

Application Note AC-1

Subject: Basics of Electrochemical Impedance Spectroscopy

Introduction

Overview

When used to study electrochemical systems, electrochemical impedance spectroscopy (EIS) can give you accurate, error-free kinetic and mechanistic information using a variety of techniques and output formats. For this reason, EIS is becoming a powerful tool in the study of corrosion, semiconductors, batteries, electroplating, and electro-organic synthesis.

Table I summarizes some of the electrochemical phenomena that have been studied using EIS. In these areas, EIS offers three advantages over dc techniques:

Small Amplitude: EIS techniques use very small excitation amplitudes, often in the range of 5 to 10 mV peak-to-peak. Excitation waveforms of this amplitude cause only minimal perturbation of the electrochemical test system, reducing errors caused by the measurement technique.

Mechanism Study: Because electrochemical impedance experiments provide data on both electrode capacitance and charge-transfer kinetics, EIS techniques can provide valuable mechanistic information.

Measurement Accuracy: Because the method does not involve a potential scan, you can make measurements in low conductivity solutions where dc techniques are subject to serious potential-control errors. In fact, you can use EIS to determine the uncompensated resistance of an electrochemical cell.

Theoretical Advantages

The main advantage of EIS is that you can use a purely electronic model to represent an electrochemical cell. An electrode interface undergoing an electrochemical reaction is typically analogous to an electronic circuit consisting of a specific combination of resistors and capacitors. You can take advantage of this analogy by using established ac circuit theory to characterize the electrochemical system in terms of its equivalent circuit.

In practice, you can correlate an impedance plot obtained for a given electrochemical system with one or more equivalent circuits. You can use this information to verify a mechanistic model for the system, or at least to rule out incorrect models. Once you choose a particular model, you can correlate physical or chemical properties with circuit elements and extract numerical values by fitting the data to the circuit model.

About This Note

Because EIS generates detailed information, sophisticated approaches are required to interpret the data and extract meaningful results. The recent increase in literature demonstrates that a better understanding of impedance theory and data interpretation has followed the advances in instrumentation. Two of the better longer works are Digby D. Macdonald's 'Transient Techniques in Electrochemistry' and J. Ross Macdonald's 'Impedance Spectroscopy.'^{37,38}

In this note, we will review basic EIS theory and describe the commonly used plot formats. We will also introduce some of the simpler methods of data interpretation. This should give you a good starting point for further study.

Research Area	Application
Corrosion (See references 1-15)	<ul style="list-style-type: none"> ◆ Rate Determinations ◆ Inhibitor and Coatings ◆ Passive Layer Investigations
Coatings Evaluation (See references 16-21)	<ul style="list-style-type: none"> ◆ Dielectric Measurements ◆ Corrosion Protection
Batteries (See references 22-28)	<ul style="list-style-type: none"> ◆ State-of-charge ◆ Materials Selection ◆ Electrode Design
Electrodeposition (See references 29-32)	<ul style="list-style-type: none"> ◆ Bath Formulation ◆ Surface Pretreatment ◆ Deposition Mechanism ◆ Deposit Characterization
Electro-Organic Synthesis (see reference 33)	<ul style="list-style-type: none"> ◆ Adsorption/Desorption ◆ Reaction Mechanism
Semiconductors (See references 34-36)	<ul style="list-style-type: none"> ◆ Photovoltaic work ◆ Dopant Distributions

Table 1: Applications Amenable to Impedance Studies

Theory

Overview

Electrochemical impedance theory is a well-developed branch of ac theory that describes the response of a circuit to an alternating current or voltage as a function of frequency. The mathematics of the theory is beyond the scope of this discussion, but we will present the basic theory here.

In dc theory (a special case of ac theory where the frequency equals 0 Hz) resistance is defined by Ohm's Law:

$$E = I R \quad (1)$$

Using Ohm's law, you can apply a dc *potential* (E) to a circuit, measure the resulting current (I), and compute the *resistance* (R) - or determine any term of the equation if the other two are known. Potential values are measured in *volts* (V), current in *amperes or amps* (A), and resistance in *ohms* (Ω). A *resistor* is the only element that impedes the flow of electrons in a dc circuit.

In ac theory, where the frequency is non-zero, the analogous equation is:

$$E = I Z \quad (2)$$

As in Equation 1, E and I are here defined as *potential* and *current*, respectively. Z is defined as impedance, the ac equivalent of resistance. Impedance values are also measured in *ohms* (Ω). In addition to resistors, *capacitors and inductors* impede the flow of electrons in ac circuits.

In an electrochemical cell, slow electrode kinetics, slow preceding chemical reactions, and diffusion can all impede electron flow, and can be considered analogous to the resistors, capacitors, and inductors that impede the flow of electrons in an ac circuit.

Figure 1 shows a typical plot of a voltage sine wave (E) applied across a given circuit and the resultant ac current waveform (I). Note that the two traces are different not only in amplitude, but are also shifted in time.

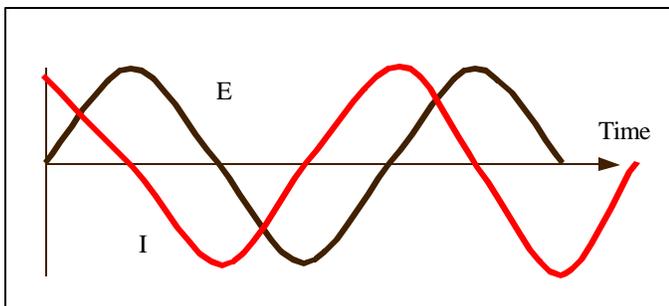


Figure 1: AC Waveforms for an Applied Potential and a Resulting Current.

What is Impedance?

The terms resistance and impedance both denote an opposition to the flow of electrons or current. In direct current (dc) circuits, only resistors produce this effect. However, in alternating current (ac) circuits, two other circuit elements, capacitors and inductors, impede the flow of electrons. Impedance can be expressed as a complex number, where the resistance is the real component and the combined capacitance and inductance is the imaginary component.

The total impedance in a circuit is the combined opposition of all its resistors, capacitors, and inductors to the flow of electrons. The opposition of capacitors and inductors is given the same name reactance, symbolized by X and measured in ohms (Ω). Since the symbol for capacitance is C , capacitive reactance is symbolized by X_C . Similarly, since the symbol for inductance is L , inductive reactance is symbolized by X_L .

Capacitors and inductors affect not only the magnitude of an alternating current but also its time-dependent characteristics - or phase. When most of the opposition to current flow comes from its capacitive reactance, a circuit is said to be largely capacitive and the current leads the applied voltage in phase angle. When most of the opposition to current flow comes from its inductive reactance, a circuit is said to be largely inductive and the current lags the applied voltage in phase angle. The more inductive a circuit is, the closer the difference in phase angle approaches 90 degrees.

It's sometimes easier to perform calculations using admittance, the reciprocal of impedance. Admittance is symbolized by Y and measured in siemens (S). Like impedance, admittance can be expressed as a complex number, where the conductance, the reciprocal of resistance, is the real component, and the susceptance, the reciprocal of reactance, is the imaginary component.

with respect to each other - that is, they are out of phase. In the case of a purely resistive network, the two waveforms would not be shifted. They would be exactly in phase, differing only in amplitude.

