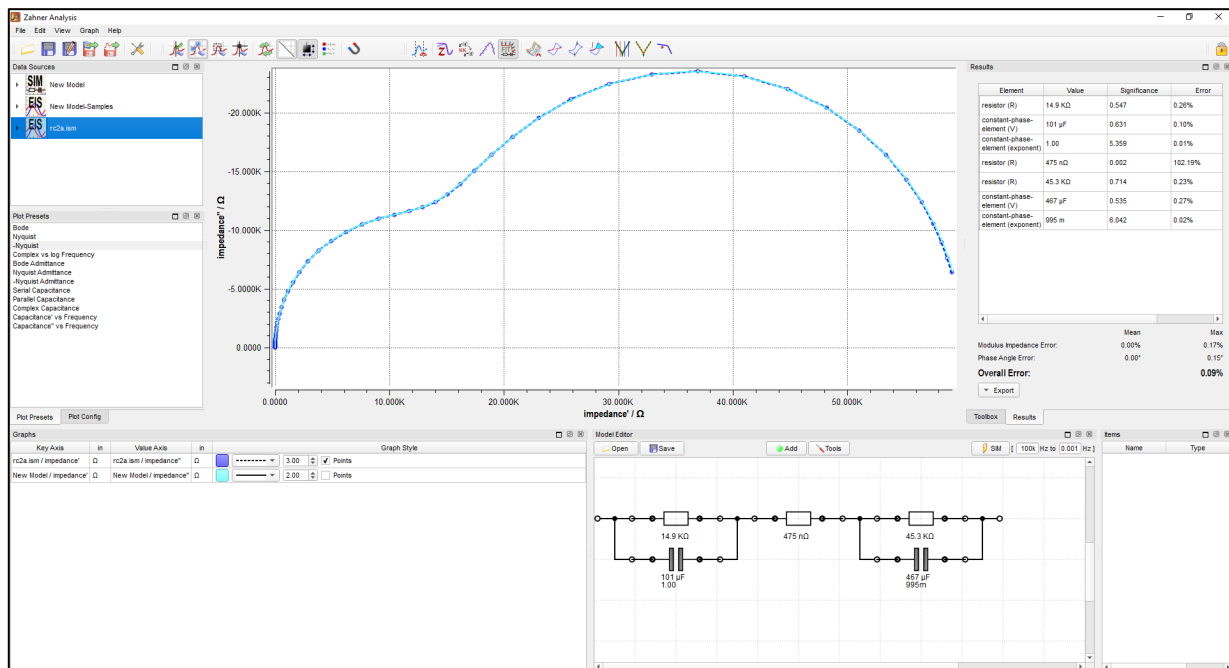


# Zahner Analysis





## Table of Contents

<b>1. Overview .....</b>	<b>2</b>
<b>2. Electrochemical impedance spectroscopy.....</b>	<b>3</b>
2.1 EIS fitting .....	3
2.2 Impedance electrical elements .....	5
2.2.1 Resistor .....	5
2.2.2 Capacitor .....	6
2.2.3 Inductor .....	6
2.2.4 Warburg impedance .....	7
2.2.5 Nernst diffusion .....	7
2.2.6 Finite diffusion .....	8
2.2.7 Homogeneous reaction impedance .....	9
2.2.8 Constant phase element .....	9
2.2.9 Young-Göhr impedance .....	11
2.2.10 Spherical diffusion impedance .....	12
2.2.11 Surface relaxation impedance .....	12
2.3 Zwei-pol Hilbert transformation (ZHIT) .....	14
<b>3. Current-Voltage curve .....</b>	<b>15</b>
3.1 Current potential (I/E) curve .....	15
3.2 Cyclic voltammetry (CV) .....	16
3.3 Tafel slope .....	17
3.4 Butler-Volmer curve .....	17



