Application Area: Corrosion

Electrochemical impedance spectroscopy of three coated aluminum samples

Keywords

Autolab Corrosion Applications: Aluminum, Aluminum Oxide, Corrosion, Coating, Electrochemical impedance spectroscopy, Fit and simulation, Metrohm Autolab

Introduction

Electrochemical impedance spectroscopy (EIS) is a powerful technique used to investigate the linear response of a system perturbed by an alternating potential (potentiostatic EIS) or current (galvanostatic EIS). For an introduction to this technique you are kindly referred to application notes AN-EIS-01 – AN-EIS-06.

EIS is widely applied in corrosion science and technology, to obtain information about the polarization resistance and time constants of the corrosion processes[1-4]. Also, experimental data are fitted to equivalent circuits, which give a deep understanding of the corrosion processes. Examples of such circuits are shown in the application note AN-COR-04.

One of the most successful protections against corrosion is the application of coating layers on metal surfaces. The coating industry relies on various techniques to test the quality of their coatings. EIS is one of the most interesting techniques, since it is relatively fast and non-destructive.

In this application note, EIS is applied on three coated aluminium samples, before and after the stepwise dissolution measurement (SDM). This technique has been reviewed in the application note AN-COR-08.

Experimental Setup

Three sheets of coated aluminum were tested; all of them with a thin coating of aluminum oxide, Al_2O_3. Two of them had an additional coating layer. The exact composition of the coatings was not made available. Therefore, further in the text, they will be referred as "pink" and "gold" coatings. Each sheet was punched to obtain disks of 1.5 cm diameter, to fit the sample holder of the Autolab 1 L corrosion cell, shown in Figure 1. The exposed area was 1 cm^2. One side of each sample was polished with 600 grit sandpaper, to remove the

coating layers and to ensure good electrical contact with the sample holder. All measurements were carried out in artificial seawater, obtained by dissolving 33 g of NaCl in one liter of Millipore water. A stainless steel counter electrode and an Ag/AgCl 3 M KCl reference electrode completed the three-electrode setup. In this note, all potential values are given with respect to the potential of the reference electrode. The electrodes were connected to an Autolab PGSTAT204 with a FRA32M impedance module, shown in Figure 1.

Figure 1 - The 1 L corrosion cell and the PGSTAT204 with the FRA32M module

The procedure

The EIS measurements were carried out before and after the SDM. A 10 mV (rms) amplitude signal was superimposed to the open circuit potential (OCP), with a frequency range from 100 kHz to 10 Hz, including a logarithmic frequency step and 10 frequencies per decade. The data before and after the SDM were compared and fitted with suitable equivalent circuits.

The equivalent circuits

In order to determine the proper equivalent circuit, a deep understanding of the system is necessary. Here a description of different coating types and their relative equivalent circuits is given[5].

In the ideal case, the non-conductive coating adheres perfectly to the metal substrate, with no surface imperfections and a flawless metal-coating interface. This situation results

in a so-called blocking electrode, described by an equivalent circuit with the uncompensated resistance R_Ω in series with the capacitance of the coating layer C_L, like in Figure 2.
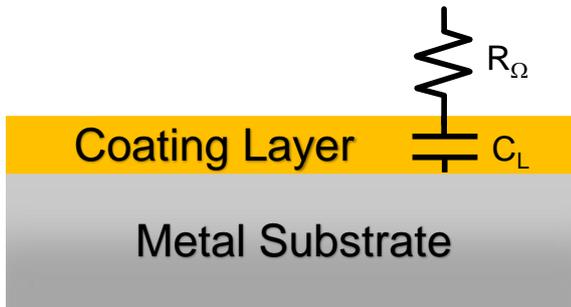
Figure 2 – Ideal, flawless non-conductive coating on a metal substrate and corresponding $R_\Omega C_L$ equivalent circuit

