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Detection of Electrode Asymmetry in Electrochemical Noise Analysis

A. Lowe, H. Eren, *Member, IEEE*, Chun Che Fung, *Member, IEEE*

***Abstract*– The electrochemical noise resistance is a calculation that can be used for estimating the rate of corrosion of a pair of metal samples purely from the electrochemical noise that they generate. Ideally these metal samples (electrodes) would be identical, but it is not uncommon, for various reasons, for the electrodes to be significantly different. In that case, the theory linking the noise resistance to the more conventional electrochemical parameter, the polarisation resistance, breaks down. This link is important because it is only via the polarisation resistance that noise resistance can be used for corrosion rate estimation. It is therefore important to be able to detect an asymmetric electrode pair. This paper describes how the cross correlation between voltage and current noise can be used to detect an asymmetry.**

***Index Terms*–Noise resistance, Electrochemical Noise Analysis, Polarisation Resistance, Asymmetric Electrodes.**

I. INTRODUCTION

Electrochemical noise (EN) [1] is the phenomenon where the potential on an electrochemically reacting element (referred to as a working electrode) is observed to fluctuate, rather than remain at a constant level. Its was first proposed by Iverson [2] in 1968 that useful information regarding the reaction might be elucidated by analysis of this "noise". Since then, there has been much interest in the field of electrochemical noise analysis, particularly in corrosion studies. A popular analysis is the noise resistance [3], [4] calculation, which can be used to estimate the rate of the reaction. Figure 1 depicts the experimental set up used for the calculation.

In Figure 1, two metal samples (the working electrodes) are placed in a corrosive environment along with a third, specially designed, reference electrode. The potential between the two working electrodes and the reference electrode is measured, as is the current flowing between the two working electrodes. In this way, simultaneous potential and current EN measurements are observed. Figure 2 shows an example pair of potential and current waveforms.

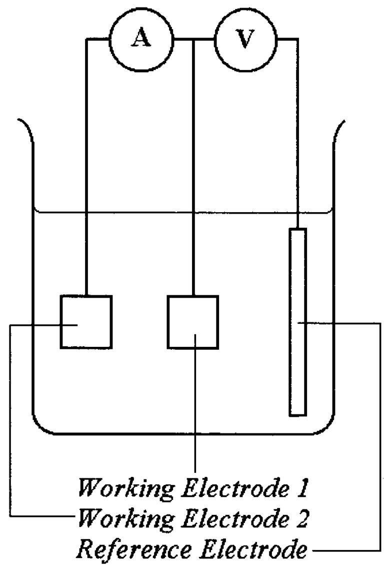

Fig. 1. Set up for a noise resistance measurement.

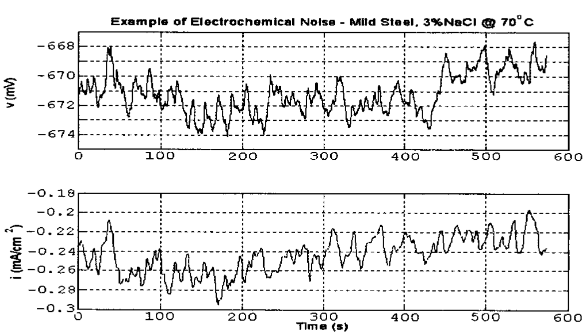

Fig 2. Example potential and current EN measurements

The theory behind the noise resistance method [3], [4] links the noise resistance to a quantity known as the polarisation resistance. The polarisation resistance [5] is a well understood and a widely used quantity that can be applied to the Stern-Geary [6] equation to infer the corrosion rate of a kinetically controlled system. As such, the link between noise resistance and polarisation resistance is an important anchor for the EN techniques. However, the theory asserts that the two working electrodes in Figure 1 must be nominally identical (ie

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symmetrical) if the noise resistance is to be representative of the polarisation resistance of the electrodes. It is therefore quite important to be able to show that a measurement does indeed come from a system with symmetric working electrodes.

This paper will describe how the cross correlation between the potential and current EN can be used to detect an asymmetric electrode pair.

II. Noise Resistance and the Equivalent Circuit

Figure 3 shows the electrical equivalent circuit used for analysis of the experimental set up of Figure 1.

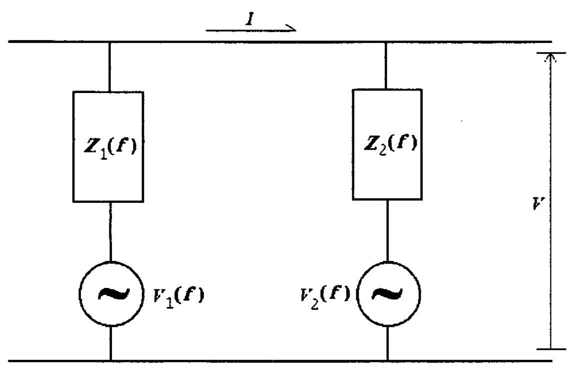

Fig 3. Equivalent circuit of the noise resistance measurement set up.

