

Introduction to EIS (Electrochemical Impedance Spectroscopy) with EC- Lab[®]/EC-Lab[®] Express

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Understand what is performed during an impedance measurement.

Understand what information can be obtained on the studied electrochemical system

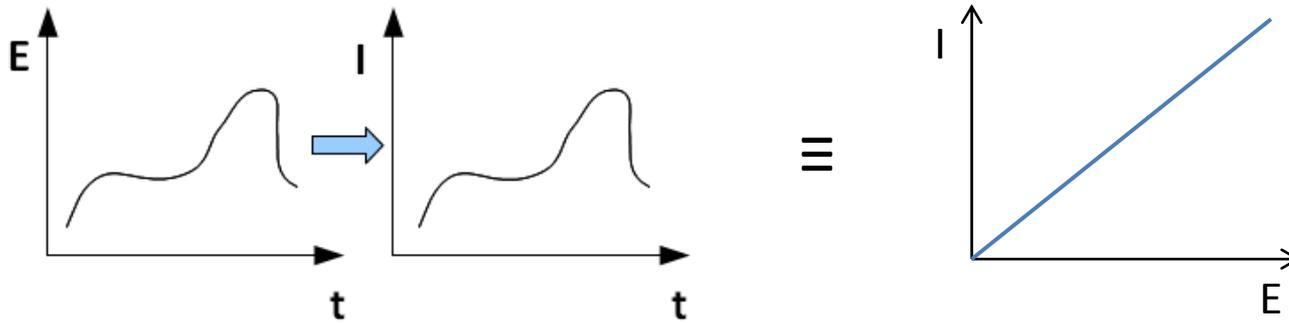
System

in electrochemistry, one electrode or more in an electrolyte... i.e. metal in salt water

Linear System

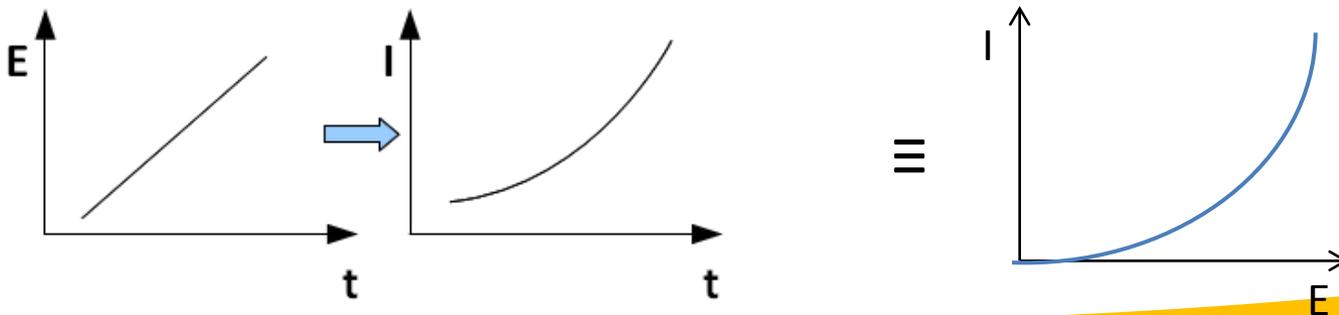
system for which **Current = $k \cdot \text{Potential}$** ($k = \text{constant}$)

Example of such a system : a resistor for which $U = RI$



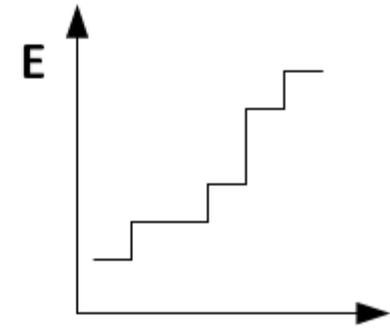
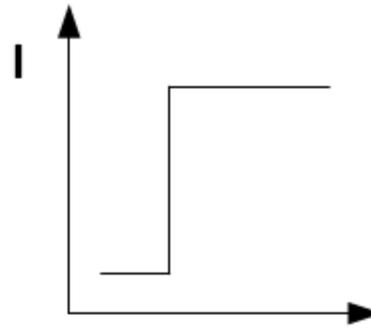
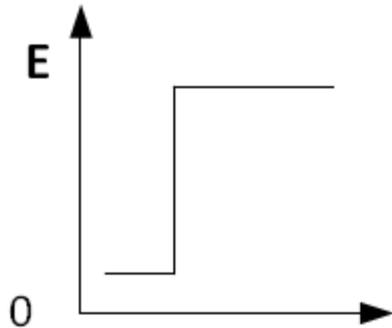
Non-Linear System

system for which **Current = $f(\text{Potential})$** ($f = \text{function that is not a constant}$). Example of such a function in electrochemistry: the Butler-Volmer relation

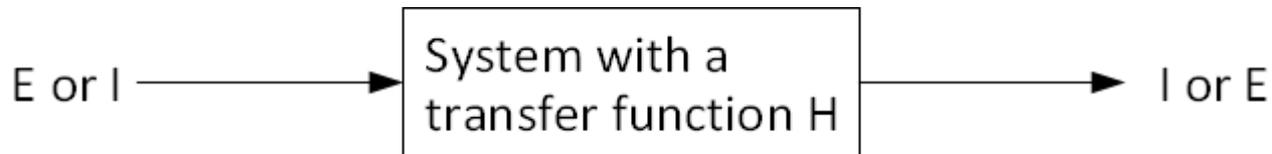


Steady-state perturbation : perturbation that is time-invariant

Ex : chronoamperometry, chronopotentiometry, staircase voltammetry (in certain conditions)



Transfer Function : function that analytically describes how a system will respond to an input



Impedance (Z) : Laplace Transform $[E(t)]$ /Laplace Transform $[I(t)]$

Two main types

1. Steady-state methods (steady-state Voltammetry or Potentiometry etc...)

- . A steady-state perturbation (E or I) is imposed on a system (Cf. Tutorials CV)
- . The response is recorded.

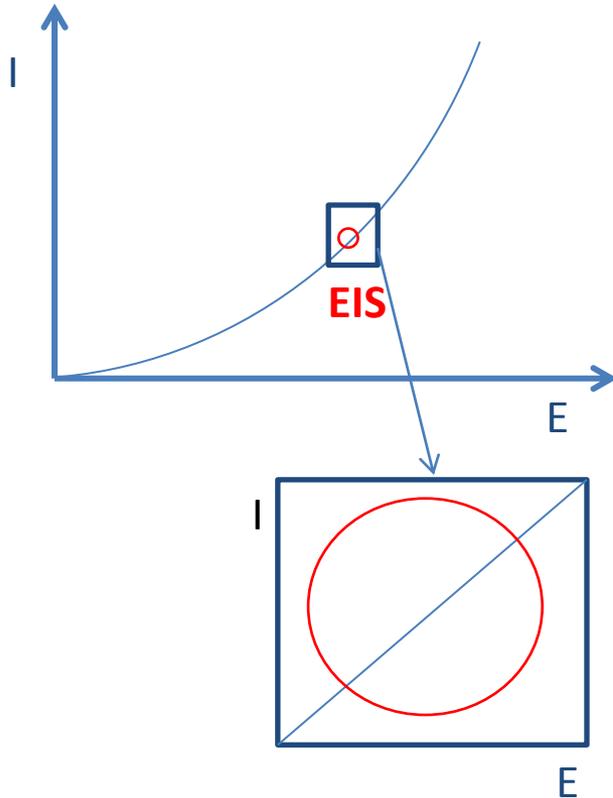
The steady-state response I vs. E
(or E vs. I) can be plotted.

