

Graphic Customization

I – INTRODUCTION

Good graphical representation makes understanding data much easier. EC-Lab® and EC-Lab® Express software provide “a trace processing tool” (Fig. 1) which allows the users to customize their own traces.

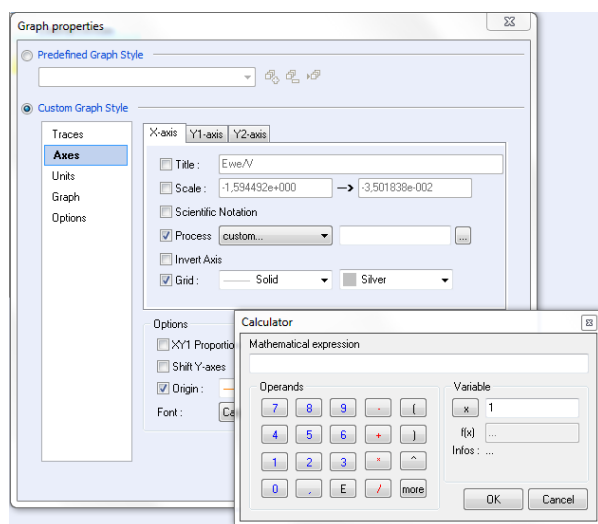


Figure 1: Traces process windows.

exp()	exponential of a number
sqr()	square of a number
sqrt()	square root of a number
abs()	absolute value
round()	round to the nearest integer
trunc()	truncates a real number to an integer
ln()	natural logarithm
log10()	logarithm base 10
logN(,)	logarithm for a specified base : LogN(Base, X)
sin()	sine of an angle in rad
cos()	cosine of an angle in rad
tan()	tangent of an angle in rad
arcsin()	inverse sine in rad
arccos()	inverse cosine in rad
arctan()	inverse tangent in rad
sinh()	hyperbolic sine of an angle in rad
cosh()	hyperbolic cosine of an angle in rad
tanh()	hyperbolic tangent of an angle in rad
arcsinh()	inverse hyperbolic sine in rad
arcosh()	inverse hyperbolic cosine in rad
artanh()	inverse hyperbolic tangent in rad
PI	3.1415926535897932385
degtorad()	conversion of degrees to radians
radtodeg()	conversion of rad to degrees

Figure 2: Mathematical functions available in calculator.

24 mathematical functions (Fig. 2) are available (button “more” of the calculator) for writing mathematical expression of X-, Y1- or Y2-axis.

In this application note, some examples of graphic customization are shown in various fields of electrochemistry.

II – RDE VOLTAMMETRY APPLICATION

The plot $\log [i/(i_{lim} - i)] = E$ could be required in order to determine the standard potential and the number of electrons involved in the redox process under stationary conditions and for Nernstian system. Consequently, this feature is used in Rotating Disk Electrodes (RDE) voltammetry investigations [1] or in the field of High Performance Liquid Chromatography (HPLC) with electrochemical detection [2].

In this context, a solution of $K_4Fe(CN)_6$ at 10 mmol.L^{-1} is studied by RDE voltammetry with RRDE-3A in aqueous electrolyte with KCl (0.1 mol.L^{-1}) as supporting salt. A Three-electrodes set-up is used with the following configuration:

- platinum electrode (surface electrode $A = 0.126 \text{ cm}^2$) as working electrode,
- Ag/AgCl electrode as reference electrode,
- alloy wire as counter electrode.

Scan rate and rotating rate are of 50 mV.s^{-1} and 500 rpm , respectively.

The corresponding voltammogram is shown in Fig. 3 and the “Wave Analysis” tool gives the i_{lim} equal to $766 \mu\text{A}$ and $E_{1/2} = 223 \text{ mV vs. Ag/AgCl}$.

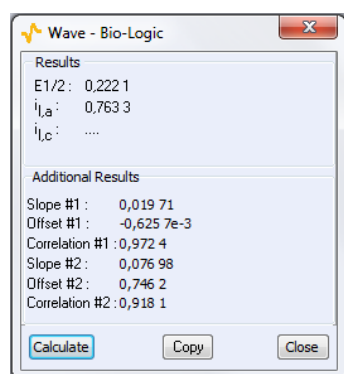
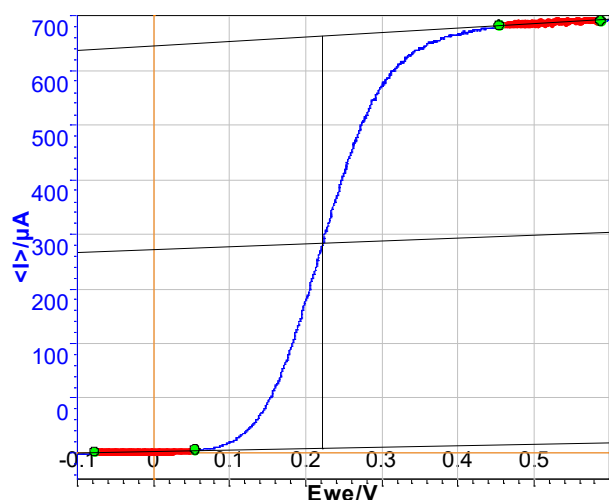


