

Evaluation of Organic Coatings with Electrochemical Impedance Spectroscopy

Part 2: Application of EIS to Coatings

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Part 1 of this series (August 2004 JCT CoatingsTech, page 46) described Electrochemical Impedance Spectroscopy (EIS) in general terms. In Part 2, the focus is on painted metal substrates and how their specific characteristics affect the EIS measurement and interpretation. Part 3 will address experimental protocols using EIS to test the performance of paints.

WHAT CAN EIS TELL US ABOUT PAINTS?

EIS can generate quantitative data that relates to the quality of a coating on a metal substrate. EIS is a very sensitive detector of the condition of a coated metal, so the EIS response can indicate changes in the coating long before any visible damage occurs. EIS is not an absolute measurement. An EIS spectrum only tells us something when we compare it to another EIS spectrum. Any experiment designed to measure coating quality must include a mechanism to stress the coating and induce its failure. By making periodic EIS measurements during the stress process, a rate of coating failure can be estimated. EIS is a nondestructive measurement, so we can use EIS to track the condition of a coated metal sample as it changes. In most cases, it is possible to identify the cause of coating failure.

In almost every experiment, the coated metal is exposed to an electrolyte, a solution chosen to either simulate a specific environment or to conduct a standardized test (ASTM B 117, for example). In almost all cases, the electrolyte contains dissolved salts so it is nicely suited for electrochemical experiments.

ASTM (D01.27.32) and ISO (TC35/SC9/WG29) will publish a Standard Practice for Electrochemical Impedance Spectroscopy (EIS) on High Impedance Coated Samples in late 2004. This Standard will provide guidelines for the collection of EIS data from high impedance samples. It will include round robin results on high impedance dummy cells, which simulate a coated metal.

AN ELECTROCHEMICAL DESCRIPTION OF AN ORGANIC COATING ON A METAL SUBSTRATE

Electrochemical techniques are typically used on conductive materials such as metals, batteries, etc. Applying an electrochemical technique to a painted sample, which is inherently nonconductive, is somewhat non-intuitive. However, when you consider that electrochemistry is very commonly used to study corrosion of metals and that paints are employed to control corrosion on metals in industrial and marine environments, then you can begin to imagine some interesting possibilities.

Why is EIS so useful for paints? It is useful because using EIS to characterize a painted metal substrate simultaneously measures two phenomena: (1) the deterioration of the organic coating caused by exposure to an electrolyte and (2) the increase in corrosion rate of the underlying substrate due to the deterioration of the coating and subsequent attack by the electrolyte.

In EIS, an AC voltage of varying frequency is applied to the sample. It is

useful to think of the frequency as a camera shutter that can be very fast (high frequency) for fast reactions and very slow (low frequency) for slow reactions. This is the technical feature that allows EIS to gather so much information on an electrochemical reaction in one experiment. And this is why EIS is more useful for coatings than DC electrochemical techniques.

As was said in Part 1, EIS can quantitatively measure both resistances and capacitances in the electrochemical cell. A resistance corresponds to electron-transfer reactions such as corrosion. The capacitance of a metal electrode in contact with an electrolyte is important information for any electrochemical system. For organic coatings, the capacitance measurement is particularly revealing. As the organic coating deteriorates with time during exposure to an electrolyte, EIS can track changes in the capacitance of the coating. The capacitance will change as the coating swells or absorbs water, for example. In addition, we can measure changes in the porosity of the coating. EIS can also simultaneously monitor the rate of corrosion of the metallic substrate which generally increases as the protective coating fails, allowing the electrolyte to contact the substrate.

To quantify these physical and chemical processes with EIS, we need an appropriate equivalent circuit. Even more frightening, we need to actually start thinking of the coated sample as a collection of electrical elements. As noted in Part 1, each element of the equivalent circuit should model a specific function of the sample. The equivalent circuit that is most commonly used to describe an organic coating on a metal

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lic substrate is shown in *Figure 1*. Not surprisingly, this equivalent circuit is more complex than the Randles cell from Part 1. Each of the circuit elements describes a "portion" of the sample that is in contact with an electrolyte. In *Figure 1*, the equivalent circuit is overlaid on a schematic of a coated metal substrate.

