

## Electrochemical Impedance Spectroscopy (EIS): 1. Basic Principles

Electrochemical Impedance Spectroscopy or EIS is a powerful technique for the characterization of electrochemical systems. The promise of EIS is that, with a single experimental procedure encompassing a sufficiently broad range of frequencies, the influence of the governing physical and chemical phenomena may be isolated and distinguished at a given applied potential.

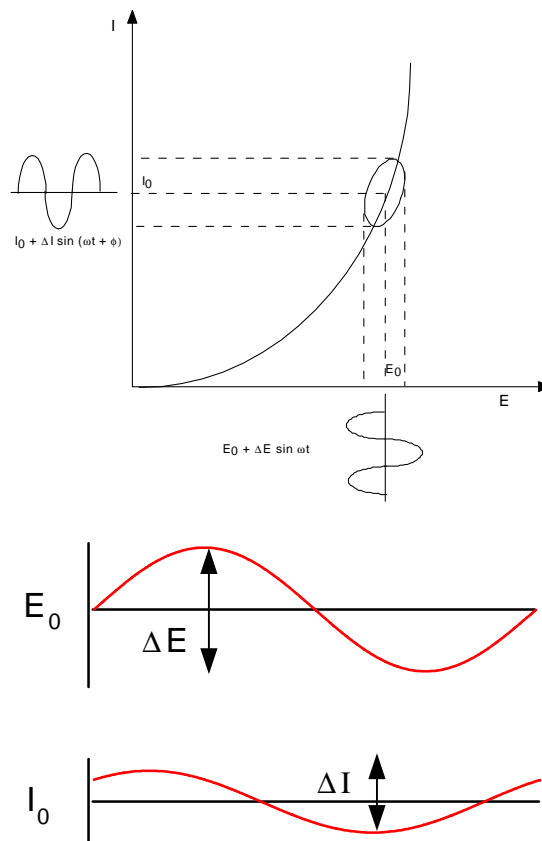
In recent years, EIS has found widespread applications in the field of characterization of materials. It is routinely used in the characterization of coatings, batteries, fuel cells, and corrosion phenomena. It has also been used extensively as a tool for investigating mechanisms in electrodeposition, electrodisolution, passivity, and corrosion studies. It is gaining popularity in the investigation of diffusion of ions across membranes and in the study of semiconductor interfaces.

### Principles of EIS measurements

The fundamental approach of all impedance methods is to apply a small amplitude sinusoidal excitation signal<sup>1</sup> to the system under investigation and measure the response (current or voltage or

<sup>1</sup> This signal is typically voltage or current but can be any other signal of interest, e.g. in the case of Electro-hydrodynamic (EHD) impedance spectroscopy, the signal is rotation speed.

another signal of interest). In the following figure, a non-linear I-V curve for a theoretical electrochemical system is shown.



A low amplitude sine wave  $\Delta E \sin(\omega t)$ , of a particular frequency, is superimposed on the dc polarization voltage  $E_0$ . This results in a current response of a sine wave  $\Delta I \sin(\omega t + \phi)$  superimposed on the dc

current  $I_0$ . The current response is shifted with respect to the applied potential. The Taylor series expansion for the current is given by

$$\Delta I = \left( \frac{dI}{dE} \right)_{E_0, I_0} \Delta E + \frac{1}{2} \left( \frac{d^2 I}{dE^2} \right)_{E_0, I_0} \Delta E^2 + \dots$$

If the magnitude of the perturbing signal  $\Delta E$  is small, then the higher order terms

$$\frac{1}{2} \left( \frac{d^2 I}{dE^2} \right)_{E_0, I_0} \Delta E^2 + \dots$$

in the first equation can be assumed to be negligible. The impedance of the system can then be calculated using Ohm's law as,

$$Z(\omega) = \frac{\Delta E(\omega)}{\Delta I(\omega)}$$

This ratio is called impedance,  $Z(\omega)$ , of the system and is a complex quantity with a magnitude and a phase shift which depends on the frequency of the signal. Therefore by varying the frequency of the applied signal one can get the impedance of the system as a function of frequency. Typically in electrochemistry, a frequency range of 100 kHz – 0.1 Hz is used.

The impedance,  $Z(\omega)$ , as mentioned above is a complex quantity and can be represented in Cartesian as well as polar co-ordinates.

In polar co-ordinates the impedance of the data is represented by,

$$Z(\omega) = |Z(\omega)|e^{j\phi(\omega)}$$

where  $|Z|$  is magnitude of the impedance and  $\phi$  is the phase shift.

