedance of the cathode was much lower than that of the anode and the current noise due to oxygen reduction on the cathode was not significant compared to that on the anode, so that the expressions of $\Psi_{V_{\text{meas}}}$ and $\Psi_{I_{\text{meas}}}$ can be reduced to:

$$\Psi_{V_{\text{meas}}} = |Z_c|^2 \Psi_{i_a} \quad \text{and} \quad \Psi_{I_{\text{meas}}} = \Psi_{i_a} \quad (13)$$

which shows that the noise impedance is equal to the impedance modulus of the cathode. Finally, owing to the high noise generated by pitting occurring on the anode, the impedance (modulus) of the cathode was determined, which is not a straightforward result. In other situations, the noise impedance may be close to the impedance modulus of the anode or simply be comprised between the impedance moduli of the electrodes.¹¹ It should be noted that, despite a higher current noise i_a on the anode, the amplitude of the potential fluctuations was lower in presence of the bias potential. This can be explained using Equation 13 in which $\Psi_{V_{\text{meas}}}$ reduces to $|Z_c|^2 \Psi_{i_a}$, which remains low because of the much lower impedance modulus of the cathode.

In conclusion, while the EN analysis is simple for symmetric systems, asymmetric systems require the measurement of both the potential and current noise and the impedance of each electrode for a thorough analysis of the stochastic behavior of the corrosion process.

CONCLUSIONS

In view of the unreliable EN results obtained in the Round-Robin tests performed on dummy cells by the ECG-COMON with most commercial potentiostats,^{2,3} often coming from the absence of

anti-aliasing filters in the measuring devices, it is important to train people to learn how to perform valid EN measurements with a commercial potentiostat equipped with such filters. This paper presents several practical experiments, consisting first in measuring the thermal noise of dummy cells, a noise of amplitude as low as that of passive electrodes, to learn how to set the parameters of the controlling software correctly and identify the noise level of the instrumentation. Then, the EN generated by pitting corrosion of aluminum in potassium chloride was investigated by using symmetric and asymmetric electrodes. Validation of the EN measurements is obtained from the quality of the overlap of the PSDs of time records sampled at different sampling frequencies. It is important to emphasize that it cannot be obtained from the analysis of data in the time domain only and that working in the frequency domain is absolutely mandatory. In addition, when the corrosion system generates an EN of relatively large amplitude, which is often the case for pitting corrosion, validation is also obtained by comparing the noise impedance, calculated from the potential and current PSDs, to the impedance modulus of the electrodes for a symmetric system, ~~or to the impedance modulus of the less noisy electrode for an asymmetric system.~~ All these recommendations concerning the validation of the EN measurements have been issued using a particular commercial potentiostat. However, they are general and can be applied to any other equally reliable EN measuring devices. In addition, the development of Equations 10 and 11 allowing the interpretation of the EN results for the dummy cells and the determination of the instrumental noise, may serve for other equipment because the measuring circuits in most commercial potentiostats are very similar. The current noise is measured by amplifying the voltage across a resistor and the potential noise by amplifying the potential difference between the WE and the RE.

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[†] Trade name

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APPENDIX A: MEASUREMENT PROCEDURE FOR EN MEASUREMENTS IN ZRA MODE

- 1) Connect all electrodes. Toggle cell on.
- 2) Input file name, choose ZRA mode, sampling frequency f_s , test time (at least $10 N / f_s$).
- 3) Set Device/I-E Stability according to f_s (usually 'Fast', see Table 2).
- 4) Set Device/Ich Filter and Vch Filter to 1 kHz if $f_s > 5$ Hz, or to 5 Hz otherwise.

- 5) Set all I-E range, Current channel, Voltage channel to auto mode, let the software choose a measure range without overload. Overload may disappear after 10 to 20 seconds.
- 6) Set all I-E range, Current channel, Voltage channel to manual mode. Try to decrease I-E range down to get a minimum setting without overload. Once the overload indicator is triggered for more than 20 s, meaning a too-low current range for the measured value, the user should set the range one order up.
- 7) Decrease voltage channel and current channel manually down to get a minimum range without overload.
- 8) For the voltage fluctuations, evaluate the peak-to-peak amplitude on the screen during the measurements, and check if this value is lower than the V_{ch} range.
- 9) For the current fluctuations, evaluate the peak-to-peak amplitude on the screen during the measurements, multiply it with the gain in V/A of the I-E converter given in Table 2 and check if this value is lower than the I_{ch} range.
- 10) If the EN is expected to increase during the experiment, it may be necessary to use higher I/E, voltage, and current ranges.
- 11) Start to record EN data.
- 12) Observe the overload indicators. Once the overload warning occurs, the data may be unreliable.
- 13) When the test is finished, toggle cell off.

