Application Area: Fundamental

EIS Data fitting – How to obtain good starting values of equivalent circuit elements

Keywords

Electrochemical impedance spectroscopy; EIS; fit and simulation; resistance; capacitance; Warburg; short circuit terminus.

Summary

Electrochemical impedance spectroscopy (EIS) is a powerful technique that provides information on the processes occurring at the electrode-electrolyte interface.

The data collected with EIS are modeled with a suitable electrical equivalent circuit, resulting from an arrangement of electrical elements, like resistors (R), capacitors (C), inductors (L), and ad-hoc elements like constant phase element (CPE) and Warburg (W). Each element is characterized by an impedance Z (Ω) described by a complex function (often frequency-dependent) with one or more parameters free to change during the fit.

The electrical equivalent circuit is the result of arranging the elements in series and/or in parallel. A combination of electrical elements in series results in a complex function $Z_{tot,series}$ (Equation 1), calculated as sum of the impedances of the electrical elements, Figure 1.

$$Z_{tot,series}\ (\Omega) = Z_1 + Z_2 \quad (1)$$

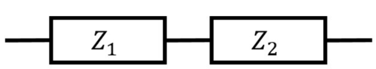

Figure 1 – A combination of electrical elements in series, with their impedances.

A combination of electrical elements in parallel results in a complex function $Z_{tot,parallel}$ (Ω) (Equation 2) calculated as the inverted sum of the inverse of the impedances of the electrical elements, Figure 2.

$$Z_{tot,parallel}\ (\Omega) = \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right)^{-1} = \frac{Z_1 Z_2}{Z_1 + Z_2} \quad (2)$$

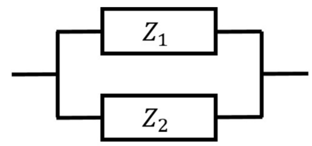

Figure 2 – A combination of electrical elements in parallel, with their impedances.

In general, the electrical equivalent circuit can be the result of an arrangement in series, in parallel, or a combination of both series and parallel of electrical elements. An example is in Figure 3.

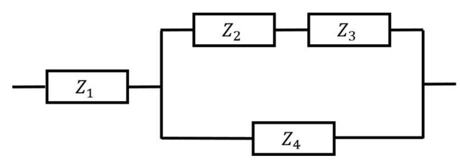

Figure 3 – A combination of electrical elements in series and in parallel, with their impedances.

In such cases, the total impedance is calculated in blocks. In this example, the Z_1 is the first block (A), in series with the second block (B), formed by the arrangement of Z_2, Z_3 and Z_4. The total impedance is given by the sum of the two blocks. The second block is composed of $Z_2 + Z_3$ (in series), in parallel with Z_4. Therefore, the total impedance Z_{tot} is given by:

$$Z_{tot}\ (\Omega) = A + B = Z_1 + \left(\frac{1}{Z_2 + Z_3} + \frac{1}{Z_4}\right)^{-1} \quad (3)$$

Finally, the impedances Z are substituted with the complex functions related to the relative electrical elements that form the equivalent electrical circuit.

NOVA exploits a nonlinear least square regression to fit the data with the function from the equivalent circuit, using the Levenberg–Marquardt algorithm. The fitting procedure will change the values of the parameters until the mathematical function matches the experimental data within a certain error margin. The goodness of the fit is represented by the χ^2 (chi-squared) value. The better the fit, the closer to 0 will be the χ^2 value.

It is necessary to have a starting value for each of the parameters in order to start the modelling calculations. Selecting reasonable starting values that are close to the expected result increases the likelihood of a successful fitting. When the algorithm needs to perform fitting from unreasonable starting values, it is likely that the fit will not be successful, i.e., the fit will result in unreasonable values of the parameters and/or a high χ^2 value, or the computation will fail completely.

In this application note, some suggestions are given in order to get good initial parameters and to perform an accurate fitting.

Experimental conditions

EIS was performed on a 3 mm Pt disk electrode in aqueous solution composed of 0.05 mol/L potassium ferrocyanide; 0.05 mol/L potassium ferricyanide and 0.1 mol/L NaCl (ferro/ferri solution).

A double junction Ag/AgCl 3 mol/L KCl reference electrode and a Pt counter electrode completed the setup.

Potentiostatic EIS measurements were performed with a Metrohm Autolab PGSTAT302N, equipped with a FRA32M module. A Metrohm Autolab RDE rotator and motor controller was used to allow the working electrode (WE) to be used in stationary or rotating conditions.

EIS measurements were performed from 100 kHz to 100 mHz, 10 mV amplitude and 10 points per decade. The offset potential was set at the half wave potential $E_{1/2}$, (i.e., the potential half way between the potentials where the Fe^{2+} oxidation and Fe^{3+} reduction peaks occur), of a cyclic voltammetry measurement (not shown here). The half wave potential was $E_{1/2} = 0.256$ V vs. Ag/AgCl.

EIS measurements were taken with the working electrode standing still (no rotation), and with the working electrode rotating at 100 RPM.

Then, an adequate equivalent circuit was selected, and the starting values of the parameters describing resistances, capacitors, Warburg, and Warburg-short circuit terminus elements were found. Finally, the fitting was performed.

For the starting values of other elements, like inductance, Warburg – open circuit terminus, and Gerischer element, simulation of EIS measurements were performed, since no experimental data were available.

Results and Discussion

Stationary working electrode

The Nyquist and Bode plot resulting from EIS measurement on a stationary WE is shown in Figure 4 and Figure 5, respectively.

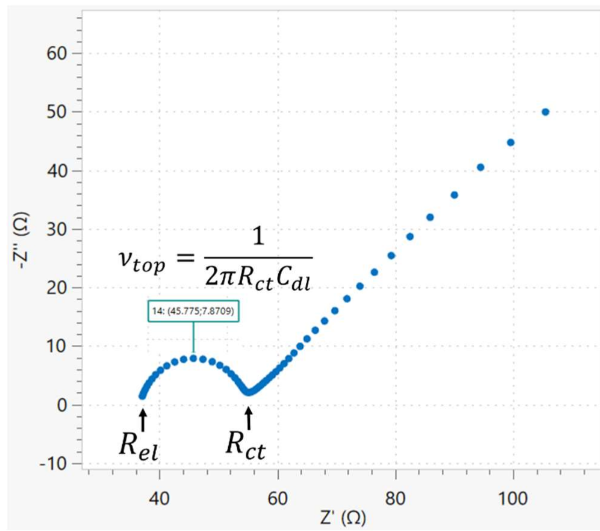

Figure 4 – Nyquist plot of a Pt working electrode in a ferro/ferri solution. No rotation is applied to the working electrode.

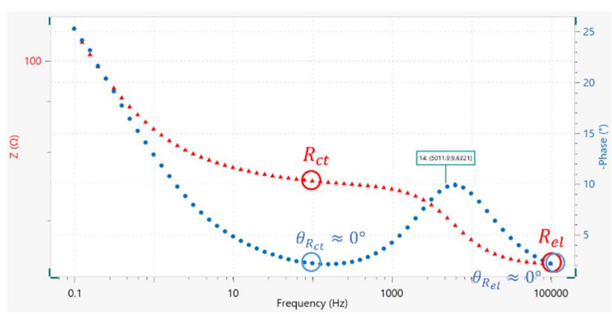

Figure 5 – Bode plot of a stationary Pt working electrode in a ferro/ferri solution. In red, the modulus vs. linear frequency (in a log-log fashion), in blue the phase vs. linear frequency (in a linear-log fashion).

