Electrochemical impedance spectroscopy (EIS) as a tool for measuring corrosion of polymer-coated fasteners used in treated wood

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Abstract

Currently, many of the polymer-coated fasteners on the market are designed for improved corrosion performance in treated wood; yet, there is no way to evaluate their corrosion performance. In this study, a common technique for measuring the corrosion performance of polymer-coated metals, electrochemical impedance spectroscopy (EIS), was used to evaluate commercial fasteners in a water extract of treated wood. Fasteners were tested in an "out of the box" condition as well as after being driven into the wood to simulate service conditions. The EIS spectra were fit to the traditional model for polymer-coated metals where the capacitors were replaced with constant-phase elements. A low frequency corrosion-time constant was measured for all of the fasteners in the out of the box condition, which implies that the barrier properties of the coating had failed before they were used.

Research has shown that wood treated with alkaline copper quaternary (ACQ) and copper azole (CuAz), which are used as replacements for chromated copper arsenate (CCA), is more corrosive to metal fasteners than wood treated with CCA (Kear et al. 2005, Simpson Strong Tie 2006, Ying and Mingliang 2007, Zelinka and Rammer, in press). One cost-effective way of protecting metals in contact with treated wood is to coat them with a non-conducting polymer or paint. These coatings produce a barrier that isolates the metal from the treated wood, and they may also contain corrosion inhibitors. Currently, the *National Design Specifications® (NDS®) for Wood Construction* does not recommend that polymer-coated fasteners be used with treated wood, although there are many polymer-coated fasteners on the market.

One reason polymer-coated fasteners have not gained design recommendation is that there are no test methods for evaluating their effectiveness. Polymer-coated metals do not undergo uniform corrosion, but rather experience local corrosion at sites where the coating breaks down. The sole standard for corrosion of metals in contact with treated wood, AWPA E12 (AWPA 2007), only addresses uniform corrosion over a metal coupon and is a comparative test. Corrosion tests on fasteners as opposed to coupons (Baechler 1949, Simm and Button 1985, Baker 1992, Zelinka and Rammer, in press) also calculate a corrosion rate using the entire surface area of the fastener. A test that can quantify corrosion on coated metal fasteners is the first step toward the implementation of coated metal fasteners for use in wood structures.

Electrochemical impedance spectroscopy (EIS) has been widely used to characterize corrosion of coated metals used in non-wood applications (Scully et al. 1993, Jones 1996,

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Loveday et al. 2004). An EIS spectrum takes minutes to run compared with the weeks needed for an exposure test. In addition, EIS is nondestructive, which allows the researcher to observe changes in the film with time. Unlike traditional salt-spray tests (ASTM 2005a), EIS does not require a subjective visual rating. EIS can measure both intact and defective coatings.

Functionally, EIS measures the electrochemical response to a small AC voltage applied over many frequencies. This electrochemical response is usually interpreted in terms of an equivalent circuit, a circuit composed of electrical components with the same frequency response as the electrochemical reaction. For example, a capacitor has the same frequency response as a reaction step when electrons or ions build up on a surface, and a resistor represents the transport of charge through materials or interfaces (Amirudin and Thierry 1995). Often, it is possible to assign physical meaning to individual elements in the equivalent circuit based upon a reaction mechanism.

The equivalent circuit in **Figure 1** has been applied by many authors to describe the corrosion response of polymer-coated materials (Scully et al. 1993, Amirudin and Thierry 1995, Jones 1996, Loveday et al. 2004). Amirudin and Thierry (1995) give a detailed history of this model as well as a detailed explanation of the physical meaning of each of the components within this model. The major concepts will be stated here for clarity.

R_u is the uncompensated solution resistance. It depends on the resistivity of the solution and the location of the reference electrode with respect to the working electrode.

C_{coat} is the capacitance of the polymer coating. This parameter is sometimes used to monitor water adsorption in the coating because the dielectric constant of water is much greater than most polymers (Rammelt and Reinhard 1992, Amirudin and Thierry 1995).

R_{pore} is the resistance to charge transport through pores, voids, and other defects in the polymer coating.

C_{dl} is the double layer capacitance that arises from dipole interactions on the metal surface.

R_p is the polarization resistance.

