# Electrochemical Impedance Spectroscopy for Coating Evaluation using a Micro Sensor

Nicholas Waters[1], Richard Connolly[2], Douglas Brown[3], and Bernard Laskowski[4]

[1,2,3,4] *Analatom Inc., Santa Clara, CA 95054, USA*

*Nicholas.waters@analatom.com*
*Richard.Connolloy@analatom.com*
*doug.brown@analatom.com*
*Bernard.Laskowski@analatom.com*

## ABSTRACT

This paper discusses a micro-linear polarization resistance (μLPR) sensor modified to perform coating evaluation by means of electrochemical impedance spectroscopy (EIS). A circuit model is used with the EIS data to measure solution resistance, pore resistance, charge transfer resistance, intact coating capacitance, and double layer capacitance. These measurements allow the end user to monitor degradation of protective coatings in real-time, through non-destructive means. This is demonstrated through an accelerated aging test using a coated metal plate with a modified μLPR sensor. A metal panel made from aluminum alloy 7075-T6 was coated with 2 mils of an epoxy-based polymer coating and 2 mils of high solids polyurethane. The sensor was adhered to the face of the coated panel in a manner that allowed the electrolyte solution consisting of 3.5% NaCl to flow between the sensor and the coated surface of the panel. EIS measurements were acquired every hour for a total of 35 hours and at the conclusion of the test, changes in key parameters within the circuit model identified the initial time and mechanism of coating degradation, in this case, delamination.

## 1. BACKGROUND

Polymer coatings are commonly applied to metal substrates to prevent contact with natural elements that initiate and perpetuate corrosion. This corrosion process requires the metal be in contact with oxygen and an electrolyte. Protective coating integrity is of utmost importance to maximize remaining useful life of equipment and minimize costs associated with maintenance and repairs. Electrochemical impedance spectroscopy (EIS) provides a means of monitoring the present condition of a protective coating. Small defects in the protective coating, if undetected and unaddressed, can lead to coating failures, thus providing pathways for the electrolyte to reach the metal substrate.

The British Standards Institution's (BSI) Publicly Available Specification for the optimized management of physical assets defines asset management as the "systematic and coordinated activities and practices through which an organization optimally and sustainably manages its assets and asset systems, their associated performance, risks and expenditures over their life cycles for the purpose of achieving its organizational strategic plan." The motivation for effective asset management is driven by owners' desire for higher value assets at less overall costs, thus extracting the maximum value from their assets (Engineering, 2012). Condition-based maintenance aims to maximize asset value by extending the useful life of assets through mitigation of unnecessary maintenance actions performed during schedule based maintenance strategies. By providing maintenance engineers with information regarding the health of the structure, maintenance can be performed on a basis of necessity unique to each asset, as opposed to schedule-based predictions formed on statistical trends of operational reliability.

Protective coatings are the first line of defense against corrosion for metal substrates. Coatings aim to prolong the integrity of metal structures by creating a barrier between the elements and the metal substrate. Removing the possibility of contact with electrolytic fluid prevents electron transfer between the anodic and cathodic portions of the metal, which prevents the oxidation-reduction reactions that lead to metal loss. EIS measurements evaluate the integrity of the protective coating and are the first indication of compromised structural health of an asset.

The micro-linear polarization resistance (μLPR) corrosion sensor presented in this paper, provides insight into the health of coated metal structures through non-destructive

---

testing. In its native configuration, this sensor is capable of identifying coating failure through changes in polarization resistance and time-of-wetness measurements which is further explained in (Brown, 2014). By measuring changes in the electrochemical properties of the coating, EIS is able to monitor coating degradation over time. Coupling EIS with linear polarization resistance provides a broader assessment of structural and coating integrity by answering "why" and "how" failure occurs on susceptible components.

EIS can be used as a non-destructive method of performing coating evaluation in real time. Impedance values of the electrochemical cell are determined by applying a sinusoidal voltage at various fixed frequencies and measuring the current response. Impedance is calculated from the current's magnitude and phase response with respect to the applied potential across an electrochemical cell. Typically, EIS measurements are represented by either Bode or Nyquist plots. After acquiring EIS data, a circuit model representing the impedance of the coating is selected that provides the best fit for experimental data. Once the appropriate model is selected, it is possible to extract values for model parameters, such as resistance and capacitance. EIS provides insight into how each parameter changes by the electrochemical properties of the coating as the coating degrades over time; this provides insight into the level and type of degradation taking place (David Loveday, 2004; Gamry Instruments, 2011).