In Cartesian co-ordinates the impedance is given by,

$$Z(\omega) = Z_r(\omega) + jZ_i(\omega)$$

where  $Z_r$  is the real part of the impedance and  $Z_i$  is the imaginary part and  $j = \sqrt{-1}$

The plot of the real part of impedance against the imaginary part gives a Nyquist Plot, as shown in Figure 1. The advantage of Nyquist representation is that it gives a quick overview of the data and one can make some qualitative interpretations. While plotting data in the Nyquist format the real axis must be equal to the imaginary axis so as not to distort the shape of the curve. The shape of the curve is important in making qualitative interpretations of the data. The disadvantage of the Nyquist representation is that one loses the frequency dimension of the data. One way of overcoming this problem is by labelling the frequencies on the curve.

The absolute value of impedance and the phase shifts are plotted as a function of frequency in two different plots giving a Bode plot, as shown in Figure 2. This is the more complete way of presenting the data.

The relationship between the two ways of representing the data is as follows:

$$|Z|^2 = (\text{Re } Z)^2 + (\text{Im } Z)^2$$

$$\phi = \tan^{-1} \frac{\text{Im } Z}{\text{Re } Z}$$

or

$$\text{Re}(Z) = |Z| \cos \phi$$

$$\text{Im}(Z) = |Z| \sin \phi$$

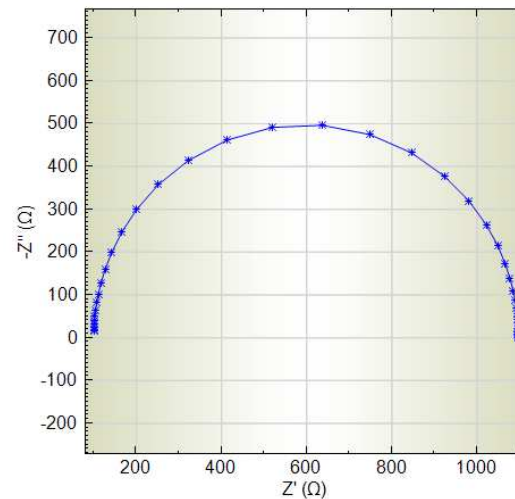


Figure 1 – A typical Nyquist plot

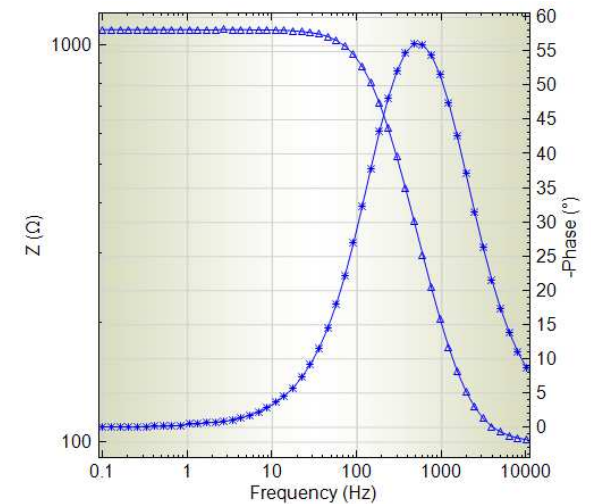
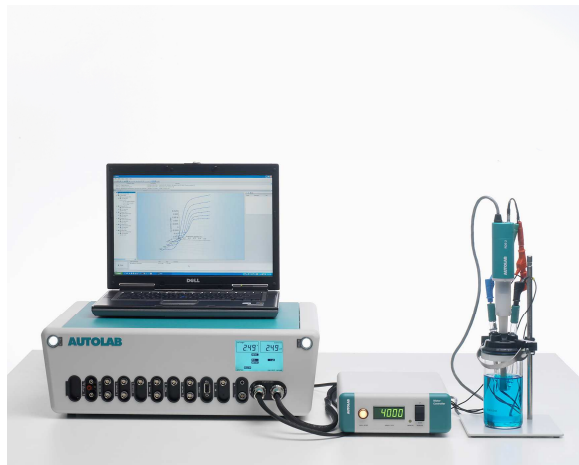


Figure 2 – A typical Bode plot

## Electrochemical Impedance Spectroscopy (EIS): 2. Experimental Set-up

A typical electrochemical impedance experimental set-up consists of an electrochemical cell (the system under investigation), a potentiostat/galvanostat, and a frequency response analyser (FRA). The FRA applies the sine wave and analyses the response of the system to determine the impedance of the system.