Polarization resistance is an important corrosion parameter that can be measured using a variety of techniques (Mansfeld 1973, Jones 1996, Scully 2000). No matter how it is determined,

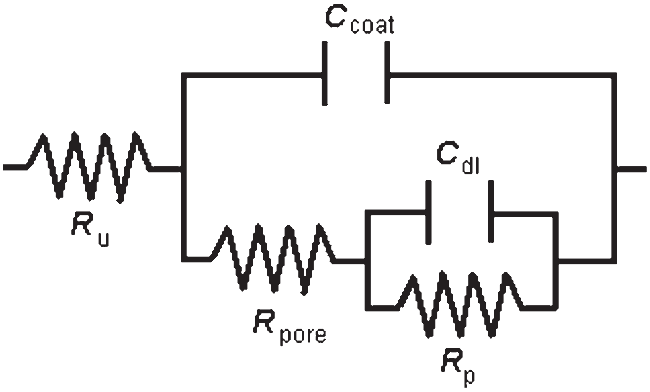

Figure 1. — Equivalent circuit model used to described metals with a non-metallic coating.

R_p is always inversely proportional to the corrosion current density i_{corr} (and thus the corrosion rate) through the Stern-Geary relation (Stern and Geary 1957, Stern and Roth 1957, Stern and Weissert 1959):

$$i_{corr} = \frac{1}{R_p}\left(\frac{\beta_a\beta_c}{2.303(\beta_a + \beta_c)}\right) \qquad [\mathbf{1}]$$

where:

β_a and β_c = the anodic and cathodic Tafel slopes, respectively.

Depending on the type and quality of the polymer coating, some of these elements may not be necessary to fit the data (Loveday et al. 2004). For perfect coatings, the coating acts as a perfect dielectric and only C_{coat} is needed to fit the data. As the coating begins to break down, the coating starts to act as a lossy dielectric, and the data exhibit a single time constant, $\tau_c = (R_{pore}C_{coat})$. After the coating has broken down to the point at which the corrosion reaction can occur, the data exhibit a second time constant, $\tau_{dl} = R_pC_{dl}$. Typical values for these parameters have been tabulated by Loveday et al. (2004), and their data showed that the corrosion time constant (τ_{dl}) occurs at lower frequencies than the coating time constant (τ_c) or in the time domain, $\tau_c << \tau_{dl}$.

Most of the literature studies on polymer-coated metals were conducted using liquid electrolytes. Treated wood is a solid electrolyte, and the baseline impedance spectra of wood has at least one time constant in the frequency range of interest to corrosion scientists (Zelinka 2006). The inherent frequency-dependent electrical properties of wood could mask the frequency response of the polymer-coated metal during impedance spectroscopy and make the results nearly impossible to interpret. But, direct current electrochemical tests of uncoated steel and galvanized steel in a water extract of treated wood have had good correlation with exposure tests of matched specimens in solid wood (Zelinka et al. 2008). Therefore, it was determined that polymer-coated fasteners in a water extract of treated wood would be tested in this study. The implications of using extracts instead of solid wood will be addressed in the Discussion section.

Experimental

Extract

The extract was made from commercially purchased southern pine (*Pinus* spp.) that was treated with ACQ to a retention of 4 kg m^{-3} (0.25 lb ft^{-3}). Then the wood was ground into sawdust and immersed in high-purity distilled water for 1 week at room temperature. The ratio of sawdust to water was 1:10 (weight basis). After the extraction period, the sawdust was separated out and the extract was stored at 1°C to minimize biological activity during storage. A portion of this extract was used in a previous study in which the polarization resistance was used to measure the corrosion of uncoated fasteners (Zelinka et al. 2008).

Fasteners

Two types of wood screws, which will be referred to as Fastener A and Fastener B, were purchased from a local retail outlet for this study. Both fasteners were advertised for exterior use with ACQ-treated lumber. Fastener A was nominally 50 mm long coated with a vinyl polymer. Fastener B was nominally 64 mm long and coated with an epoxy-based paint. Both fasteners had standard threads; the fastener heads were different but the heads were machined off prior to testing. As purchased, all of the type B fasteners had defects in the coating which were visible to the naked eye. The composition of the metal beneath the coating was not examined.

