Primer on the AC Impedance Technique

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Abstract

The AC impedance technique (electrochemical impedance technique) is an emerging technology. The technology is becoming important to the corrosion engineer in accurately predicting corrosion behavior. In fact, the technology is now moving out of the laboratory. This primer is written to provide the background necessary for the corrosion engineer to become sensitized to the technique and the rather unique role it can play in corrosion prediction.

Introduction

Theory and applications of the AC impedance technique are currently so developed that the technique can aid in practical corrosion prediction and control. A gulf exists, however, between the practical corrosion engineer and the laboratory scientist in both the understanding of and the emphasis areas for AC impedance applications. A number of reviews exist on the AC impedance technique.[1-5] The primary problem with the majority of these reviews is that they either tend to be oriented only toward the laboratory without the introduction of "real world" factors or tend to assume a reasonably advanced background in either electronics or mathematics.

Two of the listed reviews that seem to require the least background for understanding are those by EG & G Princeton Applied Research[2] and by Hladky, et al.[5] Two of the reviews are oriented to particular products.[2,3] The purpose of this short overview is to serve as a simple primer for practical corrosion engineers so that they can understand the published literature more easily as well as determine how the AC impedance technique can best serve their needs. A reasonable understanding of the referenced literature is vital in making full use of the technique. Instrumentation is reviewed elsewhere[2-4] and is not discussed here.

Corrosion processes are electrochemical in nature. As such, they involve electron transfer, which facilitates the dissolution of metal. If a means can be found to model this process, then corrosion prediction and control might be facilitated. From a practical standpoint, this outcome is the goal of most industrial efforts to use electrochemical tools.

Technique

In principle, an electrochemical process may be modeled by electrical circuit elements such as resistors, capacitors, and inductors. For example, the corrosion reaction itself can often be modeled by one or more resistors. The ability to model a corrosion process in this manner gives rise to the practical utility of the AC impedance technique. The corrosion engineer can use established AC circuit theory to characterize the electrochemical corrosion process. Such characterization can facilitate understanding and lead to more accurate predictions of corrosion rates and overall corrosion behavior.

Before examining some of the different models that might be established, a brief theoretical overview is necessary. The purpose is to introduce the physical meaning and use of imaginary numbers, which are important to interpreting the data from and creating models for the AC impedance technique. Direct current can be viewed as alternating current in the limit of zero frequency. Under conditions of direct current, e.g., zero frequency, Ohm's Law can be written as:

$$E = IR^{(1)} \qquad (1)$$

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(1)All symbols are defined at the end of the paper.

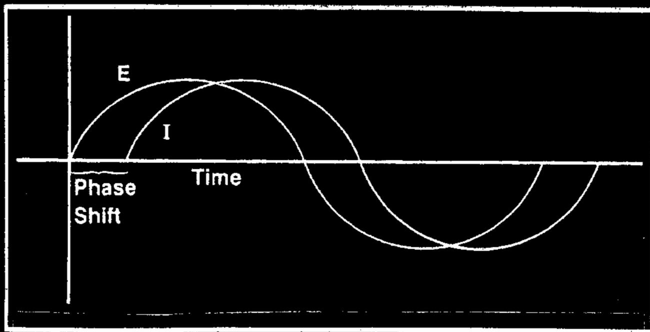

FIGURE 1 — Sinusoidal AC voltage and current signals.

In this case, the resistance is composed of only one or more actual resistors. When the frequency is not zero, as would occur from imposition of an alternating current, Ohm's Law becomes:

$$E = IZ \tag{2}$$

Under these conditions, the resistance is caused by all circuit elements that can impede the flow of current, e.g., resistors, capacitors, and inductors. The value of the resistance created by capacitors and inductors depends on frequency. The value of the resistance created by a resistor is independent of frequency.

When an AC voltage sine or cosine wave is applied across a circuit composed only of a resistor, the resultant current is also a sine or cosine wave of the same frequency, with no phase shift but with a different amplitude. If the circuit consists of capacitors and inductors, the resulting current will not only differ in amplitude but will also be shifted in time, i.e., have a phase shift. This phenomenon is shown in Figure 1.

