# Gamry Instruments Software

# Tutorials and Primers

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Gamry Software
Tutorials and Primers

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# Table of Contents

# Chapter 1 -- Introduction

## Description of this Guide

*Tutorials and Primers* contains miscellaneous written technical support and training materials, associated with Gamry Instruments' Windows based software.

## What is not in this Document

Help files included with each software package are the primary technical support tool for Gamry's software. The material in these Help files is very complete compared to Help files for most other Windows applications. Very little of the information in Help is duplicated in this document.

Help is also the gateway to access the DC105 on-line tutorial. This tutorial provides quite comprehensive training in both basic use of the DC105 software and advanced techniques.

## Notational Conventions

In order to make this manual and the online help more readable we have adopted some of Microsoft's standard notational conventions and added some of our own. These are used throughout this and other Gamry Instruments' manuals.

- Key names. The names of keys are spelled out in this manual (for example ESCAPE, ENTER, CONTROL) and appear as small capital letters. The key caps on your keyboard may abbreviate the names or represent them differently. For example, the ESCAPE key is often labeled Esc and the ENTER and TAB keys are often labeled with arrows.

- Key combinations. A plus sign between two characters indicates that the keys are pressed at the same time. An example is ALT+ESCAPE to switch between windows.

  A comma between key names indicates that the keys are pressed sequentially, pressing and releasing one key before pressing the next key.

- DIRECTION keys. The DIRECTION keys are the four pointing keys, labeled with arrows, on your computer's keypad. The name of the individual DIRECTION key refers to the direction the key points: UP, DOWN, RIGHT and LEFT.

- Italics. *Italics* indicate words and characters that you type.

- Numbered lists. A numbered list is reserved for step-by-step procedures, with the steps always performed sequentially.

- Bulleted list. The items in a bulleted list, such as this one, are grouped together because they represent similar items. The order of items in the list is not critical.

- Hexadecimal numbers. Hexadecimal numbers are used for hardware related items such as I/O addresses. The Framework and this manual use the C programming language convention: all hexadecimal numbers have a prefix of 0x. For example the default I/O addresses used by a PC4 Potentiostat card are 0x120 through 0x13F.

- File names and directories.  Inside paragraphs, references to files and directories will be in quotes, for example:  "gamry5.ini" and "\FRAMEWORK\FRAMEWORK.EXE".

- Windows buttons and menu selections.  Labels will be shown in bold type with the accelerator key underlined as shown on the screen, i.e., **<u>F</u>ile**.

# Chapter 2 – DC Corrosion Theory

## Current and Voltage Conventions

A current value of -1.2 mA can mean different things to workers in different areas of electrochemistry. To an analytical electrochemist it represents 1.2 mA of anodic current. To a corrosion scientist it represents 1.2 mA of cathodic current. In the DC105's standard techniques we follow the corrosion convention for current. Positive currents are anodic, resulting in oxidation of the metal specimen under test.

Potentials can also be a source of confusion. In the DC105, the equilibrium potential assumed by the metal in the absence of electrical connections to the metal is called the Open Circuit Potential ,$E_{oc}$. We have reserved the term Corrosion Potential, $E_{corr}$ for the potential at which no current flows, as determined by a numerical fit of current versus potential data. In an ideal case, the values for $E_{oc}$ and $E_{corr}$ will be identical. One reason the two voltages may differ is changes in the electrode surface during a voltage scan.

In the DC105, all potentials are specified or reported as the potential of the working electrode with respect to either the reference electrode or the open circuit potential. The former is always labeled as "vs $E_{ref}$" and the later is labeled as "vs $E_{oc}$". The equations used to convert from one form of potential to the other are:

$$E \text{ vs } E_{oc} = ( E \text{ vs } E_{ref}) - E_{oc}$$

$$E \text{ vs } E_{ref} = ( E \text{ vs } E_{oc}) + E_{oc}$$

Regardless off whether potentials are versus $E_{ref}$ or versus $E_{oc}$, one sign convention is used. The more positive a potential, the more anodic it is. More anodic potentials tend to accelerate oxidation of a metal specimen.
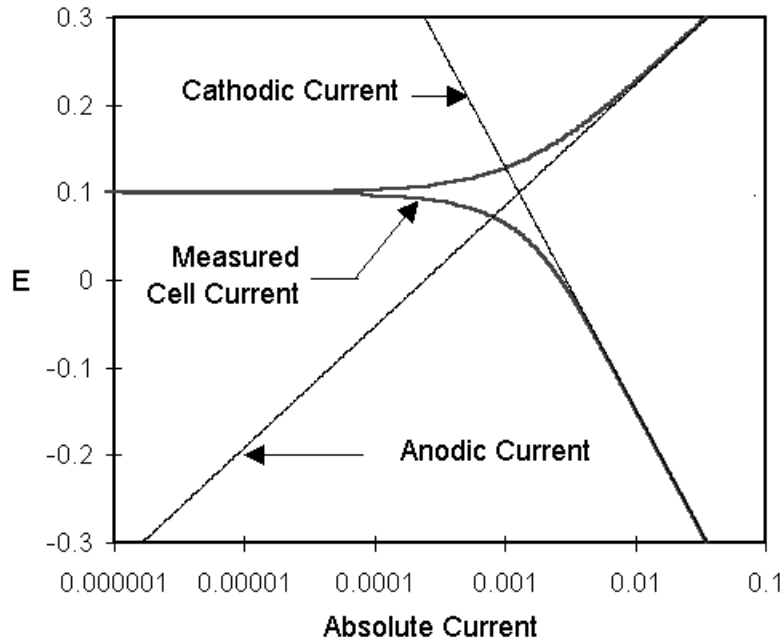
## Review of the Electrochemical Basis of Corrosion

Nearly all metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution. A thin film of moisture on a metal surface forms the electrolyte for atmospheric corrosion. Wet concrete is the electrolyte for reinforcing rod corrosion in bridges. Although most corrosion takes place in water, corrosion in non-aqueous systems is not unknown.

Corrosion normally occurs at a rate determined by an equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The other is the cathodic reaction, in which a solution species (often $O_2$ or $H^+$) is reduced, removing electrons from the metal. When these two reactions are in equilibrium, the flow of electrons from each reaction is balanced, and no net electron flow (electronic current) occurs. The two reactions can take place on one metal or on two dissimilar metals (or metal sites) that are electrically connected.

Figure 2-1 diagrams this process. The vertical axis is potential and the horizontal axis is the logarithm of absolute current. The theoretical current for the anodic and cathodic reactions are shown as straight lines. The curved line is the sum of the anodic and cathodic currents. It is the current that you measure when you sweep the potential of the metal. The sharp point in the curve results from the use of a logarithmic axis. It is actually the point where the current gets very small prior to changing sign.

**Figure 2-1**
**Corrosion Process Showing Anodic and Cathodic Current Components**



The potential of the metal is the means by which the anodic and cathodic reactions are kept in balance. Refer to Figure 2-1. Notice that the current from each half reaction depends on the electrochemical potential of the metal. Suppose the anodic reaction releases too many electrons into the metal. Excess electrons shift the potential of the metal more negative, which slows the anodic reaction and speeds up the cathodic reaction. This counteracts the initial perturbation of the system.

In the DC105, the equilibrium potential assumed by the metal in the absence of electrical connections to the metal is called the Open Circuit Potential ,$E_{oc}$.

The value of either the anodic or cathodic current at $E_{oc}$ is called the Corrosion Current, $I_{corr}$. If we could measure $I_{corr}$, we could use it to calculate the corrosion rate of the metal. Unfortunately $I_{corr}$ cannot be measured directly. However, it can be estimated using electrochemical techniques. In any real system $I_{corr}$ and corrosion rate are a function of many system variables including type of metal, solution composition, temperature, solution movement, metal history, and many others.

The above description of the corrosion process does not say anything about the state of the metal surface. In practice, many metals form an oxide layer on their surface as they corrode. If the oxide layer inhibits further corrosion, the metal is said to passivate. In some cases, local areas of the passive film break down allowing significant metal corrosion to occur in a small area. This phenomenon is called pitting corrosion, or simply pitting.

Because corrosion occurs via electrochemical reactions, electrochemical techniques are ideal for the study of the corrosion processes. In electrochemical studies a metal sample a few $cm^2$ in surface area is used to model the metal in a corroding system. The metal sample is immersed in a solution typical of the metal's environment in the system being studied. Additional electrodes are immersed in the solution, and all the electrodes are

connected to a device called a potentiostat. A potentiostat allows you to change the potential of the metal sample in a controlled manner.

With the exception of Open Circuit Potential vs Time and Galvanic Corrosion techniques, all the DC105 standard techniques use the Gamry potentiostat to perturb the equilibrium corrosion process. When the potential of a metal sample in solution is forced away from $E_{oc}$ it is referred to as polarizing the sample. The response (current or voltage) of the metal sample is measured as it is polarized. The response is used to develop a model of the sample's corrosion behavior. Both controlled potential (potentiostatic) and controlled current (galvanostatic) polarization is useful. When the polarization is done potentiostatically, current is measured, and when it is done galvanostatically, potential is measured. This discussion will concentrate on controlled potential methods, which see more common use.

Suppose we use the potentiostat to force the potential of a metal anodic (towards positive potentials) from $E_{oc}$. In Figure 2-1, we are moving towards the top of the graph. This will increase the rate of the anodic reaction and decrease the rate of the cathodic reaction. Since the anodic and cathodic reactions are no longer balanced, a net current will flow from the electronic circuit into the metal sample. The sign of this current is positive by convention. The potentiostat accurately measures the current. If we take the potential far enough from $E_{oc}$, the current from the cathodic reaction will be negligible, and the measured current will be a measure of the anodic reaction alone. In Figure 2-1, notice that the curves for the cell current and the anodic current lie on top of each other at positive potentials. Conversely, at strongly negative potentials the cathodic current dominates the cell current.

In some cases, as we vary the potential, we will first passivate the metal then cause pitting corrosion. Analysis of a curve plotting the measured current versus time or potential may allow us to determine $I_{corr}$ at $E_{corr}$, the tendency for passivation to occur, or the potential range over which pitting will occur.

## Quantitative Corrosion Theory

In the previous section we pointed out that $I_{corr}$ cannot be measured directly. In many cases you can estimate it from current versus voltage data. You can measure a log current versus potential curve over a range of about one half volt. The voltage scan is centered on $E_{oc}$. You then fit the measured data to a theoretical model of the corrosion process.

The model we will use assumes that the rates of both the anodic and cathodic processes are controlled by the kinetics of the electron transfer reaction at the metal surface. This is generally the case for corrosion reactions. An electrochemical reaction under kinetic control obeys Equation 2-1, the Tafel equation.

$$I = I^o \, e^{(2.303(E-E^o)/\beta)} \qquad\qquad \text{Equation 2-1}$$

In this equation,

|  |  |  |
|---|---|---|
| I | | is the current resulting from the reaction, |
| $I^o$ | | is a reaction dependant constant called the exchange current, |
| E | | is the electrode potential, |
| $E^o$ | | is the equilibrium potential (constant for a given reaction), |
| $\beta$ | | is the reaction's Beta Coefficient (constant for a given reaction) |
| | | Beta has units of volts/decade. |

The Tafel equation describes the behavior of one isolated reaction. In a corrosion system, we have two opposing reactions.

