



Self linear polarization resistance-theory and examples

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Abstract

Measuring the corrosion rate of a corroding metal is of interest in many situations, including monitoring industrial processes and undertaking fundamental research. The corrosion rate of a metal can be measured electrochemically by determining its polarization resistance, which is inversely proportional to the corrosion rate. What is described in this article is a technique for mathematically extracting from electrochemical noise (EN) data the polarization resistance as well as a measure of the frequency of anodic and cathodic transients. The theoretical framework for self-linear polarization resistance is based on a time-domain analysis of an electrical circuit model of an EN experiment. The analysis indicates that the polarization resistance for one electrode can be interpreted only if the second electrode alone is generating current transients during a given time record. One advantage of this approach, compared with other techniques for obtaining a polarization resistance from EN data, is that short time records, i.e. less than one minute, can be assessed. The self-consistency of the polarization resistance can be assessed with a correlation coefficient. Another advantage is that the nature of localized corrosion events can be attributed to either anodic or cathodic current transients from one of the electrodes.

List of symbols

I_m	measured transient current, A	C_1	capacitance of metal–solution interface at electrode ‘1’, F
I_t	transient current, A	C_2	capacitance of metal–solution interface at electrode ‘2’, F
V_m	measured transient voltage, V	i_1	transient from electrode ‘1’, A
V_t	transient voltage, V	i_2	transient from electrode ‘2’, A
R_{s1}	solution resistance between the reference electrode and electrode ‘1’, ohm	R_p	polarization resistance, ohm
R_{s2}	solution resistance between the reference electrode and electrode ‘2’, ohm		

1. Introduction

Assessment of the corrosion rate of a metal is of interest in many situations from monitoring industrial processes to fundamental research in laboratories. The corrosion rate of a metal can be measured electrochemically by determining its polarization resistance (R_p), which is inversely proportional to the corrosion rate [1].

Techniques that attempt to measure the polarization resistance can be divided into active and passive approaches. Active approaches such as linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) require external imposition of either potential or current. This may mask actual changes in the sample during measurement due to changes in process conditions or to changes at the metal surface

induced by active corrosion [2]. One advantage of electrochemical noise (EN) measurements is that transient current and potential phenomenon are ‘listened to’ without external polarization. Another advantage is that EN measurements appear to provide information, both quantitative and qualitative, on the nature of localized corrosion events. Attempts to quantify localized corrosion include the pitting ratio, the slope and break point of the spectral power distribution and the shot-noise analogy [3, 4]. However, a consensus has not developed regarding which one is the best approach.

Typically, EN measurements are made with two electrodes of the metal of interest and a reference electrode. The current between the sample electrodes is measured with a zero-resistance ammeter. The voltage between the coupled sample electrodes and a reference

electrode is measured. Two techniques for extracting a polarization resistance from EN data that have reached a degree of acceptance are the noise resistance and the spectral noise resistance [3, 4]. The statistically-based noise resistance is the ratio of the standard deviation of EN voltage to the standard deviation of EN current. The frequency-based spectral noise resistance is the square root of the ratio of the power spectral density of the voltage to that for the current in the low frequency limit. The accuracy of these two EN techniques depends on the length of the time record with longer time records providing greater accuracy. This is because capturing information at the more meaningful lower frequencies improves with the length of time record. However, the corrosion rate must be constant during the time record.

What is introduced in this article is a technique for mathematically extracting polarization resistance as well as for obtaining a measure of the frequency of anodic and cathodic transients from EN data. It is a refinement and further development of the technique introduced as self-linear polarization resistance (SLPR) [5]. The SLPR results for 430 stainless steel electrodes in acidic media were virtually identical to LPR results.

