Application Area: Fundamental

Electrochemical Impedance Spectroscopy (EIS)
Part 4 – Equivalent Circuit Models

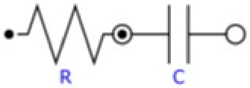
Keywords

Electrochemical impedance spectroscopy; frequency response analysis; Nyquist and Bode presentations; data fitting; equivalent circuit

Summary

The circuit elements described in the application note AN-EIS-003 can be combined in series and parallel to build equivalent circuit models, which can then be used to model the various phenomena occurring at the interface. In this note, the use of the circuit elements to build models is described.

Model 1 – A resistor and capacitor in series



Model 1 can be used, for example, to model a metal with an undamaged high impedance coating. Here, the value of R gives the resistance of the electrolyte, and the value of C gives the coating capacitance. In Figure 1, the resulting Nyquist plot is shown.

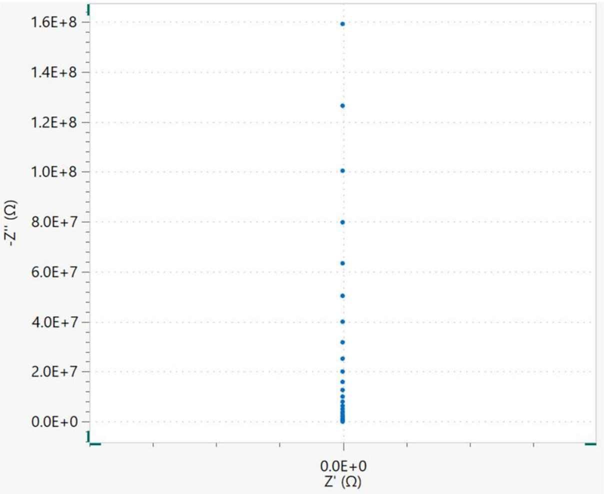


Figure 1 - A typical Nyquist plot resulting from a resistor and a capacitor in series

Model 2 – A resistor, a capacitor and an inductor in series

Model 2 can be used to model the response of a supercapacitor. Here, the value of R gives the internal resistance of the supercapacitor, and the value of C gives the capacitance value of the supercapacitor, and L can be attributed to the cables inductance. In Figure 2, the resulting Nyquist plot is shown.

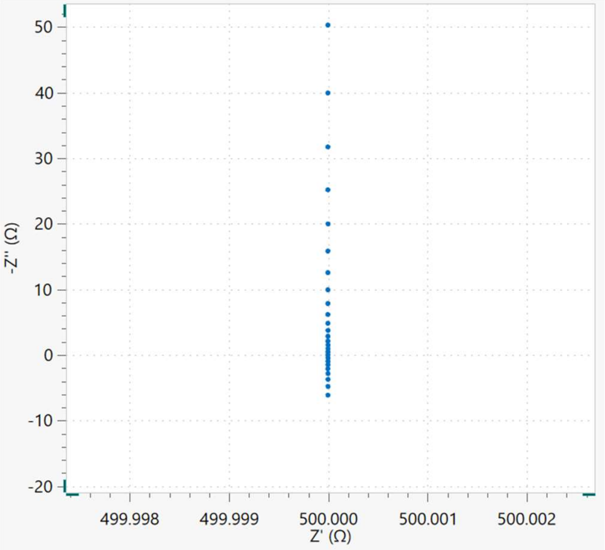
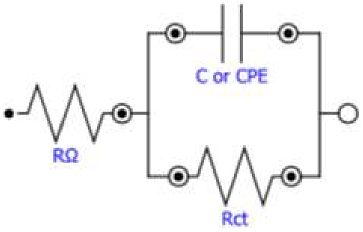


Figure 2 - A typical Nyquist plot resulting from a resistor, a capacitor and an inductor in series

Model 3 – A resistor and a capacitor in parallel. The simplest example of a Randles circuit



The Randles circuit is one of the simplest and most common cell models. It includes a solution resistance (R_Ω), a double layer capacitor C or a CPE and a generic element for the Faradaic impedance, due to the electrochemical processes. In the simplest case of the Randles circuit, the Faradaic impedance is solely the charge-transfer resistance R_{ct}. It is used to model corrosion processes and is often the starting point for other more complex models. In Figure 3 a typical Nyquist plot resulting from the equivalent circuit of Model 3. The blue dots represent the Nyquist plot of the equivalent circuit with the capacitor, the red dots, represent the Nyquist plot of the equivalent circuit with a CPE (n = 0.8).

