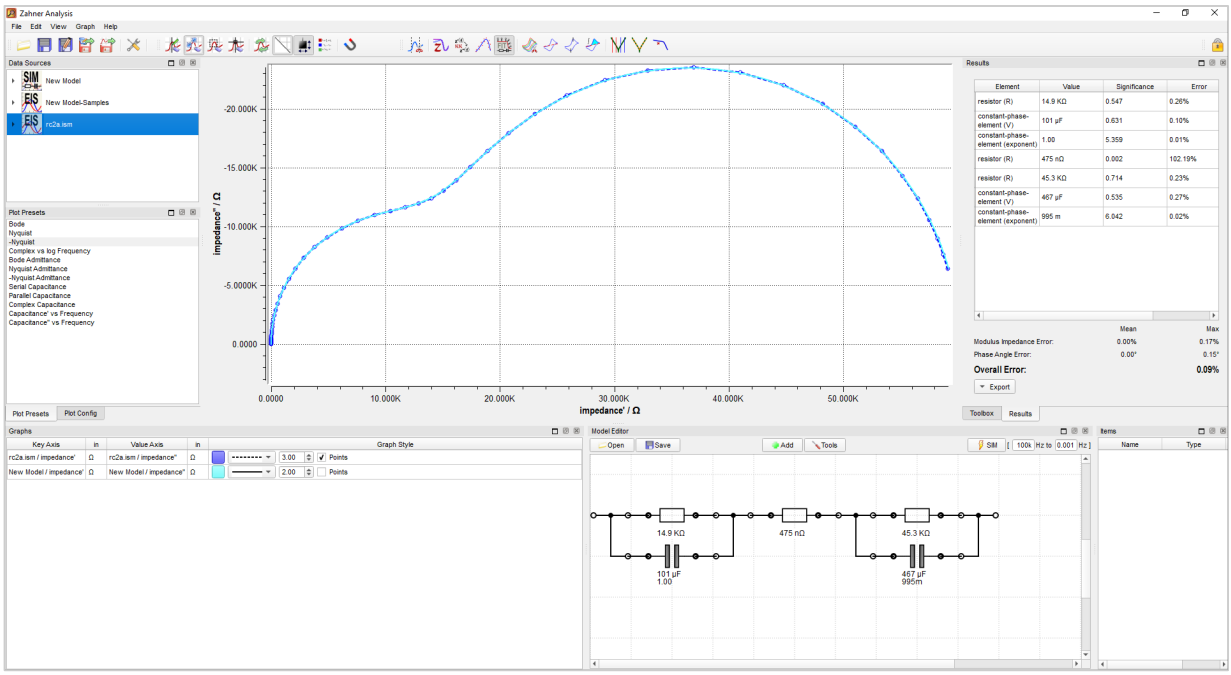
Zahner Analysis



ZAHNER

11/2023

Zahner Analysis software

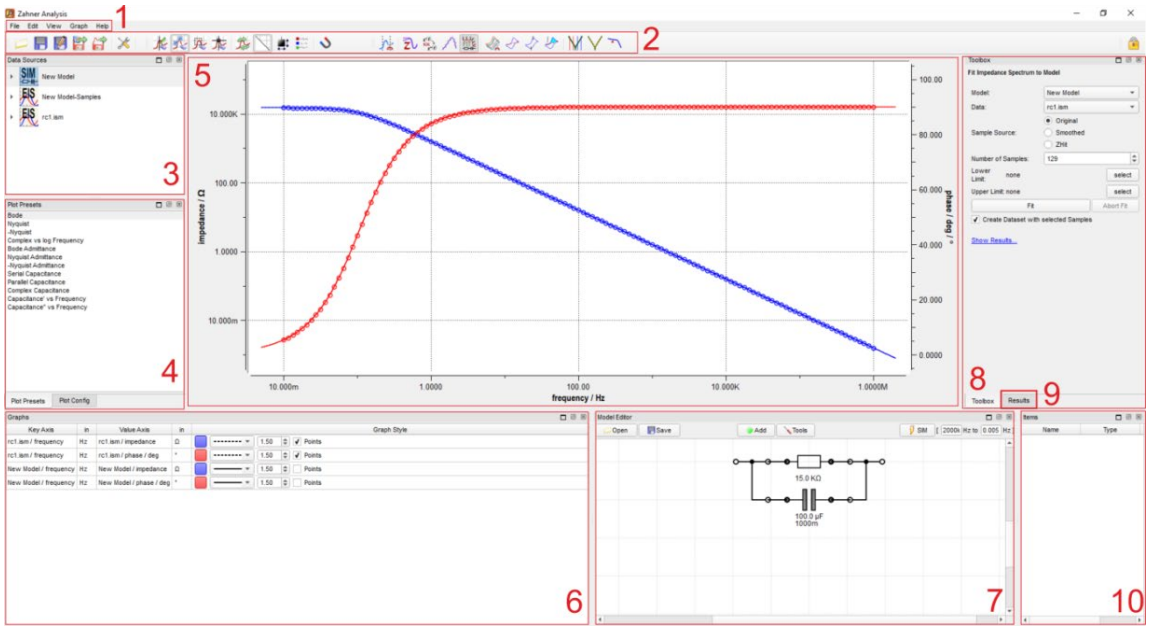
A manual evaluation of the electrochemical experimental results can be sometimes very tedious and complex, for example, fitting an impedance spectrum with an equivalent electrical circuit (EEC). In impedance spectroscopy, different graphical representations are used namely the Nyquist plot, Bode plot, and Cole-Cole plot. For a proper fitting, one has to choose such fitting parameters that the simulated curve fits the impedance spectrum in all the graphical representations. Unfortunately, different presentations may set the focus on different parts of the spectrum. Such complexities make the correct evaluation of electrochemical results very difficult. Therefore, Zahner has introduced the new Zahner Analysis software. This software provides users with a very simple platform to evaluate the results of different electrochemical measurements.

Zahner Analysis software can be used for the evaluation of the results of the following electrochemical methods

- Electrochemical impedance spectroscopy (EIS)
- Current potential curve
- Tafel slope evaluation (i.e. for the determination of corrosion rate)
- Maximum power and fill factor calculation (solar cell characterization)

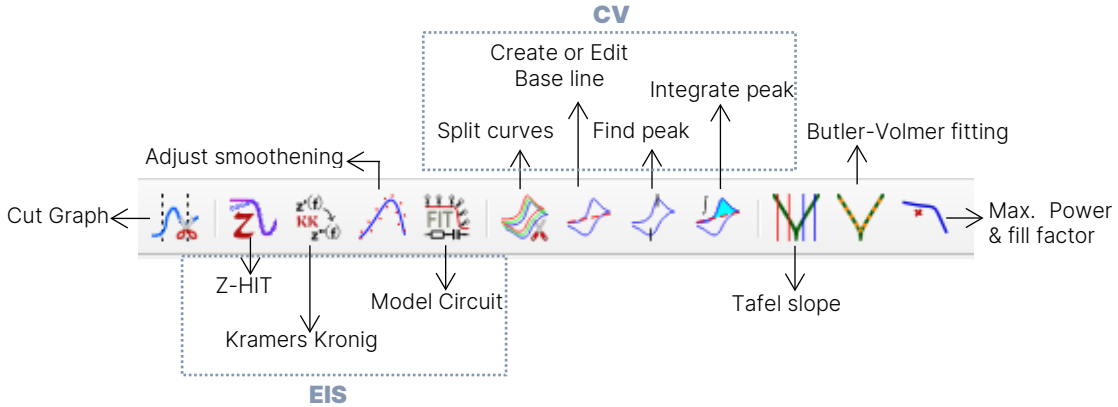
1 Overview

The main display window of the Zahner Analysis software consists of many different windows. These windows are listed below



1. Menu bar
2. Toolbar
3. Data Sources window (open files list)
4. Plot Presets (plot representations options)
5. Main graph area
6. Graphs (list of open graphs in Graph area)
7. Model circuit window – only visible after clicking the "*EIS Fit*" icon
8. Toolbox
9. Results
10. Items (cursors and/or label window)

The toolbar consists of many different icons that are designed for use in the evaluation of different electrochemical methods.



Following, a step-by-step guide is provided for the evaluation of different electrochemical measurement results. Along with the evaluation, different windows (used during evaluation) are also briefly explained.

2 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a widely used electrochemical method that provides insight into reaction kinetics. To get reliable results from EIS, it is very crucial to fit the impedance spectrum with an equivalent electrical circuit (EEC), which closely mimics the system under investigation. With the Zahner Analysis software, the user can create an EEC and fit the measured impedance spectrum with the simulation from the EEC. The software also provides information about the total error in the fitting and the significance of each electrical element used in the fitting.

2.1 EIS fitting

For fitting of an EIS spectrum, multiple steps are followed and are explained in detail below.

- **Open EIS spectrum**

For fitting of an EIS spectrum, first open a spectrum using **File → Open**. With this, the spectrum will be visible in the Graph area (***window 5***). The filename of the opened spectrum will be visible in ***window 3***. The list of the opened graph(s) is presented in ***window 6***. Here the color of the graph, its thickness, and its format can be modified.

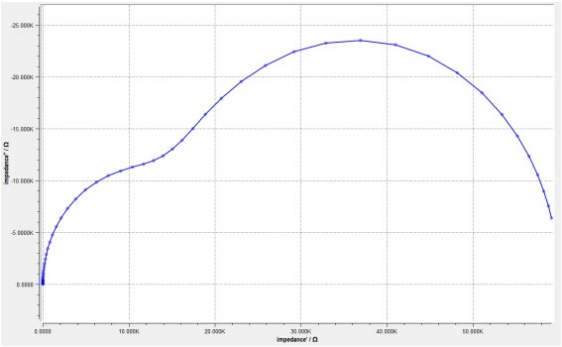
Choose desired graphical representation

For EIS, different graphical representations are possible. A suitable graphical representation can be chosen from ***window 4***. A list of the representations is provided below.

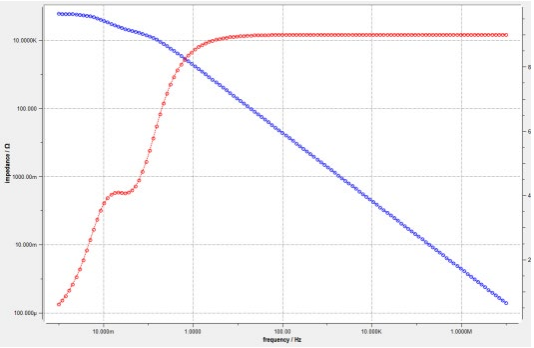
- Bode (*Y-axes*: |Z| and Phase, *X-axis*: Frequency)
- Nyquist (*Y-axis*: Z'', *X-axis*: Z')
- -Nyquist (*Y-axis*: - Z'', *X-axis*: Z')
- Complex vs Log Frequency (*Y-axes*: Z'' and Z', *X-axis*: Frequency)
- Bode Admittance (*Y-axes*: |Y| and Phase, *X-axis*: Frequency) → Y=1/Z
- Nyquist Admittance (*Y-axis*: Y'', *X-axis*: Y')
- -Nyquist Admittance (*Y-axis*: Y'', *X-axis*: - Y')
- Serial Capacitance (*Y-axes*: Resistance and Serial Capacitance, *X-axis*: Frequency)
- Parallel Capacitance (*Y-axes*: Resistance and Parallel Capacitance, *X-axis*: Frequency)
- Complex Capacitance (*Y-axis*: C'', *X-axis*: C')
- Capacitance′ vs Frequency (*Y-axis*: C', *X-axis*: Frequency)
- Capacitance″ vs Frequency (*Y-axis*: C'' *X-axis*: Frequency)

Here,

|Z| = Impedance modulus
Z' = Real part of impedance
Z'' = Imaginary part of impedance
Y' = Real admittance
Y'' = Imaginary admittance
C' = Real capacitance
C'' = Imaginary capacitance



EIS spectrum (Nyquist plot)



EIS spectrum (Bode plot)

Serial Capacitance: In serial capacitance, each impedance point is considered as the sum impedance of a resistor and a capacitor in series. Here,

$$Z = R + \frac{1}{iwC}$$

From the formula, the values of the resistance and serial capacitance are calculated.

Parallel Capacitance: In parallel capacitance, each impedance point is considered as the sum impedance of a resistor and a capacitor in parallel. Here,

$$\frac{1}{Z} = \frac{1}{R} + iwC$$

From the formula, the values of the resistance and parallel capacitance are calculated.

Complex Capacitance: In complex capacitance, real capacitance (C') and imaginary capacitance (C'') are defined as follows

$$\mathrm{C}' = \frac{\mathrm{Y}''}{2\pi f}$$

$$\mathrm{C}'' = -i\,\frac{\mathrm{Y}'}{2\pi f}$$

Here Y' and Y'' are real and imaginary admittance.