## **Zahner Analysis software**

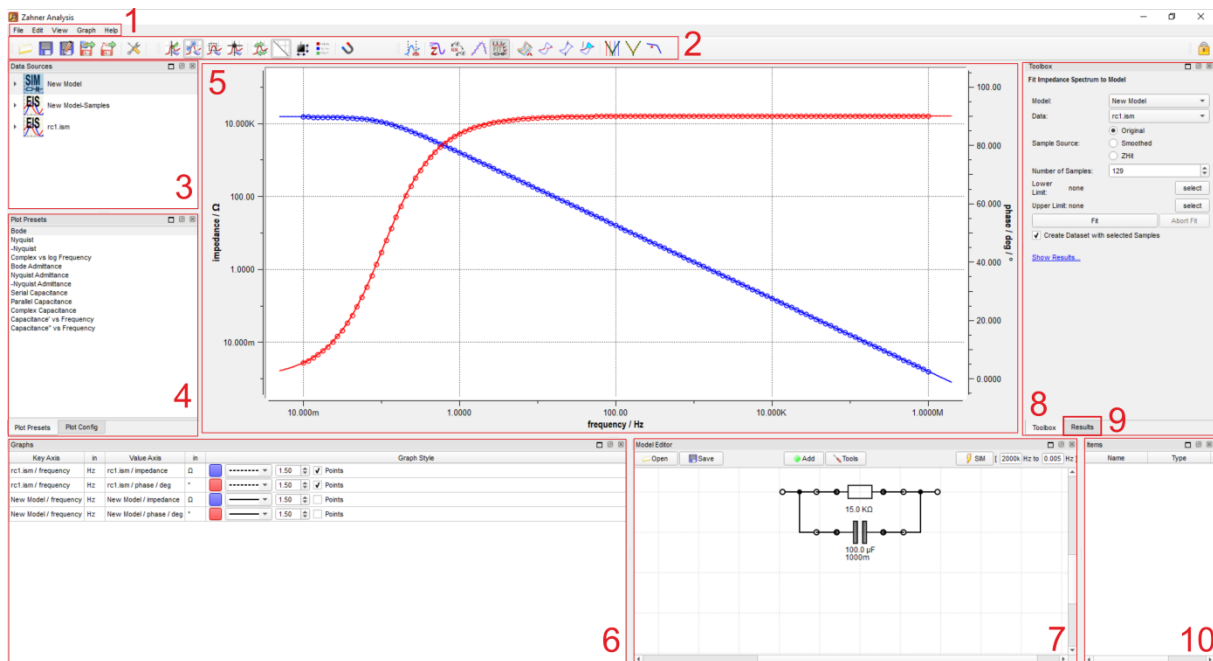
A manual evaluation of the electrochemical experimental results can be sometimes very tedious and complex, for example, fitting of an impedance spectrum with an equivalent electrical circuit (EEC). In impedance spectroscopy, different graphical representations are used namely Nyquist plot, Bode plot, 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. As there are indefinite sets of parameters which will fit the Nyquist plot but will not fit the Bode and Cole-Cole plot and only a single set of parameters (for an EEC) will fit all the graphical representations simultaneously. 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 evaluation of the results of 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)

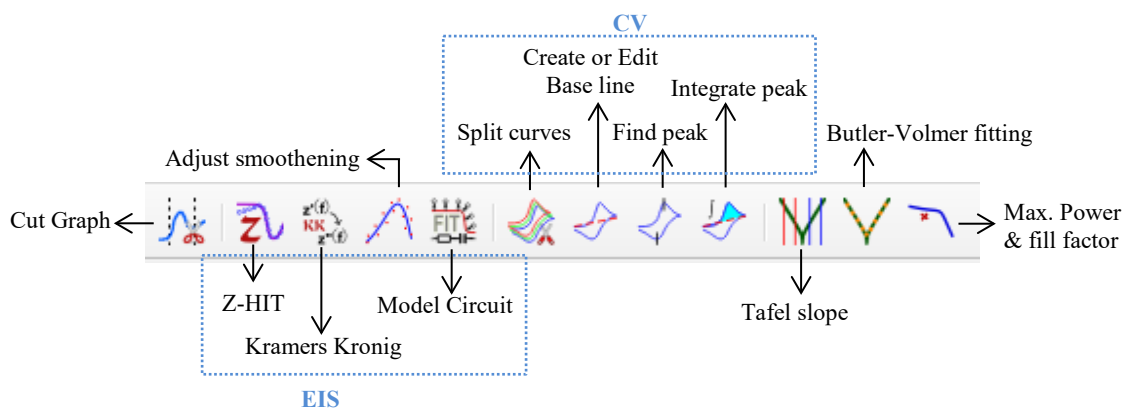
## 1. Overview

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



1. Menu bar
2. Icon bar
3. Open files list (Data Sources window)
4. Plot representation options
5. Main graph area
6. Graph list
7. Model circuit window
8. Toolbox
9. Results
10. Cursors and/or Label window

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



In the rest of this manual, 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 (EIS)

Electrochemical impedance spectroscopy (EIS) is a widely used electrochemical process that provides insight into the 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 users can fit the impedance spectrum with an EEC. The software also provides information about the total error in the fitting and the significance of each electrical element used in fitting.

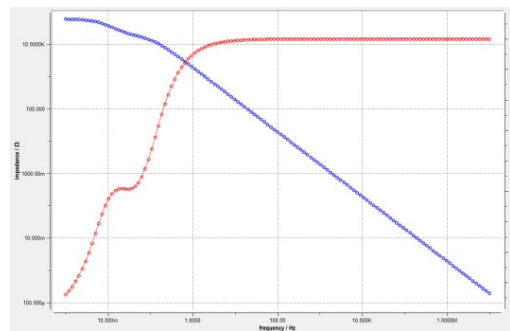
### 2.1 EIS fitting

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

#### 1. 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 format can be modified.

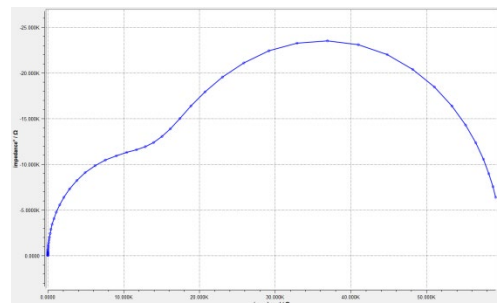


Bode plot

#### 2. Choose desired graphical representation


For EIS, different graphical representations are possible (provided below) are available in **window 4**.

