Impedance :
From the experimental side

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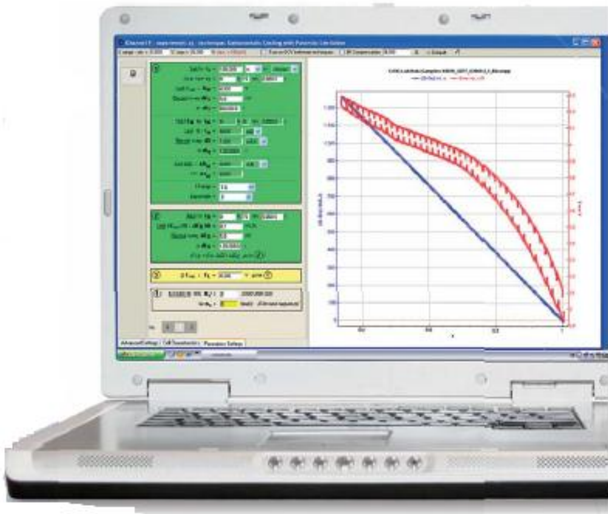
Background on EIS

Experimental set-up

- Which instruments?
- Connection
- Experimental conditions
- Cell

Monitoring software

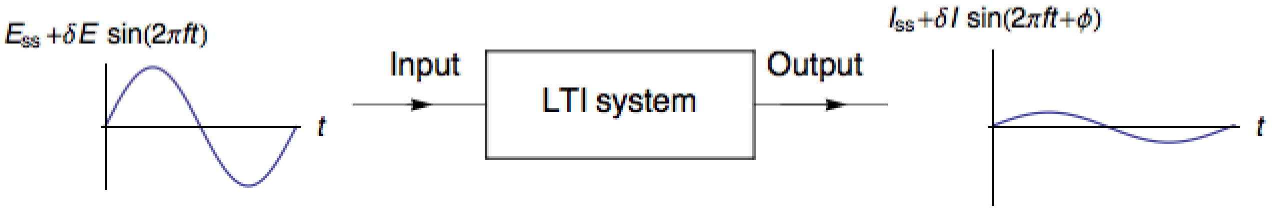
- Basic parameters (DC or AC voltage/current, frequency,...)
- Advanced parameters (Drift, Multisinus, …)
- Stack of cell



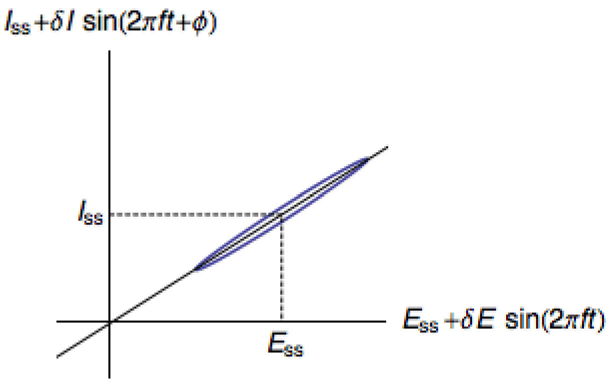
Analysis tools

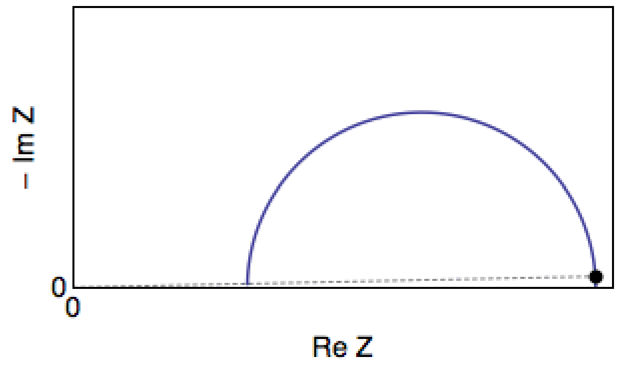
- Kramers-Kronig
- Zfit
- Mott-Schottky/capacity measurement

BACKGROUND



Current response has a the same frequency with an **amplitude δI** and **phase Φ**
Perturbation in potential, (it is also possible to perform the same in Galvano)





Increasing the frequency or amplitude → moving away from the steady state I_{ss} vs E curve

BACKGROUND

$Z = \mathcal{L}[E(t)]/\mathcal{L}[I(t)]$

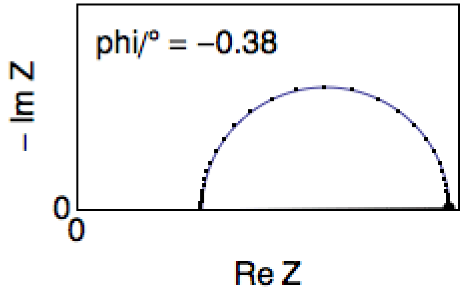
$\mathcal{L}$: Laplace Transform

The impedance is a complex number:

$Z = a + j\,b = Re(Z) + j\,Im(Z)$ (with $j^2 = -1$)

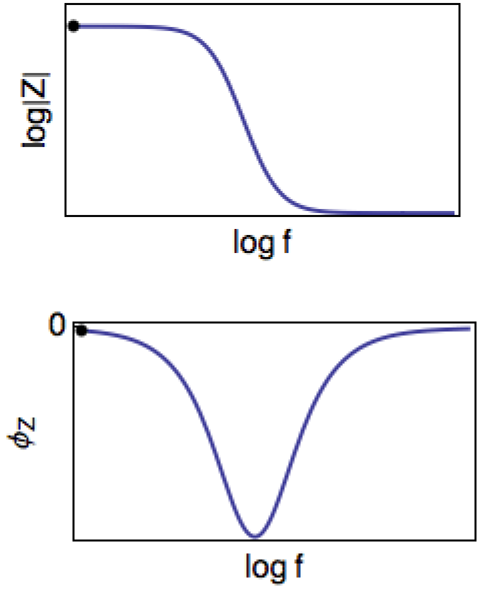
$Z = \rho(\cos\varphi + j\sin\varphi)$ with ρ the modulus and φ the phase

Nyquist diagram



In the Nyquist plot, the impedance for each frequency is plotted in the complex plane -Im(Z) *vs* Re(Z).

Bode diagram



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

How to optimize the setup?

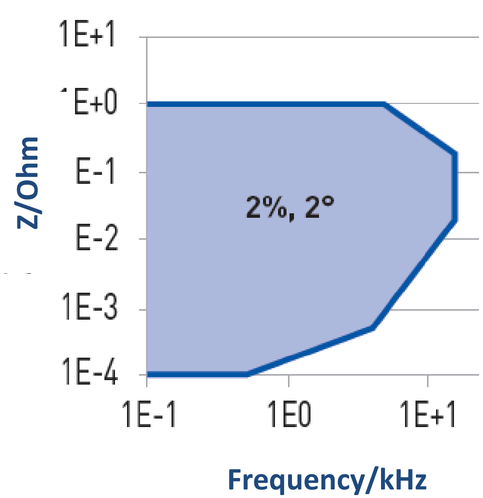
- Which instruments for my measurements?
- Connection
- Experimental conditions
- Cell

THE APPROPRIATE INSTRUMENT

Select the appropriate instrument …

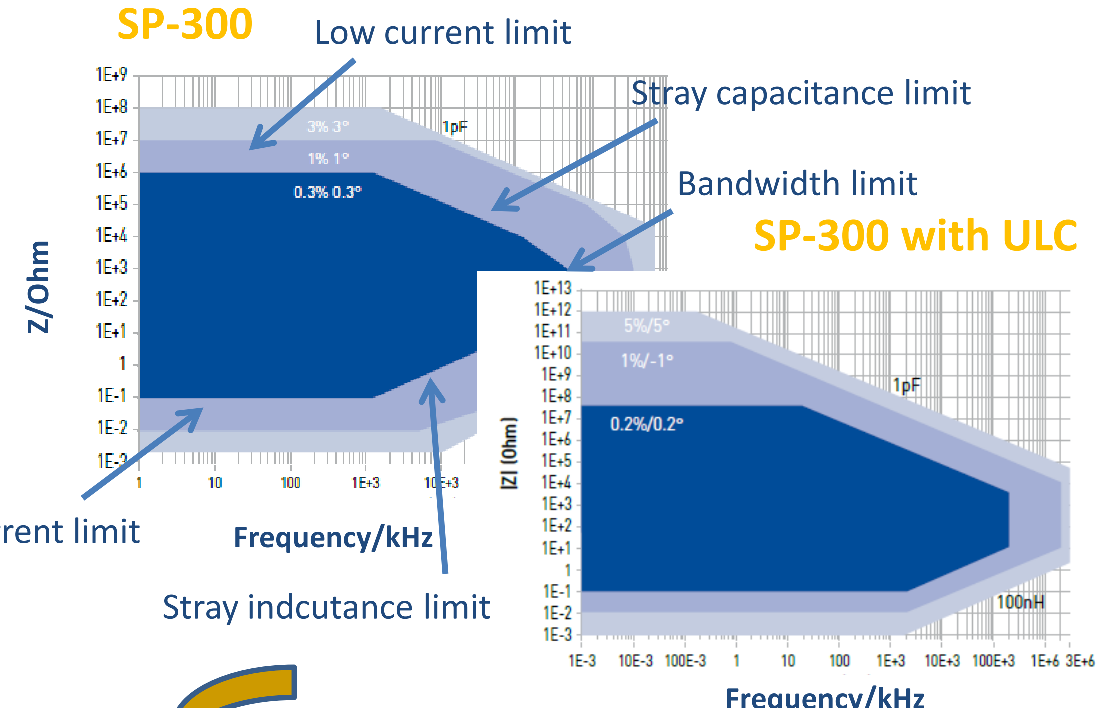
…in the optimized configuration *i.e.* low current option, high current option…

HCP-803



SP-300

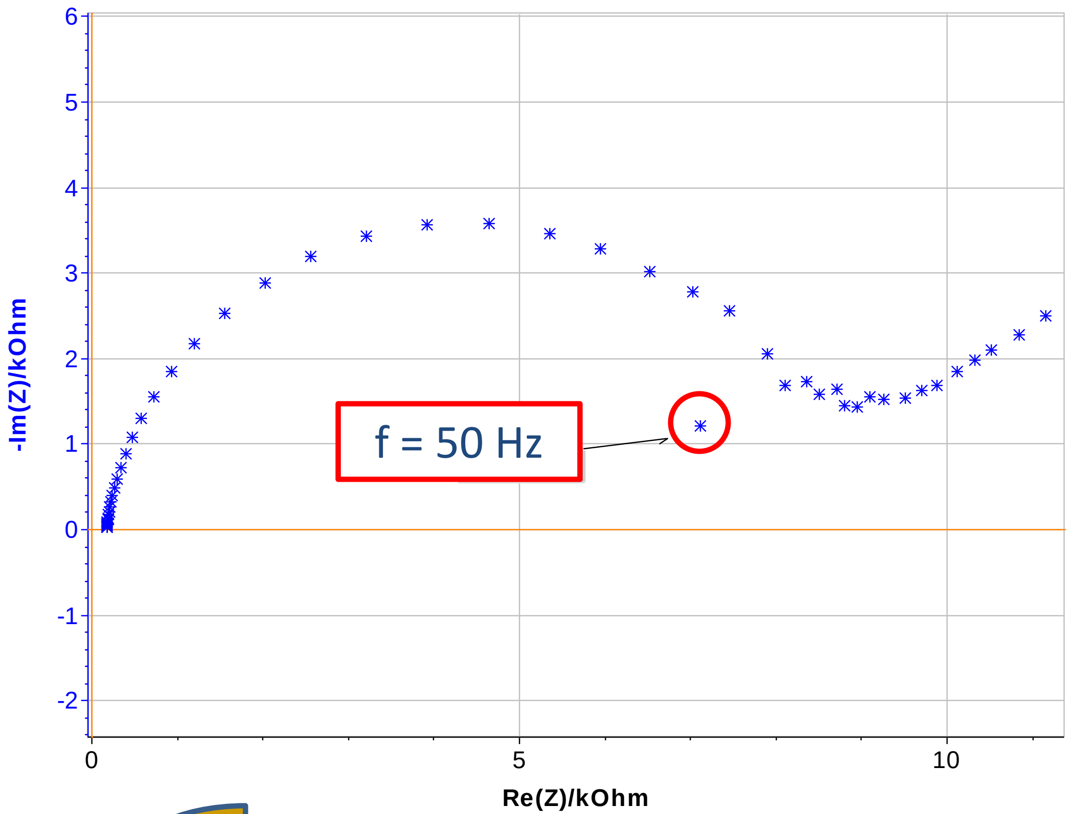
SP-300 with ULC

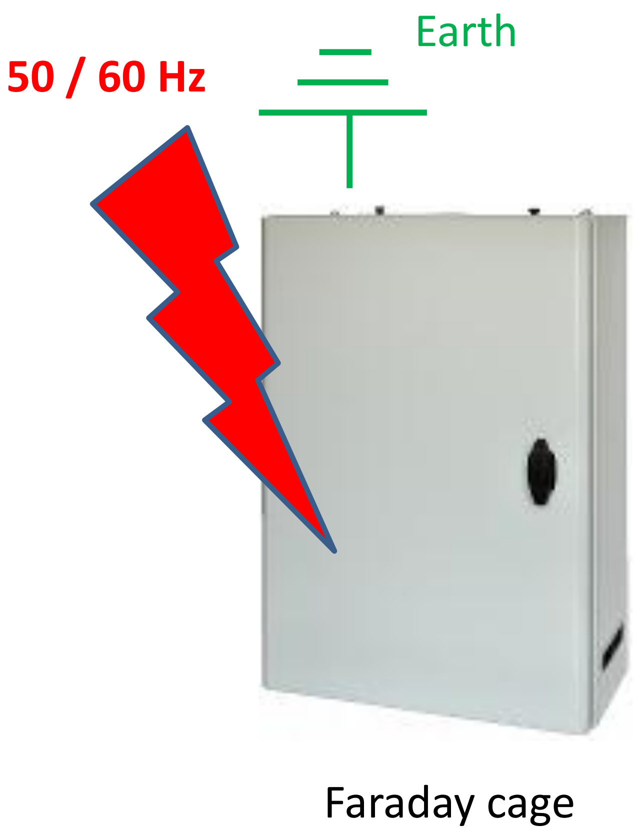


For a system with low impedance (such as battery, supercapacitor), select a potentiostat with a current booster.

For a system with high impedance (such as a coating), SP-300 with ULC can be of interest

Protect the cell from any external disturbance

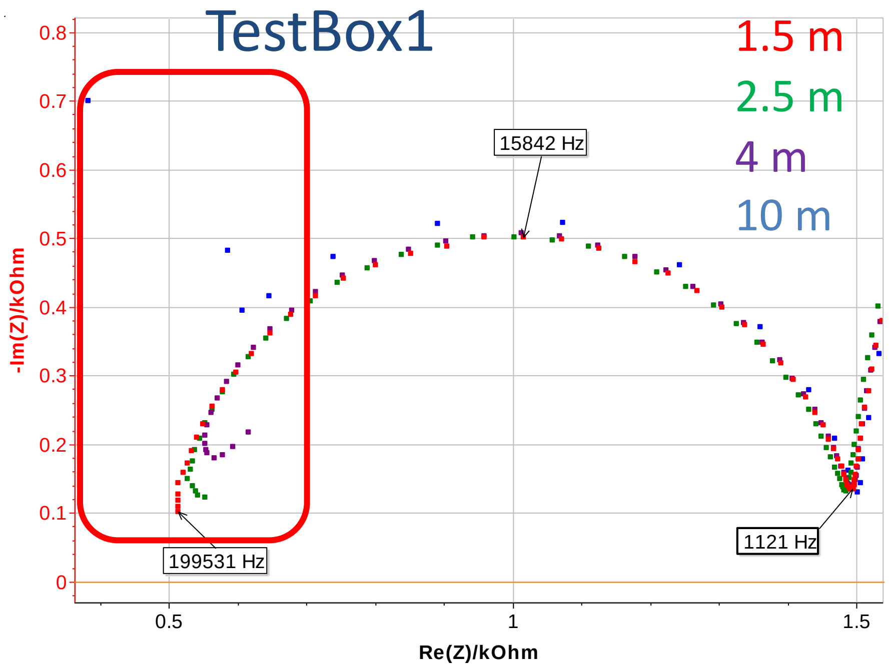




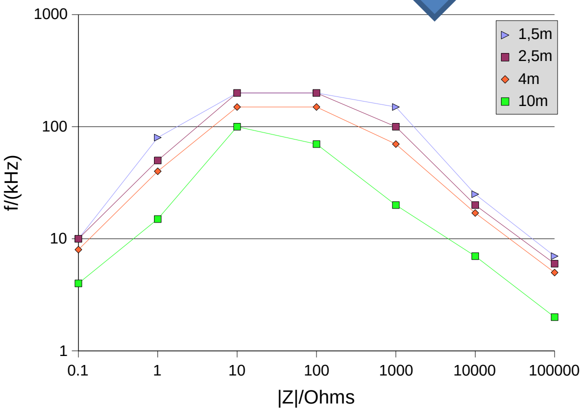
Use a Faraday cage connected to the earth of the potentiostat
Especially for low current measurements.

EXTENDED CABLE

Why?



- Because this affects the bandwith of the potentiostat.
Error is higher.



- Capacity of the extra cable is added.
Specifications given are the specifications at the end of the leads of the standard cable.