Derivation of complex capacitance:

$$\mathrm{Z} = \mathrm{Z}' + i\,\mathrm{Z}''$$

$$Y = Y' + i\,\mathrm{Y}''$$

As

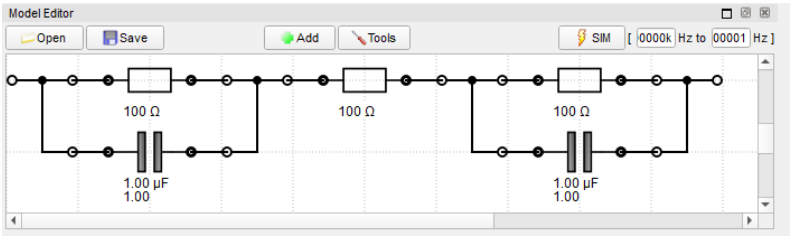
$$C = \frac{1}{iwZ} = \frac{\mathrm{Y}}{iw} = \frac{\mathrm{Y}' + i\mathrm{Y}''}{iw}$$

$$C' = \frac{\mathrm{Y}''}{w} = \frac{\mathrm{Y}''}{2\pi f} \quad , \quad C'' = -i\,\frac{Y'}{w} = -i\,\frac{Y'}{2\pi f}$$

Real and imaginary capacitances are frequency dependant capacitances and are used for characterizing the supercapacitors. Further information about the real and imaginary capacitances is provided in a research publication titled "Electrochemical Characteristics and Impedance Spectroscopy Studies of Carbon-Carbon Supercapacitors", J. Electrochem. Soc., 150 (3) A292-A300 (2003).

- Create an equivalent electrical model

When the desired graphical representation is chosen, then click on the "Model Circuit" icon ( ). This will open a new window where the EEC can be built.



For creating different electrical elements, click on "*Add*" and then choose the desired elements. Electrical elements can be connected by connecting the dots. For complex electrical circuits, sometimes the model may look messy. In such cases, the user may click on "*Tools → Auto Align*" to properly align the electrical elements in the model. Once a model circuit is created and the desired frequency range for simulation is provided, then click on SIM to generate the simulation file.

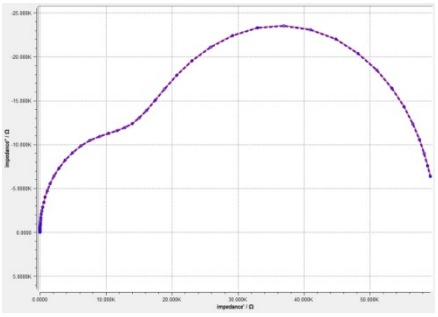
- Open the simulated model graph in the Graph window

After simulating, A "New Model" file is generated in the Data sources window (***window 3***). To open the file in the Graph window, either double-click on the file or "drag and drop" the file to the Graph window.

Note: In some graphical representations (i.e., the Nyquist plot), you may not be able to see your simulated graph, after opening it in the Graph window. This might be due to the small values assigned to the elements in the equivalent electrical circuit.

- Fit the simulated spectrum

For fitting the simulated spectrum to the measured EIS spectrum, click on the Toolbox (***window 8***). Here different fitting options i) *Original*, ii) *Smoothed,* and iii) *Z-HIT* are available. Choose the desired fitting option and then click "Fit". This will lead to the fitting of your simulated spectrum. The modified electrical element values will be visible on the "Model Circuit" and are also listed in the Results (***window 9***). Here *Value*, *Significance,* and *Error* of each electrical element are also provided. In addition, the "overall Error" of the simulated fitting is given too.



Fitted Nyquist plot

Element	Value	Significance	Error
resistor (R)	45.1 KΩ	0.713	0.11%
constant-phase-element (V)	483 µF	0.536	0.14%
constant-phase-element (exponent)	997 m	6.057	0.01%
resistor (R)	338 nΩ	0.002	99.82%
resistor (R)	14.9 KΩ	0.549	0.13%
constant-phase-element (V)	101 µF	0.633	0.04%
constant-phase-element (exponent)	1.00	5.370	0.01%

Results window

In the results window, the second resistance used in the modelling has a resistance of 338 nΩ and has a significance of 0.002. This indicates that the second resistance is not very significant in this fitting and can be removed. Removing this resistance will not affect the simulation. During EIS fitting, sometimes users are prone to use complex circuits for fitting. Here the "Significance" checks if all the electrical elements in EEC are necessary for fitting or not.

- Save the simulated spectrum

The simulated spectrum can be saved by **File → Save**, or by clicking on the save icon (). A text export is possible. For a text export, select the file in **Data Sources** you want to export and then click on **File → Text-Export** or **Text-Export Wizard**.

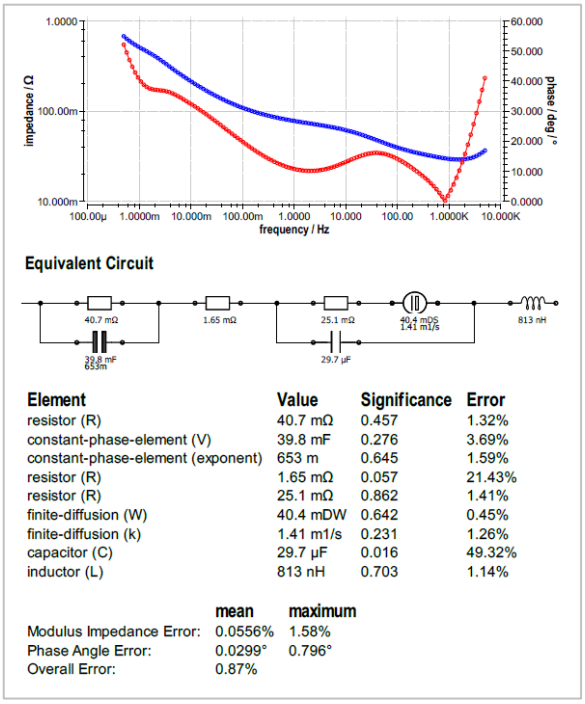
After selecting the "New Model" entry in the **Data Sources** window, one can save the fitting result by clicking on **File → Save** or **Save as**. The saved data file will be saved in Zahner .isfx file format.

Quick PDF export

In the "Result window" (*window 9*), an "Export" option is available. This allows a quick export of the results in a PDF file. A PDF export will contain the

- EIS spectrum with the fitted curve
- Equivalent electrical circuit
- Fitting parameter values with error and significance
- Additional fitting results

Such a quick export file is very useful for discussing the result (fitting/electrical circuit) with colleagues.



Element	Value	Significance	Error
resistor (R)	40.7 mΩ	0.457	1.32%
constant-phase-element (V)	39.8 mF	0.276	3.69%
constant-phase-element (exponent)	653 m	0.645	1.59%
resistor (R)	1.65 mΩ	0.057	21.43%
resistor (R)	25.1 mΩ	0.862	1.41%
finite-diffusion (W)	40.4 mDW	0.642	0.45%
finite-diffusion (k)	1.41 m1/s	0.231	1.26%
capacitor (C)	29.7 µF	0.016	49.32%
inductor (L)	813 nH	0.703	1.14%

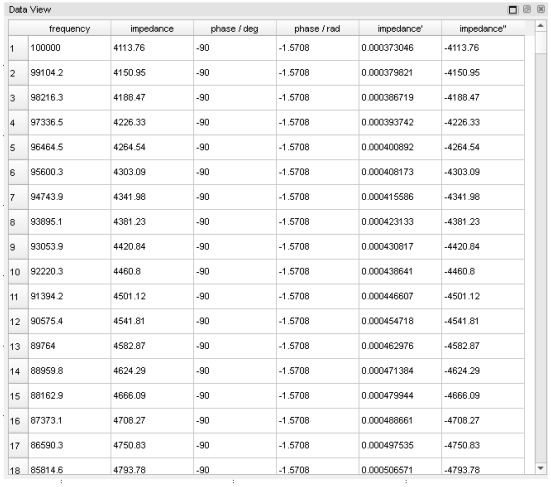
	mean	maximum
Modulus Impedance Error:	0.0556%	1.58%
Phase Angle Error:	0.0299°	0.796°
Overall Error:	0.87%	

2.1.1 Removing data points

After selecting the desired data file in the **Data Sources** window, the data table for the selected data file can also be viewed by right-clicking on the Toolbar and then enabling "*Data View*". Here, if needed, the user can remove one or more data points by

1. selecting one or more data lines by selecting the numbering on very left column

2. right-clicking with mouse and then selecting "Delete Selected Row(s)" from the drop-down menu.


Data View

	frequency	impedance	phase / deg	phase / rad	impedance'	impedance''
1	100000	4113.76	-90	-1.5708	0.000373046	-4113.76
2	99104.2	4150.95	-90	-1.5708	0.000379821	-4150.95
3	98216.3	4188.47	-90	-1.5708	0.000386719	-4188.47
4	97336.5	4226.33	-90	-1.5708	0.000393742	-4226.33
5	96464.5	4264.54	-90	-1.5708	0.000400892	-4264.54
6	95600.3	4303.09	-90	-1.5708	0.000408173	-4303.09
7	94743.9	4341.98	-90	-1.5708	0.000415586	-4341.98
8	93895.1	4381.23	-90	-1.5708	0.000423133	-4381.23
9	93053.9	4420.84	-90	-1.5708	0.000430817	-4420.84
10	92220.3	4460.8	-90	-1.5708	0.000438641	-4460.8
11	91394.2	4501.12	-90	-1.5708	0.000446607	-4501.12
12	90575.4	4541.81	-90	-1.5708	0.000454718	-4541.81
13	89764	4582.87	-90	-1.5708	0.000462976	-4582.87
14	88959.8	4624.29	-90	-1.5708	0.000471384	-4624.29
15	88162.9	4666.09	-90	-1.5708	0.000479944	-4666.09
16	87373.1	4708.27	-90	-1.5708	0.000488661	-4708.27
17	86590.3	4750.83	-90	-1.5708	0.000497535	-4750.83
18	85814.6	4793.78	-90	-1.5708	0.000506571	-4793.78

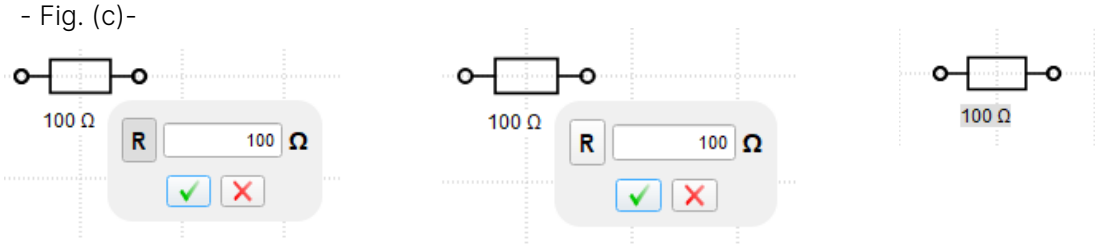
2.1.2 Start values for EIS fitting

With the fitting command, Zahner Analysis software tries to minimize the deviation between the model's transfer function (simulated data) and the measured data set. In this effort, the software can get trapped in a local minimum at some unsuitable values for the elements in the electrical circuit. Hence it is always a good practice to assign the electrical elements some starting values in the software so that the software can start fitting in the right direction. With complex electrical circuits, it is very difficult to properly fit the measured spectrum without providing suitable initial values. For example, when fitting an electrical circuit for a battery it is always a good idea to assign the resistances a value in the milli-ohm (mΩ) range and then start the fitting. As in batteries, the resistances are always very small. The user does not have to provide a specific value but assigning a random value in the correct range will suffice for the software.

In the case of complex electrical circuits, if the software does not fit the measured spectrum correctly even after assigning suitable initial values for the electrical elements, the values of a few elements can be fixed in a suited values range. After fixing the values for one/few electrical element(s), the software will not modify the fixed value(s) during the fitting of the impedance spectrum. Fitting after fixing the start values of the few elements in the electrical circuit will force the software to try to fit the spectrum only using the elements which are not fixed and this way the software will work in minimizing the difference between the model's transfer function and the measured data. Once the values of all the electrical elements are in the correct range and the software shows appropriate fitting then the fixed values can be unfixed. A fitting operation afterwards will optimize the fitting results and a good fitting will be achieved.

For fixing the value of an electrical element

1. Double-click on the electrical element, this will open the new small input window. - Fig. (a)-
2. Click on the element icon, turning the color of the R (resistance) icon to light grey. - Fig. (b)-
3. Click OK (green good mark ✓).
4. A grey shade appears on the value of the electrical element, indicating that the value is fixed. - Fig. (c)-

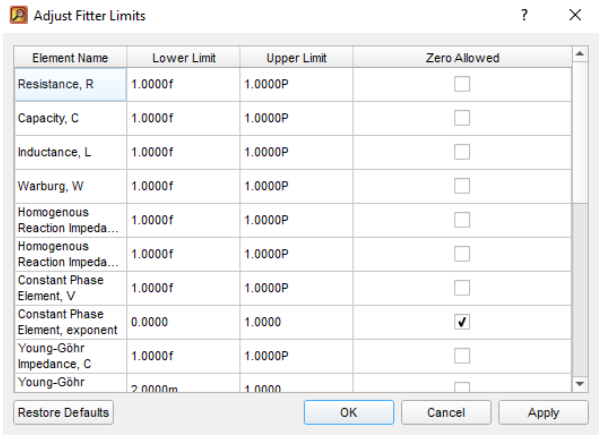


a) b) c)

For unfixing the value of the electrical element, click on the element logo again to change the color from light grey (Fig. b) to dark grey (Fig. a). This will remove the grey shade on the value of the element.

In the Zahner Analysis software, the global value range(s) can be set to the suitable value range so that the software never leaves the defined value range during fitting.

