Application Area: Corrosion

Corrosion
Part 4 – Equivalent Circuit Models

Keywords

Corrosion; Electrochemical methods; Electrochemical impedance spectroscopy; Equivalent circuit

Summary

In recent years, Electrochemical Impedance Spectroscopy (EIS) has been successfully applied to the study of corrosion systems. EIS has been used effectively to measure the polarization resistance for corrosion systems and for the determination of corrosion mechanisms for systems where DC electrochemical methods have failed.

EIS has been applied, among others, to uniform corrosion, pitting corrosion, corrosion in concrete, and corrosion underneath coatings. In this application note, some of the equivalent circuit models that are used to model corrosion systems are described.

Uniform corrosion

The most common equivalent circuit used to model corrosion of bare metal in aqueous electrolyte is the Randles circuit, shown in Figure 1.

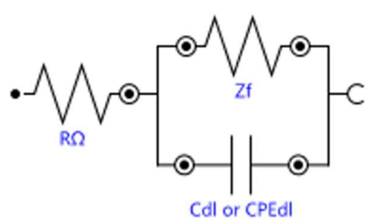

Figure 1 – A typical Randles circuit.

Where R_{Ω} is the solution resistance, due to the presence of the electrolyte between the reference and working electrodes, Z_f is a generic Faradaic impedance and C_{dl} or CPE_{dl} is the double layer capacitance or double layer constant phase element (CPE).

In the simplest Randles circuit, the polarization resistance R_p replaces the Faradaic impedance, Figure 2.

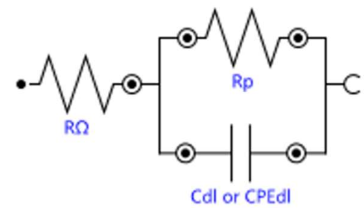

Figure 2 – The Randles circuit with the polarization resistance R_p as Faradaic impedance Z_f.

The model can be used to estimate the polarization resistance from the impedance data.

Figure 3 shows a typical Nyquist plots for a Randles equivalent circuit with a C_{dl} (blue dots) or CPE_{dl} (red dots) element. The CPE_{dl} element introduces a depression of the semicircle.

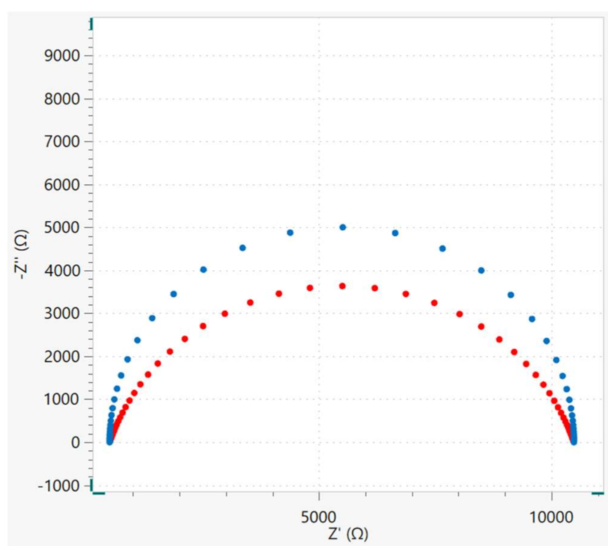

Figure 3 – Typical Nyquist plots for a Randles equivalent circuit with a C_{dl} (blue dots) or CPE_{dl} element, with N=0.8 (red dots).

For corrosion of low carbon steel in NaCl solution, the equivalent circuit shown in Figure 4 has been proposed.

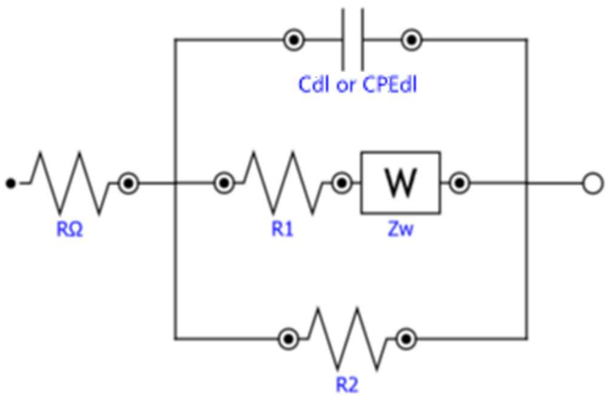

Figure 4 – Circuit For corrosion of low carbon steel in NaCl solution.