2. SLPR theory

A schematic of the electrical analogue of the electrode arrangement for EN measurement is shown in Figure 1. This is a very similar circuit to one used for an analysis in the frequency domain [6]. It is assumed that either anodic or cathodic transients can be generated at either electrode. The ground represents a sink or source for electrons. The current generated by anodic reactions on electrode '1' can be consumed on either electrode '1' or '2' through either cathodic reactions at the metal surface or capacitive processes at the metal-solution interface. Conversely, current consumed by cathodic reactions on electrode '1' can be supplied by anodic reactions on either electrode '1' or '2' or through capacitive processes. The electrode resistance corresponds to the

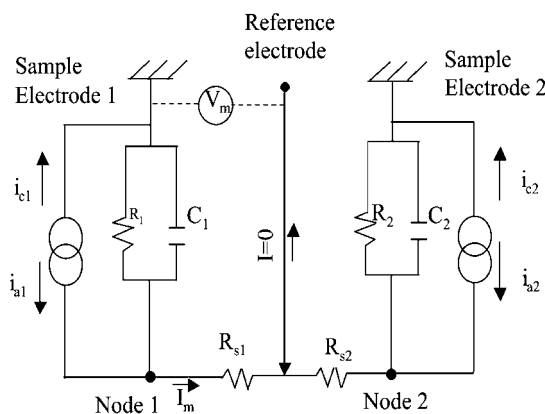


Fig. 1. Equivalent circuit diagram of an electrochemical noise arrangement with two electrodes and a reference electrode. Each electrode can generate both anodic and cathodic current transients.

polarization resistance of the corrosion reaction and the capacitor represents the capacitive effect of the metal-solution interface. The solution resistance between the reference electrode and electrode '1' is R_{s1} and that between the reference electrode and electrode '2' is R_{s2} .

The circuit in Figure 1 may be analyzed by the application of Kirchoff's Law at nodes 1 and 2 to the transient current, I_t and transient voltage, V_t . The voltage at node 1 is $I_t R_{s1} - V_t$ and that at node 2 is $-I_t R_{s2} - V_t$. At node 1, the current balance during a transient from electrode 1 is

$$i_1 = I_m - \frac{(I_t R_{s1} - V_t)}{R_1} - C_1 \frac{d(I_t R_{s1} - V_t)}{dt} \quad (1)$$

At node 2, the current balance during a transient from electrode '2' is

$$i_2 + I_m = \frac{(-I_t R_{s2} - V_t)}{R_2} + C_2 \frac{d(-I_t R_{s2} - V_t)}{dt} \quad (2)$$

In regard to node 1, the only circumstances whereby R_1 can be estimated is when the transients from electrode '1' are zero. Thus it is necessary that transients from electrode '2' reveal the polarization resistance of electrode '1'. In this case the polarization resistance for electrode '1' is

$$R_1 = \frac{V_t - I_t R_{s1}}{I_t - C_1 \frac{d(V_t - I_t R_{s1})}{dt}} \quad (3)$$

Similarly, the polarization resistance for electrode '2' is revealed where the transients from electrode '2' are zero,

$$R_2 = \frac{-(V_t + I_t R_{s2})}{I_t + C_2 \frac{d(V_t + I_t R_{s2})}{dt}} \quad (4)$$

In the general case, where electrodes '1' and '2' are each generating transient currents within the same time record, the solutions for polarization resistance are indeterminate. There are four unknowns (i_1 , i_2 , R_1 and R_2) and only two variables are measured (V_t and I_t). Even in the ideal case where the electrodes are perfectly identical ($R_1 = R_2 = R$), there are still three unknowns. Thus in time records where both electrodes are generating current transients, information on the polarization resistance of either electrode are not obtainable.

From Equations 3 and 4, the polarization resistance for the electrodes separately is theoretically obtainable from what is measured if one assumes a value for the electrode capacitance (either C_1 or C_2) and can measure the solution resistance R_{s1} and R_{s2} . The capacitance for each electrode is the product of the electrode area and the specific double-layer capacitance, which for most metal-solution interfaces is $50\text{--}100 \mu\text{F cm}^{-2}$ [3, p. 25] and therefore can be reasonably estimated.

