

***In-Situ* Corrosion Sensor for Coating Testing and Screening**

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Abstract

An *in-situ* corrosion sensor facilitates coating development and screening by detecting the early stages of corrosion well before degradation is visible. Based on electrochemical impedance spectroscopy (EIS), the sensor extends the use of this established laboratory technique from immersion only to different accelerated test conditions (such as salt fog or humidity) and ambient service environments. By enabling a direct quantitative comparison of the early stages of coating deterioration and substrate corrosion that occur in laboratory accelerated tests and service or field conditions, the laboratory tests can be validated and coatings screened more quickly.

Introduction

Development, testing, and screening of coatings are becoming increasingly more difficult as coating performance is improved. Accelerated laboratory testing (e.g., salt fog or various cyclic exposures) is required to induce coating degradation and substrate corrosion in a reasonable time frame. Such testing raises issues of degradation mechanisms (are the degradation mechanisms occurring in the test the same as those occurring during service?) and acceleration factors (if a coating lasts x months in the test, how long will it last in the field?). Visual inspection of the coated specimen is the most common means of judging the performance of the coating. This inspection is only semiquantitative (number of blisters, fraction of rusted area, etc.) and generally gives little information concerning mechanisms. It requires extensive deterioration to visually make distinctions and is unable to detect the very early stages of coating degradation. As a result, accelerated testing typically requires several months of laboratory exposure (compared to several years of ambient exposure) to allow discrimination between good coatings.

Different laboratory techniques, including electrochemical impedance spectroscopy (EIS), have been used to elucidate degradation mechanisms and to monitor the early stages of coating degradation and substrate corrosion.¹⁻⁷ Correlations between these laboratory measurements and service performance have been made. One of the principal difficulties with this approach is need for the specimen to be immersed in an electrolyte with external and, often, fragile reference and counter electrodes. This requirement limits the size and test conditions available unless clamp-on cells (beakers without bottoms) are used to temporarily expose a local area of a coated surface to an electrolyte^{8,9} as shown in Figure 1. The cells are messy and limited by the geometry and orientation of the surface they can monitor. They require access to the location being inspected and can only detect corrosion directly under the electrolyte. The presence of electrolyte alters the immediate environment of the surface at the time of testing. It may also alter the coating itself, as shown in Figure 1. A discolored spot on the coating surface developed where a portable EIS cell had been attached several months earlier although no spot was visible at the time of the initial measurement. Such an artifactual discoloration indicates that the measurement technique itself had an effect on the specimen, despite the relatively short duration of electrolyte contact

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and thorough rinsing with distilled water. As a result, researchers and engineers must be concerned with understanding what portion of the data reflects reaction to the test environment, and what portion reflects reaction to the measurement technique itself.

In this paper, we report on an *in-situ* corrosion sensor capable of detecting coating deterioration and substrate corrosion underneath a paint coating without the use of portable cells, messy electrolytes, and remote electrodes.^{10,11} Based on EIS, the sensor is sensitive to early stages of material degradation before any visual damage is present. It allows quantification of the deterioration of the actual coated panel or structure of interest during both ambient service conditions and laboratory accelerated exposures as opposed to monitoring the deterioration of the sensor itself.

Two versions of the *in-situ* sensor have been developed: a permanently attached sensor and a portable hand-held sensor. The former is suitable for corrosion inspection in inaccessible areas or for automatic or semi-automatic inspection of a particular area. A laboratory test specimen with an attached sensor is shown in Figure 2, left. The size and configuration of the sensor electrode can be adjusted for the particular specimen or structure being monitored. The hand-held sensor (Figure 2, right) is suitable for spot inspection where a permanent sensor is not desired or had not been previously placed. Table 1 compares the *in-situ* sensor with conventional EIS involving immersion or portable cells.

