Coating strategies for the protection of outdoor bronze art and ornamentation
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Electrochemical Impedance Spectroscopy (EIS) of select coatings on bronze

Abstract

Electrochemical impedance spectroscopy (EIS) analysis was undertaken in order to examine the coated, polished bronze samples prepared and studied in Phases I and II by a parallel, quantitative method. Chapters 2 and 3 describe failure ratings of coatings on bronze as determined by visual means. This chapter describes EIS of select coatings on bronze from Phase I, as well as a complete set of unweathered coatings on polished bronze from Phase II, and provides rankings of these coatings by purely electrochemical means. The unweathered samples were followed by EIS during a simulated accelerated weathering program. Phase II samples that had already undergone separate accelerated weathering were also examined by EIS for purposes of comparison. Results support the findings of coating performance on bronze as reported in Chapters 2 and 3.

4.1. Introduction

Electrochemical test methods have recently moved center stage as important tools for the quantitative characterization of coatings on metal substrates [1]. In particular, electrochemical impedance spectroscopy (EIS) has become known as a valuable method for the rapid ranking of coatings and prediction of future performance [2,3,4,5,6,7]. In order to compare EIS analysis with visually-based performance assessment as described in Chapters 2 and 3, EIS was initially performed on a small group of coated samples from Phase I [8]. Following this preliminary analysis, the complete set of unweathered samples on polished bronze from Phase II were monitored by EIS during an accelerated weathering regime consisting of cyclic salt fog/UV exposure (see Experimental Methods, below). These results were compared to EIS values obtained from a second set of Phase II coated bronze samples that had already been weathered under the National Gallery of Art accelerated weathering protocol, as described in Chapter 3.
EIS is based upon the creation of an electrochemical cell; this consists of a coated metal sample, which functions as the working electrode, in contact with an electrolyte, into which are immersed a counter electrode and reference electrode. The setup is shown schematically in Figure 1 [9].

![Schematic representation of electrochemical impedance experimental setup.](image)

**Figure 1** *Schematic representation of electrochemical impedance experimental setup.*

An alternating voltage ($V$, volts) is applied to the working electrode, and the current response ($I$, amps) is measured over a range of frequencies ($\omega$) and time. The measured time lag, or phase shift ($\theta$), between the excitation ($V(t)$) and response signal ($I(t)$) is held to arise from characteristic types of frequency absorption or response to the applied voltage and the electrolyte [10]. This principle is illustrated in Figure 2 [9].
EIS of select coatings

Figure 2 Theoretical current (I) vs. time sinusoidal waves for excitation and response signals in EIS.

Simplistically, Ohm’s Law, V/I=R, describes the EIS cell, so that the working electrode may be defined in terms of its property of resistance (R) in the chosen electrolyte and setup. For a coated metal sample, the experimental electrochemical cell is much more complicated, however, and may be better understood as analogous to an electronic circuit, with numerous resistive and capacitive elements. Therefore we define the ratio E/I (where E=electrode potential (V)) as the impedance, Z, of the sample, which is a measure of the total opposition to current flow in the alternating current circuit, such that 

\[ Z = \frac{E}{I} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \theta)} \]

Impedance is a complex quantity and is made up of two components, real and imaginary, so that impedance modulus, \(|Z|\), is defined as shown in equation (1).

\[ |Z| = \sqrt{(Z_{\text{in phase}})^2 + (Z_{\text{out of phase}})^2} \]  \hspace{1cm} (1)

For purposes of interpretation, log impedance modulus, \(|Z|\) (ohms (Ω)), is often plotted as a function of log frequency, \(\omega\) (Hz), in a so-called Bode plot. In this representation, the low frequency impedance modulus values, e.g., at 0.1 Hz, are held to be a measure of the coating’s corrosion protection of the metal; these values may be used to rank coating performance, where higher impedance values correspond to better protection [11]. In the system used for Phase I sample testing, impedance modulus was reported as a function of exposed surface area (Ω cm²).
Quantitative values at 0.1 Hz were used for coating ranking as follows: good to excellent = values of $10^9$ to greater than $10^{12}$ $\Omega$ cm$^2$ maintained after two weeks immersion; fair to good = values of $10^6$ to greater than $10^9$ $\Omega$ cm$^2$ maintained after 2 weeks immersion; poor = values of less than $10^6$ $\Omega$ cm$^2$ that do not maintain even this level of protection in immersion.