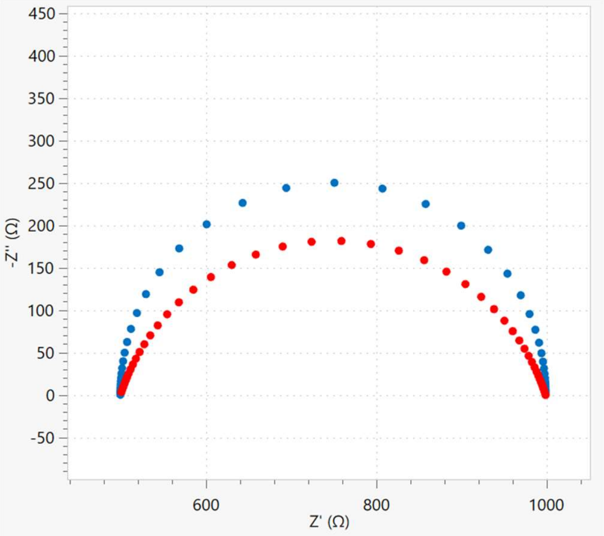
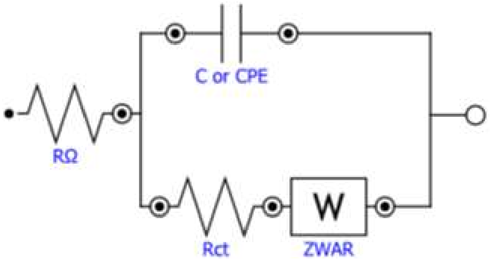


Figure 3 - A typical Nyquist plot resulting from the equivalent circuit in Model 3. The blue dots represent the results with the capacitor, the red dots, represent the results with a CPE (n = 0.8).

Model 4 – Mixed kinetic and diffusion control



It can be used to describe electrode processes when both kinetics and diffusion are non-negligible. Model 4 is a specific case of Randles circuit. It includes a solution resistance (R_Ω), a double layer capacitor C or a CPE, the charge transfer resistance and the so called Warburg element, Z_{WAR}, which contains information on the diffusion coefficient of the species. In Figure 4, a typical Nyquist plot resulting from the equivalent circuit in Model 4.

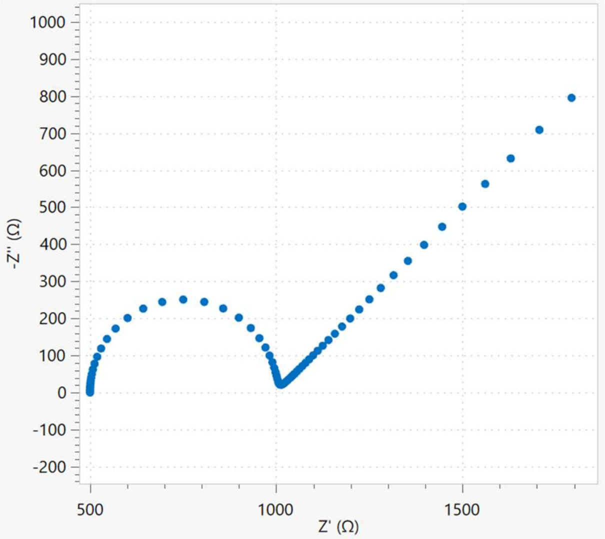
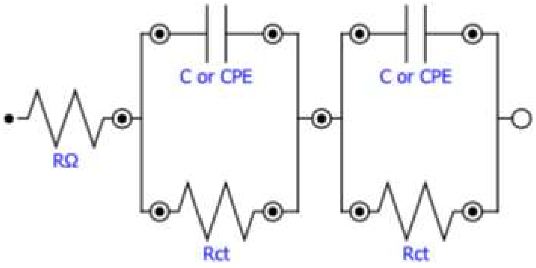


Figure 4 - A typical Nyquist plot resulting from the equivalent circuit in Model 4.

