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Detection of Electrode Asymmetry in Electrochemical Noise Analysis  
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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.


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 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.

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
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.

\[
R_n = \frac{\sigma_i}{\sigma_i}
\]  

(1)

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

\[
R_n^2 = \frac{R_1^2\sigma_{v1}^2 + R_2^2\sigma_{v2}^2}{\sigma_{v1}^2 + \sigma_{v2}^2}
\]  

(2)

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

\[
R_n = R
\]  

(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, \( \sigma_{v1}^2 \) and \( \sigma_{v2}^2 \). 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 [S]. The conditioning often contains some form of linear convolutional filter stage, e.g., [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 \( \sigma_v \) and \( \sigma_i \) represent the standard deviations of \( v \) and \( i \), respectively.

\[
r_{vi} = \frac{E[vi] - E[v]E[i]}{\sigma_v\sigma_i}
\]  

(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 \( \sigma_{v1}^2 \) and \( \sigma_{v2}^2 \).

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).

\[
r_{vi} = \frac{\sigma_{v1}^2R_2 - \sigma_{v2}^2R_1}{\sqrt{(\sigma_{v1}^2 + \sigma_{v2}^2)(\sigma_{v1}^2R_2^2 + \sigma_{v2}^2R_1^2)}}
\]  

(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 \( \sigma_1 \neq \sigma_2 \). i.e., 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.

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, \( \sigma_{p1}^2 \) and \( \sigma_{p2}^2 \). 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 \( r_{oo} \) and
predicted \( r_{ii} \).

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.

REFERENCES

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- Simultaneous Monitoring of Potential and Current Noise Signals from
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1997
Electrochemical Impedance Spectroscopy and Electrochemical Noise
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Signal Conditioning", to be published
Performance Continuously Using Electrochemical Noise Analysis", British
Table 1. Data collected from a number of dual working electrode systems, encompassing both symmetric and asymmetric.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>LP</th>
<th>EPN</th>
<th>EPN/ECN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_{pl}$</td>
<td>$R_{p2}$</td>
<td>$\sigma_{i1}^2$</td>
</tr>
<tr>
<td>SA1017</td>
<td>50 $\Omega$</td>
<td>70 $\Omega$</td>
<td>0.50</td>
</tr>
<tr>
<td>SA1019</td>
<td>60 $\Omega$</td>
<td>60 $\Omega$</td>
<td>0.31</td>
</tr>
<tr>
<td>SA1025</td>
<td>70 $\Omega$</td>
<td>90 $\Omega$</td>
<td>0.50</td>
</tr>
<tr>
<td>SA1027</td>
<td>30 $\Omega$, 120$\Omega$, 30 $\Omega$, 130$\Omega$</td>
<td>0.07, 0.93, 0.04, 0.96</td>
<td>0.45</td>
</tr>
<tr>
<td>AS1108a</td>
<td>30 $\Omega$, 40 $\Omega$</td>
<td>0.86</td>
<td>0.14</td>
</tr>
<tr>
<td>AS1108b*</td>
<td>30 $\Omega$, 40 $\Omega$</td>
<td>0.86</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*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).

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

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$r_{st}$ - Observed</th>
<th>$r_{st}$ - Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA1017</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>SA1019</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
<td>SA1025</td>
<td>-0.18, -0.19, -0.12</td>
<td>-0.12, -0.12, -0.12</td>
</tr>
<tr>
<td>SA1027</td>
<td>0.45</td>
<td>-0.44, -0.59</td>
</tr>
<tr>
<td>AS1108a*</td>
<td>0.92</td>
<td>0.93</td>
</tr>
<tr>
<td>AS1108b*</td>
<td>-0.26</td>
<td>-0.32</td>
</tr>
</tbody>
</table>

*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).