The current sine wave can be described by the equation:

$$I(t) = A \sin(\omega t + \phi) \quad (3)$$

where

$I(t)$ = instantaneous current

A = maximum amplitude

ω = frequency in radians per second = $2\pi f$

(where f = frequency in Hertz)

t = time

ϕ = phase shift in radians

Vector Analysis

Vector analysis provides a convenient method of characterizing an ac waveform. It lets you describe the wave in terms of its amplitude and phase characteristics.

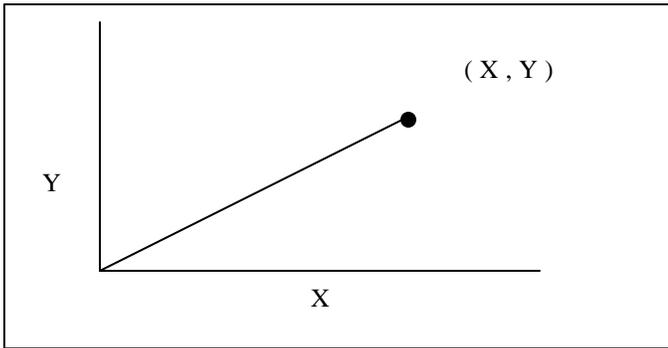


Figure 2: Vector in Terms of X and Y Coordinates

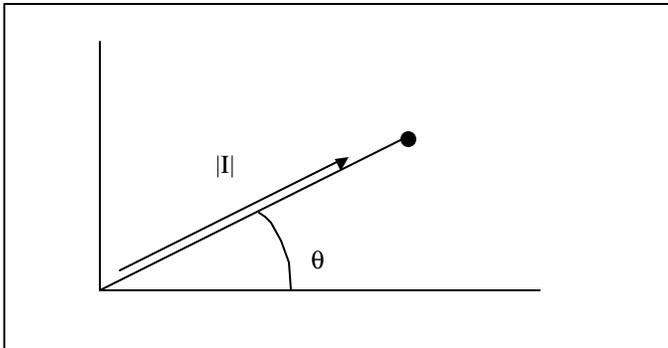


Figure 3: Vector in terms of Angle (θ) and Magnitude ($|I|$)

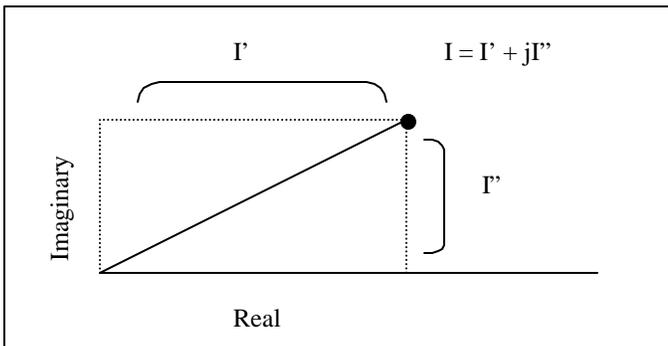


Figure 4: Vector in Terms of Real (I') and Imaginary (I'') Coordinates

For example, Figures 2, 3, and 4 show vector analyses for the resultant current waveform of Figure 1. The current waveform vector can be graphically described in a variety of ways.

Figure 2 shows how the end point of the vector can be described in terms of an (x, y) coordinate pair formed from the in-phase (x) and out-of-phase (y) components. In Figure 3, the vector is unambiguously defined by phase angle (θ) and current magnitude ($|I|$).

Figure 4 shows a third approach, often more convenient for numerical analysis. The axes are defined as real (I') and imaginary (I''). The real and imaginary components can be handled as a single number in complicated equations if the complex number notation is used. The

mathematical convention for expressing quantities in this coordinate system is to multiply the I' , or imaginary, coordinate value by $v\text{-T}$.

Using this complex number convention, an ac current vector can be defined as the sum of its real and imaginary components:

$$I_{\text{Total}} = I' + I'' j \quad (4)$$

where

$$j = \sqrt{-1}$$

Note: Although mathematicians use i to stand for $\sqrt{-1}$, electrochemists use j , to avoid confusion with i , the symbol for current.

Note that the location of the point in Figures 2, 3, and 4 has not changed - only the labels on the axes are different. The three different ways of expressing the position of the point - (x, y) pair, phase angle/magnitude, and real/imaginary coordinates, are really all the same.

The real and imaginary components of an ac current or voltage waveform are defined with respect to some reference waveform. The real component is in phase with the reference waveform, and the imaginary component, (or *quadrature component*) is exactly 90 degrees out of phase. The reference waveform allows us to express the current and voltage waveforms as vectors with respect to the same coordinate axes. This facilitates mathematical manipulation of these vector quantities.

Specifically, this allows us to use Equation 2 to calculate the impedance vector as the quotient of the voltage and current vectors:

$$Z_{\text{Total}} = \frac{E' + E'' j}{I' + I'' j} \quad (5)$$

where the ac voltage vector, E , can also be expressed as a complex number.

$$E_{\text{Total}} = E' + E'' j \quad (6)$$

The resulting vector expression for the ac impedance,

$$Z_{\text{Total}} = Z' + Z'' j \quad (7)$$

is defined in terms of the same coordinate axes as the current and voltage vectors.

By analogy with Figures 3 and 4, the absolute magnitude of the impedance (that is, the length of the vector) can be expressed as

$$|Z| = \sqrt{Z'^2 + Z''^2} \quad (8)$$

and the phase angle can be defined by:

$$\tan \theta = Z'' / Z' \quad (9)$$

Equivalent Circuit Elements

Given this basic theory, we can now look at impedance expressions for some simple electrical circuits. Table 2 shows that the impedance of a resistor has no imaginary component at all. The phase shift is zero degrees - that is, the current is in phase with the voltage. Both current and impedance are independent of the frequency.

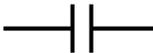
Conversely, the impedance of a capacitor has no real component. Its imaginary component is a function of both capacitance and frequency. The current through a capacitor is always 90 degrees out of phase with the voltage across it, with current leading the voltage. Because the impedance of a capacitor varies inversely with frequency, at high frequencies a capacitor acts as a short circuit - its impedance tends toward zero. At low frequencies (approaching dc) a capacitor acts as an open circuit, and the impedance tends toward infinite.

The third simple electrical component is the inductor. Like a capacitor, the current through an inductor is always 90 degrees out of phase with the voltage drop across it. However, the phase shift is in the opposite direction - the current lags behind the voltage. Also, as the frequency increases, the impedance of an inductor increases. It acts as a short circuit at low frequencies and as a large impedance at high frequencies.

To determine the total impedance of a combination of simple elements, you combine the impedance values of the individual components according to some simple rules. For two circuit elements in series, the combined impedance is simply the vector sum of the individual impedance values.

$$Z_S = Z_1 + Z_2 \quad (10)$$

In complex number representation, the real parts must be added together to form the real component of the

Circuit Element	Impedance Equation
	$Z = R + 0j$ $j = \sqrt{-1}$
	$Z = 0 - j / \omega C$ $\omega = 2\pi f$
	$Z = 0 + j \omega L$ $\omega = 2\pi f$
	$Z = \frac{R}{1 + \omega^2 C^2 R^2} - \frac{j\omega CR^2}{1 + \omega^2 C^2 R^2}$

Polarization Resistance versus Charge Transfer Resistance

You can define resistance as the slope of the steady-state potential vs. current plot. As such, it is the low frequency (dc) limit for the real part of the impedance. You can determine the polarization resistance by extrapolating the Nyquist plot to the real (x) axis as the frequency approaches 0 Hz (dc).