2. Non-steady-state methods (EIS, IMVS, IMPS, CASP, VASP, linear analog potential ramp)

- . A perturbation that is varying with time is imposed on the system.
- . The response is recorded.

The response of the system depends on its transfer function.

AC/DC differences



EIS is a local measurement at one point on the steady-state curve.

In a DC measurement, the scan rate is considered low enough for the steady state when the backward and forward I vs. E curves can be superimposed.

In an AC experiment, the amplitude of the sine wave is chosen to be small enough such that the system is considered to be linear.

Response of an LTI to a sinusoidal potential perturbation

Input (Potential) : $E(t) = E_{ss} + \delta E \sin(2\pi ft)$

Output (Current) : $I(t) = I_{ss} + \delta I \sin(2\pi ft + \varphi)$

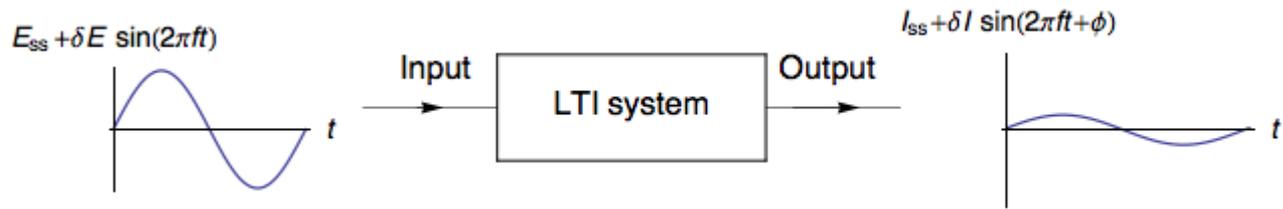
With :

E_{ss}, I_{ss} the steady-state potential and current, respectively

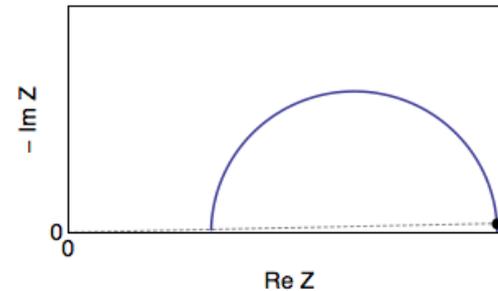
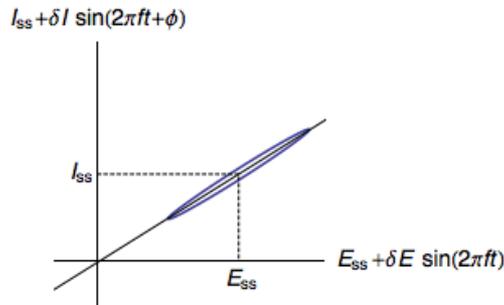
$\delta E, \delta I$ the amplitude modulation of the potential and current, respectively

f the frequency

φ the phase



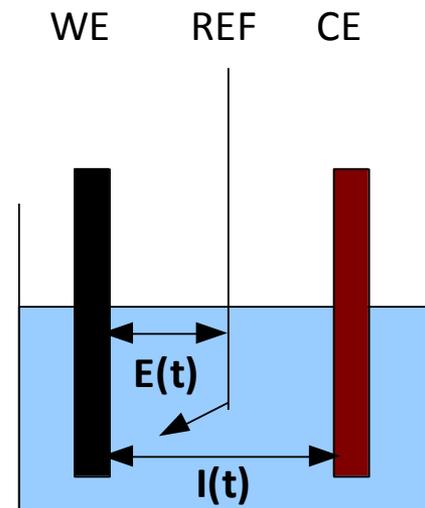
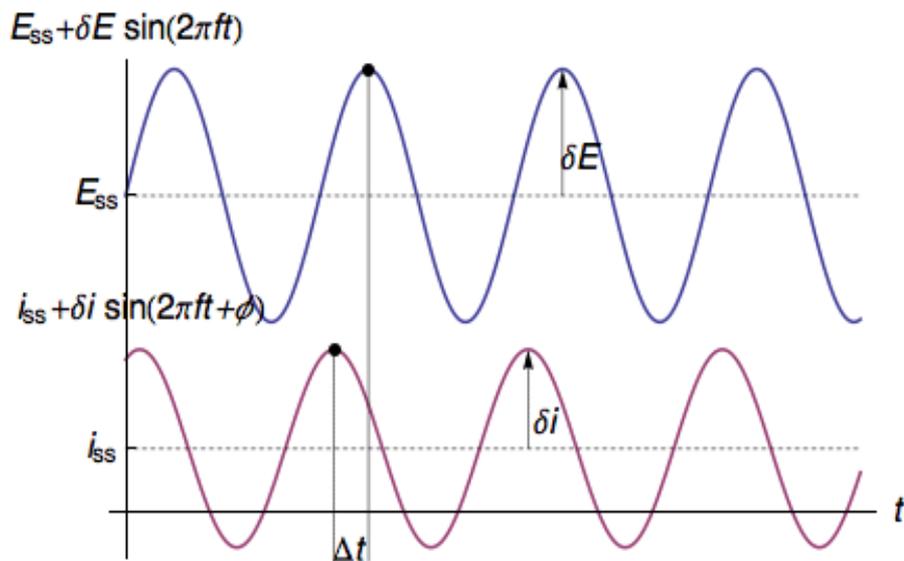
Current response has a different amplitude and is phase-shifted



Increasing the frequency \rightarrow moving away from the steady-state response

What is an impedance measurement ?

The Impedance measurement is based on the study of the response of a system subjected to sinusoidal potential (or current) modulations of various frequencies.



A three-electrode set-up is required.

$$Z = \text{Laplace Transform}[E(t)] / \text{Laplace Transform}[I(t)]$$

The results can be plotted in many different ways.

The most common are Bode (electronics) and Nyquist (electrochemists) plots.