### The Electrochemical Cell

The electrochemical cell in an impedance experiment can consist of two, three, or four electrodes. The most basic form of the cell has two electrodes. Usually the electrode under investigation is called the working electrode, and the electrode necessary to close the electrical circuit is called the

counter electrode. The electrodes are usually immersed in a liquid electrolyte. For solid-state systems, there may be a solid electrolyte or no electrolyte.

#### 1 – Two electrode cell

A two-electrode configuration for the cell is used when precise control of the potential is not critical. This arrangement is used to investigate electrolyte properties, such as conductivity, or to characterize solid-state systems.

#### 2 – Three electrode cell

A three-electrode configuration for an electrochemical cell is most common for typical electrochemical applications. A third electrode (the reference electrode) is used to determine the potential of the working electrode precisely. Since the absolute potential of a single electrode cannot be measured, all potential measurements, in electrochemical systems are performed with respect to a reference electrode. A reference electrode, therefore, should be reversible, and its potential should remain constant during the course of the measurement.

#### 3 – Four electrode cell

A four-electrode cell is used to analyse processes occurring within the electrolyte, between two measuring electrodes separated by a membrane. In this configuration, the working electrode and the counter enable current flow. This kind of a cell is usually used to study ion transport through a membrane or to perform electron or ion conductivity

measurements. A four-electrode configuration is also necessary for measurements on low impedance solids where the influence of contact and wire resistance should be minimal.

### Main Experimental Parameters

The main experiment parameters can be divided in the parameters or settings of the potentiostat and the parameters or settings of the FRA.

#### Potentiostat Parameters or Settings

##### 1 – Potentiostatic or Galvanostatic Mode

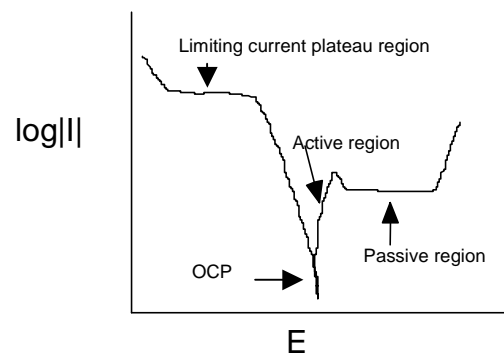
EIS measurements can be done in the potentiostatic or galvanostatic mode. In the potentiostatic mode, experiments are done at a fixed DC potential. A sinusoidal potential perturbation is superimposed on the DC potential and applied to the cell. The resulting current is measured to determine the impedance of the system.

In the galvanostatic mode, experiments are done at a fixed DC current. A sinusoidal current perturbation is superimposed on the DC current and is applied to the cell. The resulting potential is measured to determine the impedance of the system. Typically impedance experiments are done under potentiostatic control. In some cases, e.g. electrodeposition at constant current and battery research, impedance experiments can be performed under galvanostatic control.

## 2 – DC potential or current

Impedance measurements allow the investigation, in detail, of the various phenomena occurring at a certain dc potential (or current) of interest. This DC value is also referred to as the bias potential (or current). In the following figure a typical current potential curve for a corrosion of iron in passivating solution is shown. EIS measurements, in this case, can be performed at the following bias potentials or currents:

- Open circuit potential (OCP), corrosion potential or zero current
- Potential or current in the active region
- Potential or current in the passive region
- Potential or current in the limiting current plateau region



Note: Care must be taken when doing the experiments at OCP. A typical impedance scan takes around 10 minutes. For certain systems, the OCP can drift during the course of the impedance

experiment. If the OCP is measured at start of the impedance scan and the potential bias fixed at that value at the beginning of the scan, then as the experiment progresses, the OCP can change due to changes in the electrode surface. As the bias potential is fixed at the beginning of the experiment, this can result in a difference between the OCP and the potential applied to the working electrode causing in errors. It is desirable that OCP is measured dynamically at each frequency or the measurements are done under galvanostatic control at zero current, thus eliminating the problem.

## FRA Parameters or Settings

### 1 – AC Mode

Single sine or Multi sine: Typically measurements are done in the single sine mode. Multi sine (5 or 15) can be used to save time when measuring very low frequencies.

### 2 – Perturbation (sine wave) amplitude

It is important that the impedance response of a system is linear. The linearity condition implies that the impedance response is independent of the perturbation amplitude. This can be achieved by using small amplitude perturbations. A very small value can give rise to poor signal to noise ratio and hence “noisy” data. A large value can result in the violation of the linearity condition. Typically a value of 10mV is used for most electrochemical systems.

Experimentally, one can verify the linearity condition by performing the same experiment at different perturbation amplitude. The range for which the

impedance is independent of the perturbation amplitude provides the acceptable range. The largest value in this range can be used to give the highest signal to noise ratio.

