Bio**Logic**
Science **Instruments**

Staircase Potentio Electrochemical Impedance Spectroscopy and automatic successive ZFit analysis

I- Introduction

It is sometimes useful to automate measurements. With EC-Lab® and EC-Lab® Express, it is possible to automatically perform successive impedance measurements during a potential sweep with the SPEIS (Staircase Potentio Electrochemical Impedance) technique. This technique allows the user to do different potential steps in the same experiment and, for each one, do an electrochemical impedance spectroscopy measurement. For each experiment, the user defines the conditions. The main application of this technique is to study electrochemical reaction kinetics along steady-state curves. Note that the same process can be used in galvanostatic mode with the SGEIS technique.

II- Experimental part

In the first part of this application note, the measurements were done on circuit #2 of the Bio-Logic Test Box 3. This circuit is non-linear as explained in ref. [1]. Measurements were done with the SPEIS technique of the EC-Lab® software (Fig. 1)

This protocol allows the user to define the initial and final potentials (first and fourth blocks) with a number of EIS measurements (N) between the two limits. The second block allows the user to define the waiting time before the EIS experiment. The third block is relative to the EIS experiment and the definition of the EIS settings.

EIS settings are as follows: frequency sweep from 100 kHz to 50 mHz with 6 points per decade and a peak to peak amplitude of 5 mV.

P_w and N_a were set, respectively, to 1 and 2 to let the system come back to a steady-state transient period after each frequency measurement and to have an average recorded value.

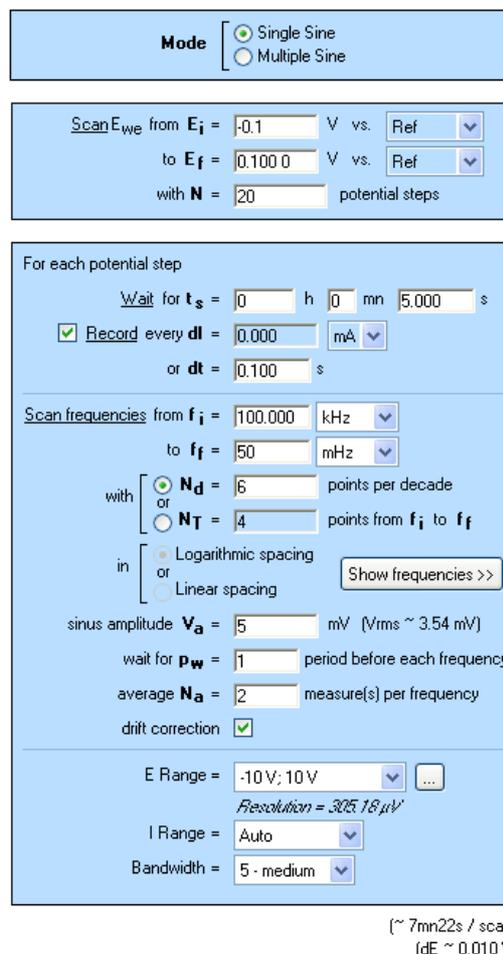Note that this experiment takes *ca.* 2 h.

Fig. 1: SPEIS "parameters Settings" window.

II-1 Determination of the diode parameters value

Cyclic voltammetry acquisition was done between - 0.2 and 0.2 V *vs.* Ref on the circuit #2 of the Test Box 3, as shown in Fig. 2 (it is possible to load the setting in the EC-Lab® software data as Cyclic Voltammetry_Test Box 3_Circuit 2.mps).
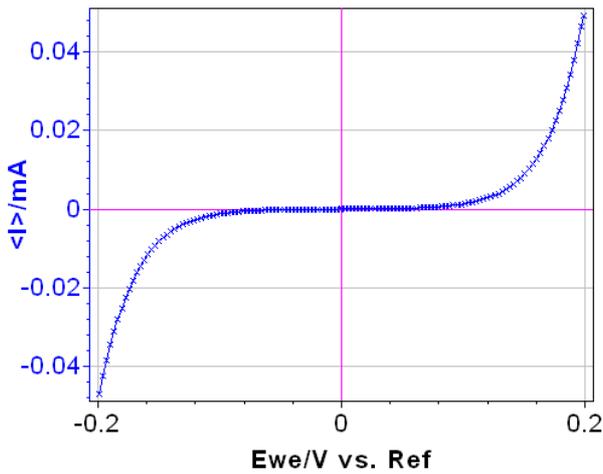
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Fig. 2: Steady-state curve _I_ _vs._ _E_we recorded using Cyclic Voltammetry technique.