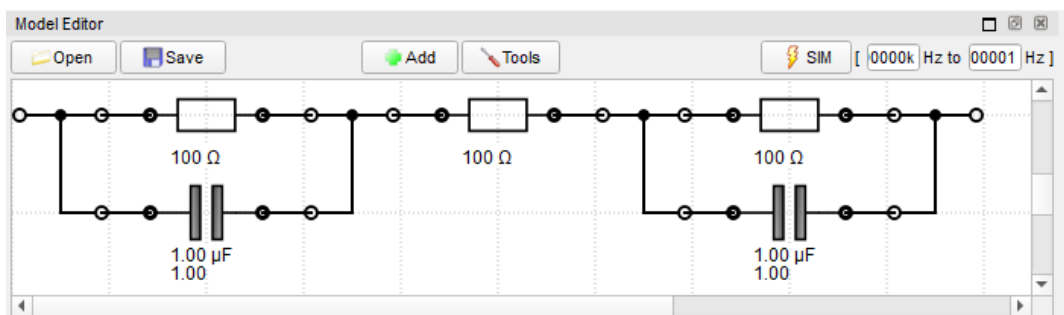
- Bode
- Nyquist
- -Nyquist
- Complex vs Log Frequency
- Bode Admittance
- Nyquist Admittance
- -Nyquist Admittance
- Serial Capacitance
- Parallel Capacitance
- Complex Capacitance
- Capacitance' vs Frequency
- Capacitance'' vs Frequency




EIS spectrum (Nyquist plot)

#### 3. Create an equivalent electrical model

Once the desired graphical representation is chosen, then click on the “Model Circuit” icon (  ). This will open a new window where the EEC is built, the frequency range is provided and the simulated graph is generated.



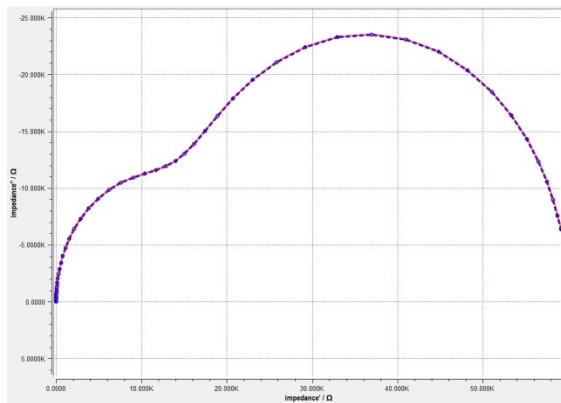
For generating different electrical elements, click on “Add” and then choose the desired elements. Electrical elements can be connected by connecting the dots. For complex electrical circuits, sometimes the model looks very messy so then click “Tools → Auto Align” to properly align the electrical elements in the model. Once a model circuit is created and the desired frequency range for simulation is provided, then click on  to generate the simulation file (**New Model**).

#### 4. 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 representation (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 of your elements in the equivalent electrical circuit.

#### 5. 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 the *Error* of each electrical element are also provided. In addition, the “overall Error” of the simulated fitting is also given.




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 modeling 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.

#### 6. Save the simulated spectrum

The simulated spectrum can be saved by **File → Save**, or by clicking on the save icon (). Also text export is possible.

**Note:** In the Zahner Analysis software, the data table can also be viewed by right-clicking on the icon bar and then enabling “Data View”.

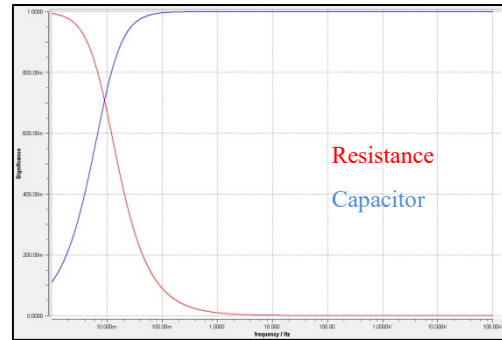
Data View						
	frequency	impedance	phase / deg	phase / rad	impedance'	impedance''
1	100000	4113.76	-90	-1.5708	0.000373046	-4113.76
2	99104.2	4150.95	-90	-1.5708	0.000379821	-4150.95
3	98216.3	4188.47	-90	-1.5708	0.000386719	-4188.47
4	97336.5	4226.33	-90	-1.5708	0.000393742	-4226.33
5	96464.5	4264.54	-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



### Significance plot:

The significance plot is a significance vs frequency plot and informs about the significance of each electrical element (used in the EEC) at different frequencies. The Figure on right shows a significance plot of a simple EEC with a parallel resistor and a capacitor.

The significance plot indicates at which frequencies which element is active.

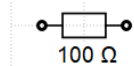


## 2.2 Impedance electrical elements

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

### 2.2.1 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

Impedance of a homogeneous conductor, e.g. the electrolytic resistance

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

Charge transfer resistance of faradaic impedance

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

## 2.2.2 Capacitor



The capacitor (C) has a phase angle of  $-90^\circ$  and 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 different phenomenon

- dielectric surface layer
- double layer
- adsorption impedance
- crystallization impedance
- general "pseudo"-capacitive behavior assigned to concentration-dependent potential ("Nerstian capacitance").

An electrostatic capacities, e.g. plate capacitor, double layer capacitance can be explained via

$$C = \frac{\varepsilon \cdot \varepsilon_0 \cdot A}{d}$$

with  $\varepsilon$  : 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  $\Theta$  = mean surface concentration parameter,  $\Gamma$  = surface access parameter

## 2.2.3 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  $90^\circ$ . 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".