The *in-situ* corrosion probe is directly suited to detect the degree of coating degradation and the amount of substrate corrosion of both test specimens and real structures. By detecting degradation from the very early stages and allowing a quantifiable comparison between field or service degradation and that observed during accelerated testing, the sensor is valuable during coating development. Additionally, because it provides a warning before structure degradation occurs, preventative maintenance of a structure can be scheduled in time to forestall corrosion damage.

Table 1. Comparison of In-Situ Corrosion Sensor with Conventional EIS

In-Situ Corrosion Sensor	Conventional EIS
<ul style="list-style-type: none"> • Suitable for field use or laboratory test chamber/immersion • Permanent electrode is available for inaccessible regions • Hand-held sensor is available for structures/areas without a permanent sensor • Arbitrary structure configurations can be inspected • Easy set-up/inspection • Inspection can detect corrosion over large area 	<ul style="list-style-type: none"> • Requires immersion or clamp-on liquid cell • Cell requires accessible, flat, horizontal area, messy electrolyte, and remote electrodes • Set-up is time consuming and must be performed for each measurement • Corrosion is detected only directly under cell. • Can cause artifactual damage to coating

Examples

The initial stage of environmental degradation of a coating is absorption of moisture. Once moisture reaches the substrate, corrosion can occur. Figure 3 shows a series of EIS impedance spectra (magnitude of the impedance as a function of frequency) that illustrate typical behavior of a coated metal. Initially the coated metal demonstrates capacitive behavior (slope of -1) with very high impedance at low frequencies. As the coating degrades, its resistance decreases (as

modeled in an equivalent circuit) and the impedance becomes independent of frequency at low frequencies.

The low-frequency response can be tracked as a function of exposure time (Figure 4). The data show degradation to occur in three stages:

- Uptake of moisture by the coating
- Incubation time for corrosion
- Substrate corrosion.¹²

Similar behavior has been seen for different coatings and different exposure conditions. The relative times and impedance values for the three stages will depend on the quality and chemistry of the coating, the metal underneath, surface treatment, and the exposure conditions. In the example shown in Figure 4, the sensor demonstrates that the waterborne coating is not as effective as the epoxy polyimide coating. The impedance of the waterborne coating drops approximately one order of magnitude more than that of the organic solvent coating, reflecting the greater moisture uptake. Partially as a result of the increased moisture concentration at the interface, the incubation period is shorter and active corrosion of the substrate occurs sooner.

The predictive ability of the sensor is illustrated in Figure 5. A variety of different coatings and substrates were exposed to cyclic immersion/drying/humidity conditions that have been correlated with service conditions by the automotive industry. Each cycle is a business day and the entire 100-cycle test lasts approximately 5 months. Earlier discrimination of coatings is desired during the testing of different formulations. Two painted sensors were applied to each of the coated specimens and measurements were taken approximately every 10 cycles during the ambient drying stage. A very good correlation was obtained between the time required for the low-frequency impedance to decrease to $10^7 \Omega$ and the amount of corroded area on the specimen at the end of the test. In all cases, at the time at which the sensor indicated coating degradation, there was no rust or other visual signs of degradation. The sensor measurements were able to predict the amount of general corrosion present on the surfaces at the end of the test.

A principal advantage of the *in-situ* corrosion sensor is its ability to monitor corrosion under a variety of conditions in addition to immersion, for which conventional remote electrode EIS measurements are possible. The measurements discussed above were taken while the specimens were lying on the laboratory bench. Measurements in other tests have been acquired while the specimens have been in humidity or salt fog chambers or in the field.

One particularly important situation where *in-situ* sensors are extremely valuable is measurement in ambient service conditions or natural exposures under aggressive conditions, such as a beach exposure site. An on-going example is a series of panels that are being exposed aboard a ship in Hawaii (Figure 6). The panels are periodically shipped to the laboratory for sensor measurements. Alternatively, the potentiostat used to interrogate the sensors could be brought to the specimens. The hand-held sensor was selected for this evaluation. Figure 6 shows that some coatings are exhibiting noticeable degradation even after 5 months based on sensor measurements. No visual difference between the various coatings can yet be seen.