The Tafel equations for both the anodic and cathodic reactions in a corrosion system can be combined to generate the Butler-Volmer equation (Equation 2-2).

$$I = I_{corr} \left( e^{(2.303(E-E_{corr})/\beta_a)} - e^{-(2.303(E-E_{corr})/\beta_c)} \right) \qquad \text{Equation 2-2}$$

where

|  |  |
|---|---|
| I | is the measured cell current in amps, |
| $I_{corr}$ | is the corrosion current in amps, |
| $E_{corr}$ | is the corrosion potential in volts, |
| $\beta_a$ | is the anodic Beta (Tafel) coefficient in volts/decade, |
| $\beta_c$ | is the cathodic Beta (Tafel) coefficient in volts/decade. |

What does Equation 2-2 predict about the current versus voltage curve? At $E_{corr}$ each exponential term equals one. The cell current is therefore zero, as you would expect. Near $E_{corr}$, both exponential terms contribute to the overall current. Finally, as you get far from $E_{corr}$, one exponential term predominates and the other term can be ignored. When this occurs, a plot of log current versus potential becomes a straight line.

A log I versus E plot is generally called a Tafel plot. The Tafel plot in Figure 2-1 was generated directly from the Butler-Volmer equation. Notice the linear portion of the log current curve in the region far from $E_{corr}$.

In practice many corrosion systems are kinetically controlled and thus obey Equation 2-2. A log current versus potential curve that is linear on both sides of $E_{corr}$ is indicative of kinetic control for the system being studied. However, there can be complications, such as:
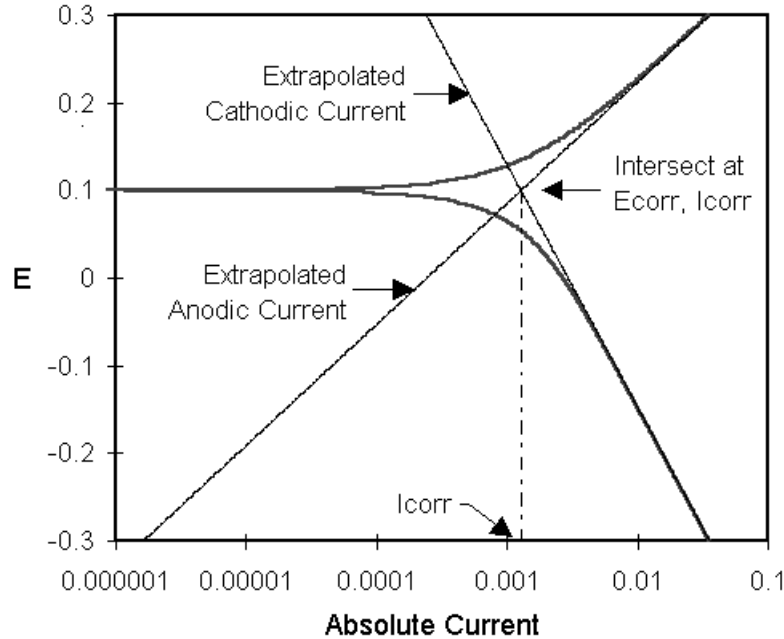
- Concentration polarization, where the rate of a reaction is controlled by the rate at which reactants arrive at the metal surface. Often cathodic reactions show concentration polarization at higher currents, when diffusion of oxygen or hydrogen ion is not fast enough to sustain the kinetically controlled rate.

- Oxide formation, which may or may not lead to passivation, can alter the surface of the sample being tested. The original surface and the altered surface may have different values for the constants in Equation 2-2.

- Other effects that alter the surface, such as preferential dissolution of one alloy component, can also cause problems.

- A mixed control process, where more than one cathodic or anodic reaction occurs simultaneously, complicates the model. An example of mixed control is the simultaneous reduction of oxygen and hydrogen ion.

- Finally, potential drop as a result of cell current flowing through the resistance of your cell solution causes errors in the kinetic model. This last effect, if it is not too severe, may be correctable via IR compensation in the potentiostat.

In most cases, complications like those listed above will cause non-linearities in the Tafel plot. The numbers that come out of a Tafel analysis on data that does not have a linear Tafel plot should be used with caution.

Classic Tafel analysis is performed by extrapolating the linear portions of a log current versus potential plot back to their intersection. See Figure 2-2 (this is Figure 2-1 reprinted with annotations that demonstrate the analysis). The value of either current at the intersection is $I_{corr}$. Unfortunately, many real world corrosion systems do not provide sufficient linear region to permit accurate extrapolation. Most modern corrosion test software performs a more sophisticated numerical fit to the Butler-Volmer equation. The measured data is fit to Equation 2-2 by adjusting the values of $E_{corr}$, $I_{corr}$, $\beta_a$ and $\beta_c$. The curve fitting method has the advantage that it does not require a fully developed linear portion of the curve.

**Figure 2-2**
**Classic Tafel Analysis**



The Equation 2-2 can be further simplified by restricting the potential to be very near to $E_{corr}$. Close to $E_{corr}$, the current versus voltage curve approximates a straight line. The slope of this line has the units of resistance (ohms). The slope is called the Polarization Resistance, $R_p$. An $R_p$ value can be combined with an estimate of the Beta coefficients to yield an estimate of the corrosion current.

If we approximate the exponential terms in Equation 2-2 with the first two term of a power series expansion ($e^x = 1+x +x^2/2...$) and simplify we get one form of the Stern-Geary equation:

$$I_{corr} = (1/ R_p) \ (\beta_a \beta_c \ / \ 2.303 \ (\beta_a + \beta_c) \ ) \hspace{2cm} \text{Equation 2-3}$$
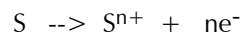
In a Polarization Resistance experiment you record a current versus voltage curve as the cell voltage is swept over a small range near $E_{oc}$. A numerical fit of the curve yields a value for the Polarization Resistance, $R_p$.

Polarization Resistance data does not provide any information about the values for the Beta coefficients. Therefore, to use Equation 2-3 you must provide Beta values. These can be obtained from separate Tafel type experiments or estimated from your experience with the system you are testing.

## Calculation of Corrosion Rate from Corrosion Current

The numerical result obtained by fitting corrosion data to a model is generally a corrosion current. We are interested in corrosion rates in more useful terms, such as a corrosion rate in millimeters per year. How is corrosion current used to generate a corrosion rate?

Assume an electrolytic dissolution reaction involving a chemical species, S:

$$S \; \longrightarrow \; S^{n+} \; + \; ne^-$$

You can relate current flow to mass via Faraday's Law.

$$Q_S = \; n \, F \, M_S \hspace{5cm} \text{Equation 2-4}$$

where

$Q_S$      is the charge in coulombs resulting from the reaction of species S,
$n$      is the number of electrons transferred per molecule or atom of S,
$F$      is Faraday's constant = 96486.7 coulombs/mole,
$M_S$      is the number of moles of species S reacting.

A more useful form of Equation 2-4 requires the concept of equivalent weight. The equivalent weight ($EW_S$) is the mass of species S that will react with one Faraday of charge. For an atomic species $EW = AW/n$ (where AW is the atomic weight of the species). For a complex alloy that undergoes uniform dissolution, the equivalent weight is a weighted average of the equivalent weights of the alloy components. Mole fraction, not mass fraction, is used as the weighting factor. If the dissolution is not uniform, you may have to measure the corrosion products to calculate EW.

Substituting into Equation 2-4 we get:

$$W_S \; = \; EW_S \, Q_S \; / \, F \hspace{5cm} \text{Equation 2-5}$$

where
$W_S$      Is the mass of species S that has reacted.

In cases where the corrosion occurs uniformly across a metal's surface, the corrosion rate can be calculated in units of distance per year. Be careful - this calculation underestimates the problem when localized corrosion occurs!

Conversion from a weight loss to a corrosion rate (CR) is straightforward. We need to know the density, d, and the sample area, A. Charge is given by $Q = I\,T$, where T is the time in seconds and I is a current. We can substitute in the value of Faraday's constant. Modifying Equation 2-5

$$CR = I_{corr}\, K\, EW\, /\, d\, A \hspace{4cm} \text{Equation 2-6}$$

CR      The corrosion rate. Its units are given by the choice of K,
$I_{corr}$      The corrosion current in amps,
K      A constant that defines the units for the corrosion rate,
EW      The equivalent weight in grams/equivalent,
d      Density in grams/$cm^3$,
A      Sample area in $cm^2$.

Table 2-1 shows the value of K used in Equation 2-6 for corrosion rates in the units of your choice.

**Table** 2-1
**Corrosion Rate Constants**

| Units for Corrosion Rate | K | Units |
| --- | --- | --- |
| mm/year (Gamry default) | 3272 | mm/( Amp cm year) |
| millinches/year | $1.288 \times 10^5$ | milliinches( Amp cm year) |

See ASTM Standard G 102, *Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements*, for further information. The standard can be obtained from ASTM, 1916 Race St., Philadelphia, Pennsylvania 19013-1187 (USA).

## IR Compensation in the DC105

When you pass current between two electrodes in a conductive solution, there will always be regions of different potentials in the solution. Much of the overall change in potential occurs very close to the surface of the electrodes. Here the potential gradients are largely due to ionic concentration gradients set up near the metal surfaces. Also there is always a potential difference (a potential drop) due to current flow through the resistance in the bulk of the solution.

In an electrochemical experiment, the potential that you wish to control or measure is the potential of a metal specimen (called the working electrode) versus a reference electrode. You are normally not interested in the potential drops due to solution resistances.

Gamry Instruments Potentiostats, like all modern electrochemical instruments, are three electrode potentiostats. It measures and controls the potential difference between a non-current carrying reference electrode and one of the two current carrying electrodes (the working electrode). The potential drop near the other current carrying electrode (the counter electrode) does not matter when a three electrode potentiostat is used.
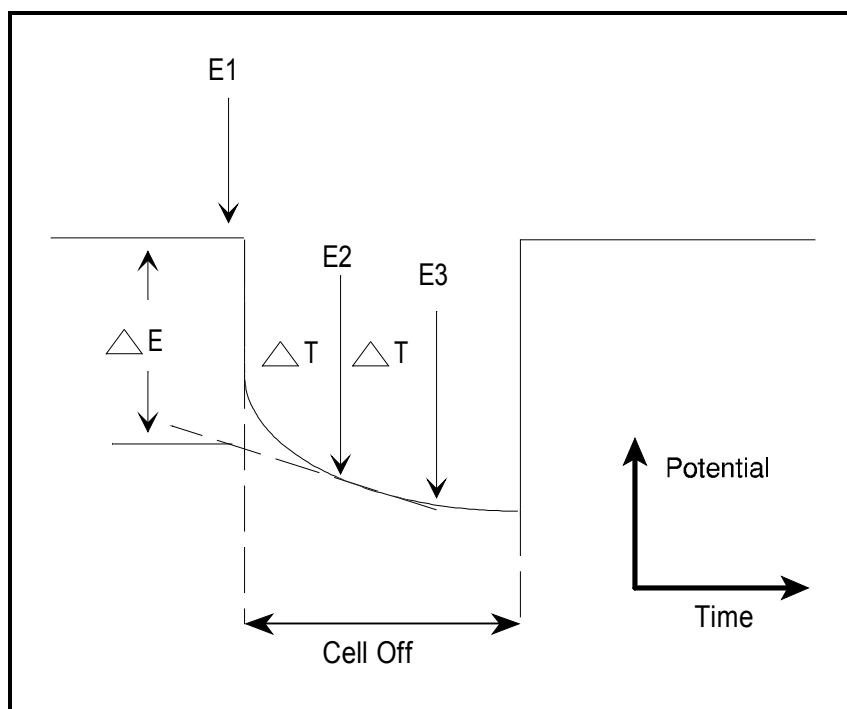
Careful placement of the reference electrode can compensate for some of the IR drop resulting from the cell current, I, flowing through the solution resistance, R. You can think of the reference electrode as sampling the potential somewhere along the solution resistance. The closer it is to the working electrode, the closer you are

to measuring a potential free from IR errors.  However, complete IR compensation cannot be achieved in practice through placement of the reference electrode, because of the finite physical size of the electrode.  The portion of the cell resistance that remains after placing the reference electrode is called the uncompensated resistance, $R_u$.