Use of sines and cosines are mathematically cumbersome. Vector analysis, however, provides a convenient method of describing the analogous circuit in mathematical terms. The relationship between such vector analysis and imaginary numbers provides the basis for the AC impedance analysis. A sinusoidal current or voltage can be pictured as a rotating vector as shown in Figure 2. In this figure, the current rotates at a constant angular frequency, f (hertz) or ω (radians-s^{-1} = $2\pi f$). For example, standard AC current can be pictured as a vector that rotates at 60 hertz or 377 radians-s^{-1}. In Figure 2, the x component defines the observed current. Therefore, it becomes the *real* component of the rotating vector. The y component is a contribution that is not observed; therefore, it is termed the *imaginary* component of the rotating vector. The mathematical description of the two components is written as:

$$\text{Real current} = I_x = |I|\cos(\omega t) \tag{3(a)}$$

$$\text{Imaginary current} = I_y = |I|\sin(\omega t) \tag{3(b)}$$

$$|I|^2 = |I_x|^2 + |I_y|^2 \tag{3(c)}$$

The voltage can be pictured as a similar rotating vector

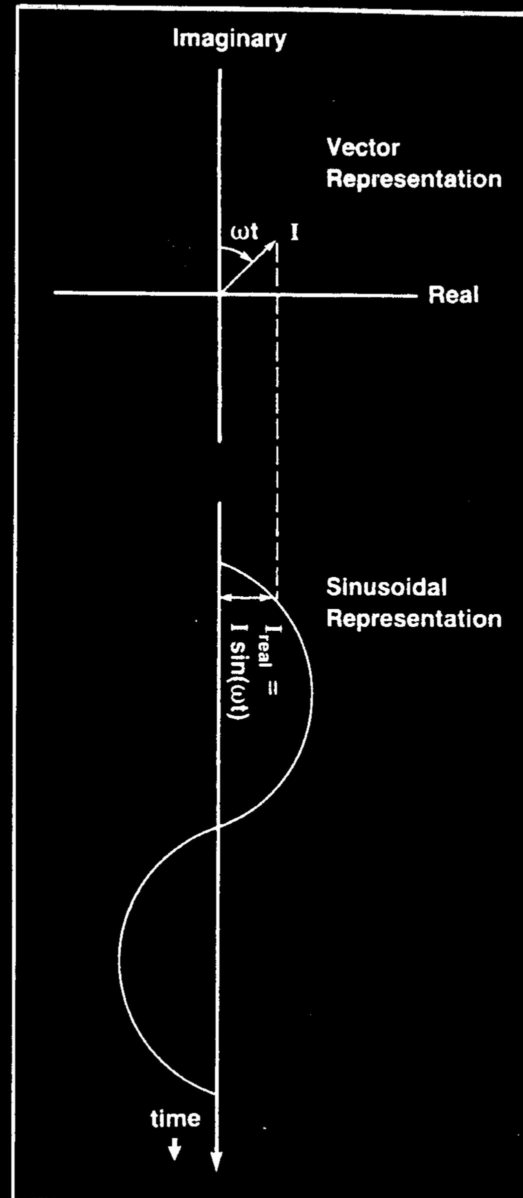

FIGURE 2 — Relationship between sinusoidal AC current and rotating vector representation.

with its own amplitude, E, and the same rotation speed, ω. As shown in Figure 3, when the current is in phase with the applied voltage, the two vectors are coincident and rotate together. This response is characteristic of a circuit containing only a resistor. When the current and voltage are out-of-phase, the two vectors rotate together at the same frequency, but are offset by an angle called the *phase angle shift*, θ. This response is characteristic of a circuit that contains capacitors and inductors in addition to resistors.

In the measurement of AC impedance, one vector is viewed using the others as a frame of reference. Thus, the reference point rotates and the time dependence of the signals (ωt) is not viewed. In addition, both the current and voltage vectors are referred to the same reference frame. The voltage vector is divided by the current vector to yield the final result in terms of the impedance (voltage divided by current), as shown in Figure 4.