Because identical procedures and equipment are used for measurements taken under these conditions and under the accelerated laboratory conditions, material degradation in laboratory tests can be directly compared to degradation occurring in the field.

Summary and Conclusions

An *in-situ* corrosion sensor has been developed that extends the applicability of electrochemical impedance spectroscopy (EIS) to monitor material degradation beyond laboratory immersion studies. Two versions of the sensor are available: a permanent electrode that is especially suited for inaccessible areas or for areas for which a corrosion history or database is desired and a portable, hand-held electrode that is especially suited for areas where a permanent sensor is not desired for aesthetics or other reasons or where only a one-time measurement is needed. Both versions provide EIS measurements identical to conventional remote electrode procedures when tested in immersion. The ability of the *in-situ* sensor to monitor material deterioration from the very initial stages in accelerated tests, such as salt fog or humidity, and during actual field service enables two applications: 1) enhanced coating development with the quantitative comparison of degradation occurring during accelerated testing and system service use and 2) *in-situ* corrosion monitoring of critical structures to allow condition-based maintenance and reduce the likelihood of unforeseen corrosion-induced failure.

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References

- ¹ F. Mansfeld, Corrosion 37, (1981): p. 301.
- ² M. Kendig, F. Mansfeld, and S. Tsai, Corros. Sci. 23, (1983): p. 317.
- ³ M. Kendig and J. Scully, "Basic Aspects of the Application of Electrochemical Impedance for the Life Prediction of Organic Coatings on Metals," Corrosion/89, paper no. 32, (Houston, TX, NACE, 1989).
- ⁴ J.R. Scully, J. Electrochem. Soc. 136, (1989): p. 979.
- ⁵ J.N. Murray, Prog. Org. Coat. 31, (1997): p. 375.
- ⁶ J.N. Murray and H.P. Hack, "LongTerm Testing of Epoxy Coated Steel in ASTM Sea Water Using EIS," Corrosion/90, paper no. 140, (Houston, TX, NACE, 1990).
- ⁷ J.A. Grandle and S.R. Taylor, Corrosion 50, (1994): p. 792.
- ⁸ A. Zdunek and X. Zhan, "A Field EIS Probe and Methodology for Measuring Bridge Coating Performance," Proc. 4th World Congress on Coating Systems for Bridge and Steel Structures, (Steel Structures Painting Council, St. Louis, MO, February 1995).
- ⁹ P.C. Su, O.F. Devereux, and W. Madych, Structural Integrity in Aging Aircraft, AD-Vol. 47, C.I. Chang, and C.T. Sun, ed., (New York, American Society of Mechanical Engineers, 1995).
- ¹⁰ G.D. Davis and C.M. Dacres, "Electrochemical Sensors for Evaluating Corrosion and Adhesion on Painted Metal Structures," U.S. Patent 5,859,537.
- ¹¹ G.D. Davis and C.M. Dacres, "Portable, Hand-Held, In-Situ Electrochemical Sensor for Evaluating Corrosion and Adhesion on Coated or Uncoated Metal Structures," patent pending.
- ¹² G.D. Davis, P.L. Whisnant, and J.D. Venables, J. Adhes. Sci. Technol. 9, (1995): p. 433.

