

In-Situ Sensor to Detect Moisture Intrusion and Degradation of Coatings, Composites, and Adhesive Bonds

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Abstract

An *in-situ* sensor, based on electrochemical impedance spectroscopy (EIS), has been developed that can detect the absorption of moisture in polymeric systems. In the case of a coated metal, moisture intrusion into the coating foretells corrosion of the substrate so that the sensor is sensitive to the very early stages of corrosion. In an adhesive bond, the sensor monitors ingress of moisture into the bondline that causes plasticization of the adhesive and hydration of an aluminum adherend. Thus, it is able to warn of impending bond degradation before delamination or even substantial weakening of the bond occurs. For a composite, the sensor detects low concentrations of absorbed moisture that can induce delamination and other damage during repair operations. The two versions of the sensor, a permanent electrode and a hand-held probe, give identical results to conventional three-electrode measurements that require immersion in the laboratory or clamp-on liquid cells. In contrast, the sensor is suitable for identical measurements under ambient service conditions as well as during laboratory accelerated testing. Applications of the *in-situ* sensor include development/screening of coatings, health monitoring of coatings and adhesive bonds to enable condition-based maintenance of structures, and inspection of composite structures prior to repair.

Introduction

Electrochemical Impedance Spectroscopy (EIS) has long been used to evaluate coatings and study corrosion in the laboratory.¹⁻⁷ Correlations have been made with EIS parameters, such as low-frequency impedance and breakpoint frequency, and performance under different conditions. Initially, a coating exhibits capacitive behavior with very high impedance at low frequency. As the coating absorbs moisture, the low-frequency impedance decreases and becomes independent of frequency (Figure 1). The low-frequency impedance is a sensitive measure of coating and substrate health; it decreases by several orders of magnitude as moisture is absorbed and substrate corrosion occurs. This change occurs well before any visual indication of deterioration.

Conventional EIS requires immersion of a specimen into an electrolyte and the use of remote counter and reference electrodes. This procedure is suited for the laboratory as long as small specimens and immersion conditions are suitable for the study. Evaluation of larger specimens is possible with the use of flat cells (beakers without bottoms) that can be clamped to a specimen or structure and filled with electrolyte. Counter and reference electrodes are then inserted into the electrolyte and EIS spectra acquired. This procedure allows measurements to be taken in the field in addition to the laboratory,⁹⁻¹¹ but requires an accessible, flat, smooth, and (preferably)

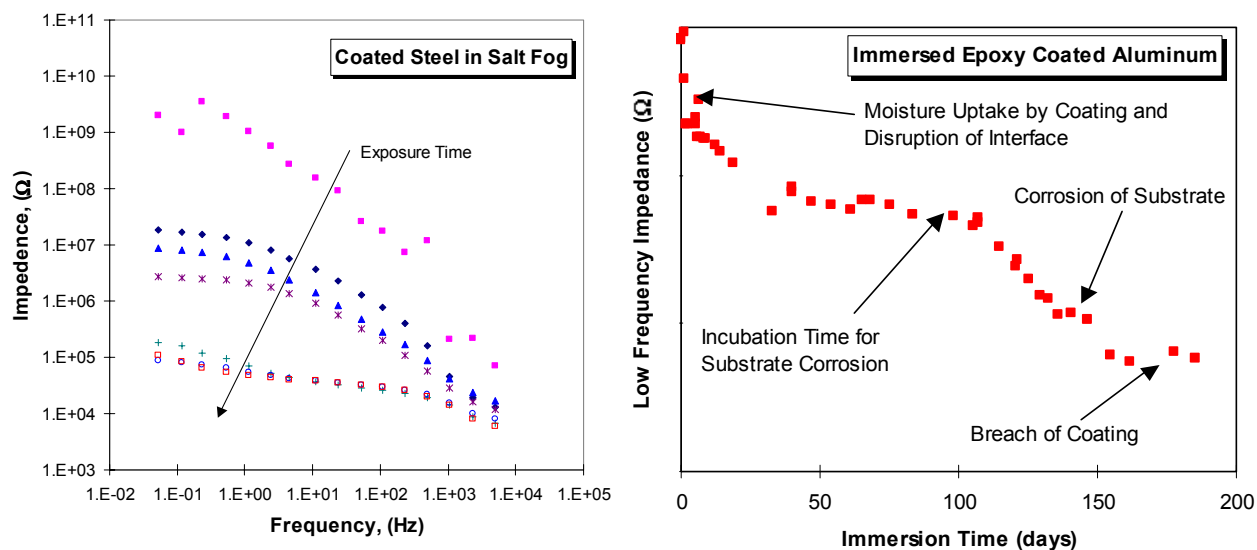


Figure 1. Left: Typical impedance spectra of a coating during degradation. Right: Low-frequency impedance as a function of exposure time showing three stages of degradation: moisture absorption, incubation, and substrate corrosion.

horizontal surface. It provides a local indication of the coating and substrate health; the measurement probes only the area wetted by the electrolyte. The process generally is time-consuming and involves mounting of the cells, handling of the fragile electrodes, allowing the specimen to come into quasi-equilibrium with the electrolyte, acquiring data, removing and storing the cells and electrodes, and rinsing the surface. In some cases, the several-hour exposure to the electrolyte can cause artifactual damage to a coating during subsequent ambient exposure (Figure 2).¹²

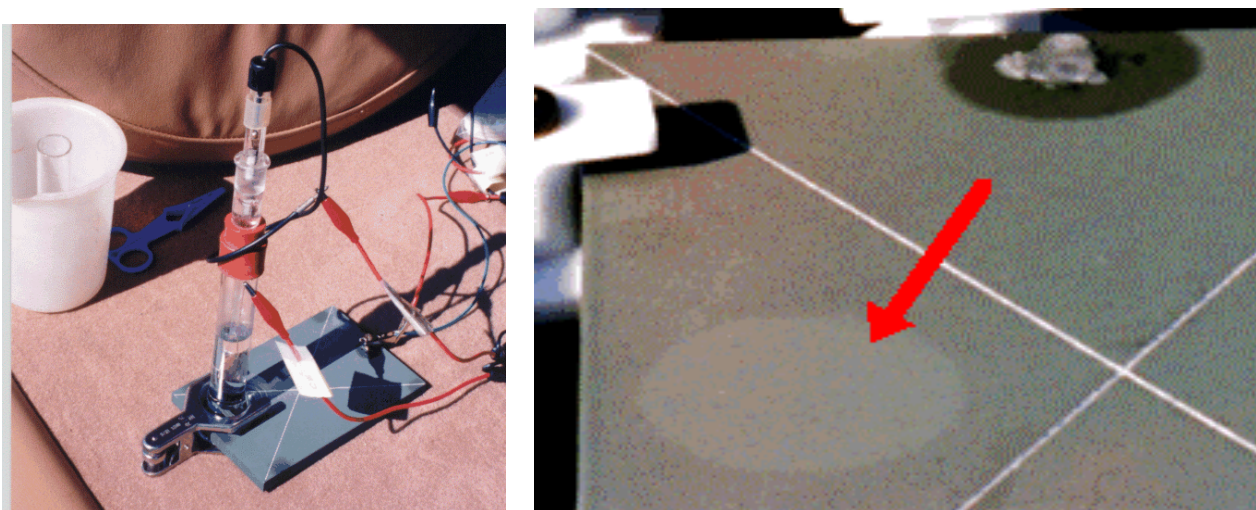


Figure 2. Left: Portable EIS cell attached to coated specimens during seacoast exposure. Individual cells contain reference and counter electrodes as well as electrolyte. Right: Faded spot that developed on the surface of coated sample at location of portable EIS cell. The cell was attached, filled with electrolyte, and removed several months before photo was taken.