## 2. LITERATURE REVIEW

Coating degradation is a costly problem that many industries face. The best way to minimize costs associated with corrosion is to mitigate the effects through preventative conservation. Similar to the metal substrate, the coating degrades over time leaving the metal exposed to the elements. Providing service engineers insight into the state of their protective coatings is not only critical when dealing with valuable equipment, but also in the preservation of historical artifacts, where corrosion is taking place on priceless historical pieces (Emilio Cano, 2010).

Proper application of the coating is one of the main factors affecting lifetime and performance. Improper application of the coating can lead to poor adhesion to the metal substrate which provides pathways for corrosive substances to undercut the coating and compromise the coating's ability to protect the metal from corrosion. EIS provides a means of monitoring and evaluating the key parameters that change as the coating degrades over time, providing the user an opportunity to intercept the degradation pathways with preventative maintenance strategies (Api Popoola, 2014; M. Taqi Zahid Butt, n.d.).

## 3. IMPEDANCE AND EQUIVALENT CIRCUIT FOR COATING EVALUATION

The use of EIS to measure coating degradation relies on impedance measurements. Impedance is a measure of a circuit's ability to resist current and is defined as the ratio of the applied voltage to the current. A small amplitude sinusoidal excitation signal is applied across the coating. The amplitude of this excitation signal must be low, as the simple linear relationship relating resistance to current and voltage, shown in Eq. (1), becomes non-linear with more complex circuits.

$$R = \frac{E}{I} \text{ , (equation for an ideal resistor)} \tag{1}$$

where E is the voltage and I is the current. In more complex non-linear systems, impedance is the metric used to represent the circuit's ability to resist the flow of current. By applying a small amplitude excitation potential to the electro-chemical cell, it is possible to observe a pseudo-linear response in the response current which is shifted in phase. This excitation potential is expressed according to Eq. (2)

$$\vec{E}_t = E_o \sin(\omega t) , \tag{2}$$

where $\vec{E_t}$ is the applied potential, $E_0$ is the amplitude of the applied potential, and ω is the radial frequency (2πf). The response current is expressed according to Eq. (3)

$$\vec{I}_t = I_o \sin(\omega t + \phi) , \tag{3}$$

where $\vec{I}_t$ is the response current, $I_o$ is the amplitude of the response current, $\omega$ is the radial frequency, and $\phi$ is the phase. The impedance is then defined as the ratio of the applied potential to the response current as shown in Eq. (4)

$$Z = \frac{E_t}{I_t} . \tag{4}$$

A potentiostat is used to apply a frequency sweep of the potential across the electrochemical cell and measure the response current. These data are then used to calculate the resulting impedance. Data is plotted using a Bode plot which displays phase and impedance as a function of frequency. EIS relies on fitting a model to impedance values based on an equivalent circuit representation of the interrogated electrochemical system. Impedance values for different circuit components are listed below in Table 1.

Table 1. Circuit components and corresponding impedance values.

| Circuit Component | Impedance $(Z)$ |
|---|---|
| Resistor | $R$ |
| Inductor | $J\omega L$ |
| Capacitor | $1/(J\omega C)$ |

*Where R = Resistance, ω is radial frequency, L is inductance,* $J=\sqrt{-1}$*, and C is capacitance.*

For a linear system and circuit components wired in series (Figure **1**), the equivalent impedance value is calculated according to Eq. (5).

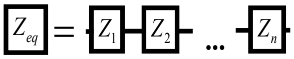


Figure 1. Circuit components wired in series.

$$Z_{eq}=Z_1+Z_2+...+Z_n \; . \tag{5}$$

For circuit components wired in parallel (Figure **2**), the equivalent impedance value is calculated according to Eq. (6).

