Application Area: Fundamental

Electrochemical Impedance Spectroscopy (EIS) Part 3 – Data Analysis

Keywords

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

Summary

The characterization of electrochemical systems with electrochemical impedance spectroscopy (EIS) requires the interpretation of the data with the help of suitable models. These models can be divided into two broad categories: equivalent circuit models and process models. The models are regressed to experimental data to estimate parameters that can describe the experimental data adequately and can be used to predict the behavior of the system under various conditions.

Equivalent circuit models

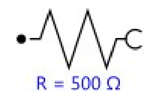
The equivalent circuit models are most commonly used to interpret impedance data. These models are built with the help of well-known passive electrical elements such as resistors, capacitors, and inductors, and distributed elements such as constant phase element and Warburg impedance. These elements can be combined in series and parallel to give complex equivalent circuits. A certain physical meaning is then assigned to the various elements of the equivalent circuit.

Resistor, R

A resistor R has an impedance Z_R of:

$$Z_R\ (\Omega) = R$$
$$|Z_R|\ (\Omega) = R \qquad 1$$
$$\theta_R\ (°) = 0$$

The impedance is independent of frequency and has no imaginary part. The current through a resistor is always in phase with the voltage, therefore no phase shift is present. In NOVA, the R element is represented by the following symbol:



Some examples of the use of a resistance to describe electrochemical phenomena are:

Ohmic resistance, R_Ω

The potential drop between the reference electrode and the working electrode, is the ohmic resistance, also known as uncompensated resistance, and can be modelled using R. The ohmic resistance depends on the conductivity of the electrolyte and the geometry of the electrode. For a rotating disc electrode, the ohmic resistance is given by:

$$R_\Omega = \frac{1}{4\kappa r} \qquad 2$$

Where, $\kappa\ (S\ cm^{-1})$ is the specific conductivity of the bulk electrolyte and $r\ (cm)$ is the radius of the disc.

For more complex geometries the ohmic resistance is determined experimentally and can be estimated by EIS.

In a Nyquist plot, the intersection of the impedance data with the real part of the axis at the high frequency end gives the ohmic resistance.

Polarization resistance, R_p

An electrode is polarized when its potential is forced away from its value at open circuit. Polarization of an electrode causes current to flow due to electrochemical reactions it induces at the electrode surface. The magnitude of the current is controlled by reaction kinetics and diffusion of reactants both towards and away from the electrode.

When an electrode undergoes uniform corrosion at open circuit, the open circuit potential (OCP) is controlled by the equilibrium between anodic and cathodic reactions resulting in anodic and cathodic currents. The OCP is the potential where the two currents are equal. The value of the current for either of the reactions is known as the corrosion current. When the two reactions are under kinetic control, the potential of the cell can be related to the current by the Butler-Volmer equation:

$$i = i_0\left(e^{2.303\frac{\eta}{b_a}} - e^{-2.303\frac{\eta}{b_c}}\right) \quad 3$$

Where,

- $i\ (A)$ is the measured cell current;
- $i_0\ (A)$ is the exchange current;
- 2.303 is the conversion factor between log_e and log_{10};
- $\eta\ (V)$ is the overpotential, defined as the difference between applied potential E and the corrosion potential E_{corr};
- $\beta_a\ (V)$ and $\beta_c\ (V)$ are the Tafel slopes of the anodic and cathodic branch, respectively.

For small η the above equation can be transformed to:

$$i_0 \approx \frac{1}{R_p}\left[\frac{\beta_a\beta_c}{2.303(\beta_a+\beta_c)}\right] \quad 4$$

The polarization resistance R_p behaves like a resistor. If the Tafel slopes are known, one can calculate i_0 from R_p. The exchange current, i_0 can then be used to calculate the corrosion rate.

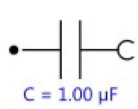
Capacitor, C

A capacitor C has an impedance of:

$$Z_c\ (\Omega) = \frac{1}{j\omega C}$$
$$|Z_C|\ (\Omega) = \frac{1}{\omega C} \quad 5$$
$$\theta_C\ (°) = -90°$$

Where $j = \sqrt{-1}$ $\omega\ (Hz)$ is the angular frequency and $C\ (F)$ is the capacitance.

The impedance of capacitors is a function of frequency and has only an imaginary part. A capacitor's impedance decreases as the frequency is raised. The current through a capacitor is phase shifted $-90°$ with respect to voltage. In NOVA, the C element is represented by the following symbol:



Some examples of the use of capacitance to describe electrochemical phenomena are provided below.