### 3 – Integration time

As the amplitude of the perturbation is decreased the signal to noise ratio becomes poor. To improve the signal to noise ratio an average of measurements over several sine waves or cycles can be taken. This process of averaging is also referred to as integration and the time needed to measure is called the integration time. Increasing integration time increases the signal to noise ratio.

### 4 – Wait for steady state

During a scan when a new frequency is applied, one needs to wait for some time for the system to stabilize before measurements can start. This can be achieved by skipping the first few cycles.

### 5 – Frequency range

In theory one must choose the widest possible frequency range to capture all the time constants of the system. In practice the frequency range is constrained by the instrument limitations and system considerations.

The highest frequency of an impedance scan is often limited by the high frequency limit of the potentiostat and the slow response of the reference electrode. Typically potentiostats can go up to 1 MHz.

The measurement time at each frequency is the inverse of the frequency. Hence, a very low frequency limit can result in a very long time for the collection of a complete scan. For example the measurement of one data point at a frequency of 1mHz will take 1000s. For systems that are changing with time (e.g. due to corrosion, growth of a film etc.) this implies that the system has changed during the course of the data collection. Therefore, the low frequency limit should be chosen to ensure minimal change in the system during data collection.

A frequency range of 100 kHz – 0.1 Hz is typically used for most electrochemical systems. The total measurement time for this frequency range is around 10 minutes.

#### 6 – Frequency distribution

The frequency can be distributed over the frequency range linearly, logarithmically or with a square root distribution. The most common distribution is logarithmic distribution.

## Electrochemical Impedance Spectroscopy (EIS): 3. Data Analysis

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

### Equivalent circuit models

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

#### Resistance, $R$

The circuit element Resistance,  $R$ , has an impedance of

$$Z = R$$

The impedance is independent of frequency and has no imaginary part. The current through a resistor is always in phase with the voltage.

Some examples of the use of Resistance,  $R$ , to describe electrochemical phenomena are:

#### 1 – Ohmic resistance, $R_{\Omega}$

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

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

where,  $\kappa$  is the specific conductivity of the bulk electrolyte,  $r$  is the radius of the disc.

For more complex geometries the ohmic resistance is determined experimentally and can be estimated by impedance spectroscopy. In a Nyquist plot, the intersection of the impedance data with the real part of the axis at the high frequency end gives the ohmic resistance.

#### 2 – Polarization resistance, $R_p$

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

by reaction kinetics and diffusion of reactants both towards and away from the electrode.

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

$$I = I_{corr} \left( e^{\frac{\eta}{\beta_a}} - e^{-\frac{\eta}{\beta_c}} \right)$$

Where,

$I$  is the measured cell current,  
 $I_{corr}$  is the corrosion current,  
 $\eta$  is the over potential,  
 $\beta_a$  is the anodic Tafel coefficient,  
 $\beta_c$  is the cathodic Tafel coefficient.

For small  $\eta$  the above equation can be transformed to:

$$I_{corr} = \frac{\beta_a \beta_c}{(\beta_a + \beta_c)} \left( \frac{1}{R_p} \right)$$

The parameter,  $R_p$ , the polarization resistance behaves like a resistor. If the Tafel constants are known, one can calculate the  $I_{corr}$  from  $R_p$ .  $I_{corr}$  can be used to calculate the corrosion rate.

### Capacitance, C

The circuit element Capacitance, C, has an impedance of

$$Z = \frac{1}{j \omega C}$$

The impedance of capacitors is a function of frequency and has only an imaginary part. A capacitor's impedance decreases as the frequency is raised. The current through a capacitor is phase shifted -90° with respect to voltage.

Some examples of the use of Capacitance to describe electrochemical phenomena are:

#### 1 – Double layer capacitance, $C_{dl}$

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

#### 2 – Coating capacitance, $C_c$

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

$$C_c = \frac{\epsilon \epsilon_0 A}{d}$$

Where,

$\epsilon$  is the dielectric constant of the coating,  
 $\epsilon_0$  is the dielectric constant of vacuum,  
 A is the area of the coating,  
 D is the thickness of the coating.

Typical dielectric constants of coatings are in the range 3-4 and of water around 80. When water penetrates the coating, its dielectric constant increases resulting in the increase in the coating capacitance. Hence,  $C_c$  can be used to measure the water absorbed by the coating.