The DC105 uses current interrupt IR compensation to dynamically correct uncompensated resistance errors.  In the current interrupt technique, the cell current is periodically turned off for a short time.  With no current through the solution resistance, its IR drop disappears.  The potential drops at the electrode surface remain constant on a rapid time scale.  The difference in potential with the current flowing and without is a measure of the uncompensated IR drop.

The DC105 makes a current interrupt measurement right after each data point is acquired.  It actually takes three potential readings: E1 before the current is turned off, and E2 and E3 while it is off.  See Figure 2-3.  Normally, the latter two are used to extrapolate the potential difference, delta E, back to the exact moment when the current was interrupted.  The timing of the interrupt depends on the cell current.  The interrupt time varies by current range and instrument.  On lower current ranges, the interrupt lasts longer.

**Figure 2-3**
**Current Interrupt Potential versus Time**



The DC105 has a second current interrupt measurement mode that involves averaging of the 2 points on the decay curve.  See the discussion of the Pstat.SetIRuptMode() function in the online help for details.

In controlled potential modes, the applied potential can be dynamically corrected for the measured IR error in one of several ways.  In the simplest of these, the IR error from the previous point is applied as a correction to the applied potential.  For example, if an IR free potential of 1 volt is desired, and the measured IR error is 0.2 volts, the DC105 will apply 1.2 volts.  The correction is always one point behind, as the IR error from one point is applied to correct the applied potential for the next point.  In addition to this common mode, the DC105 offers more complex feedback modes.  Again, see the discussion of the Pstat.SetIRuptMode() function in the online help for details.

By default in the controlled potential modes, the potential error measured via current interrupt is used to correct the applied potential.  In the controlled current modes, no correction is required.  If IR compensation is selected, the measured IR error is subtracted from the measured potential.  All reported potentials are therefore free from IR error.

# Chapter 3 – EIS Theory

## About This Chapter

This chapter presents an introduction to Electrochemical Impedance Spectroscopy (EIS) theory. This chapter has been kept as free from mathematics and electrical theory as is possible. If you still find the material presented here difficult to understand, don't stop reading. You will get useful information from this chapter even if you don't follow all of the discussions.

Five major topics are covered in this chapter:

- AC Circuit Theory and Representation of Complex Impedance Values.

- Physical Electrochemistry and Circuit Elements.

- Common Equivalent Circuit Models.

- Extracting Model Parameters from Impedance Data.

- EIS Literature.

No prior knowledge of electrical circuit theory or electrochemistry is assumed. Each topic starts out at a quite elementary level. Each topic proceeds from this simple beginning to cover more advanced material.

## AC Circuit Theory and Representation of Complex Impedance Values

## Impedance definition: concept of complex impedance

Almost everyone knows about the concept of electrical resistance. It is the ability of a circuit element to resist the flow of electrical current. Ohm's law (Equation 3-1) defines resistance in terms of the ratio between voltage E and current I.

$$R = \frac{E}{I}$$
(3-1)

While this is a well known relationship, it's use is limited to only one circuit element -- the ideal resistor. An ideal resistor has several simplifying properties:
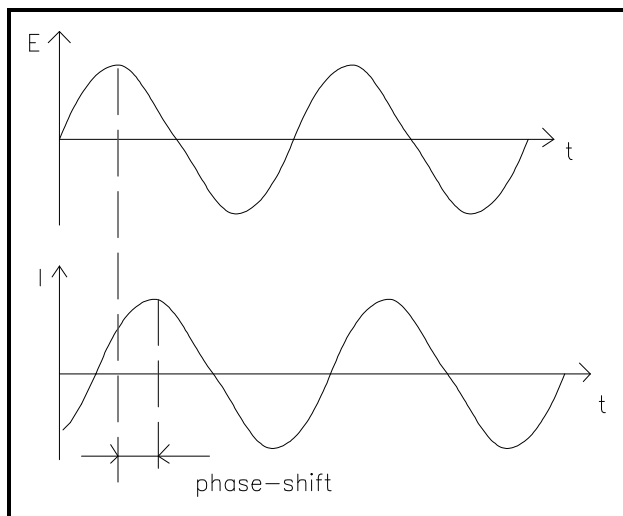
- It follows Ohm's Law at all current and voltage levels.

- It's resistance value is independent of frequency.

- AC current and voltage signals though a resistor are in phase with each other.

The real world contains circuit elements that exhibit much more complex behavior. These elements force us to abandon the simple concept of resistance. In its place we use impedance, which is a more general circuit parameter. Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current. Unlike resistance, impedance is not limited by the simplifying properties listed above.

Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell. Suppose that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal, containing the excitation frequency and it's harmonics. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series).

Electrochemical Impedance is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear. Linearity is described in more detail in a following section. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase. See Figure 3-1.

**Figure 3-1**
**Sinusoidal Current Response in a Linear System**

The excitation signal, expressed as a function of time, has the form

$$E_t = E_0 \sin(\omega t) \qquad (3\text{-}2)$$

E(t) is the potential at time t, $E_0$ is the amplitude of the signal, and $\omega$ is the radial frequency. The relationship between radial frequency $\omega$ (expressed in radians/second) and frequency f (expressed in hertz) is:

$$\omega = 2\pi f \qquad (3\text{-}3)$$

In a linear system, the response signal, $I_t$, is shifted in phase ($\phi$) and has a different amplitude, $I_0$:

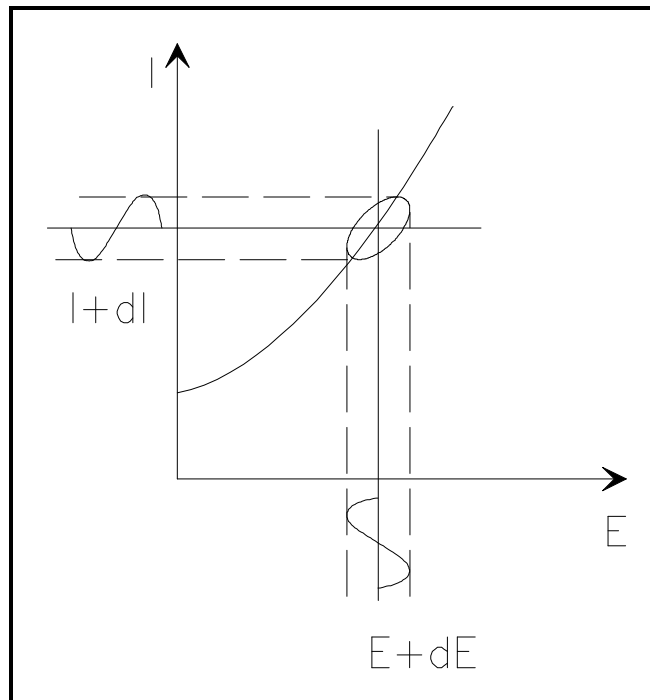$$I(t) = I_0 \cos(\omega t - \phi) \qquad (3\text{-}4)$$

An expression analogous to Ohm's Law allows us to calculate the impedance of the system as:

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)} \qquad (3\text{-}5)$$

The impedance is therefore expressed in terms of a magnitude, $Z_0$, and a phase shift, $\phi$.

If we plot the applied sinusoidal signal on the X-axis of a graph and the sinusoidal response signal I(t) on the Y-axis, an oval is plotted. See Figure 3-2. This oval is known as a "Lissajous figure". Analysis of Lissajous figures on oscilloscope screens was the accepted method of impedance measurement prior to the availability of lock-in amplifiers, frequency response analyzers, and digital signal processing.

**Figure 3-2**
**Origin of Lissajous Figure**

Using Eulers relationship,

$$\exp(j\phi) = \cos\phi + j\sin\phi \qquad\qquad (3\text{-}6)$$

it is possible to express the impedance as a complex function. The potential is described as,

$$E(t) = E_0 \exp(j\omega t) \qquad\qquad (3\text{-}7)$$

and the current response as,

$$I(t) = I_0 \exp(j\omega t - j\phi) \qquad\qquad (3\text{-}8)$$

The impedance is then represented as a complex number,

$$Z = \frac{E}{I} = Z_0\exp(j\phi) = Z_0(\cos\phi + j\sin\phi) \qquad\qquad (3\text{-}9)$$

## Data Presentation

Look at Equation 3-9 in the previous section. The expression for $Z(\omega)$ is composed of a real and an imaginary part. If the real part is plotted on the Z axis and the imaginary part on the Y axis of a chart, we get a "Nyquist plot". See Figure 3-3. Notice that in this plot the y-axis is negative and that each point on the Nyquist plot is the impedance at one frequency.

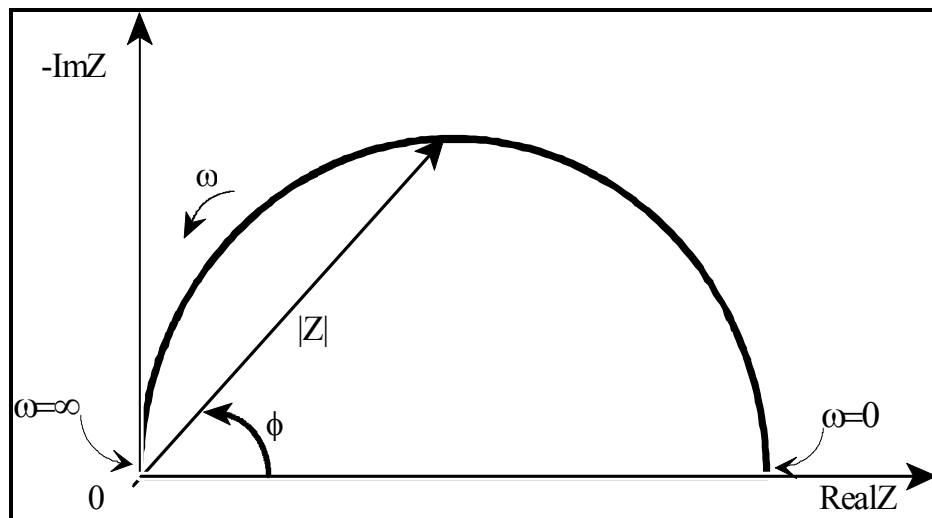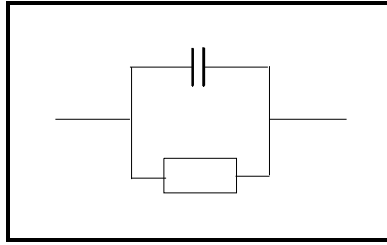**Figure 3-3**
**Nyquist Plot with Impedance Vector**



Figure 3-3 has been annotated to show that low frequency data are on the right side of the plot and higher frequencies are on the left. This is true for EIS data where impedance usually falls as frequency rises (this is not true of all circuits).