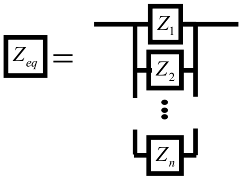


Figure 2. Circuit components wired in parallel.

$$\frac{1}{Z_{eq}}=\frac{1}{Z_1}+\frac{1}{Z_2}+...+\frac{1}{Z_n} \; . \tag{6}$$

In order to use EIS to perform coating evaluation, a circuit model is used to represent the physical system comprising the electrochemical cell. A coated metal plate is wired as the working electrode and is submerged in an electrolyte. Reference and counter electrodes are placed in the electrolyte as well. As an alternating potential is applied to the working electrode (the coated panel), the metal substrate, coating, and electrolyte form a capacitor, whose value is referred to as the coating capacitance (Cc). The metal substrate and electrolyte form parallel plates, while the coating acts as the dielectric barrier. An additional capacitor is formed when the coating begins to delaminate and electrolyte has penetrated the space between the coating and the metal substrate. The electrolyte and the metal form the two plates of the capacitor, while a single layer of water molecules (Helmholtz Plane) separates the two plates forming the dielectric. This capacitance is referred to as the double layer capacitance ($C_{dl}$). The circuit model shown in Figure 3 is commonly used to represent metal with protective coatings (Loveday, 2004; Mike O'Donoghue, 2003).

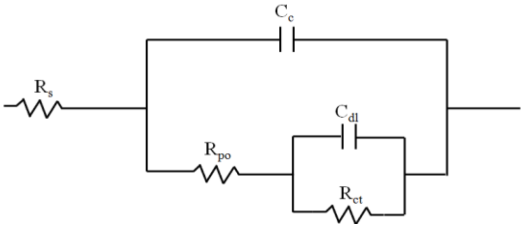


Figure 3. Equivalent circuit diagram for paint used for EIS.

In the circuit model, $R_s$ is the solution resistance, $R_{po}$ is the pore resistance, $C_c$ is the intact coating capacitance, $C_{dl}$ is the double layer capacitance, and $R_{ct}$ is the charge transfer resistance. Once the model has been fitted to the data, changes in the model's parameters offer insight into the health of the coating. For example a decrease in coating capacitance represents deterioration of the coating's ability to shield the metal substrate from the environment. Another example is the pore resistance, which provides information on the effectiveness of the coating. As pores in the paint begin to expand over time, the resistance associated with these pores decreases. This parameter provides a general indication of paint degradation (Gamry Instruments, 2011; K. M. Deen, 2009). Figure **4** provides a physical representation of the circuit model used to interpolate the impedance data.

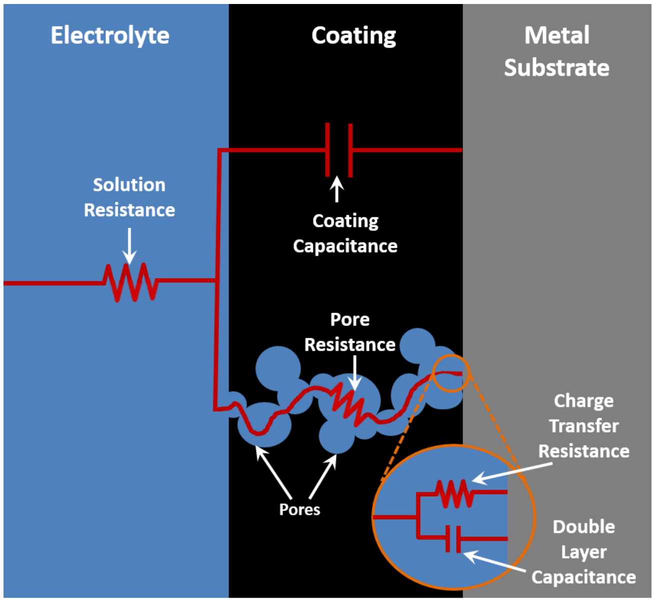
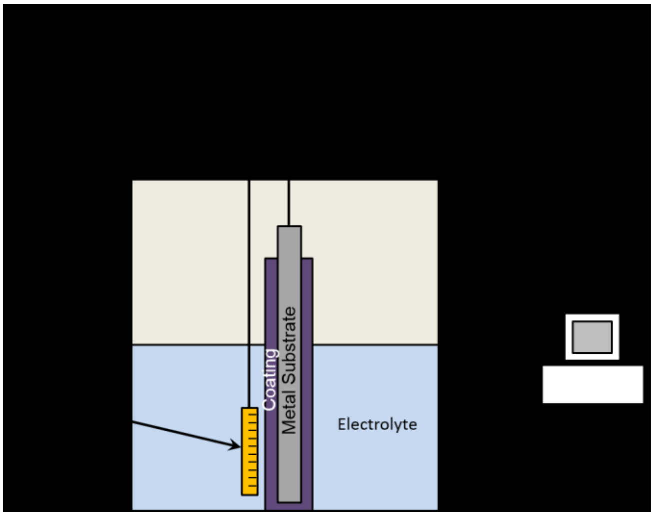


Figure 4. Physical representation of the equivalent circuit model for damaged coating.