RU: UNCOMPENSATED RESISTANCE—The resistance of the electrolyte between the working electrode and reference electrode. For studies of organic coatings, the electrolyte is very conductive, so Ru is usually very low (1-50 ohms) and can be ignored.

COATING: COATING CAPACITANCE—The capacitance of the organic coating is an important parameter to measure during coating failure. Because most coatings are relatively thick, the coating capacitance tends to be rather low—in the range of 1 nF/cm². The physical and chemical properties of the coating that affect the capacitance are:

$$C_{\text{coating}} = (\epsilon)(\epsilon_0)(A)/t \quad (1)$$

where ϵ is the dielectric constant of the coating, ϵ_0 is 8.85×10^{-14} Farads/cm, A is the area (cm²), and t is the thickness (cm).

The capacitance is related to the magnitude of the impedance ($|Z|$) by

$$|Z| = 1 / (2\pi f C_{\text{coating}}) \quad (2)$$

where f is the frequency of the applied AC voltage.

RPORE: PORE RESISTANCE—The resistance of the coating changes during exposure due to the penetration of electrolyte into the micropores of the coating. Upon immersion, the Pore Resistance can be very high ($>10^{10}$ ohm) and usually decreases with time of exposure to the electrolyte. However, it is not unusual for R_{po} to increase after long exposure times; the increase is commonly attributed to corrosion products from the metal substrate blocking the pores.

RP: POLARIZATION RESISTANCE—The corrosion rate of the metal substrate beneath the coating is described by the Polarization Resistance. For a metal in the absence of a coating, the corrosion rate can be determined from the Polarization Resistance. The Polarization Resistance is inversely proportional to the corrosion rate. A typical Polarization Resistance for a bare metal is 5000 ohm-cm². R_p must be normal-

ized because it is electrode area dependent.

CDL: DOUBLE LAYER CAPACITANCE—The coating is not the only "structural" feature of the sample that gives rise to a capacitance. There is a charge on the metal electrode and a charge in the electrolyte that are separated by the metal-electrolyte interface. Since this interface is commonly known as the "double layer" in electrochemical theory, the capacitance is called the Double Layer Capacitance and abbreviated Cdl. The value of Cdl is usually in the range of 10–40 $\mu\text{F}/\text{cm}^2$. This capacitance is much higher than C_{coating} ($\sim 1 \text{ nF}/\text{cm}^2$, or $10^{-9} \text{ F}/\text{cm}^2$), so the Cdl of even a small holiday will be apparent in the EIS response. A scratch or holiday that exposes only 0.005% of the total sample area to the electrolyte has the same capacitance ($20 \mu\text{F} * 0.005\%$) as the entire intact area of the coating (1 nF). A coating that is adhering strongly to the metal surface does not allow metal-electrolyte contact, so Cdl can sometimes be related to delamination of the coating. Cdl must be normalized because it is electrode area dependent.

The two circuit elements that initially dominate the impedance are the Coating Capacitance and the Pore Resistance. The capacitance of a typical undamaged coating with good barrier properties is about 1 nF/cm². From equation (2), the impedance of 1 cm² of this coating at 1 Hz is about 10^9 ohms and increases at lower frequencies. The Pore Resistance of this coating is exceedingly high ($>10^{12}$ ohm), so that the sample behaves as a near-perfect capacitor. The impedance is high because there is no low impedance path through the sample.

Finally, the equivalent circuit in *Figure 1* is for the general case. For a coating that is under attack by an electrolyte, the values of the circuit elements will change (sometimes dramatically) as attack proceeds, which leads to changes in the EIS response.

ELECTROCHEMICAL INSTRUMENTATION FOR EIS OF COATINGS

Because of the nonconductive nature of an organic coating, coated metal samples typically exhibit very high impedances. The barrier properties of a coating prohibit contact between the

Capacitive Drift of Eoc

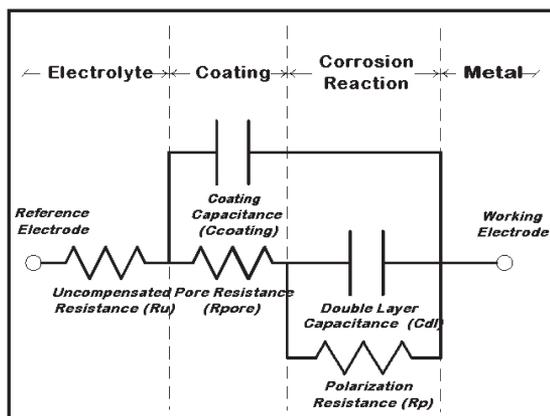
DC potential control is always used with impedance measurements to control the electrochemical reactions at the surface of the electrode while performing the impedance measurement. The DC potential applied during an EIS measurement on a coating is almost always the open-circuit potential. For a coated metal sample that is in excellent condition, it is difficult to obtain a stable value of the open-circuit potential. The nonelectroactive nature of the coatings causes the sample to behave like a capacitor, for which an open-circuit potential is undefined.