On the other hand, the first intersection of the Nyquist plot with the real axis indicates charge transfer resistance. In the simple cases, the polarization resistance and the charge transfer resistances are identical. However, for more complicated cases they may not be equal (see Figure 8).

For both types of resistance, you must subtract the solution resistance to get an accurate value.

series combination and the imaginary parts must be added to form the imaginary component of the combination.

$$Z_S' + j Z_S'' = (Z_1' + Z_2') + j (Z_1'' + Z_2'') \quad (11)$$

For example, if you have a resistor and capacitor in series, the impedance expression will be the sum of the impedance of the resistor (which has only a real part - the imaginary part is identically zero) and the impedance of the capacitor (which has only an imaginary part - the real part is zero). This is shown in Table 2.

For the more complex parallel resistor/capacitor network, the impedance expression becomes more complicated. For circuit elements in parallel, the admittance values (admittance being the inverse of impedance) must be added together. Thus, for two impedance values in parallel,

$$\frac{1}{Z_p} = \frac{1}{Z_1} + \frac{1}{Z_2} \quad (12)$$

You can build more complicated equivalent circuits from a series or parallel combination of simpler sub-circuits.

Plot Analysis

You can study an equivalent circuit by deriving its impedance equation. However, it's simpler to perform a measurement on the circuit and analyze the resulting plot. You'll get a good picture of the real and imaginary impedance components and of the phase shift characteristics as a function of frequency.

The Randles cell (see Figure 5) models the electrochemical impedance of an interface and fits many chemical systems. You can easily equate the circuit components in the Randles cell with familiar physical phenomena, such as adsorption or film formation.

$R\Omega$ is the ohmic or uncompensated resistance of the solution between the working and reference electrodes.

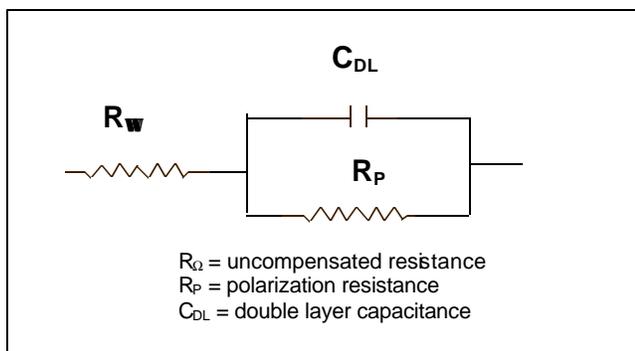


Figure 5: Equivalent Circuit for a Single Electrochemical Cell

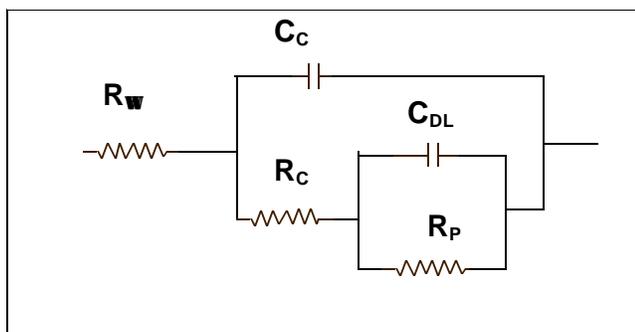


Figure 6: Equivalent Circuit for a Metal Coated with a Porous, Non-conductive Film

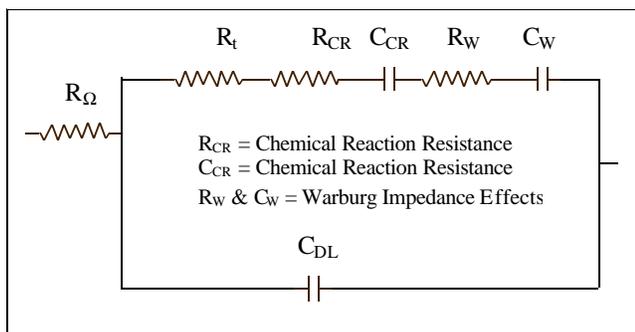


Figure 7: Equivalent Circuit for an Electrochemical Reaction Coupled to a Chemical Reaction

R_p is the polarization resistance or charge-transfer resistance at the electrode/solution interface. C_{DL} is the double layer capacitance at this interface.

If you know the polarization or charge-transfer resistance, you can calculate the electrochemical reaction rates. Double-layer capacitance measurements can provide information on adsorption and desorption phenomena. In some systems, a C_{DL} measurement may not represent the double layer capacitance. Rather, it may indicate the degree of film formation or the integrity of an organic coating.³⁹

The impedance of a capacitor diminishes as the frequency increases (see Table 2), while the impedance of a resistor is constant. Thus, above a certain frequency, the impedance of the capacitor, C_{DL} , becomes

much smaller than the impedance of the resistor, R_p . Since C_{DL} is in parallel with R_p , the capacitor acts as a short and effectively removes the resistor from the circuit. At the highest frequencies, the impedance of the capacitor will also become much smaller than $R_Ω$. Thus, the high frequency behavior of the Randles cell is controlled almost entirely by $R_Ω$.

However, at the lowest frequencies, the capacitor acts as an open circuit and is effectively removed from the circuit. The impedance of the Randles cell is then the combined resistance values of the two series resistors $R_Ω$ and R_p .

Thus, at both the high and the low frequency limits, the Randles cell behaves primarily as a resistor. The imaginary component is very small, the phase angle is close to 0 degrees, and the impedance does not change with frequency. At intermediate frequencies, the capacitor's impedance begins to have an effect and the cell becomes more capacitive. The imaginary component becomes significant, the phase angle can start to approach 90 degrees, and the cell impedance becomes frequency dependent.

Figure 6 shows an equivalent circuit proposed for a corroding metal coated with a porous, non-conductive film.⁴⁰ The additional circuit elements are the coating capacitance (C_c) and the pore resistance (R_{po}).

The circuit in Figure 7 represents an electrochemical reaction coupled to a chemical reaction. Here, R_{CR} and C_{CR} represent the resistive and capacitive effects of the chemical reaction. The boxed sub-circuit is a simplified illustration of the effects of diffusion. The enclosed resistor and capacitor, R_w and C_w , provide a rough approximation of the Warburg impedance, a value used to account for mass transfer limitations due to diffusion processes adjacent to the electrode.

To determine which equivalent circuit best describes the behavior of an electrochemical system, you must measure the impedance over a range of frequencies. The standard technique is to apply an ac voltage or current over a wide range of frequencies and measure the current or voltage response of the electrochemical system. You can then calculate the system's impedance by analyzing the response signal at each frequency.

To completely describe the behavior of an electrochemical system, you must know the values of both the in-phase and out-of-phase impedance components at a number of frequencies across the range of interest. You can calculate these values by applying Equation 5 to the real and imaginary components of the excitation and response waveforms. You can characterize most electrochemical systems quite well by gathering impedance data in the 0.001 Hz to 1×10^4 Hz frequency range.