LIST OF CAPTIONS

TABLE 1. *Gain of the V_{ch} and I_{ch} amplifiers as a function of the V_{ch} and I_{ch} range*

TABLE 2. *Current-measuring resistance, R_m , gain of the I-E converter, and upper value of the frequency bandwidth of the current channel as a function of the I-E range and I-E stability*

FIGURE 1. *PSDs of potential fluctuations measured on 1 M Ω dummy cells by the ECG-COMON in 2017 (a) with potentiostats of various origins (77 curves), (b) with the potentiostat used in this paper (36 curves).³*

FIGURE 2. *(a) 10 M Ω and (b) 1 M Ω dummy cells in a 'star' arrangement.*

FIGURE 3. *(a) potential time records sampled at various frequencies f_s and (b) corresponding PSDs. 10 M Ω dummy cell (I-E range = 6 nA, V_{ch} = 30 mV).*

FIGURE 4. *PSDs of the current fluctuations measured on a 10 M Ω dummy cell at various sampling frequencies and I-E ranges (I-E Stability "Fast", I_{ch} = 30 mV).*

FIGURE 5. *Schematic circuit of the potentiostat working in ZRA mode with predominant noise sources.*

FIGURE 6. *(a) Time records (f_s = 10 Hz, arbitrary zero of time scale) and (b) PSDs of the potential and current fluctuations due to pitting corrosion of identical aluminum disk electrodes (diameter 2.5 cm) in 1 M KCl (f_s = 10 Hz and 100 Hz); (c) Z_n and $|Z|$.*

FIGURE 7. *(a) Current-voltage curve showing the potentials V_a , V_c of two identical corroding electrodes of the same material connected through a ZRA when a bias voltage V_{bias} is superimposed; (b) time records (f_s = 100 Hz, arbitrary zero of time scale); (c) PSDs of the potential and current fluctuations due to pitting corrosion of identical aluminum disk electrodes (diameter 2.5 cm) in 1 M KCl (f_s = 10 Hz and 100 Hz); (d) Z_n and $|Z|$ of each electrode.*

TABLE 1

Gain of the Vch and Ich amplifiers as a function of the Vch and Ich range

Vch and Ich range	3 V	300 mV	30 mV
Vch and Ich gain	1	10	100

TABLE 2

Current-measuring resistance, R_m , gain of the I-E converter, and upper value of the frequency bandwidth of the current channel as a function of the I-E range and I-E stability

			I-E Stability			
			Fast	Medium Fast	Normal	Slow
I-E range	$R_m (\Omega)$	Effective gain (V/A)	frequency bandwidth upper value (Hz)			
600 mA	0.2	5	500	500	500	500
60 mA	2	50	500	500	500	500
6 mA	20	500	500	500	500	500
600 μ A	200	5×10^3	500	500	500	500
60 μ A	2 k	5×10^4	500	500	500	80
6 μ A	20 k	5×10^5	500	500	240	8
600 nA	200 k	5×10^6	500	500	24	800 m
60 nA	2 M	5×10^7	500	80	2.4	80 m
6 nA	20 M	5×10^8	50	8	240 m	8 m
600 pA	200 M	5×10^9	5	800 m	24 m	800 μ
60 pA	2 G	5×10^{10}	500 m	80 m	2.4 m	80 μ

FIGURE 1. PSDs of potential fluctuations measured on $1\text{ M}\Omega$ dummy cells by the ECG-COMON in 2017: (a) with potentiostats of various origins (77 curves); (b) with the potentiostat used in this paper (36 curves).³

FIGURE 2. (a) $10\text{ M}\Omega$ and (b) $1\text{ M}\Omega$ dummy cells in a 'star' arrangement.

FIGURE 3. (a) potential time records sampled at various frequencies f_s and (b) corresponding PSDs. $10 \text{ M}\Omega$ dummy cell ($V_{ch} = 30 \text{ mV}$).

FIGURE 4. PSDs of the current fluctuations measured on a $10 M\Omega$ dummy cell at various sampling frequencies and I-E ranges (I-E Stability “Fast”, $I_{ch} = 30 mV$).

FIGURE 5. Schematic circuit of the potentiostat working in ZRA mode with predominant noise sources.

FIGURE 6. (a) Time records ($f_s = 10$ Hz, arbitrary zero of time scale) and (b) PSDs of the potential and current fluctuations due to pitting corrosion of identical aluminum disk electrodes (diameter 2.5 cm) in 1 M KCl ($f_s = 10$ Hz and 100 Hz); (c) Z_n and $|Z|$.

FIGURE 7. (a) Current-voltage curve showing the potentials V_a , V_c of two identical corroding electrodes of the same material connected through a ZRA when a bias voltage V_{bias} is superimposed; (b) time records ($f_s = 100$ Hz, arbitrary zero of time scale) and (c) PSDs of the potential and current fluctuations due to pitting corrosion of identical aluminum disk electrodes (diameter 2.5 cm) in 1 M KCl ($f_s = 10$ Hz and 100 Hz); (d) Z_n and $|Z|$ of each electrode.