The electrometer that is built into a potentiostat measures the voltage of the sample. The electrometer is a very high impedance device. The ideal electrometer has a zero input current, but a real-world electrometer is not so perfect and exhibits an input current of several tens of picoamps. This low current is applied to the sample's capacitive coating and charges the capacitor. The result is an apparent open-circuit potential that steadily increases until it reaches the limit of the potentiostat (8–30 volts).

To circumvent this problem, the EIS experiment on good intact coatings should be performed at the open-circuit voltage of the bare, uncoated substrate in the electrolyte. The open-circuit voltage of the substrate should be measured in the electrolyte in a separate experiment. The value of the open-circuit potential is then used during the EIS measurement and specified "versus the reference electrode." The open-circuit potential of most common metals is between –1.0 and 0.5 volts.

As the coating deteriorates upon exposure to the electrolyte, the sample will assume more resistive characteristics. This condition can be recognized by a more stable value for the open-circuit potential. When this occurs, the DC potential during the EIS measurement may be defined with respect to the stable open-circuit potential for convenience.

Figure 1—Equivalent circuit of an organic coating on a metal substrate overlaid on a schematic of a painted metal surface.



electrolyte and the conductive metal substrate. This is especially true when the sample is initially immersed in the electrolyte. It is not unusual for the impedance of a fresh, intact coating to exceed 1010 ohms. During an EIS experiment, the current with this sample may be as low as 10 pA. (Remember that $I = E/Z$.) Because of these low currents, EIS measurements on coatings are not trivial and require special consideration.

An electrochemical impedance instrument consists of a potentiostat to apply the AC voltage and measure the current, associated electronics to measure the impedance, and an electrochemical cell to contain the sample. The potentiostat is the key component to address the high impedance of the coated sample. The potentiostat must have sufficient sensitivity to measure the low currents with suitable accuracy. The details of potentiostat performance in this regard were addressed in Part 1. This is very important; some EIS instruments will not have sufficient sensitivity to characterize a coating with good barrier properties.

CELLS AND SAMPLES

An electrochemical cell designed for EIS of coated metals is shown in Figure 2. The sample is clamped to the cell body and fixed in a horizontal position. The cell body contains an O-ring to form a leak-proof seal. The cell also contains a Saturated Calomel Reference Electrode and a graphite counter electrode. The electrolyte of choice is placed in the cell body and contacts the coated

metal sample. In most cases, the cell is unstirred.

The electrolyte is generally chosen to reflect service conditions. Exposing the painted metal to the exact environment it will encounter in the field is the best way to verify acceptable performance.

The electrode area of the paint sample should be 10–30 cm². This is a relatively large sample area, which has two benefits: (1) statistically, a large area has a high probability of exhibiting a defect in the coating, and (2) a large electrode area will exhibit higher currents than a smaller area.

The reference electrode in the electrochemical cell should be properly maintained. The junction material should be kept moist and the internal solution in the electrode should never be allowed to dry out. It is important to employ a low impedance junction material. The junction material is the contact to the cell and a high impedance at this point will enhance noise pick-up and may cause other instrumental problems. Follow the guidelines of the potentiostat's manufacturer.

Remember that the measured cell currents will be low, so a Faraday Cage should always be used. A Faraday Cage is a grounded conductive enclosure (i.e., a steel box) that is continuous and completely surrounds the cell and all the electrodes. It reduces current noise picked up by the working electrode and voltage noise picked up by the reference electrode. The instrument itself need not be placed inside the Faraday Cage. In most cases, the Faraday Cage is connected to an earth ground. For coated samples, a Faraday Cage is indispensable.