Bode and Nyquist plots

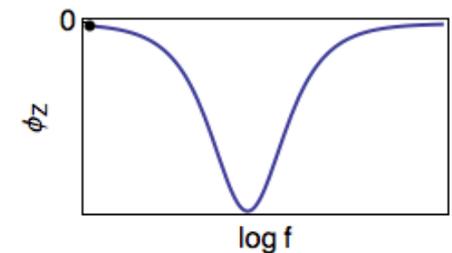
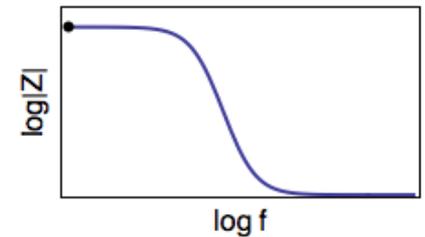
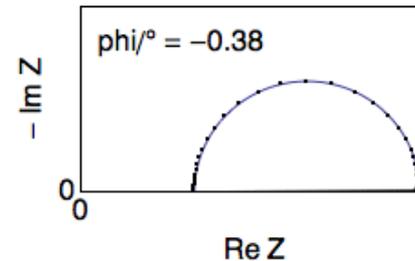
The impedance is a complex number:

$$Z = a + jb = \text{Re}(Z) + j\text{Im}(Z) \text{ (with } j^2 = -1)$$

$$Z = \rho(\cos\varphi + j\sin\varphi) \text{ with } \rho \text{ the modulus and } \varphi \text{ the phase shift}$$

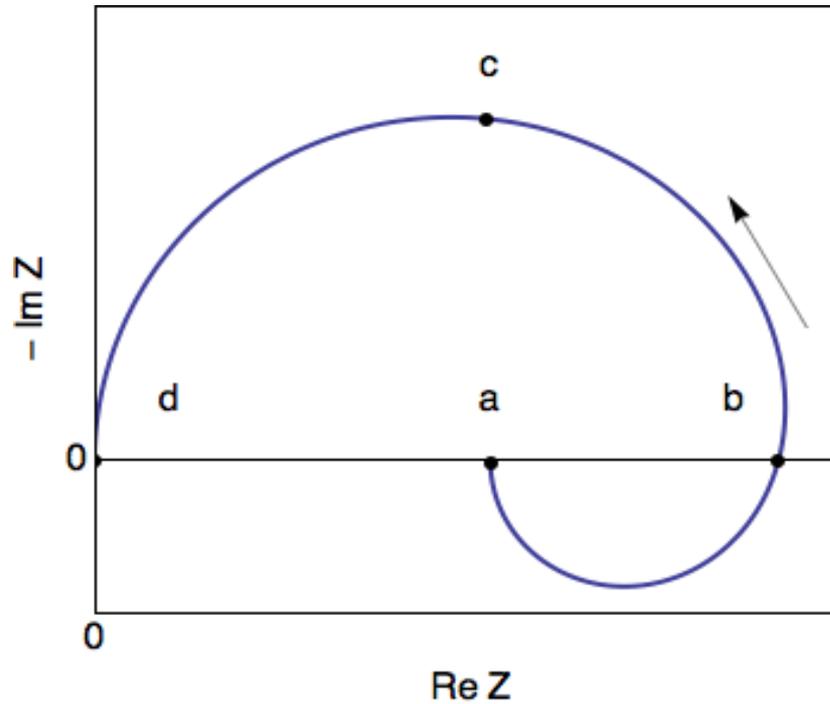
In the Bode Plot, the modulus and the phase of the impedance are plotted against the frequency of the modulation.

In the Nyquist plot, the impedance for each frequency is plotted in the complex plane $-\text{Im}(Z)$ vs. $\text{Re}(Z)$.



How can we deduce Bode plot from Nyquist plot ?

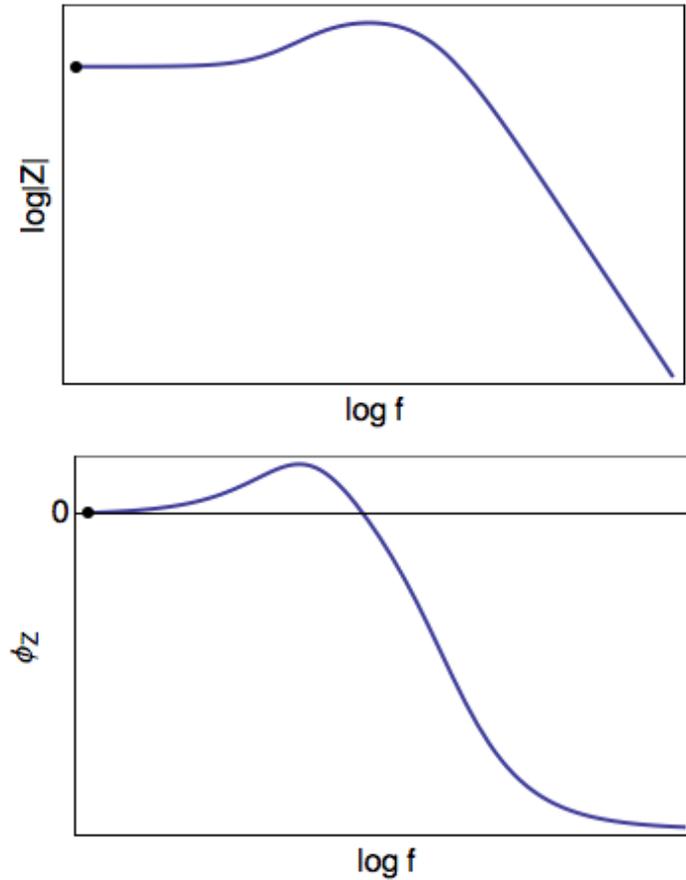
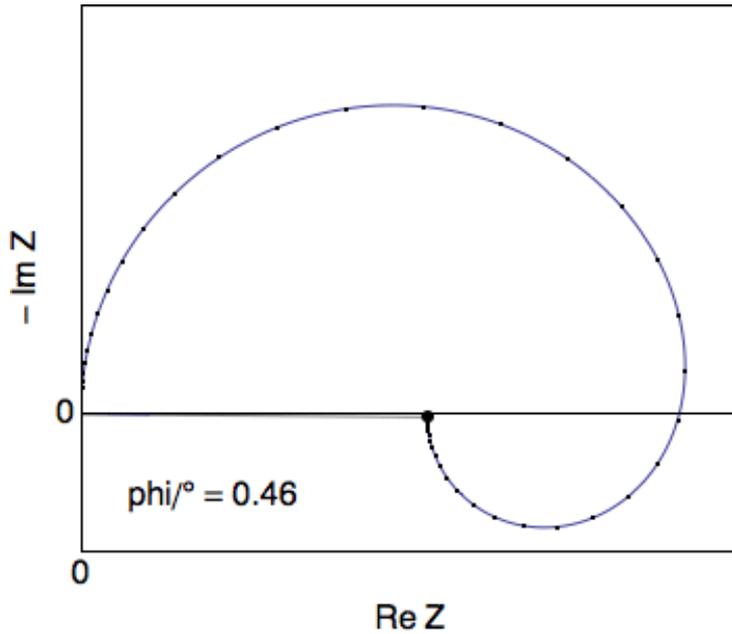
$$|Z| = \sqrt{(\text{Re}(Z))^2 + (\text{Im}(Z))^2}, \varphi_z = \arctan \frac{\text{Im}(Z)}{\text{Re}(Z)}$$

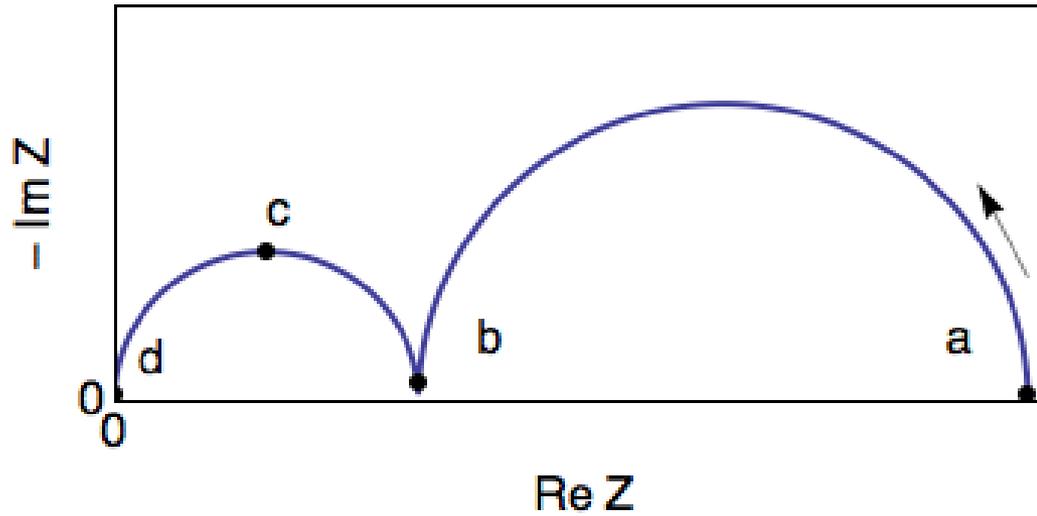


What are the phases of points a, b, c, d ?