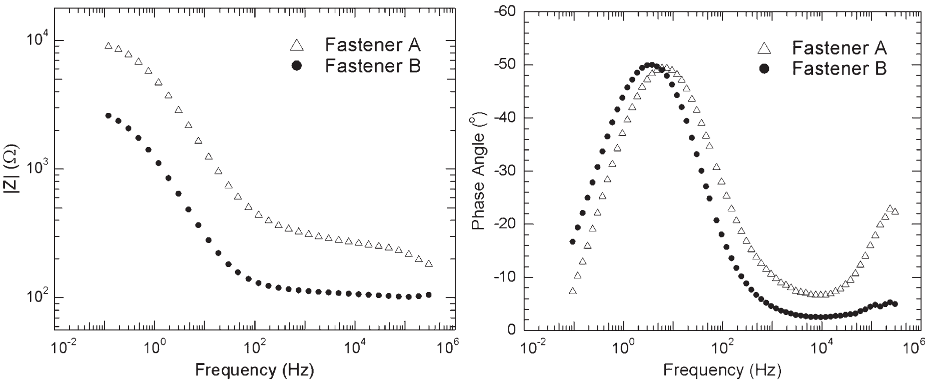

Figure 2. — Modulus and phase angle for Fastener A and B after 1 hour of exposure in an extract of ACQ-treated wood.

Because the large shear forces associated with driving the fastener may damage coatings, three different conditions were tested. Fasteners were tested:

1. out of the box, as a control;
2. after being driven into wood; and
3. after being driven through a metal plate into the wood to simulate fasteners used with connecting hardware.

The driven fasteners were installed with a power drill that was also operated in reverse to withdraw the fasteners. Once driven, the fasteners were machined such that they fit in the standard electrochemical cell described in ASTM G5 (ASTM 2005c). This was achieved by cutting the fasteners to a length of 41 mm, after which a hole was drilled and tapped so that the fastener could thread onto the standard polytetrafluoroethylene (PTFE) gasket system. A special jig was made out of PTFE so that the fastener could be gripped for machining without damaging the coating. The cut edge was completely covered by the PTFE gasket, and no corrosion was observed on the cut edge.

EIS testing procedure

Immediately prior to testing, the fastener was cleaned and degreased. The fastener was first placed in a soapy solution that was ultrasonically agitated for 5 minutes. Then it was rinsed with high-purity distilled water before being placed in another bath of high-purity distilled water and ultrasonically agitated for an additional 5 minutes. It was then quickly rinsed with acetone and rinsed twice more with high-purity distilled water before being placed in the extract.

The parameters of the EIS scan are similar to those published in ASTM G106 (ASTM 2005b). Upon being placed in the solution, the open circuit potential was measured with respect to a saturated calomel electrode (SCE) for 1 hour. The frequency was scanned between 3×10^5 and 1×10^{-1} Hz with 20 steps per decade of frequency. The amplitude of the applied voltage was 10 mV. To observe how the nonmetallic coating changed with time, impedance spectra were collected at 1, 24, 48, 168, 336, and 672 hours after immersion.

The data were fitted to an appropriate equivalent circuit using a non-linear least squares routine available in Gamry Echem Analyst Version 5.30[1] for fitting complex functions.

Results

Because impedance is a complex number with real component, Re(Z), and imaginary component, Im(Z), EIS spectra are generally plotted in either Bode or Nyquist diagrams. In a Bode diagram, both the phase angle given by arctan

$$\left(\frac{\mathrm{Im}(Z)}{\mathrm{Re}(Z)}\right)$$

and the modulus, |Z|, given by $\sqrt{(\mathrm{Re}(Z))^2 + (\mathrm{Im}(Z))^2}$ are plotted as functions of frequency. In a Nyquist diagram, Im(Z) is plotted against Re(Z), and frequency is contained implicitly. Because Im(Z) is negative for most electrochemical systems, it is customary to plot the negative of Im(Z) so that the data lie in the first quadrant. Each time constant from the equivalent circuit appears as either a semicircle in a Nyquist plot or a peak in the phase angle in a Bode plot.