In the testing system used with Phase II samples, impedance modulus was reported strictly in ohms; coatings with impedance modulus values of $|Z|_{0.1 \text{ Hz}} > 10^7\Omega$ were considered to be performing well under the cyclic weathering protocol. Absolute failure was considered to be the point at which a coated sample had an impedance modulus value of $|Z|_{0.1 \text{ Hz}} \approx 10^3\Omega$, which was close to the value obtained for the uncoated bronze. Although visual changes during testing were not taken into account in the rankings, failure was obvious either visually or from the EIS data in some samples at values greater than that of the uncoated bronze, e.g., at $|Z|_{0.1 \text{ Hz}} < 10^6\Omega$. This is discussed in greater detail below.

A complicating factor in the interpretation of performance based solely on one impedance modulus value is that impedance may actually be increased during weathering by the formation of new corrosion or a passivating layer beneath the coating. Obviously the coating has failed if this occurs, and data can be easily misinterpreted. Therefore, EIS measurements of a system undergoing weathering are particularly valuable for tracking such events. Interpretation of Bode plots may yield other information about dynamic changes taking place in the coating/metal system during progressive weathering as well. Whereas low frequency impedance is thought to arise mainly from resistance to wetting at the metal surface beneath the coating, decreases or flattening in the slope of the curve are thought to arise from increasing non-homogeneity in the coating, such as the formation of microcracking. Decreases in the impedance modulus at the high frequency end may indicate increasing porosity in the coating [12].

### 4.2. Experimental methods

The experimental EIS setup consisted of a glass cylinder clamped with an o-ring to a bronze sample, which acted as the working electrode. The glass cylinder was filled with dilute Harrison’s electrolyte (0.35 wt.% (NH$_4$)$_2$SO$_4$ and 0.05 wt.% NaCl in H$_2$O), and a saturated calomel reference electrode and a platinum counter electrode were immersed in the solution. The area of exposure on Phase I samples was 12.56 cm$^2$, and on Phase II samples was 7.07 cm$^2$. For Phase I samples, a 10 mV RMS sinusoidal potential (E) was applied to the cell with respect to the open circuit potential, and the current (I) response was scanned over a frequency ($\omega$) range of 0.1 to 5,000 Hz, over a period of time (t). For Phase II samples, the amplitude of the applied wave was 5 mV, and the frequency range was 0.1 to 10,000 Hz. Instrumentation included a Gamry Instruments PC-3 Potentiostat controlled by Gamry CMS100 software.

Prior to initial EIS measurements all coatings were free of any corrosion. The most evenly coated areas were chosen for measurement. For Phase I samples,
repeated EIS measurements were taken while the samples were in continual contact with the Harrison's electrolyte. For Phase II, set A samples, EIS measurements were taken weekly between cycles of simulated, accelerated weathering. The weathering protocol at the North Dakota State University was fashioned according to ASTM D 5894-96 "Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal (Alternating Exposures in a Fog/Dry Cabinet and a UV/Condensation Cabinet)." In the first week, the samples were placed in a QUV® cabinet, where they were exposed to four hours of exposure to 340 nm UV-A at 60 °C, followed by 4 hours of condensation at 50 °C. In the second week, the samples were placed into a Prohesion® Chamber that cycled between one hour of salt fog at 25 °C and one hour of no fog at 35 °C. The salt fog used for weathering was the dilute Harrison's electrolyte.

4.3. Results and discussion

4.3.1. Phase I samples

Preliminary EIS studies were conducted on five polished, cast bronze samples from Phase I (see Chapter 2). The five coatings tested were: StanChem waterborne acrylic urethane (#26), Incralac (#1), BTA pretreatment + Incralac (#2), Incralac + wax (#3), and BTA pretreatment + wax (#29) [13]. Initial readings indicated that StanChem waterborne acrylic urethane was the best coating, with an impedance modulus at 0.1 Hz equal to about $8 \times 10^7 \Omega \text{ cm}^2$, followed by, in order of performance, Incralac ($1 \times 10^7 \Omega \text{ cm}^2$), Incralac + wax ($4 \times 10^6 \Omega \text{ cm}^2$), BTA + Incralac ($4 \times 10^6 \Omega \text{ cm}^2$), and BTA + wax ($7 \times 10^5 \Omega \text{ cm}^2$).

