

Zfit and equivalent electrical circuits

I- Introduction

It has long been known that different electrical circuits can explain EIS data in an equivalent manner, that is, they exhibit identical impedance for all frequencies [1, 2, 3, 4].

EC-Lab[®] software is provided with a powerful tool for EIS data analysis called Zfit. This tool can perform electrical circuit identification with EIS experimental data files obtained with either Bio-Logic potentiostats/galvanostat or with other systems on the market. In fact, EC-Lab[®] software can import ASCII text files generated by other electrochemical stations and perform efficient EIS fits. The user can choose between two different minimization algorithms, Simplex and Levenberg-Marquardt, to achieve the best electrical element values.

The aim of this note is to explain how to fit EIS data with EC-Lab[®] software and show the user equivalent circuits that can fit the same EIS data file in particular conditions.

II- Fitting an experimental Nyquist impedance diagram using Zfit

The Nyquist impedance diagram shown in Fig. 1 has been measured for circuit #3 of the Bio-Logic test-box 3 using the PEIS protocol. Test circuit #3 mainly consists of two transistors. It is a model for metal passivation [5]. The Nyquist impedance diagram shown in Fig. 1 is made of two capacitive arcs well separated in frequency.

It is possible to load the PEIS_0-8V_circuit3.mpr file with EC-Lab[®] software in the following folder: C:\EC-Lab\Data\Samples.

Let us suppose that the Nyquist impedance diagram shown in Fig. 1 has been obtained for an electrochemical system, and we want to

characterize this electrochemical impedance diagram with an electrical circuit.

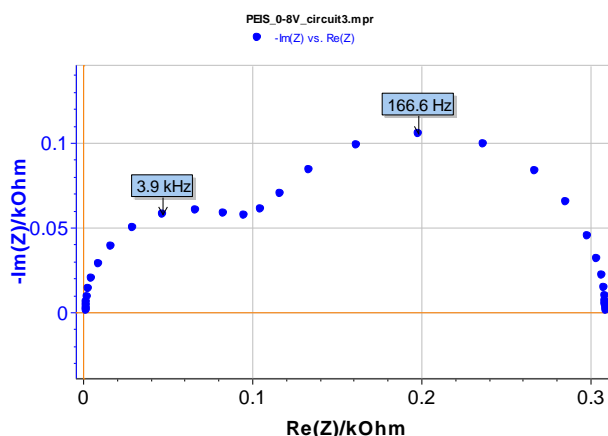


Fig. 1: Test circuit #3. Nyquist impedance diagram measured using PEIS technique. $E_{WE} = 0.8\text{ V}$, $V_a = 0.8\text{ V}$, $f_{min} = 1\text{ Hz}$, $f_{max} = 100\text{ kHz}$.

The electrical circuit shown in Fig. 2 is first selected because it matches the Faradaic impedance structure for an electrochemical system with $R_1 = R_{ct}$ and $C_1 = C_{dl}$ where R_{ct} is the charge transfer resistance and C_{dl} the double layer capacitance. The corresponding Equivalent Circuit Edition window is shown in Fig. 3.

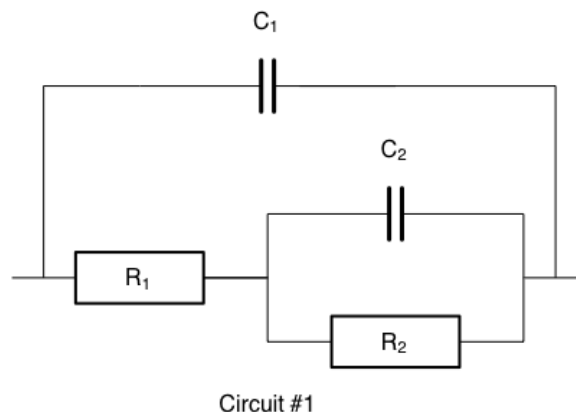


Fig. 2: Equivalent circuit #1 made of two resistors and two capacitors. Ladder circuit $C_1/(R_1+C_2/R_2)$.

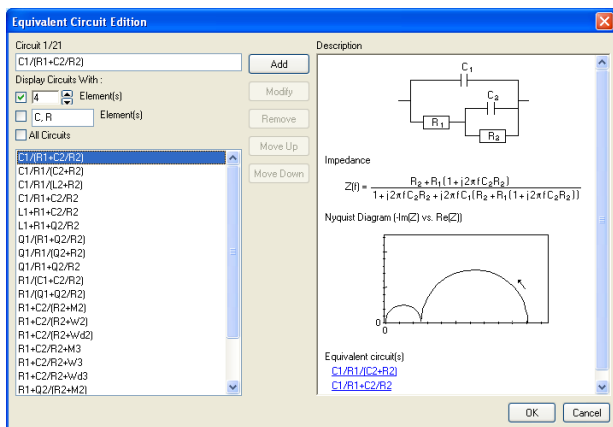


Fig. 3: Equivalent Circuit Edition window. Ladder circuit C1/(R1+C2/R2).

Clicking in the boxes for the elements and their numbers in the Equivalent Circuit Edition window is an easy method to choose an electrical circuit. The results of Zfit procedure using Randomize + Levenberg-Marquardt are shown in Fig. 4.

III- Equivalent electrical circuit

Zfit indicates known equivalent circuits in the description window (Fig. 3).

Three others circuits shown in Fig. 5, made of two *R*s and two *C*s, can be used to characterize the Nyquist impedance diagram shown in Fig. 1. It is very easy, using Zfit, to verify this quite surprising result, sometimes ignored by electrochemists.