Where R_{Ω} is the solution resistance, R_1 and R_2 are the charge transfer resistances of the anodic and cathodic reaction, respectively, C_{dl} or CPE_{dl} is the double layer capacitance, and Z_W is the Warburg impedance, used to simulate the mass-transport effects.

Figure 5 shows a typical Nyquist plot corresponding to the proposed circuit shown in Figure 4.

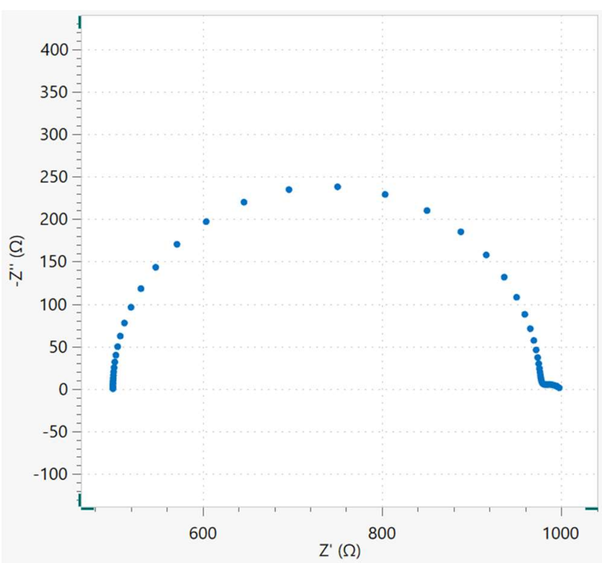

Figure 5 – A typical Nyquist plot corresponding to the circuit in Figure 4.

Coatings

Electrochemical Impedance spectroscopy has been used extensively to characterize the corrosion protection of metals by coatings.

The equivalent circuit shown in Figure 6 is often used to model a coating.

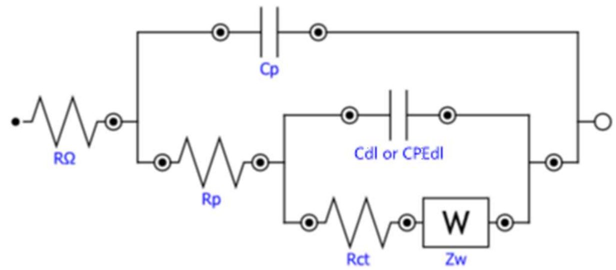

Figure 6 – A typical equivalent circuit to model a coating.

Where R_{Ω} is the solution resistance, R_p is the paint resistance, which is an indication of the coating's porosity. C_p is the paint capacitance, which quantifies the water uptake by the coating. R_{ct} is the charge transfer resistance, which provides a value of the protection of the substrate. C_{dl} is the double layer capacitance or constant phase capacitance CPE_{dl}, which can be correlated to the delamination of the coating. Z_W quantifies the mass-transport related contributions.

Figure 7 shows a typical Nyquist plot corresponding to the proposed circuit shown in Figure 6.

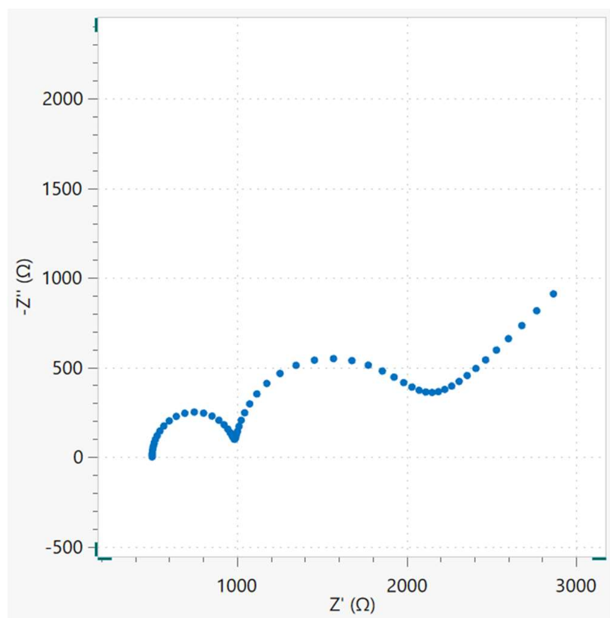

Figure 7 – A typical Nyquist plot corresponding to the circuit in Figure 6.