Impedance Plots

Overview

Once an experiment is complete, the raw data at each measured frequency consists of these components:

- The real component of voltage (E')
- The imaginary component of voltage (E'')
- The real component of current (I')
- The imaginary component of current (I'')

From this raw data you can compute the phase shift (θ) and the total impedance (Z) for each applied frequency, as well as many other impedance functions.

You can use a variety of formats to plot this data. Each format offers specific advantages for revealing certain characteristics of a given chemical system. You can discover the true behavior of a real chemical system only by looking at all of the available plotting formats.

The Nyquist Plot

Figure 8 shows one popular format for evaluating electrochemical impedance data, the Nyquist plot. This format is also known as a Cole-Cole plot or a complex impedance plane plot. In our study, we plotted the imaginary impedance component (Z'') against the real impedance component (Z') at each excitation frequency. The plot in Figure 8 illustrates the expected response of the simple circuit in Figure 5.

We saw that at high frequencies, the impedance of the Randles cell was almost entirely created by the ohmic resistance, R_{Ω} . The frequency reaches its high limit at the leftmost end of the semicircle, where the semicircle

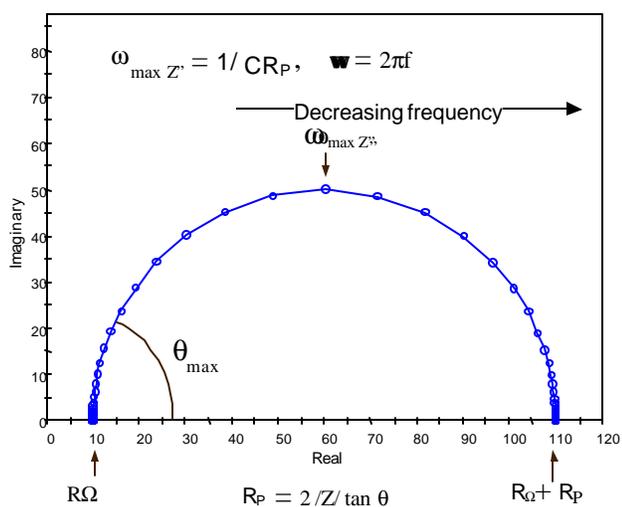


Figure 8: Nyquist Plot for a Simple Electrochemical System

touches the x axis. At the low frequency limit, the Randles cell also approximates a pure resistance, but now the value is $(R_{\Omega} + R_p)$. The frequency reaches its low limit at the rightmost end of the semicircle.

The Nyquist plot has several advantages. The primary one is that the plot format makes it easy to see the effects of the ohmic resistance. If you take data at sufficiently high frequencies, it is easy to extrapolate the semicircle toward the left, down to the x axis to read the ohmic resistance. The shape of the curve (often a semicircle) does not change when the ohmic resistance changes. Consequently, it is possible to compare the results of two separate experiments that differ only in the position of the reference electrode! Another advantage of this plot format is that it emphasizes circuit components that are in series, such as R_{Ω} .

The Nyquist plot format also has some disadvantages. For example, frequency does not appear explicitly. Secondly, although the ohmic resistance and polarization resistance can be easily read directly from the Nyquist plot, the electrode capacitance can be calculated only after the frequency information is known. As shown in Figure 8, the frequency corresponding to the top of the semicircle, $\omega(\theta = \text{MAX})$, can be used to calculate the capacitance if R_p is known.

Although the Nyquist format emphasizes series circuit elements, if high and low impedance networks are in series, you will probably not see the low impedance circuit, since the larger impedance controls plot scaling. Figure 8 illustrates this point.

The Bode Plot

Figure 9 shows a Bode Plot for the same data pictured in the Nyquist plot in Figure 8. The Bode plot format lets you examine the absolute impedance, $|Z|$, as calculated by Equation 8, and the phase shift, θ of the impedance, each as a function of frequency.

The Bode plot has some distinct advantages over the Nyquist plot. Since frequency appears as one of the axes, it's easy to understand from the plot how the impedance depends on the frequency. The plot uses the logarithm of frequency to allow a very wide frequency range to be plotted on one graph, but with each decade given equal weight. The Bode plot also shows the magnitude ($|Z|$) on a log axis so that you can easily plot wide impedance ranges on the same set of axes. This can be an advantage when the impedance depends strongly on the frequency, as is the case with a capacitor.

The $\log |Z|$ vs. $\log \omega$ curve can yield values of R_p and R_{Ω} . At the highest frequencies shown in Figure 9, the ohmic resistance dominates the impedance and $\log(R_{\Omega})$ can be read from the high frequency horizontal plateau. At the

lowest frequencies, polarization resistance also contributes, and $\log(R_{\Omega} + R_p)$ can be read from the low frequency horizontal plateau. At intermediate frequencies, this curve should be a straight line with a slope of -1. Extrapolating this line to the $\log |Z|$ axis at $\omega = 1$ ($\log \omega = 0$, $f = 0.16$ Hz) yields the value of C_{DL} from the relationship:

$$|Z| = 1/C_{DL} \quad (10)$$

where $\omega = 2\pi f$

The Bode plot format also shows the phase angle, q . At the high and low frequency limits, where the behavior of the Randles cell is resistor-like, the phase angle is nearly zero. At intermediate frequencies, q increases as the imaginary component of the impedance increases.

The q vs. $\log \omega$ plot yields a peak at $\omega_{(q=MAX)}$, the frequency, in radians, at which the phase shift of the response is maximum. The double-layer capacitance, C_{DL} , can be calculated from Equation 11.

$$\omega_{(\theta=MAX)} = \sqrt{(1 / C_{DL} R_p) (1 + R_p/R_{\Omega})} \quad (11)$$

Note that both R_p and R_{Ω} appear in this equation! It is important to remember that this frequency will not be the same as the frequency at which the Nyquist plot reaches its maximum.

The Bode plot is a useful alternative to the Nyquist plot. It lets you avoid the longer measurement times associated with low frequency R_p determinations. Furthermore, the $\log |Z|$ vs. $\log \omega$ plot sometimes allows a more effective extrapolation of data from higher frequencies.

The Bode format is also desirable when data scatter prevents adequate fitting of the Nyquist semicircle. In

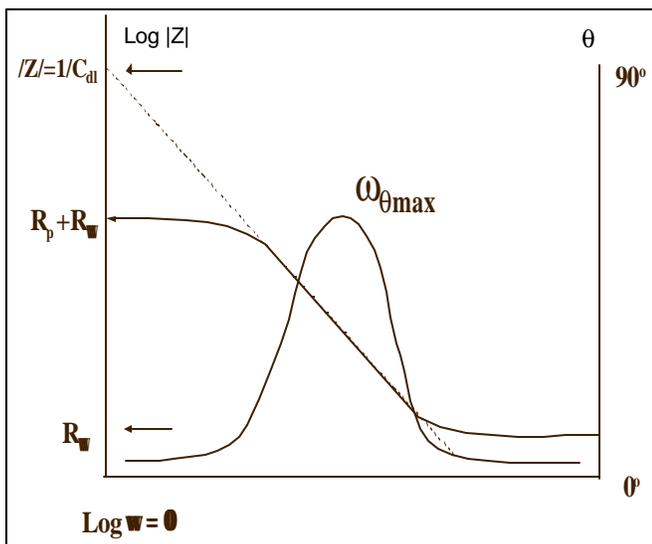


Figure 9: Bode Plot for a Simple Electrochemical System

Evaluating Capacitance from a Bode Plot

At intermediate frequencies, the impedance of the capacitor C , can control the total impedance of the Randles cell. The capacitor becomes the controlling component whenever R_{ω} and R_p differ by more than a factor of 100 or so. Under these conditions:

$$Z_C = -j / \omega C$$

And

$$\begin{aligned} \log |Z| &= \log (1/ \omega C) \\ &= -\log (\omega C) \\ &= -\log (\omega) - \log (C) \\ &= -\log (2\pi f) - \log (C) \\ &= -\log (2\pi) - \log (f) - \log (C) \end{aligned}$$

Note that the Bode plot of $\log |Z|$ vs $\log (f)$ or $\log (\omega)$ has a slope of -1 in this region.