### Constant Phase Element, CPE

Modelling an electrochemical phenomenon with an ideal capacitor assumes that the surface under investigation is homogeneous which is normally not the case. This lack of homogeneity is modelled with a CPE

$$Z = \frac{1}{(j \omega C)^\alpha}$$

where, C is the ideal capacitance and  $\alpha$  is an empirical constant,  $0 \leq \alpha \leq 1$ . When  $\alpha = 1$ , CPE acts as an ideal capacitor. Double layer capacitance and coating capacitance, described in the previous section, are usually modelled with a CPE.

### Warburg Impedance, $Z_{war}$

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

$$Z = \frac{R}{\sqrt{j\omega}}$$

Where,

R is the diffusion resistance.

Under the assumption of a finite diffusion layer thickness (Nernst hypothesis), the impedance is:

$$Z = R \frac{\tanh \sqrt{j \omega \tau}}{\sqrt{\tau}}$$

$$\tau = \frac{\delta^2}{D}$$

Where,

R is the diffusion resistance,  
 $\tau$  is the diffusion time constant  
 $\delta$  is the diffusion layer thickness  
 D is the diffusion coefficient.

**Inductance, L**

The impedance of element Inductance, L, is


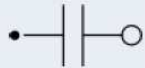

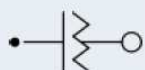
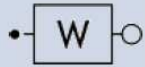

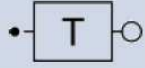

$$Z = j \omega L$$

The impedance of an inductor increases with frequency. Like capacitors, inductors have only an imaginary impedance component. But current through an inductor is phase shifted +90 degrees with respect to the voltage.

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

Inductive behaviour can also result from non-uniform current distribution, inductance of cell cables, slow response of reference electrodes and potentiostat non-idealities. In these cases, the appearance of inductance indicates an error in the EIS measurement.

The table shown on the right provides a summary of the different circuit elements that can be used for data analysis of impedance spectroscopy.

Element	Symbol	Expression
R, resistance		$Z_R = R$
C, capacitance		$Z_C = \frac{-j}{\omega C}$
L, inductance		$Z_L = j\omega L$
Q, constant phase element		$Z_Q = \frac{1}{Y_0(j\omega)^n}$
W, Warburg impedance		$Z_W = \frac{1}{Y_0\sqrt{j\omega}}$
O, cotangent hyperbolic		$Z_O = (Y_0\sqrt{j\omega})^{-1} \tanh(B\sqrt{j\omega})$
T, tangent hyperbolic		$Z_T = (Y_0\sqrt{j\omega})^{-1} \coth(B\sqrt{j\omega})$
G, Gerischer impedance		$Z_G = \frac{1}{Y_0\sqrt{(k_a + j\omega)}}$

## Electrochemical Impedance Spectroscopy (EIS): 4. Equivalent circuit models

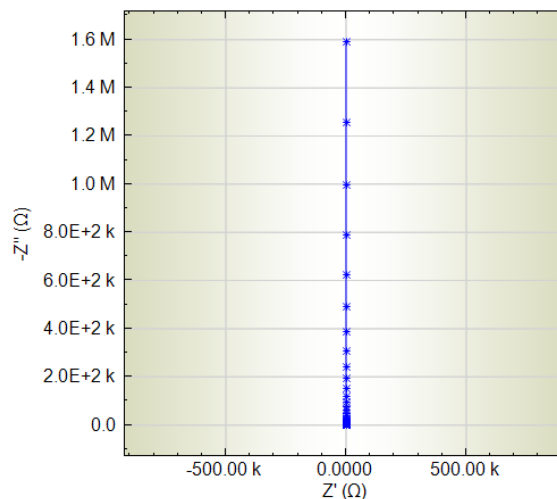
The passive circuit elements, described in the previous note on data analysis, can be combined in series and parallel to build equivalent circuit models, which can then be used to model the various phenomena going on at the interface. In this note the use of the circuit elements to build models is described.

### Model 1

A resistance and a capacitance in series

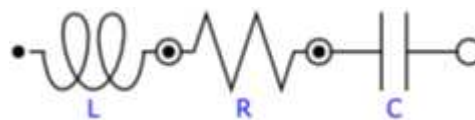


Model 1 can be used, for example, to model a metal with an undamaged high impedance coating.