Figure 3: Steady-state curves $[K_4Fe(CN)_6] = 10\text{ mM H}_2O + KCl (0.1\text{ mol.L}^{-1})$ for $u = 50\text{ mV.s}^{-1}$ and $\Omega = 500\text{ rpm}$ (top) and “Wave Analysis” result (bottom).

Current for Nernstian system under stationary condition are given by the following relationship

$$i_f = \frac{nF[X]_{init} \exp\left(\frac{nF}{RT}(E - E^0)\right)}{1 + \delta \exp\left(\frac{nF}{RT}(E - E^0)\right)} \quad (1)$$

where n is the number of electrons involved in the process, F is the Faraday number, $[X]_{init}$ is the initial concentration of X in solution, R is the Boltzmann number, T is the temperature and E^0 is the standard potential, d is the thickness of the diffusion layer and D the diffusion constant.

$$\log \left[\frac{i}{i_{lim} - i} \right] = aE - b \quad (2)$$

$$n = \frac{F}{2,3RTb} \quad (3)$$

$$E_{1/2} = -\frac{b}{a} \quad (4)$$

where i_{lim} is the limiting current, a and b are respectively the slope and y -intercept of the curve.

The resulting graphic is plotted in Fig. 4 and “Line Fit” function gives the following equation:

$$\log [i/(766 - i)] = 16.2 E + 3.251$$

According to the equations (2), (3) and (4), n is equal to 1 (mono-electronic oxidation) and $E_{1/2}$ is 201 mV vs. Ag/AgCl which is closed to the value determined previously by “Wave Analysis”.

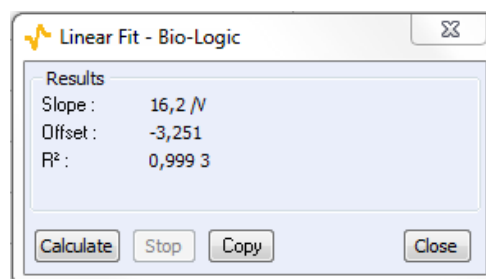
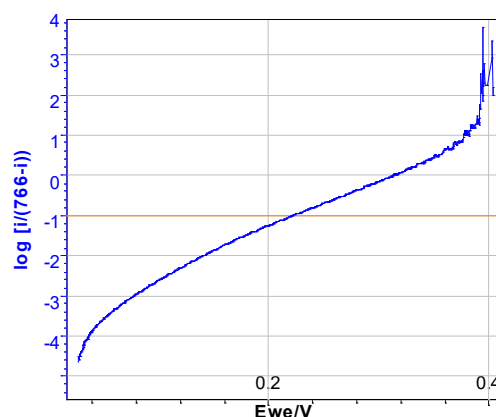


Figure 4: $\log (i/(i_{lim} - i)) = E$ plotted (top) and “Line Fit” result (bottom).

Conversely, this graphical method can be also used as a verification method for determining i_{lim} . Indeed, trials with higher ($1.05i_{lim}$) or lower

$(0.95i_{lim})$ i_{lim} exhibit non-linear behavior (Fig. 5).

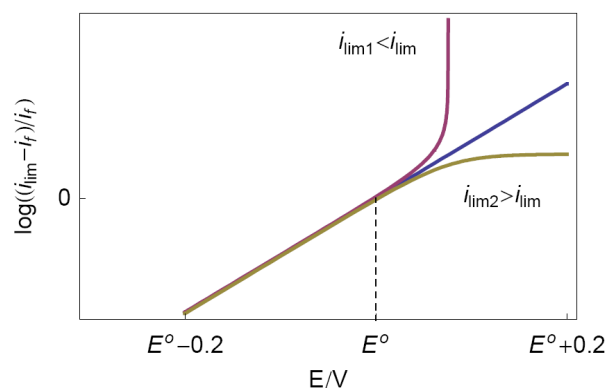
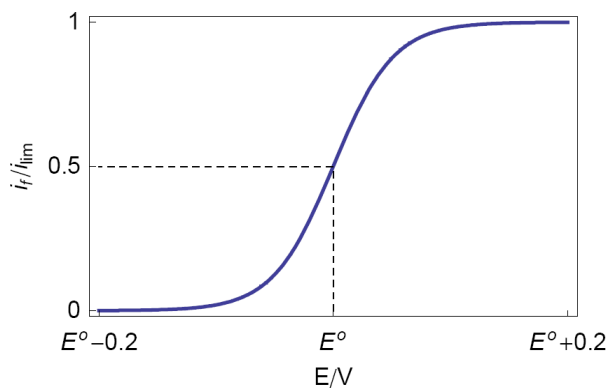