At this point $f = 0.16$ Hz, $\omega = 2\pi f = 1$ and $\log (2\pi f) = 0$

Therefore:

$$\text{Log} (|Z|) = -\log (C) \quad (\text{when } f = 0.16 \text{ Hz})$$

or

$$|Z_{(f=0.16 \text{ Hz})}| = 1/C$$

general, the Bode plot provides a clearer description of the electrochemical system's frequency-dependent behavior than does the Nyquist plot, in which frequency values are implicit rather than explicit.

On some electrochemical processes, there is more than one rate-determining step. Each step represents a system impedance component and contributes to the overall reaction rate constant. The electrochemical impedance experiment can often distinguish among these steps and provide information on their respective rates or relaxation times.

Figure 10 is typical of multiple time-constant Nyquist plots. While close inspection reveals two semicircles, one of the semi-circles is much smaller than the other, making it difficult to recognize multiple time constants.

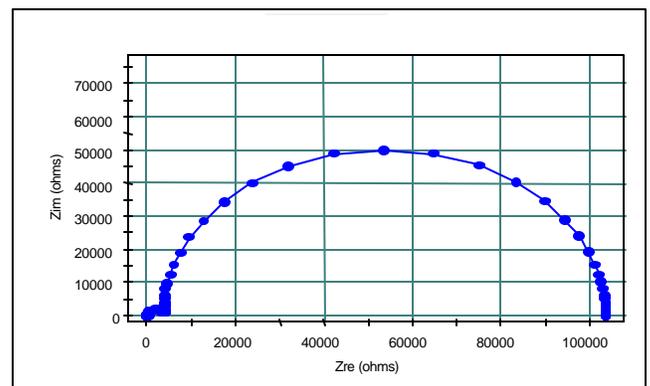


Figure 10: Nyquist Plot for a Two Time Constant Cell

Figures 11 and 12 show Bode plots for the same data shown in Figure 10. The Bode plot format lets you easily identify the frequency break points associated with each limiting step.

The Bode plot also has some disadvantages. The great est one is that the shape of the curves can change if the circuit values change. Figures 13 and 14 show Bode plots for several similar circuits. The only differences are the values of the uncompensated resistance. Note that the location ($\theta = \text{MAX}$) and height of the phase maximum depend on the value of R_{Ω} . Also note that the slope of the central portion of the log $|Z|$ plot is

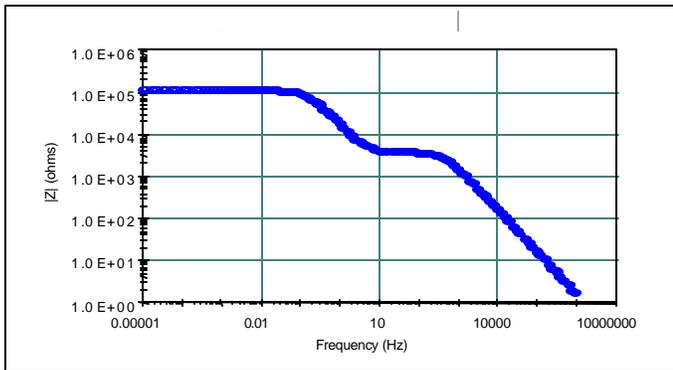


Figure 11: Bode Plot for a Two Time Constant Cell (Impedance vs. Frequency)

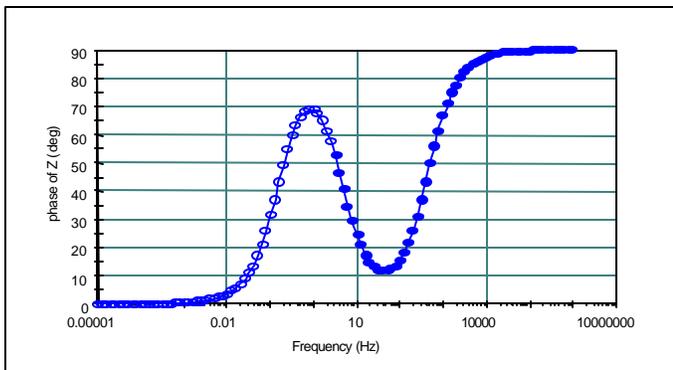


Figure 12: Bode Plot for a Two Time Constant Cell (Phase Angel vs. Frequency)

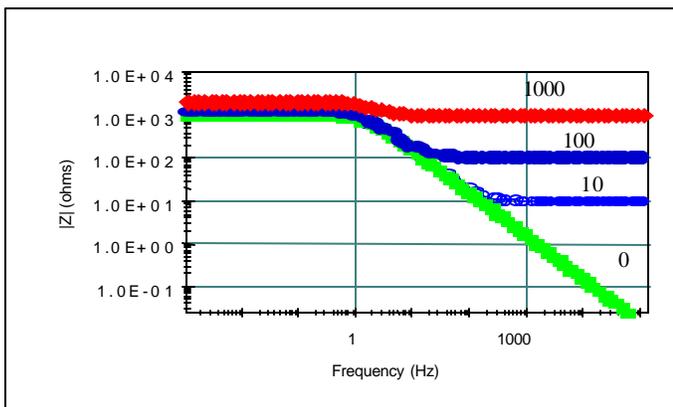


Figure 13: Bode Plots for Selected Values of R_{Ω} (Impedance vs. Frequency)

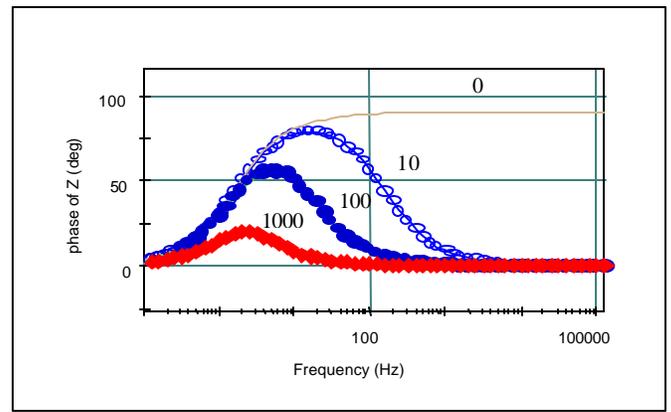


Figure 14: Bode Plots for Selected Values of R_{Ω} (Phase Angle vs. Frequency)

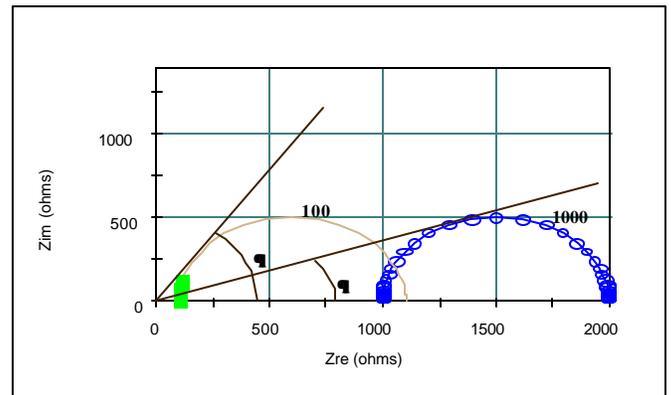


Figure 15: Nyquist Plots for Different Values of R_{Ω}

Influenced by the value of R_{Ω} as well. The R_{Ω} value can have an effect on the capacitance values calculated from Equation 1. The corresponding Nyquist plots all have the same semicircle shape (see Figure 15).