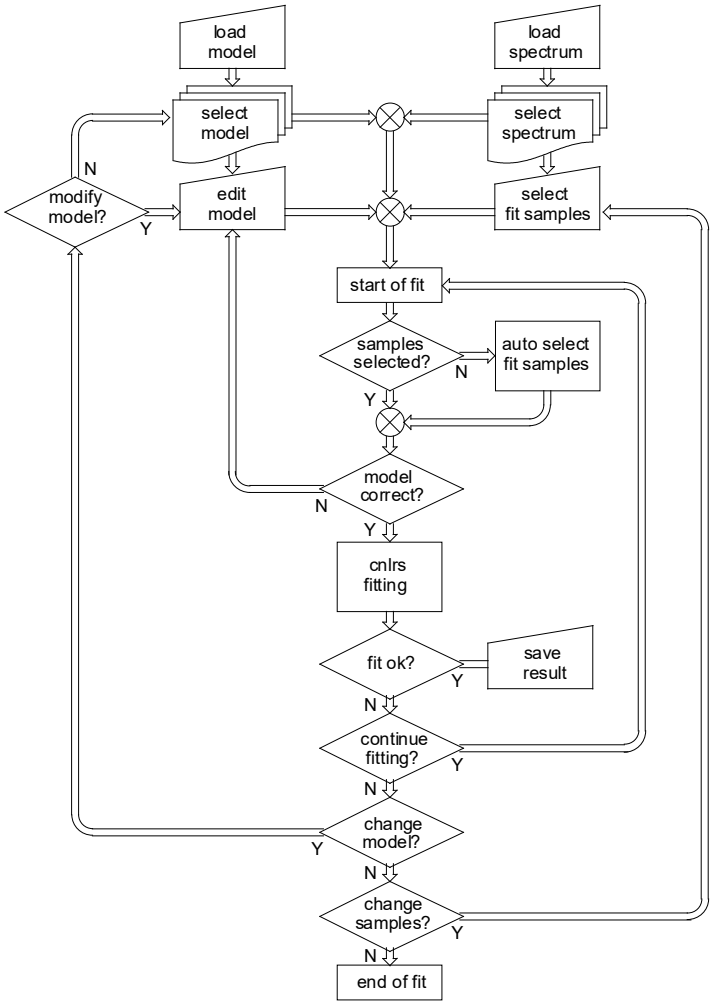
The "Adjust Fitter Limits" window can be accessed from *Edit → Settings → Evolution Methods → Adjust fitter Limits*.



2.2 How Fitter Works?

An equivalent electrical circuit can be built in the "Model Editor" window. The editor window can be opened via clicking on the "Model Editor" icon,  . In this window, new element(s) can be added by clicking on the "Add" button. Alternatively, elements can also be added using the right-click mouse menu in the "Model Editor" window. Different elements can be connected via joining the connector dots using the mouse. Once an electrical circuit is built, the user can use the "Auto Align" function to align all the elements and present the electrical circuit in an orderly representation. "Auto Align" is available in **Tools>Auto Align**. The "Auto Align" option is also available in the right-click mouse menu in the "Model Editor" window.

Once an electrical circuit is built and an appropriate frequency range is provided, using the **Fit** command, the software starts fitting the impedance spectrum according to the transfer function resulting from the equivalent electrical circuit. For the fitting, Zahner Analysis software follows a strict fitting path which is provided in the form of a flow chart.



Flow diagram exhibiting the Fitting process used by the Zahner Analysis software

Our Zahner Analysis software uses the CNRLS (complex non-linear regression least-squares fitting) algorithm in a very accurate and stable way. The algorithm is adapted to the individual parameter behavior of the impedance elements to optimize the parameters of a model, minimizing the deviation between the model's transfer function (modelled impedance spectrum) and the measured data set (measured impedance spectrum).

A logarithmic weighting function *wgt* is introduced to calculate the complex deviation between the modelled and the experimental transfer function at a particular frequency ω. The total error *E* is calculated from the least-squares sum of the differences between the *N* measured $Z_{\exp}(\omega_n)$ and the modelled data samples $Z_{theo}(\omega_n)$ at the frequencies ω_n. It is minimized during the fitting progress.

$$E = \frac{\sqrt{\sum_{n=1}^{N} wgt\left[c \log \frac{Z_{theo}(\omega_n)}{Z_{\exp}(\omega_n)}\right]}}{N}$$

n=1,2,...,N selected samples

$$wgt(real, imag) = \frac{real^2}{weight} + imag^2 \cdot weight$$

$$Z_{theo} = f(\omega, P_1, P_2, P_3, ..., P_{k-1}, P_k)$$

The default setting for *weight* in the Zahner Analysis software is 2.2222 (*weight* = $2.222\overline{2}$). An increasing value of *weight* will increase the weight of the phase angle for fitting. *clog* denotes the complex logarithm and P_i the *i*-th parameter of the transfer function which involves *k* parameters in total. The application of the *clog* operator results in the logarithmic modulus as the real part and the phase angle as the imaginary part. Compared to linear weighting, a logarithmic weighting function is advantageous due to the high dynamic range expected for the parameter values. The logarithmic scaling guarantees an equal weight of small and large parameter values as well.

Fitting is finished as soon as one of the following two conditions is fulfilled:

- an absolute error *E* smaller than 0.1% (*E*<0.001) is reached
- the relative improvement *krit* of the last iteration does not exceed $krit_{min} = 10^{-7}$.

Please note: The values of "*weight*" as well as the value of "$krit_{min}$" can be modified in Zahner Analysis software using the following:

Edit → Settings → Evolution Methods → Phase Weighting (for *weight*)
Edit → Settings → Evolution Methods → Minimal Fitting Success (for "$krit_{min}$")

2.2.1 Fitting Error

The fitting error is given in percent. A value of 100% corresponds to a factor of about 2 for the fitted parameter in a single time constant model. The fitting error should not be used to estimate parameter uncertainties because the exact value differs strongly for different impedance element parameters and different models. Instead, the fitting error should be used to estimate the quality of a fit. Fits with a final error of <3% may be taken as a good result. If the final error exceeds 10%, the model should be reconsidered.

2.2.2 Significance

The significance *S* is a measure of the 'importance' of an impedance element within a model and reflects its influence on the network impedance. It is calculated from the relative impedance modulus variation $\frac{d|Z|}{|Z|}$ caused by the relative variation of a parameter $\frac{dP}{P}$ at the frequency ω_n. The significance of the parameter is obtained from the maximum value of all samples, thus the frequency, where this parameter has the highest influence on the impedance course.

$$S_i = \max\left(\frac{d|Z_n| \cdot P_i}{dP_i \cdot |Z_n|}\right)$$

i = number of parameter
n = index of experimental data sample

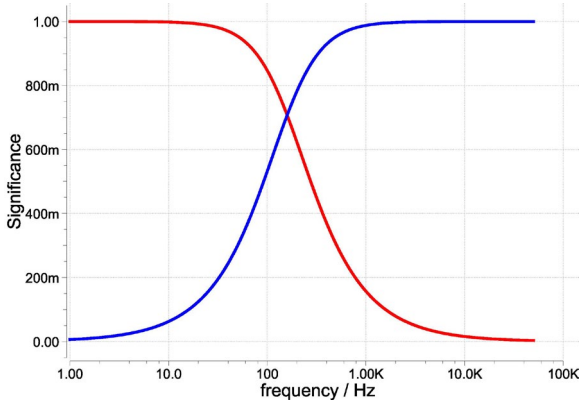
For impedance elements with a linear influence on the impedance, for instance, resistors, *S* reaches a value of one, if the element is most important within the model. This means, that there is a part within the examined frequency range, where this parameter dominates the impedance. Significance values much less than 0.01 usually indicate that the corresponding impedance element may be omitted.

Due to the non-linear influence of some parameters on the impedance, like for instance the exponent of a CPE, the significance may exceed the value 1 clearly in some cases.

Significance plot:

The diagram on the right side is called the significance plot. This shows the significance (relevance) of each element of the EEC as a function of frequency. In the diagram, a significance plot of a simple EEC with a parallel resistor and a capacitor is shown.

The significance plot can be obtained by right-clicking on the New Model file in the "Data Sources" window and then clicking on the *Significance plot*.

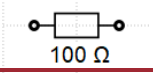


2.3 Impedance electrical elements

In Zahner Analysis software, different electrical elements can be used to construct an equivalent electrical circuit (EEC), which can mimic the physical behaviour of the system under investigation. A complete list of electrical elements is provided below

1. Resistor
2. Capacitor
3. Inductor
4. Warburg impedance
5. Nernst diffusion
6. Finite diffusion
7. Homogeneous reaction impedance
8. Constant phase element
9. Young-Göhr impedance
10. Spherical diffusion
11. Surface relaxation impedance
12. User element
13. Porous electrode

2.3.1 Resistor



The impedance of a resistor (Z_o) is independent of the frequency. It shows a Phase angle of 0 and can be described with the equation shown below

$$Z_O = R\,(\Omega)$$

This resistor can be assigned to the different parts of a system under investigation (SUI), i.e.,

- electrolyte resistance
- ohmic conductors resistance
- charge transfer resistance
- general resistance behaviour due to the hindrance of the activated processes

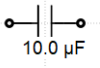
The impedance of a homogeneous conductor, e.g. the electrolytic resistance

$$R_\Omega = \frac{d}{A \cdot \sigma}$$ with d : bulk thickness, A : cross-section, σ : specific admittance

Charge transfer resistance of faradaic impedance

$$R_\eta = \frac{R \cdot T}{|z| \cdot F \cdot I^*}$$ with $I^* = \alpha \cdot I_+ - (1-\alpha) \cdot I_-$, Equilibrium: $I^* = I_0$

2.3.2 Capacitor



The capacitor (C) has a phase angle of -90° and a unit of Farad (*F*). The impedance of a capacitor (Z_C) can be explained with the equation below

$$Z_C = \frac{1}{j \cdot \omega \cdot C}$$

The impedance of the capacitor can be assigned to a different phenomenon

- dielectric surface layer
- double layer
- adsorption impedance
- crystallization impedance
- general "pseudo"-capacitive behavior assigned to concentration-dependent potential ("Nerstian capacitance").
- An electrostatic capacity, e.g. plate capacitor, double-layer capacitance can be explained via

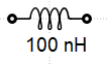
$$C = \frac{\varepsilon \cdot \varepsilon_0 \cdot A}{d}$$ with ε : permittivity, A : cross-section, d : plate distance.

Pseudo-capacitance, e.g. at adsorption

$$C_{ad} = \frac{z^2 \cdot F^2 \cdot \Gamma \cdot \Theta}{RT}$$

with Θ = mean surface concentration parameter, Γ = surface access parameter

2.3.3 Inductor



An inductor has the same features as a coil in electronics. The higher the frequency, the higher will be the impedance. Opposite to a capacitor, an inductor has a phase angle of +90°. Inductance (*L*) is measured with the unit Henry (*H*) and then the impedance of an inductor (Z_L) can be written with the equation below

$$Z_L = j \cdot \omega \cdot L$$

An inductance can be observed in the following

- wire, cable
- electronic coil
- "Pseudo"-inductive electrochemical processes, often assigned to relaxation effects, which affect the conductivity. For the latter, refer also to the "Surface relaxation impedance".

The inductance of a piece of wire

$$L \approx \frac{\mu_0 \cdot l \cdot l_0}{r}$$ with μ : permeability, l : length, r : radius of wire, $l_0 \approx 10^{-3} m$

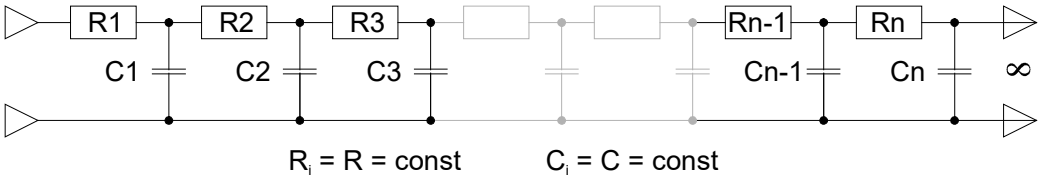
The inductance of a coil

$$L = \frac{\mu_0 \cdot \mu \cdot n^2 \cdot a}{l}$$ with n: number of turns, a: cross-section, l: length of coil

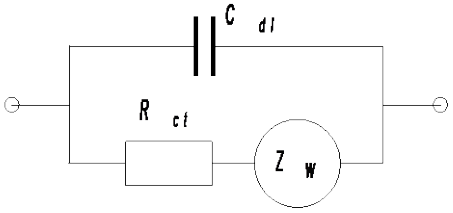
2.3.4 Warburg impedance

A Warburg impedance accounts for the impedance of a Warburg process -diffusion process (as a part of a charge transfer process)-. In Warburg impedance, one dimensional, infinite diffusion length is assumed. Warburg (W) has a unit of $\Omega s^{-1/2}$ and can be simulated with an indefinite number of R||C circuits. Warburg impedance (Z_W) is explained with the equation below

$$Z_W = \frac{W}{\sqrt{j \cdot \omega}} = \frac{W}{\sqrt{2 \cdot \omega}} \cdot (1 - j)$$



If the diffusion overvoltage dominates the overall process then the equation provided above is valid. Otherwise, the kinetic parameters of the other contributing steps may appear in the expression for Z_W. Frequently a significant charge transfer overvoltage is present. For a "Randles equivalent circuit" with the charge transfer resistance R_{ct} and the double layer capacity C_{dl}, Warburg impedance is



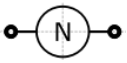
$$Z_W = \frac{W}{\sqrt{j \cdot \omega}} = \frac{W}{\sqrt{2 \cdot \omega}} \cdot (1 - j) \qquad \text{with } W = \frac{|\nu_k| \cdot p_k \cdot R \cdot T \cdot a}{z^2 \cdot F^2 \cdot c_k \cdot \sqrt{D_k} \cdot A}$$

Here p_k = reaction order, c_k = concentration at x, ν_k = stoichiometric number, D_k = Constant of diffusion, A =surface area of electrode, k = index of substance and a = coupling factor, built from partical currents, transfer coefficients.