Double layer capacitance, C_{dl}

An electrical double layer exists at the electrode/electrolyte interface. This double layer is formed as ions from the solution approach the electrode surface. Charges in the electrode are separated from the charges of these ions. The separation is of the order of angstroms. The value of the double layer capacitance depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

Coating capacitance, C_C

For polymer coated substrates, the coating capacitance C_C is given by:

$$C_C = \varepsilon_0\varepsilon\frac{A}{d} \quad 6$$

Where $\varepsilon_0\ (= 8.85E-12\ F\ m^{-1})$ is the vacuum permittivity, ε is the relative permittivity of the coating, $A\ (m^2)$ is the area of the coating, and $d\ (m)$ is the thickness of the coating.

Typical relative permittivity values of coatings range between 3 and 4; while the relative permittivity of water is around 80. When water penetrates the coating, its dielectric constant increases, resulting in an increased coating capacitance. Hence, C_C can be used to measure the water absorbed by the coating.

Inductor, L

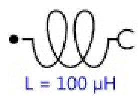
The impedance of an inductor, L, is given by:

$$Z_L\ (\Omega) = j\omega L$$
$$|Z_L|\ (\Omega) = \omega L \quad 7$$
$$\theta_L\ (°) = +90$$

Where $j = \sqrt{-1}$ $\omega\ (Hz)$ is the angular frequency $L\ (H)$ is the inductance. The impedance of an inductor increases with frequency. Like capacitors, inductors have only an imaginary impedance component. But current through an inductor is phase shifted of $+90°$ degrees with respect to the voltage.

The impedance of an electrochemical cell can sometimes appear to be inductive due to adsorption of reactants on the surface and can be modeled using Inductance.

Inductive behavior can also result from non-uniform current distribution, inductance of cell cables, slow response of reference electrodes and potentiostat non-idealities. In these cases, the appearance of inductance indicates an error in the EIS measurement. In NOVA, the L element is represented by the following symbol:

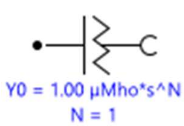


Constant Phase Element, Q (or CPE)

Modelling an electrochemical phenomenon with an ideal capacitor assumes that the surface under investigation is homogeneous, which is normally not the case. This lack of homogeneity is modelled with a Q element (or CPE), used to represent the CPE:

$$Z_Q\ (\Omega) = \frac{1}{Y_0 (j\omega)^n} \qquad 8$$

Where, $Y_0\ (S \cdot s^n)$ is the parameter containing the capacitance information, $j = \sqrt{-1}$, $\omega\ (Hz)$ is the angular frequency and n is an empirical constant, ranging from 0 to 1. It is noteworthy that when $n = 1$, the CPE behaves as a pure capacitor, while when $n = 0$, the CPE behaves a pure resistor. Furthermore, when $n = 0.5$, the CPE is the equivalent of the so-called Warburg element, described below. In NOVA, the Q element is represented by the following symbol:



Double layer capacitance and coating capacitance, described in the previous section, are usually modelled with a CPE.

Warburg, W

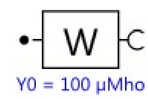
In electrochemical systems, diffusion of ionic species at the interface is common. The Warburg impedance was developed to model this phenomenon. Several expressions, based on different assumptions, are used to describe diffusion impedance. Under the assumption of semi-infinite diffusion layer, the impedance is:

$$Z_W\ (\Omega) = \frac{1}{Y_0\sqrt{j\omega}} = \frac{\sqrt{2}}{Y_0\sqrt{\omega}} - j\frac{\sqrt{2}}{Y_0\sqrt{\omega}} \qquad 9$$

$$|Z_W|\ (\Omega) = \frac{2}{Y_0\sqrt{\omega}}$$

$$\theta_W\ (°) = +45$$

Where, $Y_0\ (S \cdot \sqrt{s})$ is the parameter containing information on the diffusion, $j = \sqrt{-1}$ and $\omega\ (Hz)$ is the angular frequency. A Warburg impedance is characterized by having identical real and imaginary contributions, resulting in a phase angle of $+45°$. In NOVA, the Warburg element is represented by the W symbol:



Warburg – short circuit terminus, O

Under the assumption of a finite diffusion layer thickness (Nernst hypothesis) with short circuit terminus, the diffusion impedance is modelled by:

$$Z_O\ (\Omega) = \frac{1}{Y_0\sqrt{j\omega}} tanh\left(B\sqrt{j\omega}\right) \qquad 10$$

Where, $Y_0\ (S \cdot \sqrt{s})$ is the parameter containing information on the diffusion, $j = \sqrt{-1}$, $\omega\ (Hz)$ is the angular frequency, and $B\ (\sqrt{s})$ is given by:

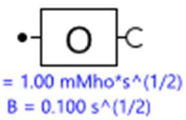
$$B = \frac{\delta}{\sqrt{D}} \qquad 11$$

Where $\delta\ (cm)$ is the diffusion layer thickness and $D\ (cm^2\ s^{-1})$ is the diffusion coefficient. It is noteworthy to point out than when B is large, the Z_O is reduced to Z_W.