After continual contact with the electrolyte for two days, a thin, foggy film formed over the samples pretreated with BTA, and 0.1 Hz impedance values for BTA pretreatment + Incralac (#2) and BTA pretreatment + wax (#29) increased, by about two or one order(s) of magnitude, respectively. This foggy film did not occur in outdoor or accelerated weathering tests, however, and appears to relate to the immersion-like conditions used in testing. As previously mentioned, a rise in impedance modulus during testing typically indicates that a corrosion patina layer has formed at the metal/coating interface. This added layer would offer increased resistance in the cell. The opaque film may thus be interpreted as an artifact of the testing, i.e., does not reflect natural outdoor weathering. Therefore, these results were discarded. At this point, the StanChem waterborne acrylic urethane coating also appeared to have fogged, possibly affecting its continued high ranking. No visual change was observed for the samples coated with Incralac (#1) or Incralac + wax (#3).

After 15 days of contact with the electrolyte, EIS rankings from $|Z|_{0.1 \text{ Hz}}$ were as follows: StanChem waterborne acrylic urethane ($9 \times 10^5 \Omega \text{ cm}^2$), Incralac + wax ($9 \times 10^5 \Omega \text{ cm}^2$), and Incralac ($3 \times 10^5 \Omega \text{ cm}^2$). Some changes in the appearance of coatings occurred. StanChem waterborne acrylic urethane (#26) was fogged and heavily pitted, seriously altering the appearance of the coating. Incralac + wax
had two small pits. The sample coated with Incralac alone had become cloudy. The impedance moduli of the Incralac coatings had both fallen in the poor performance range. The presence of BTA in the coating formulation appeared to show little or no effect on the coating system by EIS. The ranking order also continued to show a slight benefit from the addition of a wax topcoat. These results support similar conclusions in Chapter 2.

After 22 days of continual contact with the electrolyte, all coatings degraded slightly, but still held the same ranking from best to worst coatings. After 29 days, however, the StanChem waterborne acrylic urethane was omitted from EIS measurements due to its performance value far below what is considered to be a poor coating. Also, its appearance was full of pits, with highly corroded areas. These results confirm the extremely poor performance of the StanChem waterborne acrylic urethane (#26) observed in Phase I (see Chapter 2). Measurements of $|Z|_{0.1\text{ Hz}}$ for the Incralac coatings were as follows: Incralac + wax, $3.1 \times 10^5 \, \Omega \, \text{cm}^2$; and Incralac, $1.2 \times 10^5 \, \Omega \, \text{cm}^2$.

### 4.3.2. Phase II samples, set A

Further EIS analysis was coupled with a more realistic accelerated weathering protocol on Phase II coated, polished bronze samples (set A, controls) until failure or up to 238 days, whichever came first (see Experimental Methods). After an initial set of readings, periodic measurements were taken on the same sample spot between cycles of salt fog in a Prohesion® chamber and QUV® exposure, i.e., during progressive, artificial weathering, as described in the experimental section.

Bode plots for Phase II sample set A are shown in Figures 3-5. Measurements are shown up to 238 days of weathering; the number of days shown in the legends with asterisks indicates this reading followed salt fog exposure. The ranking as determined by these results, in order of worst to best, was as follows: bare bronze (#6) < BTA + wax (#2) << waterborne acrylic urethane + wax (#5) < Incralac + wax (#1) < BTA + BASF acrylic urethane + wax (#4) < Nikolas acrylic/acrylic urethane/wax (#3). This ranking is identical to the overall failure rating rankings on both polished bronze and the blasted copper roof substrates after accelerated weathering at the National Gallery of Art. Even the relative separation of these rankings after accelerated weathering seems comparable.

The Bode plot of the BTA + wax coating on polished bronze in Figure 3b shows that the initial impedance value characterizes this coating as a poor performer from the outset. After one day, the modulus actually rose; by 8 days of simulated weathering, the modulus fell to the value of the bare bronze (Figure 3a). Although there is not a clear explanation for the almost immediate rise in modulus, it should be noted that the decrease in impedance occurred not only at low frequencies, but also at high frequencies, suggesting significant increase in the porosity of the film. Results thus support performance evaluations in Phases I and II, and underscore the fact that this wax coating is in a different performance category from the other coatings tested in this study.
Figure 3a  *EIS of bare bronze (Phase II, 6A).*

Figure 3b  *EIS of BTA pretreatment + Wax on bronze (Phase II, 2A).*
Figure 4a  EIS of Waterborne Acrylic Urethane + Wax on bronze (Phase II, 5A).