Figure 2 shows the modulus and the phase angle for the coated screws 1 hour after immersion. Both fasteners exhibited a well defined time constant at lower frequencies, which can be seen by the peak in the phase angle plot. Fastener A appears to have a second peak at higher frequencies, but this peak extends past the range of frequencies measured (3×10^6 Hz). This second time constant is not observed with Fastener B.

For an ideal resistor and capacitor, the maximum phase angle should be –90°. The maximum phase angle for these data, however, occured at approximately –50°. Data whose phase angle peaks at a values below |90°| are often encountered in EIS spectra and are treated by replacing the capacitor with a constant phase element (CPE). A CPE can be modeled as a capacitor with a distribution of relaxation times (Cole and Cole 1941, Raistrick 1986, MacDonald and Johnson 1987). In the present data, this dispersion likely arises from distributions in defects and pore sizes in the fastener.

Fastener A can be fit with the traditional model (**Fig. 1**) where the capacitors have been replaced with CPEs. The best fit parameters are shown in **Table 1,** and the fit is displayed in Nyquist format in **Figure 3**.

Fastener B had only one time constant and could, therefore, be fit by a simpler model with a single CPE (**Fig. 4**). The best fit parameters are shown in **Table 1,** and the fit is displayed in Nyquist format in **Figure 5**. Prior to evaluation it could not be determined whether this time constant represents corrosion (τ_{dl}) or coating breakdown (τ_c). The time constant from this model, however, occurs at low frequencies, which suggests that it represents the corrosion time constant. In fact, the time constant is nearly the same frequency at which

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[1] Gamry Instruments, Warminster, Pennsylvania.

Table 1. — Results of complex non-linear least squares fitting of EIS spectra.

Fastener	Condition	R_u (Ω)	R_{pore} (Ω)	R_p (kΩ)	$Y_{o,coat} \times 10^6 \left(\left(\frac{A^2 s^3}{kg \cdot m^2}\right) s^{n_{coat}}\right)$	n_{coat}	$Y_{o,dl} \times 10^6 \left(\left(\frac{A^2 s^3}{kg \cdot m^2}\right) s^{n_{dl}}\right)$	n_{dl}
A	Control	< 1	300	10	1	0.5	40	0.7
	Wood	< 1	200	5	5	0.4	80	0.6
	Plate	< 1	200	3	0.9	0.5	130	0.7
B	Control	110	–	3	–	–	180	0.7
	Wood	130	–	2	–	–	160	0.7
	Plate	120	–	2	–	–	150	0.7

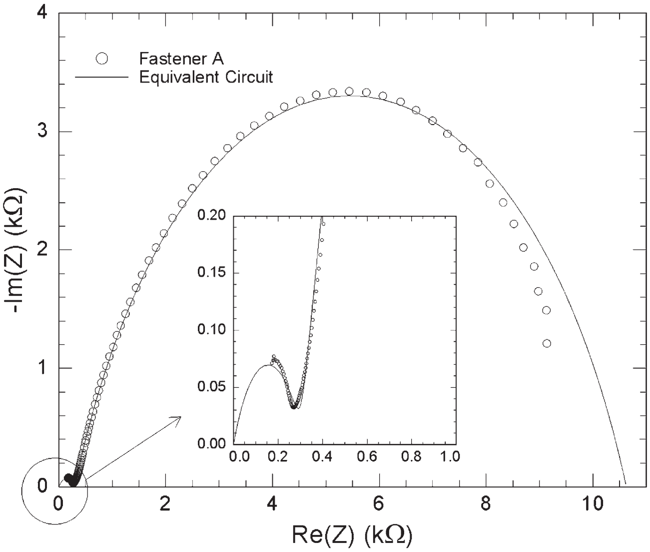

Figure 3. — Nyquist plot of Fastener A along with the equivalent circuit model fit. The coating time constant is the smaller semicircle on the left, which can be clearly seen in the inset (note the difference in scale of the inset).

τ_{dl} occurred for Fastener A, and when the magnitude of R_p is compared to published ranges of values in the literature (Loveday et al. 2004), it becomes clear that this peak results from the corrosion reaction and not the coating reaction.