Warburg is

- used for general diffusion-affected charge transfer reactions
- used for limiting case frequency behavior for all diffusion contributions at high frequencies
- a good approximation also for low-frequency diffusion behavior, when the maximum diffusion length given by the vessel dimensions is big compared to the range of the diffusion within a period of the test frequency.

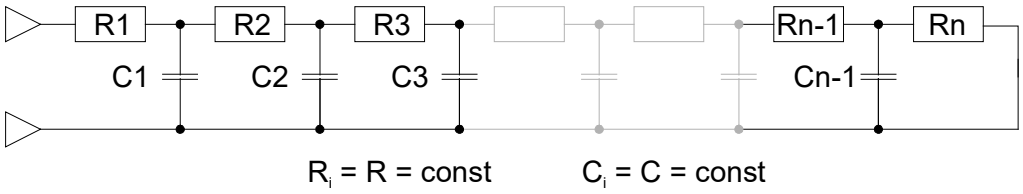
2.3.5 Nernst Impedance



The Nernst element (*N*) is used if the diffusion process is one-dimensional with finite diffusion length (limited by constant concentration). The Nernst impedance can be explained with the equation

$$Z_N = \frac{W}{\sqrt{j \cdot \omega}} \cdot \tanh \sqrt{\frac{j \cdot \omega}{k_N}}$$

The first input parameter *W* is provided as $\Omega \cdot s^{-1/2}$ like for the Warburg impedance. The second parameter (*k*) characterizes the relative reach of the diffusion compared to the finite length and is put in as 1/s. Similar to Warburg, Nernst can also be simulated with parallel R-C circuits connected in series, however here the R-C circuits are finite (contrary to Warburg).



The upper expression is valid if the diffusion overvoltage dominates the overall process. Otherwise, the kinetic parameters of the other contributing steps may appear in the expression for Z_N. Frequently a significant charge transfer overvoltage is present. This case corresponds to the "Randles equivalent circuit" (previous page) with the charge transfer resistance R_{ct} and the double layer capacity C_{dl}. We then find:

$$Z_N = \frac{W}{\sqrt{j \cdot \omega}} \cdot \tanh \sqrt{\frac{j \cdot \omega}{k_N}} \qquad \text{with } [W] = \frac{\Omega}{\sqrt{s}} \text{ and } k_N = \frac{D_K}{d_N^2}$$

d_N = thickness of layer, D_k = constant of diffusion

The Nernst impedance can be easily calculated at the boundary condition ($\omega \rightarrow 0$). As

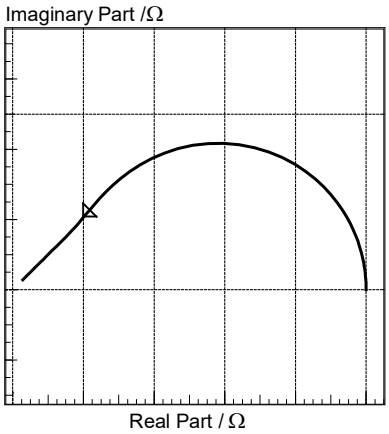
$$\lim_{x \to 0}(\tanh(x)) = x$$

so at $\omega \rightarrow 0$

$$Z_N = \frac{W}{\sqrt{k_N}}$$

At the boundary condition ($\omega \rightarrow 0$), the Nernst impedance behaves like a resistor.

The impedance spectrum of a Nernst element is provided in the image (on right). In such a system, diffusion length is finite due to a concentration assumed as constant at a certain distance from the electrode. The high-frequency part (left part in front of the arrow symbol) of the Nyquist diagram exhibits the same shape as the Warburg Impedance diagram. The low-frequency part (the right part behind the arrow symbol) is similar to an RC-element Nyquist diagram (semicircle). (The negative imaginary part is plotted upwards in the graph).



Nernst is a good approximation for the frequency behavior of the diffusion, when the free diffusion length limited for

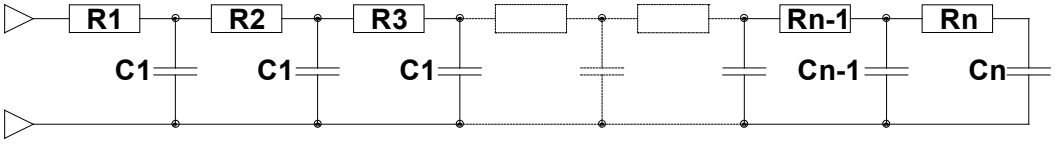
instance by convection is comparable to the range of the diffusion within a period of the test frequency (also as an approximation for a rotating disk electrode).

2.3.6 Finite diffusion

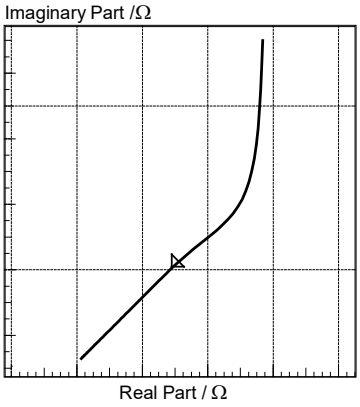
Finite diffusion (FD) is used if the diffusion process is one-dimensional with finite diffusion length limited by blocking. The impedance of the FD is explained with

$$Z_S = \frac{W}{\sqrt{j \cdot \omega}} \cdot \coth \sqrt{\frac{j \cdot \omega}{k_S}}$$

The first input parameter *W* is provided as $\Omega \cdot s^{-1/2}$ like for the Warburg impedance. The second parameter (*k*) characterizes the relative reach of the diffusion compared to the finite length and is put in as 1/s.



The upper expression is valid if the diffusion overvoltage dominates the overall process. Otherwise, the kinetic parameters of the other contributing steps may appear in the expression for Z_S. Frequently a significant charge transfer overvoltage is present. This case corresponds to the "Randles equivalent circuit" (previous page) with the charge transfer resistance R_{ct} and the double layer capacity C_{dl}. We then find:



$$Z_S = \frac{W}{\sqrt{j \cdot \omega}} \coth \sqrt{\frac{j \cdot \omega}{k_S}}$$

$$W = \frac{V}{z \cdot F \cdot \sqrt{D} \cdot A} \cdot \frac{dE}{dy}, \quad [W] = \frac{\Omega}{\sqrt{s}}, \quad k_S = \frac{D_K}{d_S^2} \qquad [k_S] = s^{-1}$$

d = thickness of layer, *D* = constant of diffusion, *A* = electrode surface, *V* = molar volume of bulk electrolyte, $\frac{dE}{dy}$ = Nernst slope

Diffusion length is finite due to a phase boundary assumed at a certain distance from the electrode. The high-frequency part (left part in front of the arrow symbol) of the Nyquist diagram exhibits the same shape as the Warburg impedance diagram. The low-frequency part (the right part behind the arrow symbol) is similar to a capacity.

Finite diffusion is a good approximation for the frequency behavior of the diffusion when the free diffusion length is blocked by a phase boundary (e.g. the vessel dimensions). This length is comparable to the range of diffusion within a period of the test frequency.

The Finite diffusion impedance can be easily calculated at the boundary condition ($\omega \rightarrow 0$). As

$$\lim_{x\to 0}(\coth(x)) = \frac{1}{x}$$

so at ω → 0

$$Z_S = W \cdot \sqrt{k_S} \cdot \frac{1}{j \cdot \omega}$$

At the boundary condition (ω → 0), the Finite diffusion impedance behaves like a capacitor.

2.3.7 Homogeneous reaction impedance

Homogenous reaction impedance (Z_H) is an impedance contribution to a diffusion process (a charge transfer reaction coupled with a first-order chemical reaction). It is also known as "Gerisher impedance". The boundary conditions assume a one-dimensional diffusion expanding from or into the volume. Homogeneous reaction impedance is calculated with the formula below

$$Z_H = \frac{W^*}{\sqrt{k + j \cdot \omega}}$$

The first input parameter *W** is provided as $\Omega \cdot s^{-1/2}$ like for the Warburg impedance. The second parameter (*k*) characterizes the relative reach of the diffusion compared to the finite length and is put in as 1/s.

$$W^* = \frac{|\nu_1| \cdot p_1 \cdot R \cdot T \cdot a \cdot q}{z^2 \cdot F^2 \cdot c_1 \cdot \sqrt{D_1} \cdot A \cdot (1+q)}$$ with $a = \frac{partial\ current \quad I_k}{exchange\ current \quad I^*}$, A: surface of electrode

$$k = \frac{j_0 \cdot p \cdot \nu}{c} \cdot (1-q)$$ with j_0: rate of homogeneous reaction $(\nu_1 s_1 + \ldots \rightarrow \nu s)$

$$q = \frac{p_1 \cdot \nu_1}{p \cdot \nu} \cdot \frac{c}{c_1}$$

2.3.8 Constant phase element

A constant phase element (CPE) is an element similar to the capacitor, but with an absolute phase angle of less than -90°. The CPE is extended through a normalization factor ω/ω_0, to enable the use of the parameter V with the dimension 'Farad'. Further information about normalization is provided here. The parameter "V" is put in as F (Farad), and the exponent α is dimensionless. α usually has a value of <1. The limit value of α=1 leads to the perfect capacitive behavior.

$$Z_{CPE} = \frac{1}{\omega_0 \cdot V} \cdot \left(\frac{j\omega}{\omega_0}\right)^{-\alpha}$$ with ω_0 = normalization factor

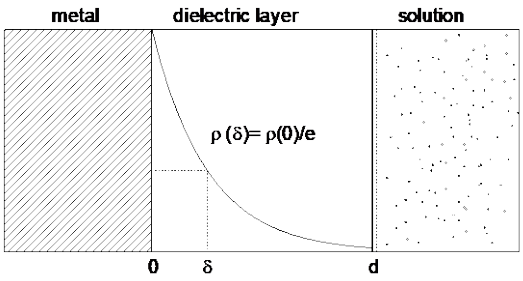
$$V \cong C \cdot \frac{\delta}{d} \qquad [V] = 1F$$ with C: layer capacity,

Physical interpretation of α

gradient of conductivity

$$\alpha = 1 - \frac{\delta}{d}$$

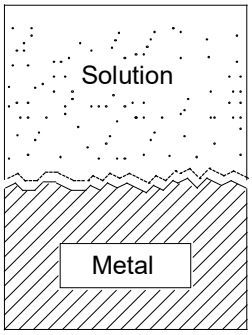
$\frac{\delta}{d}$ = relative penetration depth



fractal porous electrode

$$\alpha = \frac{1}{d_F - 1}$$

d_F = fractal dimension of porous surface



In practical measurement: Deviations from the behavior of an ideal capacitor

C - Ideal capacitor

$$Z_C = \frac{1}{C} \cdot \frac{1}{j \cdot \omega}$$

$$\log Z = \log \frac{1}{C} - \log \omega$$

slope of logZ vs. logω= -1

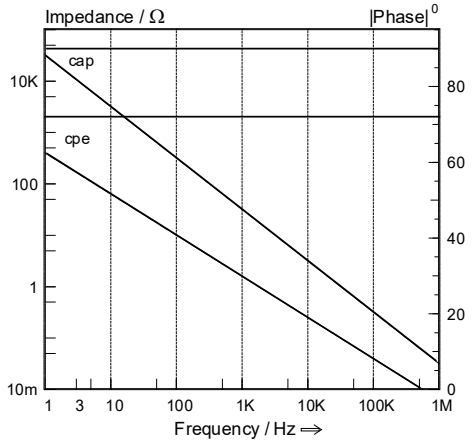
phase shift = -90°

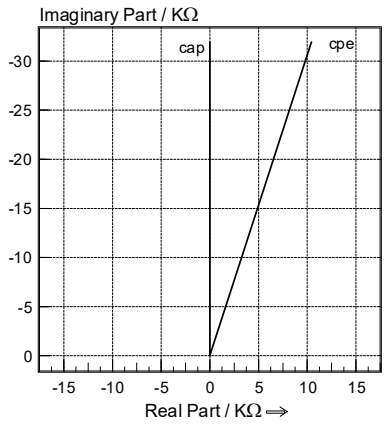
C: at logω=0

CPE - Loss Capacitance

$$Z_{CPE} = \frac{1}{Y_0} \cdot (j \cdot \omega)^{-\alpha}$$

or $$Z_{CPE} = \frac{1}{\omega_0 \cdot V} \cdot \left(\frac{j \cdot \omega}{\omega_0} \right)^{-\alpha}$$





The constant phase element is usually used for the capacitive behavior together with Ohmic contributions in distributed systems, such as porous electrodes. Due to its near omnipresence, the use of CPEs should be considered carefully. CPE character is an approximate behavior also for better-characterized systems. If the origin of the CPE is known, it should be substituted by a more accurate model, like a *Porous Electrode* or the *Young-Göhr* element.