An important limiting case to Equations 3 and 4 is where the solution resistance is much less than the polarization resistance.

$$R_1 = \frac{V_t}{I_t - C_1 \frac{dV_t}{dt}} \quad (5)$$

$$R_2 = \frac{-V_t}{I_t + C_2 \frac{dV_t}{dt}} \quad (6)$$

Further information on the nature of the current transients can be obtained by examining its sign. In the case where the polarization resistance of electrode '1' is revealed by Equation 5, the stimulus is from either a cathodic or an anodic transient from electrode '2'. If the stimulus was a cathodic transient from electrode '2', then the measured current, I_t , should contain a positive spike. If the stimulus was an anodic transient from electrode '2', then the measured current should contain a negative spike. Similarly, if the polarization resistance of electrode '2' is revealed from Equation 8, the stimulus is either a cathodic or anodic transient from electrode '1'. If the stimulus was an anodic transient from electrode '1', then I_m will contain a positive spike. If the stimulus was a cathodic transient from electrode '1' then I_m will contain a negative spike. Table 1 summarizes the interpretation of which electrode is generating anodic or cathodic transients and which electrode is expressing its polarization resistance from the sign of V_t/I_t and the direction and sign of spikes in the measured current transients (I_t).

In summary, it is the polarization resistance of the quieter electrode, in the sense of producing fewer current

Table 1. Summary of the interpretation of which electrode is generating anodic or cathodic transients and which electrode is expressing its polarization resistance from the sign of $V_t/I_t - C(dV_t/dt)$ and the skew of I_t

	Positive skew in I_t	Negative skew in I_t
Positive $V_t/[I_t - C(dV_t/dt)]$	R_1 revealed Cathodic transient from '2'	R_2 revealed Anodic transient from '1'
Negative $V_t/[I_t + C(dV_t/dt)]$	R_2 revealed Cathodic transient from '1'	R_1 revealed Anodic transient from '2'

transients, which is revealed. Thus, the distribution of expressed polarization resistances is an indication of the balance of reactivity between the two electrodes. The electrode that expressed its polarization resistance more frequently generated fewer transients than the other electrode.

3. Algorithm for implementing SLPR theory

For a given block of EN data, the first step is to determine whether there is a sufficiently clear relationship between the transient voltage and transient current, i.e. V_t vs $I_t - C(dV_t/dt)$, to warrant further examination. The second step is to evaluate the appropriate polarization resistance, either R_1 or R_2 , from Equations 5 or 6, respectively. The third step is to measure the skewness of the transient current and assess the identity of the transient stimulus as coming from either cathodic or anodic events as per Table 1. Therefore, for each block of data one of three results is possible: (i) a valid R_1 and identification of anodic or cathodic transients from electrode '2' or (ii) a valid R_2 and identification of anodic or cathodic transients from electrode '1' or (iii) no useful result.

If the solution resistance is negligible compared to the polarization resistance, the screening step for a block of EN data may be done by determining the correlation coefficient between V_t vs $I_t - C(dV_t/dt)$. If the absolute value for this exceeds a cut-off value (for example 0.8) then the data is further examined. In order to do this, however, the de-trended potential, V_t , and de-trended current, I_t , must be obtained from the raw data and then the derivative dV_t/dt must be evaluated. The de-trended measurements are obtained by the difference between the raw measurement and the fitted value for each sampling event. Fitting the raw data, both potential and current, to a fifth-order polynomial seems to be a suitable approach for obtaining average values [7]. The derivative, dV_t/dt , may be obtained numerically from the de-trended potential. Once a block of EN data has been determined to have a sufficiently high correlation

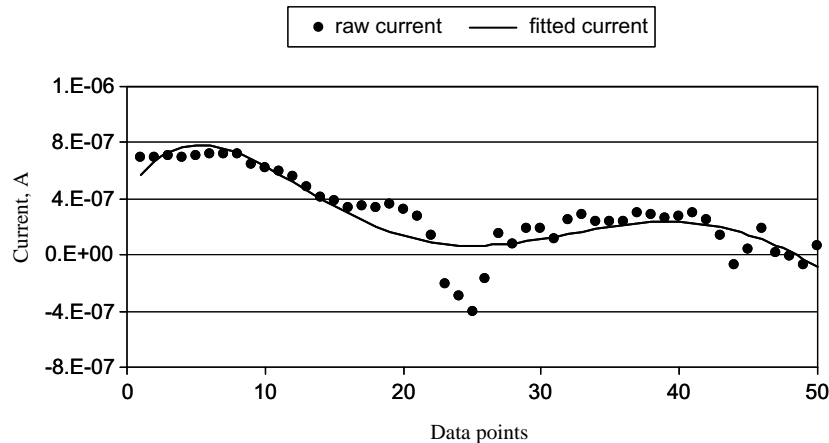


Fig. 2. Raw and fitted current between two nominally similar samples of UNS S43020 after 202 s.