This circuit, made mainly of two semi-conductor diodes [1], is a model for exponential non-linearity [2] and mimics the Butler-Volmer relationship for an electron transfer reaction without limitation by the mass transfer of the electroactive species. The current vs. potential steady-state characteristic of circuit #2 is given approximately by the following relationship:

$$I_D = I_s \left(\exp(b_1(E - E_{I=0})) - \exp(-b_2(E - E_{I=0})) \right) \quad (1)$$

or in the form of the Stern relationship [3]:

$$I_D = I_s \left(10^{(E - E_{I=0})/\beta_a} - 10^{-(E - E_{I=0})/\beta_c} \right) \quad (2)$$

I_s, β_a, β_c, and $E_{I=0}$ can be determined using the Tafel Fit analysis of EC-Lab® software (cf. Fig. 3).
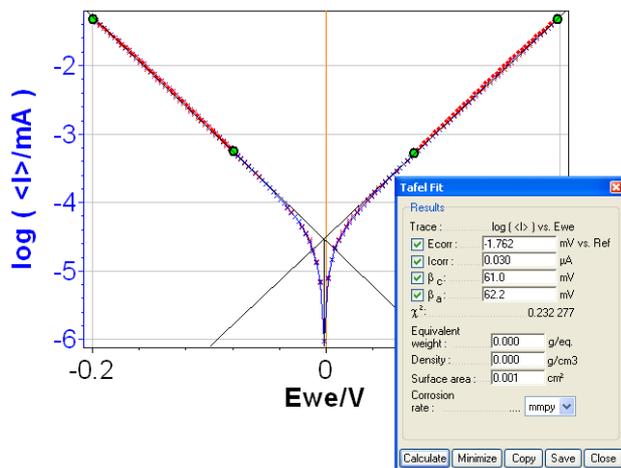

Fig. 3: Tafel Fit Analysis.

The following values are obtained: $E_{I=0}$ = - 0.002 V, I_S = 3.0 x 10^{-8} A, β_a = 0.061 V and β_c = 0.062 V for the measurement on the circuit #2 of the Test Box 3.

II-2 SPEIS Measurement

EIS experiments were done between - 0.1 and 0.1 V. Measurements were done every 10 mV implying that twenty-one impedance diagrams are measured in this potential range and are given in Fig. 4 (it is possible to load the setting and the data files in the EC-Lab® software data as SPEIS_Test Box 3_Circuit 2.mps and SPEIS_Test Box 3_Circuit 2.mpr, respectively).

As expected due to the shape of the current potential curve obtained with circuit #2 of the Test Box 3, impedance measurements are close on the anodic and the cathodic part, therefore impedance diagrams are grouped two by two.
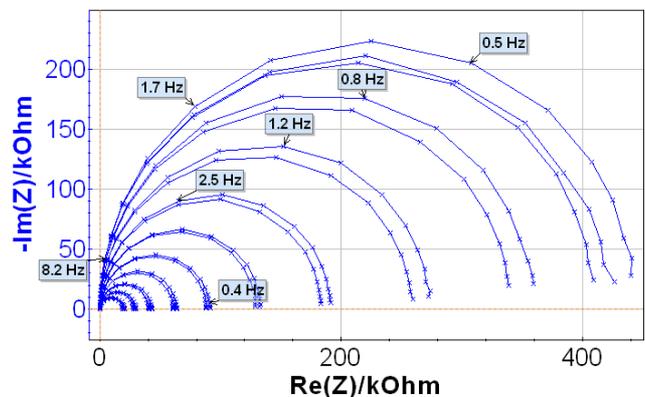

Fig. 4: Nyquist impedance diagrams along the steady-state _I_f _vs._ _E_ curve.