Avoid extended cable
Affect the EIS measurement especially at high frequencies

It is possible to evaluate the error thanks to EC-Lab:

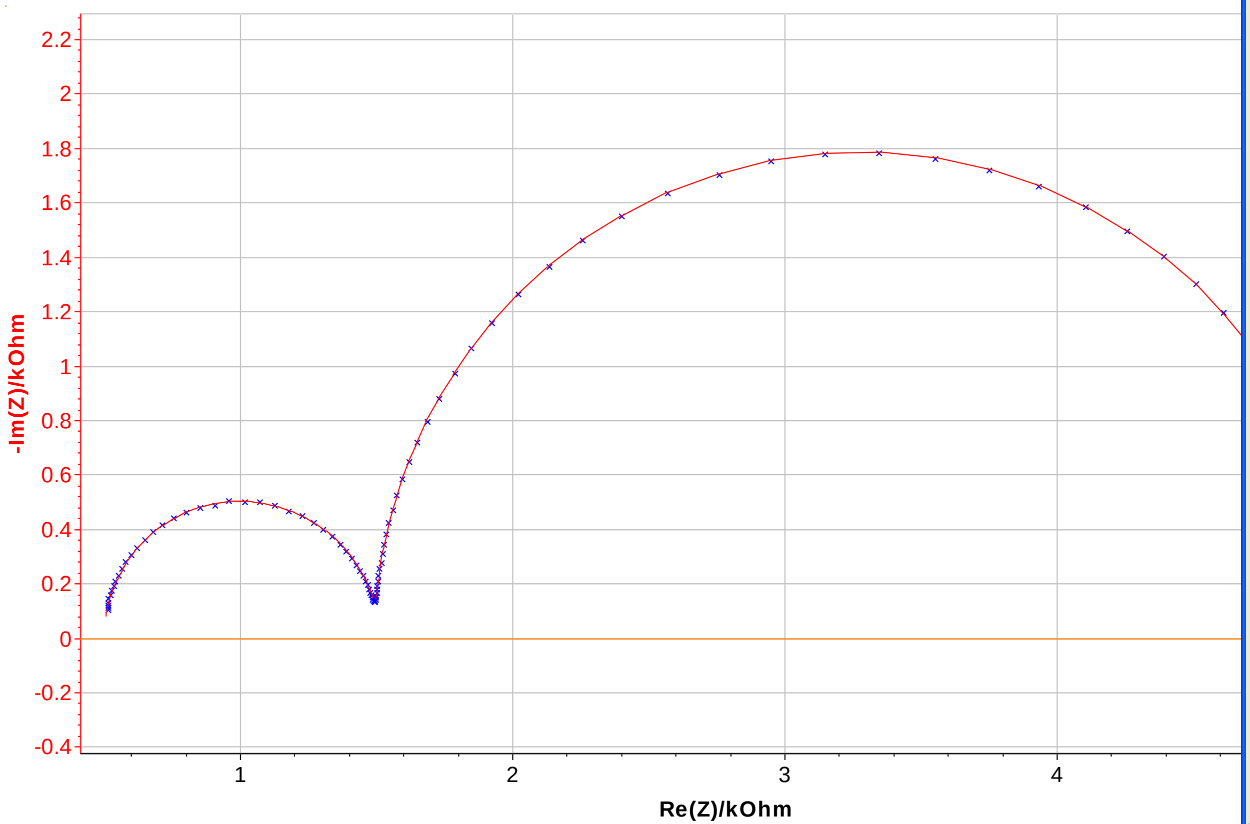
1. Fit the resulting EIS data of 1.5 m

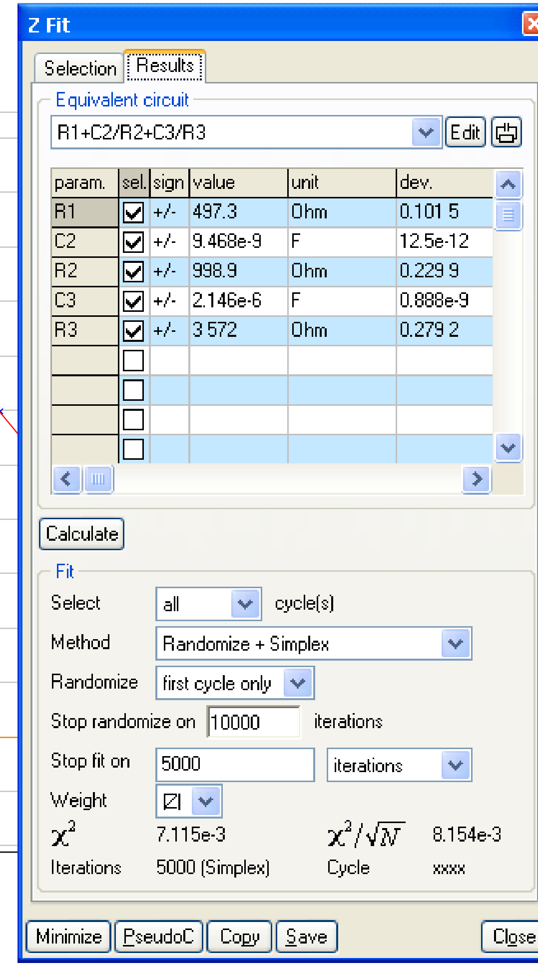
2. Use these fitted values as reference

3. Compare these reference values with the data obtained with 10 m cable
(Plot the error data *vs.* frequency, for the 1.5 m cable and for the 10 m cable)

EXTENDED CABLE

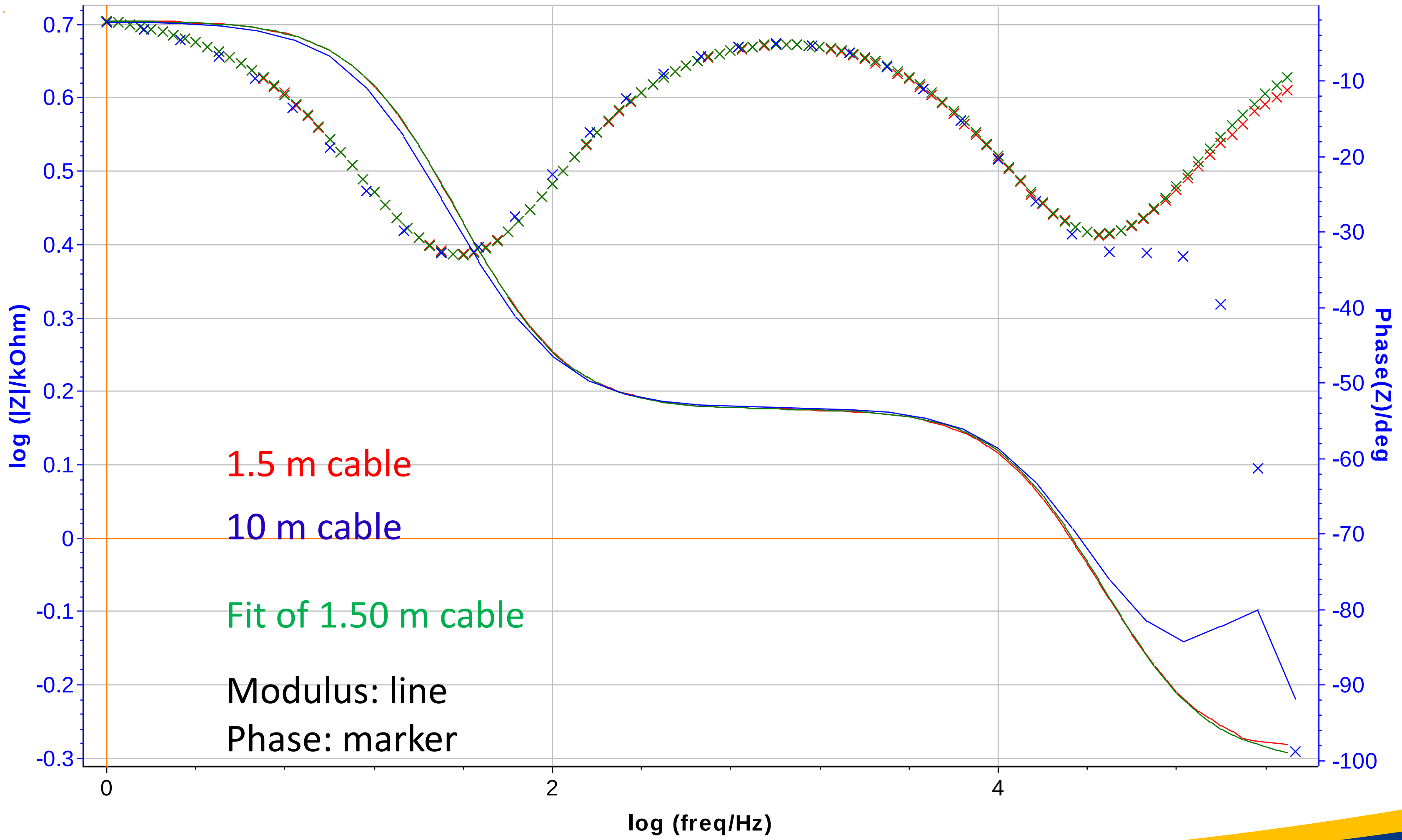
1- Fit of the EIS data obtained with 1.5 m cable





It is even clearer in the Bode plot

EXTENDED CABLE



EXTENDED CABLE

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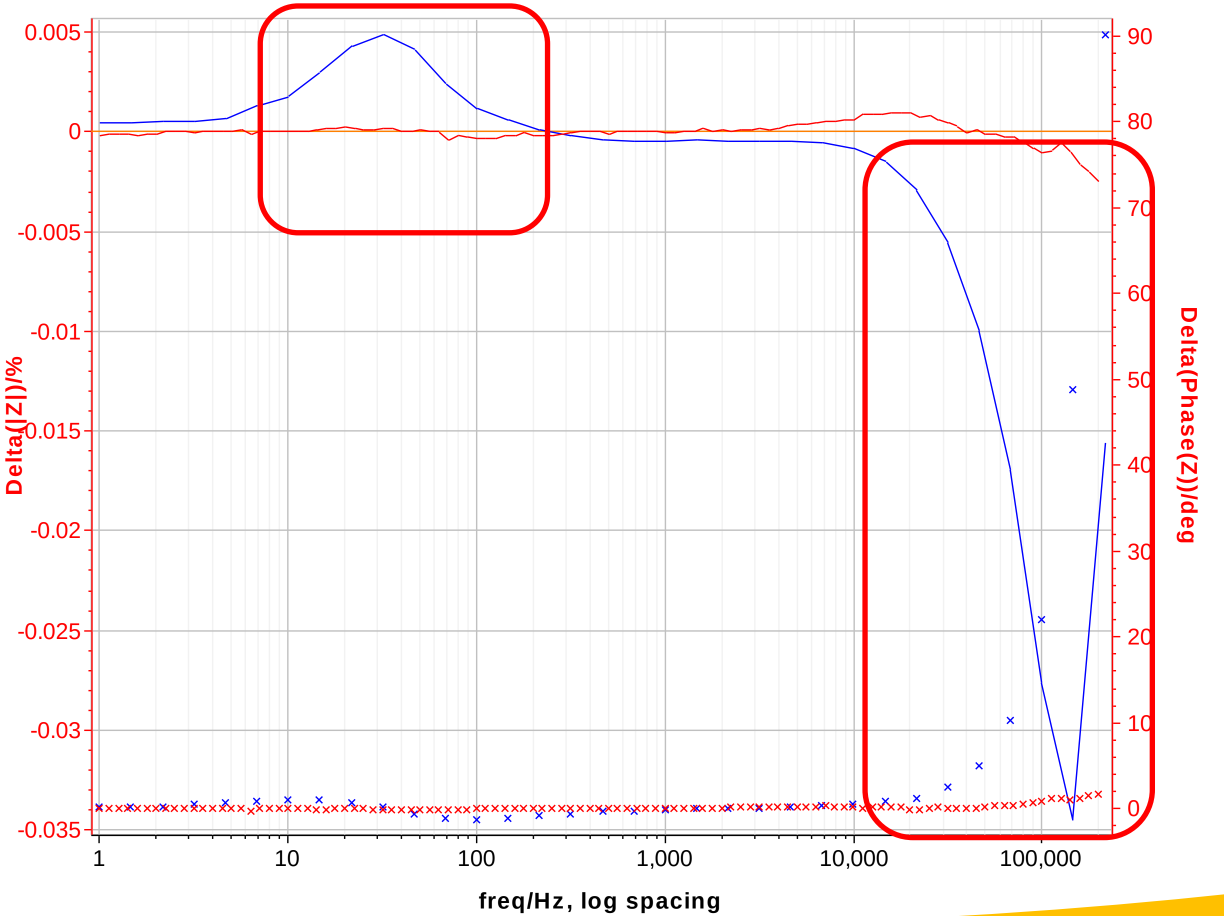
(Plot the error data *vs.* frequency, for the 1.5 m cable and for the 10 m cable)

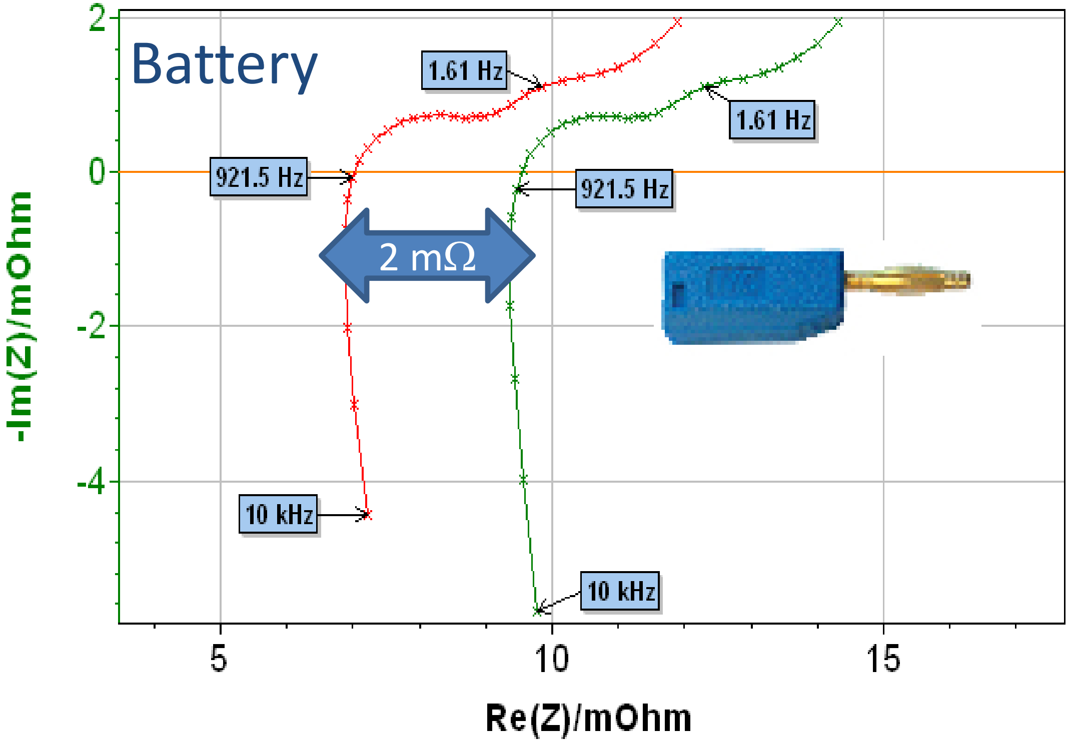


1.5 m cable

10 m cable

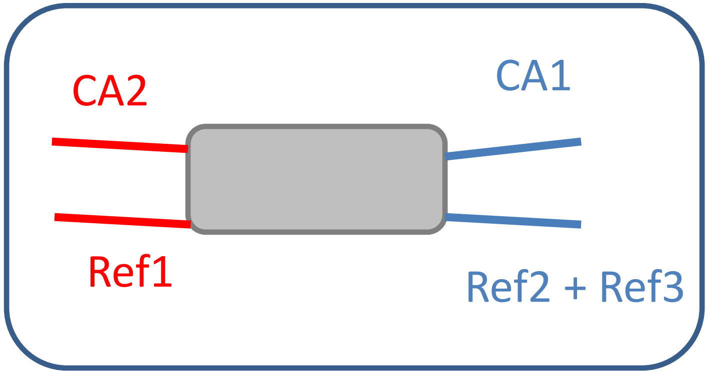
Modulus: line
Phase: marker

CONNECTION (R contact)



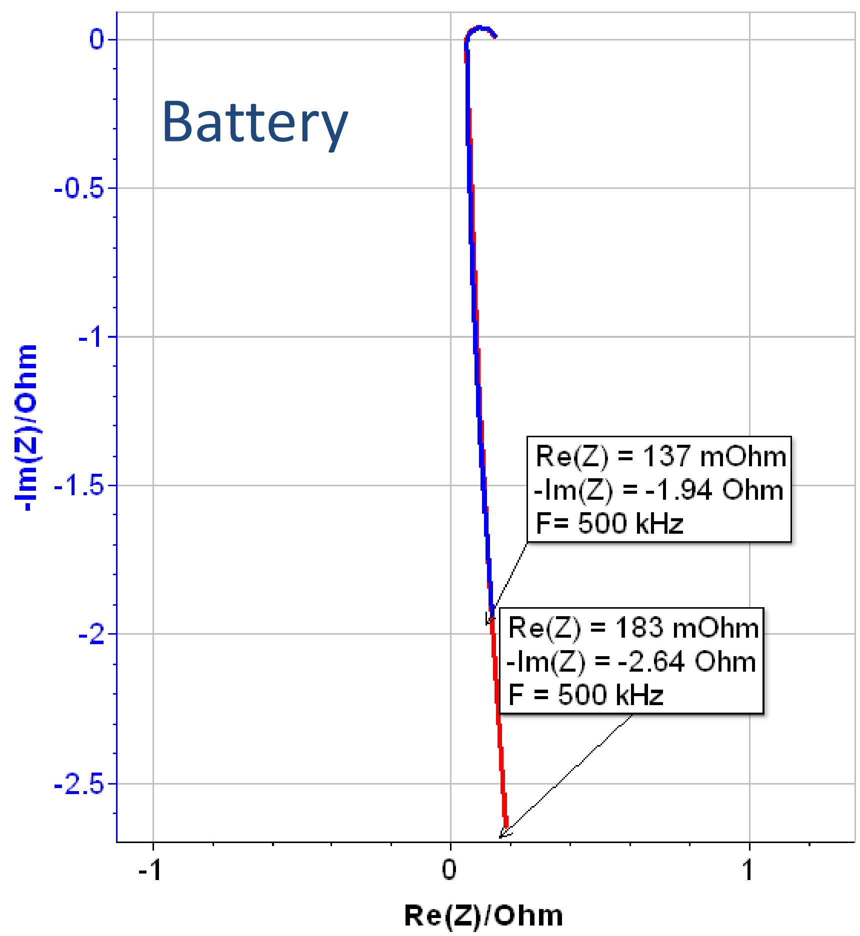
Contact resistance is no more negligible for low impedance system.