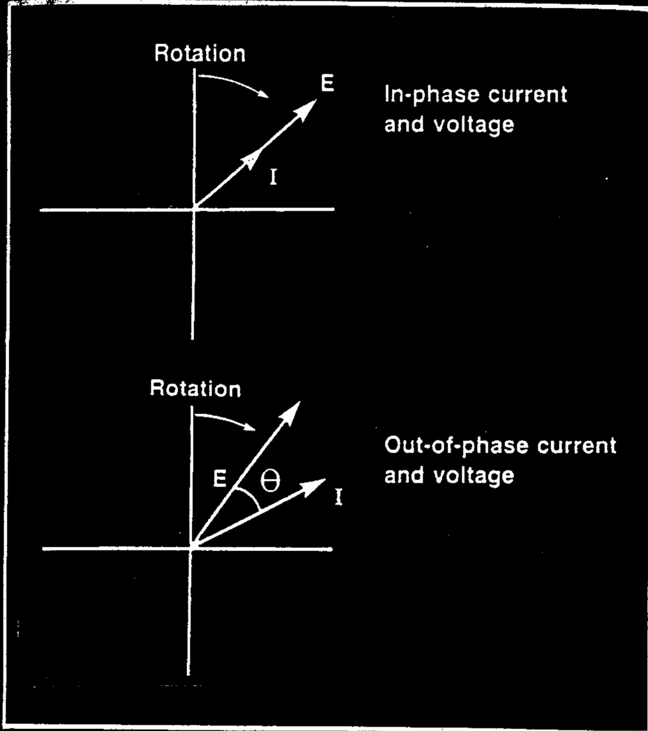

FIGURE 3 — In-phase and out-of-phase rotation of current and voltage vectors.

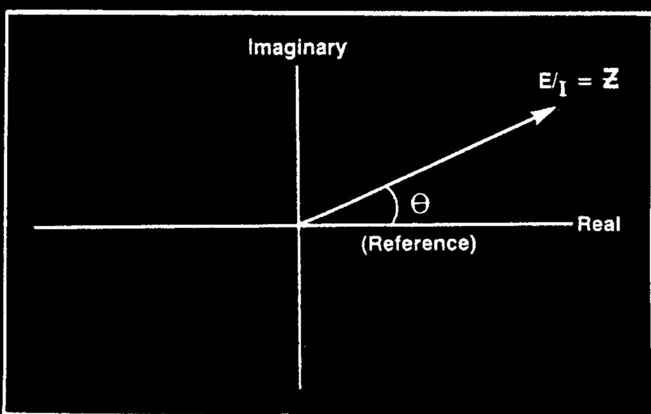

FIGURE 4 — Impedance vector.

The mathematical convention for separating the real (x) and imaginary (y) components is to multiply the magnitude of the imaginary contribution by j and report the real and imaginary values separately. The equations for AC impedance become:

$$E = E_{real} + E_{imaginary} = E' + jE'' \quad [4(a)]$$

$$I = I_{real} + I_{imaginary} = I' + jI'' \quad [4(b)]$$

$$Z = Z' + jZ'' = \frac{E' + jE''}{I' + jI''} \quad [4(c)]$$

$$\tan\phi = \frac{Z''}{Z'} \quad [4(d)]$$

TABLE 1 — AC Impedance Basic Circuit Elements

Element	AC Impedance Equation	
Resistor	$Z = R$	
Capacitor	$Z = -\frac{1}{j\omega C}$	$\omega = 2\pi f$
Inductor	$L = j\omega L$	$\omega = 2\pi f$

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad [4(e)]$$

The goal of AC impedance is to measure the impedance Z as Z' and Z'' and then to use simple circuit analogues to model the response. If the amplitude of the voltage excitation is kept low (e.g., usually 10 mV or less), the measured response may often be assumed to be composed of a linear array of resistors, capacitors, and inductors. Then, the electrode response can, in principle, be modeled in terms of such an array. The three basic circuit elements can be written as shown in Table 1.