Neither conventional immersion nor flat cell EIS is suitable for measuring ambient moisture uptake in a composite or adhesive bond. The lack of a metallic substrate to act as the working electrode would prevent EIS from being acquired from a composite with the possible exception of graphite composites. In the case of an adhesive bond, lack of electrolyte access to the adhesive would also prevent EIS from probing the bonded area. For both applications, immersing the composite or joint would cause additional moisture absorption and prevent accurate determination of moisture content.

A new, *in-situ* corrosion sensor has been developed that addresses these issues and allows EIS measurements to be taken in the field or laboratory under ambient or accelerated testing conditions.¹²⁻¹⁹ It is suitable for coated metals, composites, and adhesive bonds. As such, it extends the applicability of EIS to aging structures enabling condition-based maintenance (CBM) and to coating development and screening in exposures ranging from ambient to salt fog (ASTM B117) to cyclic accelerated testing (e.g., Prohesion, Ford APG, GM 9540P, and SAE J2334). The *in-situ* sensor is compared to conventional EIS in Table 1.

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

<i>In-Situ</i> 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 configuration • Easy set-up/inspection • Inspection can detect corrosion over large areas • Capable of detecting moisture in composites and adhesive bonds 	<ul style="list-style-type: none"> • Requires immersion or clamp-on liquid cell or similar gel/sponge cells • 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 • Not suitable to detect moisture in composites or adhesive bonds

Two versions of the sensor have been developed: a painted electrode that is permanently attached to the structure of interest and a hand-held probe that is pressed against the surface only while measurements are being acquired (Figure 3). Both versions give identical results to each other and to conventional EIS measurements during comparison immersion studies. Consequently, the procedures and analyses developed for conventional EIS can be applied directly.

The choice of sensor is dependent on the specific application. The permanent sensor is well suited for monitoring inaccessible areas of a structure and evaluating test panels in environmental chambers, such as a salt fog chamber. The hand-held sensor is best suited for spot checks of specimens without the permanent sensor or in areas where permanent sensors are not desired for reasons of aerodynamics or visual appearance. It is also well suited for inspection of composites. Both versions are suitable for monitoring adhesive bonds.

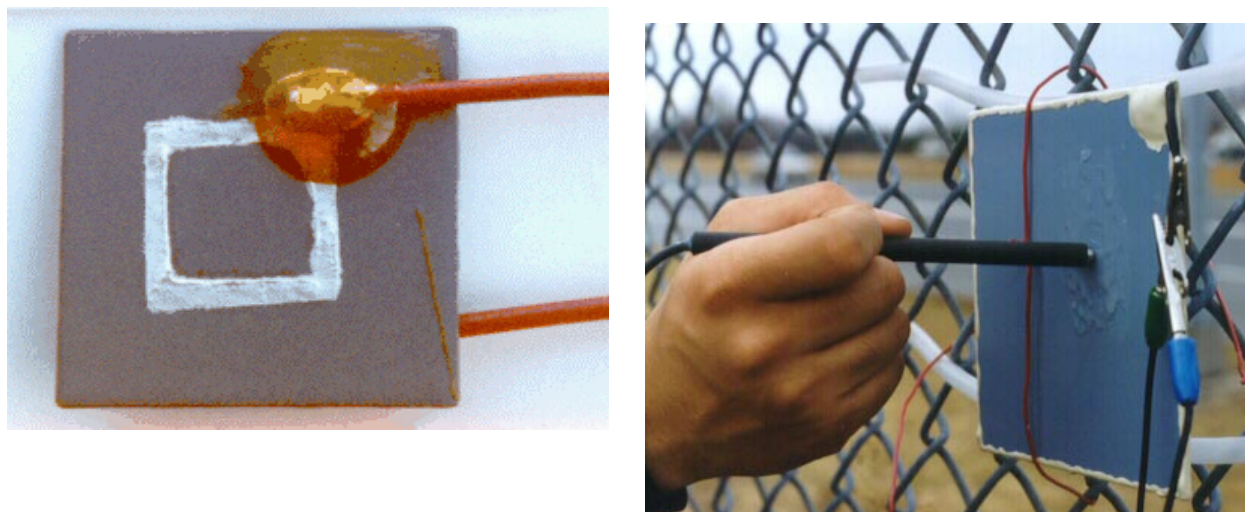


Figure 3. Left: Painted aluminum test specimen with an attached in-situ corrosion sensor. Right: Hand held in-situ corrosion sensor.

Conventional nondestructive evaluation (NDE) commonly requires extensive corrosion to detect corrosion products or thinning of the structure. NDE of composites and adhesive joints generally detect voids, delaminations, and other gross defects. Detecting moisture in a composite or an adhesive bond before serious damage is very difficult, if not impossible. Sensors, such as the ones described here, serve to provide early warning of the initial stages of damage.

Other types of corrosion sensors have also been developed. Several of these are witness-type sensors that detect corrosion of one or more components of the sensor. One example involves a bimetallic strip. The charge transfer induced by the galvanic attack of the anodic metal by the cathodic metal is monitored.²⁰ Another incorporates a bimetallic pair of electrodes onto a silicon chip along with the necessary electronics.²¹ Others involve metallic coatings on optical fibers and monitor the corrosion of the metallic coating.²² Although each operates on a different principle, the key commonality that distinguishes them from the technology reported here is that they monitor the corrosion of the sensor itself and not of the structure of interest. Accordingly, the sensors are consumed and, because they typically involve thin films, have a limited lifetime (in the case of a harsh environment, the lifetime can be very short). The information they provide is related to the corrosivity of the environment. They do not provide the information that is desired – the health of the actual coated structure.

Because they determine the corrosivity of the environment, these sensors are best suited for estimating the likelihood of a structure to corrode. Corrosivity measurements must be taken over time, they cannot be used to take a “snapshot” of a structure’s health or condition. Nonetheless, such sensors can be used as part of a condition-based maintenance procedure although they give only indirect information. They cannot be used to evaluate the effectiveness of different coatings. The alternative sensors are suitable for adhesive bonding only if they are incorporated into the bond itself during fabrication. This has been demonstrated in the case of coated fiber optics, but the invasive procedure is clearly not possible after the joint is made. None of these sensors is suitable for monitoring moisture in a composite. The only procedure currently used is to monitor the moisture released as the composite is dried in an oven.

Coated Metals

Detection of the early stages of degradation of coated metals is important in two distinct applications. The first is to facilitate distinction between different coatings in accelerated testing. The second is to detect or monitor degradation of a critical structure in the field.

Because high-performance coatings are very good, screening or ranking coating formulations can require a long-time, even with accelerated testing in the laboratory. It is not uncommon for an accelerated test to take three to five months. Making the test more aggressive can reduce the time required, but there is always a concern that different degradation mechanisms are involved compared to service conditions. If this is the case, the testing is not valid. Thus, there is a need for corrosion sensors that can detect and quantify the early stages of corrosion. There is a further need to be able to directly compare the degradation in an accelerated test to that occurring during service.

The second application involves health monitoring of critical structures in the field. Periodic inspection of both inaccessible and accessible areas of an airplane or other structure to track corrosion from the early stages would enable condition-based maintenance. In other cases, quick spot inspection of structures are desired without the need for permanent attached sensors or long-term exposure of sensors.

