Application Area: Corrosion

Evaluation of organic coatings on metals using Autolab PGSTAT based on ISO 17463 – Paints and Varnishes

Keywords

Corrosion, Coatings, ISO, Standard, accelerated cyclic electrochemical technique

Introduction

The International Standard ISO 17463 describes the determination of the anticorrosive properties of high impedance organic protective coatings on metals. This is done by exploiting the accelerated cyclic electrochemical (ACE) technique. In order to learn about the details of ISO 17463 standard, please refer to International Organization for Standardization (ISO).

This technique uses cycles composed of electrochemical impedance spectroscopy (EIS) measurements, cathodic polarizations and potential relaxation. The cathodic polarization is applied for the degradation of the coating, while EIS and potential relaxation monitor the change of the coating and its properties. The ACE technique is used to evaluate the permeability of the coating.

Experimental Setup

A Multi Autolab M204 with three PGSTAT channels and three FRA32M modules was used. The Multi Autolab M204 can accommodate up to 12 channels, and one optional module per channel, with a maximum of 6 channels and 6 modules. A typical example of Multi Autolab M204 is shown in Figure 1, with 6 channels and 6 different modules. Nevertheless, this experiment can be executed using the Autolab single channel potentiostat as well.

Figure 1 – The Multi Autolab M204 pgstat.

A Metrohm Autolab flat cell was used as electrochemical cell, suitable for measuring flat samples up to 17 cm² in size (Figure 2).

Figure 2 – The Metrohm Autolab flat cell.

The working electrode was a metal substrate, covered by the coating under study. As reference electrode, a Metrohm Ag/AgCl 3 mol/L KCl was chosen. Finally, the stainless steel counter electrode of the Metrohm Autolab flat cell was employed.

As electrolyte, an aqueous solution of NaCl 3.5% was used.

After an initial EIS measurement, to determine the initial status of the coating, a cycle of electrochemical measurements is applied n times. Each cycle consists of a cathodic polarization, followed by a relaxation process. The last step of each cycle is an EIS measurement, to determine the state of the coating after the polarization and the relaxation.

More details of the three parts of the ACE cycle are presented below:

1. Cathodic polarization

During the cathodic polarization, a constant potential is applied. If the potential is negative enough, the electrolysis of water can occur. The resulting hydroxide ions and/or hydrogen molecules can cause delamination between the substrate and the coating.

In this experiment, the potential for the cathodic polarization was set to −4 V for 20 minutes.

2. Potential relaxation

The relaxation process allows the formation of a new stable equilibrium. By recording the potential during the relaxation process, additional information about the coating and the substrate–coating interface can be obtained.

The relaxation time was set to 180 minutes.

3. EIS

The EIS measurements are used to retrieve information on the coating properties. The fitting of the EIS data can give the values of the pore resistance and the coating capacitance.

A frequency range from 100 kHz to 10 mHz was applied, with 5 points per decade, and a signal amplitude of 20 mV RMS.

Results and Discussion

In Figure 3, the plot of the potential during the relaxation time at different cycles are shown. The arrow indicates the cycle number, from the first (tail of the arrow) to the sixth (tip of the arrow).

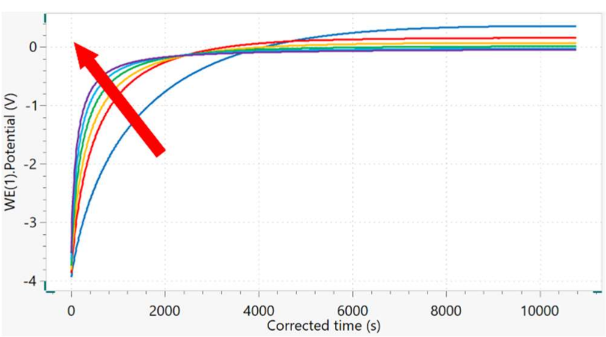

Figure 3 – Potential vs. time plot taken during the relaxation time. The arrow indicates the cycle number, from the first (tail of the arrow) to the sixth (tip of the arrow).

The cathodic polarization applied before the relaxation time induces imperfections to the coating, such as delamination to the substrate–coating interface. The sample therefore reaches the equilibrium at lower, less noble potentials, and in less time. Repeating the cathodic polarization induces more disruptions, ageing the coating.

In Figure 4, the Bode plots from the EIS measurements are shown at different cycles. The arrow indicates increasing of the cycle number.