Table 1 shows that a resistor has only a real contribution. That is, the response of a resistor would be parallel to the real axis, independent of frequency. Both the capacitor and inductor have purely imaginary contributions. Their contributions would be parallel to the imaginary axis. The object of AC impedance is to model the corrosion process in terms of circuit elements such as those shown in Table 1 and from that model to be able to make conclusions about characteristics of the corrosion process. Since measurements can be taken at the corrosion potential, the characteristics are obtainable at the alloy state found in practice.

Simple Corrosion Process

The simplest type of corrosion process would be the combination of a corrosion reaction and a double layer. One example of this type of process is uniform corrosion involving one chemical reaction. For example, the corrosion of carbon steel in 1 molar (M) sulfuric acid falls into this category.[6] The reaction

$$Fe + 2H^+ \rightarrow H_2 + Fe^{+2} \quad (5)$$

describes the corrosion reaction. This reaction can be represented by a simple resistor. The double layer is created by the fact that the surface of a metal in contact with any oxidizing agent, such as water or oxygen, is itself an oxide or hydroxide. The latter component would tend to ionize in water so that the surface becomes charged.[7] Counter-ions would be present in the liquid layer adjacent to the metal surface to balance the surface charge. This structure responds to an AC voltage signal in a way analogous to a capacitor. If the real component Z' and

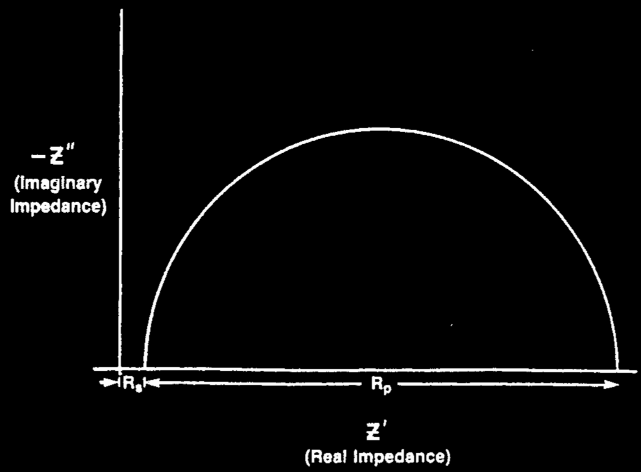

FIGURE 5 — Nyquist plot of simple charge transfer corrosion process.

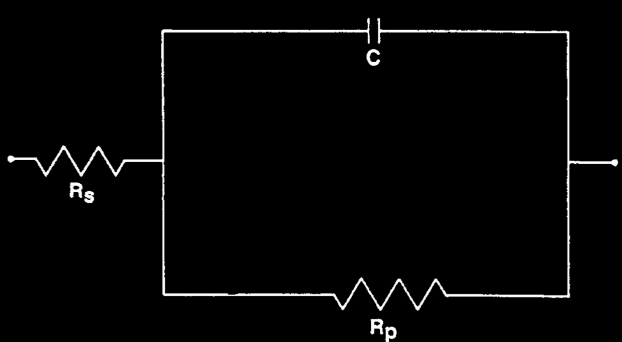

FIGURE 6 — Circuit that models impedance in Figure 5.

the negative of the imaginary component Z'', measured as a function of frequency, are plotted against each other for this type of simple corrosion process, the plot would appear as in Figure 5. This method of plotting is called the *Nyquist plot*.

For this simple process, the model circuit is that shown in Figure 6. The circuit is a resistor, R_p, in parallel with a capacitor, C. The entire parallel circuit is in series with another resistor, R_s. The utility of AC impedance lies in the fact that R_s equals the solution resistance uncompensated by the potentiostat and R_p equals the polarization resistance. For the case of carbon steel corrosion in 1 M sulfuric acid, for example, R_p is inversely proportional to the corrosion rate. This relationship is found for many processes. Use of R_p with Tafel slopes allows the corrosion rate to be estimated.[6] Thus, the AC impedance technique enables the corrosion rate to be estimated rapidly in the absence of uncompensated solution resistance and at the corrosion potential.

