Graphic Customization

I. Introduction

Good graphical representation makes easier the understanding of the data. That's why EC-Lab® and EC-Lab® Express software provide a traces processing tool (Fig. 1) which allows the user to customize its own traces.
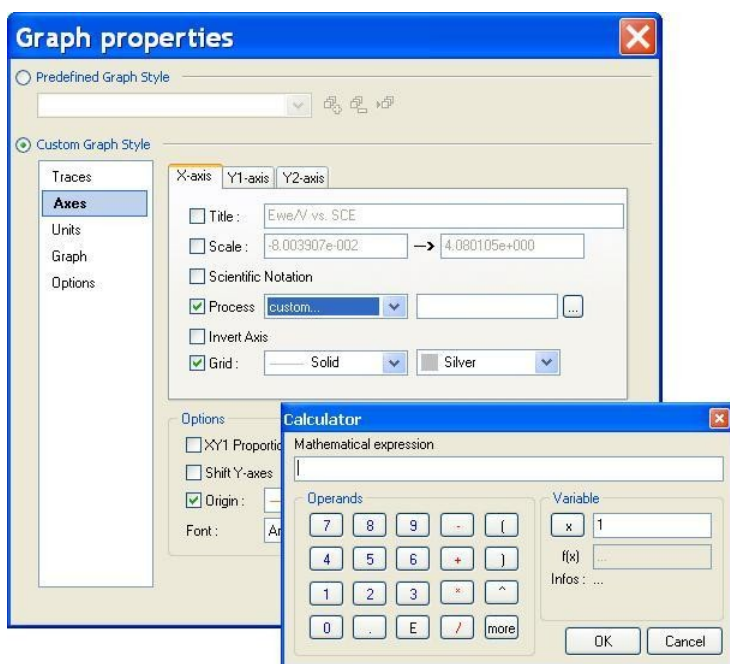

Fig. 1: Traces process windows.

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 field of electrochemistry.

N.B.: All settings and raw data files presented hereafter are available in the Data Sample folder of EC-Lab® Software as RDE_Graphic.mpr, GCPL_Graphic.mpr and EIS_Graphic.mpr.

Fig. 2: Mathematical functions available in calculator.

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 electron involved in the redox process under stationary condition and for nernstian system. Consequently, this feature is used in Rotating Disk Electrodes (RDE) voltammetry investigations [1] or in the field of the 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. Three-electrodes set-up is used and constituted as follows:

- platinum electrode (surface electrode $A = 0.126$ 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.

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Corresponding voltammogram is shown in Fig. 3 and the "Wave Analysis" tool gives the i_{lim} equal to 766 µA and $E_{1/2}$ = 223 mV *vs.* Ag/AgCl.
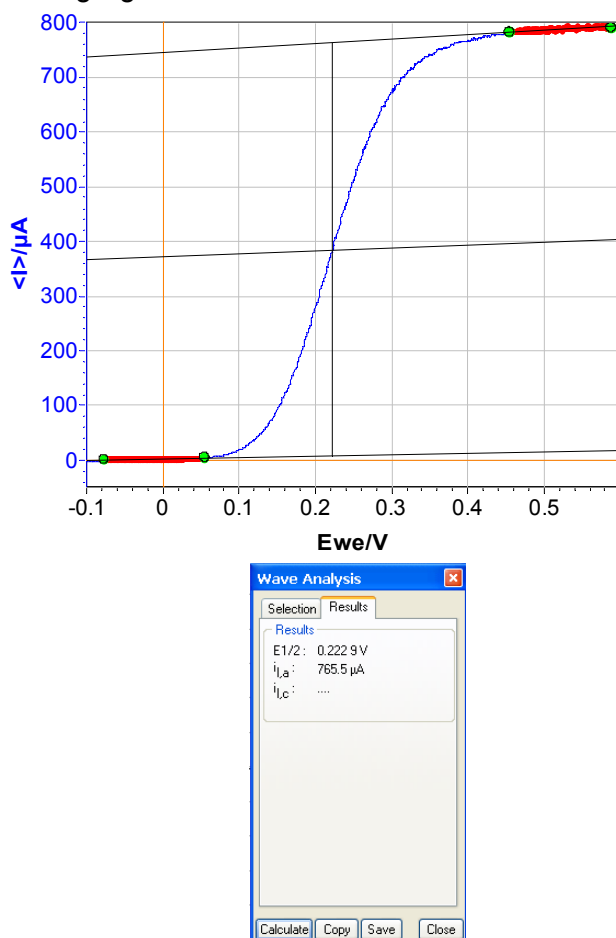

Fig. 3: Steady-state curves [K₄Fe(CN)₆] = 10 mM H₂O + KCl (0.1 mol.L⁻¹) for υ = 50 mV.s⁻¹ and Ω = 500 rpm (top) and "Wave Analysis" result (bottom).