It is also possible to make EIS measurements on samples in the field, such as pipelines, offshore platforms, or aircraft. Clearly, the cell in Figure 2 cannot be used in a field application.

DATA ANALYSIS OF COATED SAMPLES

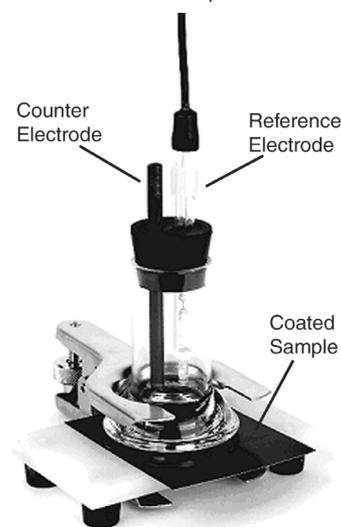
An experimental protocol that employs EIS to evaluate coating quality must include a stressing mechanism to induce the failure of the coating. The

pathway to coatings failure is monitored by making periodic EIS measurements on the sample as it is stressed. Changes in the Coatings Capacitance, Pore Resistance, Polarization Resistance, and Double Layer Capacitance can be measured and related to the rate of failure of the coating. These concepts will be discussed in Part 3 of this series.

Coating degradation proceeds through a number of stages,¹ described below. This proposed degradation route is a useful platform to describe the equivalent circuit diagrams and the EIS results expected at each stage. This is a very general case and all coatings will not show the same behavior. The degradation steps are described below and shown in Figure 3 with (1) an example of the appropriate equivalent circuit with typical values for the electrical elements, (2) a Bode plot, and (3) a Nyquist plot. It is wise (and with modern software, easy) to examine EIS data in both the Bode and Nyquist formats.

PURELY CAPACITIVE (Figure 3A): Upon initial exposure to an electrolyte, a high-performance coating with excellent barrier properties will act as an almost-perfect capacitor. At this stage, R_{pore} is extremely high. The Bode plot shows a straight line of slope -1 with high impedance at low frequency and a phase angle of -90° throughout the entire frequency range, characteristic of a pure capacitor. The capacitance value is dependent on the thickness of the coating and its dielectric constant [see equation

Figure 2—An electrochemical cell to perform EIS on a coated metal sample.



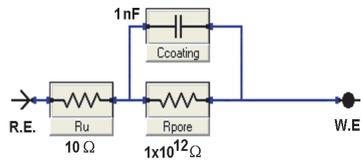


Figure 3A—Equivalent circuit of an intact paint film.

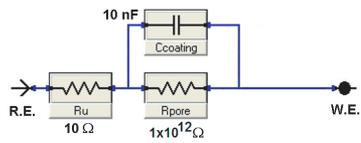
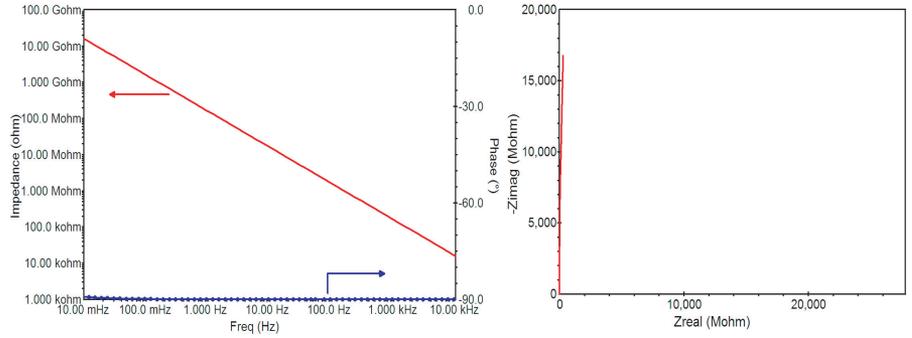


Figure 3B—Equivalent circuit for an undamaged coating with absorbed water.