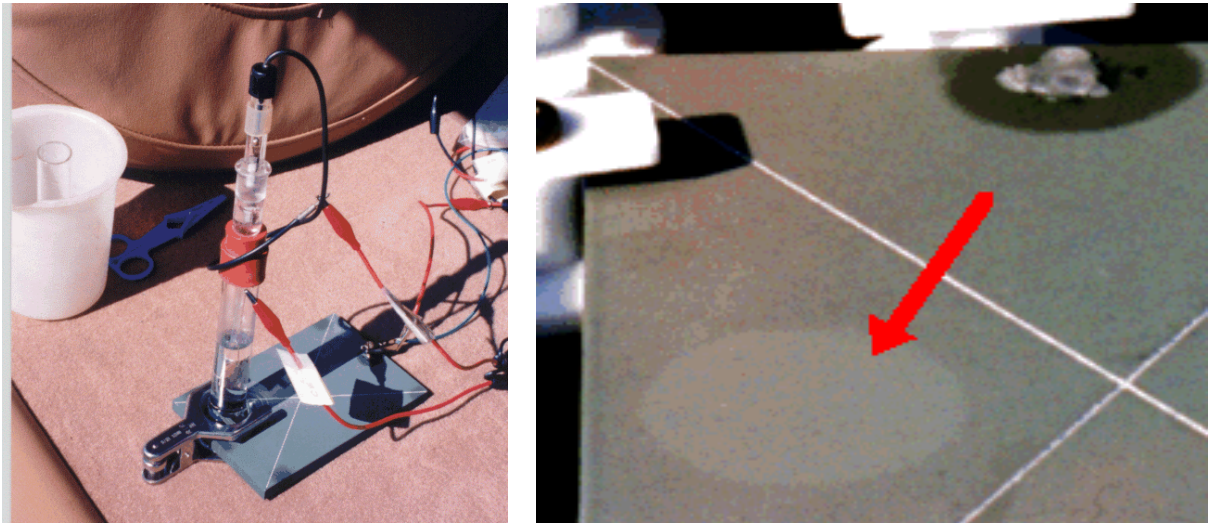


Figure 1. Left: Portable EIS cell attached to coated specimens during seacoast exposure. Individual cells contain reference and counter electrodes as well as electrolyte. Right: Faded spot that developed on the surface of coated sample at location of portable EIS cell. The cell was attached, filled with electrolyte, and removed several months before photo was taken.

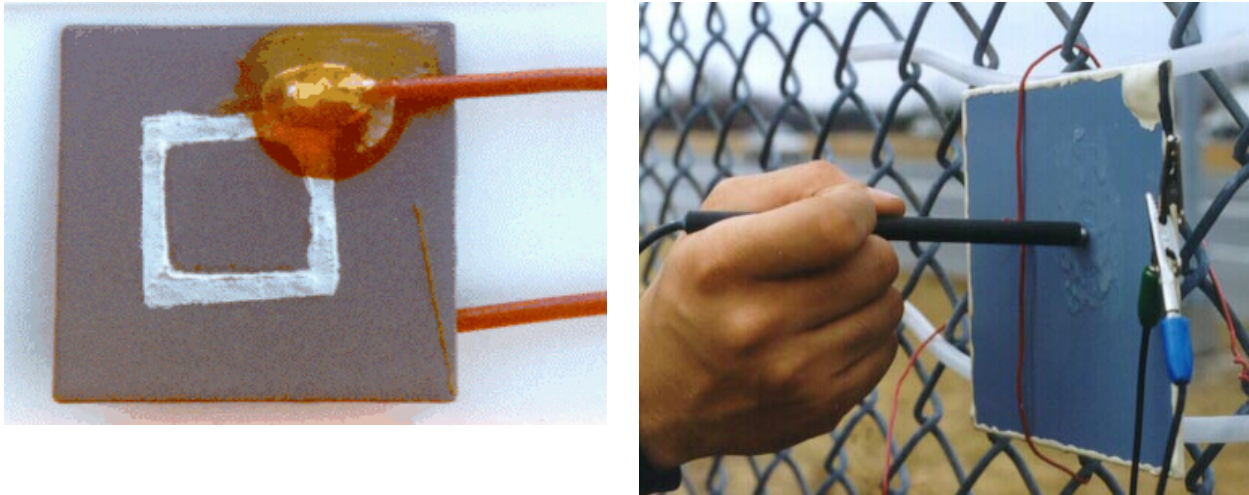


Figure 2. Left: Painted aluminum test specimen with an attached in-situ corrosion sensor. Right: Hand held in-situ corrosion sensor.