When the coating is intact, in the previous circuit, R_p the paint resistance goes to infinity and the circuit reduces to the following equivalent circuit model:

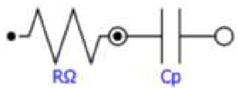

Figure 8 – A typical equivalent circuit for an intact coating.

Figure 9 shows a typical Nyquist plot corresponding to the proposed circuit shown in Figure 8.

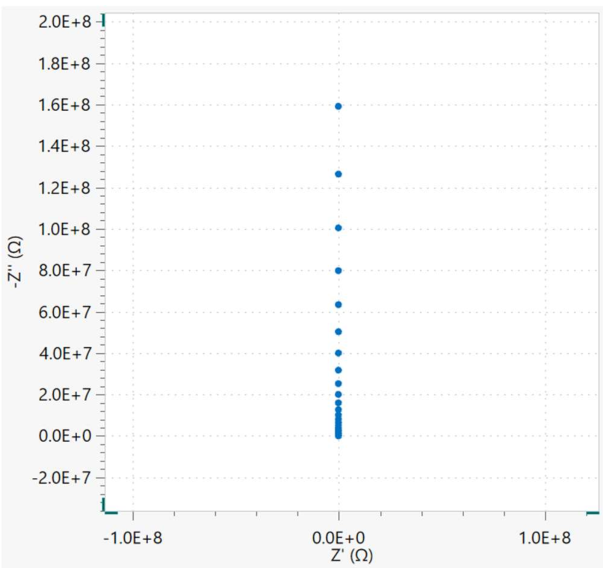

Figure 9 – A typical Nyquist plot corresponding to the circuit in Figure 8.

Corrosion in concrete

The following equivalent circuit has been proposed the corrosion of steel rebars in concrete.

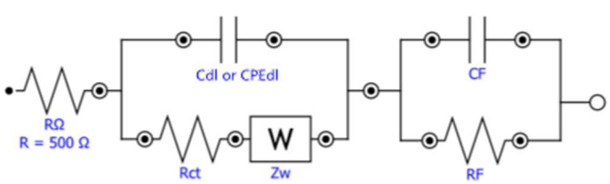

Figure 10 – A typical equivalent circuit proposed for corrosion of steel rebars in concrete.

Where R_{Ω} is the solution resistance, R_F is the resistance at the concrete/stainless steel interface, C_F is the concrete/stainless interfacial capacitance, R_{ct} is the charge transfer resistance of the corrosion reaction, C_{dl} is the double layer capacitance or constant phase element CPE_{dl}, and Z_W is the Warburg impedance related to the diffusion of oxygen to steel.

Figure 11 shows a typical Nyquist plot corresponding to the proposed circuit shown in Figure 10.

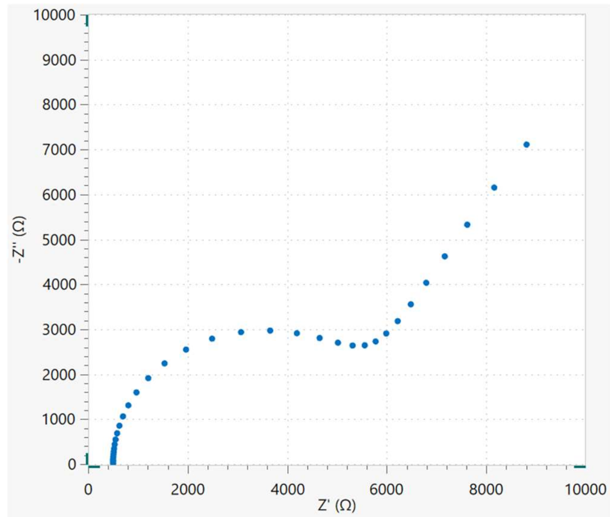

Figure 11 – A typical Nyquist plot corresponding to the circuit in Figure 10.

Conclusions

In this application note, some examples of the most used equivalent circuit used in corrosion research is given, together with examples of Nyquist plots which can be fit with the shown equivalent circuits.

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.