Figure 4b  EIS of Ineralac + Wax on bronze (Phase II, 1A).
EIS results for the waterborne acrylic urethane coating (Figure 4a) show that the $|Z|_{0.1 \text{ Hz}}$ value dropped precipitously at day 14 of weathering, and by day 49 the impedance modulus could no longer recover its resistance after a drying period. Complete failure was imminent at that point. This rather sudden decline appears to predict the dramatic failure of the waterborne coating that was observed on the naturally weathered polished bronze and 50-year-old copper roof in Phases I and II of the National Gallery of Art study. EIS of this coating also shows a decrease in impedance with weathering at the high frequency end of the graph. This feature supports findings in Phases I and II that the coating tended to lose adhesion, and may also indicate increased porosity and/or cracking.

Less dramatically, the $|Z|_{0.1 \text{ Hz}}$ value for Incralac + wax (Figure 4b) also exhibited a rapid drop from over $10^8$ to under $10^6$ Ω between days 28 and 42 of weathering. By day 70, the low frequency impedance modulus indicated rather poor performance, which continued over the next 70 days until complete failure. This mimics the rapid advance of failure noted between initial accelerated weathering of Incralac coatings in Phase I at the National Gallery of Art after 47.5 days, and the extended weathering after 7.5 months. Normal applications of Incralac coatings are expected to last 3-5 years in outdoor environments. On this basis, as well as results for the wax coating, it is tempting to correlate 15 days of the simulated weathering protocol used with EIS to about 1 year of natural outdoor weathering.

EIS analysis of the urethane coatings showed a different kind of picture from that of the other coatings (Figure 5a,b). Measurements indicate that the systems maintained initial $|Z|_{0.1 \text{ Hz}}$ values for close to 98 days of accelerated weathering. During this period, the Nikolas acrylic/urethane exhibited almost no change in the curve of the Bode plot. The BASF acrylic urethane did begin to fan downward somewhat, although it also maintained a good performance level. Gradual decrease in low frequency impedance began to occur in the Nikolas coating about day 98 of weathering and both coatings were showing some signs of pitting around 238 days. Results thus support the conclusion in Phases I and II that the Nikolas acrylic/urethane coating on polished bronze belongs to a “high performance” category compared to the other coatings. Similarly, EIS supports conclusions in Phase II that the BASF acrylic urethane coating appears to straddle high and medium performance categories.

If we examine the same data for sample set A in a different form, i.e., plotted as impedance modulus $|Z|_{0.1 \text{ Hz}}$ vs. time of weathering (Figure 6), we can discern some of the weathering trends more clearly. This graph illustrates first of all that once the impedance of the coatings started to fall, the decline was not steady with time, but oscillated up and down. These oscillations correspond to whether the samples were measured immediately following UV exposure or salt fog cycling. After Prohesion® chamber exposure, i.e., every 14 days, if the coating had imbibed a lot of moisture, the metal beneath the pores would be wetted, conductivity would be increased, and this would cause the impedance to drop. After QUV® exposure, samples would dry out, inhibiting conductivity and allowing impedance to rise again.
Figure 5a  EIS of BTA + BASF Acrylic Urethane + wax on bronze (Phase II, 4A).

Figure 5b  EIS of Nikolas Acrylic + Acrylic Urethane + Wax on bronze (Phase II, 3A).
Figure 6  Plot of Impedance modulus $|Z_{0.1\text{Hz}}|$ vs. Time of weathering for Phase II polished bronze samples under QUV/Prohesion.
After 14 days of weathering, i.e., after completion of the first salt fog cycle, all coatings except the BASF acrylic urethane showed a fall in impedance. Again, explanation for the one exception at this early stage is not readily apparent. The good physical condition of the sample and subsequent good performance suggest that the BASF coating underwent continued curing during these initial weathering cycles. This was thought to occur on the blasted copper roof sample in Phase II experiments, where a definite increase in adhesion was measured after accelerated weathering.

During subsequent weathering, both the Nikola acrylic/urethane coating and the BASF acrylic urethane coating held fairly steady for a period of time, whereas the Incralac and the waterborne acrylic urethane coatings exhibited large oscillations in impedance almost immediately upon weathering cycles. This illustrates well that the latter two coatings, and especially the waterborne coating, were initially susceptible to moisture/electrolyte ingress. While the waterborne coating failed fairly rapidly, by day 56, the Incralac coating showed small oscillations in modulus, then larger oscillations starting at about 42 days, then stabilization for a period starting at about 91 days. This suggests the formation of microcracks and/or loss of adhesion relatively early on, followed by medium performance until a coherent passivating corrosion layer formed underneath the coating. This hypothetical, new patina layer appeared to have subsequently broken down before ultimate failure at 140 days. However, as this graph shows, 91 days corresponds more truly to real failure in the Incralac coating.