A possible model to fit the data should include a resistance for the electrolyte (R_{el}), one resistance for the charge transfer (R_{ct}), a constant phase element (CPE_{dl}) or a capacitor (C_{dl}) for the double layer, and a Warburg (W_D) for the semi-infinite diffusion of the ionic species through the diffusion layer (i.e., from the bulk electrolyte to the double layer).

The electrical elements are arranged in the so-called Randles circuit, shown in Figure 6.

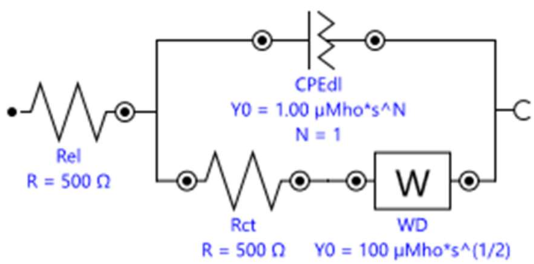

Figure 6 – The Randles circuit diagram.

The starting parameters

By default, NOVA assigns some starting values to the electrical elements (in blue, in Figure 6). The default starting values have been chosen to represent reasonable values for general electrochemical cells; however, the software has no knowledge of the actual materials being analyzed. Therefore, it is recommended to replace these starting values with any known values from the real electrochemical set up. If approximate values are known for any of the circuit element, the approximate value should be entered and the software will use that as a starting point to optimize the model.

Resistance

The impedance of a resistor Z_R contains only the real part of the complex number, Equation 4.

$$Z_R\ (\Omega) = R \qquad (4)$$

In polar coordinates, the modulus $|Z_R|$ of a resistor is the value of the resistance, when the phase θ_R is $0°$ (Equations 5).

$$|Z_R|\ (\Omega) = R$$
$$\theta_R\ (°) = 0 \qquad (5)$$

Therefore, visual observation of the Nyquist plot is often enough to have good initial starting values of the resistances. The values are the touchdown points of the Nyquist plot on the X-axis.

In Figure 4, the resistance of the electrolyte is approximately $R_{el} \approx 38\ \Omega$ and the charge transfer resistance is approximately $R_{ct} \approx 58\ \Omega - 38\ \Omega = 20\ \Omega$.

Alternatively, visual observation of the Bode plot is also possible. The $|Z_R|$ values of interest are in correspondence of $\theta_R \approx 0°$ (Figure 5).

Capacitance and constant phase element

The impedance of a capacitor Z_C contains only the imaginary part of the complex number, Equation 6.

$$Z_C\ (\Omega) = \frac{1}{j\omega C} \qquad (6)$$

Where $j = \sqrt{-1}$, $\omega\ (Hz, s^{-1})$ is the angular frequency, and C represents the capacitance value in Farad (F).

In polar coordinates, the modulus of the capacitance $|Z_C|$ is frequency-dependent, and the phase θ_C is $-90°$, Equations 7.

$$|Z_C|\ (\Omega) = \frac{1}{\omega C}$$
$$\theta_C\ (°) = -90 \qquad (7)$$

The constant phase element (CPE) is often used instead of a capacitor in order to model, for example, the non-ideality of the electrode surface or of a coating layer (roughness).

The impedance of a constant phase element Z_{CPE} is shown in Equation 8.

$$Z_{CPE}\ (\Omega) = \frac{1}{Y0(j\omega)^N} \qquad (8)$$

Where $j = \sqrt{-1}$, $Y0\ (S \cdot s^N)$ is the parameter used to calculate the capacitance (see Equations 11, 26 and 27), and N is the exponent ranging from 0 to 1. For a CPE used instead of a capacitor, $0.85 < N < 1$, approximately.

When $N = 1$, the constant phase element is equal to a capacitor with the same impedance, so Equation 8 becomes equivalent to Equation 7. Therefore, in order to get suitable $Y0$ and N starting values, the discussions about the starting values for the capacitance can be used.

To get the starting value for the $Y0$ parameter, the data can be fitted, fixing the exponent value to $N = 1$. After the initial fit, the exponent value can let be relaxed and the fit can be performed again.

Capacitance and CPE – visual observation

This method is useful only when a capacitor C_{dl} or a CPE_{dl} is in parallel with a resistor. In this example, the C_{dl} is in parallel with the R_{ct}. Both of them are in series with R_{el}, resulting in a semicircle in the Nyquist plot.

In the following discussion, the C_{dl} will be taken into account, and the results will be extended to the CPE_{dl}.

The linear frequency at which the top of the semicircle occurs, ν_{top}, is related to the capacitance value C_{dl}, according to Equation 9.

$$\nu_{top}(Hz) = \frac{1}{2\pi R_{ct} C_{dl}} \qquad 9$$

In this example, $R_{ct} \approx 20\ \Omega$.

For the value of ν_{top}, it is possible to check the index value of the data point at the ν_{top} in the Nyquist plot, with the “Toggle step through data” button in NOVA. With the help of this button, the values related to the data point selected are shown in a small window, together with the index value of the data point (data point with index 14, Figure 4).

Then, the data point with the same index value can be checked in the Bode plot, again with the “Toggle step through data” button. In the small window that appears, the frequency value is the number after the index. At high frequencies, the ν_{top} value on interest lies close to the peak of the Bode plot phase (Figure 5). In this case, $\nu_{top} \approx 5\ kHz$.

With the aid of Equation 10, C_{dl} can be calculated.

$$C_{dl}(F) = \frac{1}{2\pi R_{ct} \nu_{top}} \qquad 10$$

Resulting in $C_{dl} = 1.59E - 6\ F$.

If a CPE_{dl} is used instead of the C_{dl}, it is possible to use the C_{dl} value extracted with Equation 10 for Y0 and using $N = 1$ as starting value of the exponent.

In the following sections, capacitance values are extracted, depending on the arrangement of the capacitor, with respect to the other electrical elements.

Capacitance and CPE – Electrochemical circle fit command

With the Electrochemical circle fit command, NOVA offers the possibility to generate starting parameters for the portion of equivalent circuit related to the semicircles of a Nyquist plot. This NOVA command makes the process of obtaining starting values to fit the semicircle part of Nyquist plot very accurate and straightforward.

The command allows choosing three points along a semicircle, as shown in Figure 7.

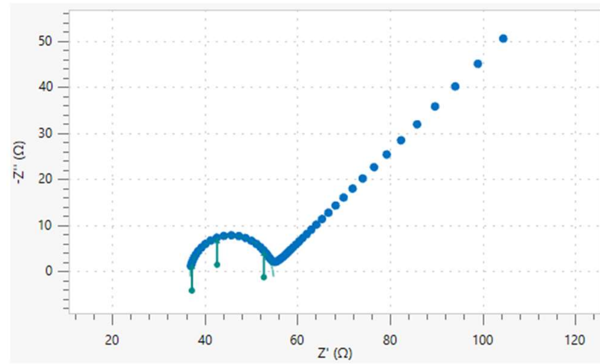

Figure 7 – The Nyquist plot from the Electrochemical circle fit command. In green, the three points chosen for the fit.

The command will automatically fit the semicircle with a [Rs(RpCPE)] equivalent circuit. The fit results are shown in Figure 8.

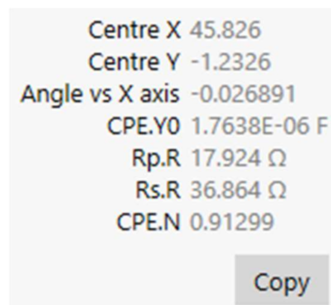

Figure 8 – The fit results of the Electrochemical circle fit command.

Clicking of the button Copy, the [Rs(RpCPE)] equivalent circuit will be copied, and it can be pasted in the Equivalent Circuit Editor of the Fit and simulation command as shown in Figure 9. This circuit diagram can now be modified to represent the actual electrochemical system by adding any relevant circuit elements. The circuit elements within the portion of the circuit that was obtained from the electrochemical circle fit command already have good starting values for the fitting.