## 4. EXPERIMENTAL RESULTS

### 4.1. Test Plan

Research is currently being conducted using a modified µLPR corrosion sensor for EIS measurements. The first EIS test cell is configured as depicted below in Figrue **5**.



Figrue 5. EIS experimental setup depicting a coated metal panel acting as the working electrode and a two electrode sensor connected to the counter and reference electrodes.

First, a metal panel made from aluminum alloy 7075-T6 is coated with 2 mils of an epoxy-based polymer coating and 2 mils of high solids polyurethane. The sensor is then adhered to the face of the panel with industrial strength epoxy. The bonding agent (industrial strength epoxy) is placed on opposing edges of the sensor so as to adhere the sensor to the surface of the painted metal plate in a manner such that the ambient environment is allowed to rapidly diffuse between the sensor and the painted substrate. The coated metal plate is then connected to a potentiostat as the working electrode. Two leads are connected to the sensor; one as the counter electrode and another as the reference electrode. A baseline EIS measurement is then taken with the sensor and panel in ambient air. The coated panel/sensor configuration is then placed in a solution containing 3.5% sodium chloride in deionized water. Another EIS measurement is taken immediately after submerging the panel/sensor configuration. EIS measurements are then taken every hour following submersion in the electrolyte solution. A circuit model is then selected based on the fit criteria between the expected and acquired EIS data.

Figure 6. Singleton corrosion test chamber used to run ASTM G85 A5 cyclic fog test.

Coating evaluation is also currently being conducted using the modified µLPR for coated panels in a Singleton corrosion test chamber, shown in Figure **6**. A panel coated with 4 mils of an epoxy-based polymer coating and 2 mils of high solids polyurethane was placed in a Singleton corrosion test chamber. Prohesion testing is being performed following the ASTM G85 Annex A5 Dilute Electrolyte Cyclic Fog/Dry Test. This test consists of a 1 hour fog at 25°C followed by a 1 hour dry-off period at 35°C. The electrolyte used for the fog is made up of 0.05% sodium chloride and 0.35% ammonium sulfate by mass in deionized water.

### 4.2. Results

To test the system's ability to perform coating evaluation in a typical laboratory environment, an experiment was conducted. A metal panel made from AA 7075-T6 measuring 7.6 cm x 1.91 cm x 0.16 cm was used for this accelerated coating evaluation experiment. Three quarters of the panel was coated with 2 mils of an epoxy-based polymer coating. A µLPR sensor was adhered to the face of the painted portion of the panel. The working lead of the potentiostat was connected to the uncoated portion of the panel. The counter electrode and reference were connected to the µLPR sensor as shown in Figure **7**. A 10 mV AC signal operating between 10 mHz and 10 MHz was utilized as the interrogation waveform. The coated panel was partially submerged in a graduated cylinder containing 3.5% sodium chloride such that only the coated portion of the plate was submerged while the uncoated portion of the plate and working electrode interface were outside the solution.

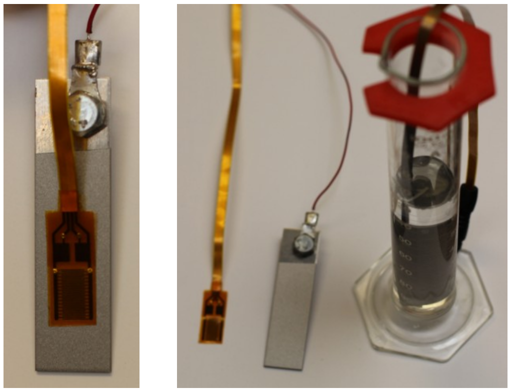
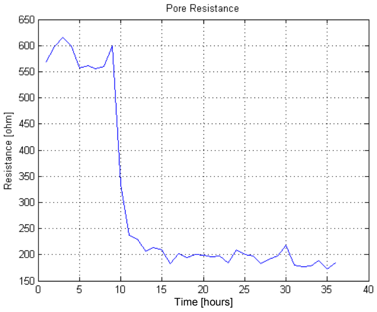
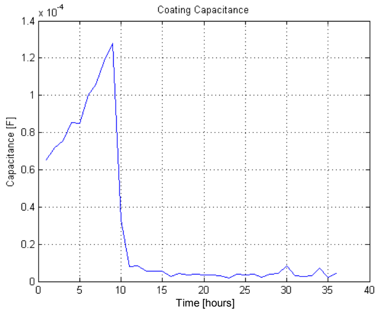