II-3 Automatic successive fits

The ZFit analysis method allows the user to analyze impedance curves [3]. This tool can fit only one EIS curve of the series (cf. Fig. 5) or all the curves successively in an automatic fashion. The settings parameters are shown in Fig. 6.
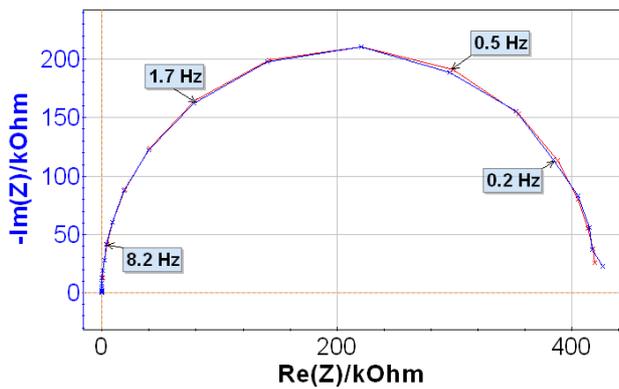
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Fig. 5: ZFit on the 11th Nyquist impedance diagram.

The equivalent electrical circuit selected in the ZFit window is given in Fig. 7. It is composed of a resistance R_1 in series with a capacitor C_2 and a resistance R_2 in parallel. Note that the value of R_1 is constant along the potential range and is around 100 Ω. However, it is not the same for the other elements of this circuit due to its non-linearity. Indeed, the impedance of this non-linear circuit depends on the value of the working electrode potential E_{we}, as showed in Fig. 4.
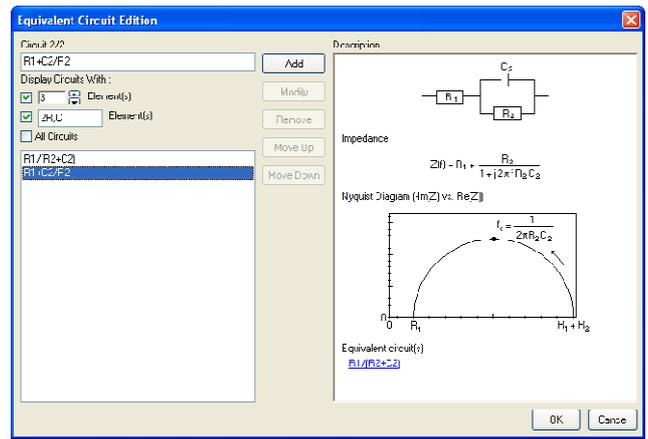

Fig. 6: ZFit analysis window.

Fig. 7: Electrical circuit selection in the ZFit analysis tool.