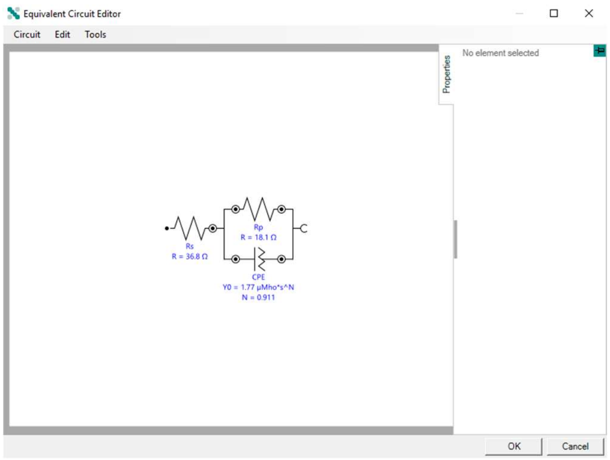

Figure 9 – The Equivalent Circuit Editor window, with the [Rs(RpCPE)] equivalent circuit copied from the Electrochemical circle fit command.

In order to complete the analysis, it is possible to calculate the effective capacitance C_{eff} with Equation 11, valid for a [Rs(RpCPE)] equivalent circuit,

$$C_{eff}\ (F) = Y0^{\frac{1}{N}} \cdot \left[\frac{1}{Rs} + \frac{1}{Rp}\right]^{\frac{N-1}{N}} \qquad 11$$

Where

- Y0 is CPE.Y0,
- N is CPE.N,
- Rs is Rs.R,
- Rp is Rp.R,

in the properties of the elements (Equivalent Circuit Editor). Finally, a Warburg can be added, and the fit can be performed.

Capacitance – capacitance calculation

The last method to get suitable initial parameters for the capacitance is to calculate the modulus of the capacitance $|C|$, Equation 12.

$$|C|\ (F) = \frac{1}{\omega |Z|} \qquad 12$$

Where $\omega\ (Hz)$ is the angular frequency $\omega = 2\pi\nu$ (ν being the linear frequency) and $|Z|\ (\Omega)$ is the modulus of the impedance.

The modulus of the capacitance can be plotted versus the linear frequency, in a log-log fashion; together with the phase, Figure 10.

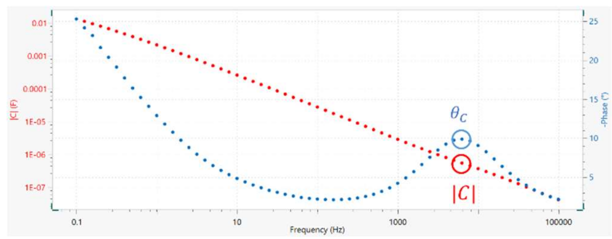

Figure 10 – The capacitance modulus and phase versus the linear frequency.

Here, the capacitance value of interest (red circle in Figure 10) occurs at the same frequency where the phase θ_C has a peak at high frequencies (blue circle in Figure 10).

In this case, the capacitance value $C_{dl}(F) = 5.63E - 7$.

It must be stressed that, since a pure capacitor has a phase shift of $-90°$, the more the phase value is away from $-90°$, the less accurate will be the calculated capacitance.

Warburg W

The Warburg element (W) is used to fit semi-infinite diffusion of species through the diffusion layer. The diffusion is semi-infinite when the lowest frequency is not enough for the charge carrier to cross the entire diffusion layer.

The impedance of a Warburg element Z_W is shown in Equation 13.

$$Z_W\ (\Omega) = \frac{1}{Y0\sqrt{j\omega}} \qquad 13$$

Where $YO\ (S \cdot \sqrt{s})$ is the parameter that contains the information about the diffusion coefficient.

A suitable starting value for $Y0$ can be extracted by performing a linear regression on the straight line in the Nyquist plot in Figure 4. The regression is shown in Figure 11.

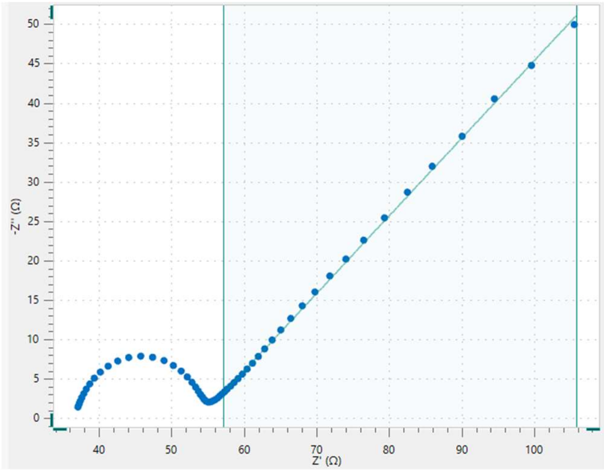

Figure 11 – The regression line on the portion of the Nyquist plot related to the Warburg diffusion (straight line).

The Warburg element W has the slope of the regression line $b \approx 1$.

In order to get the $Y0$ value, the linear function resulting from the regression must be set at $y = 0$.

Function description	y = -52.92 + 0.98281x
Correlation coefficient	0.99973
a	-52.92
b	0.98281
1/Slope	1.0175

Figure 12 – Results of the linear regression of Figure 11.

$$y = a + bx$$
$$y = 0 \rightarrow x = -\frac{a}{b} \qquad (14)$$
$$Y0 = \frac{1}{x} = \left|\frac{b}{a}\right|$$

In this example, $Y0 = 0.0186\, S \cdot \sqrt{s}$.

Data fitting with the calculated starting values

Using the new starting values that have been determined based on the experimental EIS data, it is now possible to perform fitting on the data in Figure 4 and Figure 5.

The values from the electrochemical circle fit have been used, together with the $Y0$ value for the Warburg. In Figure 13, the Randles circuit with the calculated starting parameters, which are fixed, is shown.

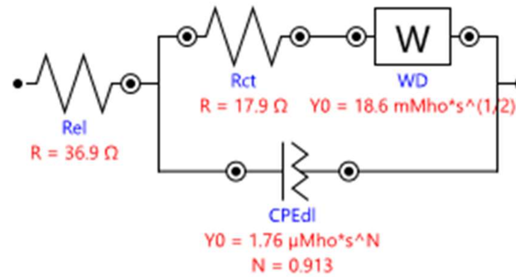

Figure 13 – The Randles circuit with the calculated starting values. The parameters are fixed.

In Figure 14, the Nyquist plot of the data (dots) and the fit results from the Randles circuit in Figure 13 are shown, resulting in $\chi^2 = 0.26$.

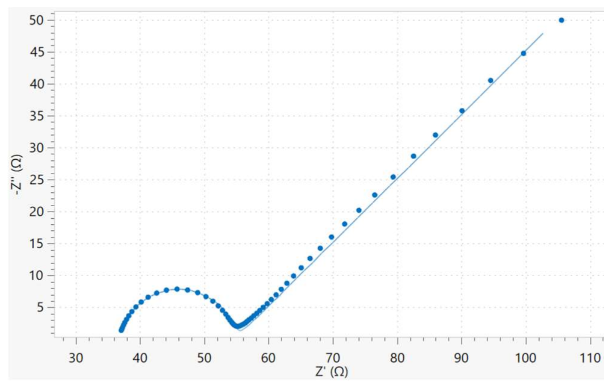

Figure 14 – The Nyquist plot of the data points (dots), together with the fit resulting by the Randles circuit in Figure 13 (line).

After the fit was performed with all the electrical elements free to relax, $\chi^2 = 0.000635$.