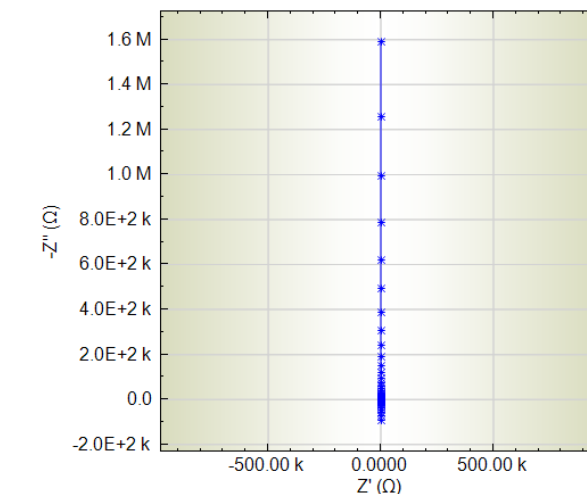


### Model 2

A resistance, a capacitance and an inductance in series

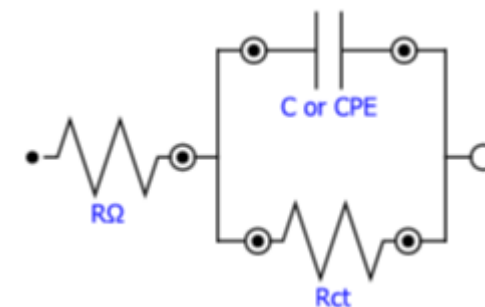


Model 2 can be used to model the response of a supercapacitor.



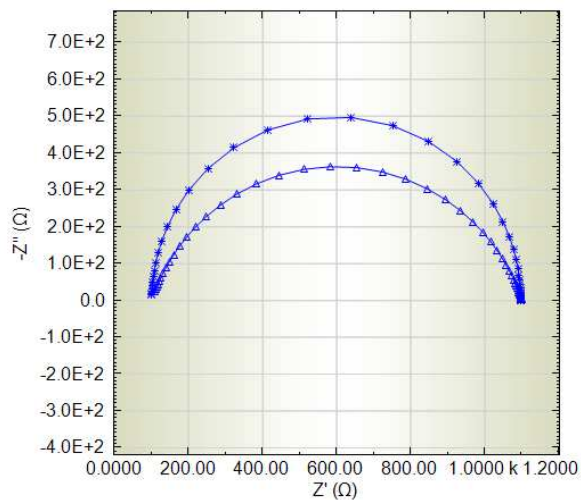
### Model 3

A resistance and a capacitance in parallel (Randles circuit)



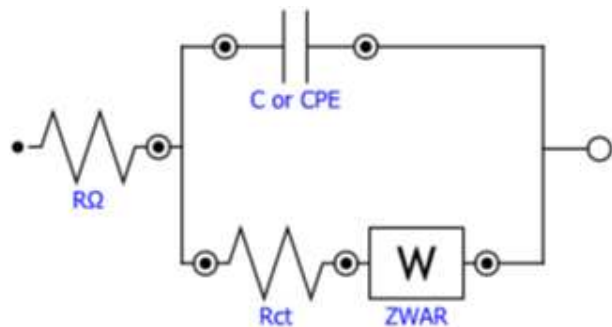
The Randles circuit is one of the simplest and most common cell models. It includes a solution resistance, a double layer capacitor or a CPE and a

polarization resistance. It is used to model corrosion processes and is often the starting point for other more complex models.

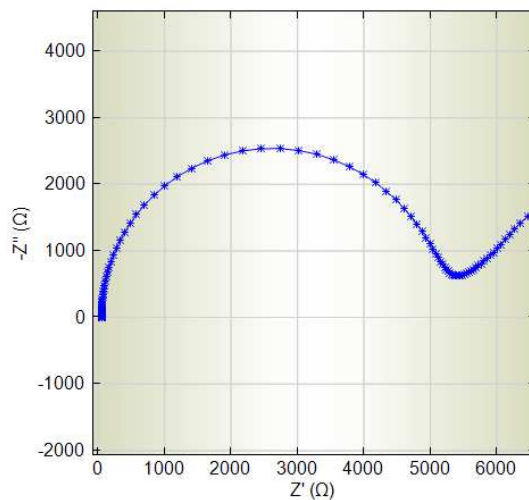


### Model 4

Mixed kinetic and diffusion control

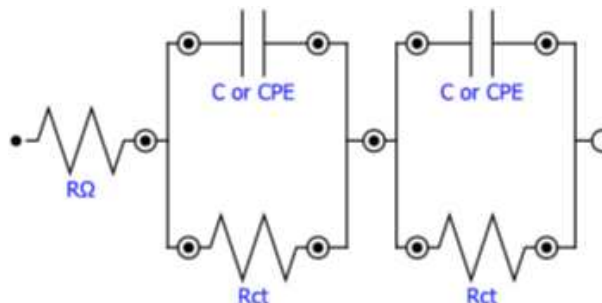


Model 4 can be used to describe electrode processes when both kinetics and diffusion are important.