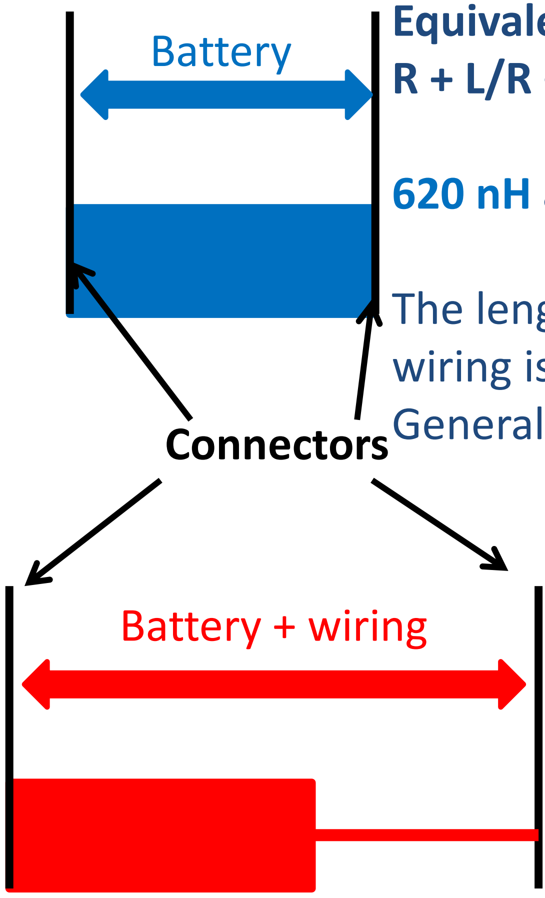
In that case, 4-point measurements has to be considered:



Affects the measurement at low level of impedance.
This is particularly relevant for battery, supercapacitor investigations…

CONNECTION (inductive effect)





Equivalent circuit:
R + L/R +R/Q

620 nH against 870 nH

The length of the extra wiring is around 25 cm. Generally this is 10 nH/cm

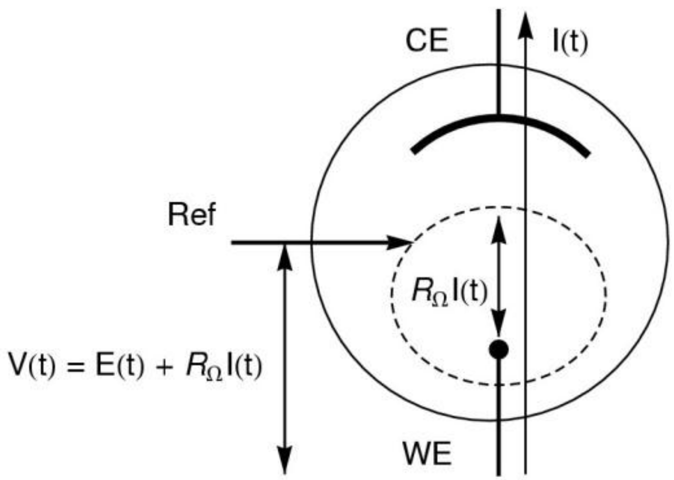
Affects the measurement at low level of impedance.
This is particularly relevant for battery, supercapacitor investigations…

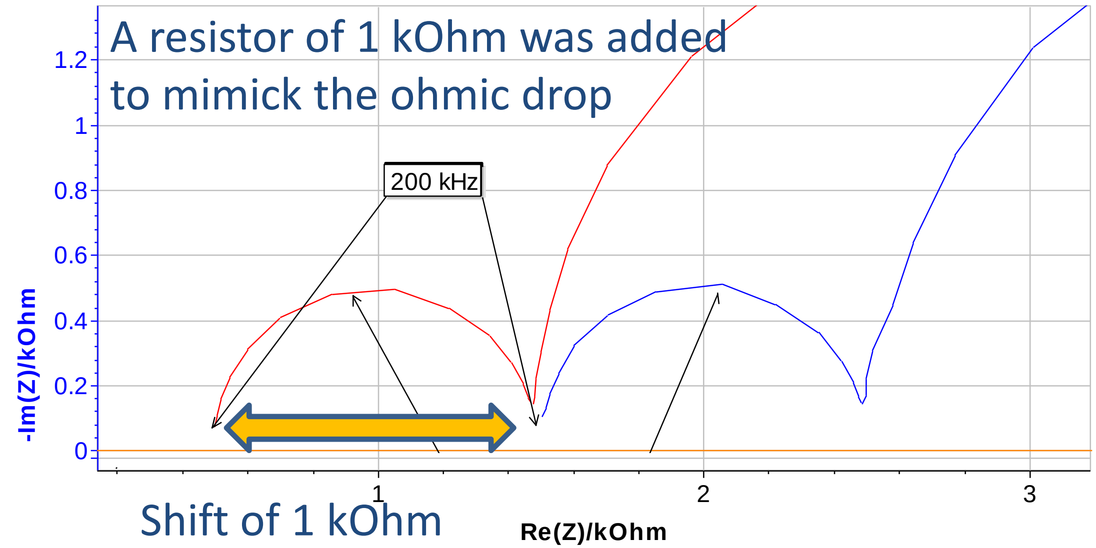
Ref: App Note 23

GEOMETRY OF THE CELL

Reduce ohmic drop of the cell by:

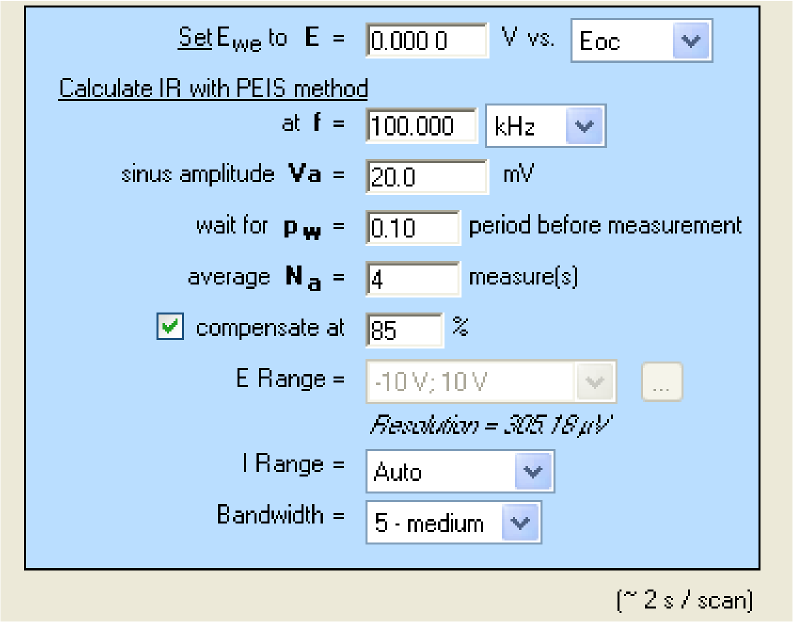
- decreasing the distance between RE and WE
- changing the Vycor glass of the RE
- …



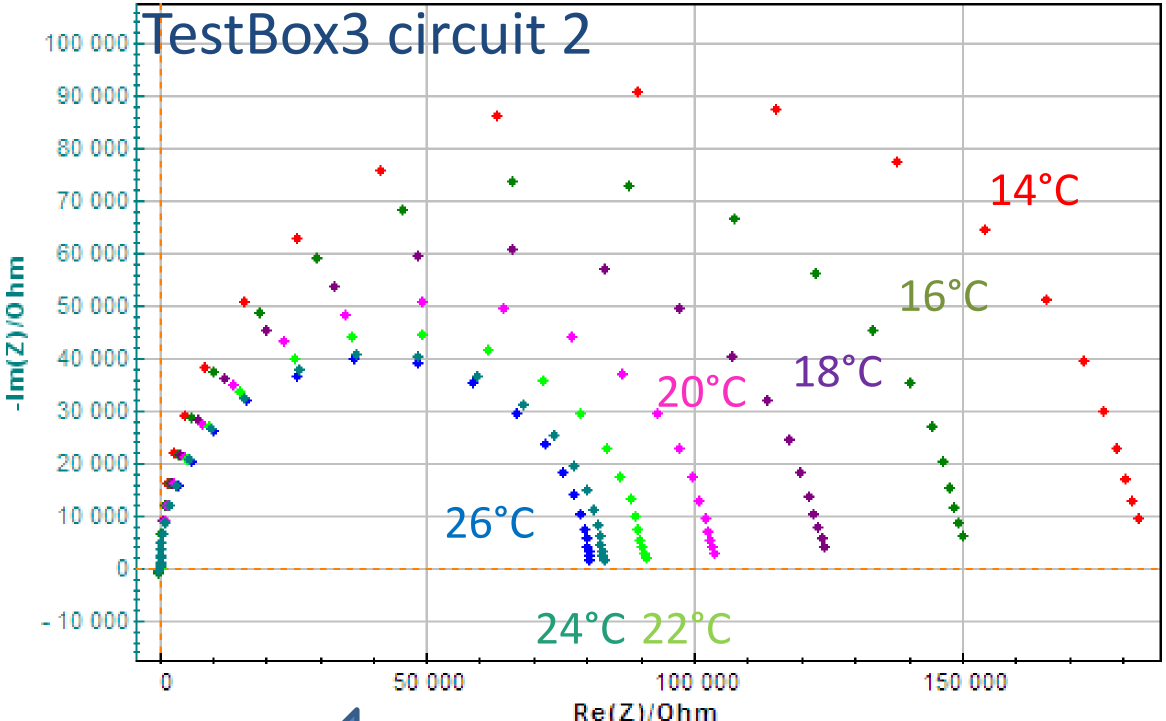


Affects the measurement of low impedance system
at high frequency (battery, supercapa, …)

Determine/compensate the ohmic drop resistance thanks to ZIR technique (measure the Re(Z) at one frequency).



Note that it is not possible to compensate ohmic drop for EIS measurement.

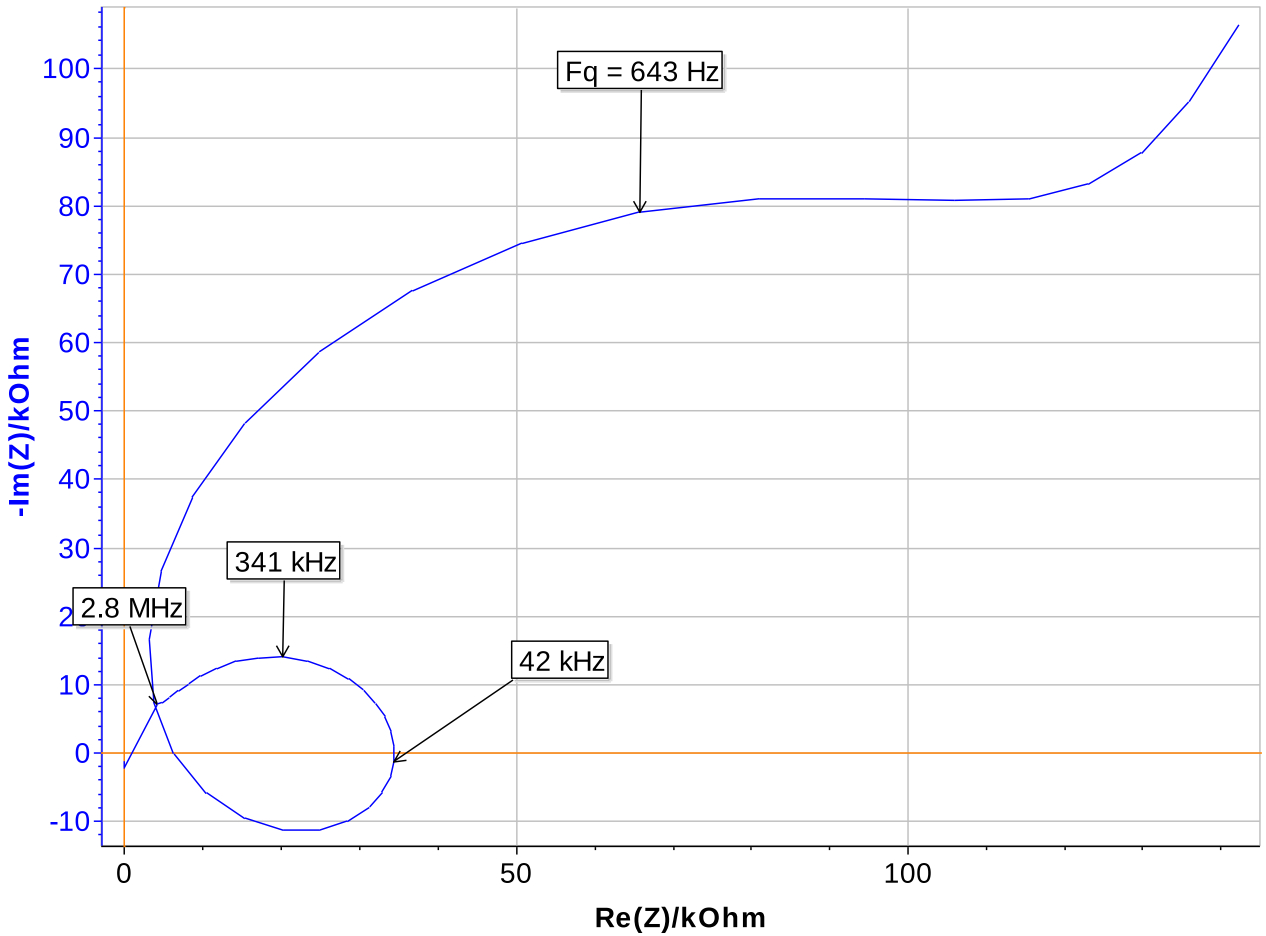


For example,
if one experiment is performed during the night and another one during the day, a difference between both spectra can be observed.

R decreases when Temp increases

Control of temperature of the cell may be required.

FUNNY BEHAVIOR !!!

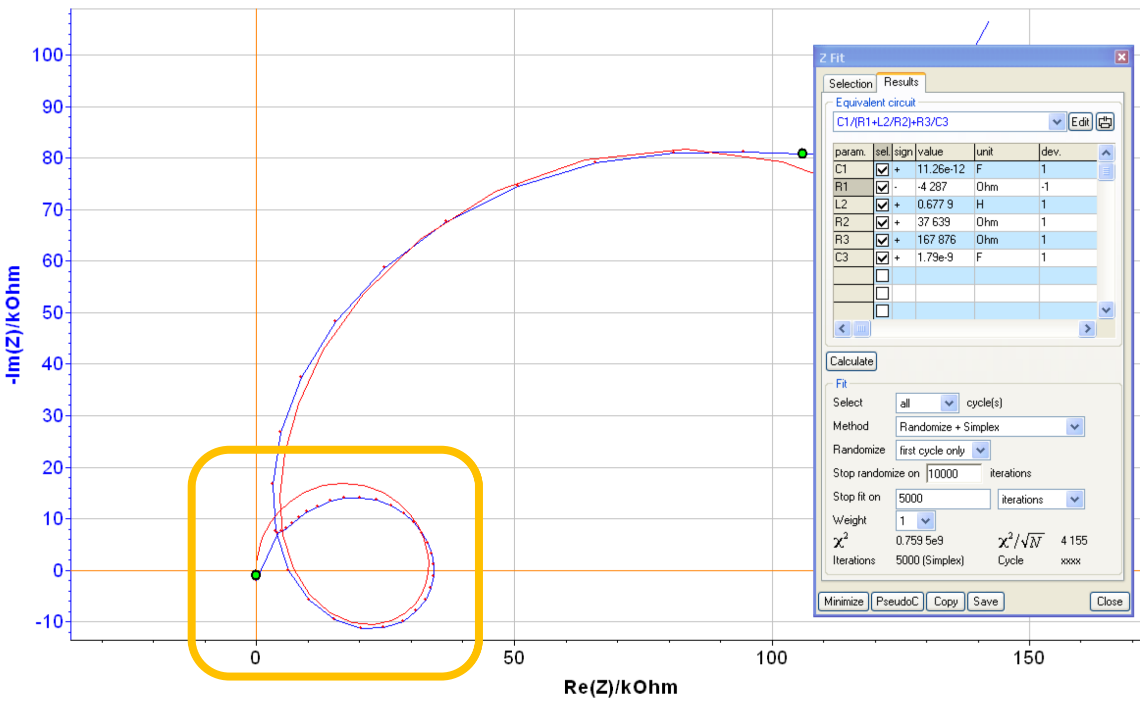


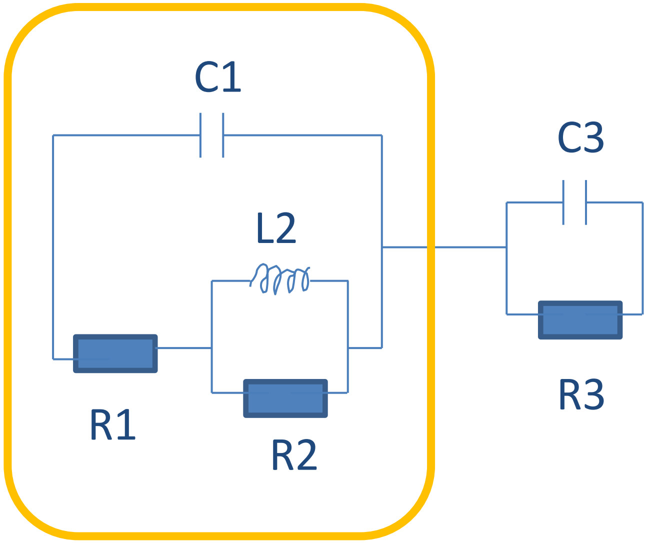
What's that?

Only artifact due to reference electrode impedance not negligible at high frequencies

Ref: Diard, Electrochim.Acta 2010, 55, 6, 1907-1911

FUNNY BEHAVIOR !!!