Inductance of a piece of wire

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

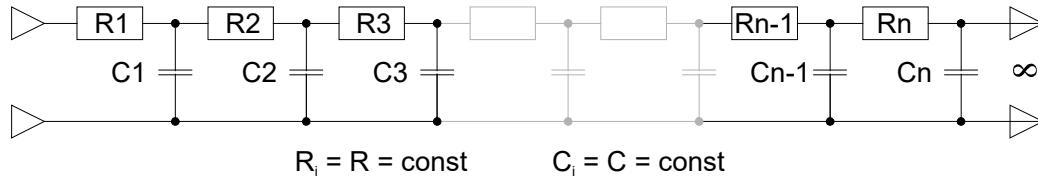
Inductance of a coil

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

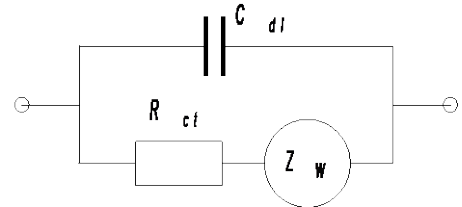
## 2.2.4 Warburg impedance

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 and 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



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

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

Warburg is used for

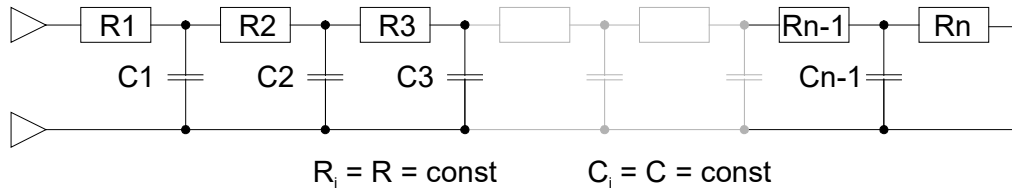
- General diffusion affected charge transfer reactions
- Limiting case frequency behavior for all diffusion contributions at high frequencies
- **W** is a good approximation also for low-frequency diffusion behavior, when the maximum diffusion length given by the vessel dimensions is big compared to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

## 2.2.5 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 below

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

The first input parameter  $W$  is provided as  $\Omega s^{-1/2}$  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).

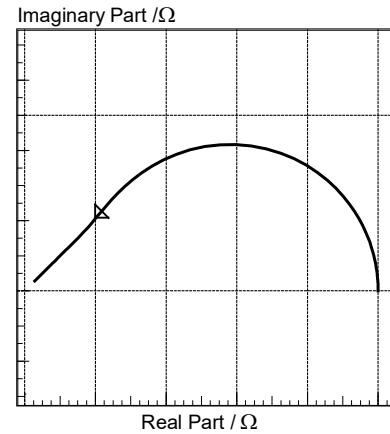


The upper expression is valid if the diffusion overvoltage dominates the overall process. Otherwise, the kinetic parameters of the other contributing steps may appear in the expression for  $Z_N$ . Frequently a significant charge transfer overvoltage is present. This case corresponds to the “Randles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

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

$d_N$  = thickness of layer,  $D_K$  = constant of diffusion

The 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).



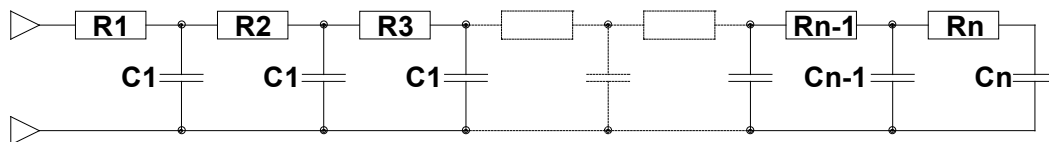
*Nernst* is a good approximation for the frequency behavior of the diffusion, when the free diffusion length limited for instance by convection is comparable to the range of the diffusion within a period of the test frequency (also as an approximation for a rotating disk electrode).

## 2.2.6 Finite diffusion

The 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  $1/s$ .



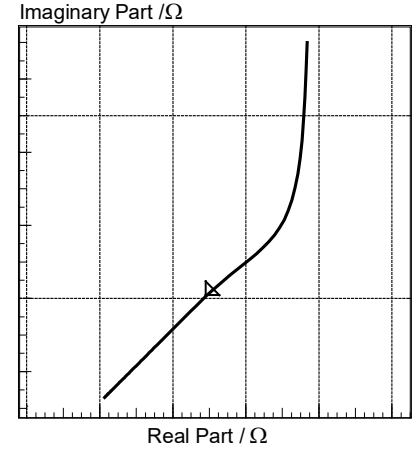
The upper expression is valid if the diffusion overvoltage dominates the overall process. Otherwise, the kinetic parameters of the other contributing steps may appear in the expression for  $Z_S$ . Frequently a significant charge transfer overvoltage is present. This case corresponds to the “Randles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

$$Z_s = \frac{W}{\sqrt{j \cdot \omega}} \coth \sqrt{\frac{j \cdot \omega}{k_s}}$$

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

$d$  = 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 the diffusion within a period of the test frequency.