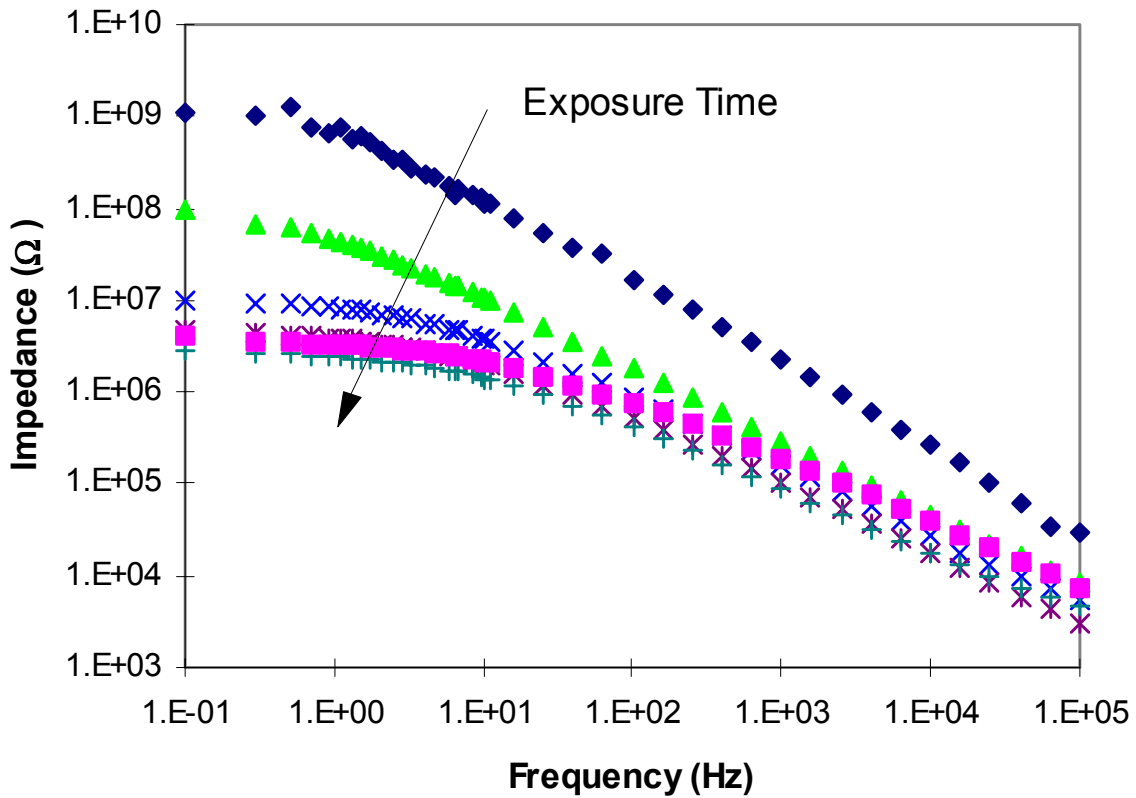


Figure 3. Impedance spectra of painted aluminum as a function of exposure time. Initially, the spectrum is capacitive (slope of -1) over nearly all frequencies. As the coating degrades, the low-frequency region becomes resistive (independent of frequency) with decreased impedance. Similar behavior is observed for all metals and most coatings although time frames may vary.