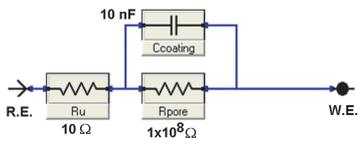
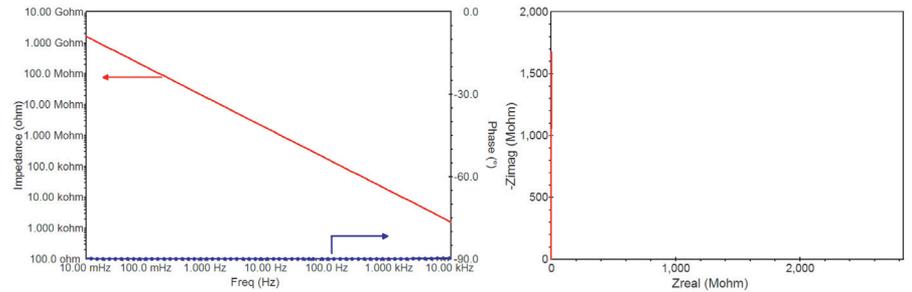


Figure 3C—Equivalent circuit for a coating that is developing a low Pore Resistance.

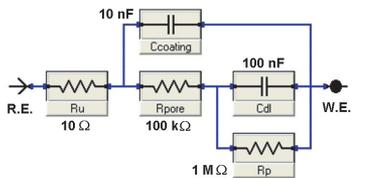
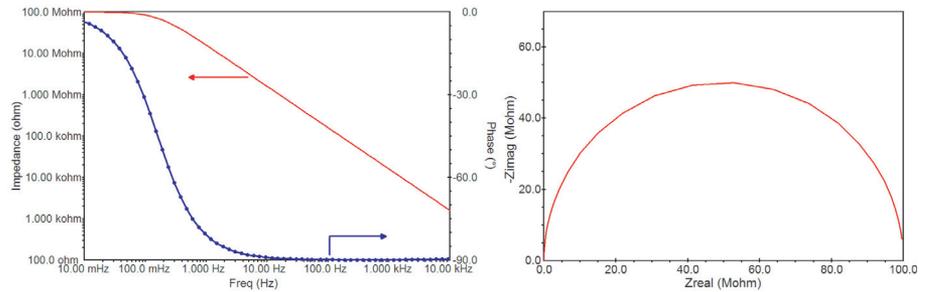


Figure 3D—Equivalent circuit for a freely corroding metal substrate.

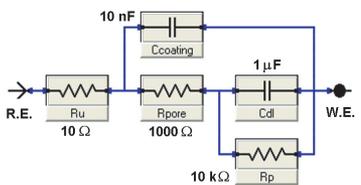
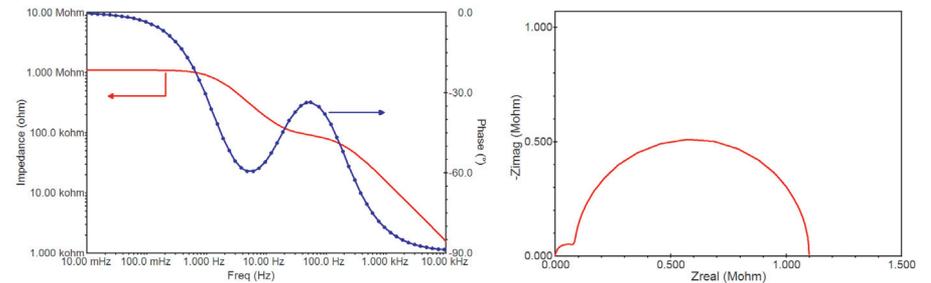


Figure 3E—Equivalent circuit for a painted metal substrate that has suffered major damage.

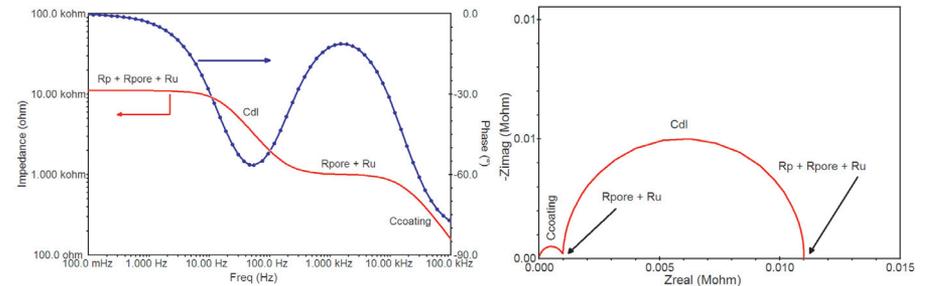


Figure 3—Degradation of an organic coating on a metal substrate. Equivalent circuit, Bode plot, and Nyquist plot for the five stages of coating failure.