### 2.2.7 Homogeneous reaction impedance

Homogeneous 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  $1/s$ .

$$W^* = \frac{|v_1| \cdot p_1 \cdot R \cdot T \cdot a \cdot q}{z^2 \cdot F^2 \cdot c_1 \cdot \sqrt{D_1} \cdot A \cdot (1 + q)} \quad \text{with } a = \frac{\text{partial current } I_k}{\text{exchange current } I^*}, A : \text{surface of electrode}$$

$$k = \frac{j_0 \cdot p \cdot v}{c} \cdot (1 - q) \quad \text{with } j_0 : \text{rate of homogeneous reaction } (v_1 s_1 + \dots \rightarrow v s)$$

$$q = \frac{p_1 \cdot v_1}{p \cdot v} \cdot \frac{c}{c_1}$$

### 2.2.8 Constant phase element

A constant phase element (CPE) is an element similar to the capacitor, but with an absolute phase angle of less than  $90^\circ$ . The CPE is extended through a normalization factor  $\omega/\omega_0$ , to enable the use of the parameter  $V$  with the dimension 'Farad'. Setting  $\omega_0$  to 1000Hz adjusts the transfer function to the impedance of a capacitor with the same 'Farad' value in the center of the typical frequency range of a double layer capacity. Set  $\omega_0$  to  $1/2\pi$  to adjust the transfer function to the literature behavior.

The parameter " $V$ " is put in as F (Farad), the exponent  $\alpha$  is dimensionless  $1 \geq \alpha$ . The limit value of  $\alpha=1$  leads to the usual capacitive behavior.

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

with  $\omega_0$  = normalization factor

$$V \cong C \cdot \frac{\delta}{d}$$

$$[V] = 1F$$

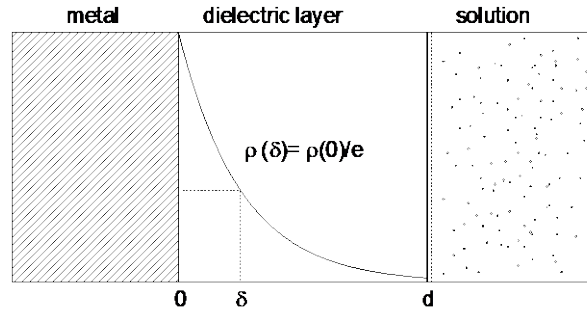
with  $C$  : layer capacity,

### Physical interpretation of $\alpha$

#### gradient of conductivity

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

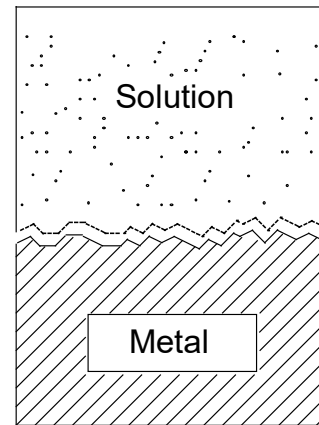
$\frac{\delta}{d}$  = relative penetration depth



#### 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  $\log Z$  vs.  $\log \omega$  = -1

phase shift =  $-90^\circ$

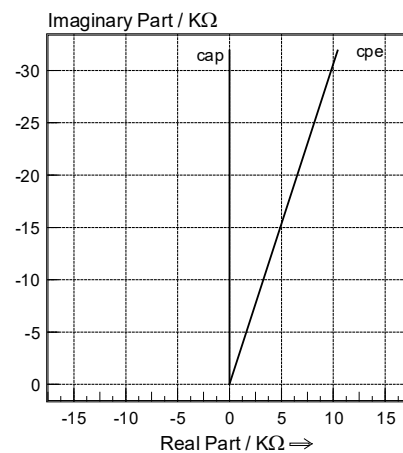
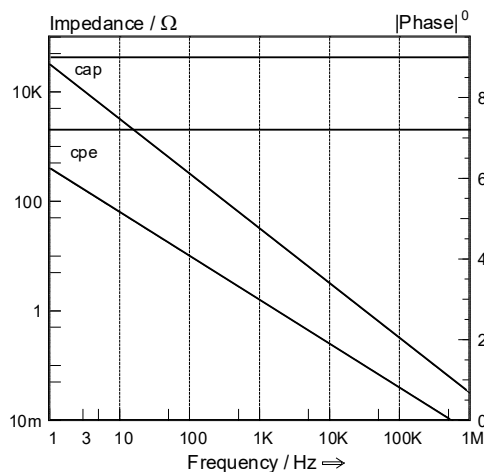
C: at  $\log \omega = 0$

#### CPE - Loss Capacitance

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

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 nearly 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 the more accurate model, like a **Porous Electrode** or the **Young-Göhr** element.