The equivalent circuit is the result of taking a linear approximation to the potential-current characteristics of an electrode about its operating points. $Z_1(f)$ and $Z_2(f)$ are the impedances of the electrodes resulting from the linear approximation and $V_1$and V_2 are the Thevenin equivalent potential EN originating from each electrode. V and I are the measured potential and current EN. In this work, for simplicity, it is assumed that the two impedances are entirely real valued with $Z_1(f)=R_1$ and $Z_2(f)=R_2$ where it follows that R_1 and R_2 are equal to the polarisation resistances of the respective electrodes. In practice, a related analysis (the spectral noise impedance [7]) can be used to account for the frequency dependent nature of the impedances.

The noise resistance is defined [3] as in Equation (1), where R_n is the noise resistance and σ_v and σ_i are the potential and current standard deviations respectively.

$$R_n = \sigma_v/\sigma_i \qquad (1)$$

By some simple circuit analysis, Equation (2) follows, where σ_{v1} and σ_{v2} are the standard deviations of V_1 and V_2 respectively.

$$R_n^2 = \frac{R_2^2\sigma_{v1}^2 + R_1^2\sigma_{v2}^2}{\sigma_{v1}^2 + \sigma_{v2}^2} \qquad (2)$$

If $R_1 = R_2 = R$, then Equation (2) reduces to Equation (3).

$$R_n = R \qquad (3)$$

Thus a requirement for the noise resistance to be equal to the polarisation resistance of the two electrodes is that the two electrodes have the same polarisation resistances.

III. Correlation Coefficient

In this work, a pair of electrodes are considered asymmetric if their Thevenin equivalent circuits have different resistances, R_1 and R_2, or if they have different noise variances, σ_{v1}^2 and σ_{v2}^2. The correlation coefficient is then proposed as a means of detecting asymmetry. Note that this is more restrictive than the requirement for the noise resistance to be equal to the polarisation resistance

In practice, the potential and current EN needs to be conditioned prior to analysis for the purpose of trend removal, amongst other reasons [8]. The conditioning often contains some form of linear convolutional filter stage, eg [4], [8], [9]. This signal conditioning is included in the analysis because it allows certain assumptions regarding the statistical characteristics of the analysed signals to be made.

Let v and i denote the filtered potential and current EN respectively. Then the correlation coefficient of v and i is defined as in Equation (4). In Equation (4), the "E" operator denotes statistical expectation and σ_v and σ_i represent the standard deviations of v and i, respectively.

$$r_{vi} = \frac{E[vi] - E[v]E[i]}{\sigma_v \sigma_i} \qquad (4)$$

The fictitious potential EN sources, v_1 and v_2, are defined as the potential EN sources of Figure 3 after application of the identical signal conditioning from which v and i are obtained. The variances of v_1 and v_2 are denoted respectively by σ_{v1}^2 and σ_{v2}^2.

Assuming (i) v_1 and v_2 to be Gaussian distributed, zero mean and statistically independent; and (ii) the impedances of Figure 3 to be purely resistive with $Z_1(f)=R_1$ and $Z_2(f)=R_2$ within the bandwidths of v_1 and v_2, the correlation coefficient in Equation (4) is found to be given by Equation (5).

$$r_{vi} = \frac{\sigma_{v1}^2 R_2 - \sigma_{v2}^2 R_1}{\sqrt{\left(\sigma_{v1}^2 + \sigma_{v2}^2\right)\left(\sigma_{v1}^2 R_2^2 + \sigma_{v2}^2 R_1^2\right)}} \qquad (5)$$

It is noted that, by the central limit theorem, the application of an infinite impulse response filter in the signal conditioning tends to validate the Gaussian assumption, and trend-removal and a band-limitation validates the zero mean assumption.

From Equation (5), it can be seen that if the correlation coefficient is non-zero, then it can be stated that $R_1 \neq R_2$ and/or $\sigma_{v1} \neq \sigma_{v2}$. ie, the resistances are not the same and/or the EN source powers are not the same. Then the electrodes cannot be considered identical. Note, however, that a correlation coefficient of zero does not necessarily imply identity of the electrodes.

The electrode symmetry may be assessed graphically as in Figures 4 and 5, where the conditioned potential and current EN are plotted on separate axes. Figure 4 is from a system with no significant asymmetry detected with a correlation coefficient of 0.088, while Figure 9 comes from an asymmetric system with a correlation coefficient of 0.60.