(1)]. The initial capacitance of the coating is in the range 0.1 nF/cm² to 1 nF/cm², depending on the coating material and thickness.

The Nyquist plot for an undamaged coating lacks significant information. The intercept on the real axis is the uncompensated resistance (10 ohms), which is indistinguishable on this plot. You will recall that the response of a capacitor to an AC waveform is phase-shifted by 90°. For this reason, the real component of the impedance is zero and the total impedance is equal to the imaginary impedance.

ABSORPTION OF WATER (Figure 3B): The impedance from the Bode plot decreases when the coating absorbs water, but maintains a linear relationship with frequency. The slope does not change and the phase angle remains at -90°. Water has a higher dielectric constant (80) than that of the typical organic coating (2 to 5), so the capacitance of the coating with absorbed water is higher than that of the dry coating [see equation (1)]. The coating may also swell during this stage, which would have the effect of decreasing the capacitance. Because of the high dielectric constant of water, the effect of water absorption usually overwhelms the effect of swelling and the capacitance increases.

The initial effect of water absorption is to change the "value" of the capacitor, so the shape of the Nyquist plot does not change. The Nyquist plot is and will remain uninteresting until we begin to see resistive elements develop in the coating.

It may be useful to measure the rate of absorption of water by the coating in the early stages of exposure. The Brasher-Kingsbury equation² provides a convenient estimate of water uptake.

$$\text{Volume Fraction H}_2\text{O} = (\log C_t/C_o)/\log \epsilon_w \quad (3)$$

where C_t is the coatings capacitance at time t , C_o is the initial coatings capacitance, and ϵ_w is 80, the dielectric constant of water.

The Coating Capacitance can be quickly measured at any time by fitting the equivalent circuit to the EIS data.

DEVELOPMENT OF PORE RESISTANCE (Figure 3C): The next significant change is the decrease in Pore Resistance that occurs as the electrolyte penetrates the coating and creates a path to the surface of the underlying metal. The value of

the Pore Resistance is much lower than when initially immersed. The Pore Resistance results in a frequency-independent plateau at low frequencies in the Bode plot. The phase angle is no longer constant with frequency and the value is 90° only at high frequencies. At this stage, there is no significant corrosion of the metal substrate.

With the development of the lower Pore Resistance, the Nyquist plot exhibits the characteristic semi-circle of a Randles-like cell. The x-intercept at low frequency (to the left) is the Uncompensated Resistance and the x-intercept at high frequencies is the sum of the Uncompensated and Pore Resistance. In this instance, the imaginary impedance was not zero at the lowest frequency employed during the EIS experiment. Extending the lower frequency range would result in better definition of the semi-circle. However, since the answers from EIS are determined from the modeling, a pretty semi-circle will not improve the quality of the results at all.

INITIATION OF CORROSION OF THE METAL SUBSTRATE (Figure 3D): As the electrolyte penetrates the coating, an ever-increasing area of the metal substrate is contacted and corrosion is initiated. The Polarization Resistance and Double Layer Capacitance are area dependent. As the exposed area increases, the observed R_p decreases ($R_p \sim 1/\text{area}$) and the observed C_{dl} increases ($C_{dl} \sim \text{area}$). It is important to note that we are observing the corrosion reaction on a very small fraction of the total coated electrode area, a tribute to the sensitivity of EIS. At this stage, there is usually no visible evidence of corrosion.

The magnitude of the total impedance at low frequency in the Bode plot continues to drop. The effects of Polarization Resistance and the Double Layer Capacitance are now impacting the Bode plot. This is signaled by a more complex Bode plot, which now exhibits two breaks, or, in the language of Impedance Spectroscopists, "two time constants." The use of "time constants" implies a kinetic phenomenon and, indeed, that is the case.

The Nyquist plot shows two semi-circles, corresponding to the two time constants. The smaller semi-circle at high frequency (to the left) is due to the Coatings Capacitance and the semi-circle at lower frequency is due to the Double Layer Capacitance. The x-inter-

cept is equal to the sum of the Pore Resistance and Polarization Resistance.