## 2.2.9 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.

$\tau$  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

$$C_Y = \epsilon_0 \cdot \epsilon_r \cdot \frac{A}{d}$$

Capacity of the layer with cross-section  $A$  and thickness  $d$

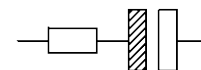
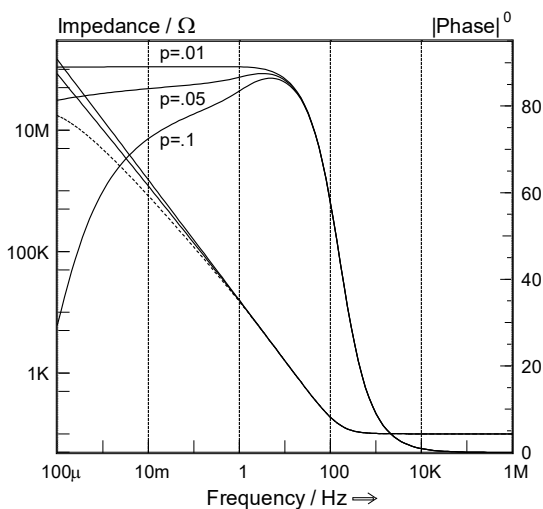
$$\tau = \epsilon_0 \cdot \epsilon_r \cdot \rho_{x=0}$$

Time constant  $\tau$  with dielectric constant  $\epsilon$  and specific resistance  $\rho$ . At  $x=0$  the highest conductivity will be observed

$$\rho_Y = \frac{\delta}{d}$$

Quotient of penetration depth  $\delta$  of conductivity and thickness  $d$  of the passive layer

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



**simulated model**

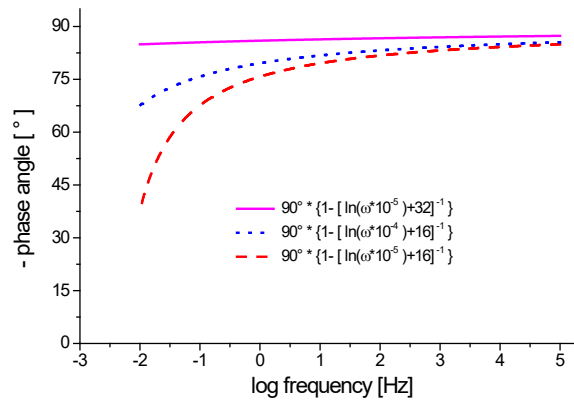
$\tau = 100\text{ms}$   
 $p = 0.1, 0.05, 0.01$   
 $C = 10\mu\text{F}$   
 $R = 100\Omega$

## The CPE approximation

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

$$\varphi = -90^\circ \cdot (1 - q) \quad \text{Phase shift } \varphi \text{ of the Young-Göhr Impedance with } q = \frac{1}{\ln(\omega \cdot t) + \frac{1}{p}}$$

1. Strong gradient in conductivity  $\delta \ll d \Rightarrow$  relative penetration depth  $p \ll 1$
2. High frequencies  $\ln(\omega \cdot t) \ll \frac{1}{p} \Rightarrow q$  constant



## 2.2.10 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 below

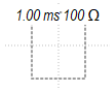
$$Z_R = \frac{W}{\sqrt{j \cdot \omega} + \sqrt{k_R}}$$

Here:  $k_R = \frac{D_K}{r^2}$  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 for the frequency behavior of the diffusion for instance in microelectrodes and microelectrode arrays with low dot densities and in the case of pitting corrosion.