In Zahner Analysis's **Menu bar → Tools**, 2 different tools are provided to determine the equivalent capacitance. The user is free to choose any tool to calculate the equivalent capacitance for his/her CPE.

CPE true capacitance calculator:

In this tool, the formula from Hsu and Mensfeld (C.H. Hsu, F. Mansfeld; Corrosion 57/ No. 9 (2001) 747-748) is used to calculate equivalent capacitance at the frequency of maximum imaginary impedance.

CPE normalization calculator:

In this tool, the normalization is carried out at a single frequency. The normalization is explained in the application note.

2.3.9 Young-Göhr impedance

Young-Göhr electrical element is used to describe a passive layer with conductivity penetrating from one side and decaying exponentially (by H. Göhr). Such conditions can be observed in "oxide layers on metal electrodes like Fe, Al, Ti, and Ta, etc.," and "organic coatings under soaking". It may substitute the CPE in several cases as a physical consistent model. Young-Göhr impedance is expressed with the formula below

$$Z_Y = \frac{p}{j \cdot \omega \cdot C} \cdot \ln \frac{1 + j \cdot \omega \cdot \tau \cdot e^{\frac{1}{p}}}{1 + j \cdot \omega \cdot \tau}$$

To avoid an excess of equivocal parameters, the three characteristic parameters are normalized:

p is dimensionless as the *relative* penetration depth of the conductivity within the dielectric.

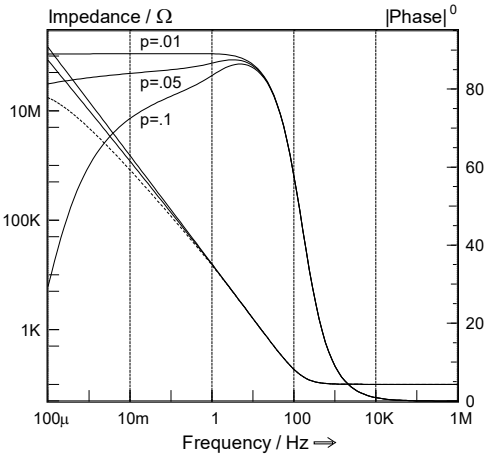
τ is the time constant of the virtual RC element built from a slice of the dielectric with its capacity and resistance at the site of the highest conductivity. The dimension is *s*.

C is the total capacity of the layer neglecting the conductivity. It can be observed as the high-frequency limit capacity and is put in as Farad.

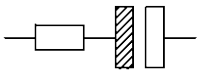
Here

$C_Y = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{A}{d}$	Capacity of the layer with cross-section A and thickness d
$\tau = \varepsilon_0 \cdot \varepsilon_r \cdot \rho_{x=0}$	Time constant τ with dielectric constant ε and specific resistance ρ At x=0 the highest conductivity will be observed
$\rho_Y = \frac{\delta}{d}$	Quotient of penetration depth δ of conductivity and thickness d

In the figure on the right, a Bode-plot is simulated for a Young-Göhr element with different penetration depths (*p*)



Simulated model:



With, τ = 100ms

p = 0.1, 0.05, 0.01

C = 10µF

R = 100Ω

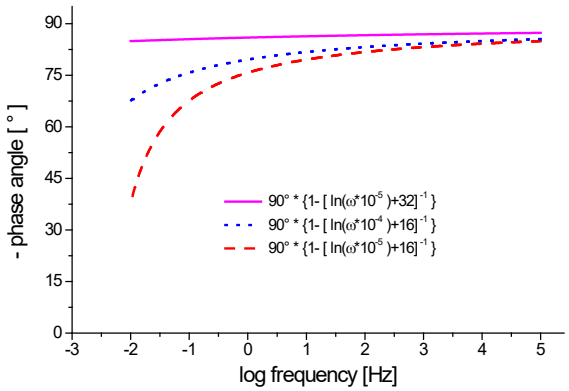
The CPE approximation

The phase in CPE can also be approximated with the Young-Göhr impedance.

$\varphi = -90^{O} \cdot (1-q)$ Phase shift φ of the Young-Göhr Impedance with $q = \dfrac{1}{\ln(\omega \cdot t) + \dfrac{1}{p}}$

1. Strong gradient in conductivity $\delta << d$ $\Rightarrow$ relative penetration depth $p << 1$

2. High frequencies $\ln(\omega \cdot t) << \dfrac{1}{p} \Rightarrow q$ constant



2.3.10 Spherical diffusion impedance

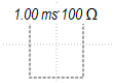
Spherical diffusion impedance (Z_R) accounts for the diffusion process as part of a charge transfer reaction. Here the boundary conditions assume a three-dimensional diffusion expanding spherically from one point in the volume. Spherical diffusion impedance is calculated from the formula

$$Z_R = \frac{W}{\sqrt{j \cdot \omega} + \sqrt{k_R}}$$

Here: $k_R = \dfrac{D_K}{r^2}$ with D_K = constant of diffusion, r = radius of sphere

The first input parameter *W* is provided as $\Omega \cdot s^{-1/2}$ like for the Warburg impedance. The second parameter (*k*) characterizes the relative reach of the diffusion compared to the finite length and is put in as 1/s.

Spherical diffusion impedance is appropriate to model the frequency behavior of the diffusion for instance in microelectrodes and microelectrode arrays with low dot densities and in the case of pitting corrosion.



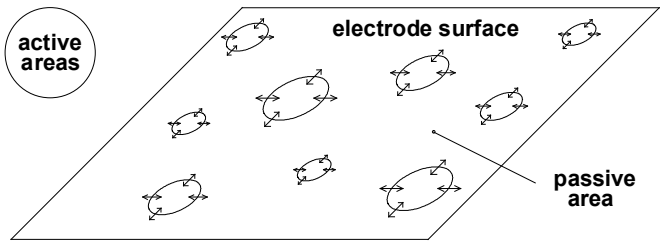
2.3.11 Surface relaxation impedance

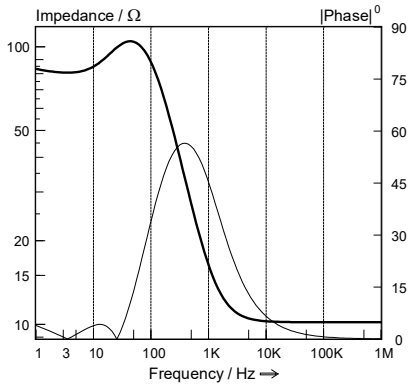
Surface relaxation impedance does not only characterize its own parameter set but imply also a certain topology of the network. For instance, it applies to the changes in the behavior of a general charge transfer reaction (CTR) under certain conditions i.e., the charge transfer reaction rate is assumed as potential-dependent, undergoing relaxation with time. The sequence to establish these models is more complicated than the input of the concentrated elements described before. Relaxation impedance (Z_F) is expressed with the formula below

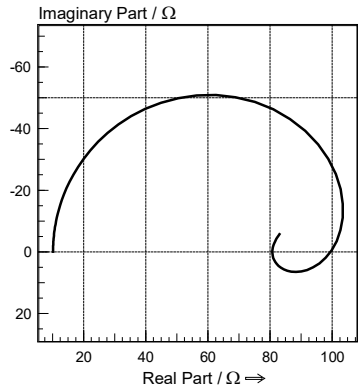
$$Z_F = \frac{R_\eta + Z_C + Z_\theta}{1 + \frac{R_\eta}{Z_k}}$$

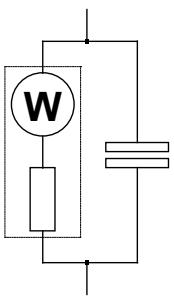
For the impedance (Z_F) to a charge transfer reaction undergoing a relaxation with time assume the following points

- the system shall be apart from the equilibrium
- the rate constant *k is assumed as potential dependent*
- the settling of k is assumed as delayed with a time constant τ









The ratio between active and passive surface areas determines the effective reaction rate. The delayed settling of that ratio to a new equilibrium state after a potential change will often cause the 'relaxation impedance'.

The surface relaxation impedance characterizes a certain property of a CTR. Therefore it is assigned to a CTR. Put in the characteristics of the relaxation first, followed by the CTR affected.

1. Parameter: count of impedance elements of the CTR, which should be affected by the relaxation.

2. Parameter: relaxation time constant in *s* of the charge transfer reaction rate.

3. Parameter: inverse strength of the potential dependence of the charge transfer reaction rate dK/dε, normalized by the Faradaic current I_f. It has the dimension Ω of a resistor.

$$Z_F = \frac{R_\eta + Z_C + Z_\theta}{1 + \frac{R_\eta}{Z_k}}$$

with R_η : charge transfer resistance

Z_C : diffusion impedance

Z_θ : coverage impedance

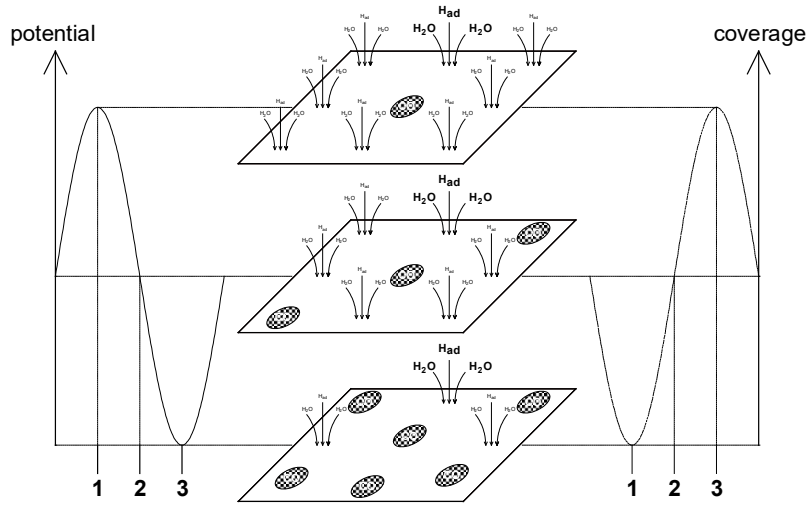
$$Z_k = \frac{1 + j \cdot \omega \cdot \tau}{I_F \cdot \frac{d \ln k}{d\varepsilon}}$$

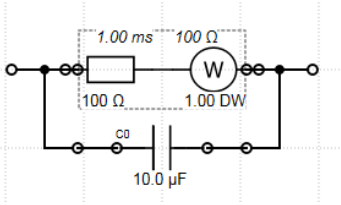
with τ : time constant of relaxation

ε : potential

$$R_k = \frac{1}{I_F \cdot \frac{d \ln k}{d\varepsilon}}$$

R_k : relaxation resistance

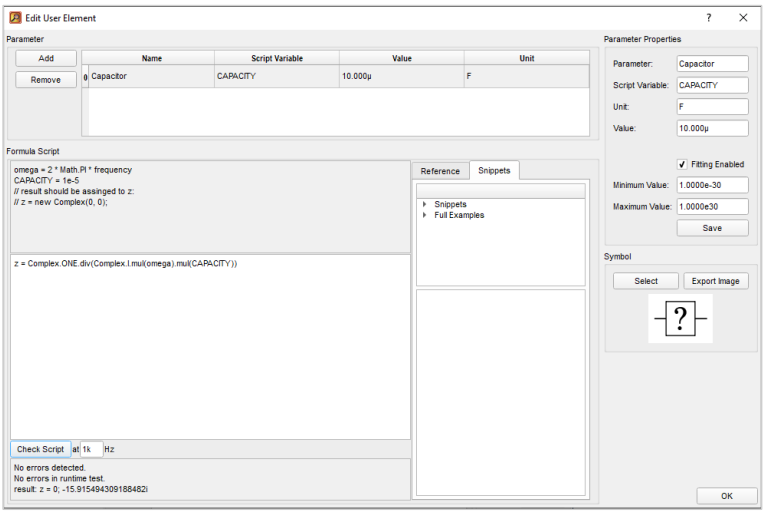




In Zahner Analysis software, in the model editor, after creating the Surface Relaxation Impedance element, other element(s) like a resistor can be created and then dragged and dropped in the Surface Relaxation Impedance element. The EEC on left is created in Zahner Analysis and contains a resistor and a Warburg in Surface Relaxation Impedance element (same EEC as on the previous page).

2.3.12 User Element

If the impedance elements provided in the Zahner Analysis software are not able to correctly represent your system then the user can build a user-defined element (User Element). A User Element ( ) in Zahner Analysis software enables you to define the transfer function fitting your special needs. To define the User Element, double-click on the User Element ( ) and then click on the “Edit User Element”. This will open up a new window, where the element is defined.



To start the customization of your User Element, click on “Add” in the “Parameter” window. Here you write the name of the “Parameter”, assign the “Script Variable” for use in the “Formula Script” window, and assign a value, and a unit. The value range can also be adjusted in the “Parameter Properties” window. In the “Formula Script” window, the script for the element can be written. In the figure above, an example of a script for a capacitor is shown.

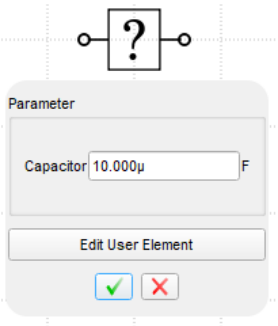
$$Z_C = \frac{1}{i \,.\, \omega \,.\, C}$$

Script for the impedance of a capacitor:

```
z = Complex.ONE.div(Complex.I.mul(omega).mul(CAPACITY))
```

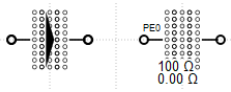
For writing the formula scripts, Javascript (library: complex.js) is used as a programming language. The user can use Javascript to customize his/her User Element. In Snippets in the “Edit User Element” window, example scripts of resistor, capacitor, and Warburg are present. The “Reference” section contains the javascript script for different mathematical functions.