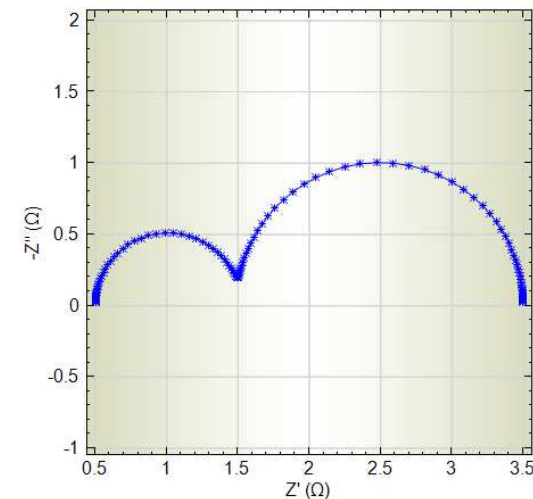


### Model 5

Two Randles circuits in series

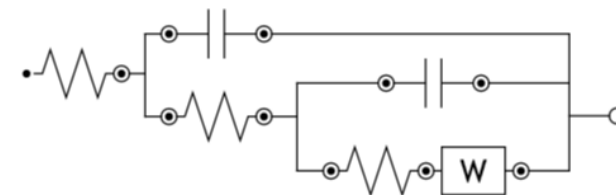


Model 5 can be used, for example, to model the response of batteries.

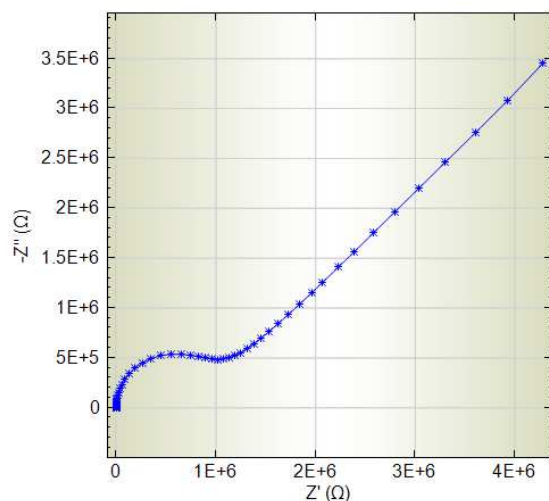


### Model 6

A complex circuit



Model 6 can be used, for example, to describe the impedance of an organic coating on a metal substrate in contact with an electrolyte.



### Non uniqueness of models

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

Moreover, it is important to keep in mind at all times that several arrangements of circuit elements are possible for a given set of data and that some equivalent circuits are mathematically identical (see application note #15).

## Electrochemical Impedance Spectroscopy (EIS): 5. Parameter Estimation

In the previous application note on equivalent circuit models, an overview of the different circuit elements that are used to build an equivalent circuit model was given. It was shown that these circuit elements provide the building blocks for more complex models. After identifying a suitable model for the system under investigation, the next step in the data analysis is estimation of the model parameters. This is done by the non-linear regression of the model to the data. Most impedance systems come with a data-fitting program. Although these programs can be used as a black box, care must be taken to avoid problems.

### Weighting the data

The fitting of a model to data is the minimization of the objective function,  $J$ , using a non-linear regression routine.

$$J = \sum_k \frac{(Z_{r,k} - \hat{Z}_{r,k})^2}{w_{r,k}^2} + \sum_k \frac{(Z_{j,k} - \hat{Z}_{j,k})^2}{w_{j,k}^2}$$

Where,

$Z_{r,k}$ ,  $Z_{j,k}$  are the real and imaginary data

$\hat{Z}_{r,k}$ ,  $\hat{Z}_{j,k}$  are the real and imaginary model

$w_{r,k}$ ,  $w_{j,k}$  are the real and imaginary weights

There are several different weighting strategies that are possible. The three most common strategies are described in this section.

#### 1 – No weighting

$$w_{r,k} = w_{j,k} = 1$$

In impedance spectroscopy the value of low frequency data points is usually much larger than that of the high frequency data points (sometimes by several orders of magnitude). When no weighting is used then the low frequency points would have higher weight than the high frequency points. This introduces a bias and can give large errors in parameter estimation. Therefore, this weighting should not be used.

#### 2 – Proportional weighting

$$w_{r,k} = Z_{r,k}$$

$$w_{j,k} = Z_{j,k}$$

Usually at high and low frequencies the imaginary part of the data goes to zero. In that case proportional weighting can cause numerical problems because of division by zero. Therefore, this weighting should not be used.