What is the shape of the Bode plot ?

All you need is a ruler

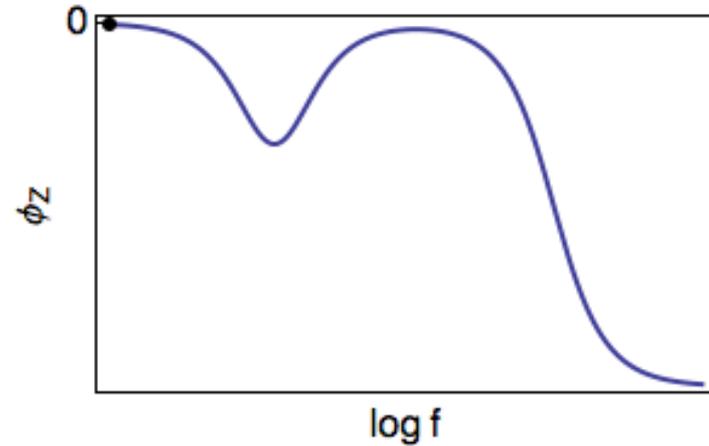
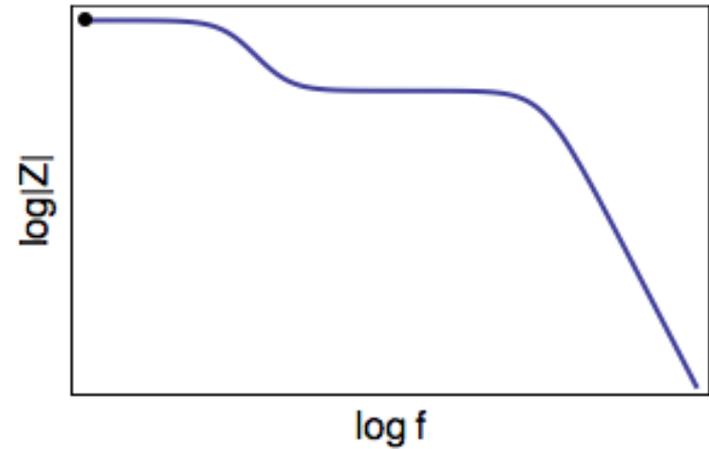
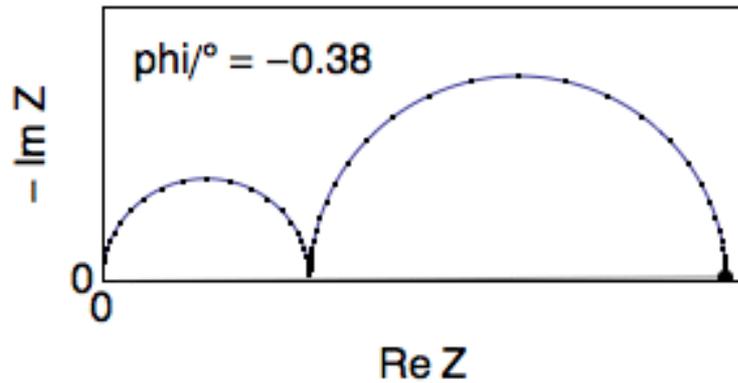




What are the phases of points a , b , c , d ?

What is the shape of the Bode plot ?

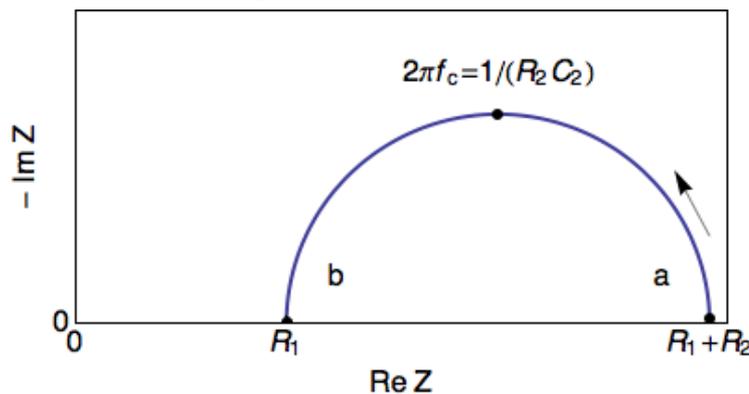
All you need is a ruler



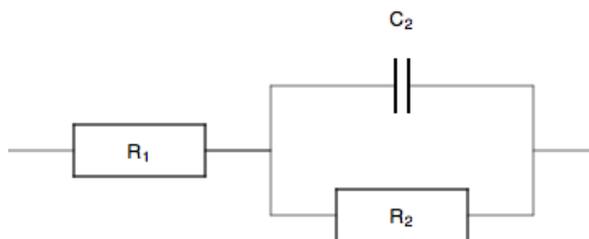
The Faradaic impedance of the reactions taking place at an electrode is equivalent to the Faradaic impedance of an electrical circuit.

Impedance measurements allow us to determine the components of this circuit and their values.

These electrical components are related to the physico-chemical characteristics of the system. Example : if you have this diagram

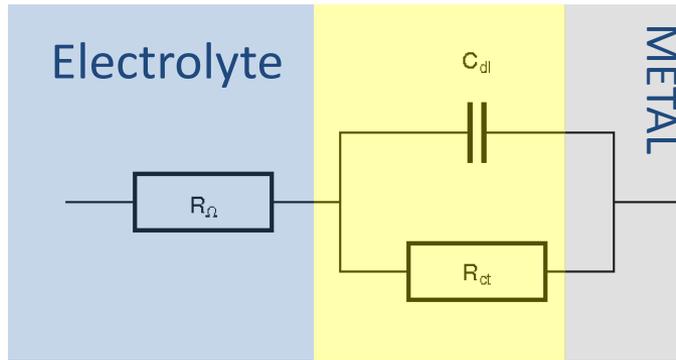


It corresponds to this equivalent circuit (but not only).