However, a coating with imperfections is the more common occurrence. Such flaws can be a non-perfect coverage of the substrate, as shown in Figure 3, where the coated area, represented by the above-mentioned $R_\Omega C_L$ circuit, is exposed together with a non-coated surface, modelled by a double layer capacitance C_{dl} in parallel with a generic faradaic impedance Z_f. The resulting equivalent circuit is shown also in Figure 3.
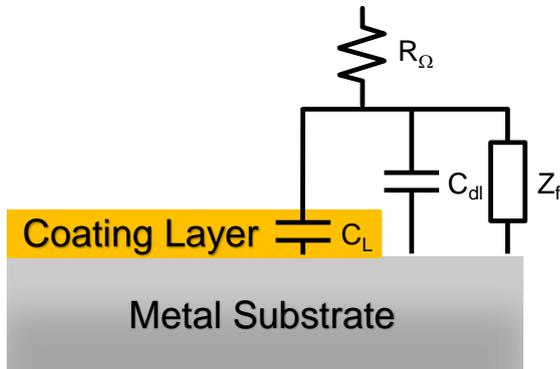
Figure 3 – A metal substrate partially coated, with the respective equivalent circuit

Pores present in the surface are also imperfections of the coating layer. A pore can be considered as a non-coated portion of substrate, like in Figure 3, but with a size so small that the exchange of the electrolyte between the pore and the bulk is hampered. Therefore, the ion concentration inside the pores could differ from the bulk. This results in an electrolyte resistance R_L different from the bulk electrolyte resistance R_Ω. In Figure 4, the presence of the pores is shown, together with the respective equivalent circuit.
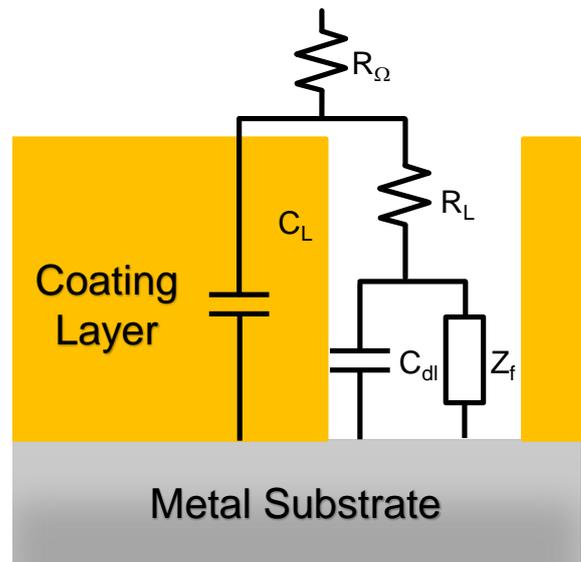
Figure 4 – A porous non-conductive coating layer, with the resulting equivalent circuit

Finally, the presence of an outer layer of coating, placed on top of the first layer, is taken into consideration. This top layer adds a second interface, modelled with a further resistance R_{L2}, in parallel with a double layer capacitance C_{L2}. The system and the resulting equivalent circuit are shown in Figure 5.
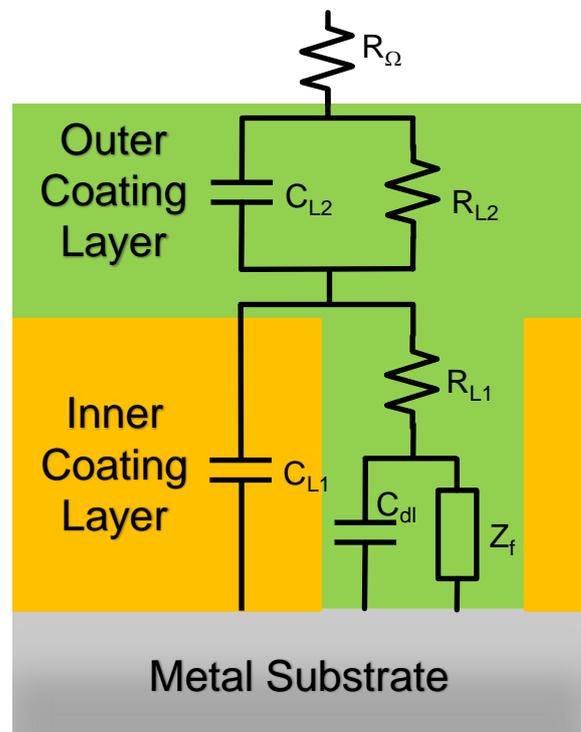
Figure 5 – Two porous non-conductive coating layers, with the equivalent circuit

Regarding the generic impedance Z_f, it is important to know the composition of the coating layers and their behavior when exposed to the electrolyte, in order to choose the proper circuit element. Examples of such elements are the constant phase element and the Warburg diffusion element.