The behavior of the remaining two top performing coatings, the Nikola acrylic/urethane and BASF acrylic urethane, is thus clearly distinguishable from the others in this analysis. The initially long, steady impedance behavior of these coatings, 77 days in the case of the Nikola coating and 61 days for the BASF coating, marks them as high performance coatings. The Nikola coating also shows itself to be the slight leader in this race. Thus, the information as plotted in Figure 6 lends more support to the findings in Chapter 3 regarding relative performance.

4.3.3. Phase II samples, set B (after accelerated weathering)

Further testing was conducted on a set of coated, polished bronze samples that had already undergone accelerated weathering at the National Gallery of Art (Phase II, set B). Results are shown in the Bode plot in Figure 7. EIS rankings are, from worst to best: BTA pretreatment + wax (#2) < uncoated bronze << Nikola waterborne acrylic urethane + wax (#5) < BTA pretreatment + BASF acrylic urethane + wax (#4) ≤ Nikola acrylic + Nikola acrylic urethane + wax (#3) ≤ Incralac + wax (#1). The results are consistent with both the EIS results for Phase II set A samples, and with the overall failure ratings shown in Chapter 3. The difference seen here is that the EIS results do not distinguish the three highest ranked coatings from each other, as they are in the above experiment or in the failure ratings (see Chapter 3). A disturbing result shown here is that the waxed samples actually fell behind the uncoated sample, which was at this point covered by a coherent layer of corrosion, i.e., patina.
The fair correspondence between EIS results of the two sets of Phase II samples indicates that the weathering protocols followed in the laboratories in North Dakota and the National Gallery of Art were basically comparable, although weathering at the North Dakota laboratory appears to have been somewhat harsher and more accelerated. EIS may thus predict behavior further ahead than the accelerated weathering conducted at the National Gallery. The increased acceleration factor in the EIS weathering protocol, as compared to accelerated methods used at the National Gallery of Art, may be ascribed in large part to a greatly increased “time of wetness” in the salt fog equipment. In the absence of automated fogging or spraying equipment at the National Gallery, approximately 5 minutes of hand spraying followed by 4 hours of 85% relative humidity did not equal the wetness achieved by 4 hours of direct fogging. Other differences in the accelerated weathering methods, such as the composition of the “acid rain” solution and duration of other cycles, may also have significance. On the other hand, the EIS experiments do not take visual changes in the coatings into account. It must be emphasized that no method of accelerated weathering or performance evaluation will ever reproduce outdoor exposure exactly, which in any case is site specific. This underscores the importance of comparing results of different methods of weathering as well as different methods of analysis in the general evaluation of coating performance.

Figure 7  EIS of Phase II, sample set B, after accelerated weathering at the National Gallery of Art.
4.4. Conclusions

Preliminary EIS work showed visual changes to the samples during testing, as well as increasing failure in the coatings. Visual evidence of a “foggy film” developing in the samples pretreated with BTA suggested a passivating layer formed as an artifact of the testing procedure, and these results were discarded. The ranking order from EIS for the remaining three coating systems tested on bronze from Phase I samples indicated a slight benefit from the addition of a wax topcoat to Incralac, although the performance of this coating was generally poor. The StanChem waterborne acrylic urethane on polished bronze (#26) performed fairly well for a time period, and then failed dramatically. This also concurs with performance evaluations for this coating on patinated substrates as described in Chapter 2, but strongly predicts dramatic failure for this coating on polished bronze, which was only slightly indicated in the Phase I study.

Additional EIS testing of Phase II polished bronze samples provided rankings for the five coatings. These results concurred with findings of the study described in Chapter 3, where the Nikolas acrylic/urethane + wax showed superior performance on polished bronze, and BTA + wax showed very inferior performance characteristics. Rankings also concurred with a mediocre performance level from Incralac + wax on the bronze, but EIS rankings indicated slightly better performance from the BTA + BASF acrylic urethane + wax coating on polished bronze than were observed in Phase II. Examination of the Bode plots and impedance modulus vs. time of weathering data yielded additional information about the coating performance that was interpreted in terms of susceptibility to porosity and/or microcracking, as well as the formation of corrosion layers underneath the coating. EIS results also appear to predict some behavior not yet seen in the natural outdoor or accelerated weathering conducted at the National Gallery of Art, in particular that of the complete breakdown of Incralac. In general, results provide strong support for the findings in Chapters 2 and 3.
References


8. Laboratory of Dr. Gordon P. Bierwagen, Dept. of Polymers and Coatings, North Dakota State University, Fargo, ND.