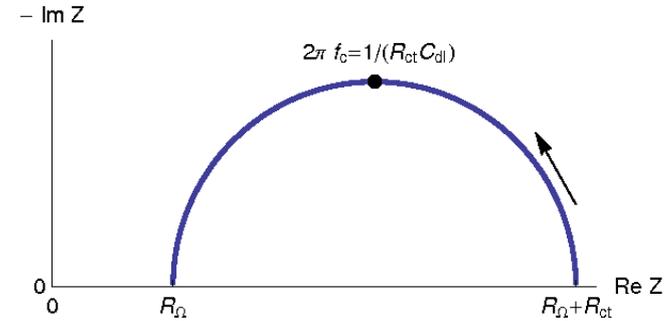


With R_1 : Ohmic drop R_Ω ; C_2 : Double layer capacitance C_{dl}

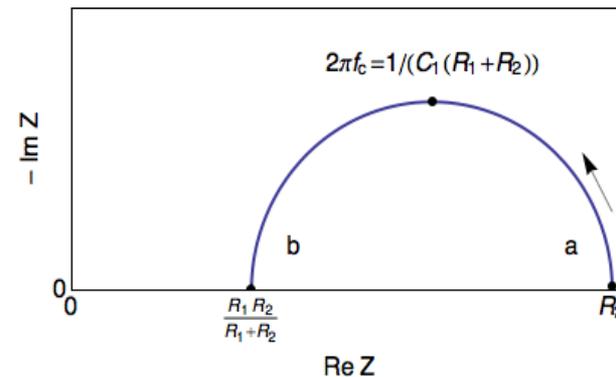
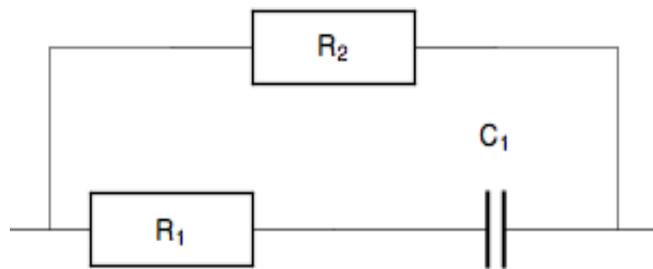
R_2 : Charge transfer resistance R_{ct}



Metal-electrolyte interface



The polarization resistance $R_p = R_{ct} + R_{\Omega}$

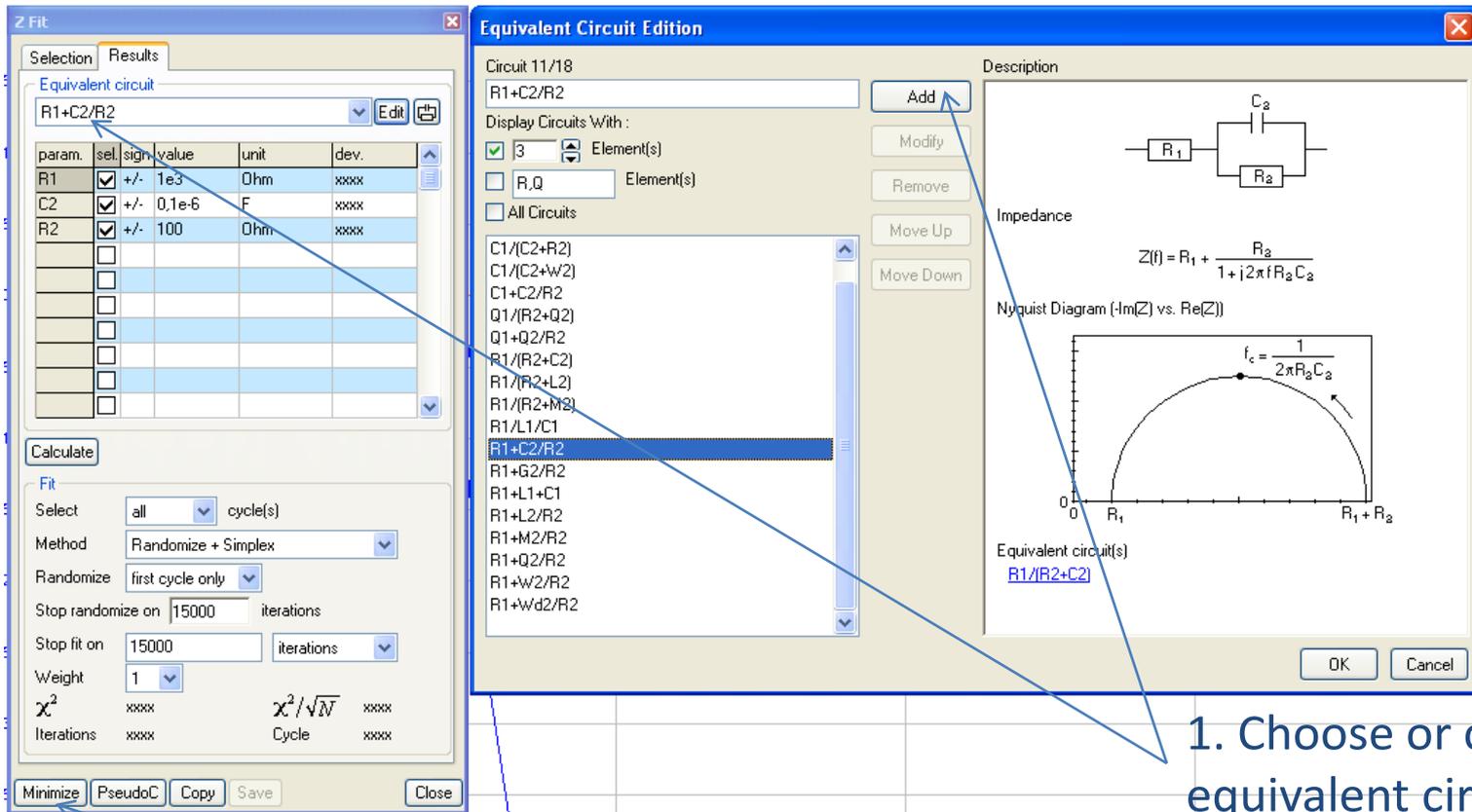


Always choose the circuit that is physically justifiable i.e. its components represent physical quantities.

Z Sim and **Z Fit** are the Impedance tools provided in EC-Lab®

Z Sim : simulates the impedance data corresponding to a given equivalent circuit

ZFit: Find the actual values associated with the components of the chosen equivalent circuit.



Z Fit window details:

param.	sel.	sign.	value	unit	dev.
R1	<input checked="" type="checkbox"/>	+/-	1e3	Ohm	xxxx
C2	<input checked="" type="checkbox"/>	+/-	0,1e-6	F	xxxx
R2	<input checked="" type="checkbox"/>	+/-	100	Ohm	xxxx

Equivalent Circuit Edition window details:

Circuit 11/18: R1+C2/R2

Display Circuits With: 3 Element(s)