The Randles Plot

The Randles plot is useful in determining whether Warburg impedance is a significant component of the equivalent circuit model. Identifying the presence of Warburg impedance can help you describe a reaction mechanism. A slope of $-1/2$ or $-1/4$ in the linear portion of the Bode plot can also indicate diffusion control.

Figure 16 shows an idealized Randles plot of Z' vs. \sqrt{w} for a diffusion-controlled system. In this case Z' and Z'' are equal and are linear functions in \sqrt{w} .

For a completely reversible system under pure diffusion control, the mass transfer (Warburg) impedance, Z_w , is given by:

$$Z_w = \frac{s\sqrt{2}}{\sqrt{w}} \quad (12)$$

where s is the Warburg coefficient, from which the diffusion coefficient may be calculated.

Warburg Impedance

The rate of an electrochemical reaction can be strongly influenced by diffusion of a reactance towards or a product away from the electrode surface. This is often the case when a solution species must diffuse through a film on the electrode surface. This situation can exist when the electrode is covered with reaction products, adsorbed solution components, or a prepared coating. Whenever diffusion effects completely dominate the electrochemical reaction mechanism, the impedance is called the *Warburg Impedance*.

For diffusion-controlled electrochemical reaction, the current is 45 degrees out of phase with the imposed potential.⁴¹ With this phase relationship, the real and imaginary components of the impedance vector are equal at all frequencies. In terms of simple equivalent circuits, the behavior of Warburg impedance (a 45 degree phase shift) is midway between that of a resistor (a 0 degree phase shift) and a capacitor (90 degree phase shift). There is no simple electrical equivalent for the Warburg impedance.

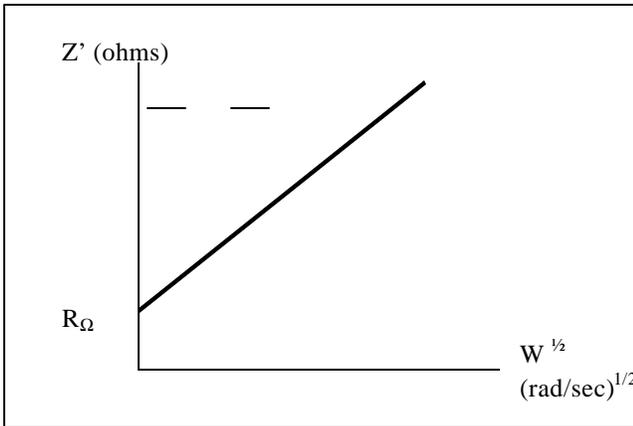


Figure 16: Idealized Randles Plot of Z' vs. ω

Thus the linearity of the Randles plot can be used as a test of diffusion control, and in certain cases the Warburg diffusion coefficient can also be calculated from the slope.

Other Plot Formats

Other plot formats optimize data interpretation for specific experimental systems. Figure 17 shows how R_a , R_p and $C_E L$ are derived from a plot of Z' vs. $\omega Z''$. For the Randles cell, this plot has the advantage of being a simple straight line. Moreover, once you know the R_p value, you can easily calculate the capacitance. This format provides a more reasonable fit of scattered data than the Nyquist plot.

You can sometimes get clearer picture of the system's behavior from a plot of Y'/ω vs Y'/ω , also known as a capacitance plot (see Figure 18). The admittance, Y , is simply the inverse of impedance.

$$Y = \frac{I}{E} = \frac{1}{Z} \quad (13)$$

It's easy to see from Equation 13 that the admittance of two circuit elements in parallel is simply the sum of the individual admittances. For this reason, plots involving admittance often emphasize circuit elements in parallel.

The impedance data shown in Figure 15 can easily be converted to the format shown in Figure 18, which permits a convenient determination of system capacitance as Y''/ω .

For a pure capacitor, $Y_c = j\omega C$, or $Y_c/\omega = jC$. Therefore, on this plot a capacitor will have only an imaginary component, and (Y_c/ω) will be independent of frequency. On the capacitance plot, a capacitor will be represented by simply a dot on the y axis.

For a resistor, $Y_R = (1/R)$ and $Y_R/\omega = (1/R)/\omega$. In contrast to the capacitor, the resistor will have only a real component, but its value will depend on the frequency. A resistor will appear as a horizontal straight line on the capacitance plot of Figure 18.

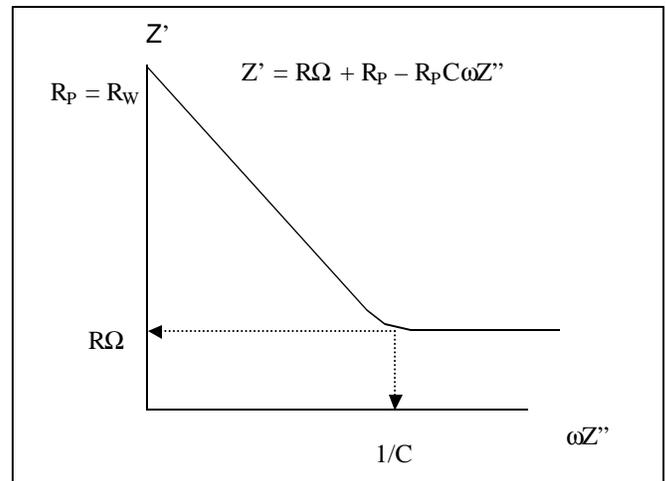


Figure 17: A Plot of Z' vs. $\omega Z''$

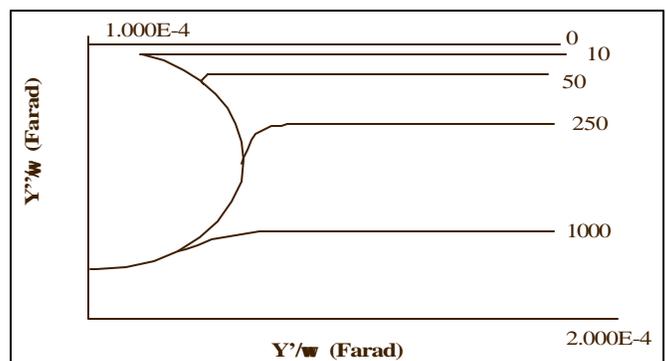


Figure 18: A Capacitance Plot

When a resistor and capacitor are in parallel, the capacitance plot is simply the sum of the impedance for the resistor and the capacitor. This will give the horizontal line shown in Figure 18. The semicircle shape is a result of the interaction of the ohmic resistance and the capacitance. The value of the capacitance can be read from the extrapolation of the semicircle to the y-axis. Under some conditions it may also be read from the Y'/w value on the horizontal line section of the plot. This is only possible if the point formed by the line and semicircle is a sharp one, as illustrated in Figure 18.

