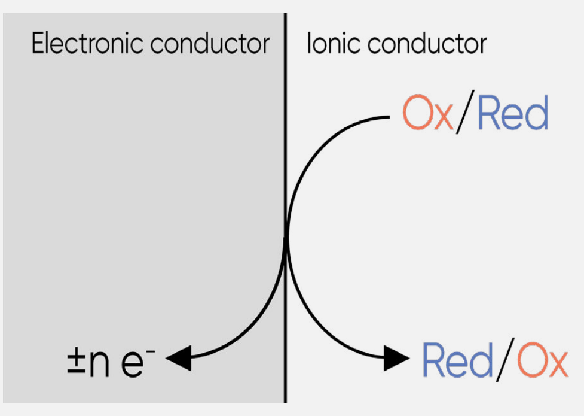
Best Laboratory Practices in Electrochemistry

Definition



Electrochemistry is a science that studies chemical reactions which most often take place at the interface between an electronic conductor (electrode) and an ionic conductor (electrolyte) and involve electrons transfer.

To carry out these measurements, a potentiostat/galvanostat is used. Usually, a three-electrode setup is used *i.e.* Working Electrode (WE), Reference Electrode (RE) and Counter Electrode (CE). A potentiostat/galvanostat applies/measures:
- a voltage between WE and RE,
- a current flow through WE and CE.

Electrochemical techniques are highly sensitive methods and precautions must be taken to prevent the collection of false or erroneous data resulting from experimental errors.

Applications		
	Electroanalytical	Sensors
	Corrosion	Coatings
	Battery	Fuel/solar cells
	Supercapacitors	Materials

Reminder

The **Redox** reaction: $Ox + ne^- \rightleftharpoons Red$

Variables

E: measured potential (V)
I: current (A)
Q: charge (C or A s) $Q = It$
1 C = 1 mA h/3.6
R: resistance (Ω)
P: power (W) $P = E\,I$
W: energy (J) $W = E\,I\,t$

The **Nernst** equation:

Thermodynamic information

$$E_{eq} = E^{O} + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]}$$

with
E^{O}: equilibrium potential in the standard conditions (V)
R: perfect gas constant (8.315 J K^{-1} mol^{-1})
T: temperature (K)
n: number of exchanged electrons
F: Faraday constant (96,487 C mol^{-1})
$[x]$: concentration of the species x (mol cm^{-3})
10^{-3} mol cm^{-3} = 1 mol L^{-1}

The **Levich** equation:

Transport information gained from RDE experiments.

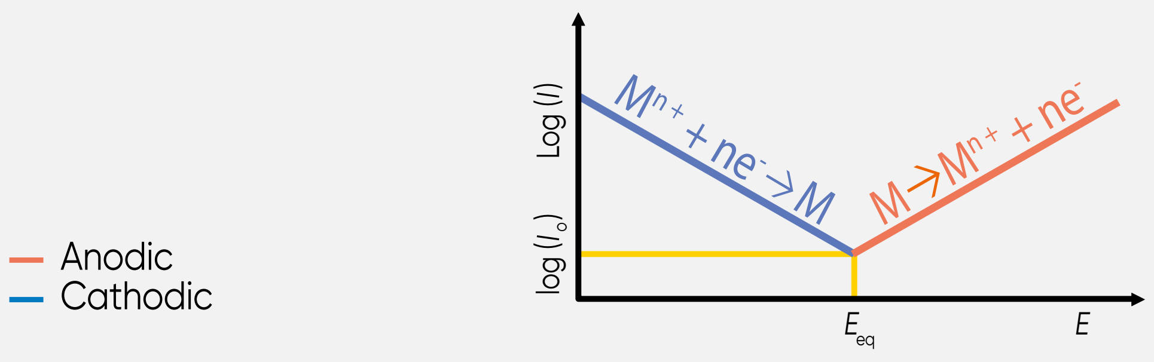
$$I_L = 0.620\, n\, F\, A\, D^{\frac{2}{3}}\, \Omega^{\frac{1}{2}}\, v^{\frac{-1}{6}}\, [x]$$

with
I_L: Levich current (A)
n: number of exchanged electrons
F: Faraday constant (96,487 C mol^{-1})
A: electrode area (cm²)
D: diffusion coefficient (cm² s^{-1})
Ω: angular rotation rate of the electrode (rad s^{-1})
1 rpm = 2π/60 rad s^{-1}
v: kinematic viscosity (cm² s^{-1})
$[x]$: concentration of the species x (mol cm^{-3})
10^{-3} mol cm^{-3} = 1 mol L^{-1}