Coating Development/Screening

Several experiments have been used to validate the *in-situ* corrosion sensors, compare their results with other measurements, and evaluate different coating systems. The predictive ability of the sensor is illustrated in Figure 4. A variety of different coatings and substrates was exposed to cyclic immersion/drying/humidity conditions that have been correlated with service conditions in the automotive industry. 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 after the full exposure, as determined by the ASTM D1654 procedure. The cold-rolled steel specimen lying above the curve experienced corrosion beginning at an unprotected edge and rapidly progressed underneath the paint. The sensor detected the corrosion once it began, but the different corrosion mechanism allowed substrate degradation to occur much more rapidly.

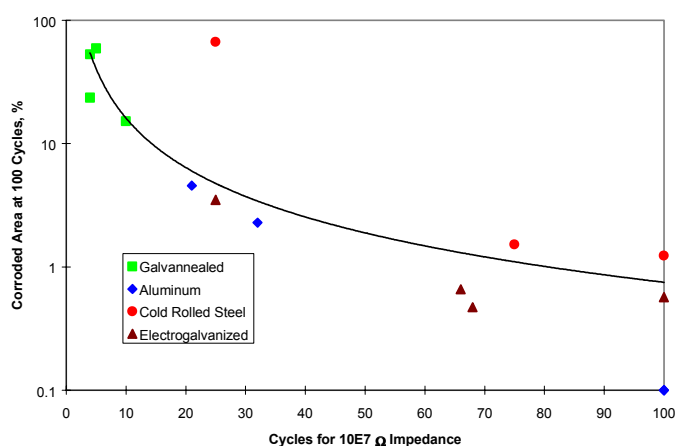


Figure 4. Corroded area after 100 cycles of a cyclic corrosion test as a function of time for the low-frequency impedance to drop to $10^7 \Omega$. Four different substrates with different coatings were tested.

Two examples of evaluation of different coating systems serve to illustrate the screening and evaluation capabilities of the sensor. In the first, a series of primers and appliqués were evaluated in a cyclic test designed to mimic shipboard exposure. Very little visual distinction could be made between the different panels at the end of the five-month test. The difference in the logarithm of the low-frequency impedances at the beginning and end of the test is plotted for the primer/appliqué matrix of Figure 5. The individual measurements are in the interior with the averages for the appliqués and primers in the front and right, respectively. The overall average is at the corner. The data clearly show that Film #1 is superior and that Film #2 gives the worst protection. For the primers, Primer #1 and Primer #2 were the best. Primer #7 is the worst. Based on these results, Film #1 with either Primer #1 or Primer #2 was recommended.

Several topcoat/primer systems were evaluated using another cyclic exposure test (Figure 6). The sensor measurements, which were taken periodically during the exposure, reflect the stability and water resistance of the topcoat. The panels were scribed and creepage or corrosion from the scribe was also measured. The creepage reflects the adhesion and inhibitive capability of the primer. The two parameters are correlated in Figure 6. In this figure, the best coatings would be near the origin – they would exhibit little moisture absorption and little corrosion at the scribe. The data clearly show that the two parameters are only partially related and that the primer and topcoat properties can be independently varied. Several coating systems showed significant water absorption but little spread of corrosion from the scribe. One showed significant corrosion at the scribe although the topcoat was very moisture resistant. Interestingly, the best coatings exhibited the best reproducibility from measurement-to-measurement and from specimen-to-specimen. The poorer coatings were more likely to have significant specimen-to-specimen variation or even changes in a single specimen over the course of taking duplicate measurements.

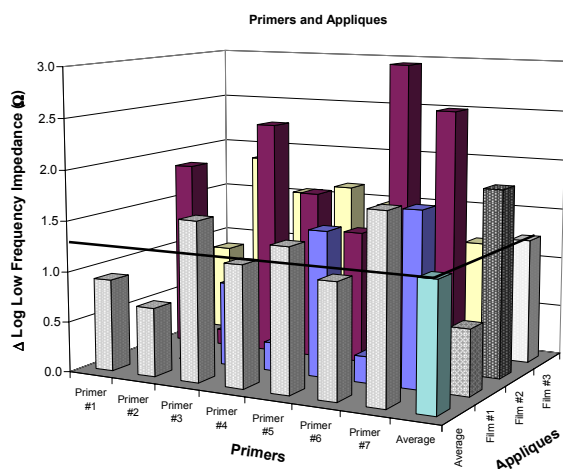


Figure 5. Difference in low-frequency impedance caused by a cyclic accelerated test for a series of primers and appliqués. Averages for each primer and for each appliqué are given on the right and front, respectively.

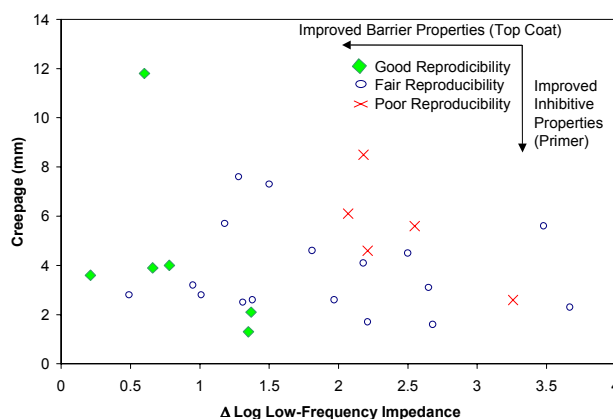


Figure 6. Creepage from a scribe as a function of the difference in log low-frequency impedance caused by a cyclic accelerated test for several top coat/primer systems. The best coatings would be near the origin. Also shown is a measure of the reproducibility from run-to-run and specimen-to-specimen. The best performing coatings have the best reproducibility.

Field Inspection

The sensors have also been used to evaluate coatings and structures in the field as illustrated by the following three examples. In the first, spot inspections were taken of primed areas inside a C-135 that was undergoing maintenance at Tinker AFB. Three areas were chosen: 1) good, original primer; 2) good primer that had been repaired at some time in the past; and 3) deteriorated primer that needed to be repaired. The sensor readily distinguished between the good and bad primers as illustrated in Figure 7. The demonstration showed that there was no problem making a ground connection to the aluminum structure and that the deteriorated primer exhibited low-frequency impedance two-to-three orders of magnitude below that of the good primers. Each measurement took only a few minutes.

The second example involves three land vehicles. One vehicle had been stored inside for several years and was in very good condition. The other two vehicles had been extensively used in a corrosive environment. Sensor measurements were taken in several areas on each vehicle. Although the later two vehicles had considerable rust, care was taken to acquire impedance spectra away from the rust in areas where the coating system looked good. The data of Figure 8 clearly show a difference between the coatings on the new and used vehicles with the impedance decreasing by two-three orders of magnitude although there were no visual differences in the areas inspected. The measured low-frequency impedance of the two used vehicles seemed to correlate with the general visual appearance – the one with the lowest impedance had the greatest rust over its body.

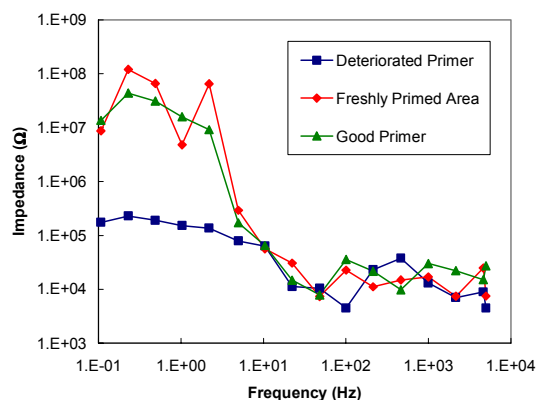


Figure 7. Impedance spectra of primed areas in the interior of a C-135.

