Determination of coating adhesion using electrochemical impedance spectroscopy

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Abstract:
Electrochemical Impedance Spectroscopy (EIS) is one of the most modern techniques available to characterize the electrical properties of organic coatings and their adhesion to metal surfaces. Numerous ways exist to study the effectiveness of polymer-metal adhesion, many of these methods are mechanical (pull-off, bending, peel test, etc.), and are therefore destructive. The unique advantages of impedance techniques are that data relating to the coatings performance can be obtained *in situ*, in a non-destructive manner, leading to a detailed understanding of the probable mechanism of adhesion loss. Obviously different organic coatings will afford different levels of protection and adhesion, but these can be effected by the penetration of polar molecules, such as water in aqueous environments, leading to electrochemical corrosion and adhesion loss. Measuring adhesion to metallic surfaces has been of considerable interest in materials science and engineering, and numerous traditional techniques exist, impedance techniques now offer a viable alternative leading to detailed information about performance and adhesion of organic coatings.

Keywords: electrochemical impedance spectroscopy, adhesion, corrosion, organic coatings, equivalent circuit

Introduction:
The performance and adhesion of organic coatings has been researched via electrochemical impedance spectroscopy[1] and many other mechanical techniques. The advantages offered by impedance techniques to analyze different coatings and their adhesion at coating and polymer-metal interfaces is at the centre of many practical and theoretical research papers[2-8]. Current studies also detail the importance of impedance interpretation and modeling techniques which have been improved by numerous research groups. Data collected via impedance techniques can be analyzed by modeling the data on known equivalent circuits which can be used to electrically simulate the obtained results, normally these have two time constants, one representing the coated surface and another for the double layer capacitance.

In aqueous media water penetration and absorption through a coating will ultimately effect the corrosion and adhesion properties at the polymer metal interface, it is clear that both of these processes are related. It is apparent that there is a direct correlation between an organic coating exposed to high humidity or condensed water and the adhesion strength which declines considerably on exposure, due to swelling, delamination, corrosion processes, etc; but these effects will ultimately depend on the quality of the coating. Therefore it is possible to draw the conclusion that the adhesion of the coating is indirectly related to corrosion processes which may be occurring at the metal surface.

For an electrochemical reaction such as corrosion to take place, water, oxygen and an ionic current flowing between the anodic and cathodic sites is required. Organic substrates generally exhibit very low ionic conductivity, preventing corrosion phenomena by isolating the anodic and cathodic sites. However, there are two separate

issues which can effect this, firstly, the presence of pores within the coating, leading to ions reaching the metallic surface through the pores. This process will ultimately lead to adhesion loss, in this instance a layer of water can form at the metal-polymer interface, the contribution of this layer with its corresponding ionic impurities can also lead to a close coupling of anodic and cathodic sites. In this instance the corrosion protection of the coating is effected dramatically. From research data it is apparent that the strength of bonding/adhesion at the metallic-polymer interface can influence corrosion processes and effectively reduce delamination and inhibit corrosion.

There are numerous way in which to study the effectiveness of polymer -metal adhesion, many of these methods are mechanical (pull-off, bending, peel test, etc.). These techniques are destructive and are used to evaluate adhesion but are not necessarily a direct measure of adhesion, primarily providing qualitative information, EIS offers a viable non-destructive alternative to these techniques.

Measurements using impedance techniques

A typical setup is shown (see Fig 1) for running impedance tests (in pstat mode) on an electrochemical cell. Electrochemical impedance tests are normally performed using a frequency response analyzer (FRA), in conjunction with a potentiostat/galvanostat. For impedance tests the bandwidth is important, and this is dependent on the bandwidth of the potentiostat being used, unlike dc tests where high loop bandwidths are not required. The 1260 frequency response analyzer, operates over a 10uHz-32MHz bandwidth stand-alone, but when operating with the 1287 Electrochemical Interface (ECI - pstat/gstat) the instrumental bandwidth is limited to the bandwidth of the pstat, which is 1MHz . Impedance tests can be run either in pstat (voltage control) or gstat (current control) mode.
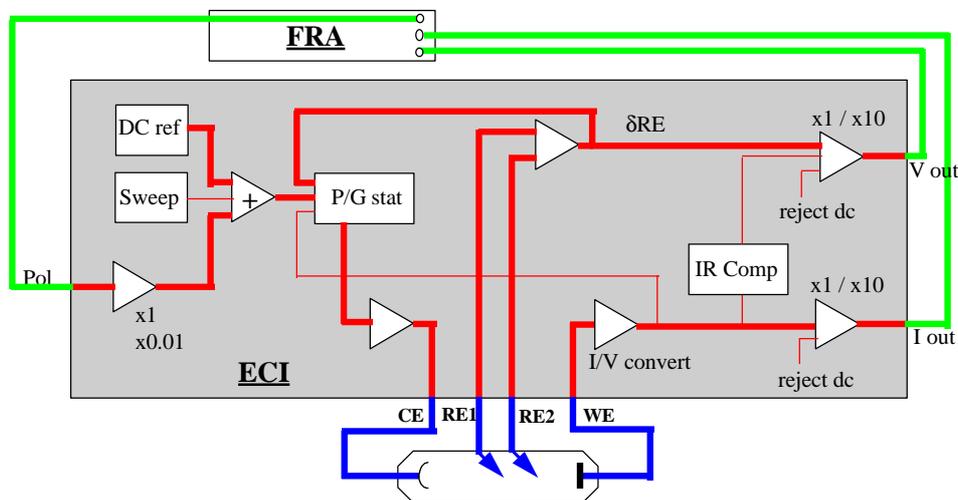