Data Interpretation

Although the simple equivalent-circuit experiments generate relatively straightforward results, typical electrochemical analyses yield more complicated plots. These complexities arise because the simple equivalent circuits do not fully describe the physical phenomena of an electrochemical system. Yet simple equivalent circuit models are frequently good approximations of real systems, and data can often be fitted to yield results of reasonable accuracy.

Several computer programs have been written to fit experimental data to a simple equivalent circuit model. Because of the complexity of this problem, all of these programs require some initial guesses for the circuit parameters.

Figure 19 shows a Nyquist plot for an iron specimen in deaerated 1N H_2SO_4 . Note that the plot is not a perfect semicircle, having an additional loop at low frequencies.

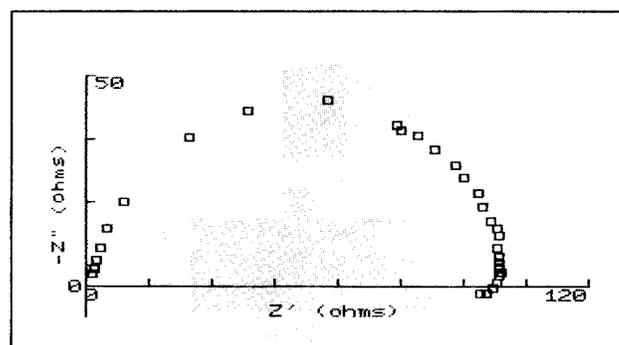


Figure 19: Nyquist Plot of Iron in Deaerated 0.1 N H_2SO_4 after 4 Hour Immersion.

This distortion has been attributed to the inductive behavior of the electrochemical system.^{42,43}

Several analytical treatments for such a plot have been proposed. Most investigators believe that it is incorrect to interpret either of the actual low frequency Z' axis intercepts as the sum of P_Ω and R_p . Instead, they use various curve-fitting techniques to obtain these values.

The Nyquist plot in Figure 19 reveals another complexity. In this plot, the center of the circle does not lie on the x-axis, but below it. To explain this depressed semicircle phenomenon, some researchers use models that assume that the surface of the electrode is not homogeneous.⁴⁴ Using this model, you can characterize different areas of the surface with different time constants. In this case, the total impedance of the surface would be the parallel combination of these areas, You can use several RC sub-circuits in parallel to model the impedance.

Appendix: Deriving the Randles Cell Impedance

You can derive the complete impedance equation for the simple Randles cell. However, since a Randles cell contains resistors and capacitors in parallel, it's easier to express the impedance values in terms of admittance, the reciprocal of impedance. Although the symbol for admittance is Y , we'll use $1/Z$ in this discussion.

The Randles cell is defined as a parallel combination of capacitance and polarization or charge transfer resistance. To calculate the total admittance of the cell, you must first add the individual admittance values of the parallel resistors and capacitors:

$$\frac{1}{Z} = \frac{1}{Z_R} + \frac{1}{Z_C}$$

Polarization Resistance

The impedance expression for polarization or charge transfer resistance (either or both symbolized here by R_p) is simple:

$$Z_R = (R_p + 0j) = R_p$$

The admittance expression is:

$$\frac{1}{Z_R} = \frac{1}{R_p + 0j} = \frac{1}{R_p}$$

Capacitance

The impedance expression for the capacitance is more complex:

$$Z_C = -j (1 / \omega C)$$

The admittance expression is:

$$\frac{1}{Z_C} = \frac{1}{(0 - j [1 / \omega C])} = \frac{1}{(-j [1 / \omega C])}$$

or

$$= \frac{\omega C}{-j} = \frac{j \omega C}{(j)(-j)} = \frac{j \omega C}{(-j^2)}$$

or finally, remembering that $j^2 = -1$:

$$= \frac{j \omega C}{-(-1)} = j \omega C$$

Parallel Combination (R_p and C)

You can calculate the admittance of the parallel combination from:

$$1/Z = 1/Z_R + 1/Z_C$$

or

$$Z = 1/R_p + (j\omega C) = 1/R_p + j(\omega C)$$

or finally, after multiplying both top and bottom by R_p :

$$Z = \frac{1}{(1/R_p) + (j[\omega C])} = \frac{R_p}{1 + j(\omega R_p C)}$$

For those unfamiliar with complex numbers:

$$\frac{1}{a+jb} = \left(\frac{1}{a+jb} \right) \left(\frac{a-jb}{a-jb} \right) = \frac{a-jb}{a^2 + b^2}$$

Thus, the impedance expression can be rewritten as:

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

Ohmic Resistance

Finally, the impedance of the ohmic resistance must be added:

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

or

$$= R_{\Omega} + \frac{R_p}{1 + (\omega R_p C)^2} + j \left(\frac{-\omega R_p^2 C}{1 + (\omega R_p C)^2} \right)$$

or

$$= Z' + jZ''$$

Although this equation is correct, its complexity obscures its meaning. It is useful, however, to check the behavior at the two frequency limits, $w=0$ and $w=\infty$. As w tends towards zero, the denominator in both terms tends toward 1. For the real term, the sum approaches $(R_{\Omega} + R_p)$ as w goes to zero. For the imaginary term, the numerator tends toward zero, so the imaginary term vanishes at the dc limit.

As the frequency increases, this behavior may not be as easy to see. In the real term, as w increases, the denominator approaches $(\omega R_p C)^2$ since that term becomes much larger than 1. Consequently, the second term ratio approaches zero and the sum (Z') becomes simply R_{Ω} . In the imaginary term, the ratio approaches

$$\frac{-\omega R_p^2 C}{(\omega R_p C)^2} = \frac{-1}{\omega C}$$

which tends towards zero as w increases. Thus, at the low frequency limit, the imaginary term vanishes and the real part approaches $(R_{\Omega} + R_p)$. At the high frequency limit, the imaginary term also vanishes, but the real term approaches R_{Ω} .