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

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

where n is the number of electron 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, δ is the thickness of the diffusion layer and D the diffusion constant.

$$\log[i/(i_{lim} - i)] = aE - b \qquad (1)$$

$$n = F/(2.3\,RTb) \qquad (2)$$

$$E_{1/2} = -b/a \qquad (3)$$

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 the equations (1), (2) and (3), 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".
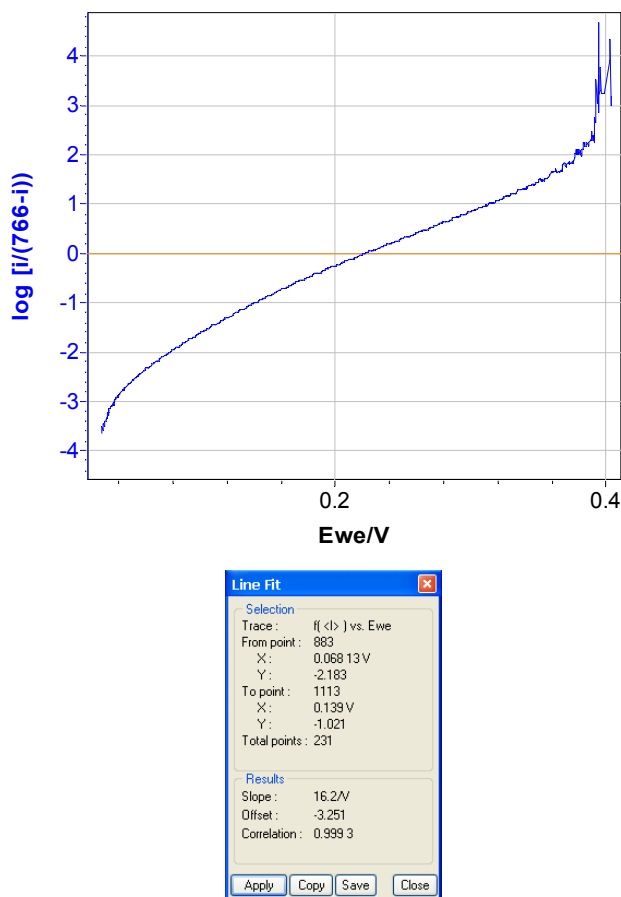

Fig. 4: log ($i/(i_{lim} - i$)) = E plotted (top) and "Line Fit" result (bottom).

On the other hand, this graphical method can be also used as verification method for determining i_{im}. Indeed, trials with higher (1.05i_{lim}) or lower (0.95i_{lim}) i_{lim} exhibit non-linear behavior (Fig. 5).
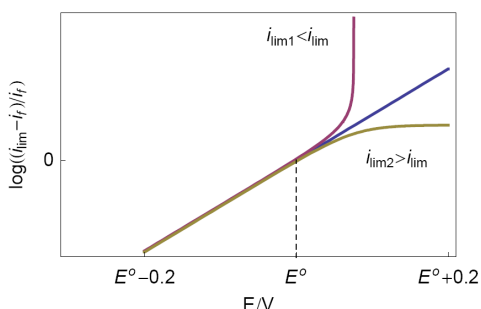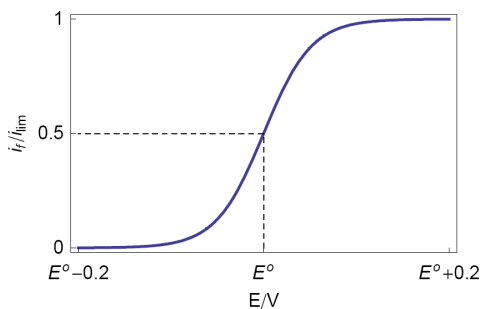
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Fig. 5: Theoretical steady state voltamogram (top) and logarithmic transform with various i_{lim} (bottom).

III. Battery application

In spite of the official unit of energy is the Joule (W.s), the calorie (1 J = 4.18 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

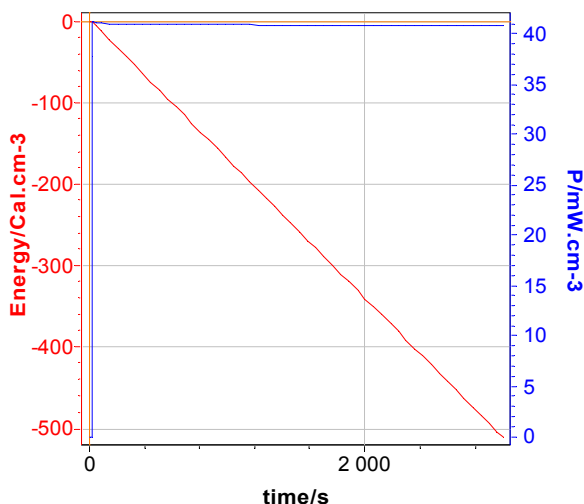On the other hand, for information, the volumic power is also plotted in Fig. 6 on the *y2*-axis.

Fig. 6: volumic energy (cal.cm-3) and volumic power (W.cm-3) *vs.* time. The volume of the battery is 160 cm3.