The **Butler-Volmer** equation:

$$I = I_0\left(\left(\exp \frac{\alpha_o nF}{RT}(E-E_{eq})\right) - \left(\exp \frac{-\alpha_r nF}{RT}(E-E_{eq})\right)\right)$$

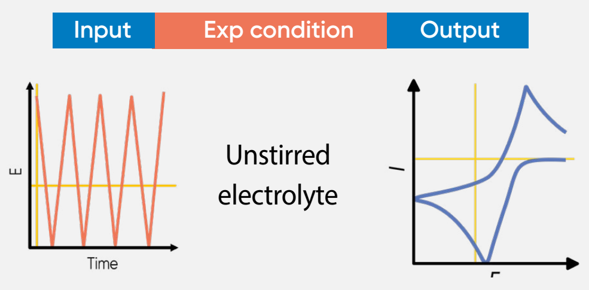
Kinetic information



with
I_0: exchange current (A)
α_x: symmetry factor (α_o+α_r=1)
R: perfect gas constant (8.315 J K^{-1} mol^{-1})
T: temperature (K)
n: number of exchanged electrons
F: Faraday constant (96,487 C mol^{-1})
E_{eq}: equilibrium potential in the standard conditions (V)
E: applied potential (V)

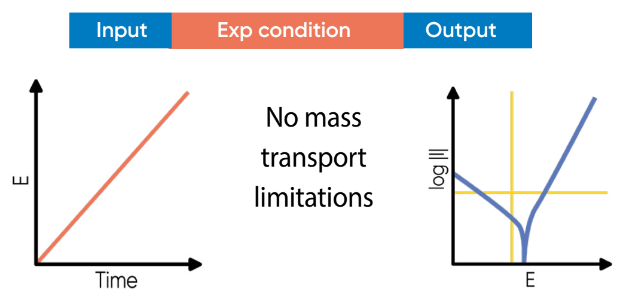
CV (Cyclic Voltammetry)

Sweep of voltage (forward and backward scan), the current is measured. This allows the user to characterize the species and mechanism of interest.



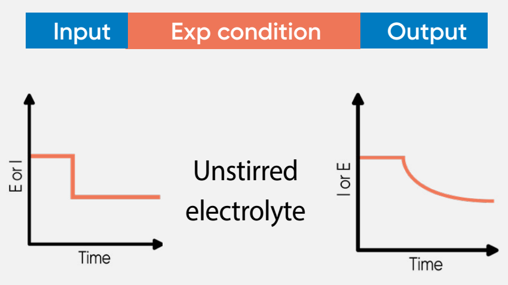
Tafel Plot

The log of absolute value of current *vs.* potential is plotted to extract kinetic constants.



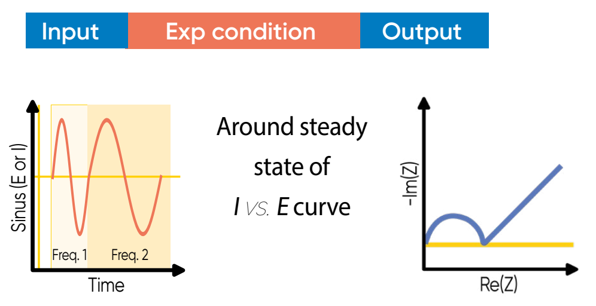
Step methods

A potential or a current step is applied to the system and its response is followed over time. The user may add species that will modify the electrode and the system response.



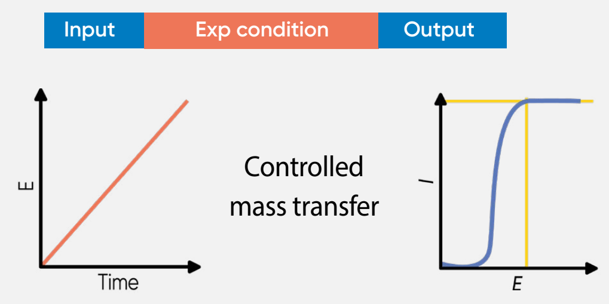
EIS (Electrochemical Impedance Spectroscopy)

A sinusoidal perturbation is applied to the cell (as potential or current) in a range of frequencies. Valuable information such as kinetic parameters or diffusion coefficients can be found. Typically, the resulting plot is a Nyquist plot *i.e.* -Im (Z) *vs.* Re (Z).