1. Mansfeld, F. "Recording and Analysis of AC Impedance Data for Corrosion Studies: 1. Background and Methods for Analysis" *Corrosion* **1981**, 37, 301-307.
2. Mansfeld, F.; Kendig, M. W.; Tsai, S. "Recording and Analysis of AC Impedance Data for Corrosion Studies: 1. Experimental Approach and Results" *Corrosion* **1982**, 38, 570-580.
3. Macdonald, D. D.; Syrett, B. C.; Wing, S. S. "Me Corrosion of Copper-Nickel Alloys 706 and 715 in Flowing Seawater: 1. Effect of Oxygen" *Corrosion* **1978**, 34, 289-301.
4. Macdonald, D. D.; Syrett, B. C.; Wing, S. S. "The Corrosion of Copper-Nickel Alloys 706 and 715 in Flowing Seawater: II. Effect of Dissolved Sulfide" *Corrosion* **1979**, 35, 367-378.
5. Lorenz, W. J.; Mansfeld, F. "Determination of Corrosion Rates by Electrochemical DC and AC Methods" *Corrosion Science* **1981**, 21, 647.
6. Feigenbaum, C.; Gal-Or, L.; Yahalom, J. "Scale Protection Criteria in Natural Waters" *Corrosion* **1978**, 34, 133-137.
7. Eppelboin, I.; Keddad, M.; Takenouti, H. "Use of Impedance Measurements for the Determination of the Instant Rate of Metal Corrosion" *J. Appl. Electrochem.* **1972**, 2, 71.
8. Keddad, M.; Mattos, O. R.; Takenoud, H. "Reaction Model for Iron Dissolution Studied by Electrode Impedance" (I and II) *J. Electrochem. Soc.* **1981**, 128, 257-274.
9. Cahan, B. D.; Chen, C. T. "The Nature of the Passive Film on Iron: II. Impedance Studies" *J. Electrochem. Soc.* **1982**, 129, 474-480.
10. Glarum, S. H.; Marshall, J. H. "An A-C Admittance Study of the Platinum/Sulfuric Acid Interface" *J. Electrochem. Soc.* **1979**, 126, 424-430.
11. Isaacs, H. S.; Olmer, L. J. "Correlation of the AC and DC Polarization Resistances of a Platinum Electrode/Zirconia Solid Oxide Electrolyte Interface" *J. Electroanal. Chem.* **1982**, 132, 59-65.
12. Glarum, S. H.; Marshall, J. H. "The A-C Response of Nickel Oxide Electrode Films" *J. Electrochem. Soc.* **1982**, 129, 535-542.
13. Bonnel, A. et al "Corrosion Study of a Carbon Steel in Neutral Chloride Solutions by Impedance Techniques" *J. Electrochem. Soc.* **1983**, 130, 753-761.
14. Dabosi, F. et al "Corrosion Inhibition Study of a Carbon Steel in Neutral Chloride Solutions by Impedance Techniques" *J. Electrochem. Soc.* **1983**, 130, 761-766.
15. *Treatise on Materials Science and Technology, Vol. 23, Corrosion: Aqueous Processes and Passive Films*; Scully, J. C. Ed.; Academic Press, Inc.: London, 1983.
16. Mansfeld, F.; Kendig, M. W.; Tsai, S. "Evaluation of Corrosion Behavior of Coated Metals with AC Impedance Measurements", *Corrosion* **1982**, 38, 478-485.
17. Padget, J. C.; Moreland, P. J. "Use of AC Impedance in the Study of the Anticorrosive Properties of Chlorine-Containing Vinyl Acrylic Latex Copolymers" *J. Coatings Tech.* **1983**, 55.
18. Walter, G. W. "Application of Impedance Measurements to Study Performance of Painted Metals in Aggressive Solutions" *J. Electroanal. Chem.* **1981**, 118, 259-273.
19. Standish, J. V.; Leidheiser, Jr., H. "The Electrical Properties of Organic Coatings on a Local Scale-Relationship to Corrosion" *Corrosion* **1980**, 36, 390-395.
20. Scantlebury, J. D. et al "Simulated Underfilm Corrosion of Coated Mild Steel Using an Artificial Blister" *Corrosion* **1983**, 39, 108-112.
21. Leidheiser, Jr., H. "Towards a Better Understanding of Corrosion Beneath Organic Coatings" *Corrosion* **1983**, 39, 189-201.
22. Sluyters, J. H. "On the Impedance of Galvanic Cells: 1. Theory" *Recueil* **1960**, 79, 1092.
23. Sluyters, J. H.; Oomen, J. J. C. "On the Impedance of Galvanic Cells: 11. Experimental Verification" *Recueil* **1960**, 79, 1101.
24. Sluyters, J. H.; Rehbach, M. "On the Impedance of Galvanic Cells: III. Applications to Alternating Current Polarography" *Recueil* **1961**, 80, 469.
25. Sluyters, J. H.; Rehbach, M. "On the Impedance of Galvanic Cells: IV. Determinations of Rate Constants of Rapid Electrode Reactions from Electrode Impedance Measurements" *Recueil* **1962**, 81, 301.
26. Zimmerman, A. H. et al "Impedance and Mass Transport Kinetics of Nickel Cadmium Cells" *J. Electrochem. Soc.* **1982**, 129, 289-293.
27. Casson, P.; Hampson, N. A.; Willors, M. J. "Fundamentals of Lead-Acid Cells: Part VII. The A. C. Response of Lead Dioxide Electrodes in Sulfuric Acid" *J. Electroanal. Chem.* **1979**, 97, 21-32.
28. McBreen, J. et al "Zinc Electrode Morphology in Alkaline Solutions: 11. Study of Alternating Charging Current Modulation on Pasted Zinc Battery Electrodes" *J. Electrochem. Soc.* **1983**, 130, 1641-1645.
29. Eppelboin, I.; Jousselein, M.; Wiar, L. R. "Impedance Measurements for Nickel Deposition in Sulfate and Chloride Electrolytes" *J. Appl. Electrochem.* **1981**, 119, 61.
30. Glarum, S. H.; Marshall, J. H. "An Admittance Study of the Copper Electrode" *J. Electrochem. Soc.* **1981**, 128, 968-979.
31. Baranski, A.; Fawcett, W. R. "Medium Effects in the Electroreduction of Alkali Metal Cations" *J. Electroanal. Chem.* **1978**, 94, 237-240.
32. Kisza, A.; Grzeszczuk, M. "Electrode Processes in Fused Organic Salts Studied by Means of Impedance Method: Part 1. The Cadmium Electrode in Fused Organic Salts" *J. Electroanal. Chem.* **1978**, 91, 115-125.
33. Franceschetti, D. R.; Macdonald, J. R. "Small-Signal A-C Response Theory for Electrochromic Thin Films" *J. Electrochem. Soc.* **1982**, 129, 1754-1756.
34. McCann, J. F.; Badwal, S. P. S. "Equivalent Circuit Analysis of the Impedance Response of Semiconductor/Electrolyte/Counter-electrode Cells" *J. Electrochem. Soc.* **1982**, 129, 551-559.
35. Etman, M.; Koehler, C.; Parsons, R. "A Pulse Method for the Study of the Semiconductor-Electrolyte Interface" *J. Electroanal. Chem.* **1981**, 130, 57-67.
36. Weber, M. F.; Schumacher, L. C.; Dignam, M. J. "Effect of Hydrogen on the Dielectric and Photoelectrochemical Properties of Sputtered TiO₂ Films" *J. Electrochem. Soc.* **1982**, 129, 2022-2028.

37. Macdonald, D. D. *Transient Techniques in Electrochemistry*; Plenum: New York, 1977.
38. Macdonald, J. R. *Impedance Spectroscopy: Emphasizing Solid Materials and Systems*; John Wiley & Sons: New York, 1987.
39. Padget; Moreland.
40. Cahan, B. D.; Chen, C. T. "Questions on the Kinetics of O_2 Evolution on Oxide-Covered Metals" *J. Electrochem. Soc.* **1982**, 129, 700-705.
41. Macdonald, J. R., p 23.
42. Gabrielli, C. *Identification of Electrochemical Processes by Frequency Response Analysis* (Monograph); Solartron Instrumentation Group 1980; pp 53-61.
43. Epelboin, I. et al] "A Model of the Anodic Behaviour of Iron in Sulphuric Acid Medium" *Electrochim. Acta* **1975**, 20, 913-916.
44. Lorenz; Mansfeld.