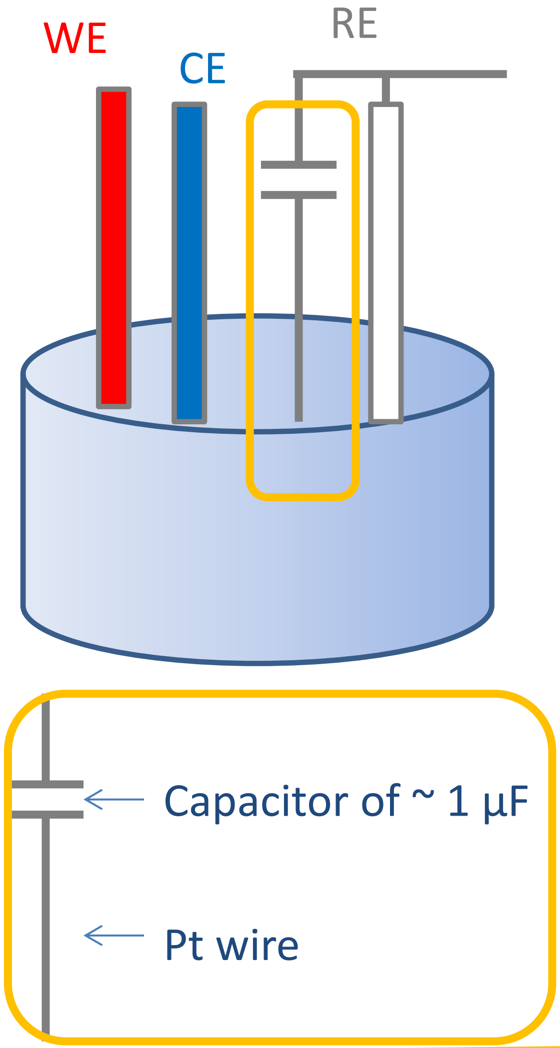


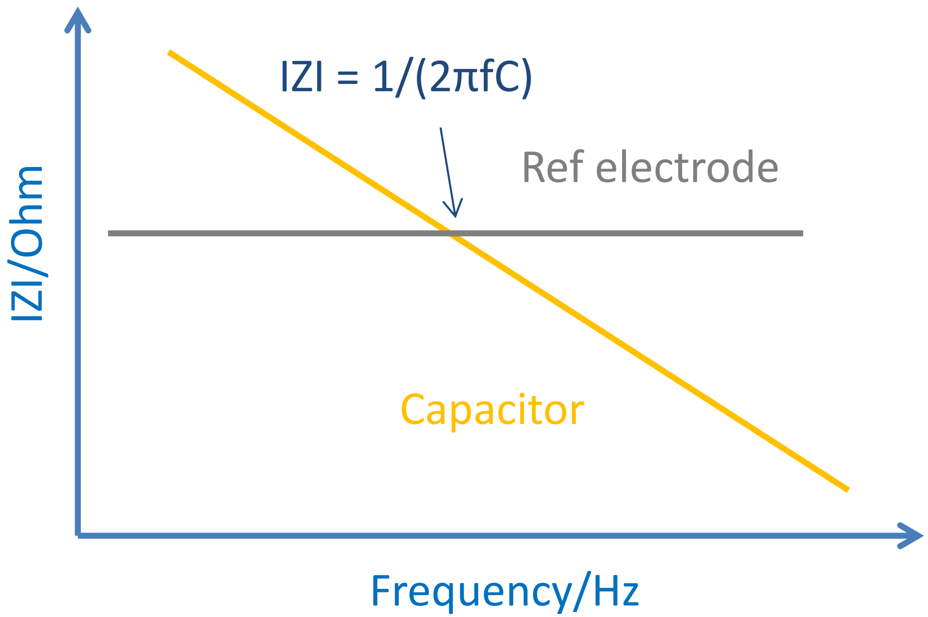
ZRef

This is due to the Ref Electrode

FUNNY BEHAVIOR !!!

A solution:



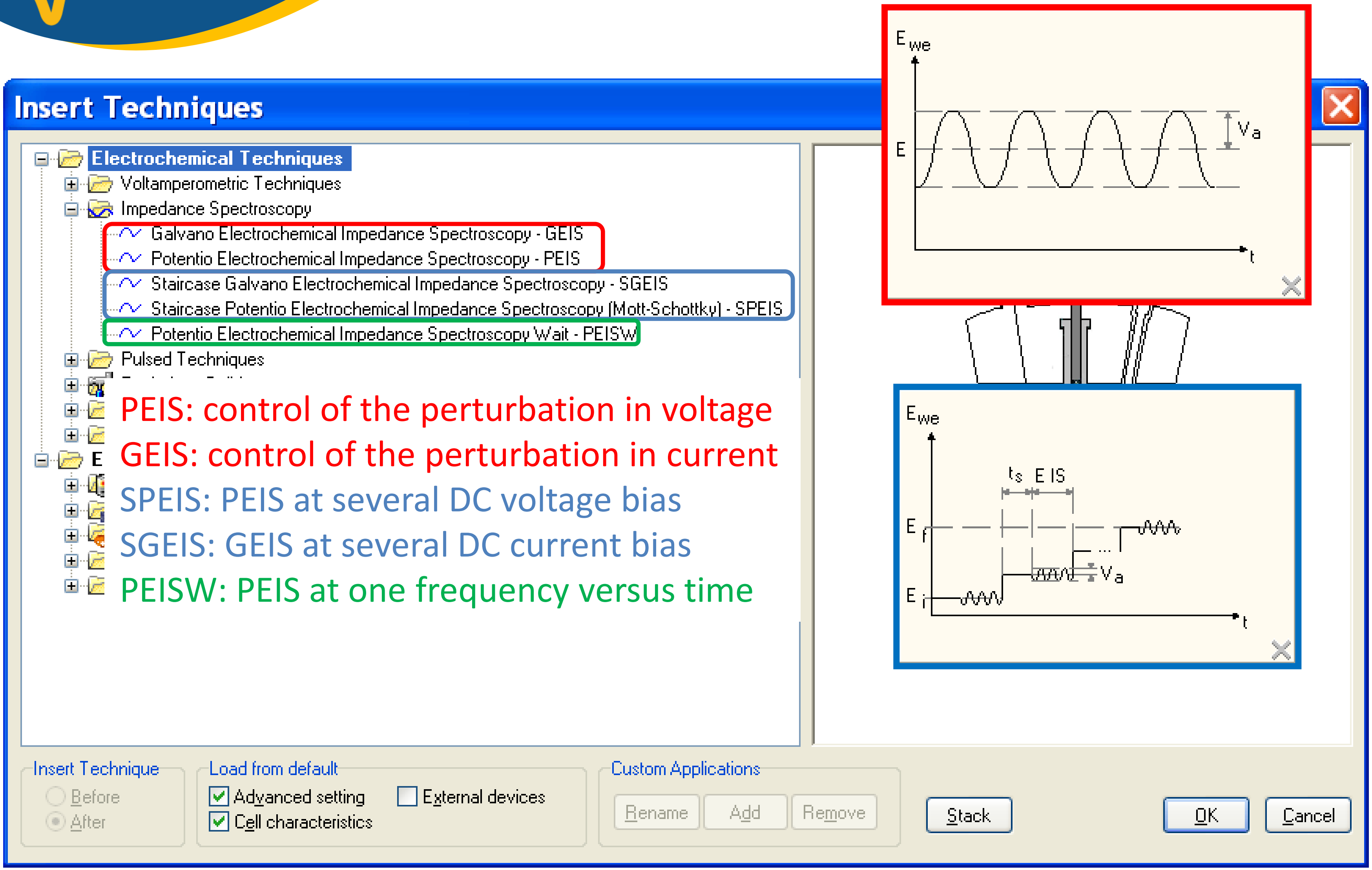


At high frequency the impedance of the capacitor is negligible

Ref: Diard, Electrochim.Acta 2010, 55, 6, 1907-1911

How to optimize the settings in EC-Lab® software?

- Which techniques in EC-Lab®/EC-Lab® Express
- Basic parameters (DC or AC voltage/current, frequency,...)
- Advanced parameters (Drift, Multisinus, …)
- Stack of cell



PEIS: control of the perturbation in voltage

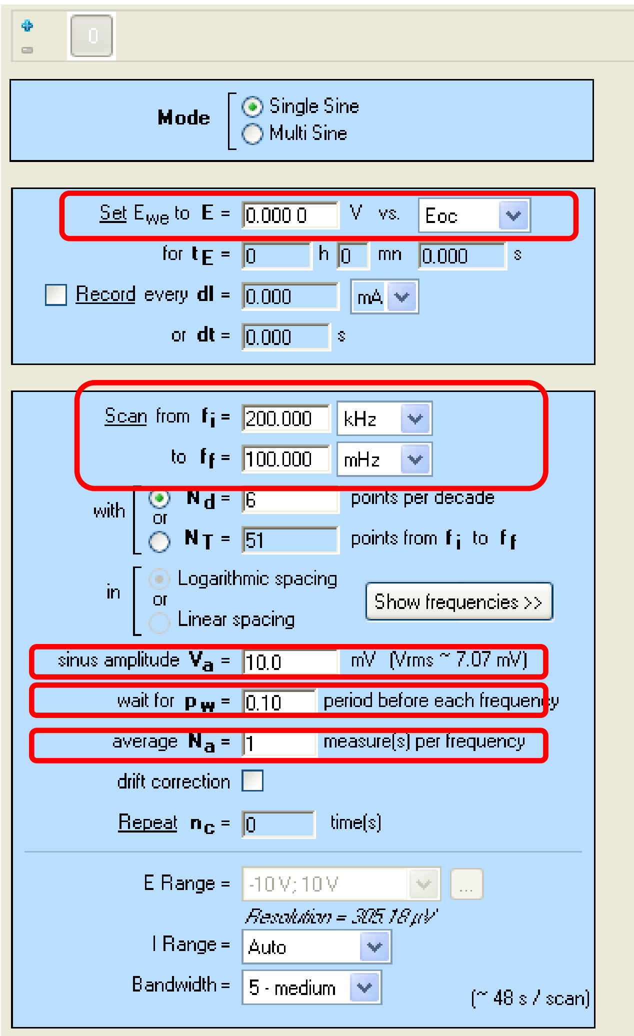
GEIS: control of the perturbation in current

SPEIS: PEIS at several DC voltage bias

SGEIS: GEIS at several DC current bias

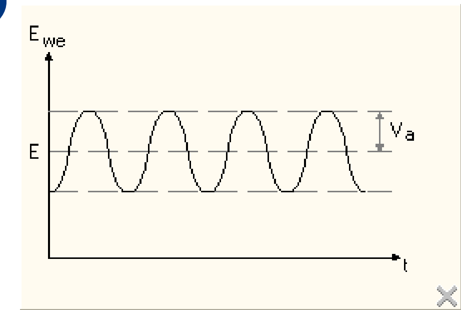
PEISW: PEIS at one frequency versus time

OVERVIEW OF EIS TECHNIQUE



$$E(t) = E_{DC} + V_a \sin(2\pi f t)$$

$$I(t) = I_{DC} + I_a \sin(2\pi f t)$$



E_{DC}/I_{DC}: defines the bias level (bias current for galvano or bias voltage for potentio) DC level

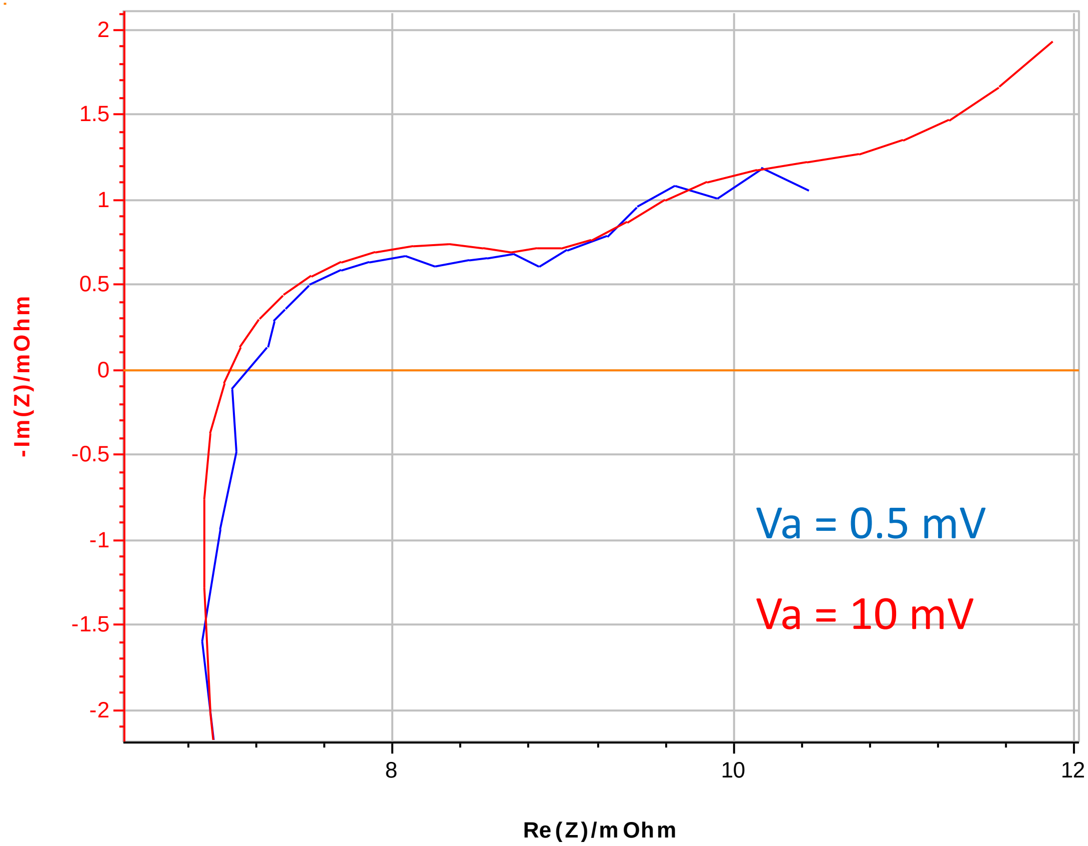
f_i/f_f: initial /final frequency

V_a/I_a: defines the amplitude of AC perturbation (be careful, it is an amplitude and not peak-to-peak or RMS amplitude)

P_w: offers the possibility to add a delay before the measurement at each frequency. This delay is defined as a part of the period. So the delay is longer for low frequencies.

N_a: repeats N_a measure(s) and average the values for each frequency.

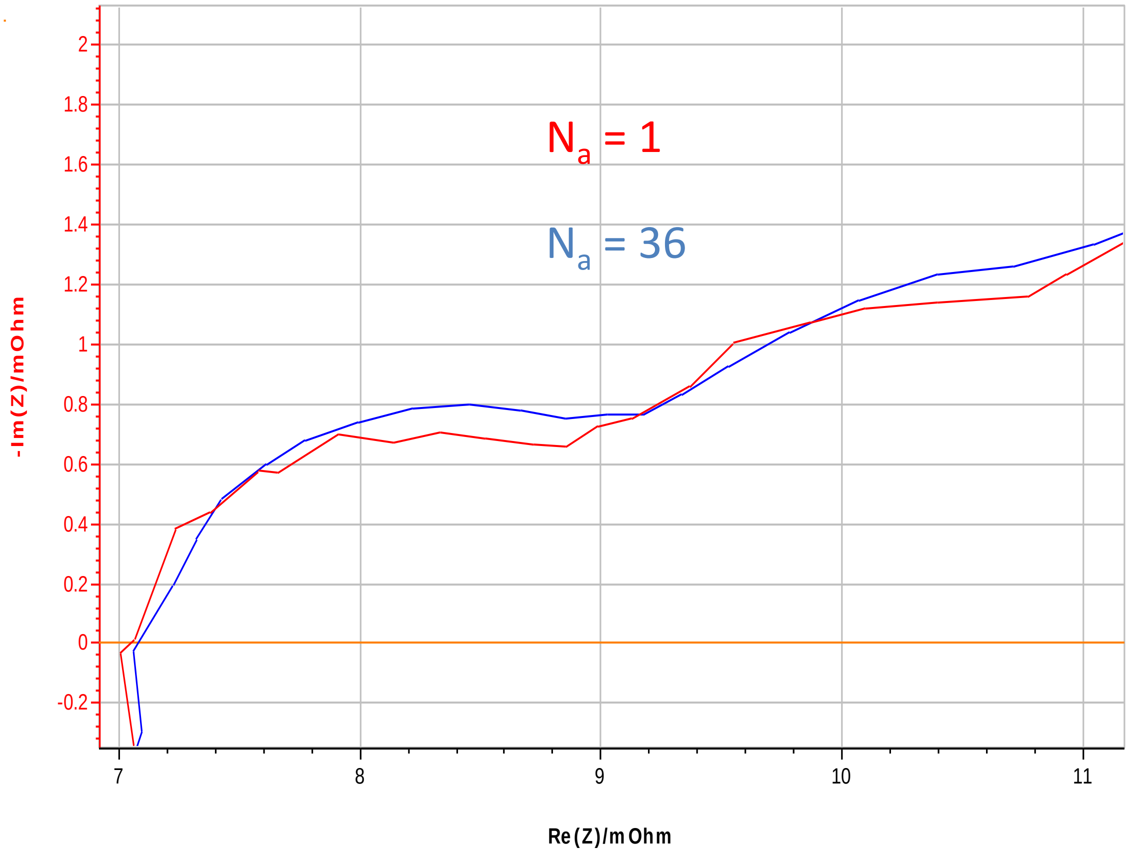
AMPLITUDE (V_a)



The resulting current and potential value should be in agreement with the accuracy of the instrument.

Amplitude of the controlled signal (V_a or I_a) should be:
- high enough to induce a significant amplitude of the response
- Small enough to keep the linear behavior of the cell.