Selected circuit: R1+C2/R2

Impedance: $Z(f) = R_1 + \frac{R_2}{1 + j2\pi f R_2 C_2}$

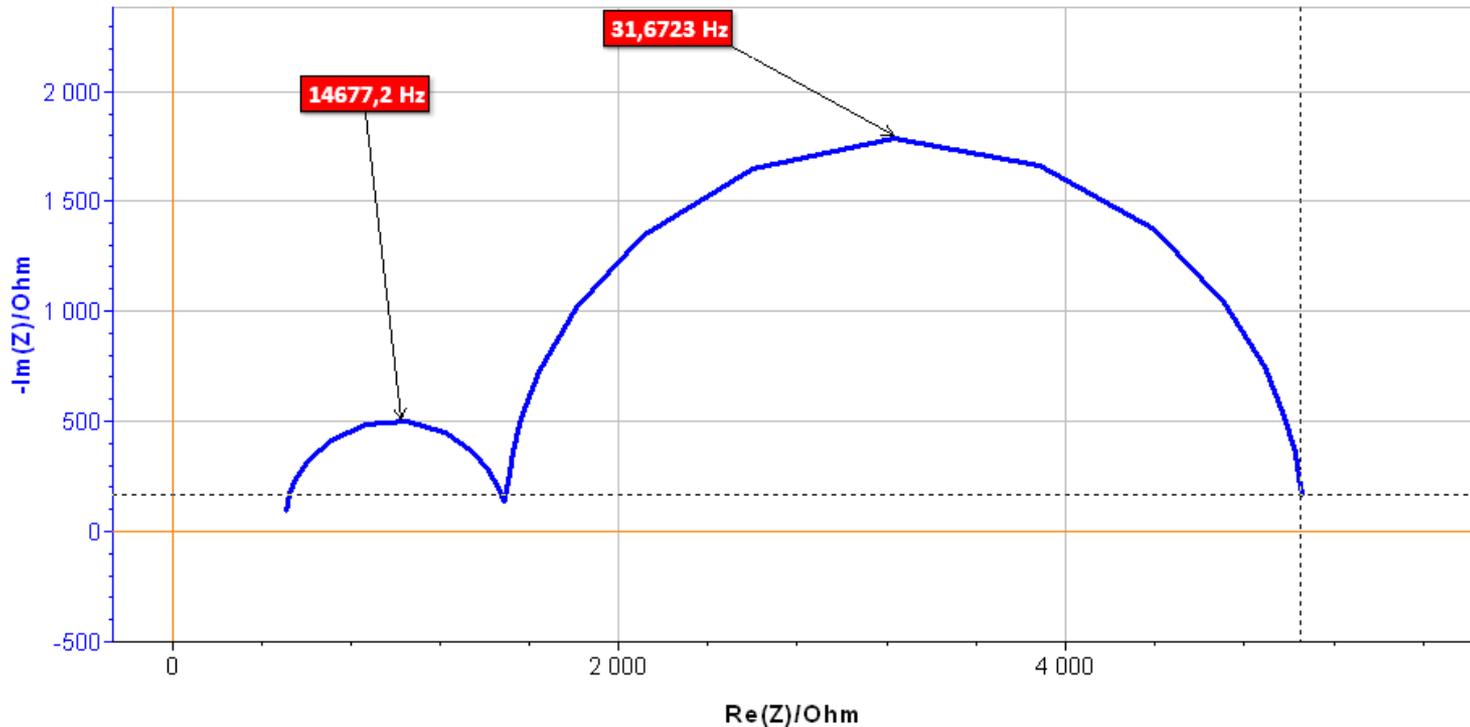
Nyquist Diagram (-Im(Z) vs. Re(Z))

Equivalent circuit(s): R1/R2+C2

1. Choose or create an equivalent circuit

2. Launch the minimization algorithm

Example 1



`\Data\Samples\EIS\PEIS_10loops.mpr`

What is the equivalent circuit ?

What are the values of the components of the circuit ?

Please refer to Application Note #9 for more details

Many available equivalent circuits

Z Fit

Selection Results

Equivalent circuit: $R1+R2/(C2+C3/R3)$

param.	sel.	sign	value	unit	dev.
R1	<input checked="" type="checkbox"/>	+/-	495.8	Ohm	0.289 3
R2	<input checked="" type="checkbox"/>	+/-	4 566	Ohm	0.412
C2	<input checked="" type="checkbox"/>	+/-	1.289e-6	F	0.823 5e-9
C3	<input checked="" type="checkbox"/>	+/-	9.667e-9	F	24.05e-12
R3	<input checked="" type="checkbox"/>	+/-	1 270	Ohm	0.762 2

Calculate

Fit

Select: all cycle(s)

Method: Randomize + Simplex

Randomize: first cycle only

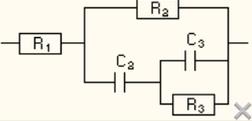
Stop randomize on: 15000 iterations

Stop fit on: 5000 iterations

Weight: 1

Error: 7.803

Iterations: 5000 (Simplex) Cycle xxxx



Z Fit

Selection Results

Equivalent circuit: $R1+C1/(R2+C3/R3)$

param.	sel.	sign	value	unit	dev.
R1	<input checked="" type="checkbox"/>	+/-	495.8	Ohm	0.289 3
C1	<input checked="" type="checkbox"/>	+/-	9.595e-9	F	23.71e-12
R2	<input checked="" type="checkbox"/>	+/-	1 006	Ohm	0.476 7
C3	<input checked="" type="checkbox"/>	+/-	2.105e-6	F	1.59e-9
R3	<input checked="" type="checkbox"/>	+/-	3 561	Ohm	0.529 9

Calculate

Fit

Select: all cycle(s)

Method: Randomize + Simplex

Randomize: first cycle only

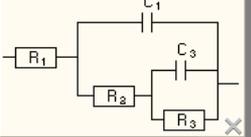
Stop randomize on: 15000 iterations

Stop fit on: 10000 iterations

Weight: 1

Error: 7.803

Iterations: 10000 (Simplex) Cycle xxxx



Z Fit

Selection Results

Equivalent circuit: $R1+C2/R2+C3/R3$

param.	sel.	sign	value	unit	dev.
R1	<input checked="" type="checkbox"/>	+/-	495.8	Ohm	0.289 3
C2	<input checked="" type="checkbox"/>	+/-	9.639e-9	F	23.92e-12
R2	<input checked="" type="checkbox"/>	+/-	996.5	Ohm	0.474 4
C3	<input checked="" type="checkbox"/>	+/-	2.109e-6	F	1.593e-9
R3	<input checked="" type="checkbox"/>	+/-	3 570	Ohm	0.521

Calculate

Fit

Select: all cycle(s)

Method: Randomize + Simplex

Randomize: first cycle only

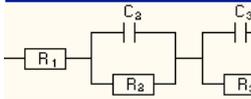
Stop randomize on: 15000 iterations

Stop fit on: 10000 iterations

Weight: 1

Error: 7.803

Iterations: 10000 (Simplex) Cycle xxxx



Z Fit

Selection Results

Equivalent circuit: $R1+C1/R2/(C3+R3)$

param.	sel.	sign	value	unit	dev.
R1	<input checked="" type="checkbox"/>	+/-	495.8	Ohm	0.289 3
C1	<input checked="" type="checkbox"/>	+/-	9.595e-9	F	23.71e-12
R2	<input checked="" type="checkbox"/>	+/-	4 566	Ohm	0.412
C3	<input checked="" type="checkbox"/>	+/-	1.28e-6	F	0.814e-9
R3	<input checked="" type="checkbox"/>	+/-	1 290	Ohm	0.774 9

Calculate

Fit

Select: all cycle(s)