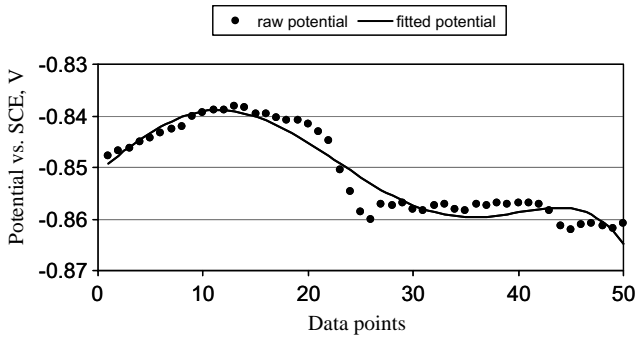


Fig. 3. Raw and fitted potential between two nominally similar samples of UNS S43020 after 202 s (same time frame as Figure 2).

then the appropriate polarization resistance can be estimated.

In summary, two parameters may be optimized for each set of EN data. The first is the number of points per block of data and the second is the cut-off criterion for the correlation coefficient between V_t and $I_t - C(dV_t/dt)$. Fewer points in the time record improve the time resolution of the estimates of polarization resistance. However, too few points in the time record decrease the likelihood that a current transient occurs. Increasing the number of points in the time record increases the likelihood that both electrodes produce current transients and causes the relationship between potential and current to be unintelligible.

4. Experimental

Two nominally identical electrodes were made from stainless steel (UNS S43020) sheet (short transverse orientation) and encased in epoxy. The exposed area of each electrode was 0.2 cm^2 , which was polished to 600 grit. The electrolyte was saline solution (3.5% NaCl) made from deionized water and reagent-grade sodium chloride. The solution resistance of this electrolyte was determined by electrochemical impedance spectroscopy to be 3–4 ohm-cm. Since the solution resistance was expected to be much less than the polarization resistance, Equations 5 and 6 were applied. The reference electrode was a saturated calomel electrode (SCE). The SCE was placed within a Luggin capillary whose tip was placed equidistant to the two electrode faces, about 1 cm away. The current and voltage measurements were made with a Gamry potentiostat (PC4) and Gamry software (ESA 400). The sampling frequency was 2 Hz. Electrode '1' was the working electrode of the potentiostat. The samples were exposed to saline solution for 20 min.

The polarization resistance for the UNS S43020 sample was also obtained by electrochemical impedance spectroscopy. The impedance was measured from 0.1 to 20 000 Hz. The counter electrode was a platinum foil. The spectra were fit to a solution resistance in series with a resistor that was in parallel with a constant phase element.

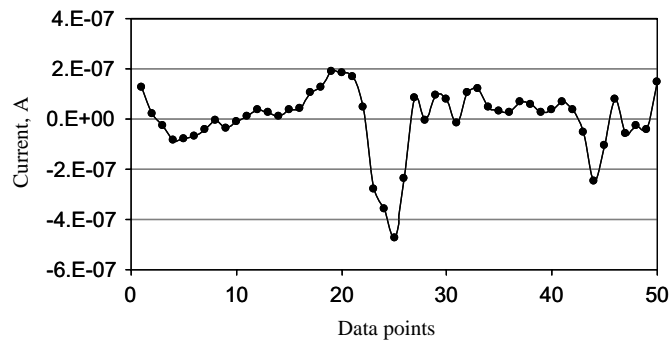


Fig. 4. De-trended current between two nominally similar samples of UNS S43020 after 202 s (same time frame as Figure 2).