AVERAGE (N_a)

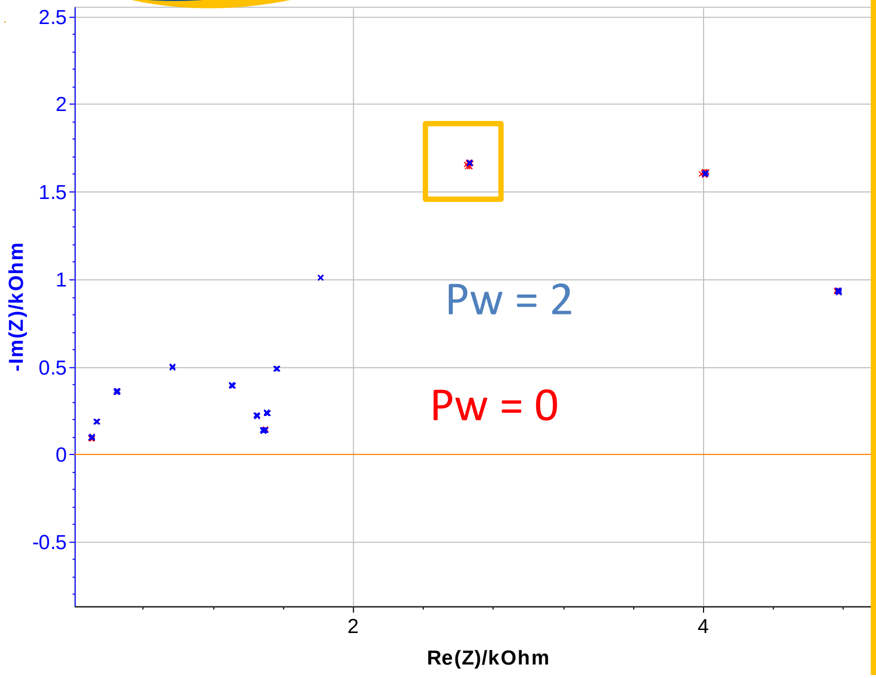


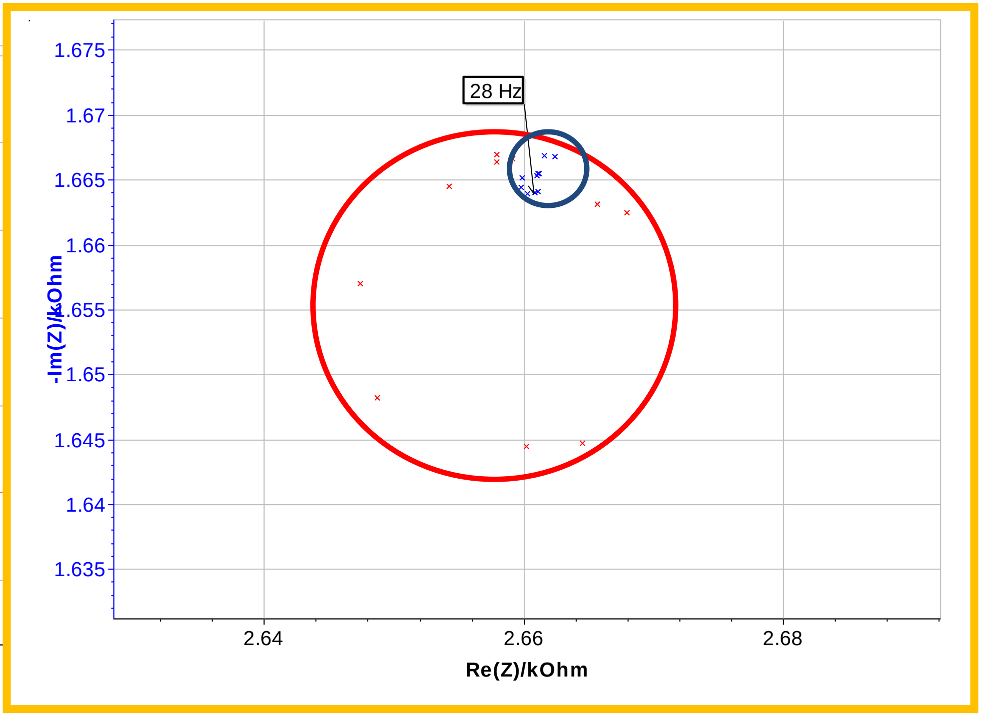
Curve with N_a = 36 is less noisy than the one with N_a = 1.

Noie is divided by the $N^{1/2}$

This average process smoothes the random error of the measurement.

WAIT PERIOD (P_w)





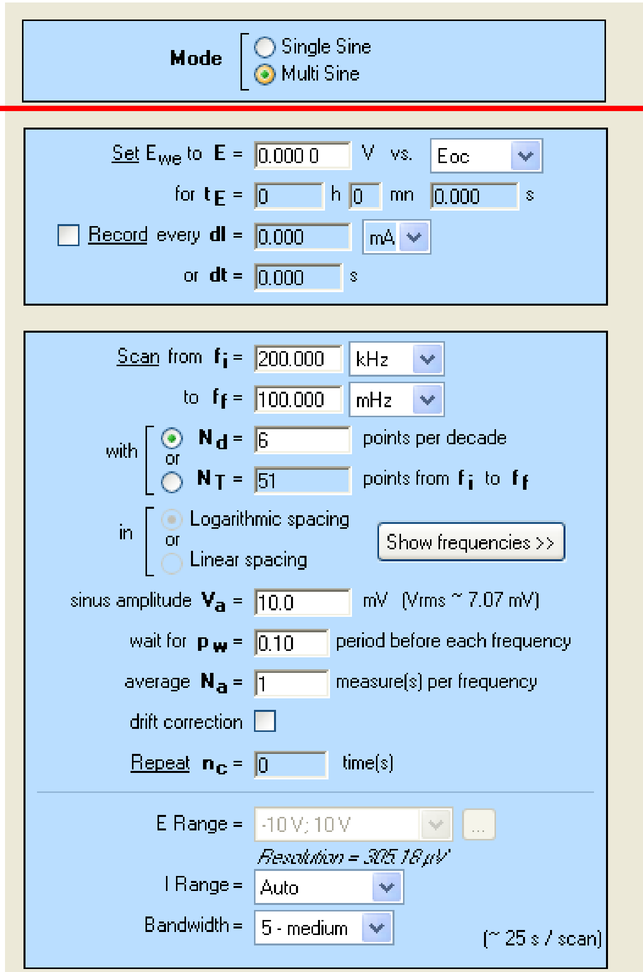
Curve with P_w = 2 is less scattered than the one with P_w = 0.

This result means that it is possible to slightly compensate a noisy shape of an EIS diagram just by increasing the P_w value and without disturbing the cell much.

Memory effect of the system

Important to activate this option when there is a big gap between two frequencies .

MULTISINE

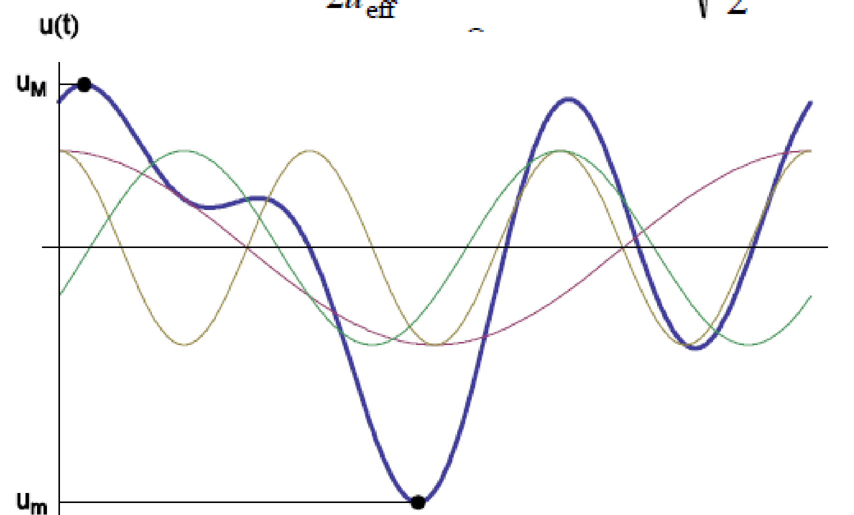


Sum of sinus

$$u(t) = A\sum_{k=1}^{N}\cos(2\Pi f_k t + \Phi_k)$$ with the phase $$\Phi_k = \Phi_1 - 2\Pi\sum_{n=1}^{k-1}\frac{(k-n)}{N}$$

Minimize the crest factor (avoid too large exciation, this might result in a measurement in the non-linear response domain of the electrochemical cell):

$$Cr(u) = \frac{u_M - u_m}{2u_{eff}}$$ with $$u_{eff} = A\sqrt{\frac{N}{2}}$$

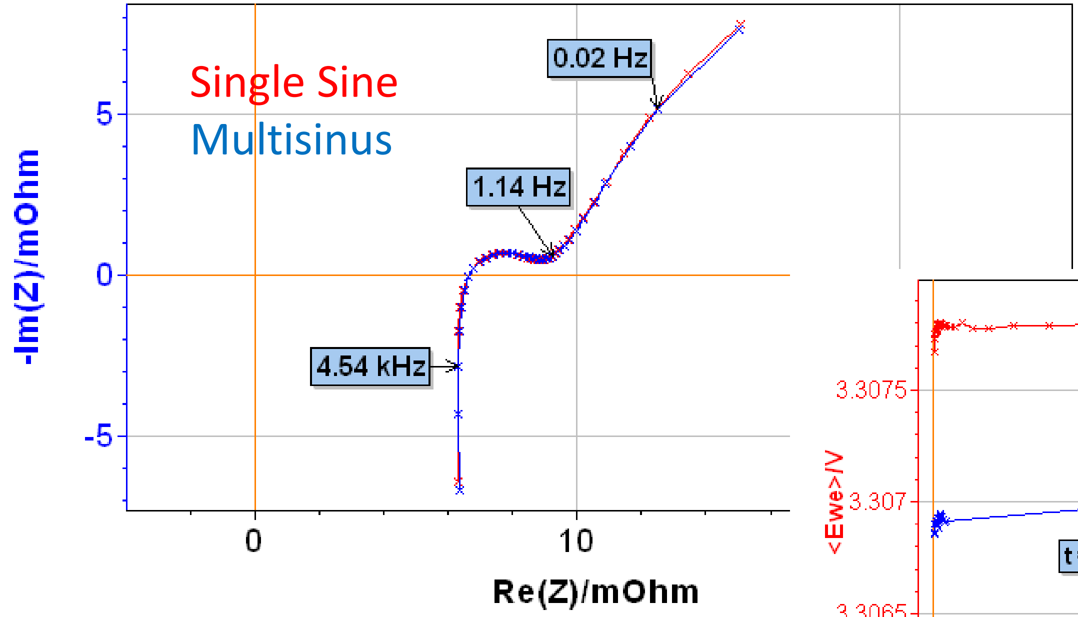


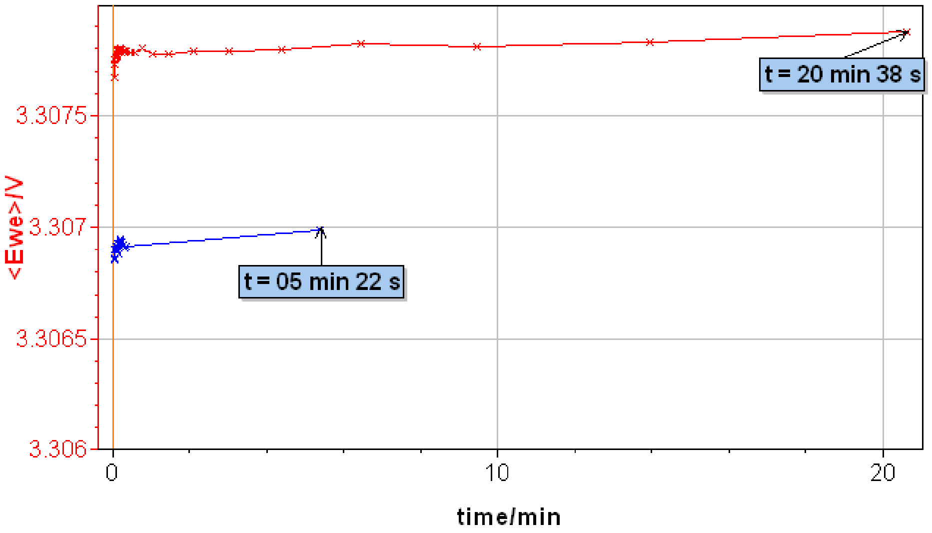
Advantages:

- Reduce time of the measurement (activated below 10 Hz)
- Avoid drifts for non-steady state system on measurement at low frequency

Same result….

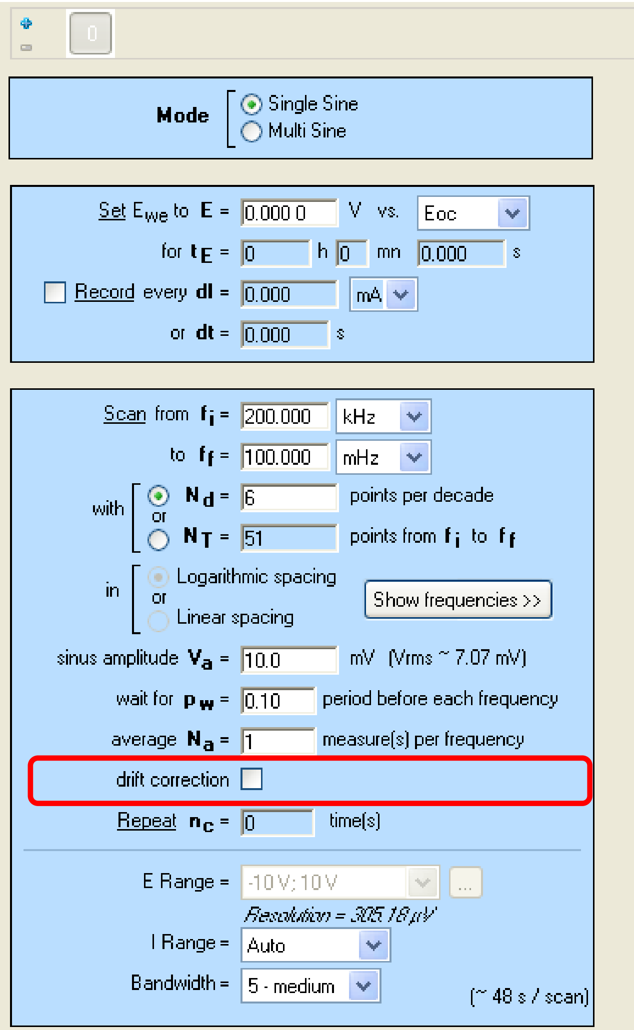
….for less time (5 mn instead of 20 mn)





This is especially important for EIS at low frequency (such as battery)

DRIFT



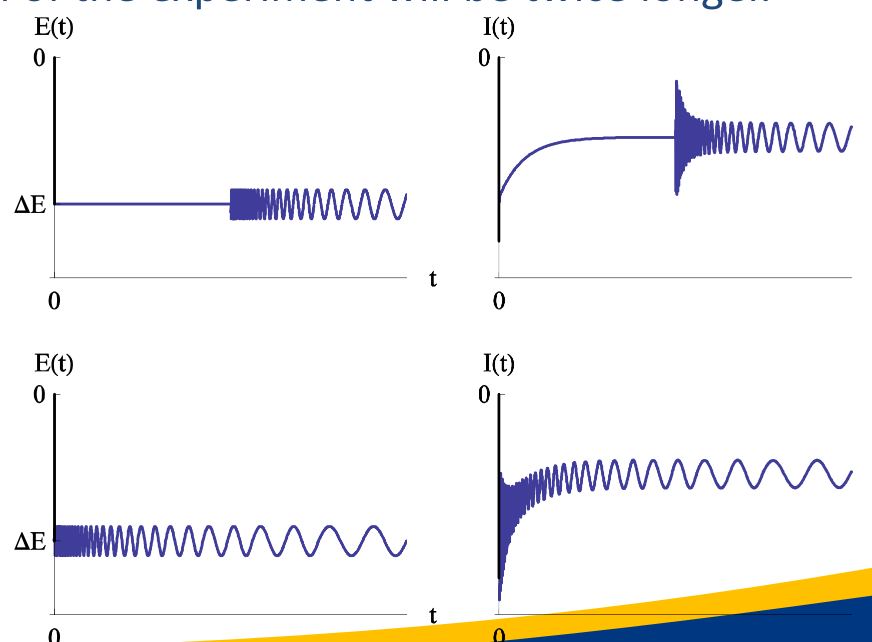
Theoretically, an EIS experiment has to be performed only on the system at its steady state but for slow system such as battery, this is almost never the case, so this option allows the user to perform EIS experiment on a system which is not yet in its steady state.

This is a patented process.

Note: Duration of the experiment will be twice longer.

