Impedance:
From the experimental side
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
Current response has the same frequency with an amplitude $\delta I$ and phase $\Phi$

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
The impedance is a complex number:
\[ Z = a + j b = Re(Z) + j Im(Z) \text{ (with } j^2 = -1) \]
\[ Z = \rho (\cos \varphi + j \sin \varphi) \text{ with } \rho \text{ the modulus and } \varphi \text{ the phase} \]

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

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
Select the appropriate instrument ...

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

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

*Ref: Brochures*
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 bandwidth 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

Ref: Tech Note 13
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)
1- Fit of the EIS data obtained with 1.5 m cable

It is even clearer in the Bode plot

Ref: Tech Note 13
EXTENDED CABLE

1.5 m cable
10 m cable

Fit of 1.50 m cable

Modulus: line
Phase: marker

Ref: Tech Note 13
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)
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...

Ref: App Note 23
Affects the measurement at low level of impedance. This is particularly relevant for battery, supercapacitor investigations...

Ref: App Note 23
Reduce ohmic drop of the cell by:
- decreasing the distance between RE and WE
- changing the Vycor glass of the RE
- ...

A resistor of 1 kOhm was added to mimic the ohmic drop

Affects the measurement of low impedance system at high frequency (battery, supercapa, ...)
Determine/compensate the ohmic drop resistance thanks to ZIR technique (measure the \( \text{Re}(Z) \) at one frequency).

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

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

Control of temperature of the cell may be required.
What’s that?

Only artifact due to reference electrode impedance not negligible at high frequencies.
This is due to the Ref Electrode

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

At high frequency the impedance of the capacitor is negligible.

IZI = 1/(2πfC)

Ref electrode

Capacitor

Frequency/Hz

IZI/Ohm

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Capacitor

Frequency/Hz

IZI/Ohm
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

Ref: EC-Lab® manual
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 galvanostatic or bias voltage for potentiostatic) 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.

Ref: EC-Lab® manual
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.
This average process smoothes the random error of the measurement.

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

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

$Na = 1$

$Na = 36$
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 excitation, 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

Ref: App. Note 19
Same result....

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

This is especially important for EIS at low frequency (such as battery)
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.
After a pulse of current

First EIS just after the current pulse is higher

Two other EIS (done after) are stable

After a pulse of current

Without drift correction

With drift correction

Ref: App. Note 17
For this kind of measurement, a three-electrode setup is required.

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

In « Cell Characteristics » tab:
EIS ON COUNTER ELECTRODE

difference is not due to the battery but to the connection

Working Electrode

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

Ref: App. Note 16
- Stack of 12 elements

- Impedance of the stack (Z_{stack}) is the sum of the impedance of each element (Z_1, Z_2, ...)

\[ Z_{stack} = Z_1 + Z_2 + Z_3 + \ldots + Z_{12} \]

Ref: App. Note 16
Some analysis tools of EC-Lab®

• Kramers-Kronig
• Zfit
• Mott-Schottky/capacity measurement
There is a relationship between $\text{Re}(Z)$ and $\text{Im}(Z)$ when:
- causal, stable and linear time invariant system
- when $f \to 0$ and $f \to \infty$

Checks the validity of the measurement

This works only for non-truncated plot.

Ref: App. Note 15
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.

Ref: Manual of EC-Lab®
**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).
Cycle: allow to fit one cycle or several cycles successively and allow one to follow the changes of the values with the cycles

Each point corresponds to one cycle of SPEIS (at different voltage)
- Fit on several cycles

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

Ref: App. Note 30
- Fit on several cycles

Raw data

Fit data
XXX_Zfitparam.mpp file is created
**Method:** Algorithm used for the fit

**Iterations:** Number of iteration

$\chi^2$ quality of the fit. $\chi^2/N$ is weighted.
MOTT-SCHOTTKY

\[
\frac{1}{C_{5c}^2} = \frac{2}{\varepsilon \varepsilon_0 N} \left( E - E_{FB} - \frac{kT}{e} \right)
\]

\( C_{5c} \) is the capacitance of the space charge region, 
\( \varepsilon \) is the dielectric constant of the semiconductor, 
\( \varepsilon_0 \) is the permittivity of free space, 
\( N \) is the donor density (electron donor concentration for an n-type semiconductor or hole acceptor concentration for a p-type semiconductor), 
\( E \) 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, ...

Ref: App. Note 24
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 $C_p$. 

Ref: App. Note 35
This allows one to plot on-line (without Zfit), $C_s$ or $C_p$ versus voltage or time.

C vs Voltage at several frequencies

$C_p/pF$

$F_q = 7.0 \text{ MHz}$

$F_q = 3.2 \text{ MHz}$

$F_q = 1.5 \text{ MHz}$

$F_q < 323 \text{ kHz}$

$<E_{we}>/V$, log spacing

Ref: App. Note 35
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

Let's move to the instruments