The ZFit tool allows the user to analyze each impedance diagram and plot the successive values of R_2 and C_2 values as a function of the working electrode potential. This result is given in Fig. 8. R_1 is not shown in this figure because as expected, the R_1 value is constant along the potential range and close to 100 Ω. In spite of the constant value of C_2 (*ca.* 0.46 x 10^{-6} F) along the potential range, this value is given with the R_2 value change in Fig. 8.
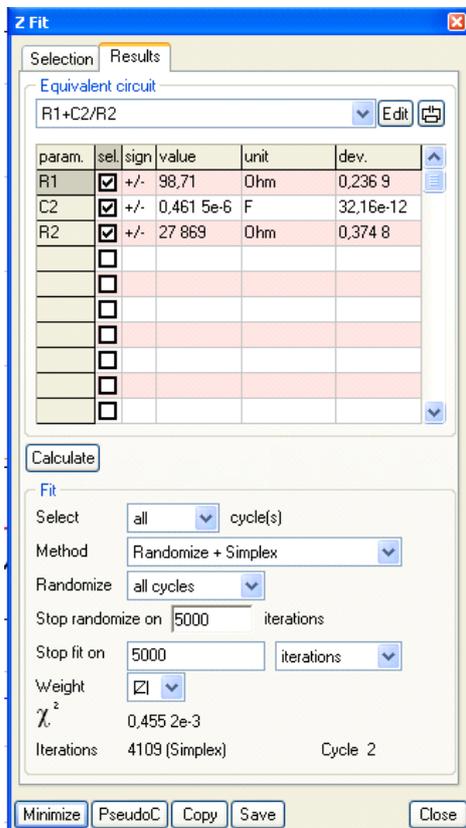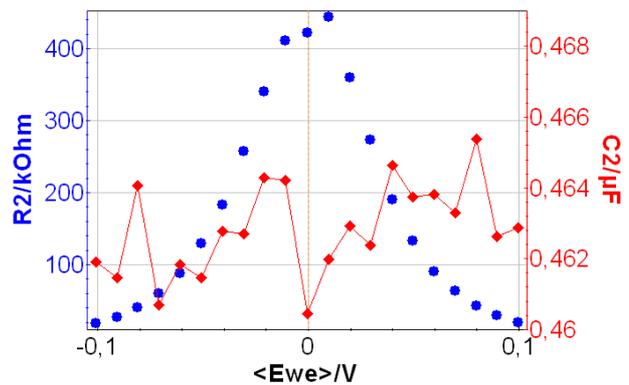

Fig. 8: Changes of the R_2 and C_2 value *vs.* E_{we}.

II-4 Determination of the circuit parameters value

Let us consider the change of R_2 obtained using ZFit and the 21 Nyquist diagrams shown in Fig. 8. For a low frequency input signal, the dynamic characteristic of the diode are of the same form as the steady-state equation (1):

$$I_D(t) = I_s \left(10^{(E(t)-E_{I=0})/\beta_a} - 10^{-(E(t)-E_{I=0})/\beta_c} \right) \quad (3)$$

Thus, the theoretical relationship for the charge transfer resistance for the circuit is given by:

$$R_t = \left(\frac{\partial I_D}{\partial E}\right)^{-1}$$

$$= \frac{1}{I_s \ln(10)\left(\dfrac{10^{(E-E_{I=0})/\beta_a}}{\beta_a} + \dfrac{10^{-(E-E_{I=0})/\beta_c}}{\beta_c}\right)} \quad (4)$$

Considering the electrical circuit given in Fig. 7 and the negligibility of R_1 compared with R_2, the previous relationship (4) can be written as:

$$R_p = \left(\frac{dI_D}{dE}\right)^{-1} = R_t \quad (5)$$

with $R_2 = R_p$.

It is thus possible to determine the I_s, β_a, β_c, and $E_{I=0}$ values using a fitting procedure such as NonlinearRegress in Mathematica software. The result is shown in Fig. 9.
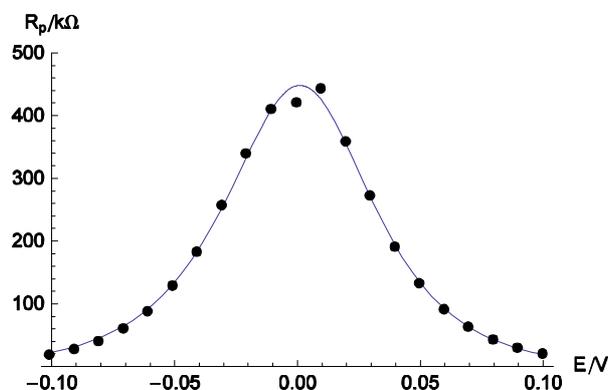

Fig. 9: Comparison of experimental data taken from Fig. 8 (dots) and theoretical curve (solid line) calculated for I_s = 2.97 x 10^{-8} A, β_a = 0.059 V, β_c = 0.064 V and $E_{I=0}$ = 0.0032 V.