Hydrodynamic (Steady-state voltammetry)

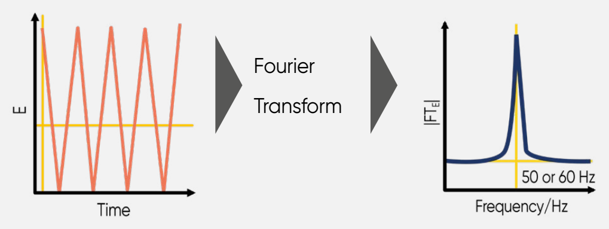
A Rotating Disc Electrode (RDE) is employed to maintain a known mass transfer rate of electroactive species from the bulk solution to the electrode surface.



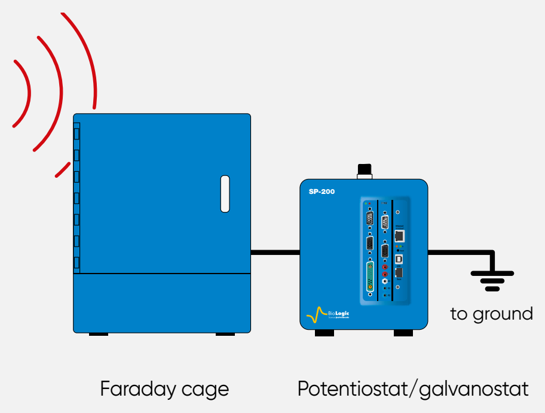
Set-up

Shielding

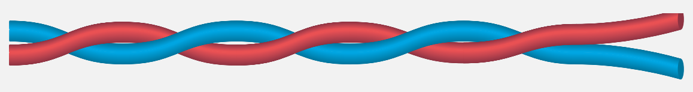
Faraday cage: when measuring low currents, the electrochemical cell should be placed in the Faraday cage and the cage must be connected to the ground of the instrument. This creates an equipotential shielding and eliminates any electromagnetic perturbation that may come from the electrical grid or other "noise" sources in your laboratory.



If the frequency of the grid is present in your data, you must improve the cell shielding. When several devices are involved in your experiment (RDE, thermostat...) make sure that all instruments share the same Earth ground.

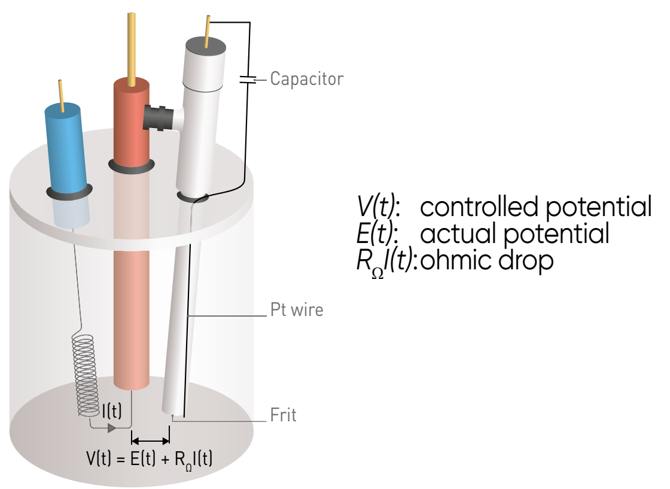


Decrease the inductive effects that result from high current passing through your circuit by employing "twisted pairs". Twist the cables that carry current to minimize electromagnetic effects that can affect your data.



Cell Geometry

Place the WE close to the RE: this will help to minimize the ohmic drop $R_\Omega I(t)$ across the electrolyte. If not set up properly, the actual potential seen by the electrode will be lower than the applied potential. EIS is recommended to measure the ohmic drop of your cell. Warning: if the ohmic drop is significant theoretical models cannot be applied to your system.



$V(t)$: controlled potential
$E(t)$: actual potential
$R_\Omega I(t)$: ohmic drop

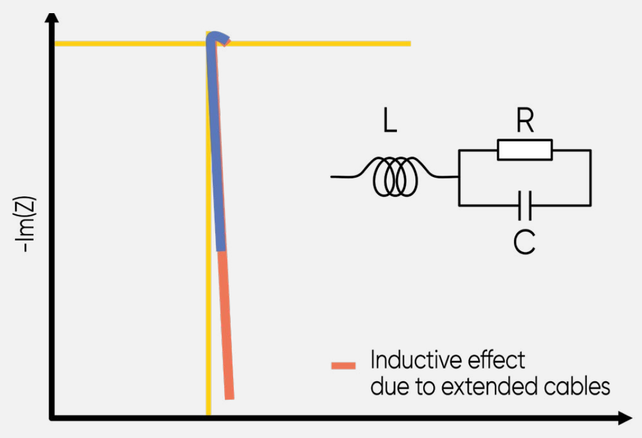
The impedance of the RE: the effect is significant especially in EIS measurement. The impedance should be low. If the impedance of the reference is too high, you may have to change the frit tip or even change the reference electrode. In some cases, for high frequency measurements a platinum wire and capacitor must be added to the RE.