If Figure 6 adequately describes the corrosion process, the plot shown in Figure 5 can be described by Equation (6).

$$Z = R_s + \frac{R_p}{1 + \omega^2 R_p^2 C^2} + \frac{j\omega R_p^2 C}{1 + \omega^2 R_p^2 C^2} \quad (6)$$

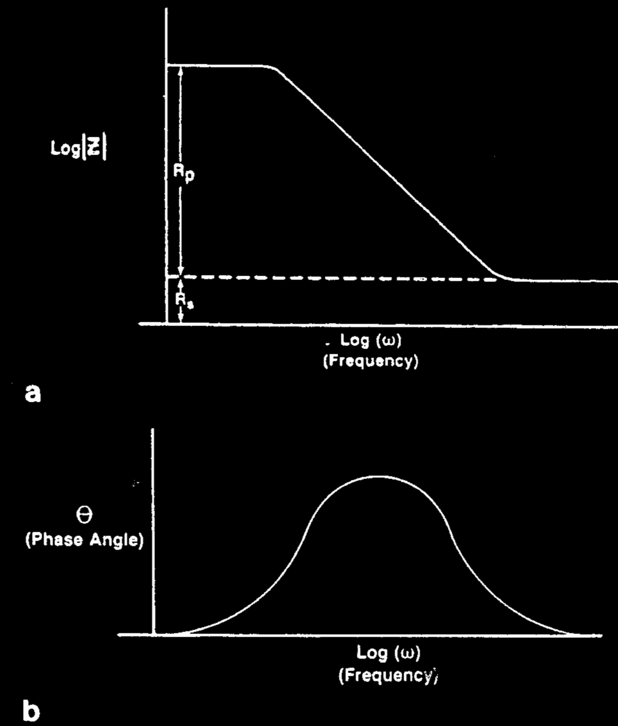

FIGURE 7 — (a) and (b): Bode type of plots of circuit in Figure 6.

Considerable attention has been paid to analyzing the circuit described by Equation (6).[1] By examining the impedance at appropriate frequency limits, accurate values of R_s, R_p, and C can be obtained. A full explanation of how Equation (6) can be used to understand the simple corrosion process shown in Figure 5 is given elsewhere.[1]

An alternative method of plotting the circuit in Figure 6 is by means of Bode plots. These plots, shown in Figures 7(a) and (b) are plots of impedance modulus, $|Z|$, versus frequency on log-log paper and the inverse of the phase angle shift versus frequency on semilogarithmic paper.

This method of plotting the data provides more information than that of Figure 5 because the frequency is explicit in Figures 7(a) and (b), but is implicit in Figure 5. Certain characteristics of these Bode plots can be used to obtain the circuit elements, R_s, R_p, and C. For example, R_s is the high frequency limiting value of Z. R_p is the difference between the low frequency limit and the high frequency limit. The double layer capacitance can be evaluated from the peak in the phase angle plot according to:

$$\omega^{\theta}max = \frac{1}{CR_p}\sqrt{1 + \frac{R_p}{R_s}} \quad (7)$$

where $\omega^{\theta}max = 2\pi f_{max}$. Further analysis can be made.[1] For a more complete discussion see Reference 1.

Unfortunately, a number of corrosion processes are not as simple as the case of one reaction dominating the process as represented by the circuit in Figure 6. These complications can arise from a number of sources.