On the Nyquist plot the impedance can be represented as a vector of length $|Z|$. The angle between this vector and the x-axis is $\phi$, where $\phi$ is the phase.

Nyquist plots have one major shortcoming. When you look at any data point on the plot, you cannot tell what frequency was used to record that point.

The Nyquist plot in Figure 3-3 results from the electrical circuit of Figure 3-4. The semicircle is characteristic of a single "time constant". Electrochemical Impedance plots often contain several time constants. Often only a portion of one or more of their semicircles is seen.
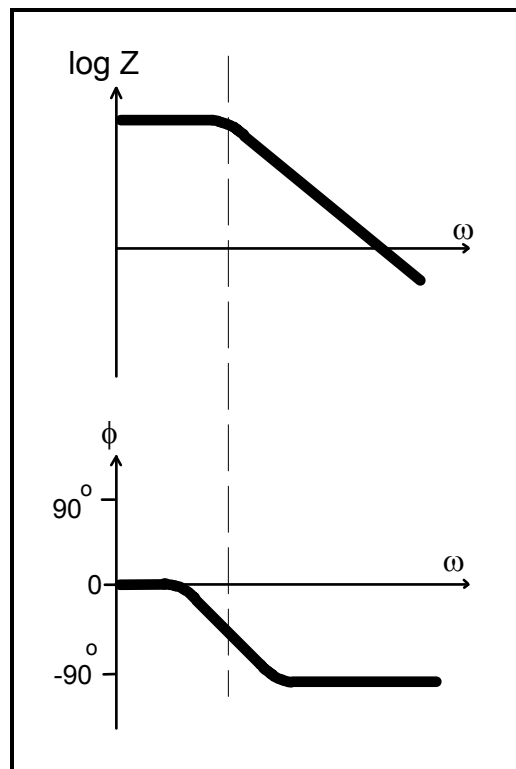
**Figure 3-4**
**Simple Equivalent Circuit with One Time Constant**



Another popular presentation method is the "Bode plot". The impedance is plotted with log frequency on the x-axis and both the log of absolute value of the impedance, $\log|Z|$, and phase-shift, $\phi$, on the y-axis.

The Bode plot for the electric circuit of Figure 3-4 is shown in Figure 3-5. Unlike the Nyquist plot, the Bode plot explicitly shows frequency information.

**Figure 3-5**
**Bode Plot with One Time Constant**

## Electrochemistry - A Linear System?

Electrical circuit theory distinguishes between linear and non-linear systems (circuits). Impedance analysis of linear circuits is much easier than analysis of non-linear ones.

The following definition of a linear system is taken from *Signals and Systems* by Oppenheim and Willsky:

> A linear system ... is one that possesses the important property of superposition: If the input consists of the weighted sum of several signals, then the output is simply the superposition, that is, the weighted sum, of the responses of the system to each of the signals. Mathematically, let $y_1(t)$ be the response of a continuous time system to $x_1(t)$ and let $y_2(t)$ be the output corresponding to the input $x_2(t)$. Then the system is linear if:
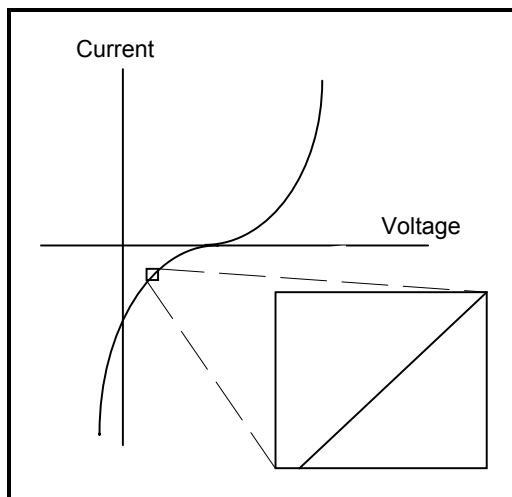>
> 1) The response to $x_1(t) + x_2(t)$ is $y_1(t) + y_2(t)$
>
> 2) The response to $ax_1(t)$ is $ay_1(t)$ ...

For a potentiostated electrochemical cell, the input is the potential and the output is the current. Electrochemical cells are not linear! Doubling the voltage will not necessarily double the current.

However, Figure 3-6 shows how electrochemical systems can be pseudo-linear. When you look at a small enough portion of a cell's current versus voltage curve, it seems to be linear.

In normal EIS practice, a small (1 to 10 mV) AC signal is applied to the cell. The signal is small enough to confine you to a pseudo-linear segment of the cell's current versus voltage curve. You do not measure the cell's nonlinear response to the DC potential because in EIS you only measure the cell current at the excitation frequency.

**Figure 3-6**
**Current versus Voltage Curve Showing Pseudo-linearity**



If the system is non-linear, the current response will contain harmonics of the excitation frequency.

Some researchers have made use of this phenomenon. Linear systems should not generate harmonics, so the presence or absence of significant harmonic response allows one to determine the system's linearity. Other researchers have intentionally used larger amplitude excitation potentials. They use the harmonic response to estimate the curvature in the cell's current voltage curve.

## Steady State Systems

Measuring an EIS spectrum takes time (often many hours).  The system being measured must be at a steady state throughout the time required to measure the EIS spectrum.  A common cause of problems in EIS measurements and their analysis is drift in the system being measured.

In practice a steady state can be difficult to achieve.  The cell can change through adsorption of solution impurities, growth of an oxide layer, build up of reaction products in solution, coating degradation, temperature changes, to list just a few factors.

Standard EIS analysis tools may give you wildly inaccurate results on a system that is not at a steady state.

## Time and Frequency Domains and Transforms

Signal processing theory refers to data domains.  The same data can be represented in different domains.  In EIS, we use two of these domains, the time domain and the frequency domain.

In the time domain, signals are represented as signal amplitude versus time.  Figure 3-7 demonstrates this for a signal consisting of two superimposed sine waves.
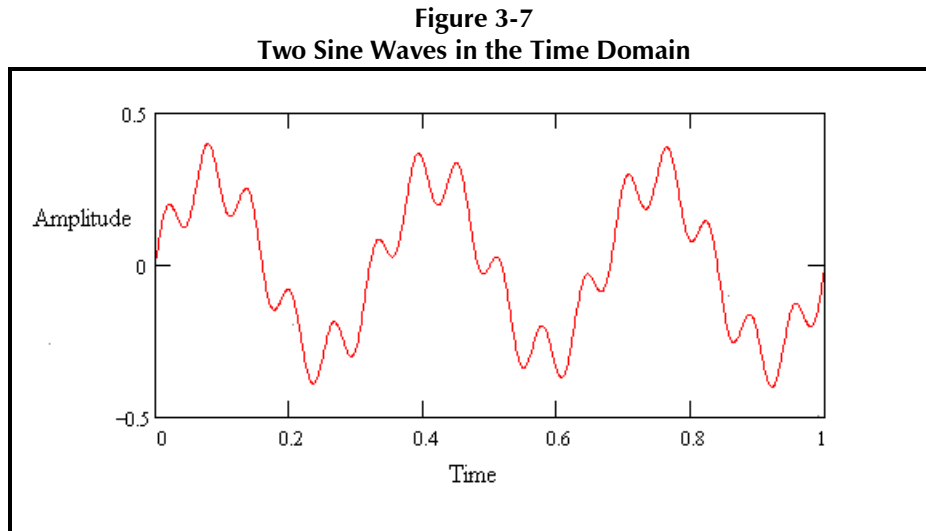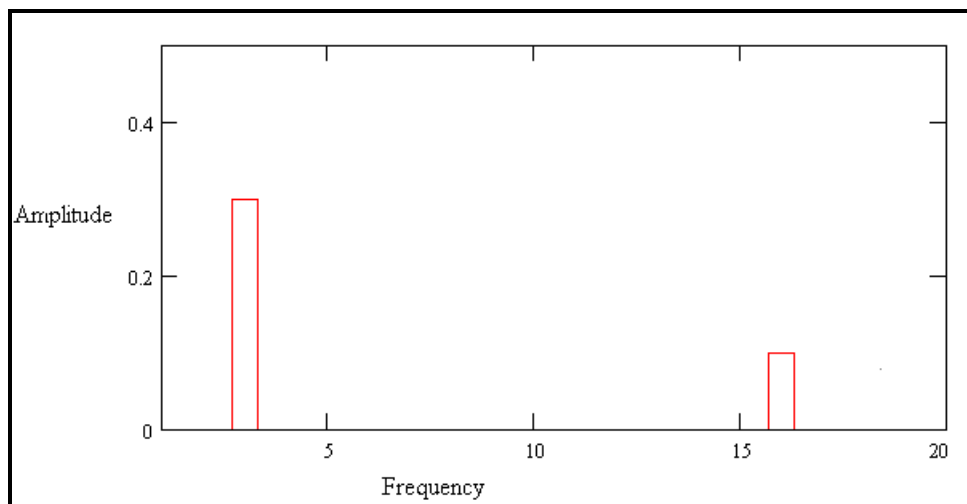
**Figure 3-7**
**Two Sine Waves in the Time Domain**



Figure 3-8 shows the same data in the frequency domain.  The data is plotted as amplitude versus frequency.

**Figure 3-8**
**Two Sine Waves in the Frequency Domain**



The Fourier transform and the inverse Fourier transform switch between the domains. The common term, FFT, refers to a fast, computerized implementation of the Fourier transform. Detailed discussion of these transforms is beyond the scope of this manual. Several of the references given at the end of this chapter contain more information on the Fourier transform and its use in EIS.

In modern EIS systems, lower frequency data are usually measured in the time domain. The controlling computer applies a digital approximation to a sine wave to the cell by means of a digital to analog converter. The current response is measured using an analog to digital computer. An FFT is used to convert the current signal into the frequency domain.

## Electrical Circuit Elements

EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as resistors, capacitors, and inductors. To be useful, the elements in the model should have a basis in the physical electrochemistry of the system. As an example, most models contain a resistor that models the cell's solution resistance.

Some knowledge of the impedance of the standard circuit components is therefore quite useful. Table 3-1 lists the common circuit elements, the equation for their current versus voltage relationship, and their impedance.

**Table 3-1**
**Common Electrical Elements**

| Component | Current Vs.Voltage | Impedance |
|---|---|---|
| resistor | E= IR | $Z = R$ |
| inductor | $E = L\, di/dt$ | $Z = j\omega L$ |
| capacitor | $I = C\, dE/dt$ | $Z = 1/j\omega C$ |

Notice that the impedance of a resistor is independent of frequency and has only a real component. Because there is no imaginary impedance, the current through a resistor is always in phase with the voltage.