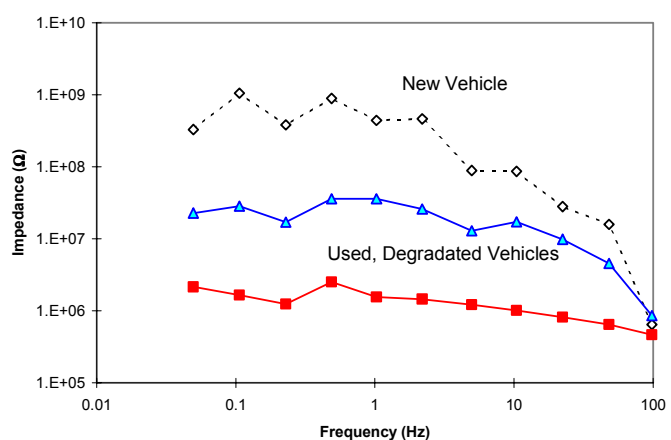


Figure 8. Impedance spectra from new and corroded land vehicles.

The final example concerns a series of coated panels that are being exposed on a ship in Hawaii. Periodically, the panels are returned to the laboratory for inspection with the handheld corrosion sensor. Although there is little visual difference in the panels, some showed a significant decrease in the low-frequency impedance after only five months of ship-board exposure. Figure 9 shows the worst case. Here the coating's low-frequency impedance decreased by approximately three orders of magnitude in the first 5 months. At that point, the coating stabilized and little change occurred over the next seven months.

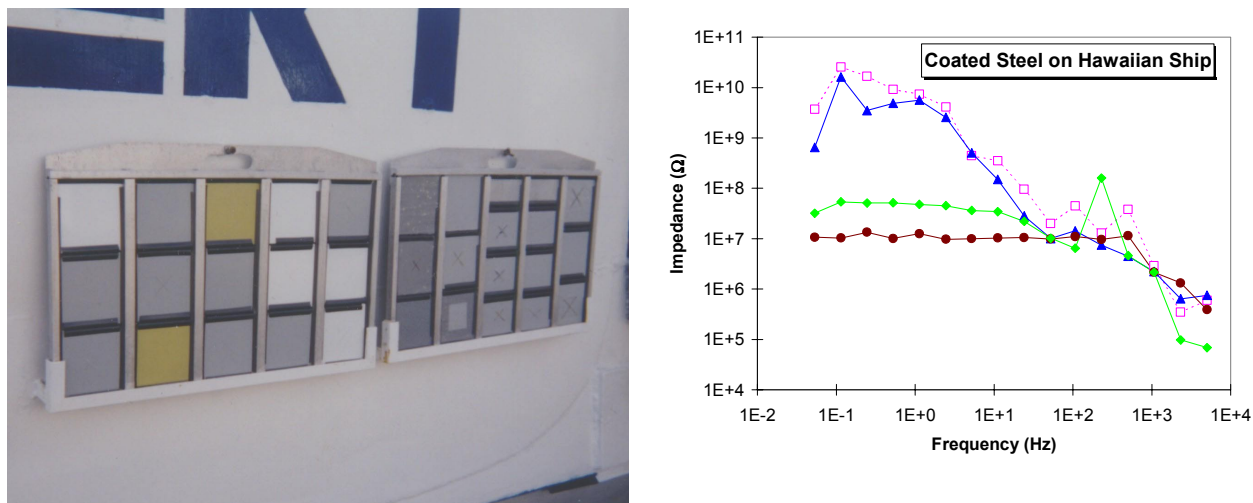


Figure 9. Left: Coated aluminum and steel panels on side of ship. Right: Impedance spectra of coated steel specimen exposed on a Hawaiian ship. The exposure times are as-received and 2, 5, and 12 months exposure.

Composites

Absorption of moisture in composites of Navy and Air Force aircraft can cause significant damage in two ways:

- Moisture can enter honeycomb structures and corrode the thin aluminum honeycomb.
- When an aircraft is repaired, the heat required to cure the adhesive will cause the moisture to become steam. The resulting pressure can cause more damage than that originally being repaired.

The first mechanism will greatly weaken the composite structure. In at least two cases, rudders on the F/A-18 have failed in-flight with loss of 80-90% of one of the rudders. Failure analysis of the remaining section indicated extensive honeycomb corrosion near the mid-hinge point due to moisture ingress via the grounding terminal. Fillet bond failure between the core and the graphite/epoxy skin leading to skin delamination was also noted in the lower recovered section.²³

In another example, x-rays detected water in an F/A-18 rudder. The engineering investigation showed aluminum corrosion products in the drained fluid. Ultrasonic C-scans showed a large area of attenuation around the mid-hinge point. Porta Pull plugs from that area showed very low strengths with higher strengths in the surrounding areas. All plugs showed varying degrees of adhesive failure mode.

Moisture in the composite, in the adhesive between the composite and the core, or in the core itself can cause significant damage during repair when the moisture turns to steam and internal pressure can exceed bond strengths. The repair failures are more pronounced with the use of 350°F-curing adhesives and have led to change orders authorizing the use of 250°F-curing adhesives during Depot level composite repairs.²⁴ Figure 10 shows an example of such repair-induced damage. During the curing of the repair patch on the left, additional delamination, marked by the black line surrounding the patch, occurred as residual moisture turned into steam.



Figure 10. F/A-18 trailing edge flap following repair showing additional moisture-induced delamination during the repair operation.

Glass Polyimide Composites

Sensor measurements obtained from glass polyimide specimens demonstrate very similar behavior to coated metals because of the nonconductive nature of the composite. Two sensor electrodes were placed on the same side of the composite to simulate inspection of an aircraft where two-sided access was not available. Complementary measurements on opposite sides of the panel gave very similar results. Representative spectra and low-frequency impedance measurements are shown in Figure 11. The spectra showed a mainly capacitive impedance behavior although a resistive low-frequency region is seen following moisture adsorption. The low-frequency impedance versus moisture content relationships are given for both sensor orientations. Two points can be immediately derived from these spectra:

- Sensors oriented to make measurements from the same surface (same-sided) or through the material thickness (opposite-sided) give equivalent impedance results,
- A logarithmic impedance decrease is seen for moisture levels in the range of 0.6% to > 2.0%.

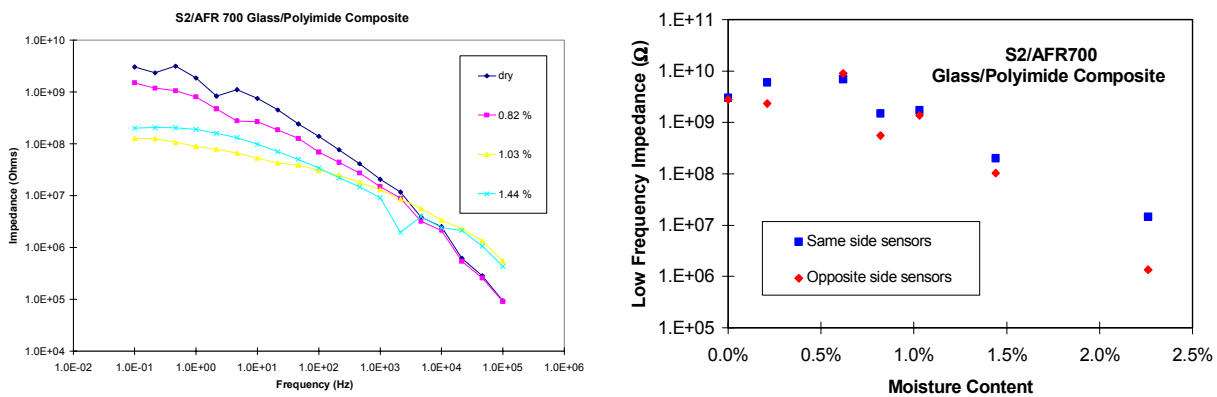


Figure 11. Left: EIS spectra for a glass/polyimide composite using same-sided measurements. Right: Low-frequency impedance versus moisture content for both sensor orientations,