These results show the good agreement between the dynamic state and the steady state, meaning that theory can explain them both simultaneously.

III- Automatic ZFit analysis of non-stationary electrochemical system

Sometimes, electrochemical systems, such as corroding electrodes, batteries, or electrochemical cells operating in finite dimensions media, are non-stationary, *i.e.* they change with time. Automatic ZFit can be used to study this change of the electrochemical system with time.

An example of the change with time of a system is given in Fig. 10. These 16 successive Nyquist diagrams are recorded on the diffusion plateau during the oxidation of NaBH$_4$ [5,6,7]:

$$\mathrm{BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-}$$

All the Nyquist diagrams present the same shape and are made of two capacitive loops with decreasing modulus with time. EIS measurements were carried out using the PEIS protocol, the repetition of the measurement period is done 15 times. Setting parameters are shown in Fig. 11.
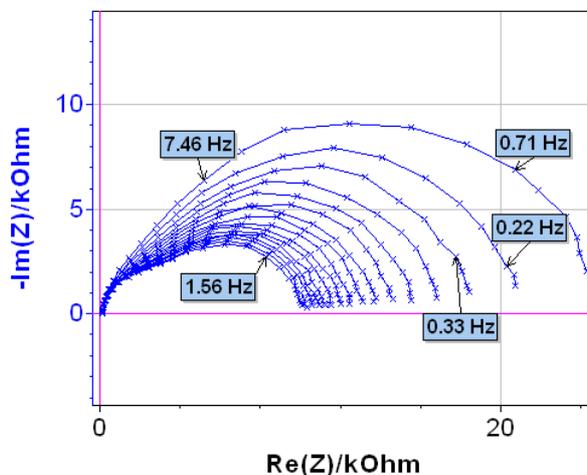

Fig. 10: Nyquist impedance diagrams plotted on the diffusion plateau for the NaBH$_4$ oxidation on an Au rotating disk electrode. *By courtesy of G. Parrour and M. Chatenet/LEPMI.*

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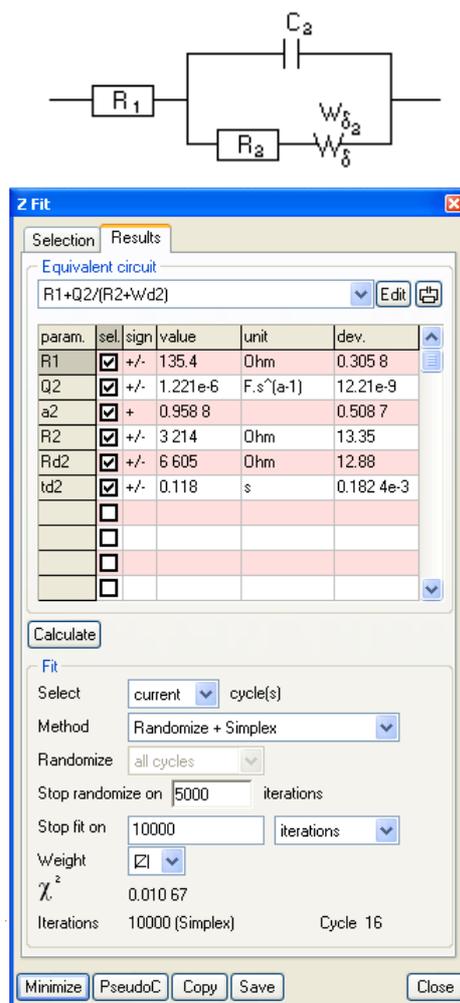
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Fig. 11: PEIS "parameters Settings" window.

Fig. 12: Equivalent circuit and ZFit analysis window.