The impedance of an inductor increases as frequency increases. Inductors have only an imaginary impedance component. As a result, an inductor's current is phase shifted 90 degrees with respect to the voltage.
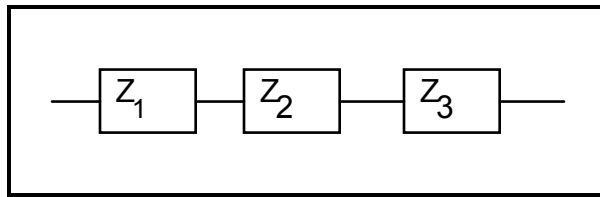
The impedance versus frequency behavior of a capacitor is opposite to that of an inductor. A capacitor's impedance decreases as the frequency is raised. Capacitors also have only an imaginary impedance component. The current through a capacitor is phase shifted -90 degrees with respect to the voltage.

## Serial and Parallel Combinations of Circuit Elements

Very few electrochemical cells can be modeled using a single equivalent circuit element. Instead, EIS models usually consist of a number of elements in a network. Both serial and parallel combinations of elements occur.

Fortunately, there are simple formulas that describe the impedance of circuit elements in both parallel and series combinations.
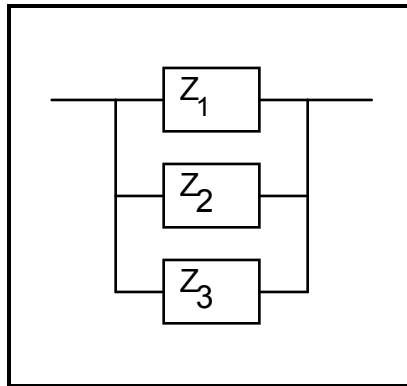
**Figure 3-9**
**Impedances in Series**



For linear impedance elements in series you calculate the equivalent impedance from:

$$Z_{eq} = Z_1 + Z_2 + Z_3$$

(3-10)

**Figure 3-10**
**Impedances in Parallel**

For linear impedance elements in parallel you calculate the equivalent impedance from:

$$\frac{1}{Z_{eq}} = \frac{1}{Z_1 + Z_2 + Z_3} \qquad\qquad (3\text{-}11)$$

We will calculate two examples to illustrate a point about combining circuit elements. Suppose we have a 1 Ω and a 4 Ω resistor is series. The impedance of a resistor is the same as its resistance (see Table 2-1). We thus calculate the total impedance as:

$$Z_{eq} = Z_1 + Z_2 = R_1 + R_2 = 1\,\Omega + 4\,\Omega = 5\,\Omega$$

Resistance and impedance both go up when resistors are combined in series.

Now suppose that we connect two 2 µF capacitors in series. The total capacitance of the combined capacitors is 1 µF.

$$Z_{eq} = Z_1 + Z_2 = \frac{1}{j\omega\,C_1} + \frac{1}{j\omega\,C_2}$$

$$= \frac{1}{j\omega\,(2e-6)} + \frac{1}{j\omega\,(2e-6)}$$

$$= \frac{1}{j\omega\,(1e-6)}$$

Impedance goes up, but capacitance goes down when capacitors are connected in series. This is a consequence of the inverse relationship between capacitance and impedance.

## Physical Electrochemistry and Equivalent Circuit Elements

### Electrolyte Resistance

Solution resistance is often a significant factor in the impedance of an electrochemical cell.  A modern 3 electrode potentiostat compensates for the solution resistance between the counter and reference electrodes.  However, any solution resistance between the reference electrode and the working electrode must be considered when you model your cell.

The resistance of an ionic solution depends on the ionic concentration, type of ions, temperature and the geometry of the area in which current is carried.  In a bounded area with area A and length l carrying a uniform current the resistance is defined as:

$$R = \rho \frac{l}{A}$$ (3-12)

where $\rho$ is the solution resistivity. The conductivity of the solution, $\kappa$, is more commonly used in solution resistance calculations.  Its relationship with solution resistance is:

$$R = \frac{1}{\kappa} \cdot \frac{l}{A} \quad \Rightarrow \quad \kappa = \frac{l}{RA}$$ (3-13)

Standard chemical handbooks list $\kappa$ values for specific solutions.  For other solutions, you can calculate $\kappa$ from specific ion conductances.  The units for $\kappa$ are Siemens per meter (S/m).  The Siemen is the reciprocal of the ohm, so 1 S = 1/ohm.

Unfortunately, most electrochemical cells do not have uniform current distribution through a definite electrolyte area.  The major problem in calculating solution resistance therefore concerns determination of the current flow path and the geometry of the electrolyte that carries the current.  A comprehensive discussion of the approaches used to calculate practical resistances from ionic conductances is well beyond the scope of this manual.

Fortunately, you don't usually calculate solution resistance from ionic conductances.  Instead, it is found when you fit a model to experimental EIS data.

### Double Layer Capacitance

A electrical double layer exists at the interface between an electrode and its surrounding electrolyte.  This double layer is formed as ions from the solution "stick on" the electrode surface.  Charges in the electrode are separated from the charges of these ions.  The separation is very small, on the order of angstroms.

Charges separated by an insulator form a capacitor.  On a bare metal immersed in an electrolyte, you can estimate that there will be approximately 30 $\mu$F of capacitance for every $cm^2$ of electrode area.

The value of the double layer capacitance depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

## Polarization Resistance

Whenever the potential of an electrode is forced away from it's value at open circuit, that is referred to as polarizing the electrode. When an electrode is polarized, it can cause current to flow via electrochemical reactions that occur at the electrode surface. The amount of current is controlled by the kinetics of the reactions and the diffusion of reactants both towards and away from the electrode.

In cells where an electrode undergoes uniform corrosion at open circuit, the open circuit potential is controlled by the equilibrium between two different electrochemical reactions. One of the reactions generates cathodic current and the other anodic current. The open circuit potential ends up at the potential where the cathodic and anodic currents are equal. It is referred to as a mixed potential. The value of the current for either of the reactions is known as the corrosion current.

Mixed potential control also occurs in cells where the electrode is not corroding. While this section discusses corrosion reactions, modification of the terminology makes it applicable in non-corrosion cases as well.

When there are two simple, kinetically controlled reactions occurring, the potential of the cell is related to the current by the following (known as the Butler-Volmer equation).

$$I = I_{corr} \left( e^{(2.303(E-E_{corr})/\beta_a)} - e^{-(2.303(E-E_{corr})/\beta_c)} \right) \tag{3-14}$$

where

$I$       is the measured cell current in amps,
$I_{corr}$    is the corrosion current in amps,
$E_{oc}$    is the open circuit potential in volts,
$\beta_a$    is the anodic Beta coefficient in volts/decade,
$\beta_c$    is the cathodic Beta coefficient in volts/decade.

If we apply a small signal approximation (E-Eoc is small) to equation 3-14, we get the following:

$$I_{corr} = \frac{\beta_a \beta_c}{2.303 \ (\beta_a + \beta_c)} \left( \frac{1}{R_p} \right) \tag{3-15}$$

which introduces a new parameter, $R_p$, the polarization resistance. As you might guess from its name, the polarization resistance behaves like a resistor.

If the Tafel constants are known, you can calculate the $I_{corr}$ from $R_p$ using equation 3-15. $I_{corr}$ in turn can be used to calculate a corrosion rate.

We will further discuss the $R_p$ parameter when we discuss cell models.

## Charge Transfer Resistance

A similar resistance is formed by a single kinetically controlled electrochemical reaction. In this case we do not have a mixed potential, but rather a single reaction at equilibrium.

Consider a metal substrate in contact with an electrolyte. The metal molecules can electrolytically dissolve into the electrolyte, according to:

$$Me \iff Me^{n+} + ne^{-} \tag{3-16}$$

or more generally:

$$Red \iff Ox + ne^{-} \tag{3-17}$$

In the forward reaction in the first equation, electrons enter the metal and metal ions diffuse into the electrolyte. Charge is being transferred.

This charge transfer reaction has a certain speed. The speed depends on the kind of reaction, the temperature, the concentration of the reaction products and the potential.

The general relation between the potential and the current is:

$$i = i_0 \left[ \frac{C_O}{C_O^*} e^{\left(\frac{\alpha n F \eta}{RT}\right)} - \frac{C_R}{C_R^*} e^{\frac{-(1-\alpha)nF\eta}{RT}} \right] \tag{3-18}$$

with,

| | |
|---|---|
| $i_0$ | = exchange current density |
| $C_O$ | = concentration of oxidant at the electrode surface |
| $C_O{}^*$ | = concentration of oxidant in the bulk solution |
| $C_R$ | = concentration of reductant at the electrode surface |
| F | = Faradays constant |
| T | = temperature |
| R | = gas constant |
| $\alpha$ | = reaction order |
| n | = number of electrons involved |
| $\eta$ | = overpotential ( $E - E_0$ ) |

The overpotential, $\eta$, measures the degree of polarization. It is the electrode potential minus the equilibrium potential for the reaction.

When the concentration in the bulk is the same as at the electrode surface, $C_O = C_O^*$ and $C_R = C_R^*$. This simplifies equation 3-18 into:

$$i = i_0 \left( \exp(\alpha \frac{nF}{RT} \eta) - \exp(-(1-\alpha)\frac{nF}{RT} \eta) \right) \qquad (3-19)$$

This equation is a form of the Butler-Volmer equation. It is applicable when the polarization depends only on the charge transfer kinetics.

Stirring will minimize diffusion effects and keep the assumptions of $C_O = C_O^*$ and $C_R = C_R^*$ valid.

When the overpotential, $\eta$, is very small and the electrochemical system is at equilibrium, the expression for the charge transfer resistance changes into:

$$R_{ct} = \frac{RT}{nFi_0} \qquad (3-20)$$

From this equation the exchange current density can be calculated when $R_{ct}$ is known.

## Diffusion

Diffusion can create an impedance known as the Warburg impedance. This impedance depends on the frequency of the potential perturbation. At high frequencies the Warburg impedance is small since diffusing reactants don't have to move very far. At low frequencies the reactants have to diffuse farther, thereby increasing the Warburg impedance.

The equation for the "infinite" Warburg impedance is:

$$Z = \sigma(\omega)^{-\frac{1}{2}} (1-j) \qquad (3-21)$$

On a Nyquist plot the infinite Warburg impedance appears as a diagonal line with a slope of 0.5. On a Bode plot, the Warburg impedance exhibits a phase shift of 45°.

In equation 3-21, $\sigma$ is the Warburg coefficient defined as:

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left( \frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right) \qquad (3-22)$$

In which,

| | |
|---|---|
| $\omega$ | = radial frequency |
| $D_O$ | = diffusion coefficient of the oxidant |
| $D_R$ | = diffusion coefficient of the reductant |
| A | = surface area of the electrode |
| n | = number of electrons transferred |
| $C^*$ | = bulk concentration of the diffusing species (moles/cm³) |

This form of the Warburg impedance is only valid if the diffusion layer has an infinite thickness. Quite often this is not the case. If the diffusion layer is bounded, the impedance at lower frequencies no longer obeys the equation above. Instead, we get the form:

$$Z_O = \sigma\omega^{-\frac{1}{2}} \ (1-j) \ \tanh(\delta(\frac{j\omega}{D})^{\frac{1}{2}})$$ 

(3-23)

with,

        $\delta$         = Nernst diffusion layer thickness
        D        = an average value of the diffusion coefficients of the diffusing species

This more general equation is called the "finite" Warburg. For high frequencies where $\omega\to\infty$, or for an infinite thickness of the diffusion layer where $\delta\to\infty$, equation 3-23 simplifies to the infinite Warburg impedance.