In its steady-state

Not in its steady-state



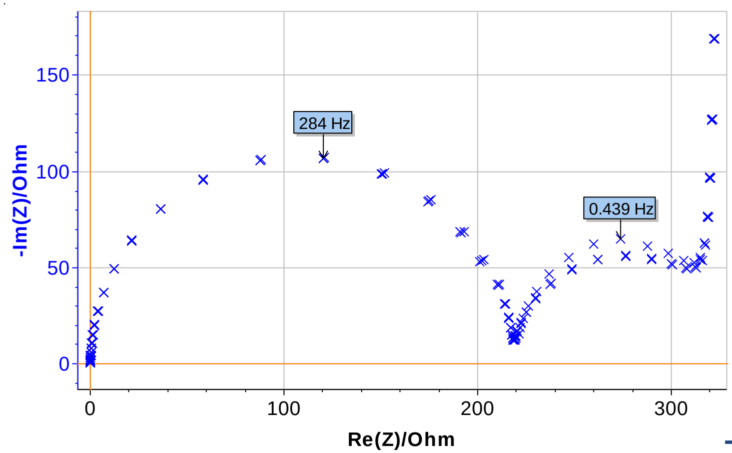
Ref: App. Note 17

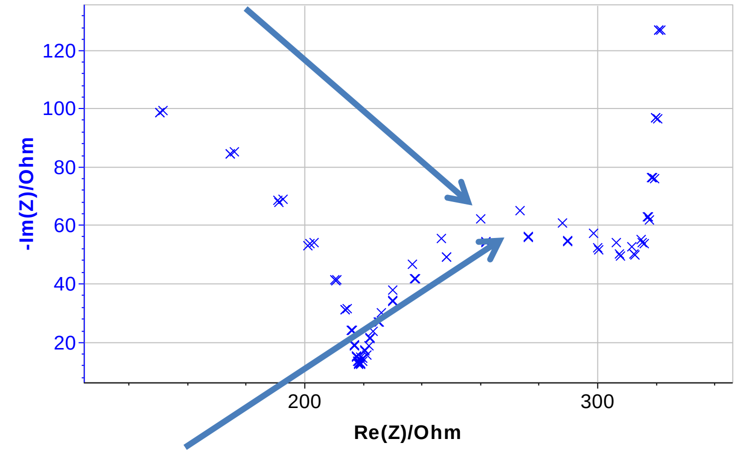
DRIFT

After a pulse of current

First EIS just after the current pulse is higher

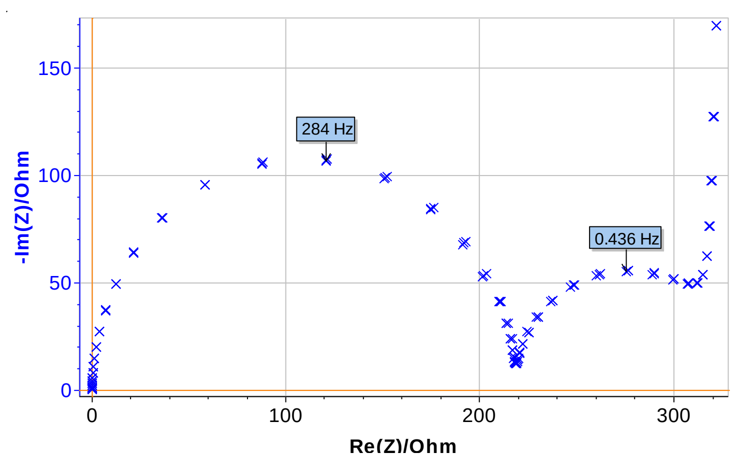
Without drift correction

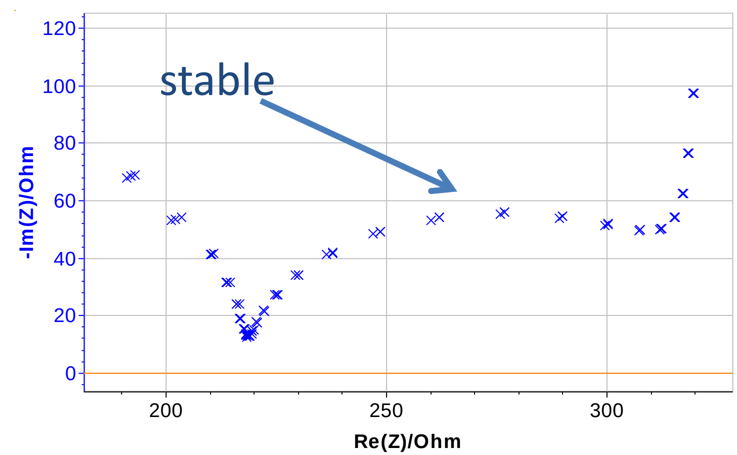




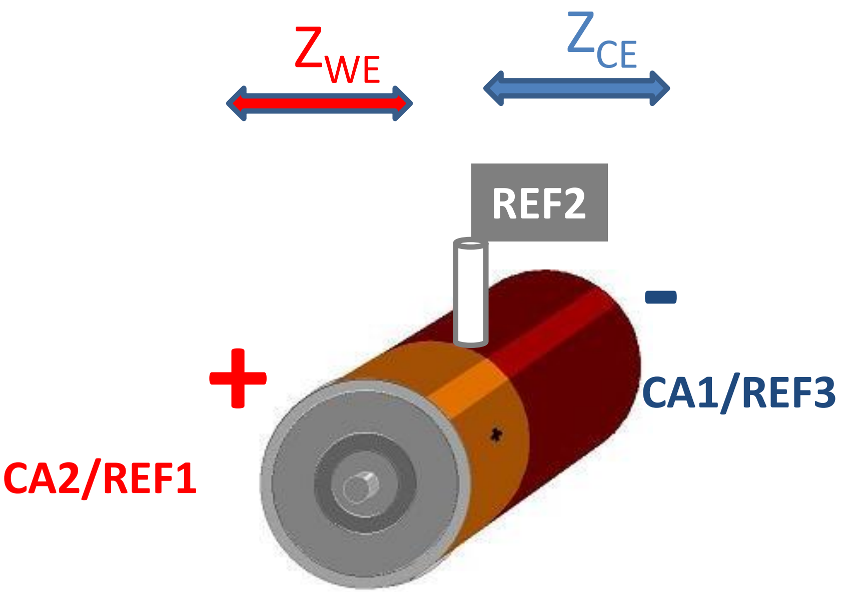
Two other EIS (done after) are stable

With drift correction

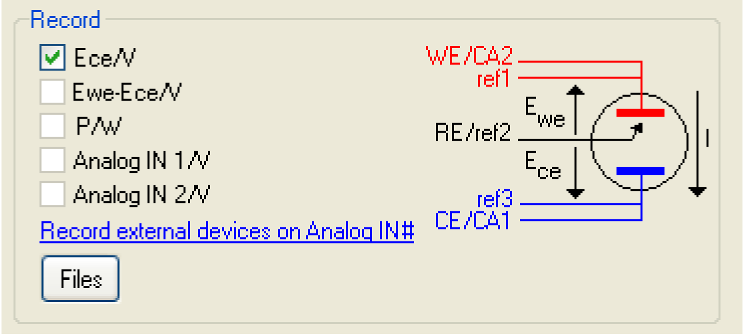




For this kind of measurement, a three-electrode setup is required.

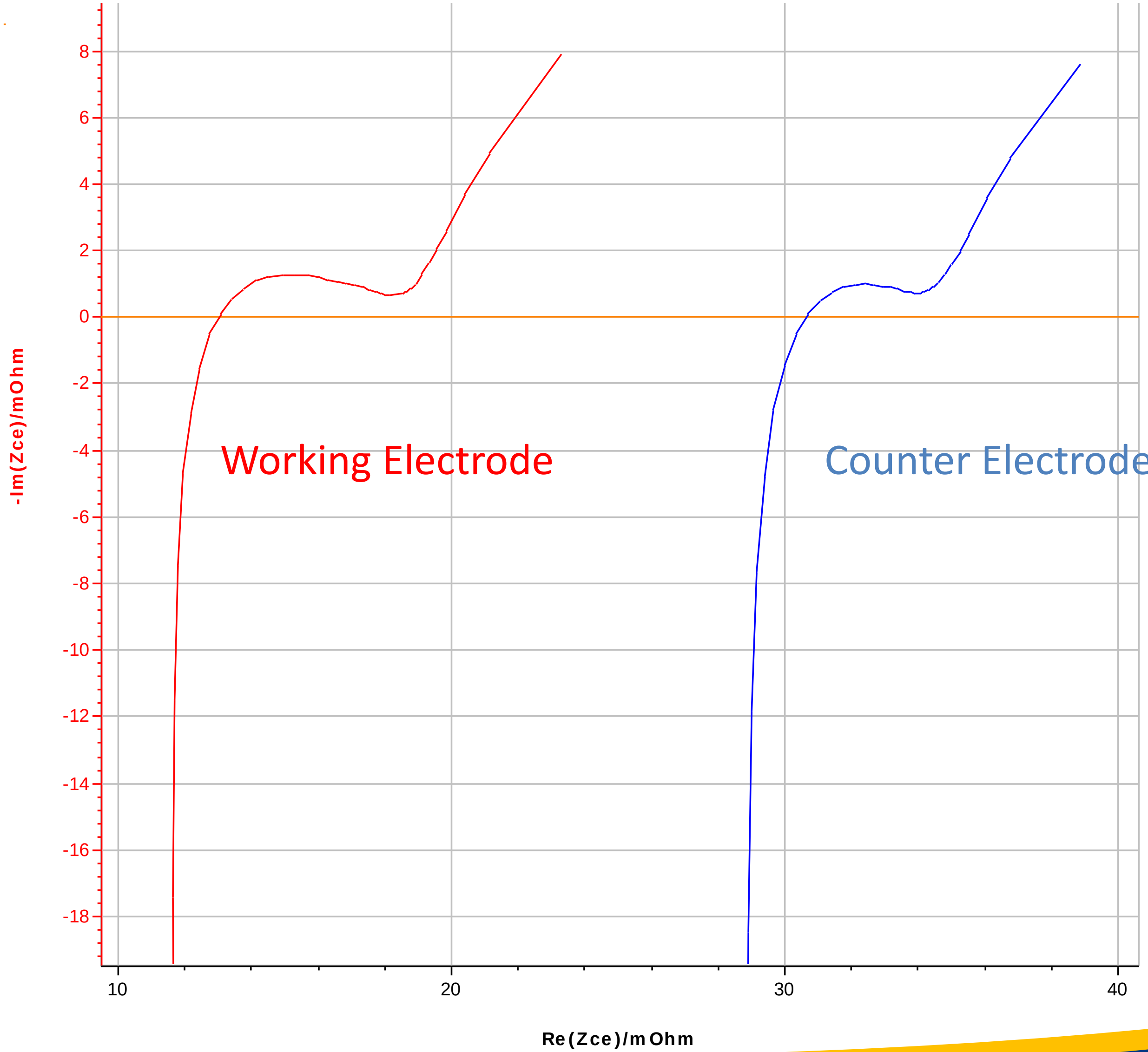


In « Cell Characteristics » tab:



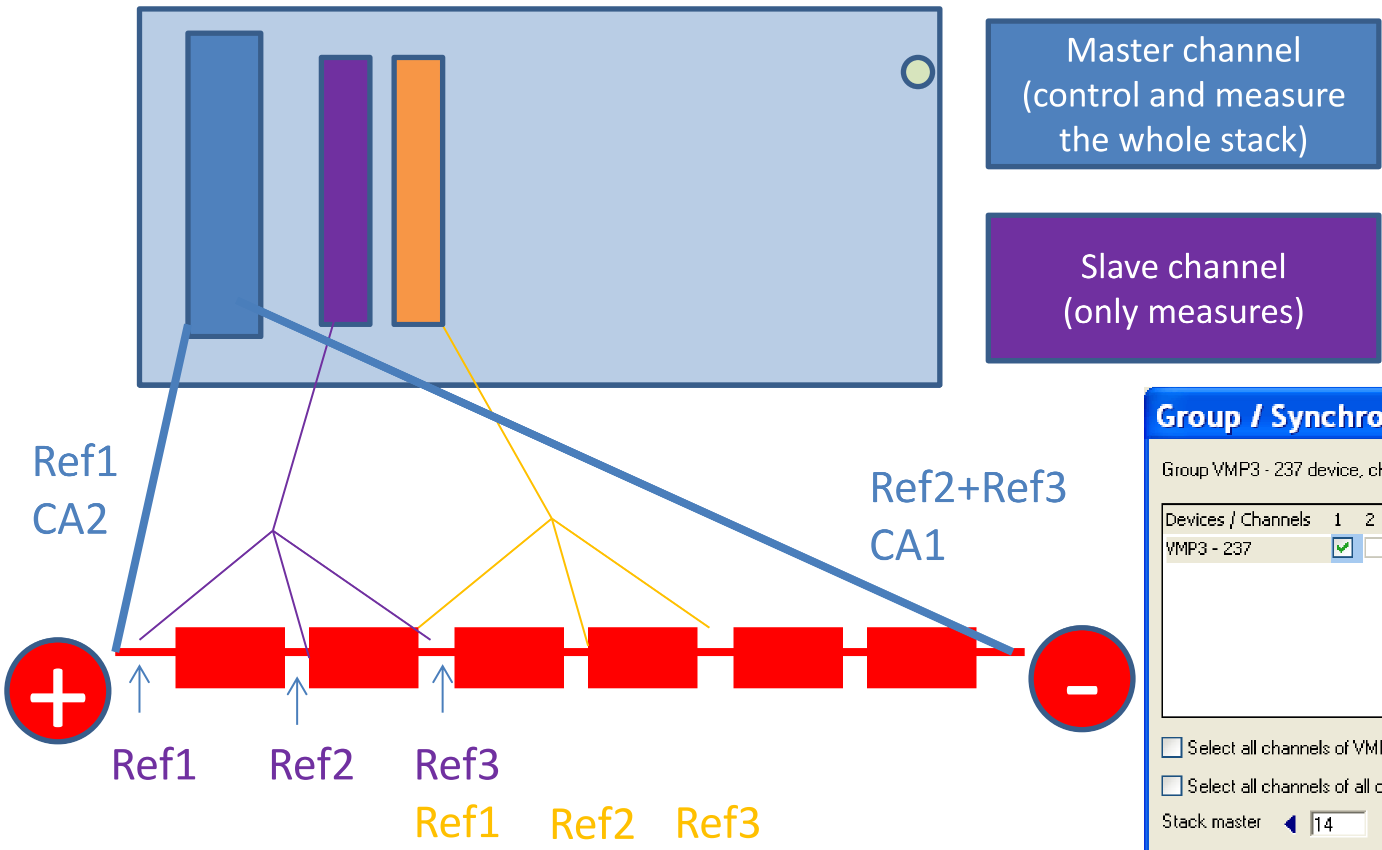
Simultaneous and independent measurment on the two sides of a system. Battery, fuel cell, supercapacitor with a ref electrode.

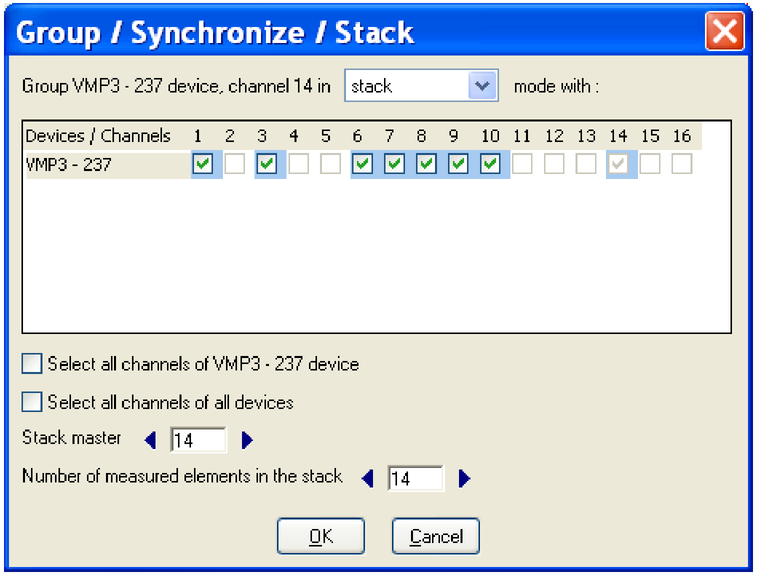
EIS ON COUNTER ELECTRODE



difference is not due to the battery but to the connection

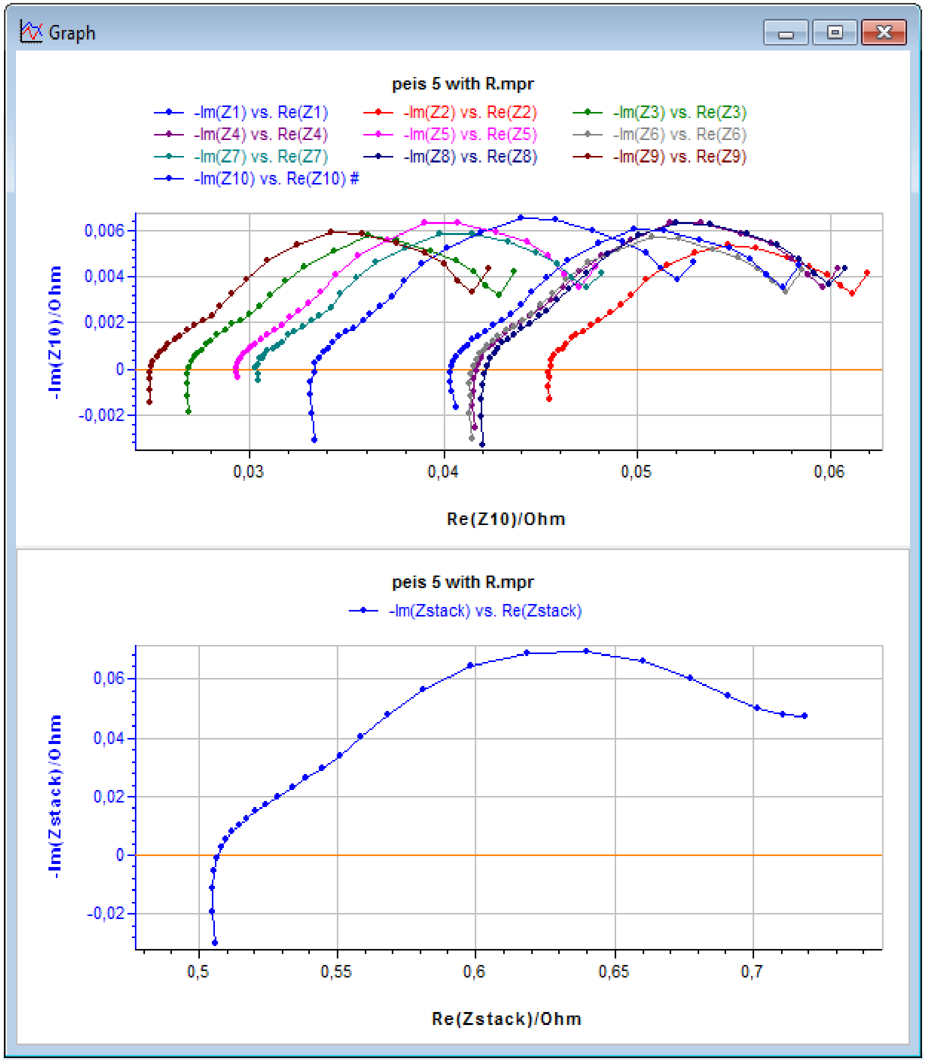
EIS ON STACK OF CELL



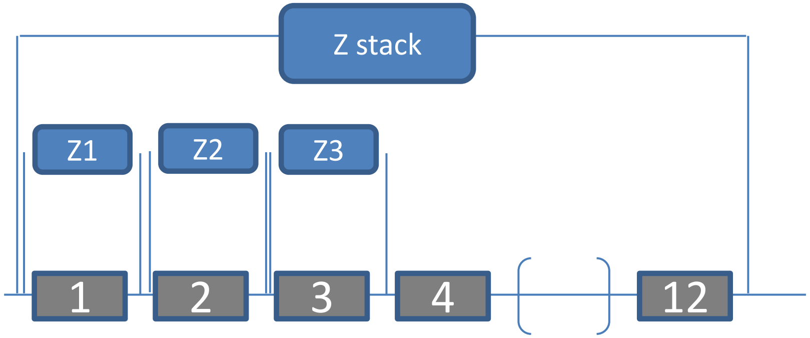


Simultaneously measurment on a whole stack and the behavior follow up of each cell.
Battery, fuel cell, supercapacitor with a ref electrode.