## 2.2.11 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 of 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

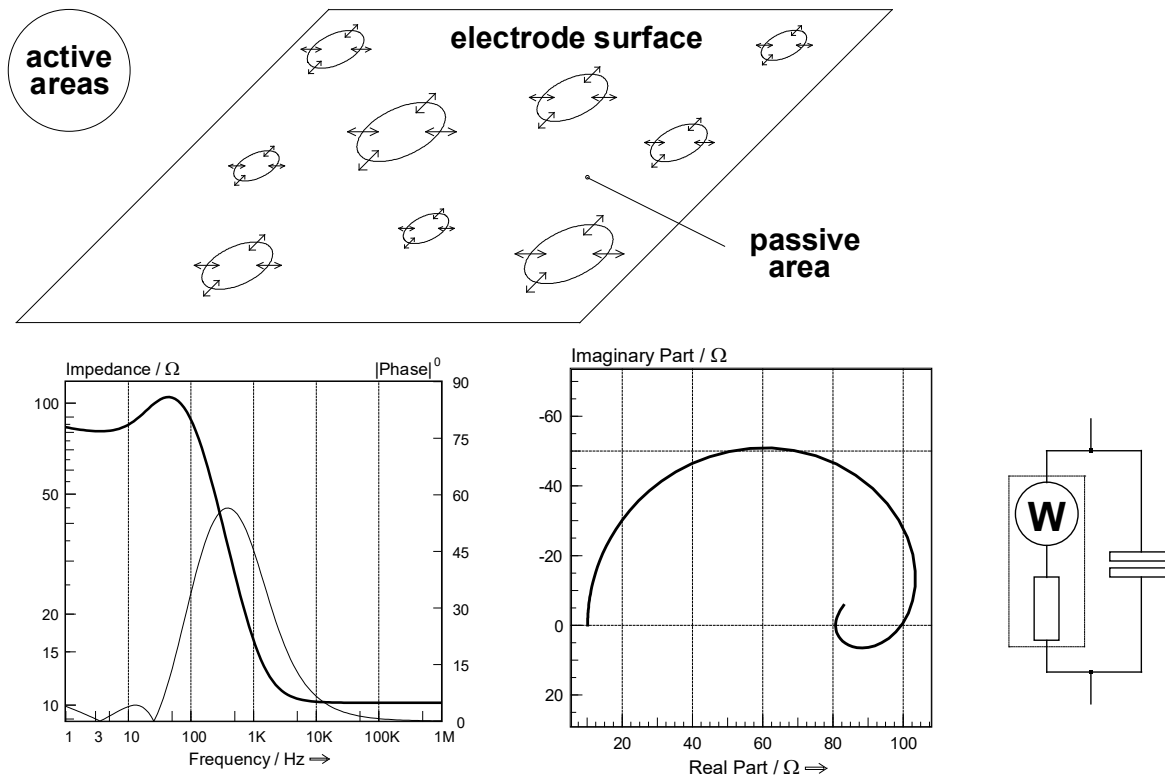


$$Z_F = \frac{R_\eta + Z_C + Z_\theta}{1 + \frac{R_\eta}{Z_k}}$$

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 equilibrium
- the rate constant  $k$  is assumed as *potential dependent*
- the settling of  $k$  is assumed as delayed with a time constant  $\tau$

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  $dK/d\varepsilon$ , normalized by the Faradaic current  $I_f$ . It has the dimension  $\Omega$  of a resistor.

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

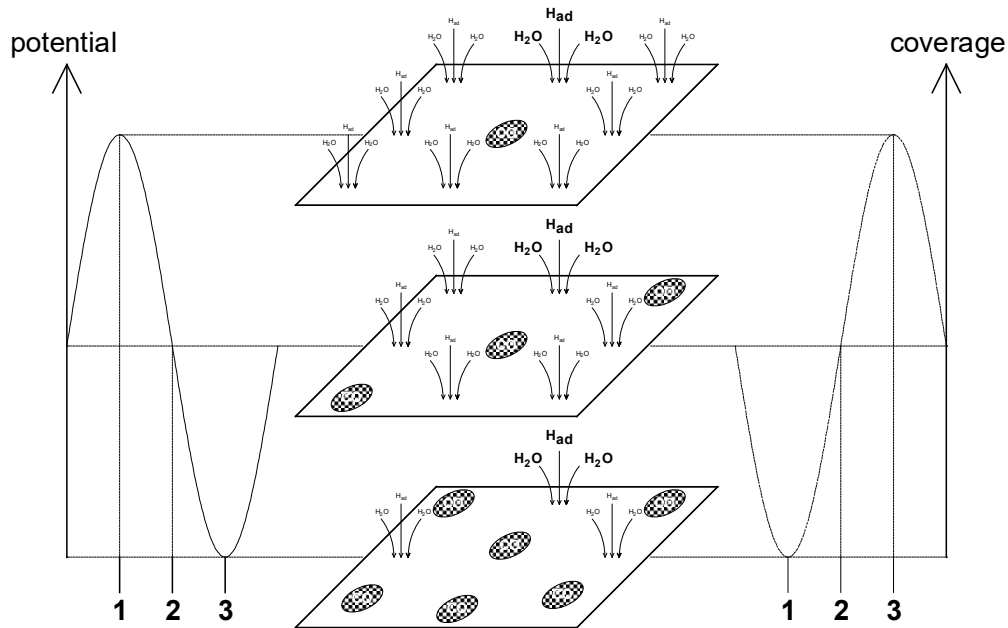
with  $R_\eta$  : charge transfer resistance  
 $Z_C$  : diffusion impedance  
 $Z_\theta$  : coverage impedance

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

with  $\tau$  : time constant of relaxation  
 $\varepsilon$  : potential

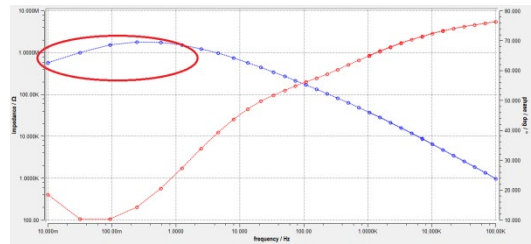
$$R_k = \frac{1}{I_F \cdot \frac{d \ln k}{d \varepsilon}}$$

$R_k$  : relaxation resistance



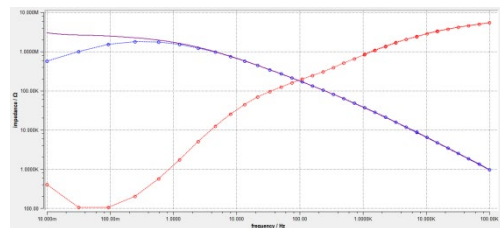
## 2.3 Zwei-pol (two-pole) Hilbert transformation (Z-HIT)

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 red circle).



Unlike impedance, the phase of a system is much 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 (Z). The **Z-HIT** calculates the impedance data  $Z(f)$  from the Phase data  $\varphi(f)$  after the following equation.

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



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 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.