Graphite-Epoxy Composites

Selected EIS spectra for a Navy graphite-epoxy material are shown in Figure 12. Same-side and opposite-side measurements gave similar results as did measurements with the electrodes oriented along the outer fiber direction and at 45° to this direction. The overall impedance values for these composites are generally lower than the impedance values for the glass/polyimide composites just discussed. Also, the change in impedance as a function of moisture content is less pronounced in the graphite-epoxy composites as compared with the glass-polyimide specimens. We attribute both of these effects to the presence of the conductive graphite fibers in the composite structure, which serve to both lower the overall impedance and to alter the effects of moisture absorption. In most cases, the impedance behavior remained capacitive over the entire frequency range and did not have a low-frequency resistive component. Nonetheless, spectra information could be correlated with moisture levels. To better understand and track the changes these composites underwent as a result of absorbing moisture, equivalent circuit modeling was used. This approach uses the data collected at all frequencies but is dependent on the choice of circuit model.

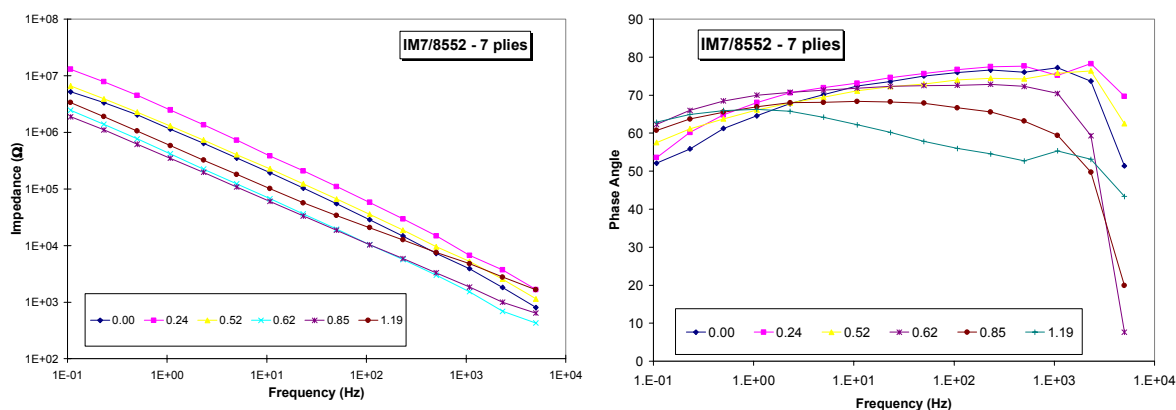


Figure 12. EIS spectra of the IM7/8552, 7 ply specimen following different periods of humidity exposure. The moisture uptake (in percent) is given in the legend. Plots are shown in Bode magnitude (left) and phase (right) formats.

Equivalent circuit analysis focused on identifying circuits that were physically significant with the intention of identifying circuit elements particularly sensitive to changes in the quantity of moisture absorbed. The method was based on tracking the changing values of several moisture-sensitive circuit elements as a function of moisture content. Identifying and monitoring the trends of more than one circuit element increases confidence in this method of moisture content prediction.

The model selected for the monolithic samples is shown in Figure 13. The model consists of three parallel R/CPE combinations in series with a “solution” resistance. This circuit was designed to describe the expected behavior of same-side contact measurements. The first and third R/CPE loops were constrained to be equal. Each was intended to describe the signal response of the resin-rich layer at the composite surface. The middle loop, R2/CPE2, was intended to model the behavior of the composite interior, where the signal is governed with the graphite fiber system. Although exact material values such as resistivity and dielectric constant were not known

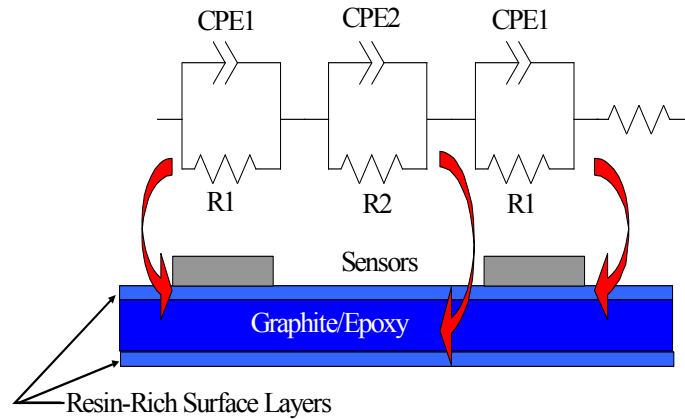


Figure 13. Equivalent Circuit Modes for monolithic composites. The circuit should be able to model similarly constructed materials by varying the values of the individual circuit elements.

for the composite material, reasonable estimates were applied during model fitting in order to further constrain the parameters in favor of a physically realistic result.

Equivalent circuit modeling of the data shown in Figure 12 revealed several parameters with sensitivity to moisture content. Examples of correlations between moisture content and particular circuit elements modeled for the 7-ply IM7/8552 sample spectra are shown in Figure 14. The parameters vary with moisture in a regular way. By fitting models to data in multiple formats and by tracking several moisture-sensitive parameters, it becomes possible to predict values of moisture content for these types of materials more reliably than by tracking only one parameter.

