



# An alternative to the use of a zero resistance ammeter for electrochemical noise measurement: Theoretical analysis, experimental validation and evaluation of electrode asymmetry<sup>☆</sup>



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## ABSTRACT

The measurement of current and potential noise during corrosion generally requires two electrodes, coupled by a zero resistance ammeter (ZRA), and a reference electrode. Statistical methods then enable estimation of the noise resistance, if the electrodes are identical. In this work, a resistor is used instead of a ZRA and, consequently, the electrodes potentials are partially decoupled. This enables evaluation of electrode asymmetry and the reliability of the estimated noise resistance. Additionally, the simplification of the current-measuring circuit ensures that no instrumental noise due to active electronic components within the ZRA is fed back to the corroding electrodes.

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## 1. Introduction

When a metal electrode is immersed in a corrosive electrolyte, anodic and cathodic reactions occur simultaneously on its surface. Generally, the anodic reaction involves the oxidation of the metal to metal ions, which are released into the environment, while the cathodic reaction involves the reduction of species present in the environment, such as molecular oxygen or hydrogen ions [1]. The rate at which the anodic and cathodic reactions proceed can fluctuate with time but, overall, the rate of the anodic and cathodic reactions are balanced, at open-circuit potential, in order to preserve electroneutrality [2]. Generally, the rate of the anodic reaction increases with increasing electrode potential, while the rate of the cathodic reaction increases with decreasing electrode potential. Consequently, the average corrosion potential represents the potential at which the average rates of anodic and cathodic reaction are balanced. However, if for example, a rapid increase of the anodic reaction rate proceeds, some of the charge generated by metal oxidation can be transiently stored in the capacitance that is generated due to charge separation at the metal-solution interface, known as the double-layer capacitance, before being consumed by the cathodic reaction on the electrode surface [3,4]. As a result, a fluctuation in the corrosion potential is observed; initially, the potential decreases rapidly due to the charging of the double layer capacitance

and, subsequently, it recovers as a result of the progressive consumption of charge by the cathodic reaction [5]. The described process is known as an anodic event, and a similar description can be given for cathodic events. Depending on the material-environment combination, anodic or cathodic events can be relatively large and occasional, such as for a passive material suffering metastable pitting, or relatively small and frequent, such as for materials undergoing active corrosion [6,7]. Consequently, larger potential and current transients are observed in the first case compared with the second case. Thus, the corrosion type can be determined analyzing the potential and current noise by statistical methods [8–10], spectral analysis [6,8,10–12], by wavelet [13–16] and Hilbert [17,18] transforms or others methods [19,20].

For two galvanically coupled electrodes comprising equal areas of the same material, when one event occurs on the surface of one electrode some charge associated with that event is consumed on the same electrode and some charge is consumed on the other electrode [3,21]. In this case, one-half of the charge generated on one electrode is consumed on the same electrode, and one-half of the charge is consumed on the other electrode [21]. If the galvanic coupling between the two electrodes is realized with a zero-resistance ammeter, the coupling current can be measured simultaneously with the potential of the electrodes.

Thus, the process of electrochemical noise generation intrinsically originates from electrode asymmetry; at a particular time, for example, the anodic activity on one electrode transiently exceeds the anodic activity of the other electrode, and a current flowing through the external circuit can be measured [21]. However, if the electrochemical noise signal is acquired for a sufficiently long time, on average, the two electrodes might be considered to behave

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as identical (or closely similar), in the sense that, on average, the duration and number of anodic and cathodic transients generated by one electrode is identical (or closely similar) to the duration and number of anodic and cathodic transients generated by the other electrode. From the previous, it follows that two electrodes can behave as identical on a long timescale, but they can be significantly asymmetrical on a shorter timescale. Except for some cases such as coated electrodes or stainless steel electrodes, it has been shown that, for two identical electrodes, and under the assumptions that (i) two identical electrodes have identical resistances (impedances), (ii) a noiseless reference electrode is used to measure the potential and (iii) the electrolyte is sufficiently conductive to neglect the electrolyte resistance, the noise resistance (impedance), defined as the square root of the variance (power spectral density) of the electrodes potential divided by the variance (power spectral density) of the coupling current, provides a close estimation of the polarization resistance (electrode impedance) [3,11,22–25].