#### 2 – Modulus weighting

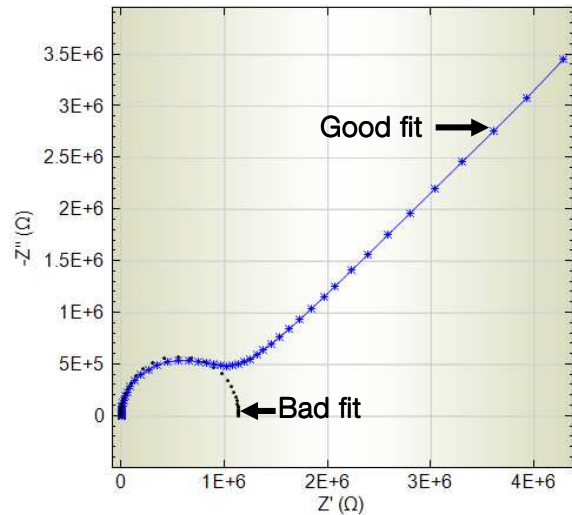
$$w_{r,k} = w_{j,k} = |Z|$$

Weighting the data by the absolute value of impedance is the most recommended weighting strategy and is the default weighting in the AUTOLAB software.

### Initial Guess

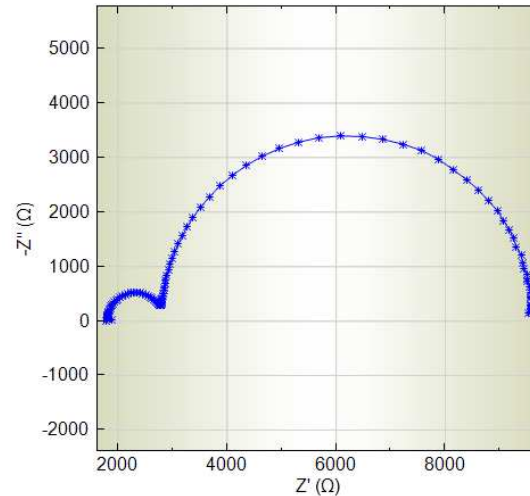
The models in impedance spectroscopy are highly non-linear in parameter space, which implies that the objective function can have several local minima. An initial guess of the parameters is required to begin the regression procedure. A poor choice of the initial guess can result in the procedure terminating at a local minimum with, for example, wrong estimates for the model parameters. A good initial guess requires some experience. An examination of asymptotes and inflexion points in the Nyquist and Bode diagrams can give some clues for making a good initial guess.

In the following figure the errors that can be introduced due to bad initial guess are illustrated. The circles represent the experimental data. The solid line is the result of fit to the data using a good initial guess, and the dotted line represents the result with a poor initial guess. One can see that a poor initial guess can result in poor fit of the model to the data.



### Non-uniqueness of circuit models

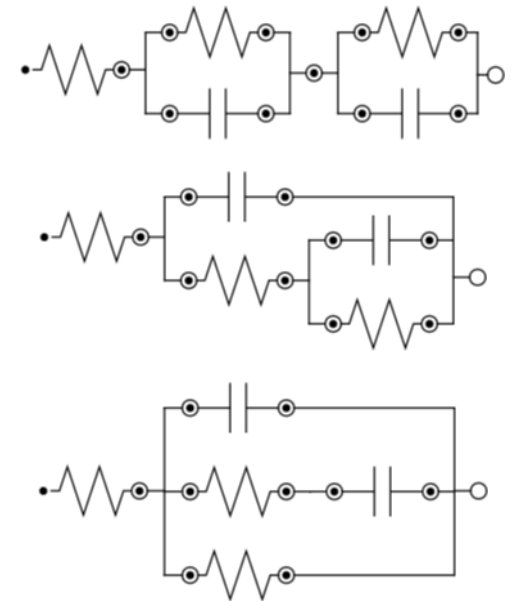
The impedance spectrum, shown in the following figure, shows two clearly defined semi circles.



An equivalent circuit that consists of two RC time constants can model this spectrum. The two RC time constants can be produced by combining the resistances and capacitances in three different ways resulting in three equivalent circuits shown in the following figure. All three circuits when fitted to the data would give an identical fit, with only the circuit parameters being different.

In this case, there is no unique equivalent circuit that describes the spectrum. One cannot assume that an equivalent circuit that produces a good fit to a data set represents an accurate physical model of the cell. One needs prior knowledge or complementary experiments to determine the appropriate model for the data. This is one of the limitations of impedance spectroscopy.

### Equivalent Circuit Models with Two Time Constants



The three equivalent circuits shown above are mathematically identical.