In the “Edit User Element” window, the symbol can also be exported. You can also customize the symbol and then later import it back via the “Select” option in the “Symbol” section. For customizing the symbol, different programs like inkspace can be used.

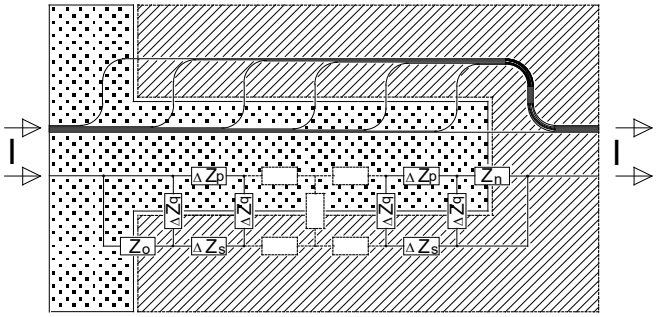


Once the user has written the script for the User Element, click on “Check Script” to see if there are some errors. If no error is present then click ok and you will be brought back to the “Model Editor” window.

2.3.13 Porous Electrode



The complexity of the Porous Electrode element (*PE*) depends on the application. Generally, the *PE* working principle is as follows: the impedance components of a porous system, for instance, its electro-active surface ***q*** within the pores, is first put in conventionally "as if" belonging to a smooth, undistributed system. You can define the electro-active surface model without functional restrictions, but consider that the meaning of some parameters may change when the impedance element is used within a pore. If you use the *PE* in its more complex form, you may consider other characteristic partial impedance besides the electro-active surface ***q***, in particular the pore ground impedance ***n*** and the top layer impedance ***o***. In this case, you have to define ***o*** and ***n*** as uncommitted partial impedances first. Next is the description of the electro-active surface ***q*** in the form of partial impedance. Finally put in the *PE* characteristic parameters, integral pore electrolyte resistance ***p***[Ω], and integral solid resistance ***s***[Ω] and connect it to ***q*** using the same scheme shown below. Note, that this will complete the circuit, although the circuit builder still indicates open partial schemes!



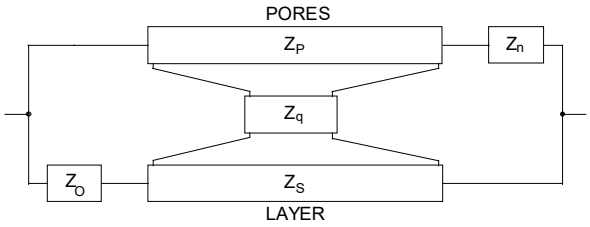
Z_S impedance of the porous layer

Z_p impedance of the pores containing electrolyte

Z_q Impedance of the interface *porous layer/pore*

Z_o impedance of the interface *porous layer/electrolyte*

Z_n impedance of the interface *porous layer/bulk*



$$Z_S = Z_{\parallel} + Z^* \cdot \frac{C + (1-C)\cdot 2\cdot p\cdot s + S\cdot(p^2\cdot q_n + s^2\cdot q_0)}{S\cdot(1+q_n\cdot q_0) + C\cdot(q_n+q_0)}$$

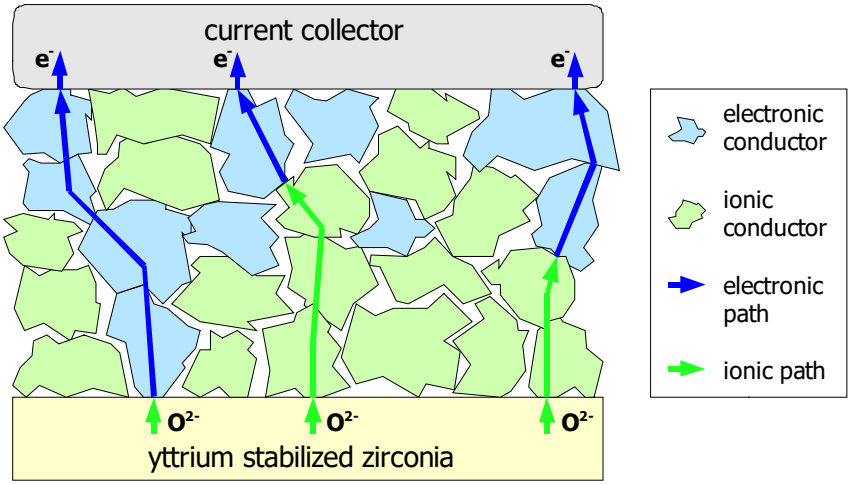
$$Z^* = \sqrt{(Z_p+Z_s)\cdot Z_q}\,, \quad Z_{\parallel} = \frac{Z_p\cdot Z_s}{Z_p+Z_s}\,, \quad C = \cosh\left(\frac{Z_p+Z_s}{Z^*}\right), \quad S = \sinh\left(\frac{Z_p+Z_s}{Z^*}\right)$$

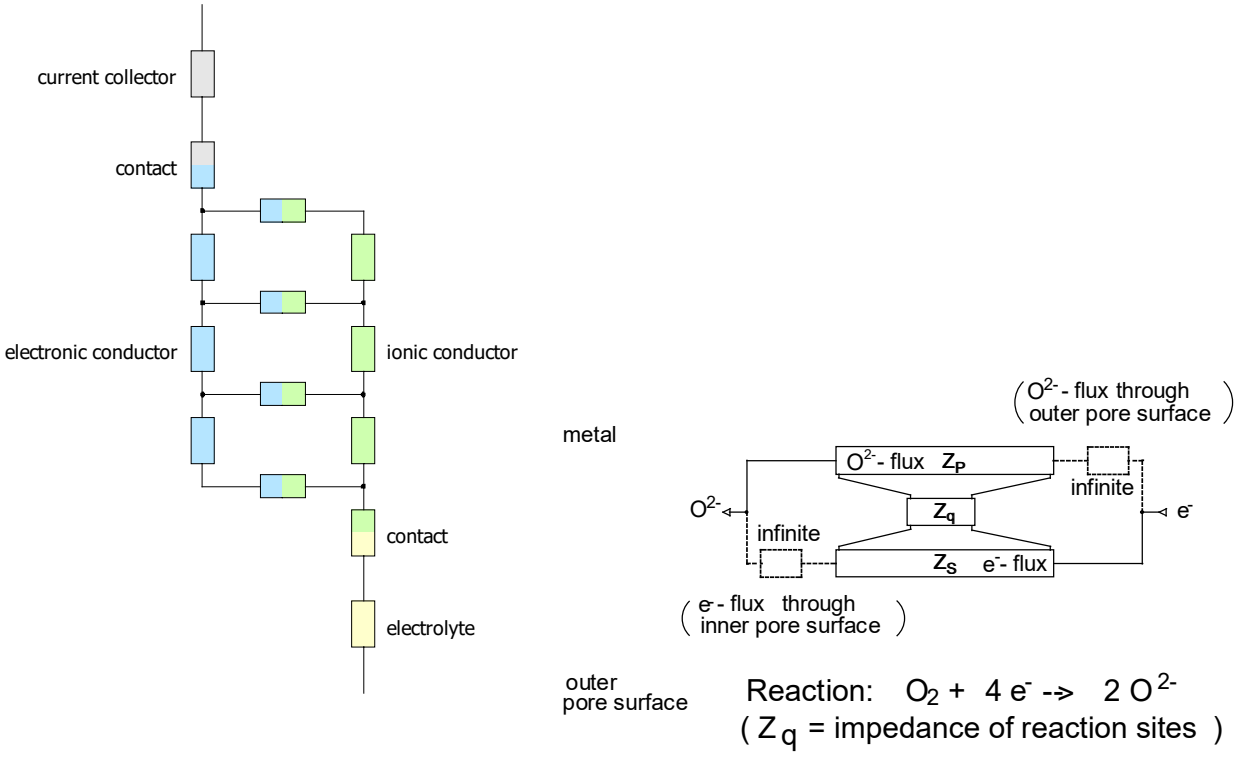
$$p = \frac{Z_p}{Z_p+Z_s}\,, \quad s = \frac{Z_s}{Z_p+Z_s} = 1-p\,, \quad q_0 = \frac{Z^*}{Z_0}\,, \quad q_n = \frac{Z^*}{Z_n}$$

H.Göhr et al., *Kinetic Properties of Smooth and Porous Lead / Lead Sulfate Electrodes*, 34th I.S.E. Meeting, Ext. Abstracts, Erlangen, (1983)

This early model is based on the assumption of uniform pores following Cavalieri's principle. It was shown later by L. Bay & Key West, *Solar Energy Materials and Solar Cells* **87 (2005)** 613-628, that this model is also appropriate if electronic and ionic conductivity in the matter is distributed over space, building current paths in form of a ladder network (Z_O and Z_n must then be omitted).

Göhr´s Porous Electrode Impedance, Applied as Differential Ladder Network to the SOFC Cathode



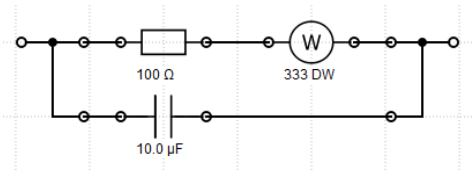


Appearance

Batteries, fuel cells, surface layer of corroding electrodes, and non-homogeneous oxide layers.

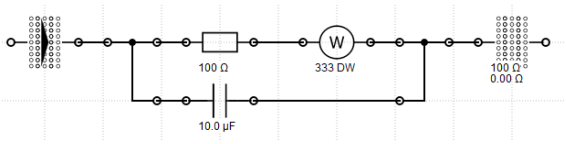
Example

Let us build up *PE* circuits of different complexity in ascending order.



Let us start with the definition of a Randle circuit, where we stop without adding a (concentrated) electrolyte resistance. The description looks like this:

R = 100 Ω, C = 10 µF, W = 333 $\Omega s^{-1/2}$



Next, we add the PE model to complete the description of the electrode. Then we yield:

R = 100 Ω, C = 10 µF, W = 333 $\Omega s^{-1/2}$

Electrolyte resistance R_p = 100 Ω

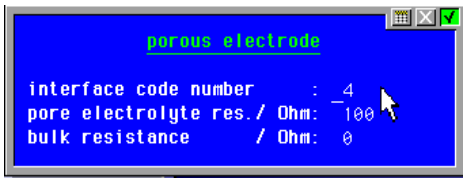
Solid/Bulk resistance R_s = 0 Ω

Please recognize that we put the bulk resistance as zero, assuming it is negligible due to the metallic character of the bulk compared to the electrolyte. At least one of both resistances must be different from zero. In the electrical circuit, the bulk resistance and the electrolyte resistances in *PE* element are represented with , whereas other resistances/capacitances in the pore are represented with the normal resistor and capacitor elements. Here the user has to define in the software which parameters belong to the *PE*. This is accomplished with the **start porous electrode** element .

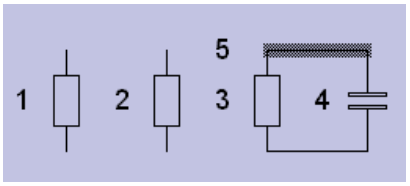
If we omit the diffusion impedance (Warburg) in the Randle circuit, we will find the porous electrode properties of the model after De-Levie (a chain latter behaviour).

Let us now build up the most complex form of the *PE* impedance, which includes both, the top surface as well as pore ground impedance *o* and *n* (currently only available in SIM application of Thales software).

In this case, we have to put in first the top surface impedance *o* as a partial scheme (13Ω), next the pore ground impedance *n* (26Ω) as a second partial scheme (we use resistors, but there is no restriction in complexity). Then we built up the *q*-interface for the electro-active pore area in a third partial scheme (here without diffusion impedance). Then we put in the *PE* characteristics, now with a code number of four, and complete the circuit by putting the *PE* in series to *q*.

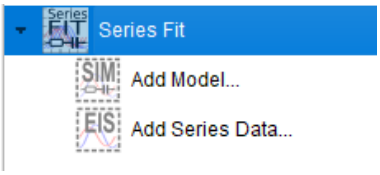


1	13	Ω
2	26	Ω
3	100	Ω
4	10	µF
5	4	
	100	Ω
	0	Ω

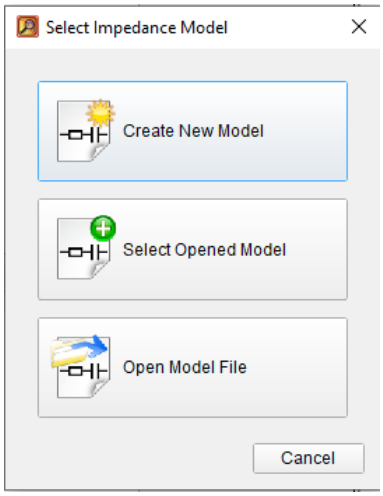


2.4 EIS – Series Fit

In Zahner Analysis, multiple impedance spectra can be fitted with a single EEC in one go. In Zahner Analysis software, the function of simultaneous fitting is called Series Fit.