Figure 5: Theoretical steady state voltamogram (top) and logarithmic transform with various i_{lim} (bottom).

III – BATTERY APPLICATIONS

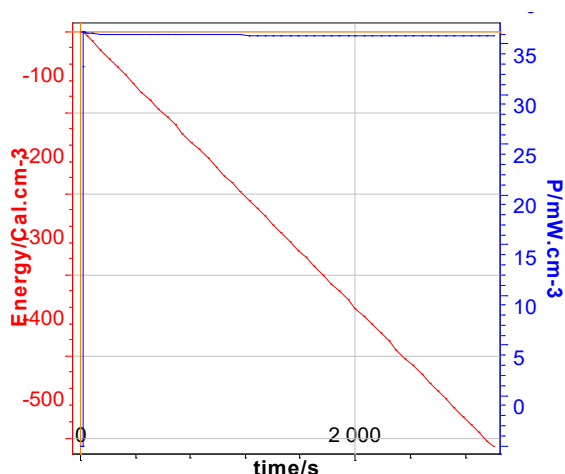


Figure 6: volumic energy (cal.cm^{-3}) and volumic power (W.cm^{-3}) vs. time. The volume of the battery is 160 cm^3 .

In spite of the official unit of energy being the Joule (W.s), the calorie ($1 \text{ J} = 4.18 \text{ cal.}$) is also used as energy unit in the medical area, and particularly, for implantable battery. In this context, the volumic energy of battery in calorie is plotted vs. time

Conversely, for information, the volumic power is also plotted in Fig. 6 on the y2-axis. In this context, discharge (GCPL technique) of LiFePO_4 battery is carried out with a 8 A booster connected to a VMP3.

N.B.: To have power values, power must be ticked in the “Advanced Setting” before starting measurement.

IV – EIS APPLICATIONS

Impedance is the field of electrochemistry where graphical representation is at its most relevant [3,4], for, as an example, the determination of the Constant Phase Element (CPE) parameter.

Investigations are performed with VSP instrument driven by EC-Lab® software in a solution of HCl (0.1 M). The three-electrode set-up is used with:

- rotating Disk Electrode (RDE) of iron as the working electrode with a surface area of 3.14 mm^2 ,
- platinum wire as counter electrode,
- saturated Calomel Electrode (SCE) as reference electrode.

Experiments are carried out with an electrode rotation speed of 800 rpm

Resulting Nyquist plot is shown in Fig. 7.

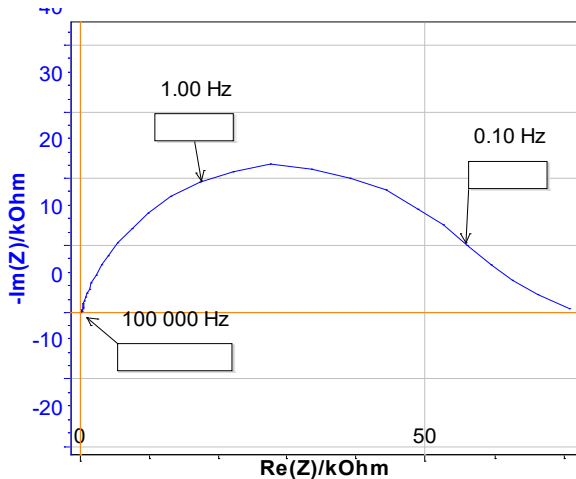


Figure 7: Nyquist plot.

Let us consider the equivalent circuit shown in Fig. 8 which is valid in the high frequency area.

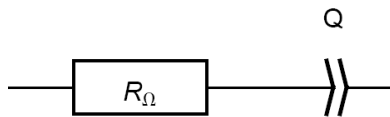


Figure 8: Equivalent circuit R in series with a CPE, noted Q.