If the observed behavior is caused by the corrosion reaction, the data raise the question of why the properties of the coating did not appear in the spectra. These fasteners had visible defects in their as-purchased condition. It is hypothesized that these defects cause R_{pore} to essentially become short-circuited and no longer measurable.

Driven fasteners

The spectra for fasteners driven into wood, or through a metal plate into wood, have the same general shape as the control fasteners, which means that the data can be fit with the same models. The only difference between the control fasteners (**Fig. 2**) and the driven fasteners (**Fig. 6**) is that the modulus |Z| has lower values for the driven fasteners. The results of the model fit are given in **Table 1**. The driven fasteners have lower values of R_p, which corresponds physically to a higher corrosion rate. There is no statistical difference between R_p values for fasteners driven through the plate into wood and those driven directly into the wood. These results are consistent with a more damaged coating, with more exposed area, and more corrosion, which is not surprising considering the shear forces associated with insertion.

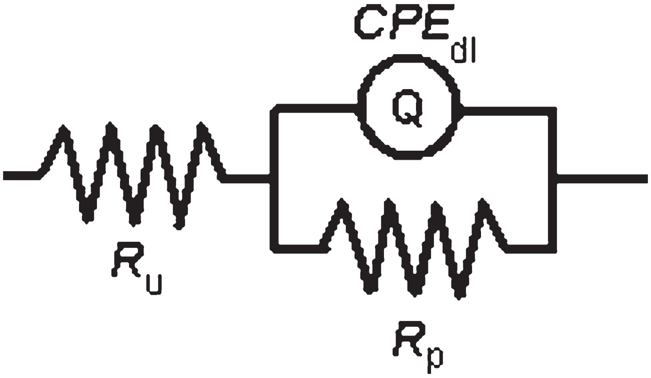

Figure 4. — The data from Fastener B contain only one time constant and can be fit with this simpler model, where R_u is the uncompensated solution resistance, R_p is the polarization resistance, and CPE_{dl} is the double layer constant phase element.

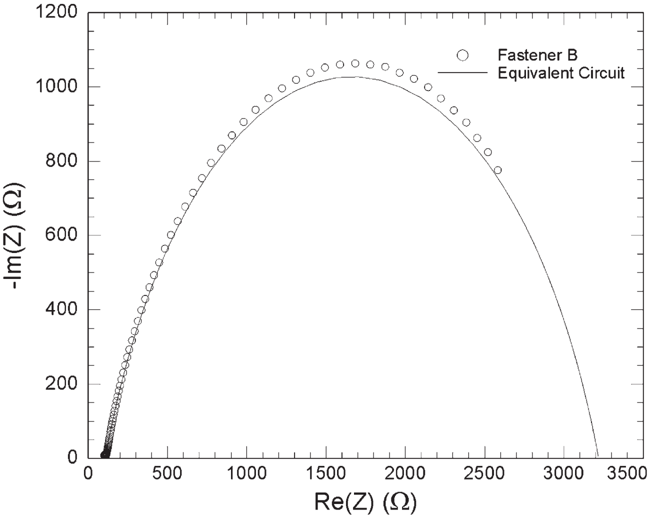

Figure 5. — Nyquist plot of Fastener B along with the equivalent circuit model fit. The data only contain one time constant, τ_{dl}.

Time progression of EIS data

For the fasteners tested in this study, the corrosion time constant appeared immediately after exposure, which

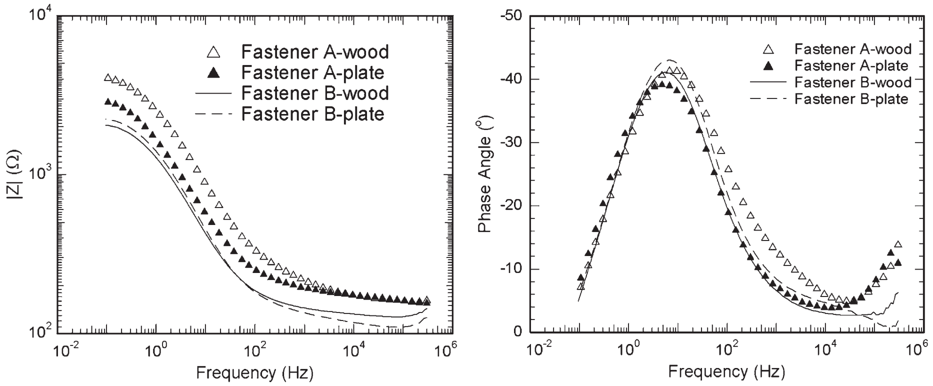

Figure 6. — EIS spectra of fasteners driven into the wood or through a plate into the wood.