Prior to Series Fit, first open only the first impedance spectrum, create an EEC and by following the instructions from section 3 fit the first spectrum. After fitting, from Menu Bar, click on the **File → New → Series Fit**. This will create a **Series FIT** entry in **Data Sources**. Clicking on the small arrow right to the Series Fit will reveal the entries for the **Add Model** and **Add Series Data**.



To add a model for the series fit, double-click on **Add Model**. This will open a sub-window and provide the user with three possibilities, where the user can

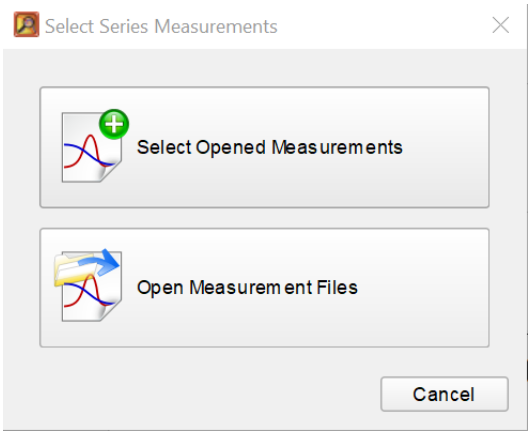
- Create a new model
- Select the already opened model
- Open an already saved model file

In case, the user has already fitted the first spectrum then the user can use the second option and select the already opened model for the Series Fit.

The opened model will be added under the Series Fit entry in the **Data Sources** window.

After selecting the model, to add impedance spectra for the series fit, double-click on **Add Series Data**. This will open a sub-window with the options

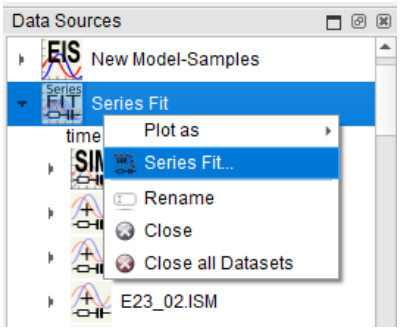
- Select Opened Measurements
- Open Measurement Files

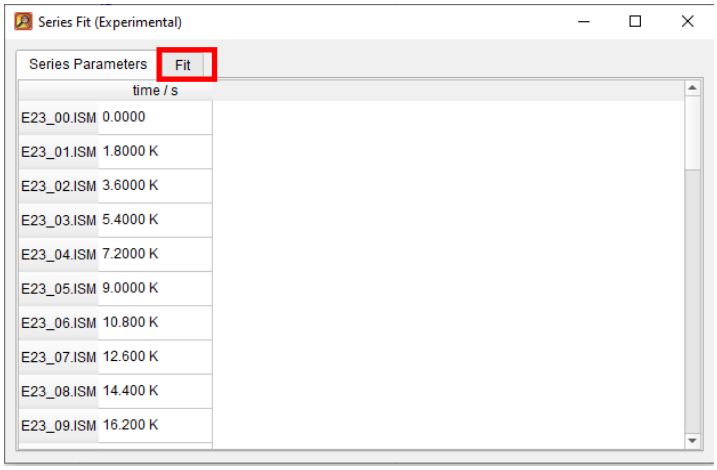


Here user can take the second option and open all the files which he/she wants to fit in one go using the Series Fit. The opened data files will be added under the Series Fit entry in the **Data Sources** window.

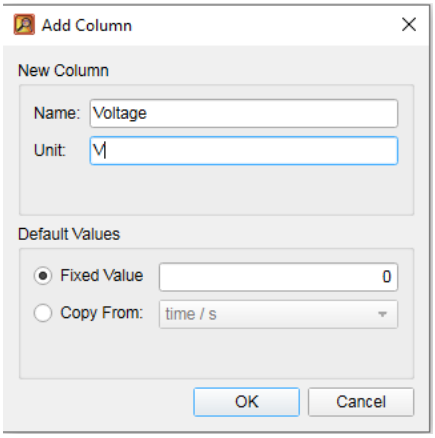
Now, in the **Data Sources** window, right-click on the Series Fit entry and from the drop-down menu, choose the “Series Fit” option. This will open a Series Fit sub-window where all opened impedance

files are listed with the parameter they were measured against. In the following example, the impedance files were measured against time.

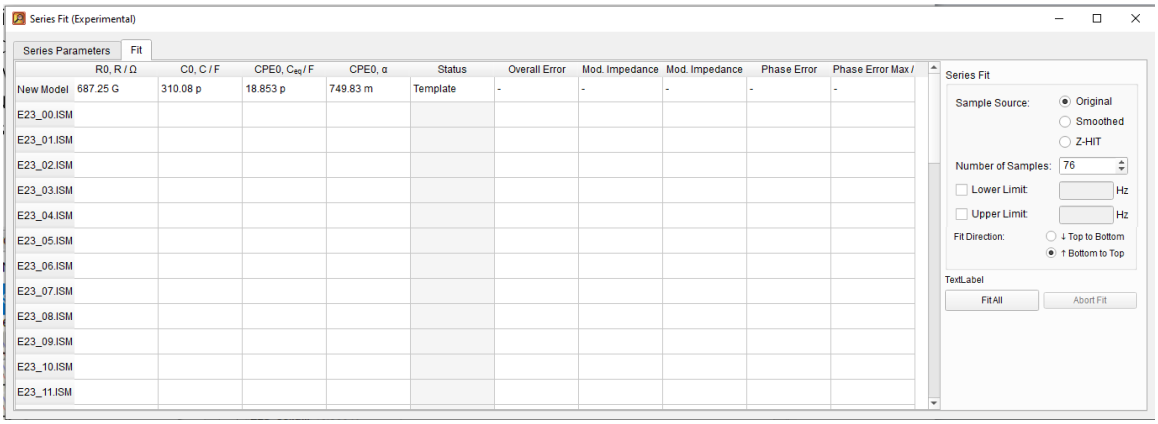




The user may also add an arbitrary parameter for the series fit. For adding an arbitrary parameter, right-click with the mouse in the empty window in the Series Fit window and then from the drop-down menu choose **add column**. In the example on the right, data fields for the new column are shown. The user may provide here a **Name,** a **Unit** and may assign a fixed value to the arbitrary parameter or copy the value from an existing column (if present).



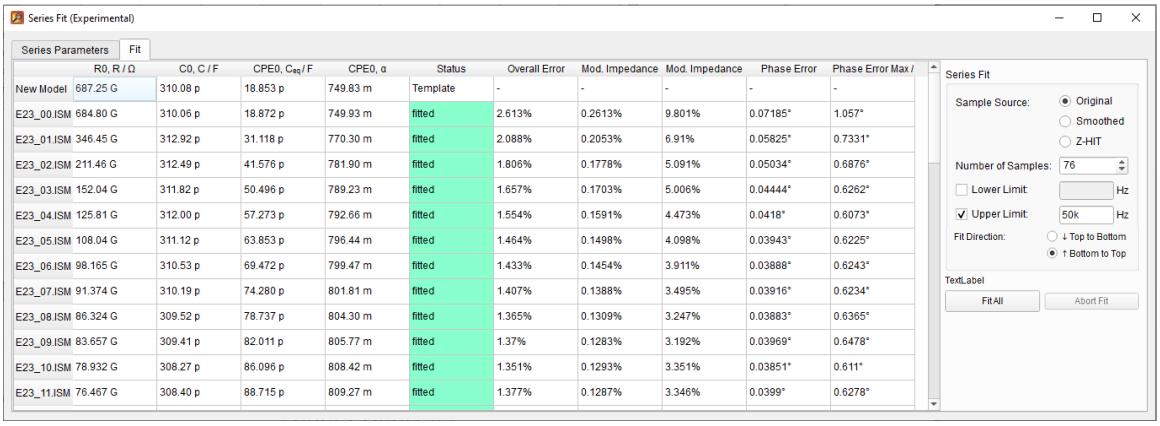
The "Fit" (marked red) in the Series Fit window reveals the sub-window with the fitting options. Here the user can set the fitting options and start the fitting process.



The benefit of first fitting a single impedance spectrum before starting the series fit is that the first fit provides useful starting values to the model for the Series Fit. Similarly, the fitter uses the fitting results of the previous fit as the start values for fitting the next impedance spectrum in the series

fitting. Clicking on **Fit All** will start the fitting of all impedance spectra. Fitting will finish when the status for each file changes to **fitted**.

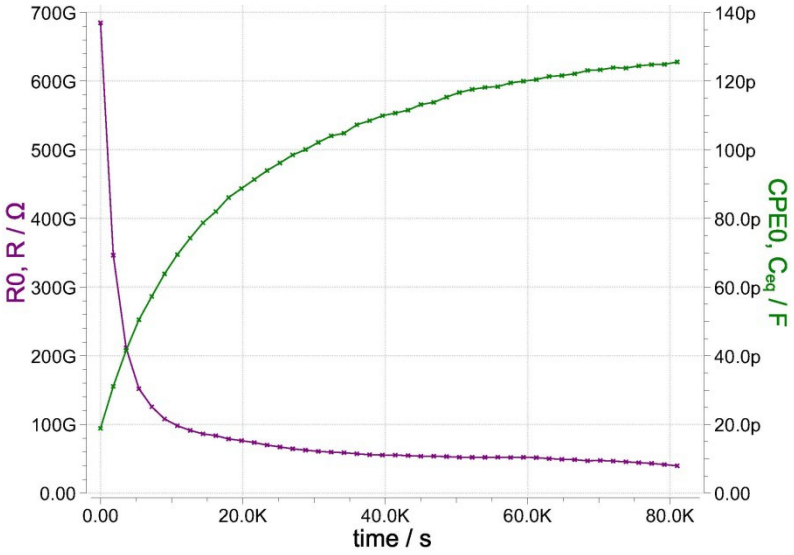
The user has the option to start fitting either from top of the list or the bottom.



	R0, R / Ω	C0, C / F	CPE0, C_{eq} / F	CPE0, α	Status	Overall Error	Mod. Impedance	Mod. Impedance	Phase Error	Phase Error Max /
New Model	687.25 G	310.08 p	18.853 p	749.83 m	Template	-	-	-	-	-
E23_00.ISM	684.80 G	310.06 p	18.872 p	749.93 m	fitted	2.613%	0.2613%	9.801%	0.07185°	1.057°
E23_01.ISM	346.45 G	312.92 p	31.118 p	770.30 m	fitted	2.088%	0.2053%	6.91%	0.05825°	0.7331°
E23_02.ISM	211.46 G	312.49 p	41.576 p	781.90 m	fitted	1.806%	0.1778%	5.091%	0.05034°	0.6876°
E23_03.ISM	152.04 G	311.82 p	50.496 p	789.23 m	fitted	1.657%	0.1703%	5.006%	0.04444°	0.6262°
E23_04.ISM	125.81 G	312.00 p	57.273 p	792.66 m	fitted	1.554%	0.1591%	4.473%	0.0418°	0.6073°
E23_05.ISM	108.04 G	311.12 p	63.853 p	796.44 m	fitted	1.464%	0.1498%	4.098%	0.03943°	0.6225°
E23_06.ISM	98.165 G	310.53 p	69.472 p	799.47 m	fitted	1.433%	0.1454%	3.911%	0.03888°	0.6243°
E23_07.ISM	91.374 G	310.19 p	74.280 p	801.81 m	fitted	1.407%	0.1388%	3.495%	0.03916°	0.6234°
E23_08.ISM	86.324 G	309.52 p	78.737 p	804.30 m	fitted	1.365%	0.1309%	3.247%	0.03883°	0.6365°
E23_09.ISM	83.657 G	309.41 p	82.011 p	805.77 m	fitted	1.37%	0.1283%	3.192%	0.03969°	0.6478°
E23_10.ISM	78.932 G	308.27 p	86.096 p	808.42 m	fitted	1.351%	0.1293%	3.351%	0.03851°	0.611°
E23_11.ISM	76.467 G	308.40 p	88.715 p	809.27 m	fitted	1.377%	0.1287%	3.346%	0.0399°	0.6278°

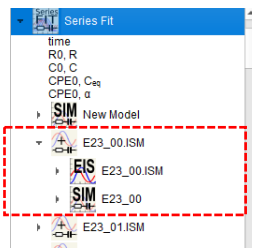
The fit results show the fitting results for each file. Upon closing the Series Fit window, one lands back to the main Zahner Analysis window. In the Zahner Analysis window, double-clicking on the Series Fit entry in the **Data Sources** window will plot the fitting results against the measurements parameter. Prior to this, removing all currently shown graphs from the graph window is mandatory.

In the example on the right, one can see the change in charge transfer resistance and the CPE against the measurement parameter (time).



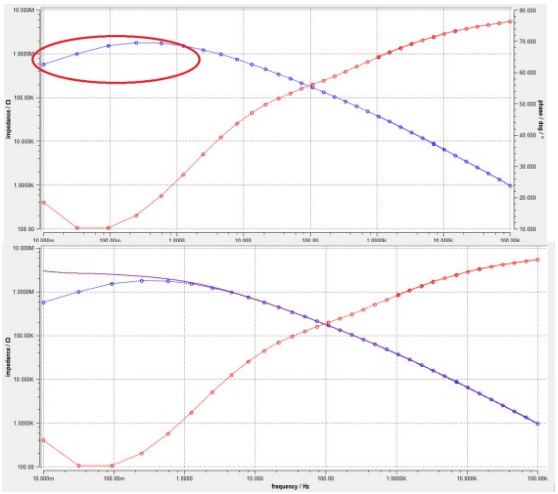
After selecting the Series Fit entry in the **Data Sources** window, one can save the results of the Series Fit by clicking on **File → Save** or **Save as**. The saved data file will be saved in Zahner's series fit (.zsfx) file format.