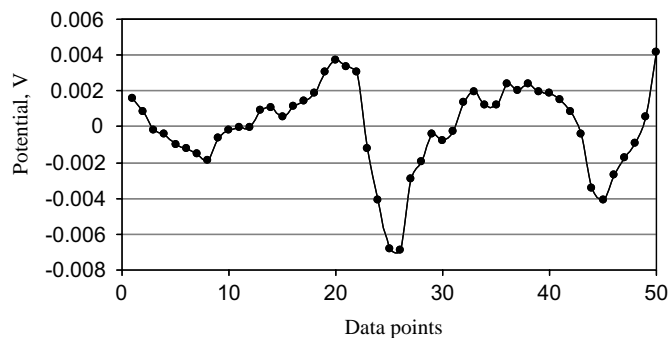


Fig. 5. De-trended potential between two nominally similar samples of UNS S43020 after 202 s (same time frame as Figure 2).

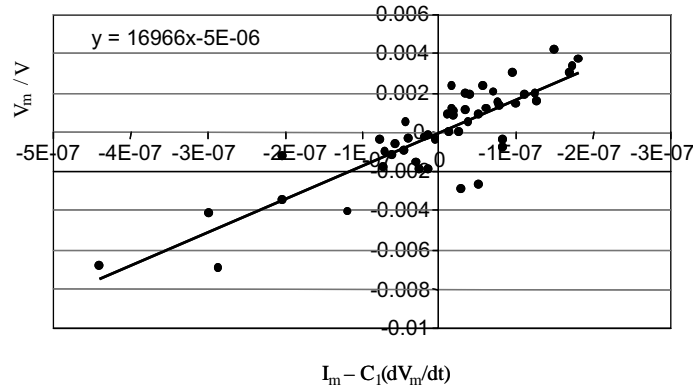


Fig. 6. De-trended potential (V_t) vs $I_t - C_1(dV_t/dt)$ for the same data presented in Figures 2–5.

5. Results and discussion

The EN data was processed by setting the number of points for each assessment to 50 points (25 s) and the cut-off criterion for the correlation coefficient was set to 0.8. The derivative dV_t/dt was obtained numerically using the 5-point, equally spaced central difference technique [8]. The capacitance of the metal-solution interface was calculated as the product of electrode area and a specific capacitance of $100 \mu\text{F cm}^{-2}$ [3].

Figures 2–6 pertain to the same block of 50 points taken 202 s after commencement of data collection. This set revealed the R_p for electrode ‘1’ by an anodic transient from electrode ‘2’. Figure 2 shows the raw and fitted current and Figure 3 shows the raw and fitted potential for the same time frame. There was a large downward spike near the middle of the data in both the current and raw potential near the middle of this period. The de-trended current and potential for these data are shown in Figures 4 and 5, respectively. The de-trended curves were obtained by subtracting the fitted curve from the raw data. The polarization resistance for electrode ‘1’ is revealed as the slope ($16\,966 \Omega$) in Figure 6, which is a plot of V_t vs $I_t - C_1 dV_t/dt$ as per Equation 5. The correlation coefficient for this data set was 0.85.

The polarization resistance, as measured by EIS, for three experiments was 18 110, 16 250 and 17 430 Ω . The polarization resistance obtained by SLPR was in good agreement.

In summary, 51 data blocks exhibited a correlation coefficient that exceeded the cut-off of 0.8 over a 20-min period. Thus in this system, about 2% of EN data

revealed a polarization resistance. Table 2 is a summary of the transients for this data set. The results indicate that although the electrodes were nominally similar, they were quite different in their reactivity. It is also of interest that a significant percentage (37%) of the transients were due to cathodic processes. Since bubbles were not visible, the cathodic transients could have been due to dissolved metal ion reduction as occurs during de-alloying.

6. Conclusions

SLPR theory was developed from a time-domain analysis of an electrical circuit model of an EN experiment. The analysis indicates that an estimate of polarization resistance is obtainable only if one electrode is generating transients during a given time record. SLPR theory also provides a means of quantifying the frequency of cathodic and anodic transients. In some cases, this information is of more interest than a measure of the polarization resistance.

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Table 2. Summary of the nature of current transients for blocks of EN data where the correlation coefficient between V_t and $I_t - C(dV_t/dt)$ exceeded 0.8. Nominally similar electrodes of UNS S43020 were exposed to saline solution for 20 min

Current transient type	Electrode source	Occurrence in 20 min	Percentage
Cathodic	‘1’	1	2
Anodic	‘1’	2	4
Cathodic	‘2’	18	35
Anodic	‘2’	30	59