Fig. 1 EIS Measurement configuration

During impedance tests the 1287 ECI is responsible for maintaining the correct dc and ac level on the cell at all times. The reference level is now the summation of the dc programmed level in the pstat and the ac reference level which is input from the ac measurement unit - the FRA. It is typical to have an attenuator on the pstat input from the FRA so that it can operate at a higher signal level to ensure that a good signal to

noise ratio is maintained. The control loop operates to maintain the programmed potential level across the cell.

The signals measured on the working electrode and between RE1 and RE2 are amplified by the potentiostat and output to the FRA as voltage signals. The potentiostat also provides dc rejection facilities (since the FRA only analyses the ac components of the signals and any dc will only serve to reduce the sensitivity of the FRA readings). The 1287 ECI can also provide iR compensation facilities which offset the voltage waveform output to the FRA by an amount equal to the previously measured solution resistance multiplied by the current passing through the cell. This helps to minimize any loss of measurement sensitivity due to the effects of high solution resistance. If the samples to be measured have a very high impedance - typical of organic coatings prior to breakdown (>100 Mohm) it is better to use a 1287 ECI in the system since it has high impedance reference inputs and better current sensitivity.

Impedance tests for coatings performance are generally performed over the 10mHz - 100kHz frequency range using a 5-20mV ac signal, the collected data is analyzed using Zplot to model the data and obtain values relating to the appropriate equivalent circuit model.

Analysis of coating performance using EIS techniques

Electrochemical Impedance Spectroscopy techniques can be used to determine the quantity of water that has penetrated the coating, from this it is possible to gauge the solubility of the coating. The data obtained from EIS measurements can be correlated directly to allow analysis of the following phenomena:

- blister formation[9]
- water permeation
- swelling, of the coating
- loss of adhesion, including delamination.
- corrosion

The uptake of water in organic coatings can be determined directly from capacitance measurements. The dielectric constants of organic coatings are generally small, and hence it is normal for them to be an order of magnitude smaller than that of water which has a dielectric constant around 80 at ambient temperatures. For this reason the adsorption of a small amount of water can significantly effect the capacitance of the film. The capacitance (1) of the organic coating can be determined directly from the dielectric constant of the coating ε, the dielectric constant of a vacuum ε_o, the thickness, d, of the dielectric and the surface area A:

$$C = \varepsilon\varepsilon_0 \frac{A}{d} \qquad (1)$$

From the immersion (or exposure) of the coating to water the penetration/adsorption process begins (see Fig 2) this leads to a rapid increase in the film capacitance - shown as phase 1, eventually it is normal for the coating to become saturated leading to a plateau where the capacitance remains constant - phase 2. If, however there then follows a further increase in capacitance - shown as phase 3, there has been further accumulation of water normally at the polymer-metal interface indicating adhesion loss and the possible on-set of corrosion. The time period that elapses before the on-set of

phase 3 is normally related to the coating thickness, electrolyte conditions and strength of adhesion.
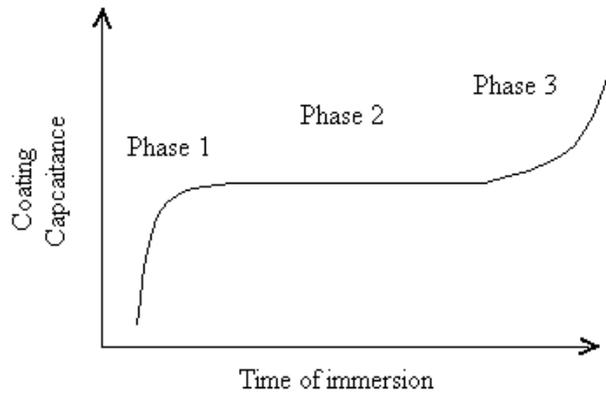

Fig. 2 Capacitance variation in an organic coating
as a function of immersion time