Diffusion Control

The rate of a chemical reaction may be strongly in-

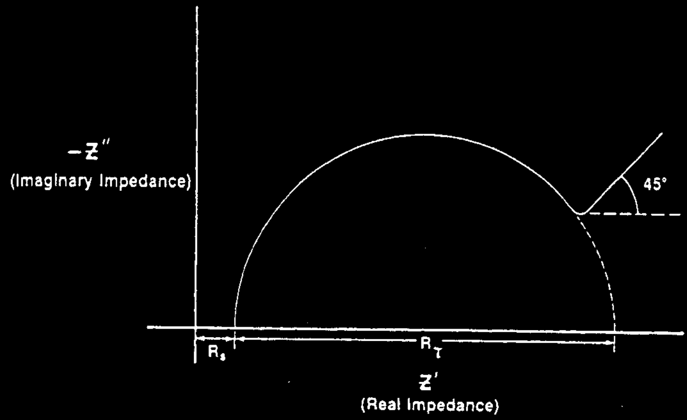

FIGURE 8 — Nyquist type of plot of simple charge transfer process in the presence of diffusion.

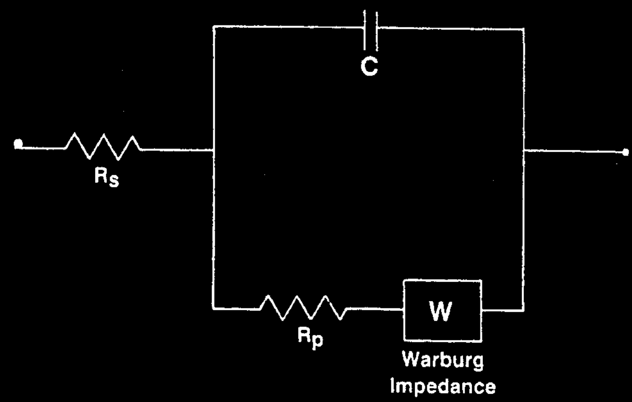

FIGURE 9 — Circuit that models impedance in Figure 8.

fluenced by the diffusion of one or more of the reactants or products to or from the surface. This situation can arise when diffusion through some type of surface film becomes the dominating process. This process may result in the surface being covered with reaction products or adsorbed solution components. An example of this type of corrosion process that has extreme practical importance is the corrosion of carbon steel in concentrated sulfuric acid. Such corrosion has been shown by Ellison and Schmeal to be controlled by the diffusion of $FeSO_4$ from a saturated film at the surface to the bulk fluid.[8]

The AC impedance response to a corrosion process dominated by diffusion control frequently has a unique characteristic known as the *Warburg impedance*. The Nyquist plot created by this phenomenon is shown in Figure 8. In the low frequency limit, the current is a constant 45 degrees out-of-phase with the potential excitation. The impedance response may ultimately deviate from this relationship and return to the real axis at very low frequencies.[9] The practical significance of this result is that if the diffusion control is in the fluid phase, the corrosion process might be sensitive to fluid flow.

The equivalent circuit is shown in Figure 9. The term W is the Warburg impedance. It creates the conditions so that the real and imaginary components of the impedance are equal at lower than a certain frequency. The value of Z for a diffusion controlled system varies inversely with the square root of the frequency. By appropriate manipulation of the data in Figure 8, the appropriate values of the circuit elements can be evaluated.[2,3] For example, for a reversible reaction under pure diffusion control, the Warburg impedance is given by:

$$Z_W = \frac{\sigma}{\sqrt{\omega}} - j\,\frac{\sigma}{\sqrt{\omega}} \qquad (8)$$

The Warburg coefficient, σ, can be used to calculate a diffusion coefficient. As indicated in Figure 8, the extrapolation of the high frequency semicircle back to the real axis yields R_T, a quantity that may be inversely proportional to the rate of the charge transfer corrosion process.

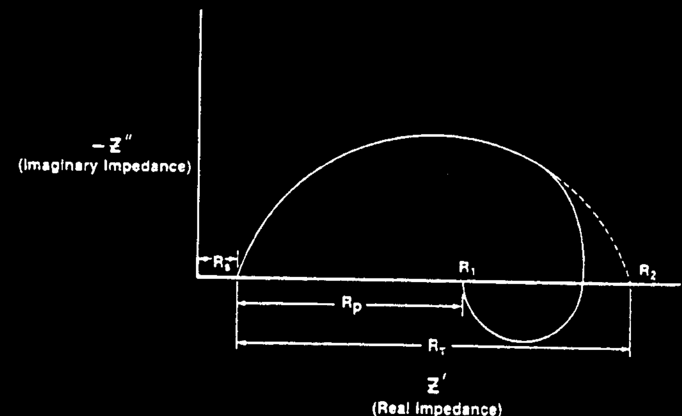

FIGURE 10 — Nyquist type of plot of simple charge transfer corrosion process in the presence of pseudo-inductance.

