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Using electrochemical impedance spectroscopy to predict the corrosion resistance of unexposed coated metal panels

F. Louis Floyd[a], Sundaresan Avudaiappan[b], Jason Gibson[b], Bhaumik Mehta[b], Pauline Smith[c], Theodore Provder[d,*], John Escarsega[e]

[a] PO Box 31208; Independence, OH 44131, United States
[b] Eastern Michigan University; Ypsilanti, MI, United States
[c] U.S. Army Research Lab; Aberdeen Proving Grounds, MD, United States
[d] Polymer & Coatings Consultants, LLC, Solon, OH, United States
[e] US Army Research Lab; Aberdeen Proving Grounds, MD, United States

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ABSTRACT

The goal of the current work was to determine if electrochemical impedance spectroscopy (EIS) testing of a series of coated but unexposed metal panels could predict the corrosion results of other sections of the same coated panels that were subjected to both continuous and cyclic corrosion testing. Variables included metal, pretreatment, primer, and topcoat. EIS results were shown to be strongly dependent upon the time-of-residence in the electrochemical cell prior to commencement of testing, and to the choice of electrolyte used in the cell. Good correlations between EIS and corrosion testing were seen for topcoat effects, but not for pretreatment effects. EIS results appear to relate mostly to barrier properties rather than electrochemical properties of coatings. It is suggested that the variation seen in EIS solution resistance values (R_s) can be utilized to quantify total system error. Total error was estimated by three techniques: total R_s variation, panel replicate variation, and EIS reading replication. The three approaches yielded similar results: total error for equivalent circuit components expressed in $\log_{10}$ form was on the order of 50%, expressed as percent standard deviation.

1. Introduction

Electrochemical impedance spectroscopy (EIS) scans have been used for over 40 years to measure the properties of coated metal panels, and to infer relative performance of those coated panels in corrosive or other environments. There are several hundred references in the literature to EIS scans of coated metals, including journals, books, and government contract reports. Only a few are cited here, to provide context for the present report.

Activity in this field started in the 1940's (see Bacon et al. [1] for example) and proceeded slowly until 1970's, after which it accelerated sharply with the introduction by Solatron (UK) and Princeton Applied Research (U.S.) of automated EIS instruments. Today's suppliers include Solatron, Zahner, Eco-Chemie, and Radiometer who all use frequency response analyzers; AMETEK (formerly PAR) who use a lock-in amplifier, and Gamry who use sub-harmonic sampling with discrete Fourier Transform. The present study employs Gamry instrumentation.

EIS scans are accomplished by vertically mounting an open cylindrical cell containing electrolyte and the various electrodes onto a horizontal flat coated panel, attaching the electrodes, electrically isolating the entire system, pushing the start button. The instrument applies an AC voltage (typically 10 mV in amplitude), measures the resulting current and calculates the resulting impedance, all as a function of AC frequency from high (MHz) to low (mHz). There is a phase lag between applied voltage and measured current, which produces both a real and imaginary component to the impedance measured at each frequency.

Results are commonly reported as a plot of imaginary vs. real components of impedance (Nyquist plots) or impedance vs. frequency and phase angle vs. frequency (Bode plots). One can also calculate the values of various circuit components from a model equivalent circuit applied to the results. Later sections consider these in greater detail.

It is generally agreed among workers in the field that to be valid, EIS measurements must adhere to the following four rules [2]:

- Causality: the observed response is due only to the applied perturbation (no significant spurious signals).
- Linearity: system obeys Ohm's Law, $dE/dI = Z$. Impedance (Z) is independent of the magnitude of the applied perturbation.

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* Corresponding author. Tel.: + 1 440 914 0611.
E-mail address: tprovder@att.net (T. Provder).

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[Requires small amplitudes, on the order of 10 mV of applied perturbation.]
- Stability: system does not change over time, and returns to its original state after the perturbation is removed. [*E* and *I* after a run are the same as before the run.]
- Continuity: finite values exist for highest and lowest frequencies, and are continuous in between.

Unfortunately, it is fairly common for publications on EIS measurements of coated panels to overlook one or more of the above rules.

1.1. Tutorials and critical reviews

Taylor [3] provides a good basic introduction on the use of EIS measurements to observe the changes in film properties over time while immersed in an electrolyte solution, such as the decline in resistance and increase in capacitance caused by the absorption of water. On the other hand, Al-Janabi, et al., [4] report that in some circumstances impedance (*Z*) can actually increase at long exposure times, which they attribute to the clogging of pores with corrosion products. There is an example of such behavior in the present work.

Geenen [5] provides an excellent summary of EIS techniques for studying coatings, covering the behavior of the individual circuit components with increasing exposure time, and the role of flaws in the film by measuring the effect of laser-induced model flaws. The present authors found this work to be lucid, comprehensive, and quite helpful.