The corresponding impedance is given by:

$$Z = Z_Q = \frac{1}{Q(i2\pi f)^\alpha}$$

If $R_\Omega = 0$, the magnitude and imaginary part of the impedance are written [5,6]:

$$|Z| = \frac{1}{Q(2\pi f)^\alpha}$$

$$\Rightarrow \log|Z| = -\alpha \log f - \log(Q(2\pi)^\alpha)$$

$$\text{Im } Z = -\frac{\sin(\alpha\pi/2)}{Q(2\pi f)^\alpha}$$

$$\Rightarrow \log|\text{Im } Z| = -\alpha \log f - \log\left(\frac{Q(2\pi)^\alpha}{\sin(\alpha\pi/2)}\right)$$

Therefore plotting $\log|Z|$ or $\log|\text{Im } Z|$ vs. $\log f$ yields to a straight line with a slope given by $-\alpha$ (Fig. 9) at high frequency.

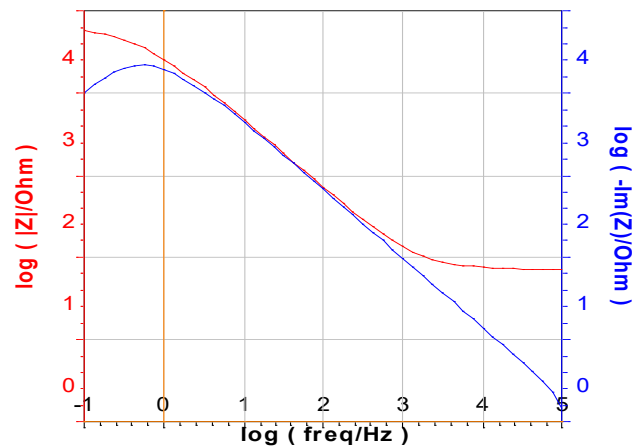


Figure 9: Bode representation and $\log(-\text{Im } Z)$ vs. \log frequency.

If $R_\Omega \neq 0$, the impedance is given by:

$$Z = R_\Omega + \frac{1}{Q(i2\pi f)^\alpha}$$

and the magnitude is written:

$$|Z_Q| = \sqrt{R^2 + \frac{1}{Q^2(2\pi f)^{2\alpha}} + \frac{2R \cos(\alpha\pi/2)}{Q(2\pi f)^\alpha}} \Rightarrow$$

$$\log|Z_Q| = \frac{1}{2} \log\left(R^2 + \frac{1}{Q^2(2\pi f)^{2\alpha}} + \frac{2R \cos(\alpha\pi/2)}{Q(2\pi f)^\alpha}\right)$$

while the expression of the imaginary part of the impedance remains unchanged. Only the plot of $\log|\text{Im } Z|$ vs. $\log f$ yields to a straight line for $R_\Omega \neq 0$.

The coming from the Line Fit of the two representations are recorded in Tab. I. The comparison of the two values determined by the two graphical methods and the values determined in Application Note #21 [7] are in good agreement.

Table I: Summary of the α parameters.

	$\log(-\text{Im } Z)$	Bode	Z Fit from [7]
α	0.8397	0.8113	0.8407

V – CONCLUSION.

Examples given in this note show the capabilities of the EC-Lab® graphic tool.

However, there are far more examples and other customizations are also available to meet the needs of each user.

This application note can be complemented by the technical notes #22 [8] and #23 [9].

Data files can be found in :

*C:\Users\xxx\Documents\EC-Lab\Data\Samples\EIS\EIS_Graphic ;
Battery\GCPL_Graphic and Fundamental Electrochemistry\RDE_Graphic*

REFERENCES

- 1) B. Trémillon, G. Durand, *Électrochimie. Caractéristiques courant-potentiel: théorie (partie 1)*, Techniques de l'ingénieur, Paris, (1993).
- 2) A. Aoki, T. Matsue, I. Uchida, *Anal. Chem.*, 64 (1992) 44.
- 3) M. E. Orazem, N. Pébère, B. Tribollet, *J. Electrochem. Soc.*, 153 (2006) B129.
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- 5) J.-P. Diard, B. Le Gorrec, C. Montella, *Exercices de cinétique électrochimique. II. Méthode d'impédance*, Hermann, Paris, (2005).
- 6) J.-P. Diard, B. Le Gorrec, C. Montella, [Handbook of EIS](#), (2017).
- 7) [Application Note #21](#), "Measurements of the Double Layer Capacitance"
- 8) [Technical Note #22](#), "Graphic Properties, Part I: Graph Style Definition"
- 9) [Technical Notes #23](#), "Graphic Properties, Part II: Graph Representation Definition"

Revised in 08/2019