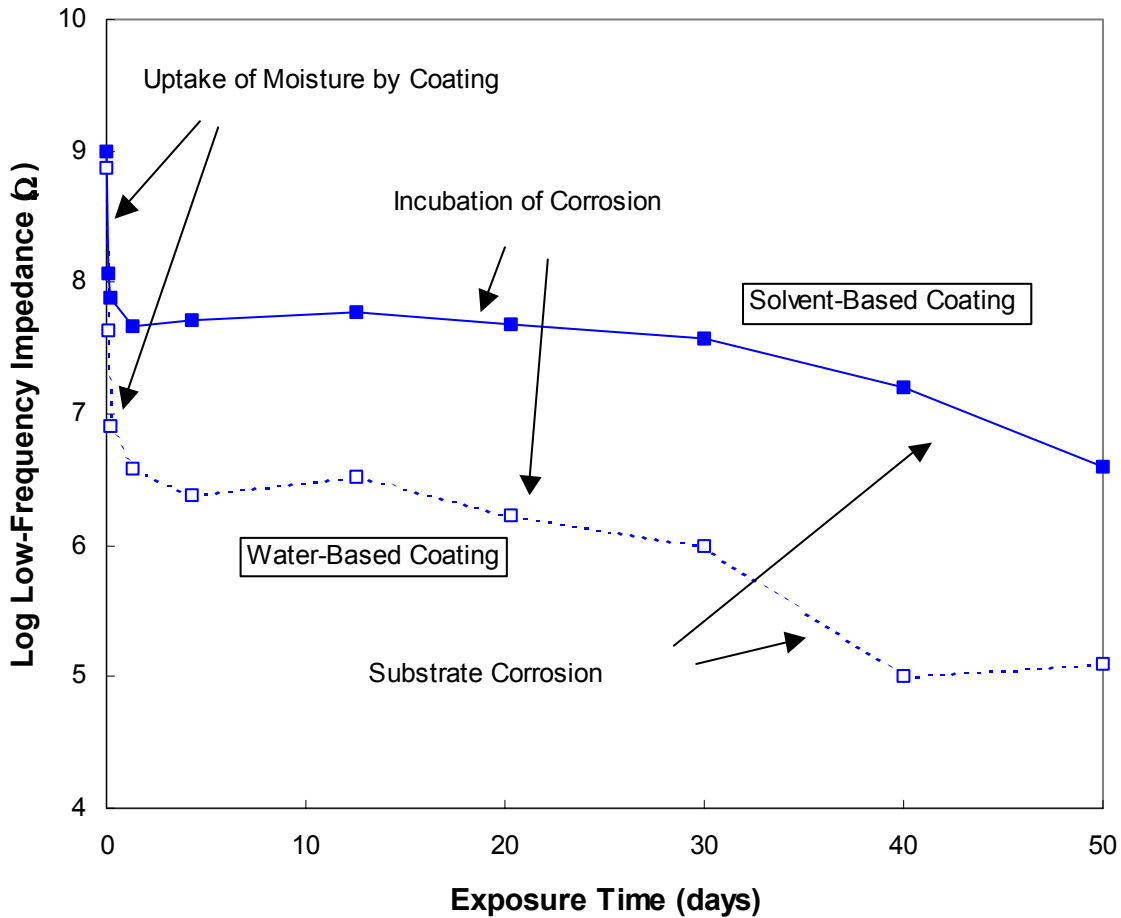


Figure 4. Low frequency impedance as a function of time for 2024 and 6061 aluminum specimens coated with either an epoxy polyimide or a waterborne epoxy. A urethane topcoat was used in both cases. The waterborne coating was clearly less effective than the epoxy polyimide. The coatings were immersed in water at room temperature during the experiment duration.