## Coating Capacitance

A capacitor is formed when two conducting plates are separated by a non-conducting media, called the dielectric. The value of the capacitance depends on the size of the plates, the distance between the plates and the properties of the dielectric. The relationship is:

$$C = \frac{\varepsilon_o \, \varepsilon_r \, A}{d}$$ 

(3-24)

With,

        $\varepsilon_o$       = electrical permittivity
        $\varepsilon_r$       = relative electrical permittivity
        A       = surface of one plate
        d       = distances between two plates

Whereas the electrical permittivity is a physical constant, the relative electrical permittivity depends on the material. Table 3-2 gives you a few useful $\varepsilon_r$ values.

**Table 3-2**
**Typical Relative Electrical Permittivities**

| Material | $\varepsilon_r$ |
|---|---|
| vacuum | 1 |
| water | 80.1 (20°C) |
| organic coating | 4 - 8 |

Notice the large difference between the electrical permittivity of water and that of an organic coating. The capacitance of a coated substrate changes as it absorbs water. EIS can be used to measure that change.

## Constant Phase Element

Capacitors in EIS experiments often do not behave ideally.  Instead they act like a constant phase element (CPE) as defined below.

The impedance of a CPE has the form:

$$Z = A(j\omega)^{-\alpha} \tag{3-25}$$

When this equation describes a capacitor, the constant $A = 1/C$ (the inverse of the capacitance) and the exponent $\alpha = 1$.  For a constant phase element, the exponent $\alpha$ is less than one.

The "double layer capacitor" on real cells often behaves like a CPE instead of like a capacitor.  Several theories have been proposed to account for the non-ideal behavior of the double layer but none has been universally accepted.  In most cases, you can safely treat $\alpha$ as an empirical constant and not worry about its physical basis.

## Virtual Inductor

The impedance of an electrochemical cell can also appear to be inductive.  Some authors have ascribed inductive behavior to adsorbed reactants.  Both the adsorption process and the electrochemical reaction are potential dependent.  The net result of these dependencies can be an inductive phase shift in the cell current .

Inductive behavior can also result from non-homogeneous current distribution, cell lead inductance and potentiostat non-idealities.  In these cases, it represents an error in the EIS measurement.

## Common Equivalent Circuit Models

In the following section we show some common equivalent circuits models.  These models can be used to interpret simple EIS data.  Many of these models have been included as standard models in the EIS300 analysis package.

To elements used in the following equivalent circuits are presented in Table 3-3.  Equations for both the admittance and impedance are given for each element.
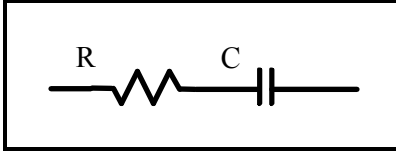
**Table 3-3**
**Circuit Elements Used in the Models**

| Equivalent element | Admittance | Impedance |
|---|---|---|
| R | $1/R$ | $R$ |
| C | $j\omega C$ | $1/j\omega C$ |
| L | $1/j\omega L$ | $j\omega L$ |
| W (infinite Warburg) | $Y_0\sqrt{(j\omega)}$ | $1/Y_0\sqrt{(j\omega)}$ |
| O (finite Warburg) | $1/Y_0\sqrt{(j\omega)}Coth(B\sqrt{(j\omega)})$ | $Tanh(B\sqrt{(j\omega)})/Y_0\sqrt{(j\omega)}$ |
| Q (CPE) | $Y_0(j\omega)^{\alpha}$ | $1/Y_0(j\omega)^{\alpha}$ |

The dependent variables used in these equations are R, C, L, $Y_O$, B and $\alpha$. The EIS300 uses these as fit parameters.

## Model #1 -- A Purely Capacitive Coating

A metal covered with an undamaged coating generally has a very high impedance. The equivalent circuit for such a situation is in Figure 3-11.

**Figure 3-11**
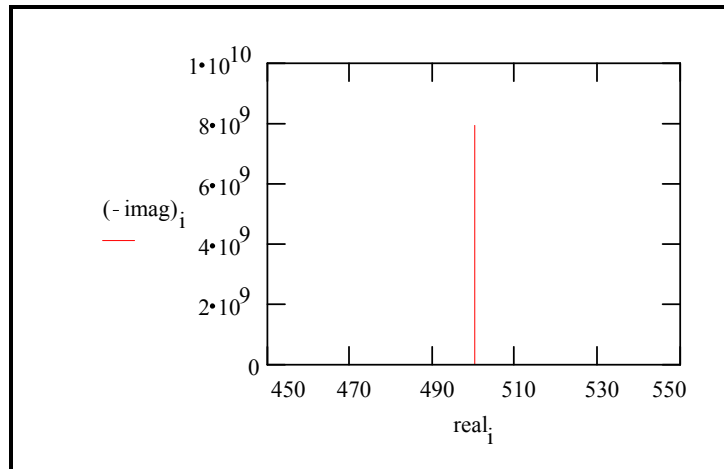**Purely Capacitive Coating**



The model includes a resistor (due primarily to the electrolyte) and the coating capacitance in series.

A Nyquist plot for this model is shown in figure 3-12.  In making this plot, the following values were assigned:

$R = 500 \; \Omega$ (a bit high but realistic for a poorly conductive solution)
$C = 200 \; pF$ (realistic for a 1 $cm^2$ sample, a 25 $\mu M$ coating, and $\varepsilon_r = 6$)
$F_i = 0.1 \; Hz$ (lowest scan frequency -- a bit higher than typical)
$F_f = 100 \; kHz$ (highest scan frequency)

**Figure 3-12**
**Typical Nyquist Plot for an Excellent Coating**



The value of the capacitance cannot be determined from the Nyquist plot.  It can be determined by a curve fit or from an examination of the data points.  Notice that the intercept of the curve with the real axis gives an estimate of the solution resistance.

The highest impedance on this graph is close to $10^{10} \; \Omega$.  This is close to the limit of measurement of most EIS systems.

The same data are shown in a Bode plot in Figure 3-13. Notice that the capacitance can be estimated from the graph but the solution resistance value does not appear on the chart. Even at 100 kHz, the impedance of the coating is higher than the solution resistance.

**Figure 3-13**
**Typical Bode Plot for an Excellent Coating**



Water uptake into the film is usually a fairly slow process. It can be measured by taking EIS spectra at set time intervals. An increase in the film capacitance can be attributed to water uptake.

## Model #2 -- Randles Cell

The Randles cell is one of the simplest and most common cell models. It includes a solution resistance, a double layer capacitor and a charge transfer or polarization resistance. In addition to being a useful model in its own right, the Randles cell model is often the starting point for other more complex models.

The equivalent circuit for the Randles cell is shown in Figure 3-14. The double layer capacity is in parallel with the impedance due to the charge transfer reaction.

**Figure 3-14**
**Randles Cell Schematic Diagram**



Figure 3-15 is the Nyquist plot for a typical Randles cell. The parameters in this plot were calculated assuming a 1 cm$^2$ electrode undergoing uniform corrosion at a rate of 1 mm/year. Reasonable assumptions were made for the $\beta$ coefficients, metal density and equivalent weight. The polarization resistance under these conditions calculated out to 250 $\Omega$. A capacitance of 40 $\mu$F/cm$^2$ and a solution resistance of 20 $\Omega$ were also assumed.

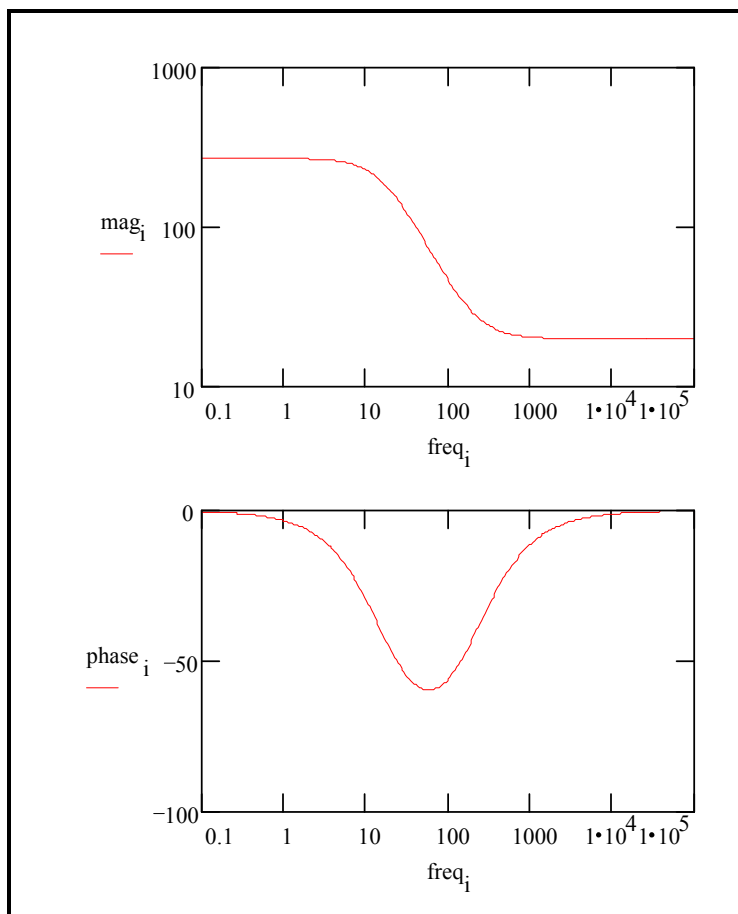**Figure 3-15**
**Nyquist Plot for 1 mm/year Corrosion Rate**

The Nyquist plot for a Randles cell is always a semicircle. The solution resistance can found by reading the real axis value at the high frequency intercept. This is the intercept near the origin of the plot. Remember this plot was generated assuming that $R_s = 20\ \Omega$ and $R_p = 250\ \Omega$.

The real axis value at the other (low frequency) intercept is the sum of the polarization resistance and the solution resistance. The diameter of the semicircle is therefore equal to the polarization resistance (in this case $250\ \Omega$).

Figure 3-16 is the Bode plot for the same cell. The solution resistance and the sum of the solution resistance and the polarization resistance can be read from the magnitude plot. The phase angle does not reach 90° as it would for a pure capacitive impedance. If the values for $R_s$ and $R_p$ were more widely separated the phase would approach 90°.