In Table 1, the comparison between the starting values and values after the fit for the electrical elements of the Randles circuit of Figure 3 is shown.

Table 1 - Comparison between starting values and fitted values for the electrical elements of the Randles circuit of Figure 6.

Element	Starting values	Values after the fit
$\boldsymbol{Rel}\ (\boldsymbol{\Omega})$	36.9	36.89
$\boldsymbol{Rct}\ (\boldsymbol{\Omega})$	17.9	17.29
$\boldsymbol{CPEdl\ Y0}\ (\boldsymbol{S \cdot s^N})$	1.76E-6	3.83E-6
$\boldsymbol{CPEdl\ N}$	0.913	0.923

$WD\ Y0\ (S \cdot \sqrt{s})$	0.0186	0.0177

The starting values are very close to the fitted values; therefore, such starting values are a good approximation, which lead the fit towards the best results.

Rotating working electrode

A rotation applied to the working electrode reduces the width of the diffusion layer. In such cases, it is possible that low frequency applied results in the charge carriers reaching the end of the diffusion layer. As result, the Warburg semi-infinite diffusion model, and the representative Warburg circuit element (W) are no longer applicable. Now the transmission line is terminated with a semicircle at low frequencies; giving rise to a new electrical element, i.e., the Warburg – short circuit terminus (O).

Warburg – short circuit terminus, the O element

Figure 15 and Figure 16 show the Nyquist and Bode plots obtained when the same Pt disk electrode is rotated at 100 RPM.

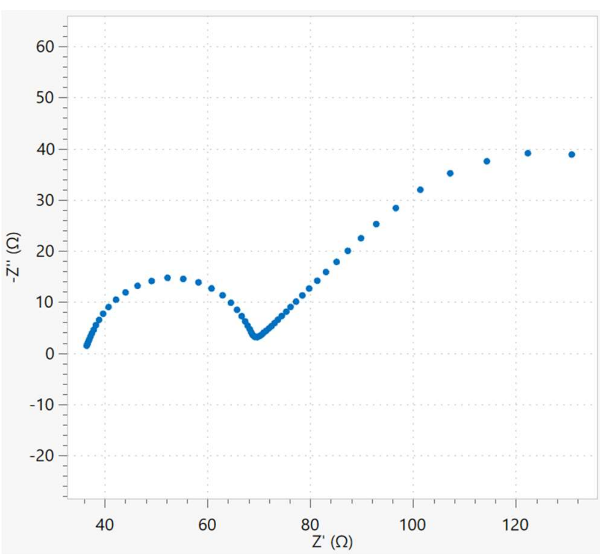

Figure 15 – Nyquist plot of a Pt working electrode rotating at 100 RPM in a ferro/ferri solution.

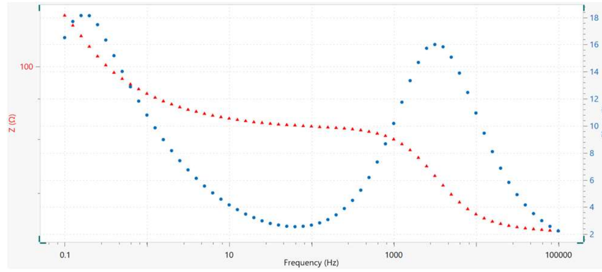

Figure 16 – Bode plot of a Pt working electrode rotating at 100 RPM in a ferro/ferri solution.

A comparison of the two Nyquist plots of Figure 15 and Figure 4 reveals that the high frequency data (i.e., the semicircle) is similar for the stationary and rotating electrodes. Therefore, the discussion from the previous section still applies.

Regarding the low-frequency portion of the plots, the Warburg – short circuit terminus (O) is used.

The impedance of such element is shown in Equation 15.

$$Z_O(\Omega) = \frac{1}{Y0\sqrt{j\omega}} \tanh(B\sqrt{j\omega}) \qquad 15$$

Where $YO\ (S \cdot \sqrt{s})$ is the parameter which contains the information about the diffusion coefficient and B $(\sqrt{s})$ is the square root of the diffusion time.

In the case of the Warburg – short circuit terminus element, it is necessary to calculate the starting values of the two parameters, $Y0$ and B.

Regarding the $Y0$ parameter, a regression line is performed, restricted on the portion of the Nyquist plot where the data points are arranged in a straight line, Figure 17.

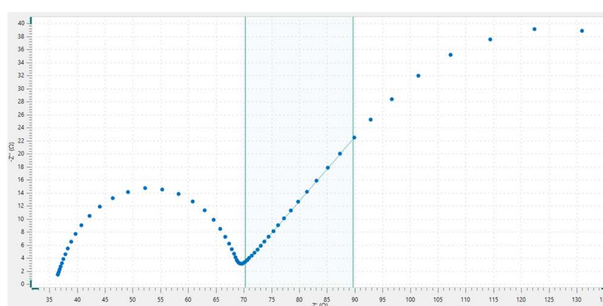

Figure 17 – The regression line on the portion of the Nyquist plot related to the Warburg diffusion (straight line).

Also in this case, the slope of the regression line $b \approx 1$. The fit results (Figure 18) and Equation 14 are used to calculate the $Y0$ value.

Function description	y = -65.842 + 0.98208x
Correlation coefficient	0.99988
a	-65.842
b	0.98208
1/Slope	1.0183

Figure 18 – Results of the linear regression of Figure 17.

In this example, $Y0 = 0.0148\ S \cdot \sqrt{s}$.

Regarding the B parameter, an electrochemical circle fit can be performed on the portion of the semicircle at low frequencies.

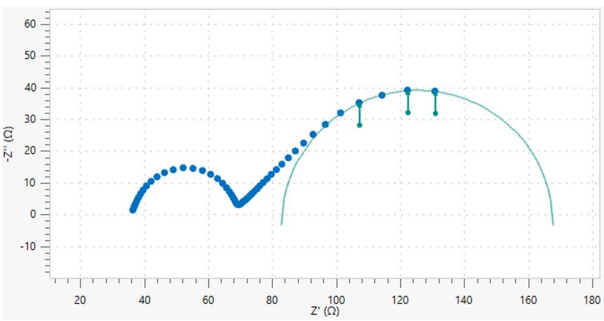

Figure 19 – The electrochemical circle fit on the portion of the Nyquist plot related to short terminus of the Warburg.

The results are shown in Figure 20.

Centre X	125.47
Centre Y	-3.3652
Angle vs X axis	-0.026815
CPE.Y0	0.016047 F
Rp.R	84.899 Ω
Rs.R	83.016 Ω
CPE.N	0.94964

Figure 20 – The results of the electrochemical circle fit of Figure 19.

With the electrochemical circle fit results, it is possible to calculate the starting value of the B parameter. Recalling Equation 9,

$$B\ (\sqrt{s}) = \frac{1}{\sqrt{\nu_{top}}} = \sqrt{2\pi R_p C_{eff}} \qquad 16$$

In this example, the effective capacitance $C_{eff}\ (F)$ must be calculated from the values of CPE.Y0 and CPE.N, with the Equation 11, where Y0 is CPE.Y0, N is CPE.N, Rs is Rs.R and Rp is Rp.R in Figure 20.

In this example, $C_{eff}\ (F) = 0.0157$ and $B\ (\sqrt{s}) = 2.88$.

The resulting equivalent circuit is shown in Figure 21.

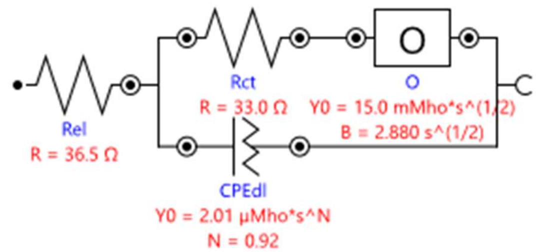

Figure 21 – The equivalent circuit with the calculated starting values. The parameters are fixed.