EIS ON STACK OF CELL



- Stack of 12 elements
- Impedance of the stack (Zstack) is the sum of the impedance of each element (Z1, Z2, ...)



Some analysis tools of EC-Lab®

- Kramers-Kronig
- Zfit
- Mott-Schottky/capacity measurement

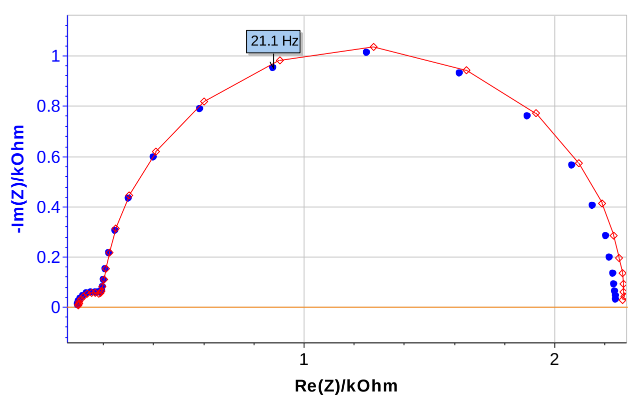
KRAMERS-KRONIG

There is a relationship between Re(Z) and Im(Z) when:
- causal, stable an dlinear time invariant system
- when $f \to 0$ and $f \to \infty$

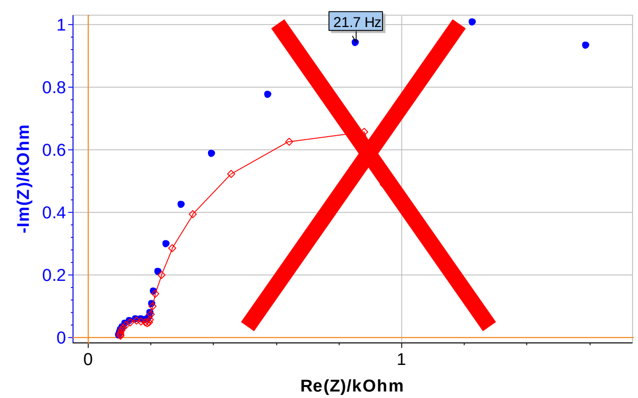
Checks the validity of the measurement

This works only for non-truncated plot.

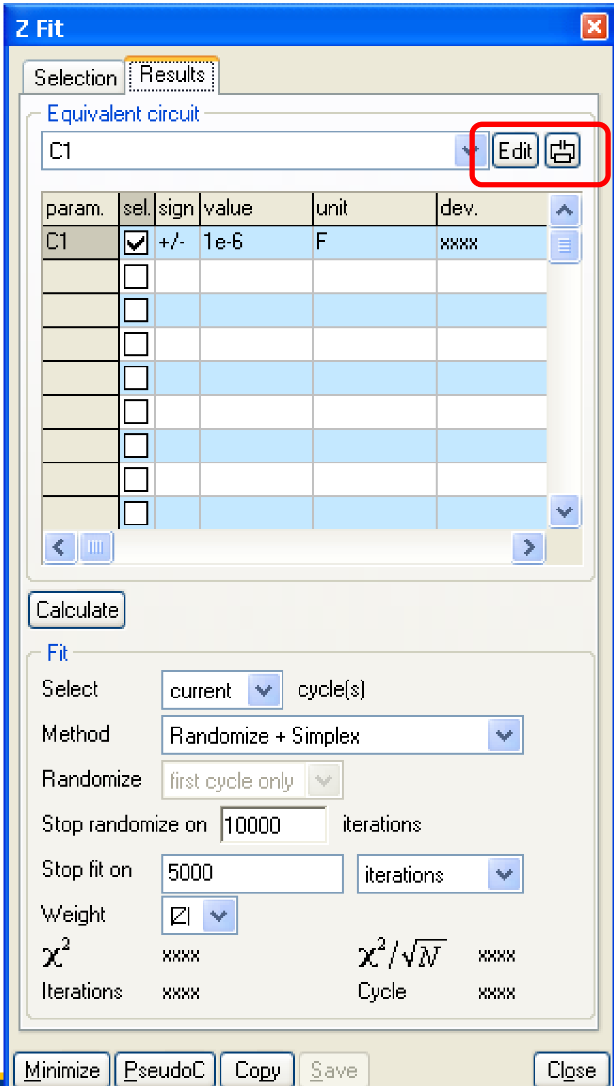
Applicable

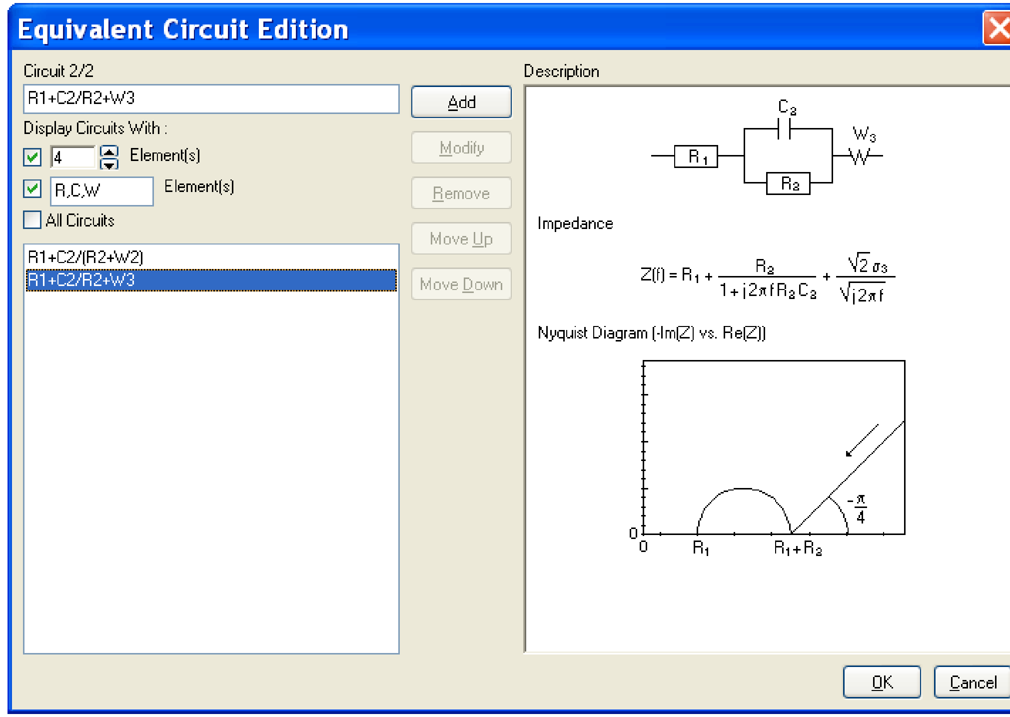


Non-applicable



EIS DATA FITTING (ZFIT)

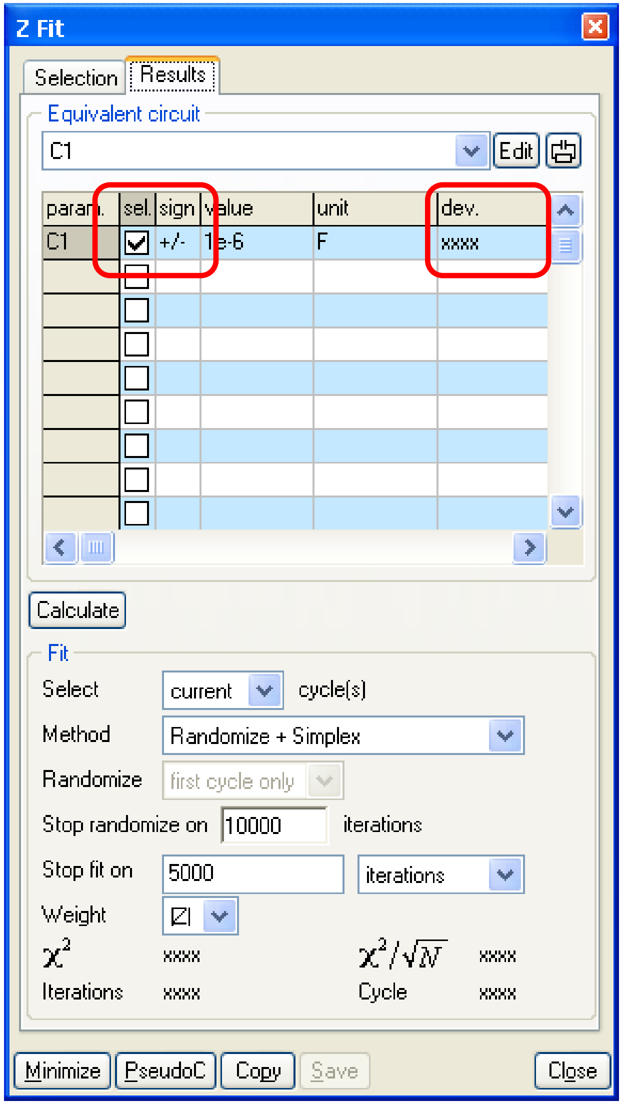




9 elements:

- R: resistor,
- L: self/inductor,
- C: capacitor,
- Q: constant Phase Element (CPE),
- W: Warburg Element simulating the semi-infinite diffusion,
- W_d: Warburg Diffusion Element simulating the convective diffusion,
- M: restricted Linear Diffusion Element,
- G: Gerischer Element.

EIS DATA FITTING (ZFIT)

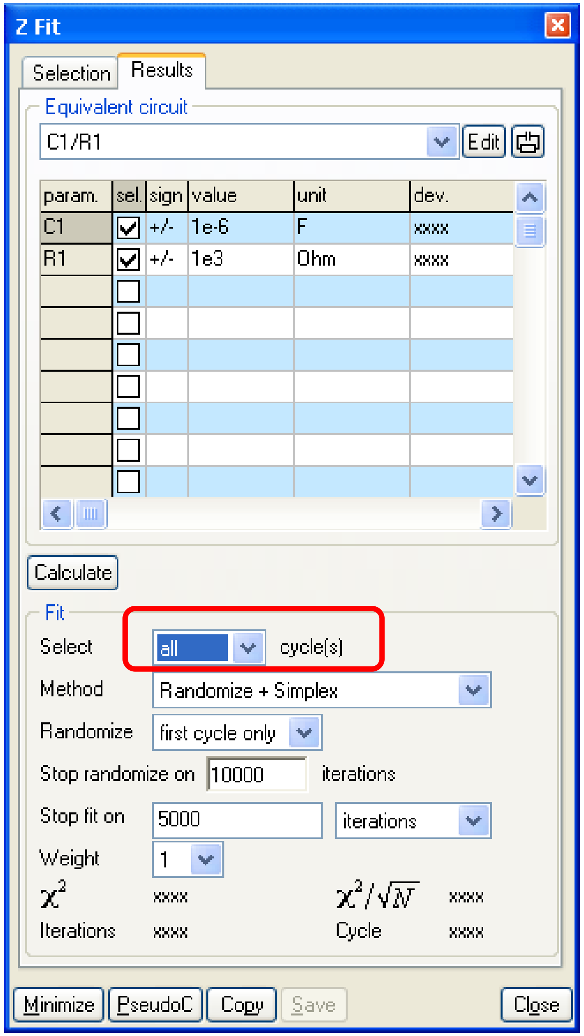


Sel: if this parameter is checked the corresponding value will be used in the fit as defined value (non minimized)

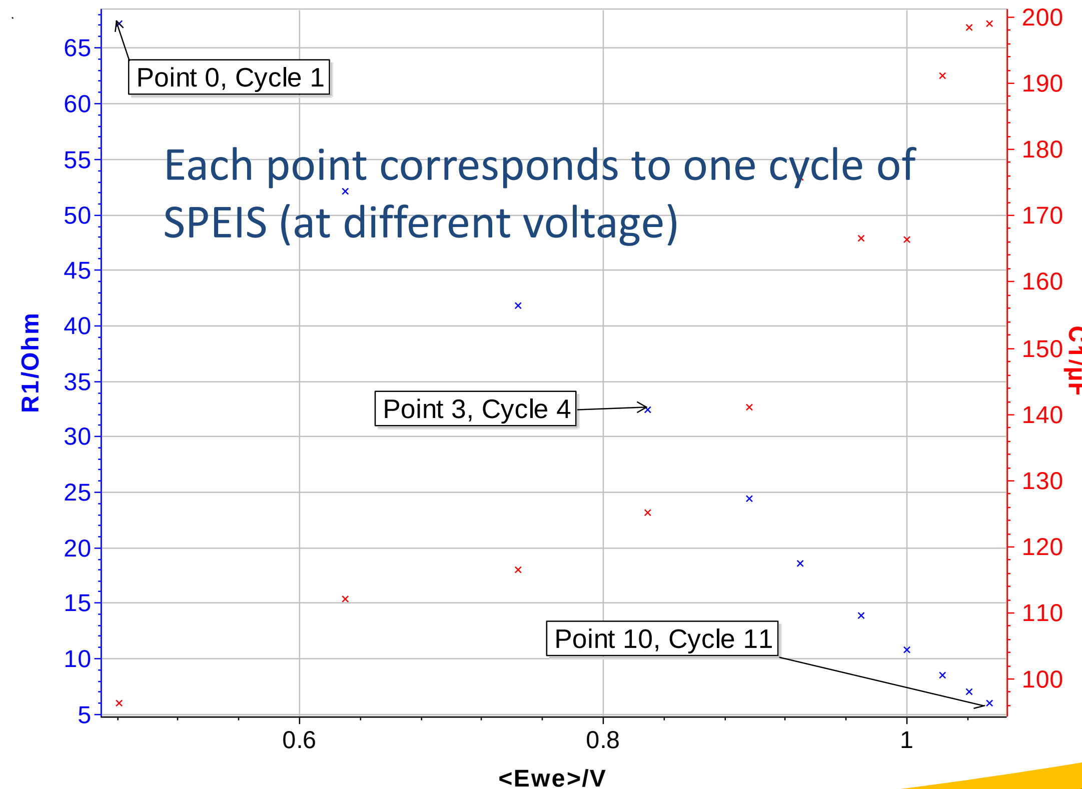
Sign: selection of the sign allowed for the parameter. + and/or -.

Dev: confidence interval (like a standard deviation).

EIS DATA FITTING (ZFIT)



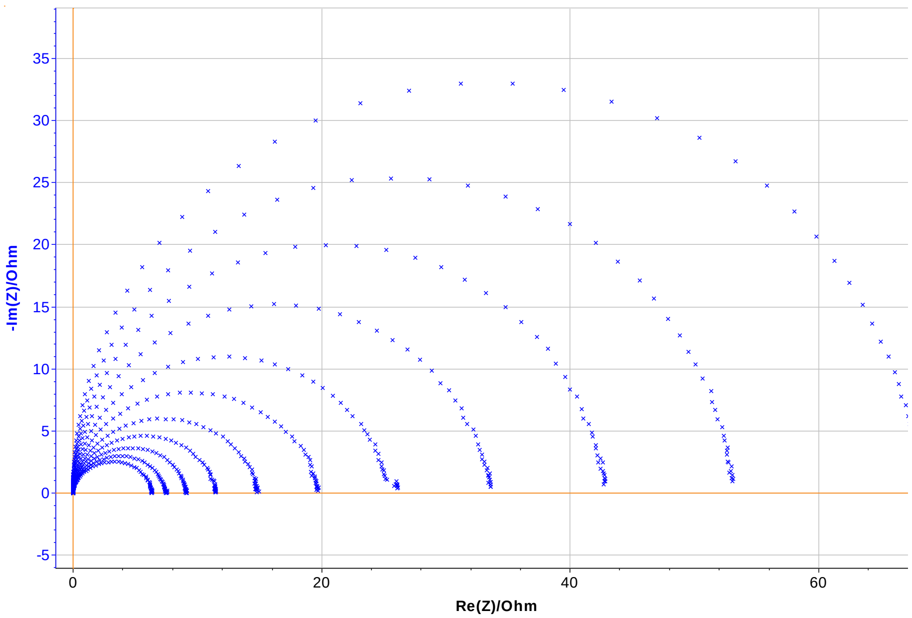
Cycle: allow to fit one cycle or several cycles successively and allow one to follow the changes of the values with the cycles