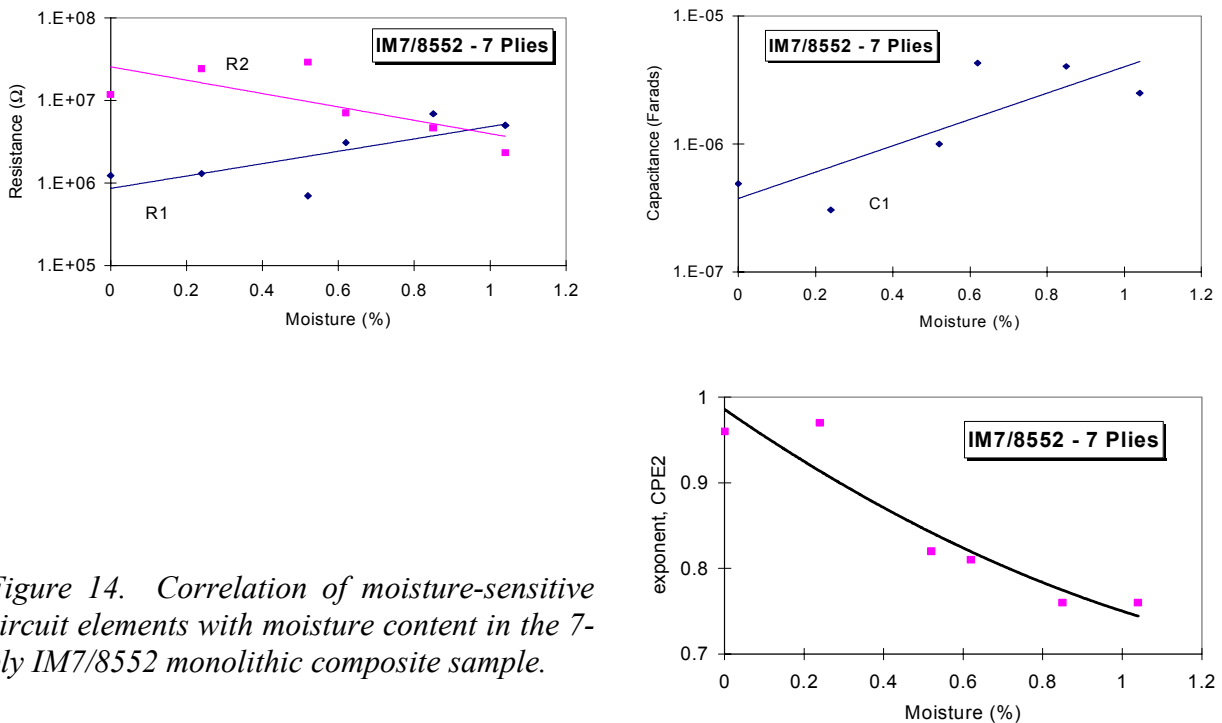


Figure 14. Correlation of moisture-sensitive circuit elements with moisture content in the 7-ply IM7/8552 monolithic composite sample.

Graphite-Epoxy Honeycomb Composites

The honeycomb composites presented a challenging measurement situation because of the diversity of the different components. Several arrangements of electrode placement were devised in order to test as many of the component materials as possible. These electrode arrangements included placement on opposite sides (on the surfaces of the two graphite-epoxy sheets sandwiching the core material) and on the same side, as well as placing one electrode on the graphite-epoxy surface and making contact to the core material or to the adhesive backing with the other electrode lead.

The most straight-forward results were collected from an IM7/8552 composite with the Nomex core, locating the sensor electrodes at the graphite/epoxy surface and at the core. Figure 15 shows the low-frequency impedance values versus moisture content. The useful range of sensitivity in this case is roughly 0.15 % to 0.50%, in which the impedance steadily decreases as moisture content increases. It is believed that the Nomex core absorbed moisture more readily than the graphite-epoxy composite and controlled the impedance measurements.

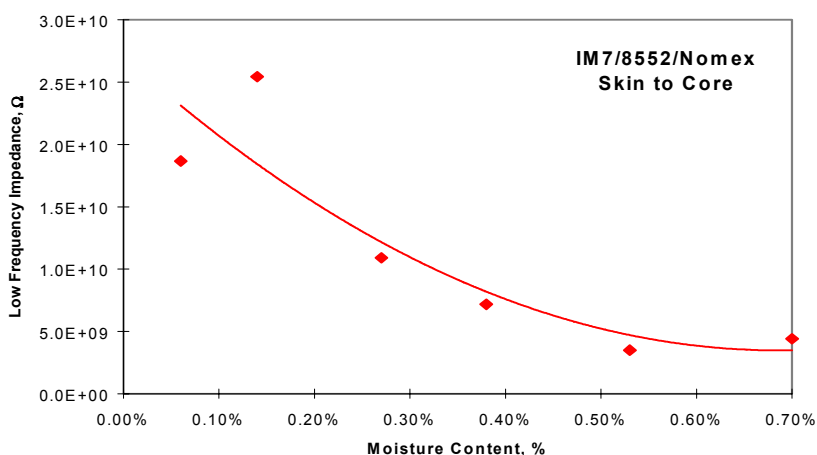


Figure 15. Impedance versus moisture content for honeycomb composite with IM7/8552 skin and Nomex core. Electrodes located on skin and on core.

For aluminum core honeycomb composite specimens, equivalent-circuit analysis was needed. The model of Figure 16 consists of two loops in series and a third imbedded loop. The R1/CPE1 parallel combination is a collapsed version of the monolithic composite circuit and is included to account for moisture absorption in the skin. The R2/C2 parallel combination with the imbedded R3/C3 parallel loop is based on a standard circuit model often used for the analysis of coated metals. In this case, R2/C2 represents moisture absorption in the adhesive joining the core and the skin. The R3/C3 portion represents activity at the adhesive/core interface. A final resistor is again placed in series with the circuit to represent any small “solution” resistance.

Figure 17 shows some moisture-sensitive parameters from equivalent circuit modeling of an AS4/3501-6/Al honeycomb. The situation of the honeycomb composite is complicated by the variety of materials present, and the differing rates at which they absorb moisture. Ideally, the model parameters will reveal not only how much moisture is in the system, but also in which materials it has accumulated. Continued evaluation of this complex combination of materials is necessary to develop the moisture sensor system to provide this information.

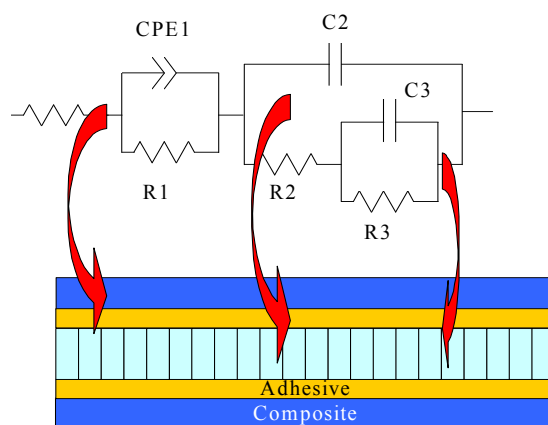


Figure 16. Equivalent Circuit Models the AS4/3501-6, FM300, Al core honeycomb composite. The circuit should be able to model similarly constructed materials by varying the values of the individual circuit elements.

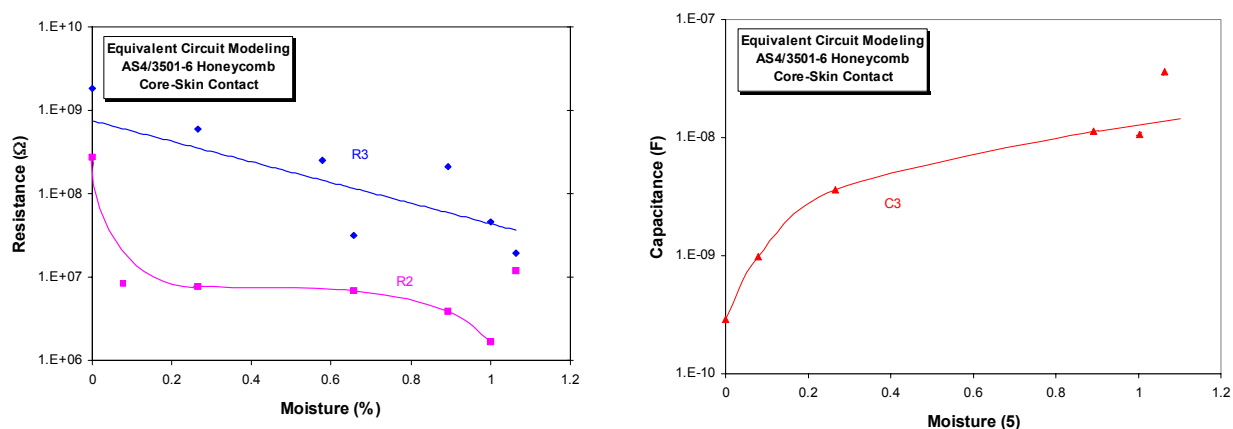


Figure 17. Correlation of moisture-sensitive circuit elements with moisture content in the AS4/3501-6 honeycomb composite sample.