In Table 2, the comparison between the starting values and the values resulting from the fit is shown.

Table 2 - Comparison between starting values and fitted values for the electrical elements of the circuit of Figure 21.

Element	Starting values	Values after the fit
$Rel\ (\Omega)$	36.5	36.5
$Rct\ (\Omega)$	33	31.7
$CPEdl\ Y0\ (S \cdot s^N)$	2.01E-6	3.88E-6
$CPEdl\ N$	0.92	0.93
$O\ Y0\ (S \cdot \sqrt{s})$	0.015	0.0188
$O\ B\ (S \cdot \sqrt{s})$	2.88	1.76

Also in this case, the starting values are close to the values obtained with the fit.

Starting values of other elements and circuits.

The following examples are related to EIS data, or portions of EIS data taken by simulating different circuits containing capacitors and resistors in series, and inductors. Finally simulations of Randles circuits with Warburg – open circuit terminus and Gerischer elements are studied.

Capacitance – [RC]

When a capacitor is in series with a resistor, a way to get a suitable starting value is to plot the modulus of the capacitance (Equation 12) versus the linear frequency in a log-log fashion. The resulting plot is shown in Figure 22, for the case of $R = 0.05\ \Omega$ and $C = 1\ \mu F$.

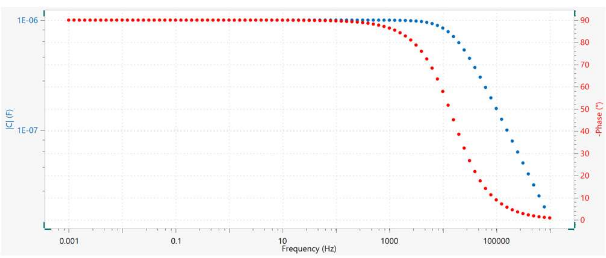

Figure 22 – The Bode plot of the capacitance modulus vs. linear frequency.

Here, the capacitance value can be extracted at low frequencies, where the phase reaches $-90°$.

If the data do not reach $-90°$, the starting values of the resistance (visual observation) and any starting value of the capacitance are often good enough to have a good fit.

Inductance L – high frequencies

Inductive behavior occurring at high frequency is usually ascribed to the electrons movement in the cell cables of the potentiostat. The electrons in one wire resonate at high frequencies, creating an oscillating magnetic field which induces a current in the nearby cable.

This inductive effect is shown in the Nyquist plot as data points in the second quadrant (positive Z' and positive Z'', plotted as negative $-Z''$).

Most of the times, there is no interest in the inductive behavior at high frequencies, since it is not related to the electrochemical system of interest. In these cases, the Windower command can be used to remove the irrelevant data, i.e., to exclude the high-frequencies inductive behavior.

However, for low-impedance devices, such as capacitors, supercapacitors, shunt resistors, and fuel cells, there could be an interest in the inductance at high frequencies.

The impedance Z_L of an inductor contains only the imaginary part of the complex number (Equation 17).

$$Z_L\ (\Omega) = j\omega L \qquad 17$$

Where $L\ (H, \Omega \cdot s)$ is the inductance.

In polar coordinates,

$$|Z_L|\ (\Omega) = \omega L$$
$$\theta_C\ (°) = +90 \qquad 18$$

In an inductor, the current signal is ahead of the voltage signal with a phase angle of $+90°$ (Equation 18). Therefore, a Bode plot of a circuit with inductive behavior will show negative values of the $-\theta$ (°) versus linear frequency plot.

The inductance at high frequencies can be in series with a resistor, [RsL], or in parallel with a resistor Rp and in series with a resistor Rs, [Rs(RpL)].

Inductor in series with a resistor – [RsL]

In Figure 23, a typical Nyquist plot of a resistor Rs in series with an inductor L.

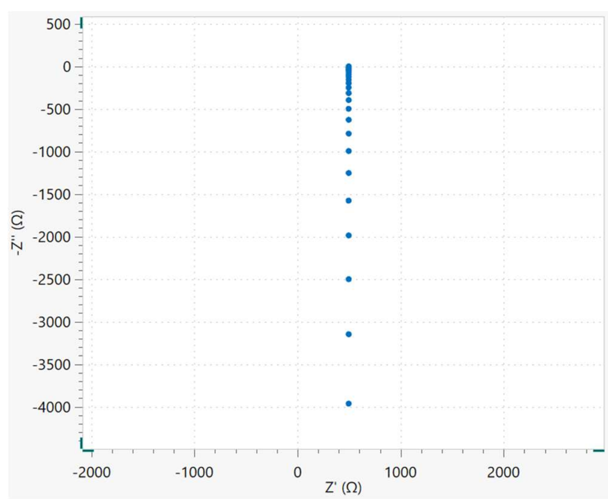

Figure 23 - Nyquist plot of an inductor in series with a resistor.

In Figure 24, the Bode plot for the same system is shown.

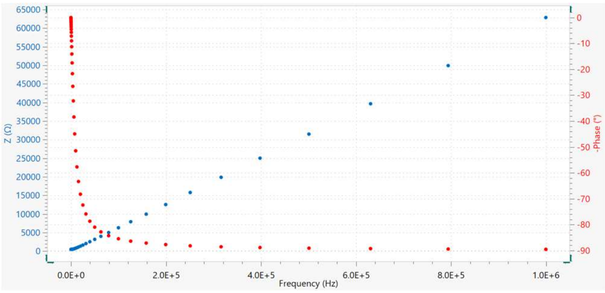

Figure 24 - Bode plot of an inductor in series with a resistor, in a linear-linear fashion.

If a regression line is performed on the modulus of Z vs. linear frequency plot, the slope divided by 2π is the inductance L, since

$$|Z_L|\ (\Omega) = \omega |L|$$

$$|L|\ (H) = \frac{|Z_L|}{\omega} = \frac{|Z_L|}{2\pi\nu} = \frac{slope}{2\pi} = \frac{b}{2\pi} \quad 19$$

The bigger the value of the inductance and the more data points in the high-frequency portion of the Bode plot, the more accurate the inductance value will be.

In this example, $Rs = 500\ \Omega$ and $L = 10\ mH$. In Figure 25, the regression line is shown.

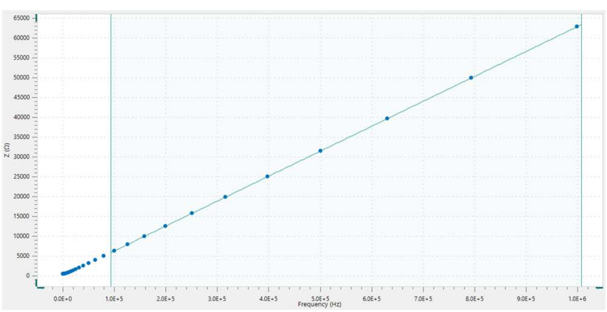

Figure 25 – The regression line for a [LR] system.

In Figure 26, the results of the regression of Figure 25.

Function description	y = 42.595 + 0.06277x
Correlation coefficient	1
a	42.595
b	0.06277
1/Slope	15.931

Figure 26 – The regression results for a [LR] system.

Here, it can be seen that if the slope b is divided by 2π, the inductance $L = 10\ mH$.

Inductor in parallel with a resistor – [Rs(RpL)]

In the case of a [Rs(RpL)] arrangement, the Nyquist plot shows a partial semicircle in the second quadrant, Figure 27.