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 application

The impedance is certainly the field of electrochemistry where graphical methods are the most useful to better interpret and evaluate data [3,4], for example, the determination of the α parameter of Constant Phase Element (CPE).

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 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 at 800 rpm as rotation speed of the electrode.

Resulting Nyquist plot is shown in Fig. 7.

Fig. 7: Nyquist plot.
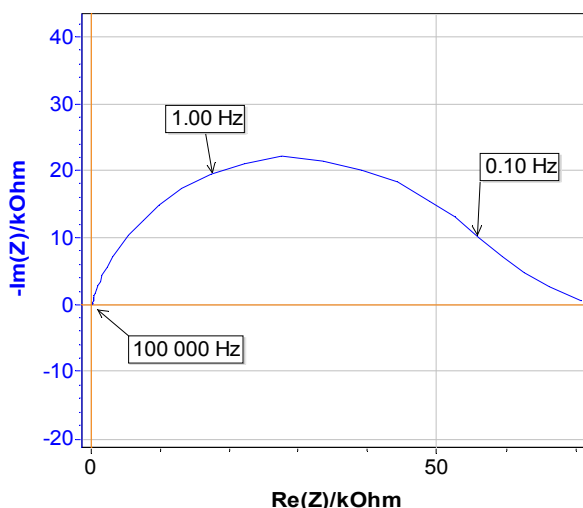
Let us consider the equivalent circuit shown in Fig. 8 which is valid in the high frequency area.

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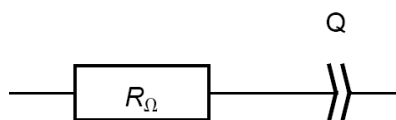Web: www.bio-logic.info

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Q

Fig. 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]:

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

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

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

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

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

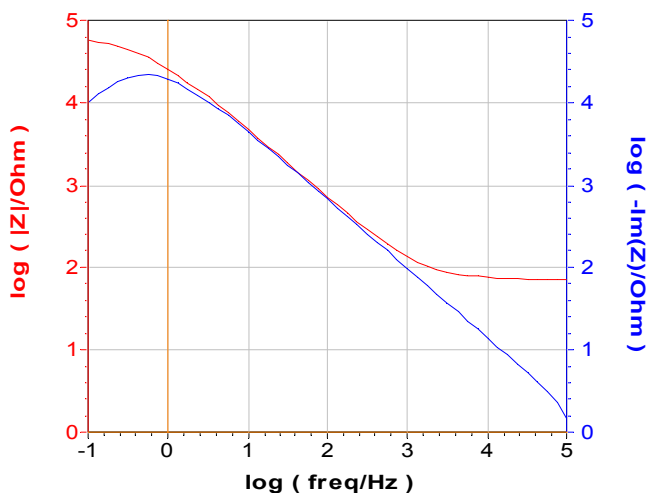**Fig. 9: Bode representation and log (-Im Z) vs. log frequency.**

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 $\log|\mathrm{Im}\,Z|$ *vs.* $\log f$ yield to a straight line for $R_\Omega \neq 0$.

The α coming from the Line Fit of the two representations are recorded in Tab. 1. 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.

Tab.1: Summary of the α parameters.

	log (-Im Z)	Bode	Z Fit from [7]
α	0.8397	0.8113	0.8407

Conclusion.

Examples given in this note show the capabilities of the EC-Lab® graphic tool. But they are not exhaustive and others customization are also available in order to meet the need of each user.

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

References

[1] Électrochimie. Caractéristiques courant-potentiel: théorie (partie 1), B. Trémillon, G. Durand, ed. Techniques de l'ingénieur (Paris) 1993.

[2] Multichannel Electrochemical Detection with a Microelectrode Array in Flowing Streams. A. Aoki, T. Matsue, I. Uchida, Anal. Chem. 1992, 64, 44-49.

[3] Enhanced Graphical Representation of Electrochemical Impedance Data. M. E. Orazem, N. Pébère, B. Tribollet, J. Electrochem. Soc. 2006, 153, B129-B136.

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[4] Constant Phase Element Behavior in the Poly(o-toluidine) Impedance Response. M. J. Rodiguez-Presa, R. I. Tucceri, M. I., Florit, D. Posadas, J. Electroanal. Chem. 502 (2001), 82–90.

[5] Exercices de cinétique électrochimique. II. Méthode d'impédance, J.-P. Diard, B. Le Gorrec, C. Montella, ed., Hermann (Paris) 2005.

[6] Handbook of Electrochemical Impedance Spectroscopy. J.-P. Diard, B. Le Gorrec, C. Montella,http://www.bio-logic.info/potentiostat/notes.html#heis

[7] Measurements of the Double Layer Capacitance, Application Note #21, http://www.bio-logic.info/potentiostat/notes.html

[8] Graphic Properties – Part I: Graph Style Definition, Technical Note #22, http://www.bio-logic.info/potentiostat/notes.html

[9] Graphic Properties – Part II: Graph Representation Definition, Technical Notes #23, http://www.bio-logic.info/potentiostat/notes.html

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