**Figure 3-16**
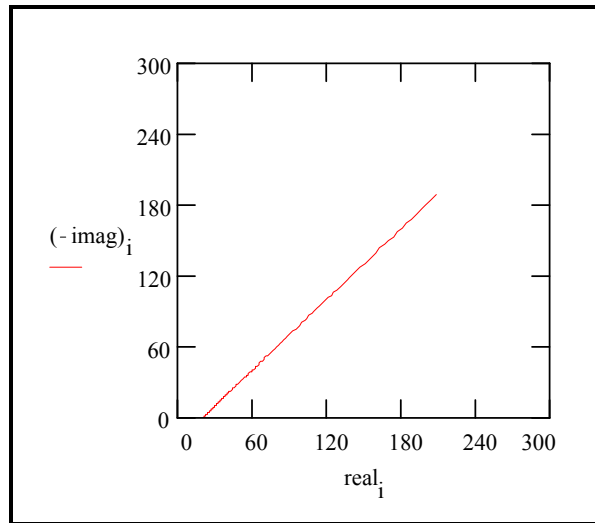**Bode Plot for 1 mm/year Corrosion Rate**

## Model #3 -- Mixed Kinetic and Diffusion Control

First consider a cell where semi-infinite diffusion is the rate-determining step, with a series solution resistance as the only other cell impedance.
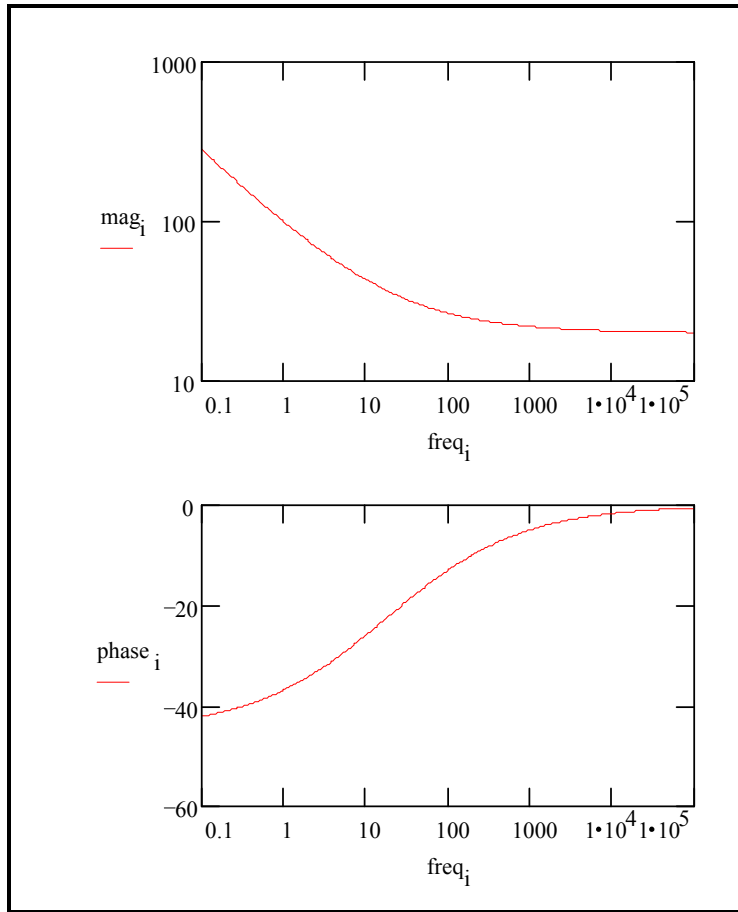
A Nyquist plot for this cell is shown in Figure 3-17. $R_s$ was assumed to be 20 Ω. The Warburg coefficient calculated to be about 120 Ωsec$^{-1/2}$ at room temperature for a two electron transfer, diffusion of a single species with a bulk concentration of 100 μM and a typical diffusion coefficient of 1.6 x10$^{-5}$ cm$^2$/sec. Notice that the Warburg Impedance appears as a straight line with a slope of 45°.

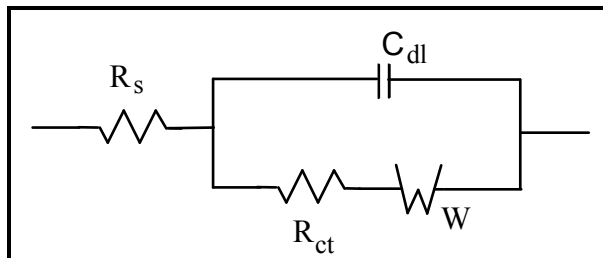**Figure 3-17**
**Nyquist Plot for a Warburg Impedance**

The same data is plotted in the Bode format in Figure 3-18.  The phase angle of a Warburg impedance is 45°.

**Figure 3-18**
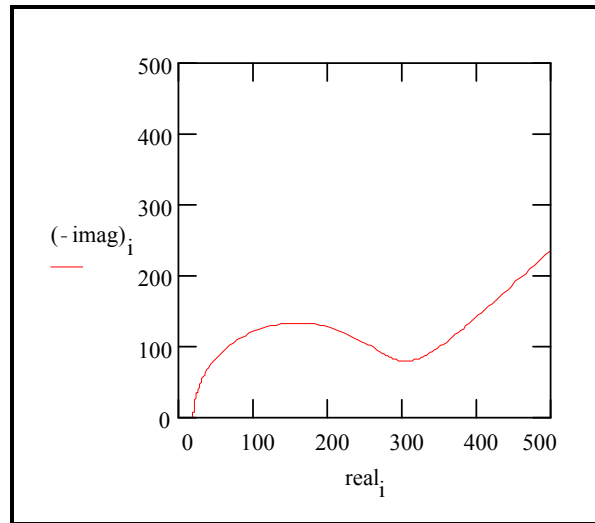**Bode Plot for a Warburg Impedance**



Adding a double layer capacitance and a charge transfer impedance, we get the equivalent circuit in Figure 3-19.

**Figure 3-19**
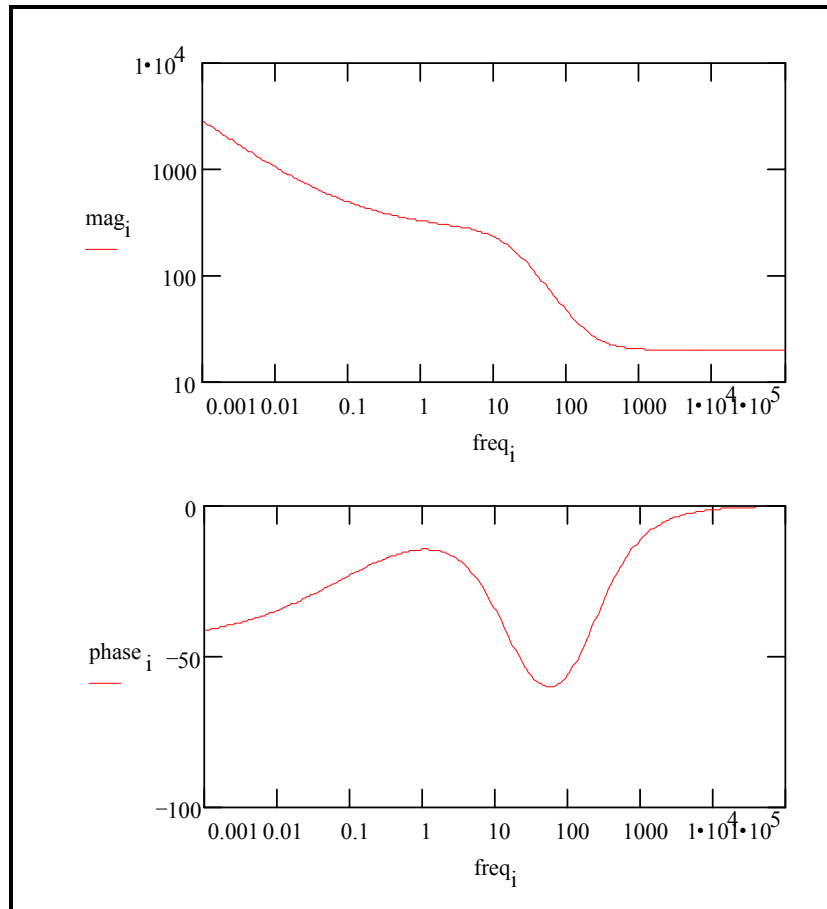**Equivalent Circuit with Mixed Kinetic and Charge Transfer Control**



This circuit models a cell where polarization is due to a combination of kinetic and diffusion processes.  The Nyquist plot for this circuit is shown in Figure 3-20.  As in the above example, the Warbug coefficient is assumed to be to be about 150 $\Omega$ sec$^{-1/2}$.  Other assumptions:  $R_s = 20\ \Omega$, $R_{ct} = 250\ \Omega$, and $C_{dl} = 40\ \mu F$.

**Figure 3-20**
**Nyquist Diagram for Mixed Control Circuit**



The Bode plot for the same data is shown in Figure 3-21. The lower frequency limit was moved down to 1mHz to better illustrate the differences in the slope of the magnitude and in the phase between the capacitor and the Warburg impedance. Note that the phase approaches 45° at low frequency.

**Figure 3-21**
**Bode Plot for the Mixed Control Circuit**

# Model #4 -- Coated Metal

The impedance behavior of a purely capacitive coating was discussed above. Most coatings degrade with time, resulting in more complex behavior.

After a certain amount of time, water penetrates into the coating and forms a new liquid/metal interface under the coating. Corrosion phenomena can occur at this new interface.
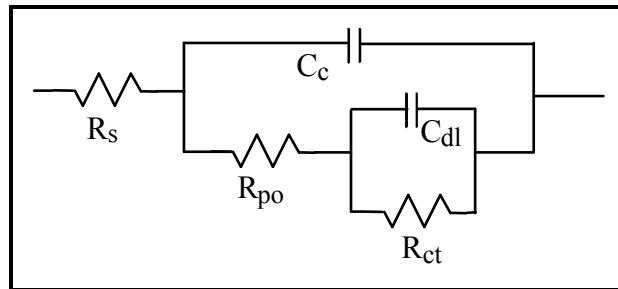
The impedance of coated metals has been very heavily studied. The interpretation of impedance data from failed coatings can be very complicated. Only the simple equivalent circuit shown in Figure 3-22 will be discussed here.

Even this simple model has been the cause of some controversy in the literature. Most researchers agree that this model can be used to evaluate the quality of a coating. However, they do not agree on the physical processes that create the equivalent circuit elements. The discussion below is therefore only one of several interpretations of this model.

$C_c$ represents the capacitance of the intact coating. Its value is much smaller than a typical double layer capacitance. Its units are pF or nF, not µF. $R_{po}$ (pore resistance) is the resistance of ion conducting paths that develop in the coating. These paths may not be physical pores filled with electrolyte.

On the metal side of the pore, we assume that an area of the coating has delaminated and a pocket filled with an electrolyte solution has formed. This electrolyte solution can be very different from the bulk solution outside of the coating. The interface between this pocket of solution and the bare metal is modeled as a double layer capacity in parallel with a kinetically controlled charge transfer reaction.

**Figure 3-22**
**Equivalent Circuit for a Failed Coating**



When you use EIS to test a coating, you fit a data curve to this type of model. The fit estimates values for the model's parameters, such as the pore resistance or the double layer capacitance. You then use these parameters to evaluate the degree to which the coating has failed.
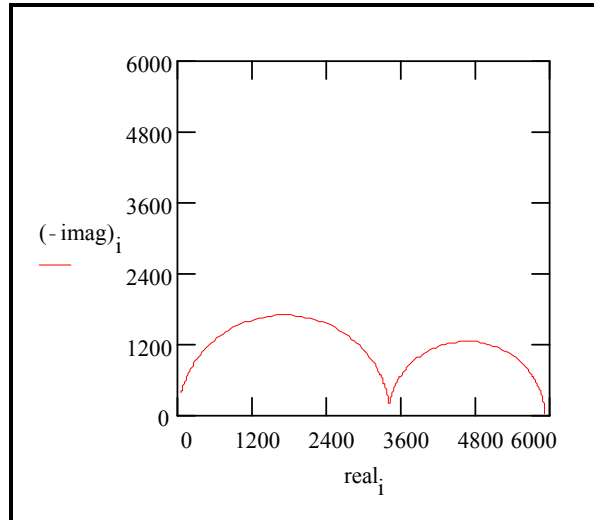
In order to show a realistic data curve, we need to do this operation in reverse. Assume that we have a 10 cm$^2$ sample of metal coated with a 12 μM film and that we have 5 delaminated areas. 1% of the total metal area is delaminated. The pores in the film that access these delaminated areas are represented as solution filled cylinders with a 30 μM diameter.