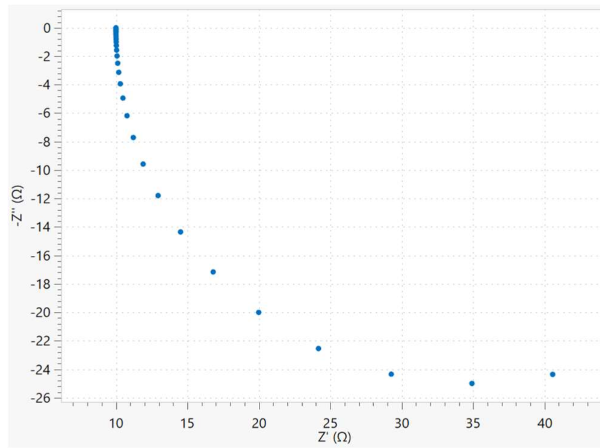

Figure 27 – The Nyquist plot for a [Rs(RpL)] system.

It is possible to calculate the inductance modulus |L|, with Equation 19, and plot it versus the linear frequency, as in a Bode plot, together with the phase $-\theta$, Figure 28.

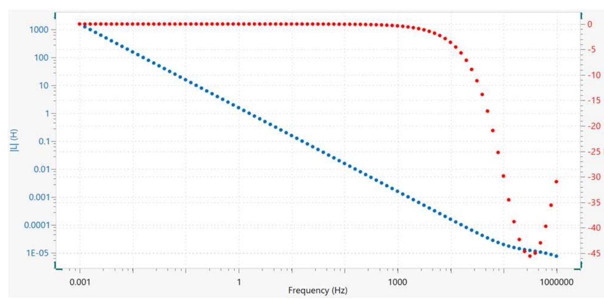

Figure 28 – The inductance modulus and the phase, vs. linear frequency, for a [Rs(RpL)] system.

The inductance value can be found at the same frequency where the $-Phase$ (°) has a minimum. In this example, the inductance value is approximately $L \approx 10\ \mu H$.

Inductance L – low frequencies

The inductive behavior can occur at low frequencies, as results of a change in the number of sites where the charge transfer occurs. A typical example is adsorption of one species, followed by desorption.

The resulting Nyquist plot has a semicircle in the negative part of the $-Z''$ Axis (second quadrant of the plot), as shown in Figure 29.

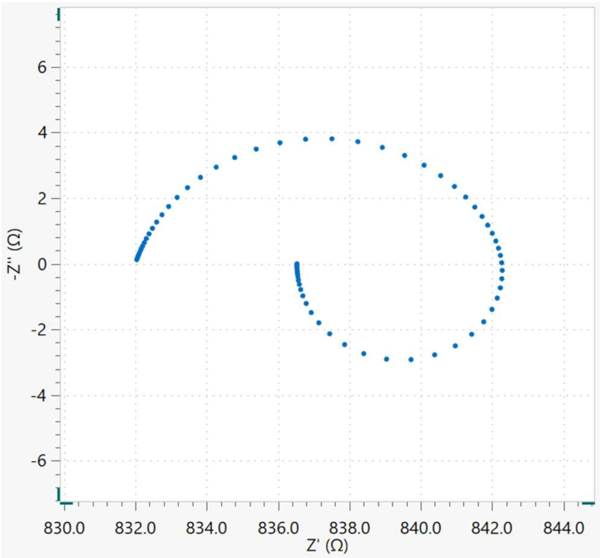

Figure 29 – An example of Nyquist plot, where an inductive effect at low frequencies is present, as a semicircle in the second quadrant.

In the example of Figure 29, the Nyquist plot can be modeled with the equivalent circuit in Figure 30.

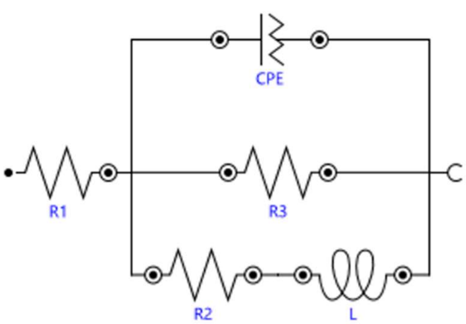

Figure 30 – An example of equivalent circuit where an inductive effect at low frequencies is present, as a semicircle in the second quadrant.

In order to get suitable starting values for the semicircle at low frequencies, the semicircle at positive $-Z''$ values has to be resolved first. This can be achieved with the Electrochemical circle fit command. The results are shown in Figure 31.

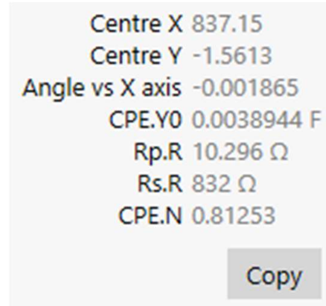

Figure 31 – The results of the Electrochemical circle fit, for the semicircle at positive $-Z''$ of Figure 29.

The electrochemical circle fit at positive $-Z''$ values gives suitable starting points for R1 (Rs.R); R3 (Rp.R); CPE.Y0 and CPE.N.

For the semicircle at low frequencies, so at negative values of $-Z''$, another Equivalent circle fit can be used. In this case, the resulting CPE has to be converted in an inductance value. This can be achieved first calculating the effective capacitance C_{eff}, with the aid of Equation 11. Then, the linear frequency point where the bottom of the semicircle occurs, $\nu_{min,L}$, is used to turn the effective capacitance into the desired inductance value, according to Equation 20.

$$L\ (H, \Omega \cdot s) = \frac{1}{\left(2\pi\nu_{min,L}\right)^2 C_{eff}} \qquad 20$$

The value of $\nu_{min,L}$, can be taken from the Bode phase plot and corresponds to the X-axis value where the minimum of $-Phase$ (°) versus linear frequency occurs, as shown in Figure 32.

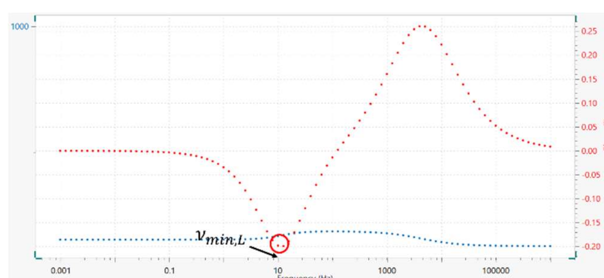

Figure 32 – The Bode plot corresponding to the Nyquist plot in Figure 29. The X-axis value where the minimum of the $-Phase$ (°) vs. linear frequency occurs is $\omega_{min,L}$.

In this example, $\nu_{min,L} \approx 10\ Hz$.

The results of the Electrochemical circle fit for the semicircle at low frequencies are shown in Figure 33.

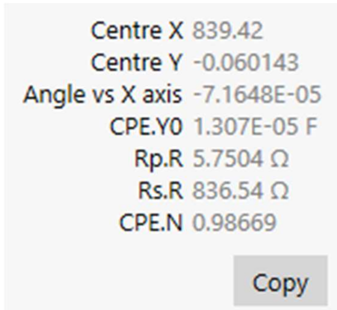

Figure 33 – Results of the Electrochemical circle fit for the semicircle at low frequencies.

From these values, the value of R2 is Rp.R, and the inductance is calculated, being $L\,(H) = 13.45$.

In Figure 34, the initial values of the fit, blue line, are superimposed at the data of Figure 29, blue dots.