Method: Randomize + Simplex

Randomize: first cycle only

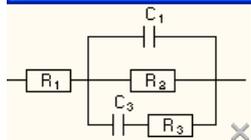
Stop randomize on: 15000 iterations

Stop fit on: 10000 iterations

Weight: 1

Error: 7.803

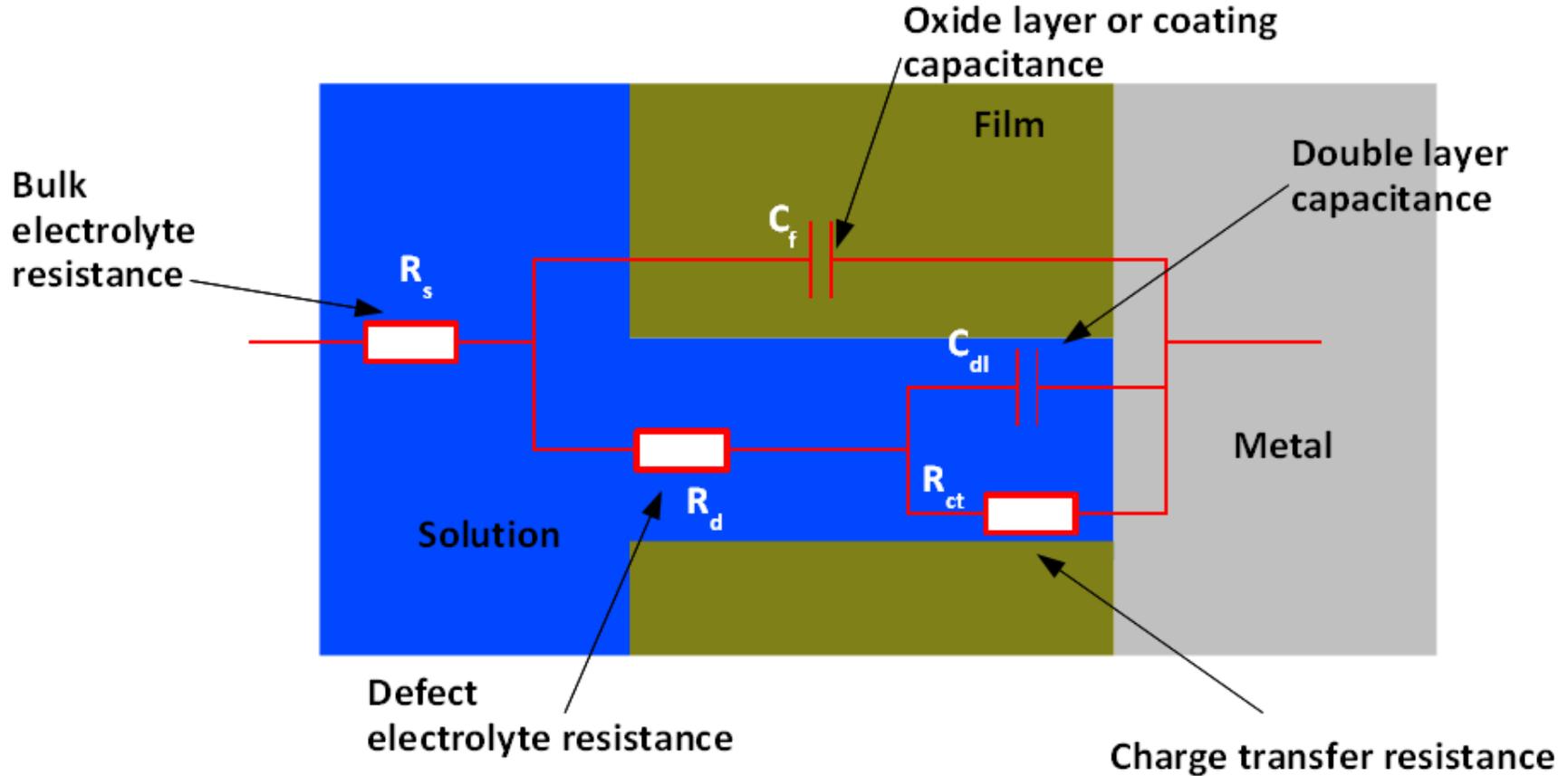
Iterations: 10000 (Simplex) Cycle xxxx



Which one should be chosen ?

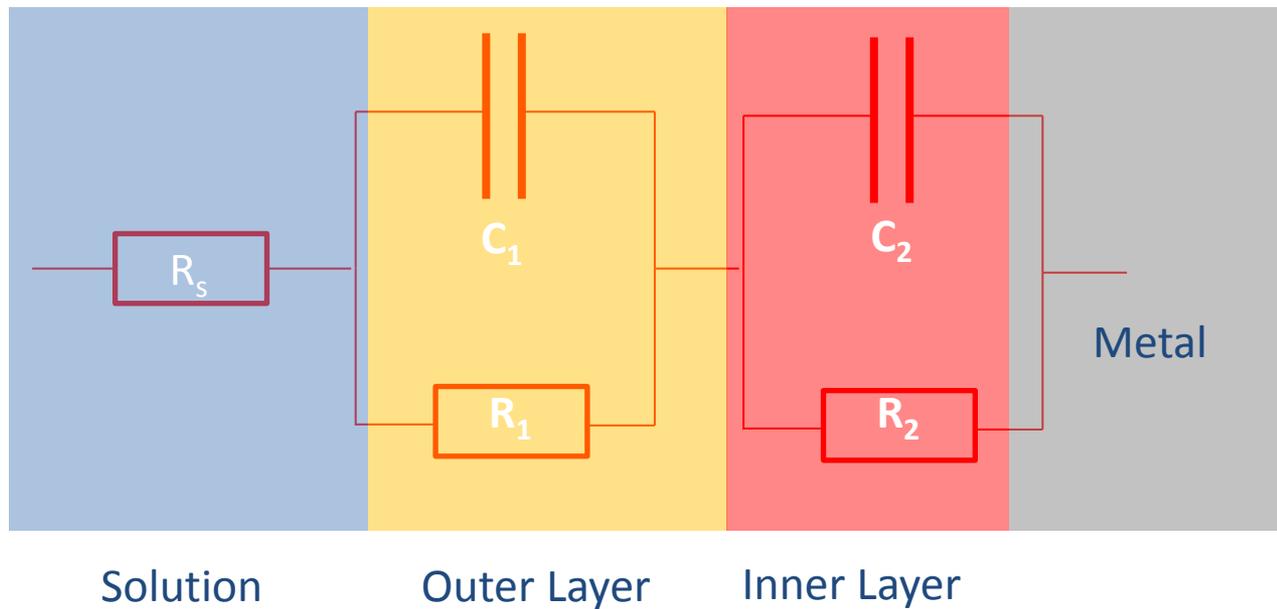
It depends on your system

If the tested material was a metallic sample coated with an oxide layer or a defective polymer then equivalent circuit 2 could be chosen.