### **3. Current-Voltage curve**

#### **3.1 Current-potential (I/E) curve**

## 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.

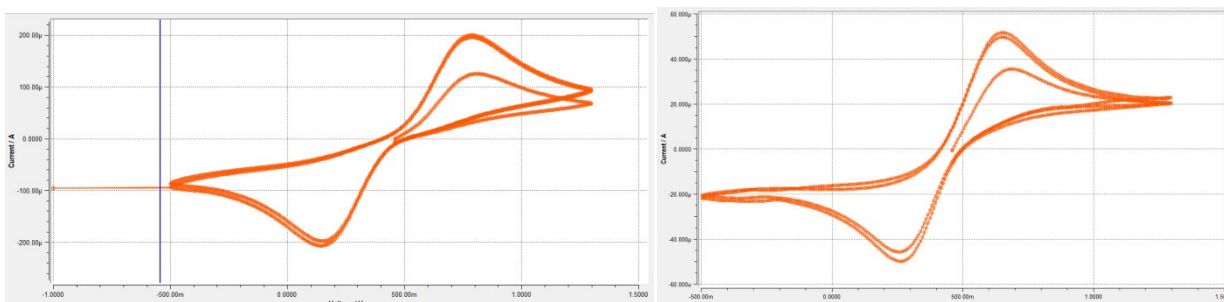
### 1. Open the measured CV

Open the measured current potential curve from **File → Open**. Like EIS, different representations of the current potential 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

### 2. Trim the CV

For trimming the artefact 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.




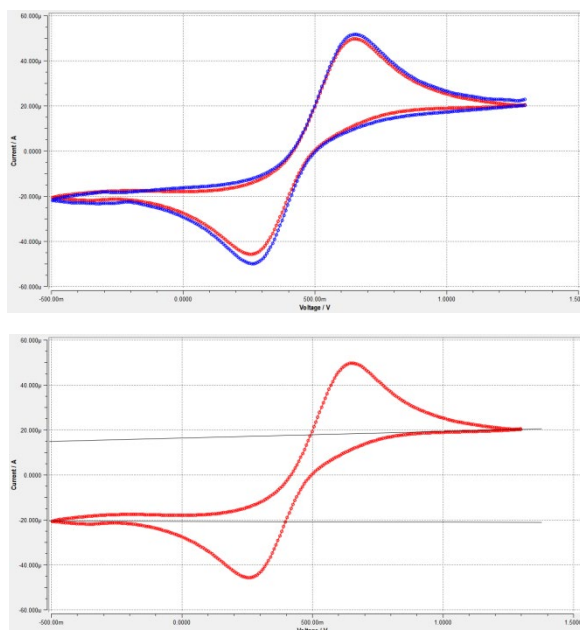
### 3. Split curve

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. (Delete CV from the Data Source window -**window 3**-).

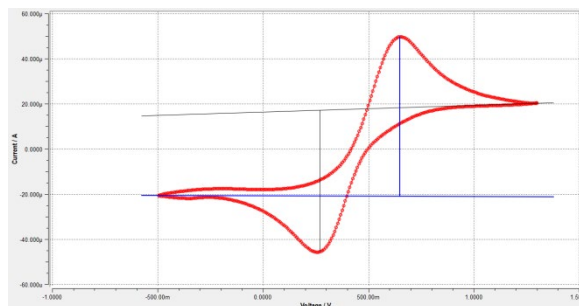
### 4. Draw the Baseline(s)

Draw the baseline 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.




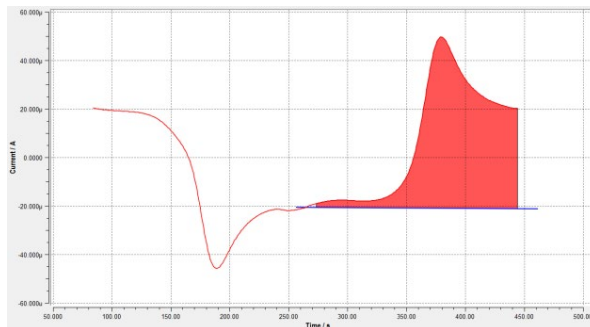
## 5. Peak position

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

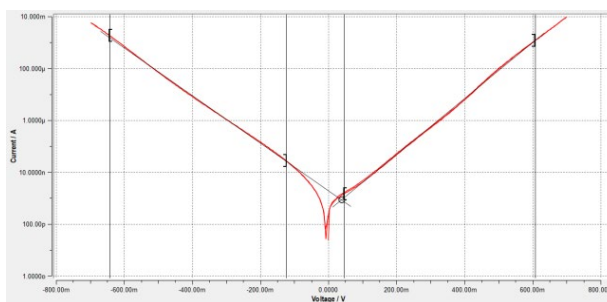
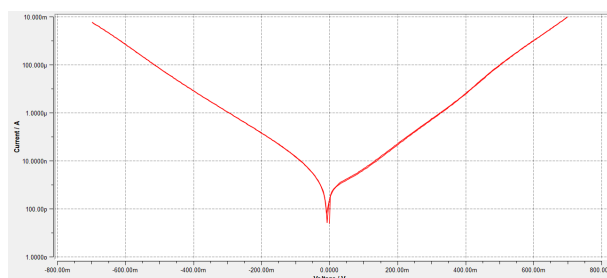
To integrate the area under peak, click on the icon . Then in the "Toolbox" window, set the baseline, "start of peak" and "end of peak". If previously baseline was drawn then that baseline will be automatically chosen. For choosing the start of the peak click "Select" icon and then on the Graph window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




## 3.3 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 potential* 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 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 the *Area of Electrode* (cm<sup>2</sup>), *Density* (g/cm<sup>3</sup>), and *Equivalent Weight* (g/mol). The calculated slope and the corrosion rate are shown in the *Toolbox* window.



## 3.4 Butler-Volmer

Butler-Volmer (BV) parameters can also be calculated from a *log Current vs Potential* 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.