Results and discussion

In all the measurements, the presence of pores was considered. For the fitting of the data collected before the SDM, the equivalent circuits mentioned in the previous section were considered. For the oxide-coated sample, the equivalent circuit in Figure 4 was selected for the gold-coated and pink-coated samples and the equivalent circuit in Figure 5 was used. The unknown nature of the coatings required selection based on best fit obtained which was generic impedance Z_f .

In the following sections, the Nyquist plots of the three samples are presented, before and after the SDM. For each Nyquist plot, the blue dots represent experimental data and the black line is the corresponding fit, performed with the equivalent circuit drawn in the top left corner of the plot. Only the choice of the equivalent circuits, in relation to the experimental data and with the above-mentioned models will be discussed. The values of the circuit elements will not be part of the discussion.

Aluminum oxide

In Figure 6, the Nyquist plot of the oxide sample before the SDM is shown. The chosen equivalent circuit resembles the one used to model the presence of pores in the coating (Figure 4).
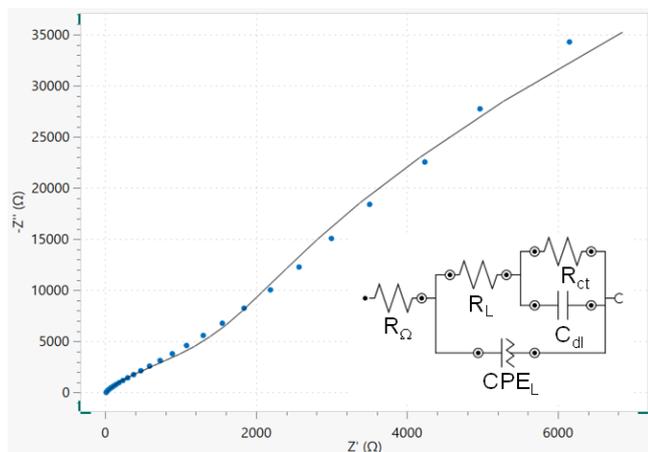
Figure 6 – Nyquist plot of the oxide sample, before the SDM

The double layer capacitance C_L of the oxide layer was replaced with a constant phase element (CPE_L), to take into account the roughness of the surface. The generic impedance Z_f was found to be close to a charge transfer resistance R_{ct}.

After the SDM, i.e., after the corrosion process, the Nyquist plot of the oxide sample (Figure 7) presents a 45° line at low frequencies, which could be addressed to the ion diffusion inside the pores and fit with a Warburg element. The ions could be a product of the corrosion process.
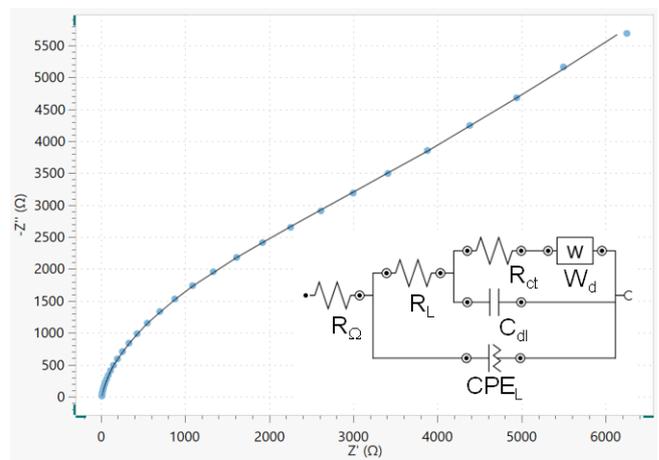
Figure 7 – Nyquist plot of the oxide sample, after the SDM

Gold-coated aluminum

In the case of the gold-coated sample, a two-layer coating model was selected as the gold coating was applied above the oxide layer. This results in the Nyquist plot shown in Figure 8. Also in the equivalent circuit employed in the data fitting, capacitors have been replaced with constant phase elements. The generic impedance Z_f was selected to be an interface, with the charge transfer resistance R_{ct} in parallel with the constant phase element CPE_{dl}.
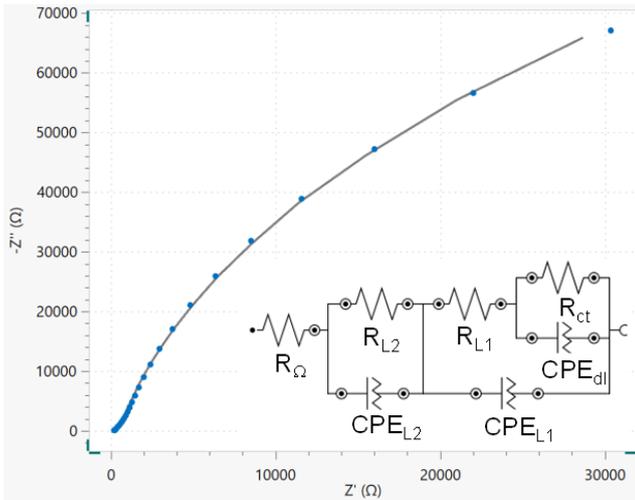
Figure 8 – Nyquist plot of the gold-coated sample, before the SDM