Adhesive Bonds

Detection of degradation or potential degradation of an adhesive bond before bond failure would be a significant improvement over current technology that generally requires separation or, at least, a kissing unbond (a bond in which the two surfaces are in intimate contact, but which cannot transfer any stress). Because the primary cause of environmentally induced degradation of a bonded joint is moisture intrusion into the bondline,²⁵⁻²⁷ detection of moisture is one way to achieve this goal. For high-performance surface treatments that provide a high density of physical bonds (mechanical interlocks) and are resistant to hydration, bondline moisture requires a long time before hydration of the adherend surface causes joint failure.¹⁸ Thus use of the electrochemical sensor or other moisture-detecting device could provide ample warning before irreversible structure damage occurs to the joint.

With the sensor technology reported here, the two metal adherends act as extensions to the sensor electrodes. Consequently, the entire bondline is interrogated and the area of greatest moisture concentration dominates the measurement.

Tensile Button Tests

Tensile button test specimens were prepared by bonding aluminum stubs to aluminum plates with different surface treatments. Specimens were placed in high humidity or immersed in water. Periodically, the specimens were removed and sensors were attached to the stub and substrate. EIS measurements were then taken. The impedance spectra for an adhesive bond closely resemble those of a coated metal. Initially, the spectra are capacitive in nature with high impedance at low frequencies. As the adhesive absorbs moisture, the low-frequency spectrum decreases in impedance and becomes resistive. This behavior reflects moisture ingress into the pores of a polymer and formation of pathways of relatively low resistance. The decrease of the low-frequency impedance for a phosphoric acid anodized (PAA) specimen is shown in Figure 18 and reflects the absorption of moisture. This specimen exhibited a fairly steady impedance decrease. For these measurements, the data are dominated by the region of the specimen with the lowest impedance. In this case, the data represent the impedance of the near-edge region of the bondline where moisture saturation first occurs.

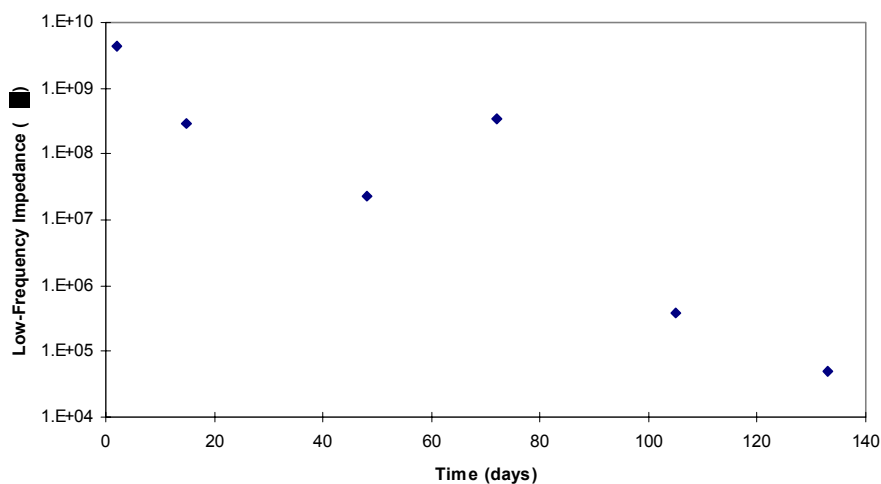


Figure 18. Geometric mean of the low frequency impedance as a function of exposure time for a PAA-treated button pull specimen.

The effect of this moisture absorption on the tensile pull strength strongly depends on the surface treatment. This dependence is illustrated in Figure 19. The initial decrease in pull strengths from approximately 38 MPa to 27 MPa corresponds to a decrease in the cohesive strength of the adhesive as moisture is absorbed. For PAA specimens, the length of time available for this experiment (approximately five months) under these conditions (humidity, followed by immersion) was insufficient to induce hydration. Accordingly, the microcomposite interphase formed by the porous PAA oxide²⁸ and the adhesive remained stable and stronger than the cohesive strength of the adhesive so that failure was almost entirely within the adhesive. Similar behavior was also observed for grit blasted and FPL-etched specimens, with the exception of an FPL surface at the end of the experiment where the strength decreased by approximately 50% and partial interfacial failure occurred as the result of hydration. In contrast, because the sanded surfaces exhibit no evolved microroughness, their bonds to the epoxy adhesive rely more on secondary bonds, such as van der Waals forces, which are readily disrupted by moisture. The locus of failure in this case gradually shifted to increasingly more interfacial with the interfacial region beginning along one segment of the edge and growing along the circumference and toward the center.

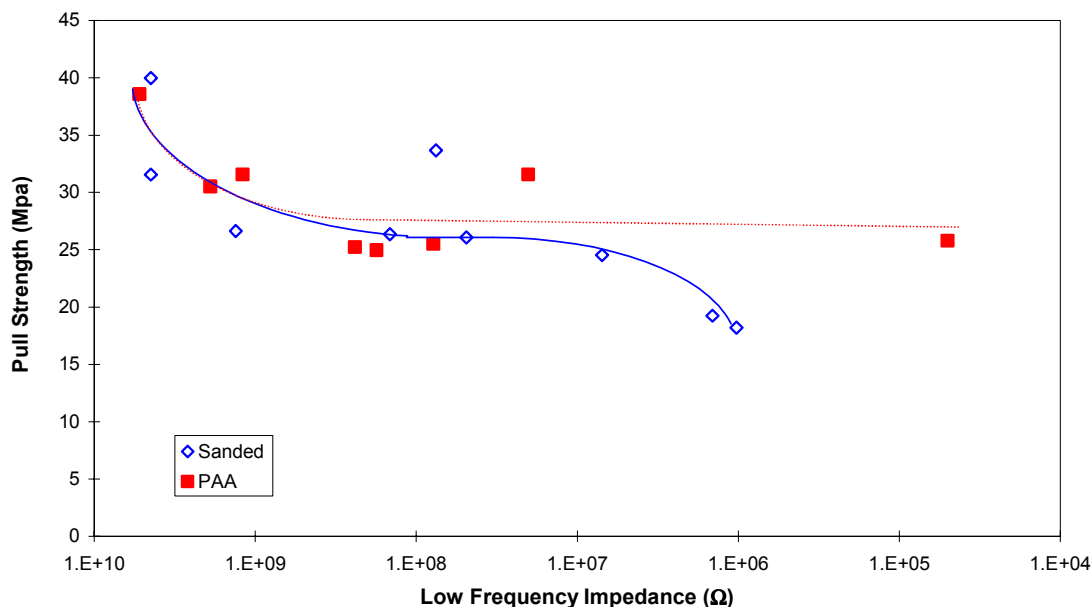


Figure 19. Tensile pull strengths as a function of low-frequency impedance for PAA and sanded aluminum surfaces.

Wedge Tests

Wedge test double-cantilever-beam specimens are more commonly and appropriately used to evaluate the durability of adhesive bonds. By driving a wedge into one end and exposing the specimen to high humidity and temperature, a very aggressive test condition is achieved with the crack tip being exposed directly to moisture while under opening stress. Poor surface treatments fail with one hour compared to months for the tensile button tests just discussed. Good surface preparations can usually be evaluated in three to ten days. Boeing correlated the performance of wedge tests with the service performance of bonded aircraft components.²⁹

Sensor electrodes were attached to both adherends of the wedge test specimens. A special non-conducting wedge was used to prevent the two adherends from shorting. Joints tested in the wedge test configuration exhibit similar behavior to the tensile button specimens and coated metals. Initially, the adhesive shows completely capacitive behavior. As moisture is absorbed, the low-frequency region of the spectra becomes resistive in nature with the extent of the resistive region generally increasing to higher frequencies as more moisture is absorbed.