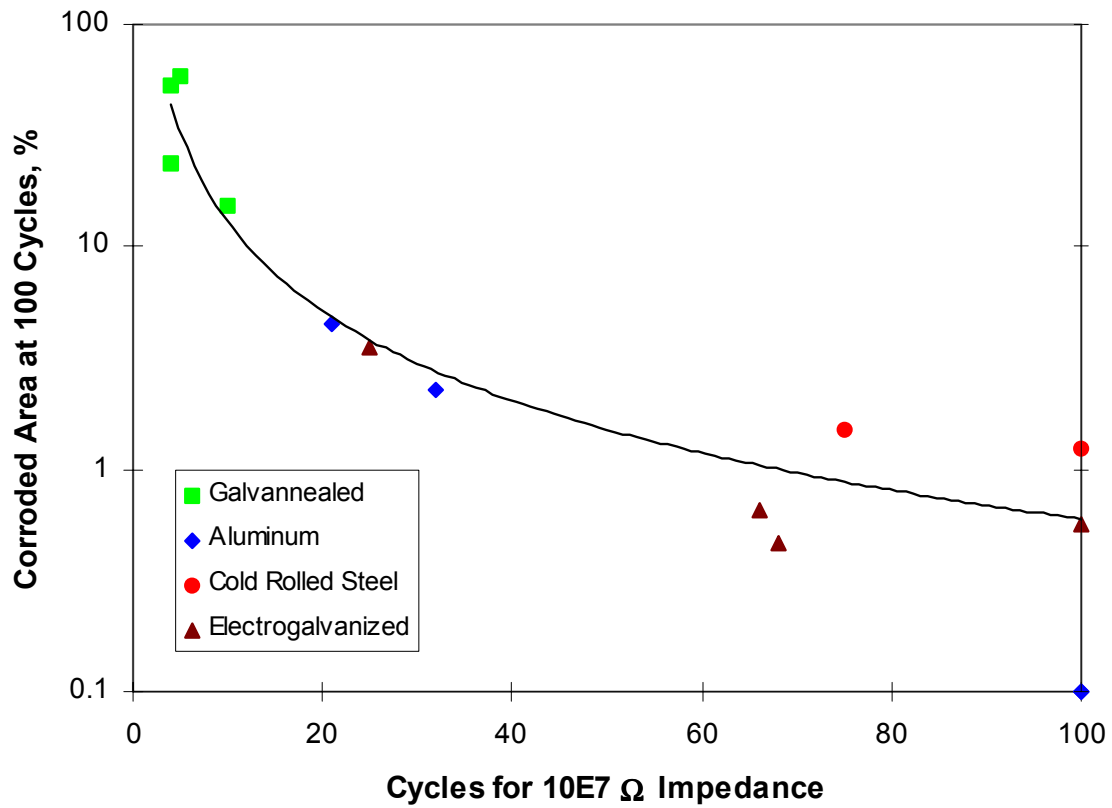


Figure 5. Corroded area after 100 cycles of a cyclic corrosion test as a function of time required for the low frequency impedance to drop to $10^7 \Omega$. Four different substrates with different coatings were tested.

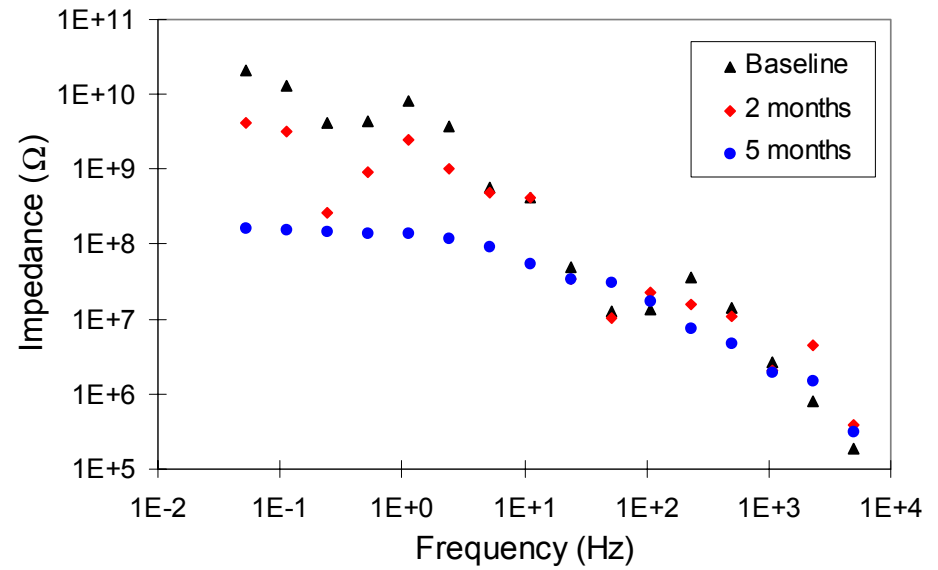


Figure 6. Left: Test panels mounted on ship. Right: Sensor measurements showing degradation of a coating exposed on a ship in Hawaii.