With some coatings, the degradation process becomes diffusion-controlled as the system progresses toward active corrosion. Diffusion control is a very common process in electrochemistry and, since the coating impedes the movement of chemical species, not unexpected with coatings. The chemical species associated with diffusion in coatings is oxygen and cations (from the electrolyte) diffusing toward the metal and corrosion products diffusing away from the metal. When the electrochemical process is diffusion controlled, it is relatively easy to recognize from a Nyquist plot.³

MAJOR COATING DAMAGE (Figure 3E): During this final stage, the impedance is dominated by the general corrosion of the substrate. The total impedance at low frequencies in the Bode plot has decreased to an even lower value. It is not uncommon for the total impedance to change by 5-6 orders of magnitude between the initial immersion and destruction of the coating. In most cases, two time constants are apparent in the Bode plot of impedance magnitude. Note that the frequency range on the x-axis is different in this figure. Because of the lower impedances, the coating capacitance is only evident at higher frequencies. Active corrosion at the metal surface is often accompanied by delamination of the coating and formation of blisters. This is signaled by an increase in the Double Layer Capacitance and a slight decrease in the Coating Capacitance. Clogging of the pores by the corrosion products from the surface of the metal sometimes causes the Pore Resistance to increase.

The Nyquist plot usually exhibits two time constants and the semi-circles are often better defined than earlier in the deterioration process.

With a little experience, it is possible to quickly glean qualitative information on the coating from a visual inspection of the EIS curve. For example, the total impedance at low frequency is the sum of the Polarization Resistance, Pore Resistance, and Uncompensated Resistance, while the impedance at the break in a "two time constant" Bode plot is due to the Pore Resistance and Uncompensated Resistance. For paint studies, the Uncompensated Resistance can usually be ignored. The high frequency "capacitive" region (so-called

because the impedance is dependent on frequency) of the Bode plot is due to the Coating Capacitance. The second capacitive region is due to the Double Layer Capacitance. The same is true in a Nyquist plot, but may not be as visibly apparent as in the Bode plot. These regions are labeled in *Figure 3E*.

Despite these qualitative short cuts, we advise the EIS newcomer to trust in equivalent circuit modeling to calculate the quantitative data. As the coating deteriorates, the changes in the EIS curve can be very subtle and easy to overlook. The mathematics of the curve-fitting algorithm is rigorous and will easily identify the equivalent circuit elements and their values that are necessary to describe the condition of the coating and the metal substrate.

PREDICTING DELAMINATION FROM EIS MEASUREMENTS

Adhesion of a paint film to the metal substrate is a key measure of performance. Adhesion has both chemical and physical aspects. Adhesion is typically measured semi-quantitatively by a simple physical test such as ASTM D610, D714, D1654, D3359, and D6677.

EIS may provide information on the loss of adhesion. Specifically, the

Polarization Resistance and Double Layer Capacitance may relate to the adhesion of the film to the surface. R_p and C_{dl} , which are characteristics of the bare metal, will not become apparent in the EIS measurement until the electrolyte traverses the coating and contacts the metal. The resulting under-film corrosion may cause loss of adhesion of the paint film to the substrate.

However, it is possible for the characteristics of the paint film to complicate the measurement of R_p and C_{dl} . If the barrier properties of the coating are good (despite the presence of under-film corrosion), then the high value of R_{pore} may cloak the presence of R_p and C_{dl} . R_p and C_{dl} will only be apparent in the EIS measurement if their impedance is of the same order of magnitude as R_{pore} . In effect, the EIS characteristics of a coating with excellent barrier properties may mask under-film corrosion.

Therefore, in the case where the barrier properties remain good, the use of R_p and C_{dl} to predict delamination may be questionable. If R_p and C_{dl} cannot be measured, then EIS will not work. If R_p and C_{dl} can be measured, EIS may be useful.

EIS cannot be used to measure the loss of adhesion that results from the physical properties of the coating and the substrate.

SUMMARY

The focus of this article was electrochemical impedance measurements on coatings. We introduced the electrochemical description of an organic coated metal surface and a general equivalent circuit model of this surface was proposed. Some of the pitfalls of the actual measurement were noted and then the five stages of coatings degradation were described.

In the final article, we will discuss how coating scientists use the various methods available to get an understanding of failures modes of coatings. These protocols include methods of stressing the coating, such as cabinet tests, used in conjunction with electrochemical impedance measurements. [CT](#)

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