It depends on your system

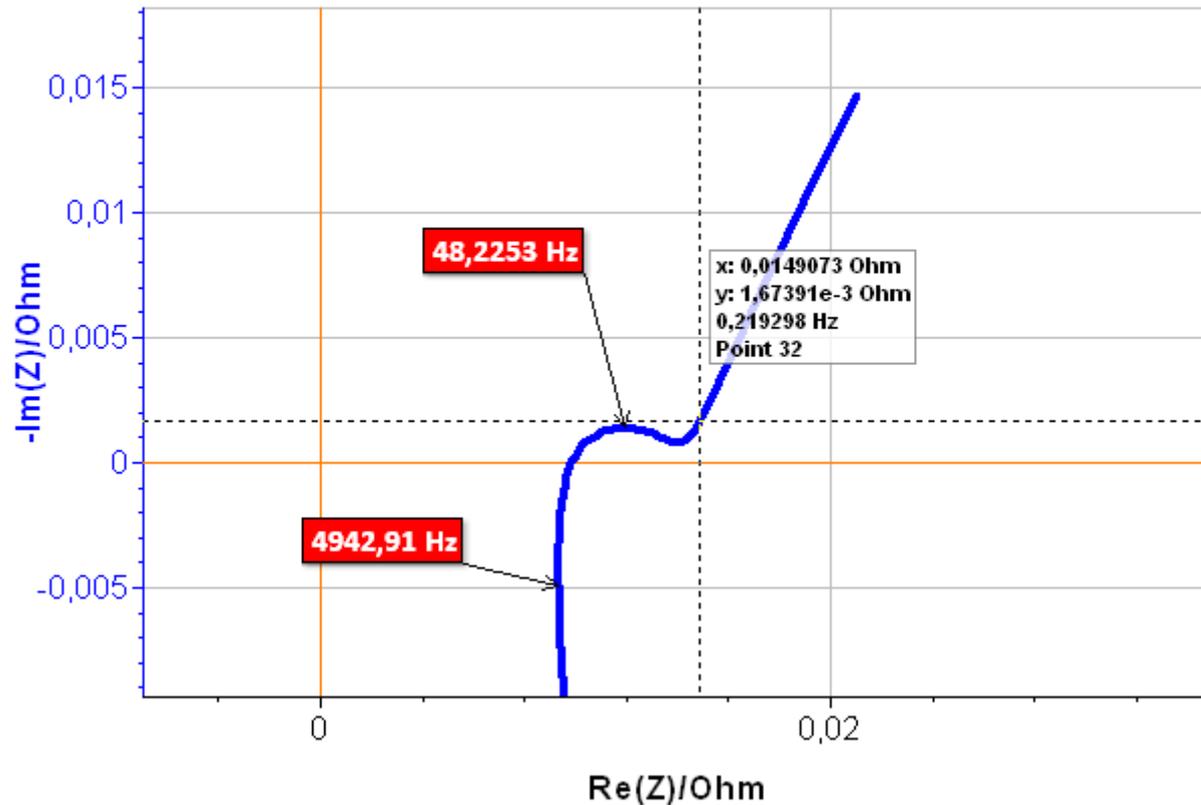
If the tested material was a metallic sample with a double oxide layer then circuit 3 could be chosen.



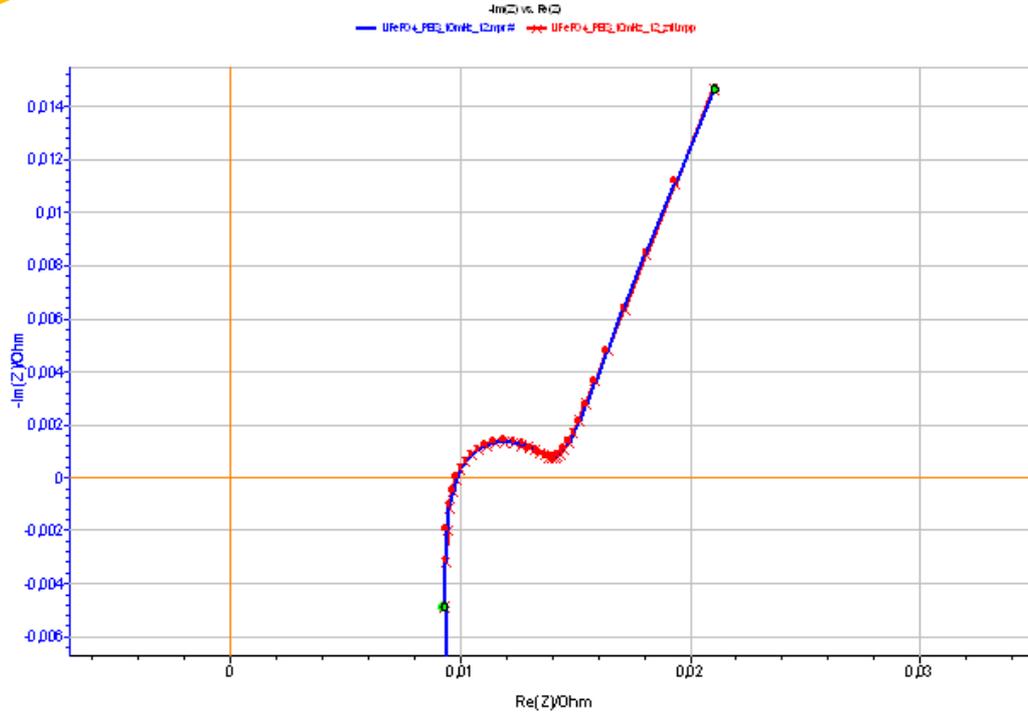
Example 2

LiFePO4_PEIS_10mHz_12.mpr

— -Im(Z) vs. Re(Z)

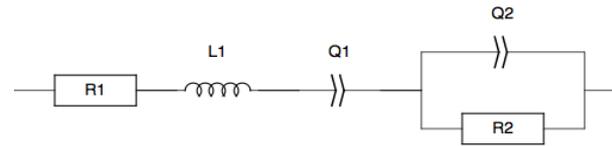


Data used in the application note #19 : \Data\Samples\EIS\LiFePO4_PEIS_10mHz_12.mpr

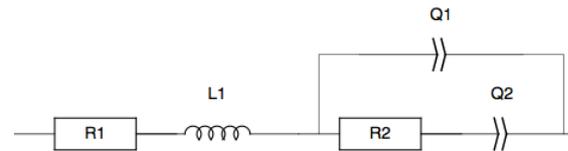


2 possible equivalent circuits :

1. $R1 + L1 + Q1 + (Q2/R2)$



2. $R1+L1+Q1/(R2+Q2)$



- . L1 is a self inductance (electrical component generating a magnetic field when a current is flowing through it).
- . Q1 is a CPE (Constant Phase Element). It is a mathematical component used instead of C when the experimental impedance graph is not semi-circle but a depressed semi circle. It means that the system in question does not behave like an ideal capacitor.

From the equivalent circuit, we can deduce that :

- . R1 is the resistance associated to the electrolyte and the electrical connections.
- . L1 is the inductance related to the electrical connections.
- . A battery is composed of two electrodes, and hence two interfaces, which makes it complicated to associate each electrical component to each electrode.
- . Tentatively, if we consider equivalent circuit 1 : Q1 can be associated to the first electrode (+ or -) and Q2/R2 to the second electrode (+ or -).

- . The transfer function of a system submitted to a current perturbation is the impedance
- . There are two ways to show impedance data : Bode and Nyquist
- . It is easy to switch from one representation to the other.
- . Impedance data can be interpreted using EC-Lab[®] Z Sim and Z Fit.
- . Electrical circuits can be used as equivalent to the expression of the faradaic impedance of a given system.
- . For one impedance graph, several equivalent circuits are possible.
- . The most adequate one is the one that makes sense, physically speaking.
- . Examples were given for coatings and batteries.