Based on the previous consideration, the values of noise resistance [3,22,24,26] or noise impedance [27–30], or their time evolution [31–34], have been used extensively to evaluate quantitatively the behavior of corroding electrodes. Under the conditions where the value of the noise resistance, or the low-frequency limit of the noise impedance spectrum, can be considered representative of the value of the polarization resistance, their values can be used to estimate the corrosion rate from the Stern–Geary equation [35], provided that Tafel coefficients have been previously determined for the specific material–environment combination. This results from the unique advantage of electrochemical noise with respect to other electrochemical techniques, where virtually no perturbation to the corrosion process is introduced by the measurement. Direct (DC) or alternating (AC) current electrochemical techniques rely on imposing an electrical perturbation to the corroding electrode in order to produce a response from which information on the corrosion process is obtained. Thus, inevitably, the Faradic current associated with the applied signal affects the rate of anodic and/or cathodic reactions on the electrode surface and modifies, to a different extent depending on the technique selected, the equilibria that would be attained on a freely-corroding electrode. On the contrary, electrochemical noise only measures the fluctuations in current and potential that are naturally generated under free-corrosion condition and it is ideal for long term and real-time corrosion monitoring.

The validity of the estimation of the noise resistance, however, relies on two a priori assumptions, namely (i) that nominally identical electrodes have identical impedances [29,36,37] and (ii) that the noise produced by the external circuit used to measure the current is significantly less than the noise generated by the corroding electrodes [38,39]. To some extent, the first assumption can be verified by considering various statistical parameters related to the potential or current noise such as average values, skewness, and correlation coefficient [40,41]. The previous parameters might provide an indication of the symmetry between the two electrodes, but their physical meaning is not straightforward and a unique criterion to evaluate the reliability of the estimation of the noise resistance by evaluating the asymmetry related parameter remains the subject of debate. The second assumption is, in principle, easier to verify by using an appropriate dummy cell for the evaluation of the instrument noise [39]. However, the noise generated by the circuitry within the zero resistance ammeter depends also on the electrode impedance [38,39] and, therefore, different dummy cells with different impedances must be used to completely characterize the instrumental noise. Further, due to the intrinsic asymmetry between the current-measuring circuit and the voltage-measuring circuit, particular care must be taken during instrumental design in order to minimize errors during the measurement. This is due to the fact that, for a specimen on the centimeter scale, the relatively small current fluctuations (nanoamps to tens of microamps) occur

across the zero mean value, while the relatively small potential fluctuations (tenths of millivolts or tens of millivolts) are overlapped to a significant DC bias (hundreds of millivolts).

In addition, from the point of view of the corrosion process, it should be noted that the instrumental (current) noise generated by the zero-resistance ammeter during the current measurement is fed back to the corroding electrodes and there is the possibility that this could affect the behavior of the system [42]. Finally, but not less importantly, a non-ideal or non-perfectly calibrated ZRA might also introduce a small bias between the two electrodes, thereby affecting the corrosion process significantly.

In this work, an alternative approach to the measurement of electrochemical noise is introduced. Specifically, the two corroding electrodes are connected by a measuring resistor instead of a zero resistance ammeter. The corrosion events on each electrode produce current fluctuations, which result in a potential drop across the measuring resistor. Thus, the potentials of the two electrodes are not identical. The two individual potentials can then be physically measured by using two voltmeters, individually connected to a reference electrode (assumed noiseless) and to one of the two corroding electrodes. By using this configuration, the perturbation produced by the measurement on the corroding surface is due to the current flowing across the voltmeter from the reference electrode to the working electrode, and it is generally negligible, due to the high impedance of the voltmeter. Further, and unlike for the case of the measurement by ZRA where the current flows across the active electronics of the instrument, if the voltmeter is not perfectly calibrated the value of the reading might not reflect exactly the electrode potential, but this does not result in a perturbation to the corroding surface.

In summary, the measurement configuration proposed here has several advantages over the usual configuration, including (i) the possibility that noise generated by active electronics is fed back to the corroding system is excluded, (ii) the current can be calculated from the difference between the measured electrode potentials (similar), avoiding asymmetry between the current-measuring circuit and the voltage measuring circuit and (iii) due to the non-identical potentials of the two electrodes, differences in individual electrode behavior can be readily evaluated.

## 2. Theory

### 2.1. Physical implications of connecting two electrodes by a measuring resistor

Considering that a distinct advantage of the electrochemical noise technique is that no perturbation is introduced to the corrosion process, the physical effect of connecting two corroding electrodes by a measuring resistor must be examined initially (Fig. 1). If a corroding electrode and a reference electrode are immersed in an electrolyte, the corrosion potential can be measured without introducing significant perturbation to the corrosion process provided that the impedance of the voltmeter is high compared with the impedance of the corroding electrode. If this assumption is verified, the current flowing between the reference electrode and the corroding electrode is negligible, and the corrosion process is unperturbed. Thus, all the charge associated with, for example, an anodic event on the electrode is consumed by the cathodic reaction on that electrode. If a second identical electrode and a second reference electrode are immersed in the same electrolyte, each of the two electrodes corrodes independently; all the charge generated by one event on one electrode is consumed on the same electrode, and the corrosion potentials of the two electrodes are uncorrelated. Thus, the introduction of a second disconnected electrodes does not introduce a perturbation to the fundamental corrosion process on the first electrode and viceversa (Fig. 1a).

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