Moisture uptake is governed by the adhesive, there is little dependence on surface preparation although the response of the bond to absorbed moisture is dependent on surface preparation. The influences of adhesive and surface preparation are shown in Figure 20. FM-73 adhesive, a 250°F-curing adhesive, absorbs a relatively large amount of moisture and the low-frequency impedance drops three orders of magnitude for the two surface preparations. In contrast, FM-300 adhesive, a 350°F-curing adhesive, absorbs much less moisture and the low-frequency impedance drops only one and a half orders of magnitude for the same exposure conditions and time.

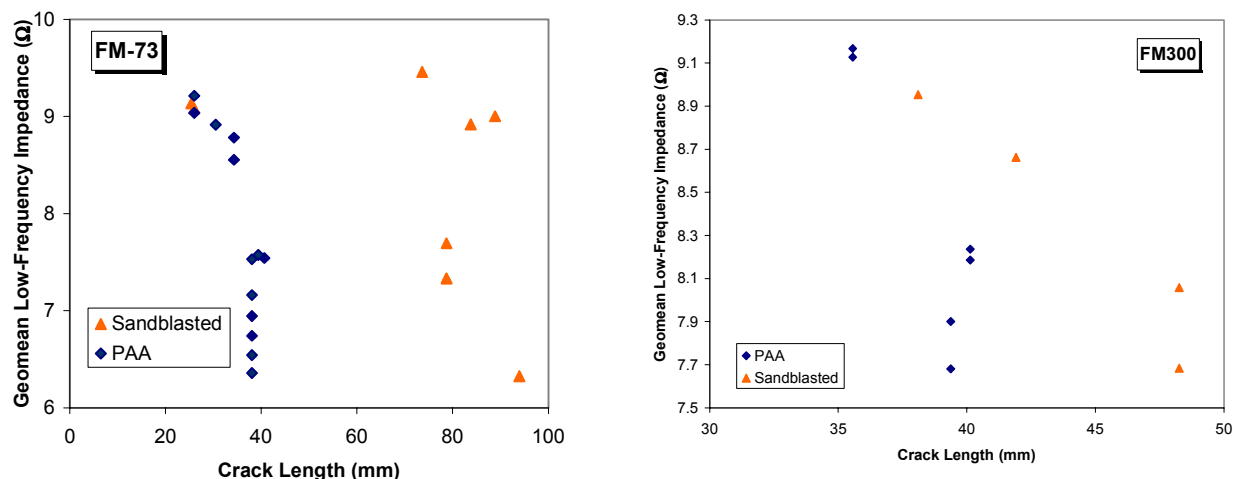


Figure 20. Low-frequency impedance as a function of crack length for PAA and sandblasted wedge test specimens. Left: FM-73; Right: FM-300. Note the different impedance and crack length scales.

The response of the bondline to this absorbed moisture is governed by the type of interfacial bonds and the stability of the interface (Figure 20 and Figure 21). For sandblasted specimens, for which the crack propagates interfacially, the initial, rapid crack growth occurs with minimal change in the low-frequency impedance. For these weak interfaces, which rely predominately on secondary forces that are easily disrupted by moisture,²⁵⁻²⁷ the crack propagates as soon as moisture reaches the interface – before it has a chance to absorb into the bulk adhesive and change the impedance. Over time, this absorption occurs and the impedance decreases, but the crack has arrested or is growing very slowly as it reaches the point of sustainable stress. For the PAA specimens, crack propagation is within the adhesive and the limiting factor governing crack propagation under these conditions and times is not the interface, but rather, the weakening of the adhesive due to moisture absorption. For the FM-73 adhesive, there is a distinct relationship between the low-frequency impedance (absorbed moisture) and crack growth until the crack arrests after approximately one centimeter of propagation. A similar relationship is likely for FM-300 adhesive, but the data are limited in this region. At the arrest point, the adhesive continues to absorb moisture, but without additional crack growth.

The utility of tracking moisture absorption in a bondline as a means of health monitoring an adhesive joint is dependent on the adherend surface preparation and the resulting failure mechanism. The use of EIS or other moisture-sensitive probes is best suited for situations where relatively long exposure to moisture results in joint failure from plasticization or other weakening of the adhesive or from hydration or other corrosion of the adherend surface. PAA adherends are one example in which these conditions are met. For these joints, the impedance spectrum significantly changes in shape and the low-frequency impedance decreases by one to three orders of magnitude well before hydration of the oxide and joint failure. Thus there is ample time to warn of impending bond degradation and preventative action can be taken.

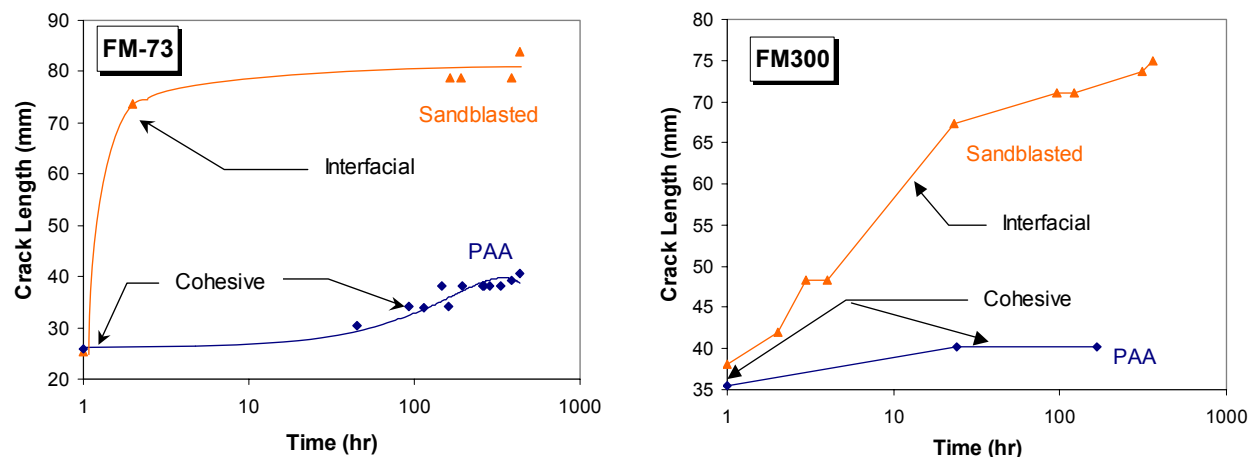


Figure 21. Wedge test crack growth for PAA and sandblasted specimens. Left: FM-73. Right: FM-300

This ability to warn is in contrast to the situation with sandblasted adherends where crack propagation occurs interfacially with the very first ingress of moisture to the interface. The smooth adherends, without a high density of physical bonds, fail as soon as a small amount of moisture reaches the interface. There is no need for the adhesive to absorb moisture and for the moisture to be in contact with the interface for an extended period of time. Fortunately, these types of surface preparations and the resulting bonds are not used where strong, durable joints are required. Structures for which these bonds are acceptable would not be candidates for bondline health monitoring.

Summary and Conclusions

A suite of sensors based on electrochemical impedance spectroscopy (EIS) are being developed that enable moisture absorption and corrosion to be detected and monitored for painted metal structures, composites, and adhesive joints. Both handheld and permanent mounted sensors are available for specific needs. Because the sensors monitor the actual structure of interest instead of a component of the sensor, they have direct applicability to 1) coating evaluation and screening, 2) health monitoring of critical coated and bonded structures, 3) spot checks of critical structures, 4) moisture detection in composites prior to repair operations, and 5) laboratory investigations of degradation mechanisms.

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