Tait [6] has written an excellent text on electrochemical corrosion testing, including EIS measurements, covering not only theory but also step-by-step practice in the use of the various techniques. The text also covers experimental error and the need for replication (he asserts a minimum of five). In this context, Tait cautions the reader to not discard extreme values (aka flyers, outliers) unless they are the result of known causes.

Amirudin and Thierry [7], of the Swedish Corrosion Institute, provide an excellent critical review of the use of EIS measurements to study the degradation of coated metals. They caution that just because many equivalent circuits of varying complexity can be employed does not necessarily mean that they are valid, have been confirmed by other techniques, or represent physical reality. They also assert that a number of commonly accepted practices are not yet settled, viz., the significance of the coating resistance, the utility of the breakpoint frequency, and the alternate use of constant phase elements and capacitance in equivalent circuits.

Silverman [8] provides a recent tutorial on and critical review of the use of electrochemical techniques to predict corrosion behavior. He notes that the demand for quicker assessments of corrosion behavior prompted the development of electrochemical techniques, which can produce useful results in 1–3 days. He also notes that while the technique is easy to use, the interpretation of results can be quite difficult. He likens the difficulty in trying to solve for several unknowns using only one equation. As such, he is one of the few authors to point out that EIS measurements cannot of themselves provide all the information needed to reliably predict corrosion results, but must instead be used in combination with other techniques to provide the desired results. This view is echoed by Fontana [9], Haynes [10], Baboian [11], and Silverman [12].

1.2. Equivalent circuit models

On occasion, an equivalent circuit model has been employed to calculate circuit components which are claimed to relate separately to the coatings and the substrate (or interface). The most common form of circuit model is a two-time-constant model with resistances and capacitances related to each of the coating and the substrate (or interface). All models also contain an uncompensated solution resistance which is presumed to be invariant.

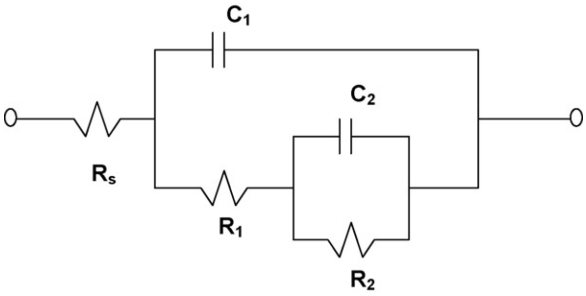

Fig. 1. Equivalent circuit model with two time constants.

In 1993 Mansfeld [13] described the use of a simple two-time-constant equivalent circuit for the interpretation of EIS measurements of coated aluminum panels, and the use of those circuit components to determine the protective properties of coatings and their degradation with exposure time in corrosive environments. Considerable data scatter was shown for the circuit components, and smoothing suggestions were offered. He also introduced a pitting model for aluminum alloys, that involved a different model circuit that correlated nicely with the observed growth rate of the pits.

Kern et al. [14] recently proposed an alternate model to account for blistering that employs an additional set of capacitances and resistance in parallel with the elements shown in Fig. 1.

In the present work, we chose to go with the simpler model as shown in Fig. 1, since it provided an adequate fit to our data.

1.3. Rapid electrochemical assessment of paint (REAP; aka AC/DC/AC tests)

In 1996, Kendig et al., [15] first proposed that one could combine EIS measurements with DC-driven delamination experiments to provide a rapid assessment of paint quality applied to steel (REAP; aka AC/DC/AC test). Their process involved running an EIS scan initially, and then again after 24 h of immersion in 0.5 M NaCl solution. A parallel cathodic delamination experiment is run to determine delamination rate from a scribe. The DC potential of the sample is held either at OCP or at −0.600 V vs. SCE if no stable OCP could be obtained. The results are combined via multiple regression into a model that correlates to continuous salt fog results, although the data scatter is rather large. One EIS equipment manufacturer (Gamry) has automated this process for their instruments.

Suay et al. [16] picked up on the concept in 2003 and developed a different cycle to accomplish the same mission, also on steel. Suay's process involves running an EIS scan (∼1.5 h), followed by a cathodic polarization test driven by an applied DC voltage (−3 V relative to OCP; 30 min), followed by a relaxation period of an hour, then followed by another EIS scan (∼1.5 h). The sequence is repeated 20 times. The results are combined with a parallel measure of cathodic delamination test that involves exposure to voltage of −0.60 V vs. Ag/AgCl for 24 h, then taping the scribe to determine the extent of delamination from the scribe. This is said to provide meaningful results in as little as a few days.

In 2005, Poelman et al. [17], applied Suay's technique to coatings for aluminum, and reported good results.

1.4. Other uses of EIS

Various authors have used EIS measurements to characterize

- the utility of pretreatments [18–20],