Inductance

The Nyquist plot will frequently have a low frequency portion that lies below the real axis. This behavior seems to arise from one of a number of sources,[3,10,11,12] for example, some types of adsorption processes. There is no uniform agreement as to the cause of inductive type of behavior. Indeed, this inductance may aptly be termed *pseudo-inductance* since the processes giving rise to inductance are probably not like those of a real inductor.[13] An example of an impedance response in the presence of inductance is shown in Figure 10.

The polarization resistance R_p is defined as R_1-R_S while the charge transfer resistance R_T is defined as R_2-R_S. There is controversy over which value is inversely proportional to the corrosion rate. Usually, R_1-R_S is used for corrosion rate calculations. Under some circumstances R_2-R_S seems to be more appropriate,[11] although this case may be unique.[10] In either case, evaluations of R_S, R_p, and R_T are important because either or both R_p and R_T may be related to the corrosion rate or corrosion process. Again, R_S is the solution resistance.

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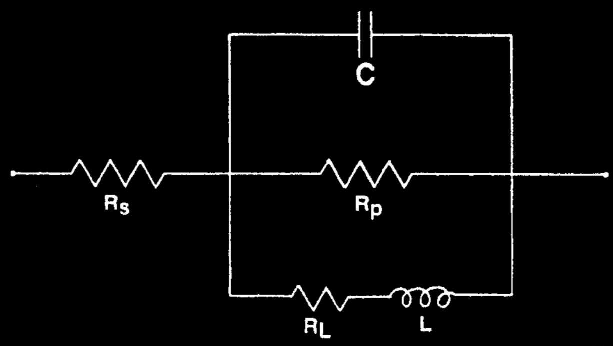

FIGURE 11 — Circuit that models impedance in Figure 10.

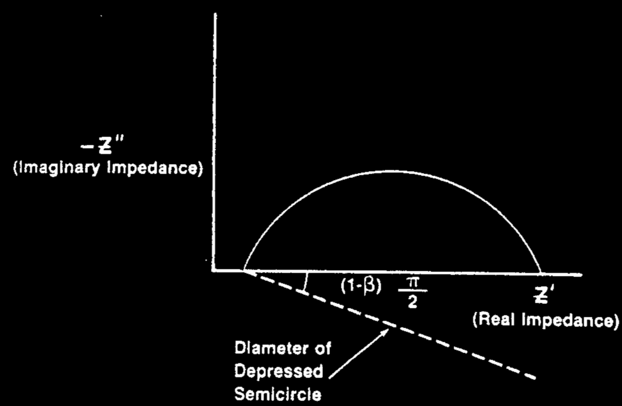

FIGURE 12 — Nyquist type of plot showing depression below the real axis.

proportional to the corrosion rate. Usually, R_1-R_S is used for corrosion rate calculations. Under some circumstances R_2-R_S seems to be more appropriate,[11] although this case may be unique.[10] In either case, evaluations of R_S, R_P, and R_τ are important because either or both R_P and R_τ may be related to the corrosion rate or corrosion process. Again, R_S is the solution resistance.

If there is one time constant, the circuit giving rise to the response in Figure 10 might be modeled as shown in Figure 11. Such a circuit may prove useful in the analysis of the response. This circuit can be solved as long as R_P can be estimated.[13] The accuracy of the values of R_P and R_L so calculated can be ascertained by comparing the calculated Nyquist and Bode plots with the measured Nyquist and Bode plots. Thus, the corrosion rate can be estimated in the presence of inductance.