Figure 7. Photo of sensor and coated panel configuration (left) and sensor, coated panel with working electrode, and graduated cylinder with panel partially submerged in solution of 3.5% sodium chloride (right).

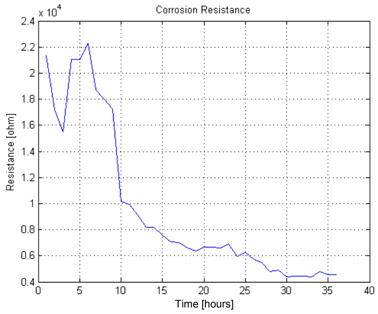
Data collection was set at one-hour intervals. The plots shown display the changes in $R_{po}$, $C_c$, $R_{ct}$, and $C_{dl}$ over the 35 hours of data collection for the submerged panel. Once the panel is placed in the solution, the coating begins to absorb electrolyte through its pores. This process causes the coating thickness to expand. As the coating absorbs fluid, the dielectric constant for the coating increases, causing an increase in coating capacitance, which is observed in the first 8 data sets, as shown in Figure **8**. After around 9 hours, a drastic drop in $R_{po}$, $C_c$, and $R_{ct}$ was observed, indicating electrolyte penetrated through to the metal substrate (coating failure). At the time of coating failure it was observed that there was an increase in $C_{dl}$. This increase in capacitance can be attributed to electrochemical reactions occurring on the surface of the metal. After removing panel from the solution, regions of paint delamination were present across both faces of the plate.



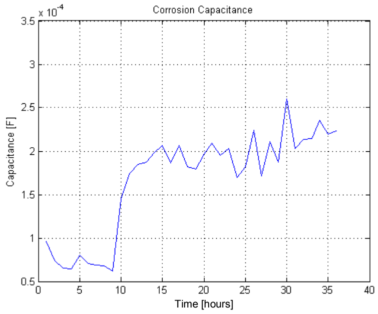
(a)



(b)



(c)



(d)

Figure 8. Plots of the pore resistance (a), coating capacitance (b), charge transfer resistance (c), and double layer capacitance (d) collected at 1 hour intervals.

## 5. CONCLUSION

In this paper, a μLPR sensor was used with EIS for coating evaluation. An accelerated corrosion test was performed on a coated metal plate. EIS data was collected over 35 hours which showed a sharp decrease in $R_{po}$, $C_c$, and $R_{ct}$ and a sharp increase in $C_{dl}$ during the duration of the experiment. The data showed failure of the protective coating 9 hours into the test, due to the thin coating layer and high salt concentration. Key parameters were evaluated within the circuit model to identify the mechanism of coating degradation. Further, this experiment showed the shielding present on Analatom's micro-sensor was sufficient to reduce the effects of ambient electromagnetic interference when operating outside of a Faraday cage.

## 6. FUTURE WORK

Future work is necessary to further understand the relationship between mechanisms of coating failure and key modeling parameters. This will involve operating under more stringent conditions, such as in a corrosion chamber running the ASTM B117 profile. Testing within a corrosion chamber presents challenges due to the additional electromagnetic interference generated by the chamber and the inability to enclose the electrochemical cell within a Faraday cage. Multiple coating types will need to be tested. Experiments involving coated metal samples with controlled coating defects need to be conducted to attain information with regard to the fault propagation rate as well as the radius of detection for the µLPR sensor.

## REFERENCES

Engineering Asset Management: Issues and Challenges. University of Cambridge, Cambridge, UK, Executive Briefing, 2012 Service Week Workshop on the Future of Asset Management, 2012.