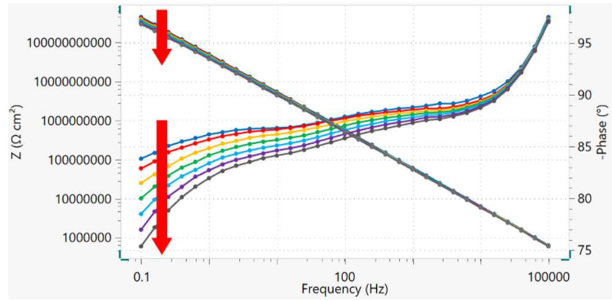

Figure 4 – Bode plot taken before and during the six cycles. The arrow indicates the cycle number, from before the cycles, (tail of the arrow) to the sixth (tip of the arrow).

Here, it can be noticed that the modulus of the impedance decreases with increasing the cycle number, while the phase is increasing (the negative phase values are plotted). This can be due to the water absorbed by the coating (water intake), during the experiment.

The EIS data were fitted with the equivalent circuit shown in Figure 5.

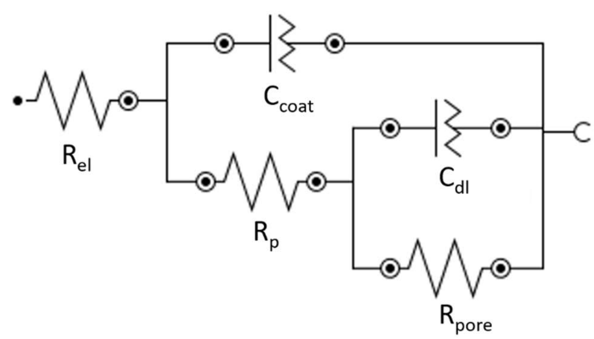

Figure 5 – The equivalent circuit used for fitting the EIS data.

From the fit results, the pore resistance R_{pore} (Ω) and the coating capacitance C_{coat} (F) per cycle were extracted and plotted versus the cycle number, Figure 6 and Figure 7, respectively.

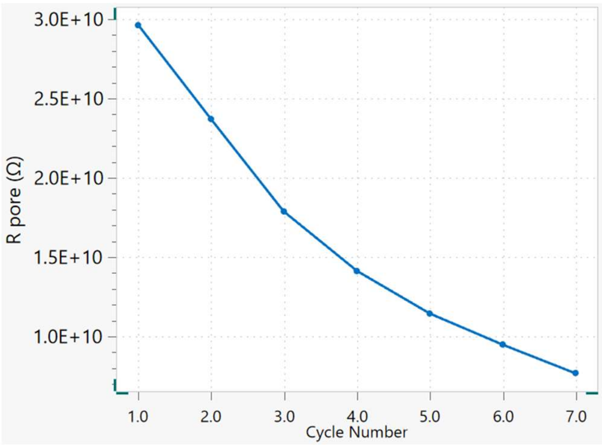

Figure 6 – Pore resistance taken before the polarization step (Cycle 1), and at other cycles (Cycles 2–7).

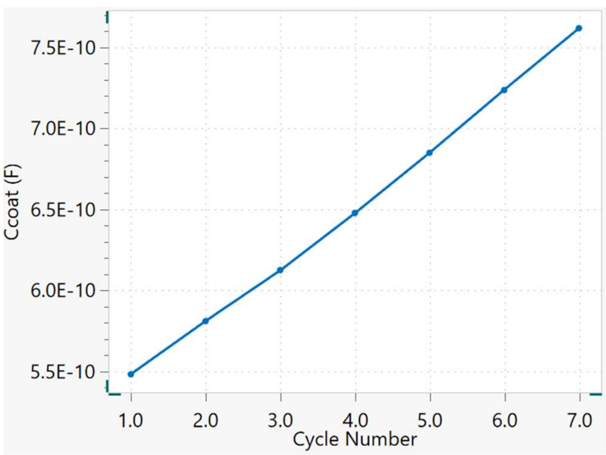

Figure 7 – Coating capacitance taken before the polarization step (Cycle 1) and at other cycles (Cycles 2–7).

Here, it can be seen that the pore resistance decreases after each cycle while the coating capacitance increases, possibly due to water intake of the coating during the experiment.

Conclusions

This application note shows the compliance of the Metrohm Autolab PGSTAT M204 and flat cell with the standard ISO 17463. A coating on a metal substrate was analyzed with electrochemical impedance spectroscopy, followed by cycles formed by cathodic polarization, a relaxation time and an electrochemical impedance spectroscopy.

From the plots of the voltage versus relaxation time and the Bode plots, it is possible to monitor the ageing of the coating and evaluate its properties.

The impedance spectroscopy data were fitted with a suitable equivalent circuit, and the values of the pore resistance and coating capacitance were monitored during the cycles.

Date

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/en/products/electrochemistry**.