Depression of Nyquist Semicircle

In real systems, the Nyquist type of semicircle for a simple corrosion process often exhibits some depression below the real axis; an example is shown in Figure 12. The cause of this behavior is believed to be a repartitioning of time constants around a central value.[3] Two explanations have been offered. The depression may be caused by increased surface roughness or by geometrical effects leading to a nonuniform repartitioning of the current density on the surface.[3] The practical significance of this depression of the semicircle is the fact that Figure 12 and not Figure 5 often represents the appearance of a real Nyquist plot of even a simple charge transfer process. Examples that can fit this characteristic include carbon steel in 1 M sulfuric acid and carbon steel in water.[14,15] Thus, the ability to extract the polarization resistance from this type of curve is important if the data are to be used for corrosion rate estimates. The circuit creating such depression is best described by:[14]

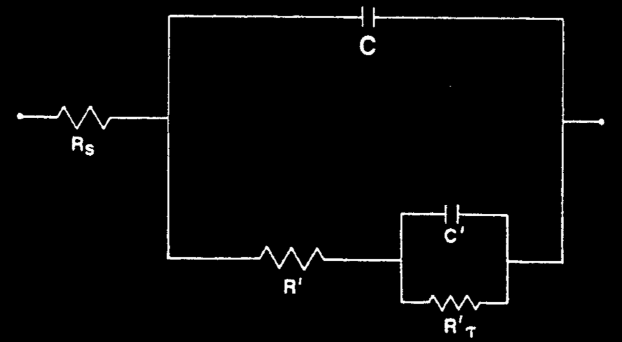

FIGURE 13 — Complex circuit that models a coated metal.

$$Z = R_S + \frac{R_P}{1 + (j\omega\tau)^\beta} \qquad (9)$$

In Equation (9), the phenomenological term $(j\omega\tau)^\beta$ replaces the term $j\omega R_P C$ for the case when $\beta < 1$. In Figure 5, $\beta = 1$. The value of R_P can still be estimated by curve-fitting the semicircle and by allowing both the radius and origin to vary.[14,15] Thus, corrosion rates can still be estimated even in the presence of such depression.

More Complex Phenomena

When a metal is coated with a porous nonconducting film, the equivalent circuit must simultaneously take account of the polarization resistance caused by the corrosion process (R_P) and the pore resistance (R'). The circuit can appear as shown in Figure 13.[16] In Figure 13, corrosion is assumed to occur only under the coating. The circuit can be analyzed mathematically to retrieve the values of the various circuit elements.[14] In fact, Figure 13 could also represent corrosion in a simulated pit or crevice.[14]

Sometimes, two or more time constants can arise for a corrosion process.[17] The causes can be a multistep reaction in which both steps have comparable rates, an adsorbed intermediate, and electrocrystallization, among others. These phenomena require more complex equivalent circuits. However, the procedure for analyzing these complex responses still requires the proposal of an equivalent circuit and then the examination of the predicted versus measured frequency response to verify the model. Even in these cases, the value of the polarization resistance(s) can be estimated from an appropriate model so that the corrosion rate and behavior can be understood and corrosion predictions can be made.

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Symbols

C = capacitance (farad $-cm^{-2}$)
E' = real component of voltage (volts)
E'' = imaginary component of voltage (volts
E = complex voltage (volts)
f = frequency (s^{-1})
I' = real component of current ($amp\text{-}cm^{-2}$)
I'' = imaginary component of current ($amp\text{-}cm^{-2}$)
I = complex current ($amp\text{-}cm^{-2}$)
j = $\sqrt{-1}$
L = inductance (henry)
R_S = solution resistance ($ohm\text{-}cm^2$)
R_p = polarization resistance ($ohm\text{-}cm^2$)
R_T = charge transfer resistance ($ohm\text{-}cm^2$)
Z' = real component of impedance ($ohm\text{-}cm^2$)
Z'' = imaginary component of impedance ($ohm\text{-}cm^2$)
Z = complex impedance
β, τ = phenomenological coefficients caused by depression of the Nyquist plot below the real axis
θ = phase angle (deg)
ω = frequency ($radians\text{-}s^{-1}$)

Subscripts

x = in-phase component
y = out-of-phase component

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