RE selection: select the appropriate RE according to your application (pH, chloride free, temperature).

Proper Cell Connection

Minimizing contact resistance: a 4-point connection to a low impedance device (battery, supercapacitor...) separates the current-carrying lead from the voltage-sensing lead. This ensures that there is no current passing through the voltage-sensing lead and improves measurement accuracy.

Do not use extension cables: when measuring low impedance. Extension cables, especially unshielded ones, can add inductive effects to EIS measurements.



	H_2/H^+ (RHE)	Ag/AgCl	Hg/HgO	$Ag/AgNO_3$	$Hg/HgSO_4$	Hg/Hg_2Cl_2
Aqueous	■	◧	◧	◧	◧	◧
Alkaline solutions	■	◧	■	◧	◧	◧
Sea water	■	◧	◨	◧	◧	◨
Organic media	◧ *	◨	◨	■	◨	◨
Hydrofluoric acid	■	🟧	🟧	🟧	🟧	🟧

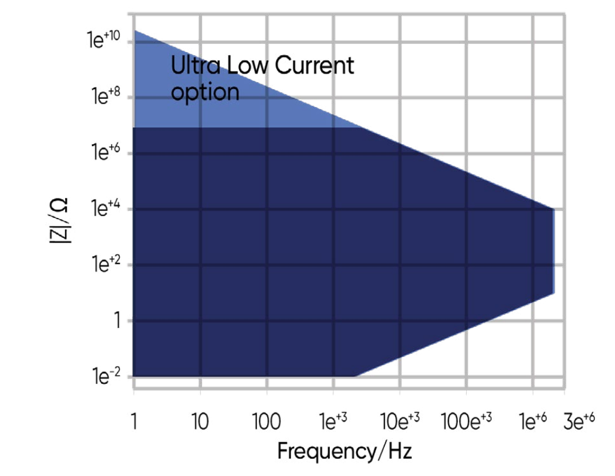
■ Recommended ◧ Acceptable ◨ Not recommended 🟧 Risk of damage

* *Only with protic solutions*

Signal Processing

Hardware Configuration

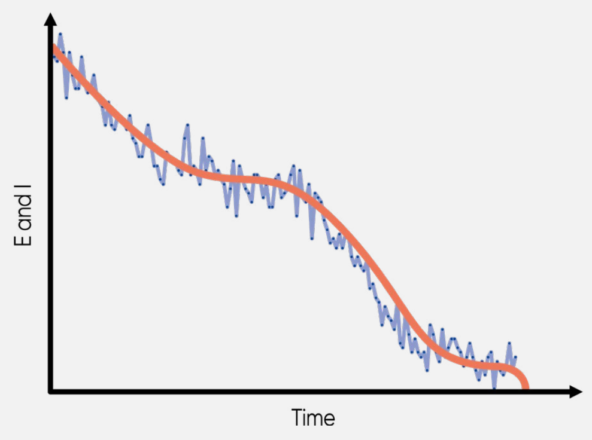
Specifications: check if expected E/I correspond to the configuration of the instrument (resolution/accuracy). Low or high current options may be required.



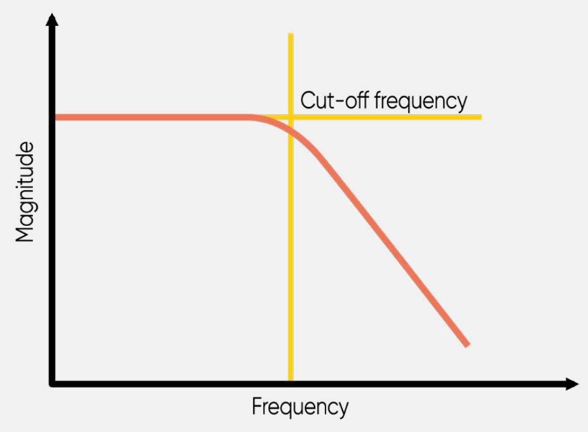
Contour plot in different configurations where: $\frac{\Delta Z}{Z} < 1\%$ $\Delta\Phi < 1°$

Data Processing

Averaging: if the data is too noisy, averaging may be employed. Signal averaging reduces noise levels by the square root of N where N is the number of samples taken for the average. Thus, to reduce noise by a factor of two, four samples should be taken in the average.



Filtering: some instruments offer low-pass filters as part of the hardware and can be turned on or off by the user. Low-pass filters allow signals with frequencies below the cutoff frequency to be measured.



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