For a rotating disc electrode, the diffusion layer thickness is given by:

$$\delta = \frac{1.61 \cdot D^{1/3} \nu^{1/6}}{\sqrt{\omega_{RDE}}} \qquad 12$$

Where $D\ (cm^2\ s^{-1})$ is the diffusion coefficient, $\nu\ (cm^2\ s^{-1})$ is the kinematic viscosity of the solution and $\omega_{RDE}\ (rad\ s^{-1})$ is the angular frequency of the rotating disc electrode. In NOVA, the Warburg – short circuit terminus element is represented by the O symbol:



Warburg – open circuit terminus, T

Under the assumption of a finite diffusion layer thickness (Nernst hypothesis) with open-circuit terminus, the diffusion impedance is modelled by:

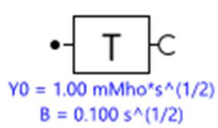
$$Z_O\ (\Omega) = \frac{1}{Y_0\sqrt{j\omega}} coth\left(B\sqrt{j\omega}\right) \qquad 13$$

Where $Y_0\ (S \cdot \sqrt{s})$ is the parameter containing information on the diffusion, $j = \sqrt{-1}$, $\omega\ (Hz)$ is the angular frequency and $B\ (\sqrt{s})$ is given by:

$$B = \frac{\delta}{\sqrt{D}} \qquad 14$$

Where $\delta\ (cm)$ is the diffusion layer thickness and $D\ (cm^2\ s^{-1})$ is the diffusion coefficient. This element is used, for example, to model the finite diffusion of species across a thin film.

In NOVA, the Warburg – open circuit terminus element is represented by the T symbol:



Gerischer, G

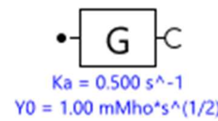
If a first order chemical reaction is present with the electrochemical reaction under investigation, the Gerischer element can be used.

The impedance of a Gerischer element is given by:

$$Z_G = \frac{1}{Y_0\sqrt{K_a + j\omega}} \qquad 15$$

Where $Y_0\ (S \cdot \sqrt{s})$ is the parameter containing information on the diffusion, $K_a\ (Hz)$ is the reaction rate of the first order chemical reaction, $j = \sqrt{-1}$, and $\omega\ (Hz)$ is the angular frequency.

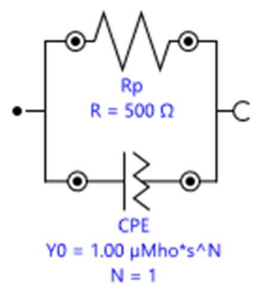
In NOVA, the Gerischer element is represented by the G symbol:



Effective capacitance from CPE values

As shown before, the CPE element does not give the capacitance value, but a parameter $Y_0\ (S \cdot s^n)$ which contains the capacitance information. In order to extract the capacitance value, three cases are listed, deepening on the placement of the CPE in an equivalent circuit.

In the case of a CPE in parallel with a resistor, (RpCPE),

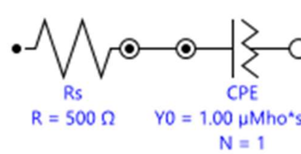


the effective capacitance can be calculated with the following Equation:

$$C_{eff}\ (F) = Y_0 \cdot (\omega_{max})^{n-1} \qquad 16$$

Where ω_{max} is the angular frequency where imaginary part of the impedance reaches its maximum value, i.e., the top of the semicircle.

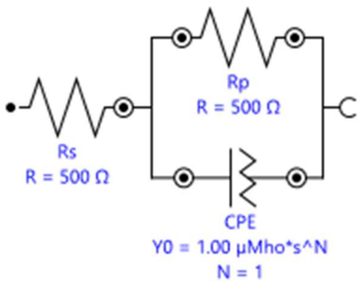
In the case of a CPE in series with a resistor Rs, [RsCPE],



the effective capacitance can be calculated with the following Equation:

$$C_{eff}\ (F) = Y_0^{\frac{1}{n}} \cdot \left(\frac{1}{Rs}\right)^{\frac{n-1}{n}} \qquad 17$$

In the case of a CPE in parallel with a resistor Rp and this arrangement is in series with a resistor Rs, [Rs(RpCPE)]



the effective capacitance C_{eff} can be calculated with the following Equation:

$$C_{eff}\ (F) = Y_0^{\frac{1}{n}} \cdot \left[\frac{1}{Rs} + \frac{1}{Rp}\right]^{\frac{n-1}{n}} \qquad 18$$

Conclusions

In this application note, insights on the electrical elements used to build up equivalent circuits are given. Moreover, the properties of the elements are listed, together with examples of utilization. Finally, formulas to extract the effective capacitance from the CPE values are given.

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