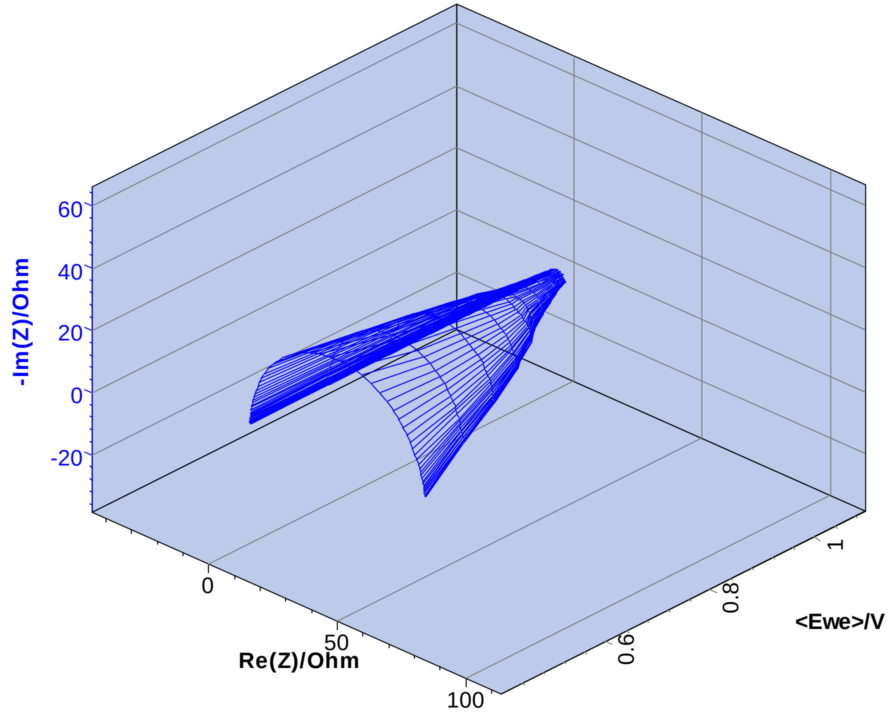


Ref: App. Note 30

EIS DATA FITTING (ZFIT)

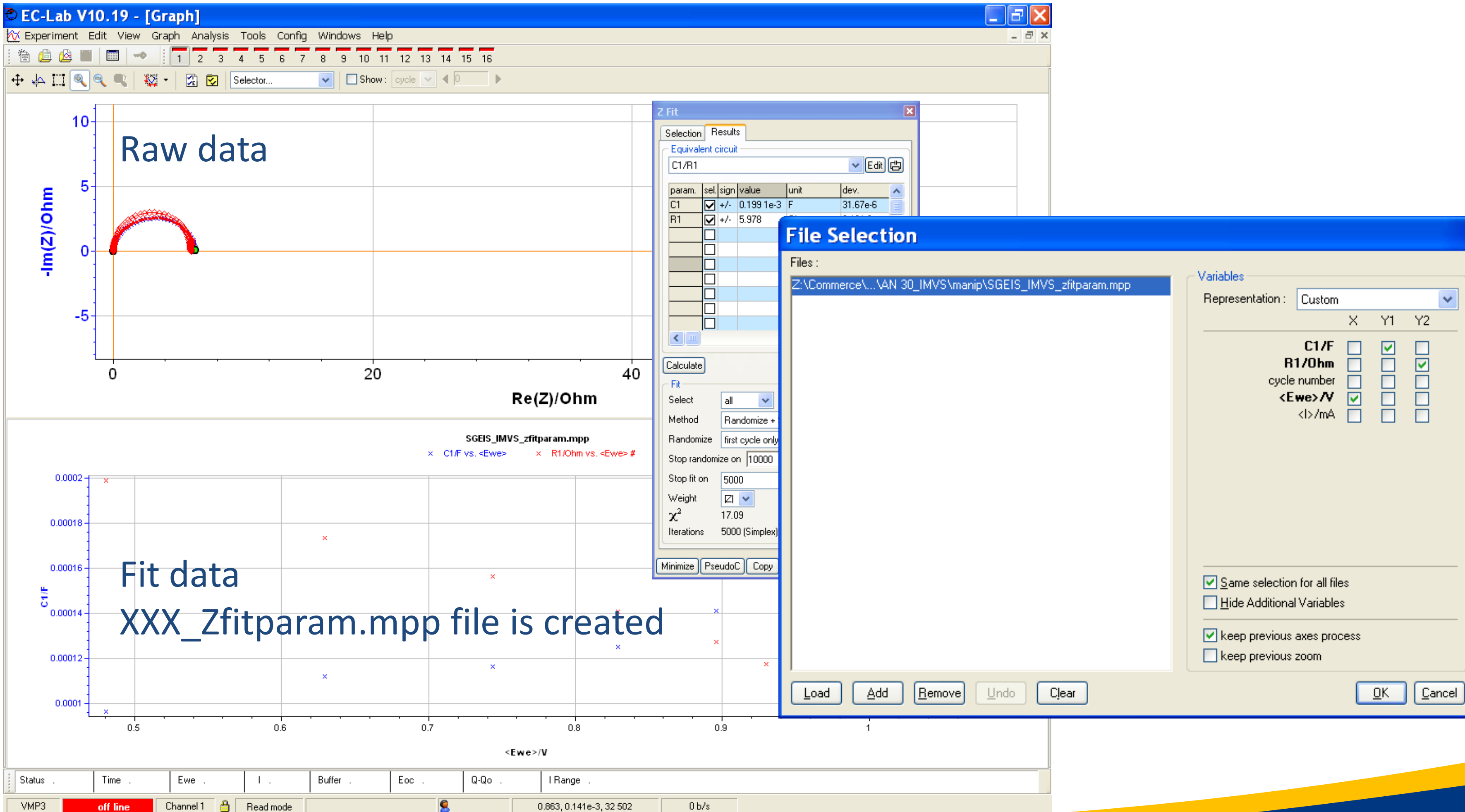
- Fit on several cycles



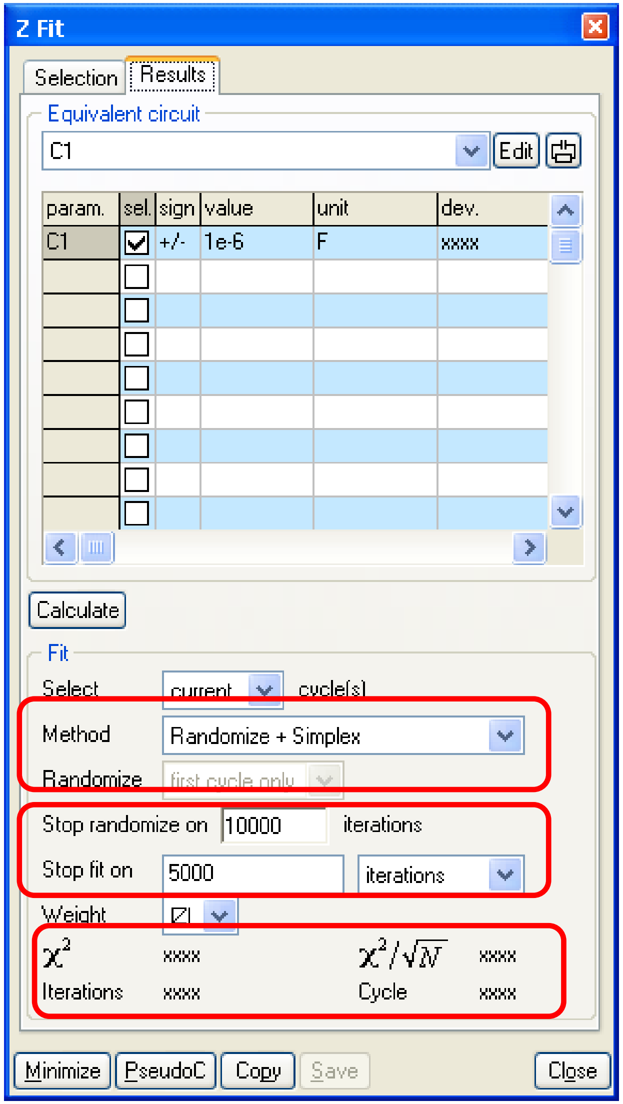


Follow up of the element values variations with time/potential/current..

- Fit on several cycles



EIS DATA FITTING (ZFIT)



Method: Algorithm used for the fit

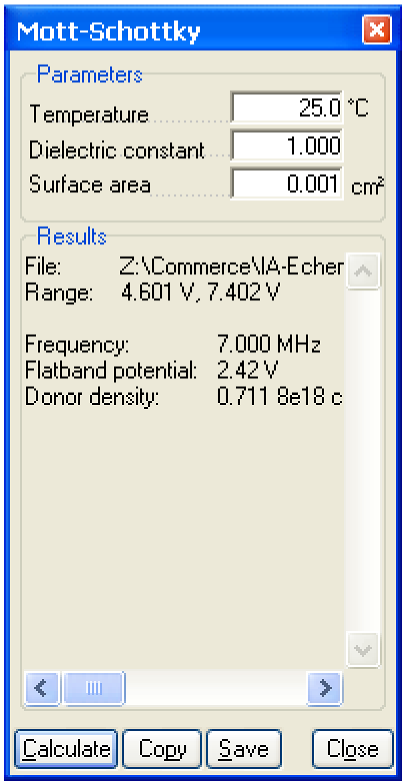
Iterations: Number of iteration

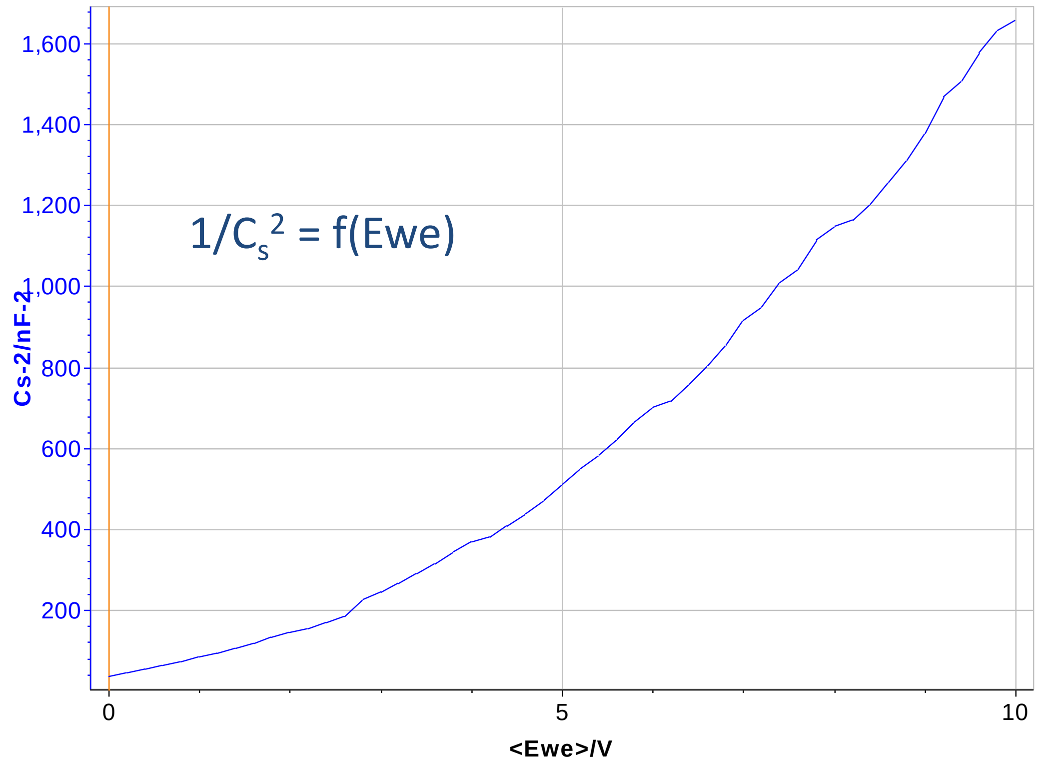
χ^2 quality of the fit. χ^2/N is weighted.

MOTT-SCHOTTKY

$$\frac{1}{C_{SC}^2} = \frac{2}{e\varepsilon\varepsilon_0 N}\left(E - E_{FB} - \frac{kT}{e}\right)$$

C_{sc} is the capacitance of the space charge region,
ε is the dielectric constant of the semiconductor,
ε_0 is the permittivity of free space,
N is the donor density (electron donor concentration for an n-type semi-conductor or hole acceptor concentration for a p-type semi-conductor),
E is the applied potential,
E_{FB} is the flatband potential.



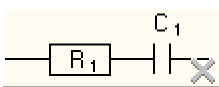


Determination of the flatband potential and the donor density
For semi-conductor, such as PV cell, …

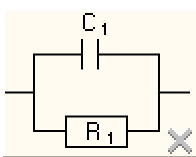
CAPACITY in the MPR FILE

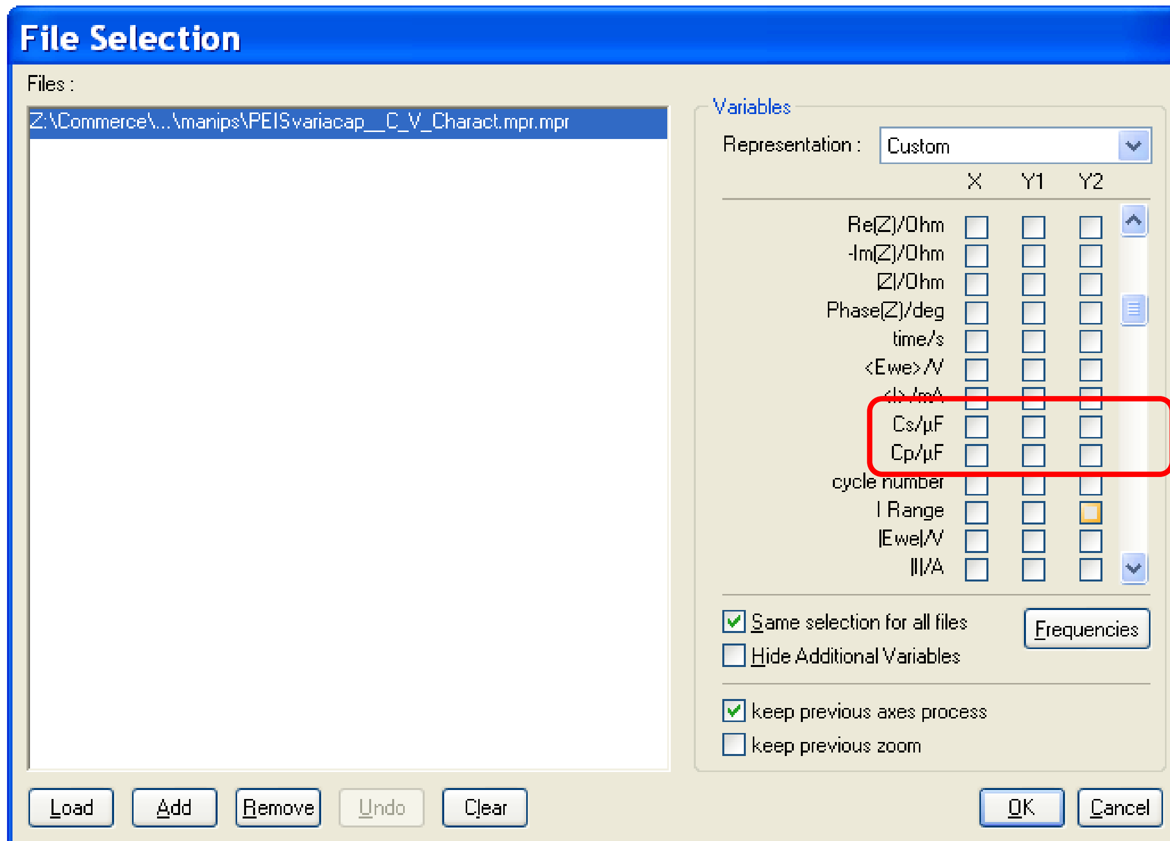
If the equivalent circuit is modeled by R/C_p or $R+C_s$, the mpr file of the EIS techniques (PEIS, GEIS, SPEIS, SGEIS, PEISW) includes already the capacity value C_s and C_p.

C_s



C_p

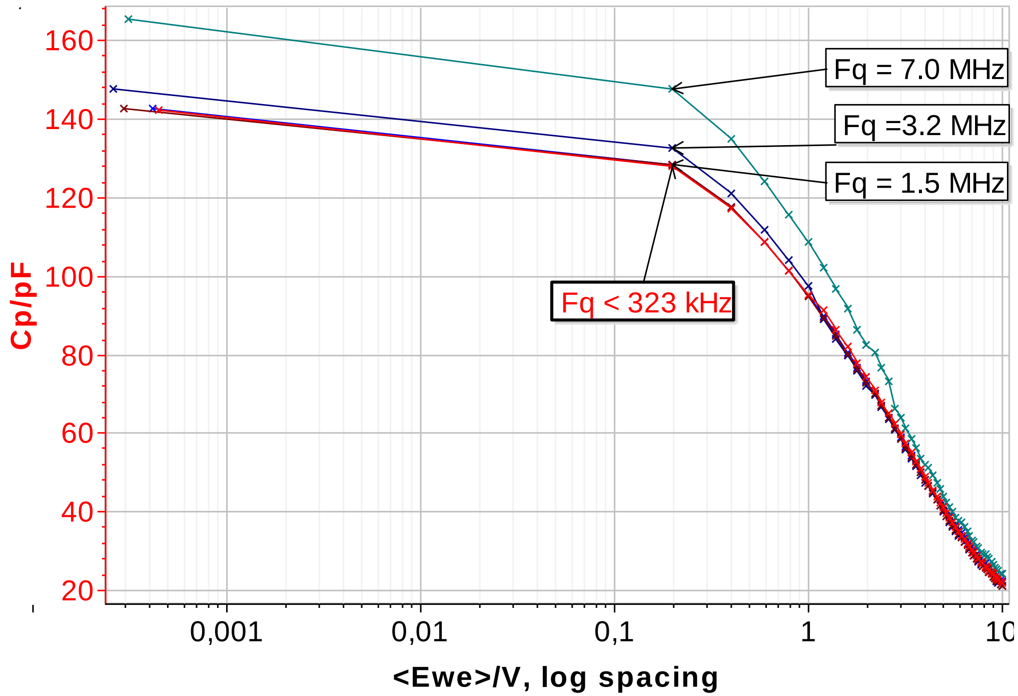




CAPACITY in the MPR FILE

This allows one to plot on-line (without Zfit), C_s or C_p versus voltage or time.

C vs Voltage at several frequencies



MORE INFO…….

Feel free to visit our web site, some application notes or EIS handbook may be helpful for your applications:

http://www.bio-logic.info/potentiostat/notesan.html

Thank you for your attention

Lets move to the instruments