Brown, D. W., Connolly, R. J., Darr, D. R., & Laskwoski, B. C. (2014). *Linear Polarization Resistance Sensor Using the Structure as a Working Electrode* (pp. 1-7), July 8-10, Nantes, France.

Loveday, D., Peterson, P., and Rodgers, B. 2004. Evaluation of Organic Coatings with Electrochemical Impedance Spectroscopy. *JCT coatingstech*, 2(13), pp.22-27.

Cano, E., Lafuente D., and Bastidas, D. M. , 2010. Use of EIS for the Evaluation of the Protective Properties of Coatings for Metallic Cultural Heritage: a Review. *J. Solid State Electrochem*, 14(3), pp.381-91.

Hyndman, R. J., & Koehler, A. B. (2006). Another look at measures of forecast accuracy. *International Journal of Forecasting*, vol. 22, pp. 679-688. doi:10.1016/j.ijforecast.2006.03.001.

Gamry Instruments, 2011. *Rapid Electrochemical Assessment of Paint*. Application Note. Warminster, PA: Gamry Instruments.

Deen, K. M. and Khan, I. H. 2009. Corrosion Protection Evaluation of Mild Steel Painted Surface by Electrochemical Impedance Spectroscopy. *Journal of Quality and Technology Management*, V1, paper 6.

Popoola, A., Olorunniwo, O. E., and Ige, O.O., 2014. Corrosion Resistance Through the Application of Anti-Corrosion Coatings.

Butt, M. T. Z., Deen, K.M., and Majeed, U. n.d. Evaluation of the Protective Performance of Epoxy Coated Mild Steel by Electrochemical Impedance Spectroscopy. Online. University of the Punjab.

O'Donoghue, M., Garrett, R., Datta, V., and Roberts, P., 2003. Electrochemical Impedance Spectroscopy: Testing Coatings for Rapid Immersion Service. *Materials Performace*, pp.36-41.

## BIOGRAPHIES

**Nicholas Waters, M.S.** earned his bachelor's degree from the University of California, Davis in Applied Mathematics. In 2012, he earned his master's degree in Ocean Engineering from Florida Atlantic University under the advisement of Dr. Pierre Philippe Beaujean. His graduate field of study was focused on machine condition monitoring and development of a vibration condition monitoring system for a 20 kW ocean turbine. Currently, Nicholas works for Analatom, Inc. in Santa Clara, CA as a project engineer. His current responsibilities include writing and submitting proposals for grants, conducting corrosion experiments with Analatom's µLPR sensor, and researching the µLPR sensor's ability to be repurposed to perform EIS for coating evaluation.

**Richard Connolly, Ph. D.** is the Senior Research Engineer for Analatom. Dr. Connolly holds a bachelor of science degree in chemical engineering and a doctor of philosophy degree in biomedical engineering. He is a fellow of the National Science Foundation and is an expert in interfacing engineering devices with skin. He has extensive experience in electrochemistry, bioelectrics, gene therapy, and plasma physics. Much of this experience was gained developing novel electrical systems for the prevention and treatment of disease. During his tenure at Analatom he has overseen testing and validation of electrochemical structural health monitoring technologies for aerospace and civil engineering applications.

**Douglas Brown, Ph. D.** is the Senior Systems Engineer for Analatom. Dr. Brown has eight years of experience developing and maturing prognostics & health management (PHM) and fault-tolerant control systems in avionics applications. He received the B.S. degree in electrical engineering from the Rochester Institute of Technology in 2006 and the M.S./Ph.D. degrees in electrical engineering from the Georgia Institute of Technology in 2008 and 2011, respectively. He is a recipient of the National Defense Science and Engineering Graduate (NDSEG) Fellowship and has received several best-paper awards for his work in PHM and fault-tolerant control.

**Bernard Laskowski, Ph. D.** Obtained a Ph.D. in Physics from the University of Brussels, Brussels, Belgium. As president of Analatom Inc,.Bernard managed 85 university, government, and private industry contracts. He received the U.S. Small Business Administration Administrator's Award for Excellence. He licensed MEMS technologies and obtained patents for the Analatom MEMS projects. Responsible for having obtained $3.5 M in US Air Force, Army, and Navy government seed funding for SHM MEMS projects.