Low frequency data collected using EIS shows considerable sensitivity and variation to changes in the impedance/phase angle - due to the uptake of water. From the data collected below it is apparent that different coating thickness will effect dramatically the effectiveness of the coating to an aggressive environment. The data shows a series of five similar films of varying thickness' exposed to a saline solution. The Bode plot clearly shows that analysis of the low frequency part of the spectrum indicates which films provide the most effective protection. The higher the impedance at low frequency the more effective the coating, for the samples with no visible corrosion / adhesion loss the impedance levels remain at around 10^7ohms at 0.1Hz.
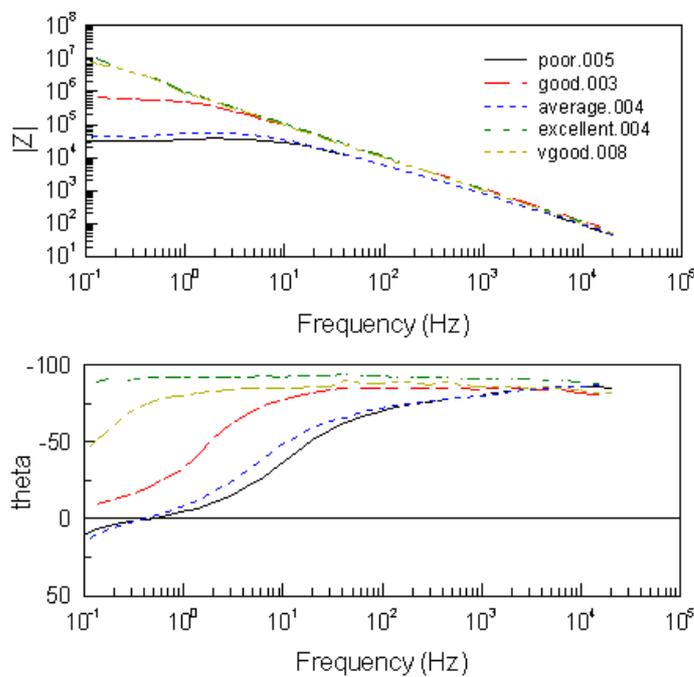

Fig. 3 Bode diagram showing the difference in electrical
properties between different coatings

Equivalent circuit modeling[10] is a standard tool for the interpretation of impedance data. The circuits which are used to model this type of data are usually comprised of Rs, the electrolyte/solution resistance, followed by a coating capacitance Cc in parallel with Rp, the pore resistance. An element called Zw (diffusional element) is also included to represent the electrochemical processes taking place at the coating-metal interface. This element Zw is often represented as Cdl (the double layer capacitance) in parallel with Rct (charge transfer resistance) in corroding coated metals. This particular model is extremely popular as it is suitable for many different systems where there are macro coating defects. The coating capacitance Cc is usually plotted as a function of the immersion time in solution, as previously discussed. The value of the coating capacitance increases with the uptake of water into the coating. The double layer capacitance Cdl represents the wet area under the coating, which is the area in contact with the electrolyte. It is primarily effected by surface roughness, surface oxidation, accurate measurement of this parameter is easily performed using EIS giving an indication of any delamination which is taking place The pore resistance Rp relates to the diffusion of electrolyte through the organic coating via the pore, which can effect the barrier properties of the coating; the parameter Rp is the ionic resistance of the coating which is inversely proportional to the area of surface defects (pores).
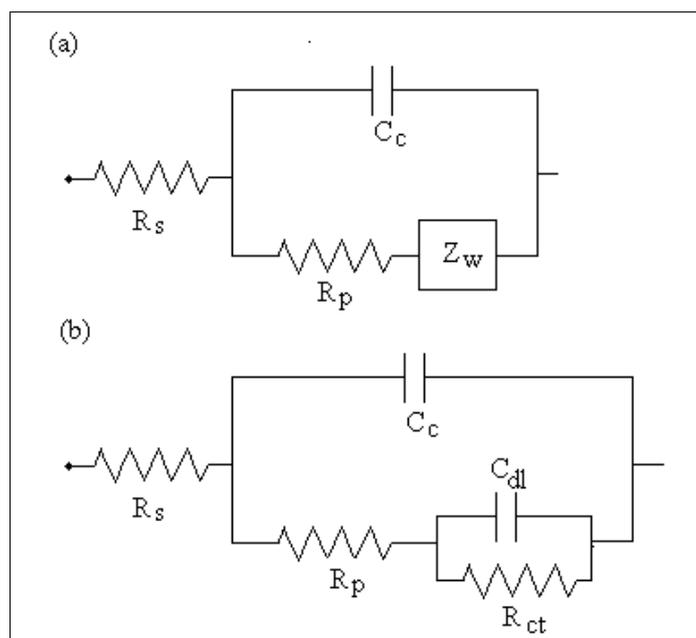

Fig 4. Standard equivalent circuit models for coated metals (a), with (b) representing a corroding coated metal

Conclusion

From the current research EIS has been shown to characterize the behavior of organic coatings in terms of water uptake, adhesion loss, other coating phenomena (blistering, delamination) and the on-set of corrosion. EIS has proved to be a technique which will allow the *in-situ*, non-destructive analysis of coatings to determining adhesion loss. The direct use of EIS techniques will enable manufacturers and researchers to determine detailed information about the properties of these coatings in conditions which will reflect the environments of the actual application, giving detailed data

relating to the performance and quality of the coating in terms of potential adhesion loss. Recent developments in impedance technology now enable researchers to study high impedance coatings and perform localized impedance measurements[11-12] at solid/liquid interfaces to map surface properties directly, including; blister formation, delamination and corrosion phenomena.

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