The parameters used to develop the curves are shown below:

| | | |
|---|---|---|
| $C_c$ | = 4 nF | Calculated for 10 cm$^2$ area , $\varepsilon_r$ = 6 and 12 μM thickness |
| $R_{po}$ | = 3400 Ω | Calculated assuming $\kappa$ = 0.01 S/cm |
| $R_s$ | = 20 Ω | Assumed |
| $C_{dl}$ | = 4 μF | Calculated for 1% of 10 cm$^2$ area and assuming 40 μF/cm$^2$ |
| Rct | = 2500 Ω | Calculated for 1% of 10 cm$^2$ area and using Polarization Resistance assumptions from an earlier discussion |

With these parameters, the Nyquist plot for this model is shown in Figure 3-23. Notice that there are two well defined time constants in this plot.
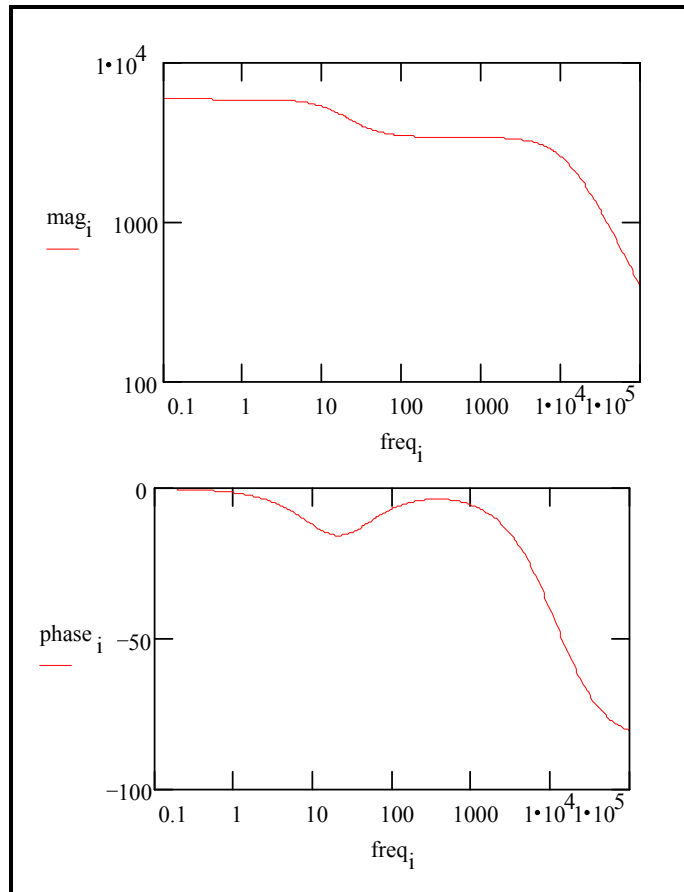
**Figure 3-23**
**Nyquist Plot for a Failed Coating**

The Bode plot of the same data is shown in Figure 3-24.  The two time constants are visible but less pronounced on this plot.

The Bode plot does not go high enough in frequency to measure the solution resistance.  In practice this is not a problem, because the solution resistance is a property of the test solution and the test cell geometry, not a property of the coating.  Therefore, it is usually not very interesting when you are testing coatings.

**Figure 3-24**
**Bode Plot for a Failed Coating**

# Extracting Model Parameters from Data

## Modeling Overview

EIS data is generally analyzed in terms of an equivalent circuit model. The analyst tries to find a model whose impedance matches the measured data.

The type of electrical components in the model and their interconnections controls the shape of the model's impedance spectrum. The model's parameters (i.e. the resistance value of a resistor) controls the size of each feature in the spectrum. Both these factors effect the degree to which the model's impedance spectrum matches a measured EIS spectrum.

In a physical model, each of the model's components is postulated to come from a physical process in the electrochemical cell. All of the models discussed earlier in this chapter are physical models. The choice of which physical model applies to a given cell is made from knowledge of the cell's physical characteristics. Experienced EIS analysts use the shape of a cell's EIS spectrum to help choose among possible physical models for that cell.

Models can also be partially or completely empirical. The circuit components in this type of model are not assigned to physical processes in the cell. The model is chosen to given the best possible match between the model's impedance and the measured impedance.

An empirical model can be constructed by successively subtracting component impedances from a spectrum. If the subtraction of an impedance simplifies the spectrum, the component is added to the model, and the next component impedance is subtracted from the simplified spectrum. This process ends when the spectrum is completely gone (Z=0).

As we shall see, physical models are generally preferable to empirical models.

## Non-linear Least Squares Fitting

Modern EIS analysis uses a computer to find the model parameters that cause the best agreement between a model's impedance spectrum and a measured spectrum. A non-linear least squares fitting (NLLS) algorithm is used.

NLLS starts with initial estimates for all the model's parameters. Starting from this initial point, the algorithm makes changes in several or all of the parameter values and evaluates the resulting fit. If the change improves the fit, the new parameter value is accepted. If the change worsens the fit, the old parameter value is retained. Next a different parameter value is changed and the test is repeated. Each trial with new values is called an iteration. Iterations continue until the goodness of fit exceeds an acceptance criterion, or until the number of iterations reaches a limit.

NLLS algorithms are not perfect. In some cases they do not converge on a useful fit. This can be the result of several factors including:
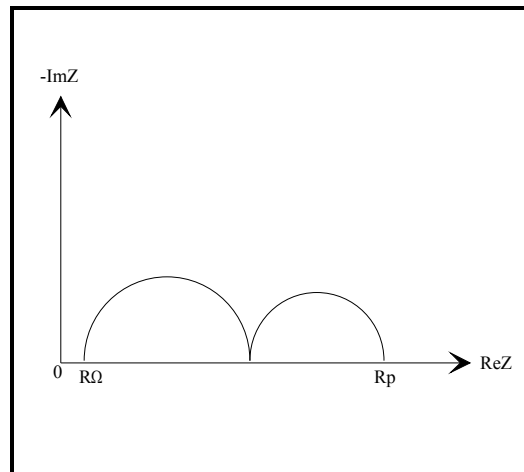
- An incorrect model for the data set being fitted.
- Poor estimates for the initial values.
- Noise

In addition, the fit from an NLLS algorithm can look poor when the fit's spectrum is superimposed on the data spectrum. It appears as though the fit ignores a region in the data. To a certain extent this is what happens. The NLLS algorithm optimizes the fit over the entire spectrum. It does not care if the fit looks poor over a small section of the spectrum.
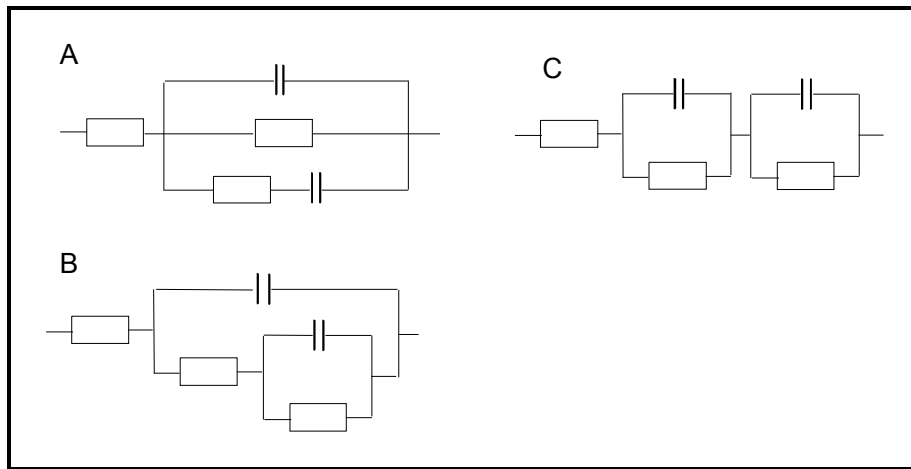
## Uniqueness of Models

The impedance spectrum shown in Figure 3-25 shows two clearly defined time constants.

**Figure 3-25**
**Two Time Constant Spectrum**

This spectrum can be modeled by any of the equivalent circuits shown in Figure 3-26.

**Figure 3-26**
**Equivalent Circuit Models with Two Time Constants**



As you can see, there is not a unique equivalent circuit that describes the spectrum. You cannot assume that an equivalent circuit that produces a good fit to a data set represents an accurate physical model of the cell.

Even physical models are suspect in this regard. Whenever possible, the physical model should be verified before it is used. One way to verify the model is to alter a single cell component (for example increase a paint layer thickness) and see if you get the expected changes in the impedance spectrum.

Empirical models should be treated with even more caution. You can always get a good looking fit by adding lots of circuit elements to a model. Unfortunately, these elements will have little relevance to the cell processes that you are trying to study. Drawing conclusions based on changes in these elements is especially dangerous. Empirical models should therefore use the fewest elements possible.

## Literature

The following sources were used in preparing this chapter. The reader is encouraged to consult them for additional information.

*Impedance Spectroscopy; Emphasizing Solid Materials and Systems* , J.R. Macdonald, Wiley Interscience publications, 1987.

*Electrochemical Methods; Fundamentals and Applications*, A.J. Bard, L.R. Faulkner, Wiley Interscience publications, 1980.

*Electrochemical Impedance: Analysis and Interpretation*, J.R. Scully, D.C. Silverman, and M.W. Kendig, editors, ASTM, 1993.

*Physical Chemistry*, P.W. Atkins, Oxford University Press ,1990.

*Signals and Systems*, A.V. Oppenheim and A.S. Willsky, Prentice-Hall, 1983.

*The Use of Impedance Measurements in Corrosion Research; The Corrosion Behavior of Chromium and Iron Chromium Alloys*, J.A.L. Dobbelaar, PhD thesis TU-Delft, 1990.

*Characterization of Organic Coatings with Impedance Measurements; A Study of Coating Structure, Adhesion and Underfilm Corrosion*, F. Geenen, PhD thesis, TU-Delft, 1990.

*Identification of Electrochemical Processes by Frequency Response Analysis*, C. Gabrielle, Solartron Instrumentation Group, 1980.

*Comprehensive Treatise of Electrochemistry; Volume 9 Electrodics: Experimental Techniques*; E. Yeager, J.O'M. Bockris, B.E. Conway, S. Sarangapani, Chapter 4 "AC Techniques", M. Sluyters-Rehbach, J.H. Sluyters, Plenum Press, 1984.

Mansfeld, F., "Electrochemical Impedance Spectroscopy (EIS) as a New Tool for Investigation Methods of Corrosion Protection", Electrochimica Acta 35(10), pp 1533-1544, 1990.

Walter, G.W., "A Review of Impedance Plot Methods Used for Corrosion Performance Analysis of Painted Metals", Corrosion Science 26(9), pp 681-703, 1986.

Kendig, M., J. Scully, "Basic Aspects of Electrochemical Impedance Application for the Life Prediction of Organic Coatings on Metals", Corrosion 1990 (1), pp 22.