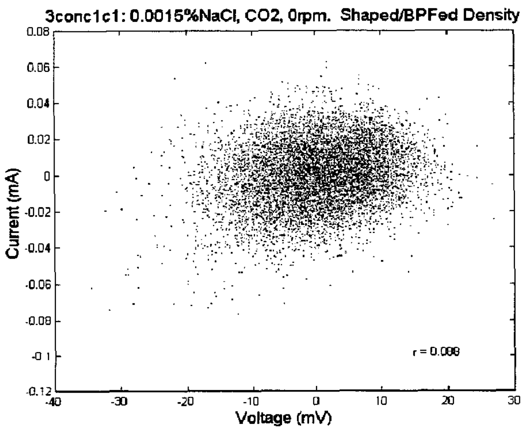

Fig. 4. Potential/current density plot for a symmetrical electrode pair.

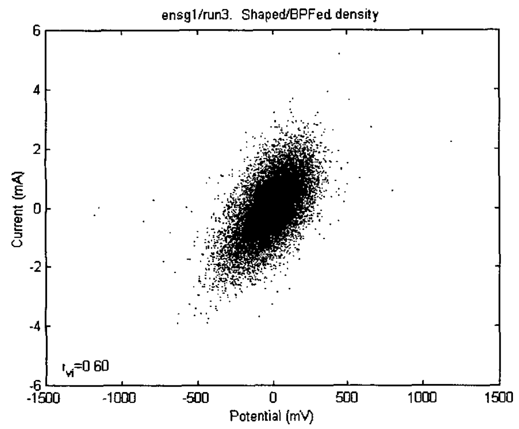

Fig. 5. Potential/current density plot for an asymmetric electrode pair.

IV. Experimental Verification

A series of experimental tests were performed to verify the theory. A linear polarisation (LP) measurement was performed separately on each of the two electrodes to obtain their polarisation resistances, R_{p1} and R_{p2}, followed by potential EN measurements (EPN) to assess their EN signal variances, σ_{v1}^2 and σ_{v2}^2. Then a dual potential/current EN measurement (EPN/ECN) was performed on the coupled electrodes, from which the correlation coefficient can be estimated by Equation (4) (with the expectation replaced with a time average). This estimated value is then compared with the value as predicted by Equation (5), using the data from the LP and EPN measurements. Table 1 summarises the results and Table 2 gives the comparison between the observed r_{vi} and predicted r_{vi}.

In table 2, there is excellent agreement between the observed and predicted correlation coefficients. The discrepancy in sign for the SA1027 measurement is likely due to confusion of the polarity of the instrument connections.

V. Conclusions

The correlation coefficient has been proposed as a means of detecting an asymmetric electrode pair in electrochemical noise resistance measurements. This allows the results of a noise resistance calculation to be used with more confidence.

Experimental data has been presented to validate the theory.

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Table 1. Data collected from a number of dual working electrode systems, encompassing both symmetric and asymmetric.

	Experiment	LP		EPN		EPN/ECN
		R_{p1}	R_{p2}	σ_{v1}^2	σ_{v2}^2	r_{vi}
SA1017	Pair of 3.02 cm^2 mild steel electrodes immersed in buffered, CO_2 saturated, 1% NaCl at 50 °C.	50 Ω	70 Ω	0.50	0.50	0.16
SA1019	Repeat of SA1017	60 Ω	60 Ω	0.31	0.69	0.39
SA1025	Repeat of SA1017. Three *v/i* noise measurements taken during the course.	70 Ω	90 Ω	0.50	0.50	-0.18, -0.19, -0.12
SA1027	A 1 cm^2 and a 9 cm^2 electrodes immersed in buffered, CO2 saturated, 1% NaCl at 50 °C. Two sets of measurements taken during the course. Second *v/i* measurement invalidated due to interference from other laboratory equipment.	30 Ω, 30 Ω	120Ω, 130Ω	0.07, 0.04	0.93, 0.96	0.45
AS1108a	A 3% NaCl cell coupled to a 0.3% NaCl cell via a NO_3 salt bridge. Both cells with 3.02 cm^2 mild steel electrodes and buffered, CO_2 saturated solution, held at 60 °C. *v/i* noise measurement with reference in 3% cell.	30 Ω	40 Ω	0.86	0.14	0.92
AS1108b	AS1108a, with reference in 3% cell for the *v/i* measurement.	30 Ω	40 Ω	0.86	0.14	-0.26

Table 2. Comparison between the correlation coefficient as observed from EPN/ECN measurement and as predicted by Equation (13).

Experiment	r_{vi} - Observed	r_{vi} - Predicted
SA1017	0.16	0.16
SA1019	0.39	0.39
SA1025	-0.18, -0.19, -0.12	-0.12
SA1027	0.45	-0.44 -0.59
SA1108a*	0.92	0.93
SA1108b*	-0.26	-0.32

*Noise resistance from the EPN/ECN measurements used to estimate salt bridge resistance, which was added in series to the appropriate polarisation resistance prior to substitution into Equation (13)