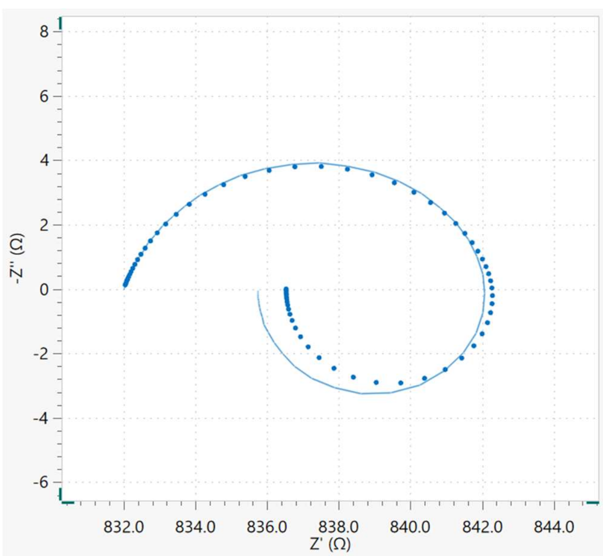

Figure 34 – Initial values of the fit done with the equivalent circuit of Figure 30, superimposed at the data of Figure 29.

In this case, the fit was performed first relaxing the parameters of the constant phase element and the inductance, then the values of the resistances.

Warburg – open circuit terminus, the T element

In the case of a thin film electrode able to exchange ions, the ions can diffuse in the vacancies of the crystals composing the electrode, resulting in a Warburg-like behavior in the Nyquist plot. However, the applied frequencies can be low enough for the charge carriers to reach the end of the electrode, where there is no room to diffuse anymore. This results in a capacitor-like behavior at low frequencies.

These two effects are combined in a Warburg – open circuit terminus element (T), whose impedance Z_T is given by

$$Z_T\,(\Omega) = \frac{1}{Y0\sqrt{j\omega}}\coth(B\sqrt{j\omega}) \tag{21}$$

Where $Y0\,(S \cdot \sqrt{s})$ contains information about the diffusion coefficient, and $B\,(\sqrt{s})$ is the square root of the diffusion time.

A simulation of Nyquist plot corresponding to a Randles circuit with a T element is shown in Figure 35.

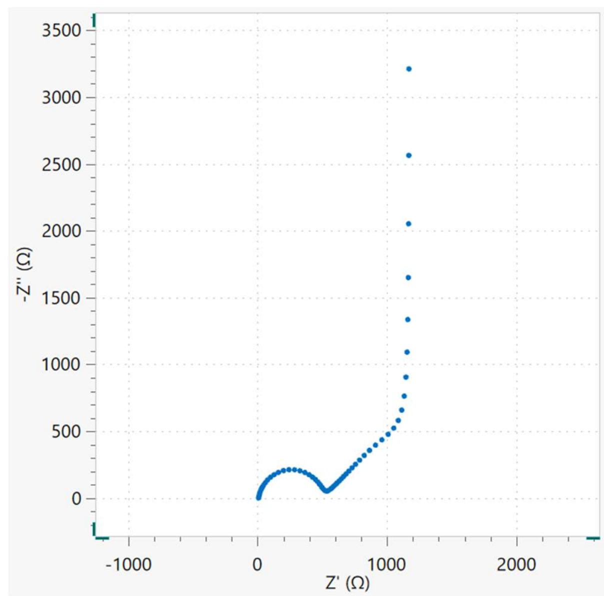

Figure 35 – The Nyquist plot of a Randles circuit with the T element.

In Figure 36, the Randles circuit with the T element.

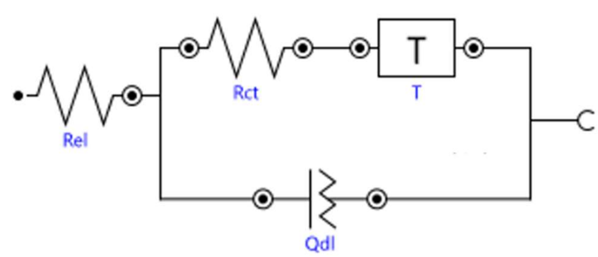

Figure 36 – The Randles circuit with the T element.

For the Warburg – open circuit terminus element, it is necessary to calculate the starting values of $Y0$ and B.

Regarding $Y0$, a regression line can be performed, restricted on the linear portion of the Nyquist plot, Figure 37.

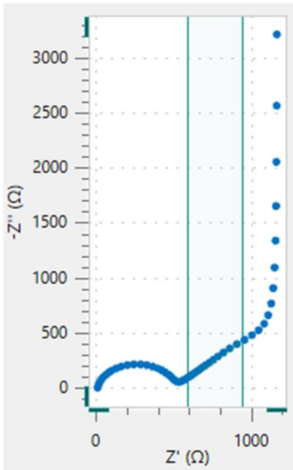

Figure 37 – The regression line on the portion of the Nyquist plot related to the Warburg diffusion (straight line).

Also in this case, the slope of the regression line $b \approx 1$. The fit results (Figure 38) and Equation 14 are used to calculate the $Y0$ value.

Function description	y = -485.21 + 0.9683x
Correlation coefficient	0.99982
a	-485.21
b	0.9683
1/Slope	1.0327

Figure 38 – Results of the linear regression of Figure 37.

In this example, $Y0 = 0.002\ S \cdot \sqrt{s}$.

Regarding the B parameter, a Windower command can be used to select the low-frequency data relative to the capacitance (Figure 39), and fit them with an [RC] circuit.

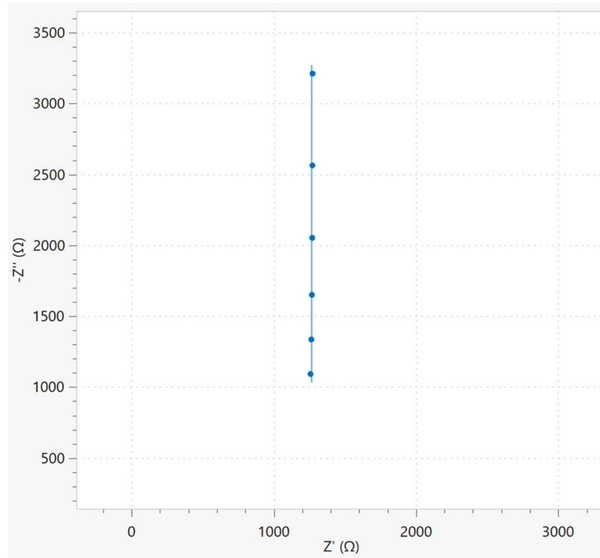

Figure 39 – The selection of the Nyquist plot of Figure 35 related to the capacitance (blue dots) and the fitted values (blue line).

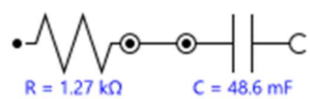

Figure 40 – The equivalent circuit used to fit the data in Figure 39.

Once the values of R and C are obtained, the B value can be calculated:

$$B\ (\sqrt{s}) = \sqrt{2\pi RC} \qquad 22$$

In this example, the R and C values from fitting the low-impedance data with the [RC] circuit give $R = 1.27\ k\Omega$ and $C = 48.6\ mF$, resulting in $B = 19.57\ \sqrt{s}$.

The example in Figure 35 was taken with $Y0 = 0.005\ S \cdot \sqrt{s}$ and $B = 10\ \sqrt{s}$. Therefore, the starting values are close to the data from the Nyquist plot.

Homogeneous chemical reaction - the Gerischer element G

In some circumstances, a homogenous chemical reaction can occur together with the electrochemical redox reactions.

In this case, the Gerischer element is used, limited to cases in which the chemical reaction is of the first order.

The impedance Z_G of a Gerischer element is given by

$$Z_G(\Omega) = \frac{1}{Y0\sqrt{K_a + j\omega}} \qquad 23$$

Where $Y0$ $(S \cdot \sqrt{s})$ is the parameter containing the information about the diffusion and K_a (s^{-1}) is the reaction rate of the first order chemical reaction.