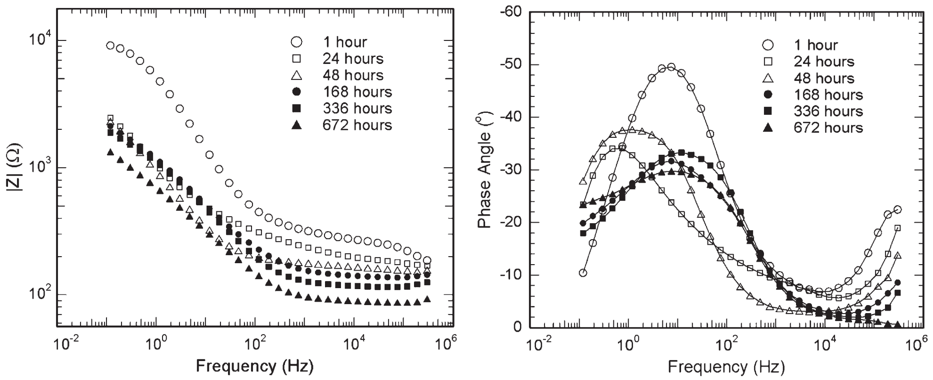

Figure 7. — Time progression of the EIS spectra for Fastener A. The peaks broaden and move toward lower frequencies.

suggests that substantial defects existed in the coating before testing. Corrosion products were visible with the naked eye after 24 hours of exposure for Fastener B and after 48 hours of exposure for Fastener A. Therefore, the time progression of the spectra from this study will be different than the traditional time progression for polymer-coated metals (Loveday et al. 2004) and have a different interpretation.

At times less than 2 weeks (336 hours), changes in the spectra were similar for all of the fasteners tested, independent of whether the fastener was driven or if it was Fastener A or B. For reference, the time progression of Fastener A out of the box is shown in **Figure 7**. There are several key changes; the spectra broaden out, the peaks in phase angle move to lower frequencies, and the polarization resistance decreases (the corrosion rate increases).

Data collected at times greater than or equal to 336 hours could not be fit with an equivalent circuit model because the spectra contained broad, unidentifiable peaks. Since the fasteners contained more than one defect, these broad peaks may be caused by competing corrosion reactions at different defects on the fastener surface. It may not be important that the spectra at these times could not be fit with an equivalent circuit because the coating has failed by this point.

Discussion

In the present study, it is not clear how changes in the EIS spectra with immersion time correspond to changes in fastener performance. Previously, a correlation had been found between 1-year exposure data and fasteners polarized *immediately* after immersion (Zelinka et al. 2008). It is doubtful that this correlation holds in the current work because many polymeric coatings fail by water adsorption in the coating, and the extract contains much more water than solid wood. In other words, the difference in corrosiveness between the extract and solid wood is greater for polymer-coated fasteners than for uncoated fasteners. But because both coated and uncoated fasteners exhibited a corrosion time constant upon immersion even in the out of the box condition, the evolution of the coating with time is irrelevant because the coating contained defects prior to the beginning of the test.

Conclusions and recommendations

The original intent of this research was to examine the viability of EIS as a tool for quantifying the corrosion of polymer-coated fasteners. How the coating properties changed after the fastener had been driven into the wood was also expected to be examined. But, a corrosion time constant was immediately observed for fasteners tested in the out of the box condition. That a corrosion time constant was observed in this condition means that the barrier properties of the polymer coating were damaged before the consumer could use the fastener.

Currently, ASTM subcommittees are developing acceptance criteria for polymer-coated metals used in contact with treated wood. Because the corrosion time constant is able to be separated from the adsorption time constant, EIS could be useful as a "pass-fail" acceptance criteria for polymer coatings. Tests could be conducted in either the out of the box or driven into wood conditions.

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