Analysis of the Nyquist diagram changing with time can be made using the ZFit tool of EC-Lab® (or EC-Lab® Express) software. The Randles circuit R1+C2/(R2+Wd2) was selected (Fig. 12) taking account of the shape of the Nyquist impedance diagrams (Fig. 10). An example of the fit is given in Fig. 13 for the 16th impedance diagram.

It is then possible, using ZFit, to automatically plot the change of R_1, C_2, R_2, R_{d2} or t_{d2} as a function of the number of Nyquist diagrams. As an example, the changes of R_2, R_{d2} and C_2 are shown in Fig. 14.

As a consequence, automatic ZFit analysis of successive impedance diagrams can be used for monitoring non-stationary electrochemical systems such as corroding electrodes or batteries.
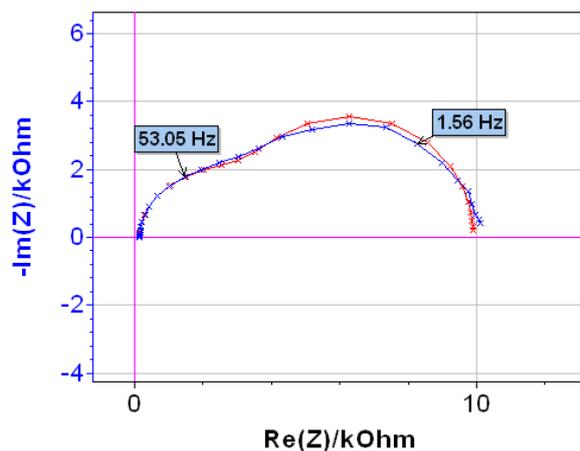

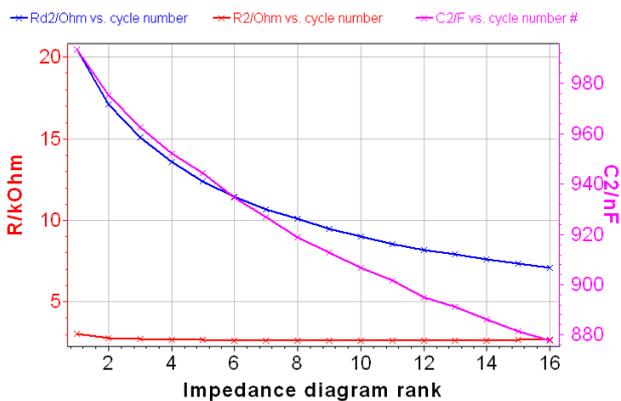Fig. 13: 16th Nyquist diagram (blue) and result of the fit (red).

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Fig. 14: Change with time of R_2, R_{d2}, and C_2

IV- Conclusions

The SPEIS method allows the user to automate EIS measurements along a steady-state or a non-stationary curve. Moreover EC-Lab® (or EC-Lab® Express) software is a well-adapted tool to simultaneously analyze successive impedance diagrams. EC-Lab® software (or EC-Lab® Express) allows the user to simplify experimental protocols and data treatments.

References:

[1] Bio-Logic Application Note #9 (http://www.bio-logic.info)

[2] J.-P. Diard, B. Le Gorrec, C. Montella, J. Electroanal. Chem., 432 (1997) 27-39.

[3] Bio-Logic Application Note #10 (http://www.bio-logic.info)

[4] Bio-Logic Application Note #14 (http://www.bio-logic.info)

[5] M. Chatenet, F. Micoud, I. Roche, E. Chainet, Electrochim. Acta, 51 (2006) 5459.

[6] M. B. Molina-Concha, M. Chatenet, J.-P. Diard, in Proceedings of the 20th Forum

sur les Impédances électrochimiques, Ed. C. Gabrielli, Paris 17 Dec. 2007.

[7] G. Parrour, Etude du mécanisme d'électrooxydation du borohydrure de sodium, Rapport de Master, Institut Polytechnique de Grenoble, 2008.

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