A Randles circuit containing a Gerischer element is shown in Figure 41.

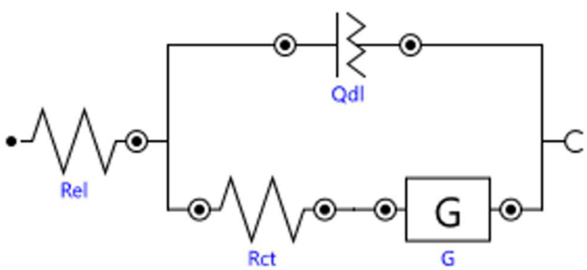

Figure 41 – The Randles circuit with the G element.

In the case of a Randles circuit containing a Gerischer element, a typical Nyquist plot is shown in Figure 42.

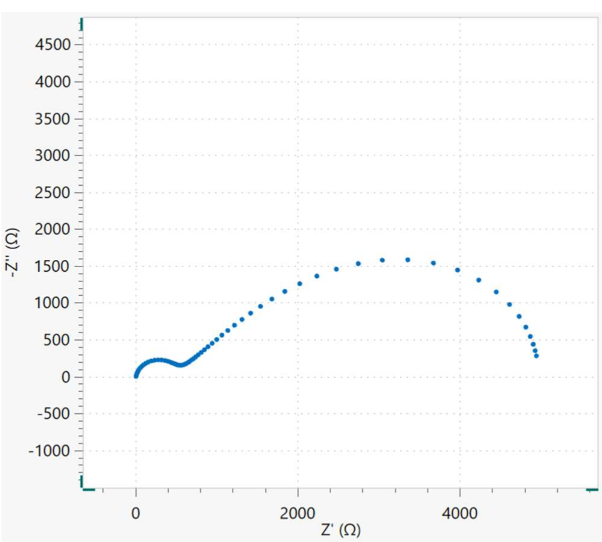

Figure 42 – The Nyquist plot of a Randles circuit with the G element.

Also in this case, it is needed to find the starting values of $Y0$ and K_a.

Regarding $Y0$, a regression line can be performed, restricted on the linear portion of the Nyquist plot, Figure 43.

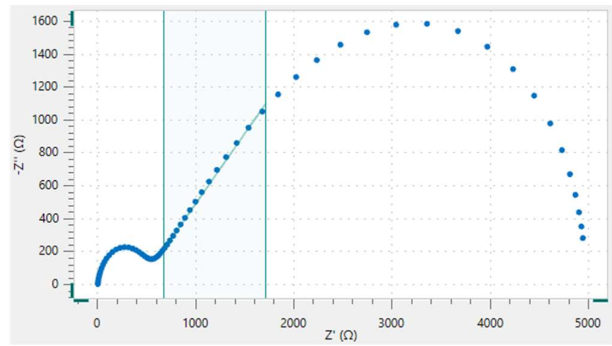

Figure 43 – The regression line on the portion of the Nyquist plot related to the Warburg diffusion (straight line).

Also in this case, the slope of the regression line $b \approx 1$. The fit results (Figure 44) and Equation 14 are used to calculate the $Y0$ value.

Function description	y = -362.96 + 0.85181x
Correlation coefficient	0.99927
a	-362.96
b	0.85181
1/Slope	1.174

Figure 44 – Results of the linear regression of Figure 43.

In this example, $Y0 = 0.0023\ S \cdot \sqrt{s}$.

Regarding the value of the rate constant K_a, it is possible to perform an electrochemical circle fit on the low-frequency part of the Nyquist plot which looks like a large quarter circle (Figure 45).

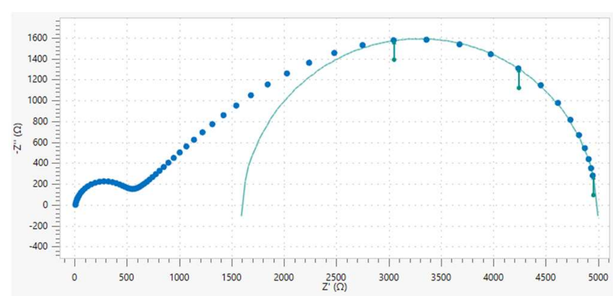

Figure 45 – The electrochemical circle fit applied to the low-frequency part of the Nyquist plot of Figure 42.

From the results of the electrochemical circle fit (Figure 46), the effective capacitance C_{eff} can be calculated (Equation 11).

Centre X	3297.2
Centre Y	-109.19
Angle vs X axis	-0.033103
CPE.Y0	0.0035184 F
Rp.R	3399.7 Ω
Rs.R	1597.3 Ω
CPE.N	0.95916

Figure 46 - The results of the electrochemical circle fit.

In this example, $C_{eff} = 0.003725\ F$.

Then, the K_a value can be calculated with Equation 24.

$$K_a(s^{-1}) = \frac{1}{2\pi R_p C_{eff}} \qquad 24$$

In this example, $K_a = 0.013\ s^{-1}$.

The simulation in Figure 42 was taken with a Gerischer element, whose parameters were $Y0 = 0.001\ S \cdot \sqrt{s}$ and $K_a = 0.05\ s^{-1}$. Therefore, the starting values are close to the data from the Nyquist plot.

Effective capacitance values from CPEs

As mentioned before, it is possible to calculate the effective capacitance C_{eff} with Equation 25, valid for a [Rs(RpCPE)] equivalent circuit,

$$C_{eff}\ (F) = Y0^{\frac{1}{N}} \cdot \left[\frac{1}{Rs} + \frac{1}{Rp}\right]^{\frac{N-1}{N}} \qquad 25$$

In the case of a CPE in series with a resistor, [RsCPE], the effective capacitance can be calculated with the following Equation:

$$C_{eff}\ (F) = Y0^{\frac{1}{N}} \cdot \left(\frac{1}{Rs}\right)^{\frac{N-1}{N}} \qquad 26$$

In the case of a CPE in parallel with a resistor, and this arrangement is not in series with another resistor, (RpCPE), then the effective capacitance can be calculated with the following Equation:

$$C_{eff}\ (F) = Y0 \cdot (\omega_{max})^{N-1} \qquad 27$$

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

Conclusions and final suggestions for EIS data fitting

The suggestions listed here are useful general tips on performing an accurate fit on EIS data, when the equivalent circuit is selected and the starting values of the electrical elements are found.

1. It is preferable not to fit the electrical elements all at once, but it is recommendable to fix the values of the elements that have already good starting values, like the resistors, and perform the fit.
2. Then, relax the previously-fixed elements and perform the fit again.
3. Often, it is advisable to leave the exponents of the CPE as last items to relax, since a small change of the exponent can change substantially the fit result.

The order described above works for most of the fit procedures.

In the case of recursive experiments, for example hydrodynamic EIS with higher rotation rate for subsequent repetitions, the fit results of the first EIS can be used as starting points to fit the following EIS measurements. This, of course, is valid if the same equivalent circuit can be adopted to model the data in all the repetitions.

In the case of complicated equivalent circuits, the Windower command can be used to select portions of the data, and fit such portions with suitable equivalent circuits in order to get starting values for the specific circuit elements. Then the entire data set can be fitted with the combination of the equivalent circuits previously employed.

Following these suggestions, the user can create an equivalent circuit model with accurate quantitative results even for very complicated systems.

References

The discussion about the Warburg – closed and open terminus is taken from the book A. Lasia – Electrochemical Impedance Spectroscopy and Its Applications, Springer, 2014.

The discussion about the effective capacitance of Equation 11, 26 and 27 is taken from the book M.E. Orazem and B. Tribollet – Electrochemical Impedance Spectroscopy, Wiley, 2008.

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**.