In addition, in the **Data Sources** window, now each impedance data entry contains two sub-entries (marked red in the image on right). One of the measured data and second of the fitting data so the user can see the fitting results of each measurement.



2.5 Zwei-pol (two-pole) Hilbert transformation (Z-HIT)

A principle requirement of electrochemical impedance spectroscopy is the stability of the system under investigation. In some systems, fulfilling this requirement is very difficult, especially at low-frequency measurements where the time required for a single measurement increases exponentially. An example of such a system is a coating immersed in water/liquid. With time the coating absorbs water and its impedance decreases. This decrease in impedance is visible during EIS measurement at low frequencies (area marked with the red circle).



Unlike impedance, the phase of a system is much more stable. So it is possible to reconstruct the impedance from the phase with Z-HIT. For calculating, ZHIT in Zahner Analysis software, click on the ZHIT icon ( ). The ***Z-HIT*** calculates the impedance data Z(f) from the Phase data φ(f) after the following equation.

$$\ln\left|H(\omega_o)\right| \approx const. + \frac{2}{\pi}\int_{\omega_s}^{\omega_0}\varphi(\omega)\, d\ln\omega + \gamma\cdot\frac{d\varphi(\omega_o)}{d\ln\omega}$$

The result is plotted as a curve (lilac) in a graph together with the original measurement data (blue symbols) and the phase curve (red). By comparing the curve and the measurement data visually you can decide whether your object was in a steady state during measurement or not. Furthermore, ***Z-HIT*** allows you to re-create impedance data from the phase data in case a measurement was disturbed.

Z-HIT is a unique function that offers a very reliable tool to judge steady-state and treat steady-state violations in experimental data.

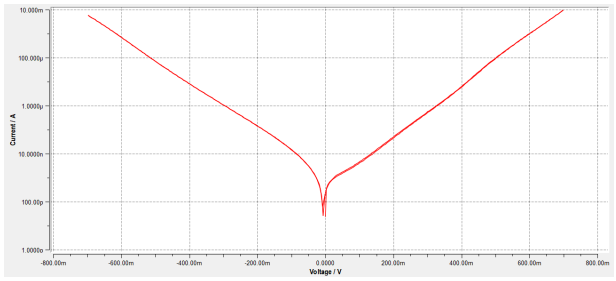
Further detailed info about Z-HIT is provided on the Z-HIT Wikipedia page and the technical note.

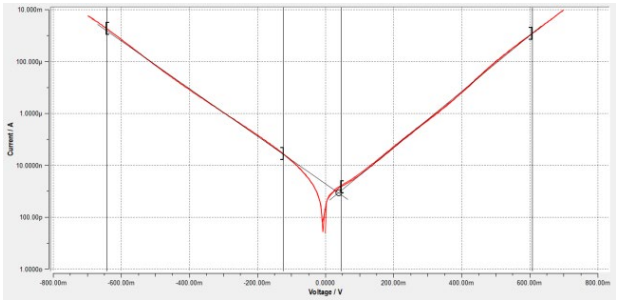
3 Current-Voltage curve

3.1 Current-Voltage (I/E) curve

I/E curves are measured in the Tafel slopes format. Evaluation of the Tafel slope is described in the sections below.

3.1.1 Tafel slope





Tafel slopes are of great importance in electrochemistry and provide insight into the reaction kinetics. In Zahner Analysis software, Tafel slopes can be easily calculated from the measured ***log Current*** vs ***Voltage*** graph.

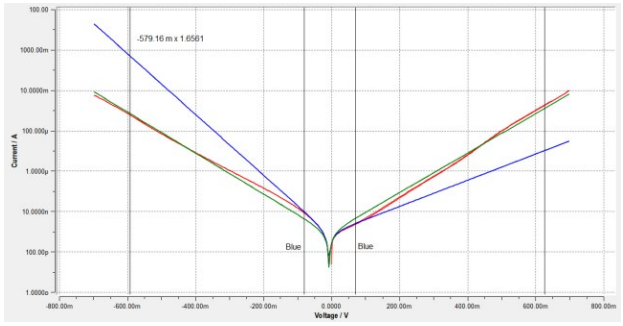
For measuring the Tafel slope, click on the Tafel slope icon ( ) and then in the *Toolbox* window, set the 2 cursors for the cathodic arm and 2 for the anodic arm, indicating points between which the slope should be calculated.

Besides the Tafel slope, the **corrosion rate** can also be calculated. For the corrosion rate calculation, the user has to provide

- *Area of Electrode* (cm^2),
- *Density* (g/cm^3),
- and *Equivalent Weight* (g/mol).

The calculated slope and the corrosion rate are shown in the *Toolbox* window.

3.1.2 Butler-Volmer



Butler-Volmer (BV) parameters can also be calculated from a ***log Current*** vs ***Voltage*** graph. For calculating the BV parameters, click on the *Butler-Volmer* icon ( ) and then click on the *Toolbox* window to set the two cursors on the cathodic and anodic arm to simulate a Butler-Volmer curve. In the image (on right), two simulated BVs are shown. The blue BV is simulated with the two cursors close to the center of the graph, whereas the green BV curve is simulated with the cursors at the far end of the measured BV curve. The results of the simulated curves will be shown in the Toolbox window.

3.2 Cyclic voltammogram

In this section, a step-by-step guide is provided to analyze a cyclic voltammogram (CV) in the Zahner Analysis software.

1. Open the measured CV

Open the measured current-voltage curve from **File → Open**. Like EIS, different representations of the current-voltage curve are possible and can be set from the Plot representation window (***window 4***). A list of the available graphic representation is provided below

- Linear I vs U
- Linear I (Linear U) vs time
- Log I vs U
- U vs Log I
- Linear I vs time
- U vs Linear I
- Normalized I vs U
- Norm (sqrt) I vs U

Normalized current:

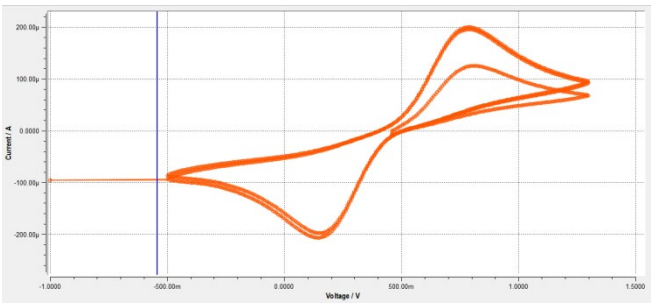
$$I = \frac{Current}{Scan\ rate} \quad , \quad \text{unit} = \frac{Ampere}{(Volt/Second)} = \frac{As}{V}$$

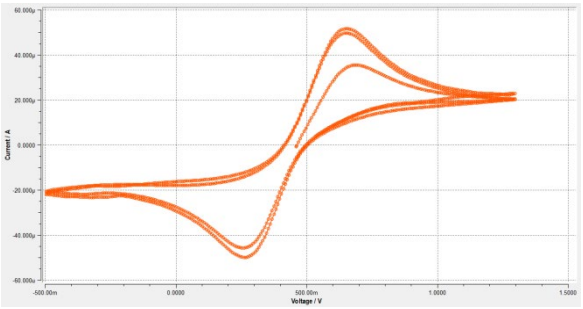
Normalized (sqrt) current:

$$I = \frac{Current}{\sqrt{(Scan\ rate)}} \quad , \quad \text{unit} = \frac{Ampere}{\sqrt{(Volt/Second)}}$$

2. Trim the CV

For trimming the artifact on the left side of the CV, first click on the "Cut Graph" icon  and then click on the curve where trimming should be done. Upon clicking, choose a cursor on the graph, and then in the "Toolbox", click on remove left/right to remove the part on the left or right from the cursor, respectively.

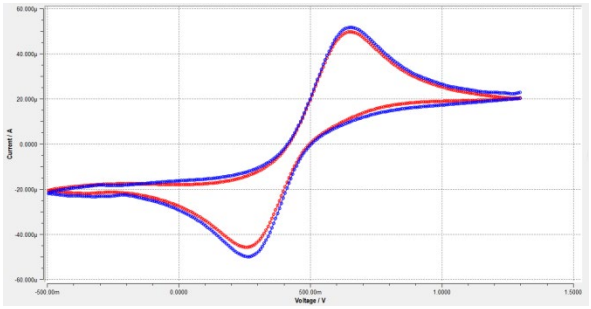




3. Split curve

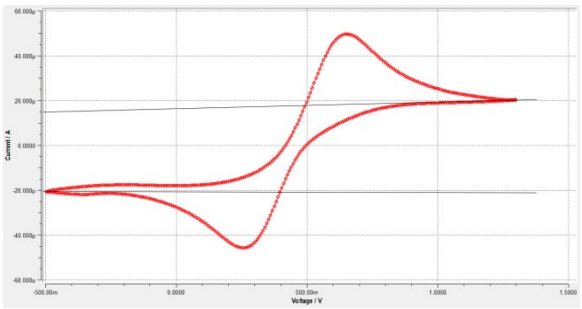
Split the curve by clicking the icon and then click “Split” in the Toolbox window. This will split the curve into multiple curves and will assign the splitted curves the pre-decided colors. If the user wants to change the colors then it is possible from the (*window 6*). Splitting will also generate new files with individual CVs and these files will be listed in the Data Source window (*window 3*).

For the rest of the evaluation, only one splitted CV will be used.



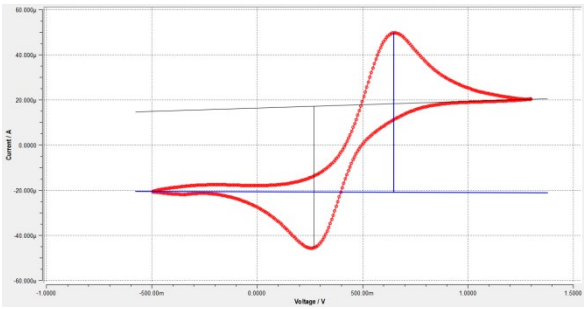
4. Draw the Baseline(s)

Draw the baseline by clicking on the icon and then sketch the desired baseline on the main graph window. If the user wants to draw more than one baseline then click on “New Baseline” in Toolbox to draw the additional baseline.



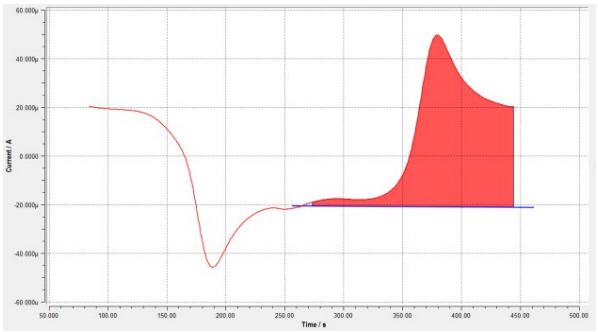
5. Peak position

To measure the peak position, click on the peak position icon and then with the mouse click on the peak of the CV. The peak position and additional information about the peak will be listed in the “Cursor and label window” (*window 10*).



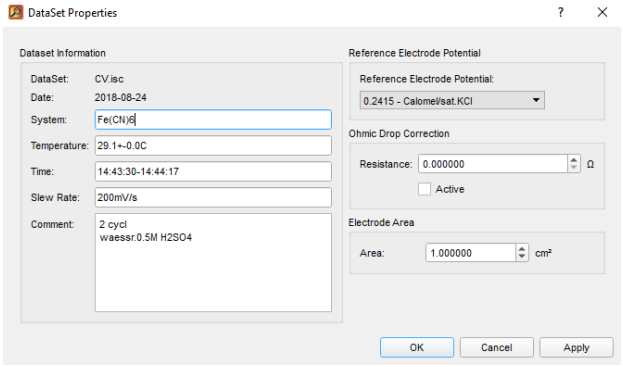
6. Peak area integration

To integrate the area under peak, click on the icon. Then in the “Toolbox” window, set the baseline, “start of peak” and “end of peak”. If previously, a baseline was drawn then that baseline will be automatically chosen. For choosing the start of the peak click the “Select” icon and then on the Graph window click on the CV where the peak is starting and then repeat the same process to select the end of the peak. In the end, clicking on the “Integrate Charge” will integrate the peak. The integrated peak will be shown only “Linear I vs time” representation.



3.3 Current-Voltage graph properties

The Zahner Analysis software allows setting reference electrode, ohmic drop correction, and electrode area for the current-voltage graphs.



For setting the reference electrode, ohmic drop resistance, and the electrode area, right-click with the mouse on the file name in the "Data Source" window and then click "Properties". This will open the "Data Set Properties" window where the above-mentioned parameters can be used. In addition, this window also includes comments and technical details which were provided during the measurement in the Thales software.

For reference electrode setting, a user-defined reference electrode option is also provided, where the user can specify the potential of his/her reference electrode which is not available in the list.

To see the changes in the Graph window, by changing the settings in the "Data Set Properties", window, the graph should be in *Current (A/cm²)* settings and not *Current (A)* settings. This setting can be changed by clicking on the "Reference Area"  icon in the Toolbar.