Model 5 – Two Randles circuits in series



Model 5 can be used, for example, to model the response of batteries. Here, each R and C (or CPE) in parallel can represent one electrode of the battery. In Figure 5, a typical Nyquist plot resulting from the equivalent circuit in Model 5.

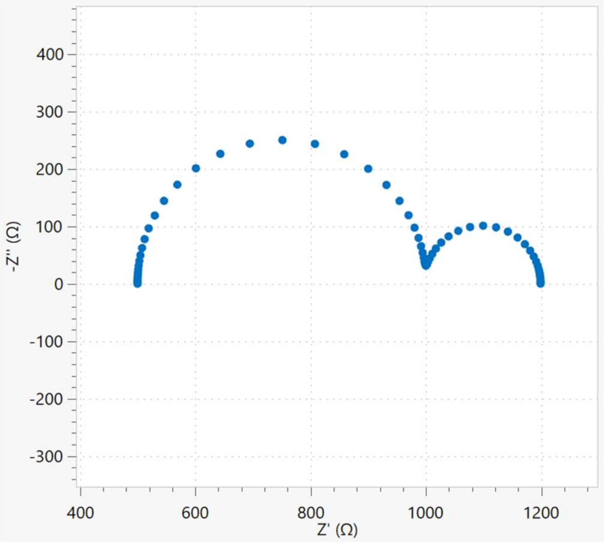
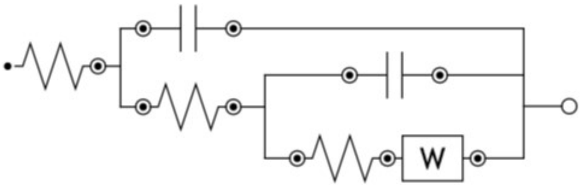


Figure 5 - A typical Nyquist plot resulting from the equivalent circuit in Model 5.

Model 6 – Example of a complex circuit



Model 6 can be used, for example, to describe the impedance of an organic coating on a metal substrate in contact with an electrolyte. In Figure 6, a typical Nyquist plot resulting from the equivalent circuit in Model 6.

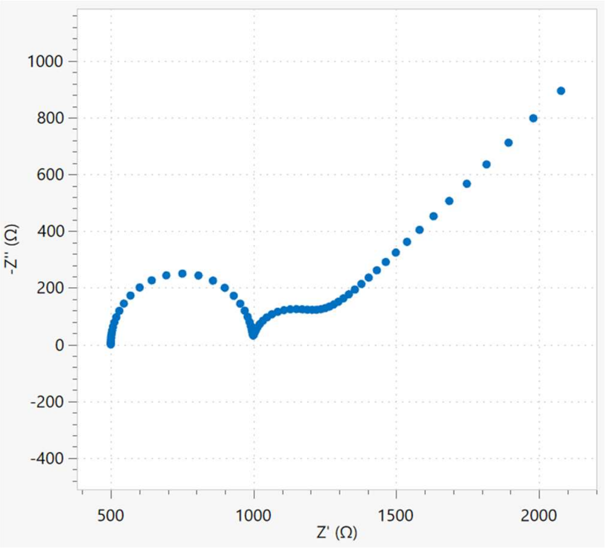


Figure 6 - A typical Nyquist plot resulting from the equivalent circuit in Model 6.

Non uniqueness of models

It is important to keep in mind that the equivalent circuit modelling is a method that aims to match a theoretical model of an electrochemical interface with an experimental set of data. Proper assignment of the circuit elements can only be performed when sufficient information on the chemical and electrochemical phenomena taken place at the interface is available.

Moreover, it is important to keep in mind that several arrangements of circuit elements are possible for a given set of data, and that some equivalent circuits are mathematically identical.

Conclusions

This application notes shows how electrical elements can be arranged, in order to build simple and complex equivalent circuits for fitting EIS data. The resulting Nyquist plots for all the circuits are shown as well.

Date

September 2019 AN-EIS-004

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 **http://www.metrohm.com/electrochemistry**.