Figure 10 – Nyquist plot of the pink-coated sample, before the SDM

The corrosion process alters the properties of the coatings, as the Nyquist plot of Figure 9 suggests.

Figure 9 – Nyquist plot of the gold-coated sample, after the SDM

Pink-coated aluminum

In the last example, the pink layer was applied over the oxide layer, like in the case of the gold-coated sample. However, before the SDM, Figure 10 shows that the Nyquist plot was an almost vertical line at low frequencies. The best fit was obtained neglecting the faradaic impedance Z_f and adding a CPE in series, CPE_{dl}, which represents the interface between the metal and oxide surface. This could be an indication of a good-quality coating.

After the SDM, however, the best fit was obtained with a double layer capacitance C_{dl} instead of the CPE_{dl}. This is shown in Figure 11. This could mean that the coating suffered less with the corrosion process induced by the SDM compared to the other two samples, and no faradaic process occurred at the aluminum-pore interface.
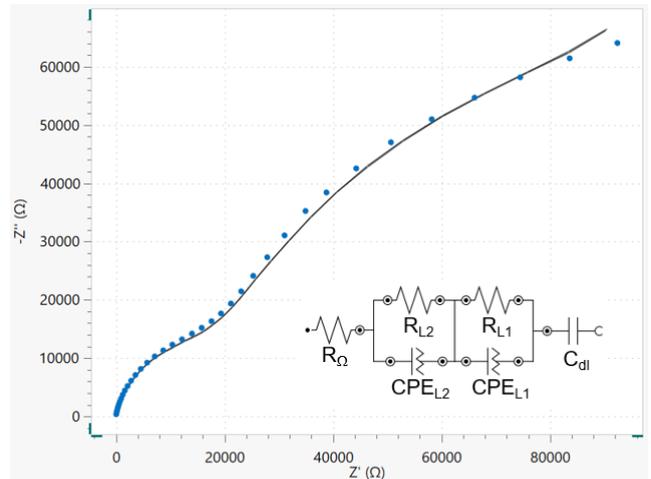
Figure 11 – Nyquist plot of the pink-coated sample, after the SDM

The three Nyquist plots after the SDM in Figure 12 show the comparison between the impedances of pink-coated sample, the oxide and gold-coated sample.
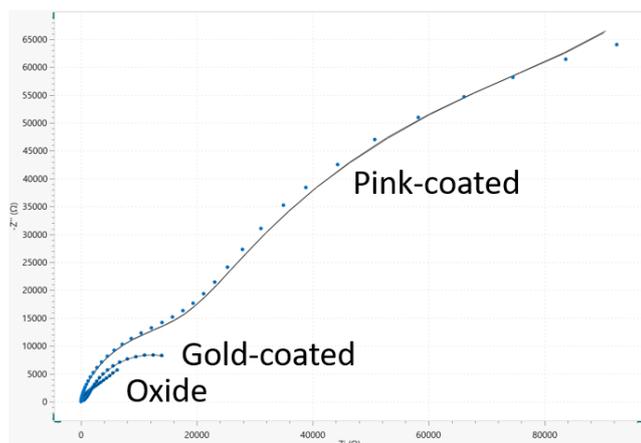
Figure 12 – Nyquist plot of the three samples, after the SDM

The pink coating seemed to have the best performances against corrosion, at least during the SDM.

Conclusions

The electrochemical impedance spectroscopy (EIS) is a fast, non-destructive and powerful technique, widely used in corrosion science. Provided a good knowledge of the system under investigation, EIS can give valuable insights about the quality of the coatings against corrosion. This application note shows how with an Autolab PGSTAT204, Autolab 1 L corrosion cell with NOVA software controlling the experiment it is possible to perform EIS on samples of aluminum, coated with different materials.

References

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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**.