The results of the Zfit procedure using randomize+Levenberg-Marquardt for the three circuits shown in Fig. 5 are given in Fig. 6 to Fig. 8. The sums of square of residuals, χ^2 , are very closed for the four circuits, with $\chi^2 \sim 1.13$. The four circuits are therefore indistinguishable, and all of them can be used to characterize the Nyquist impedance diagram shown in Fig. 1.

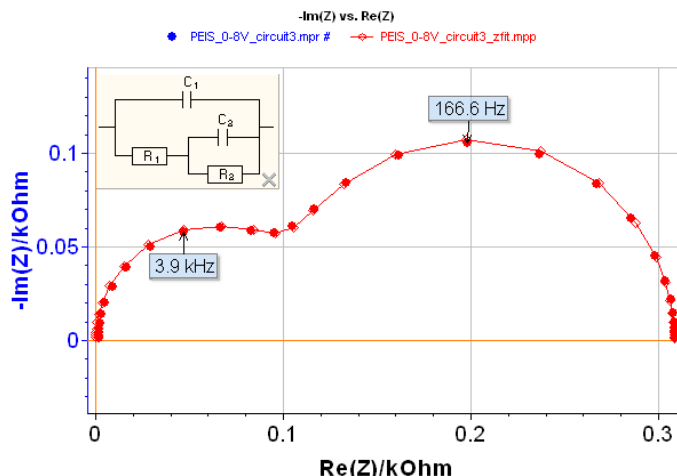
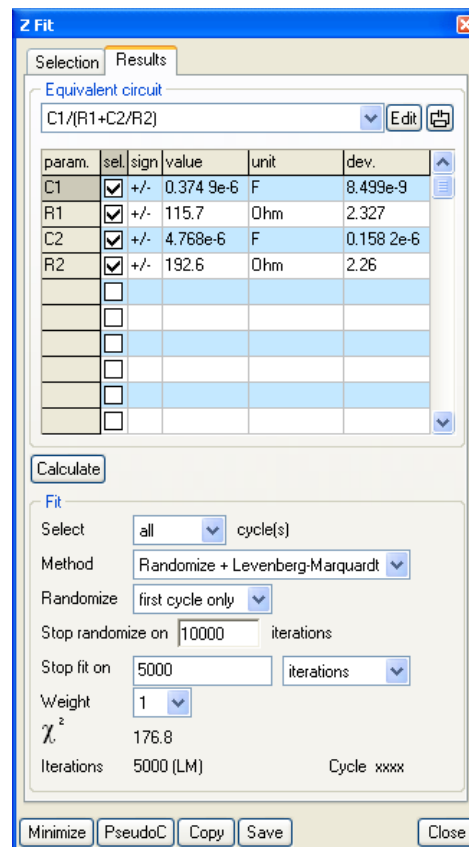


Fig. 4: Zfit window for circuit #1. Ladder circuit C1/(R1+C2/R2).

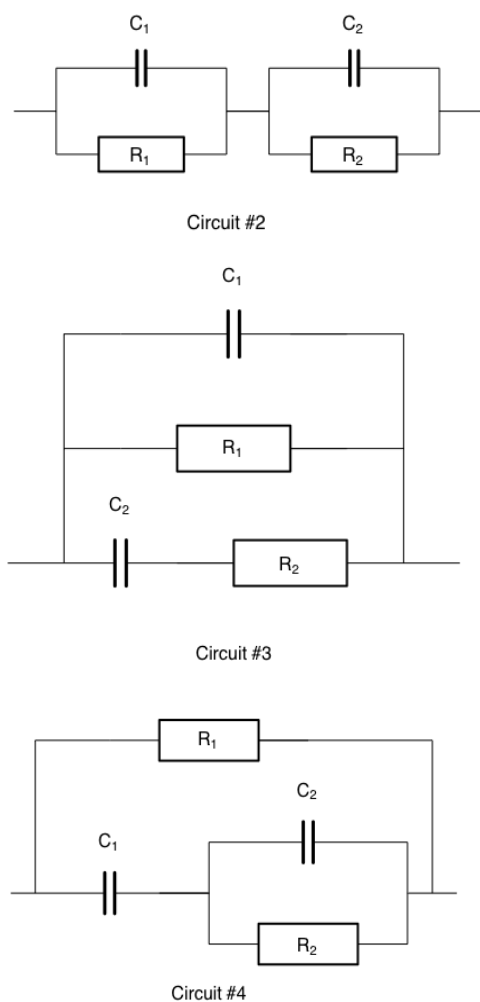


Fig. 5: Three electrical circuits made of two R s and two C s equivalent to circuit #1. Circuit #2: Voigt circuit $C1/R1+C2/R2$, circuit #3: Maxwell circuit $C1/R1/(C2+R2)$, circuit #4: ladder circuit $R1/(C1+R2/C2)$.

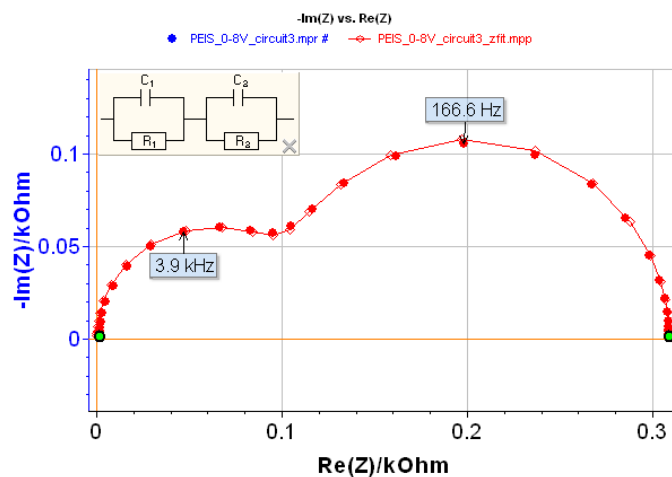
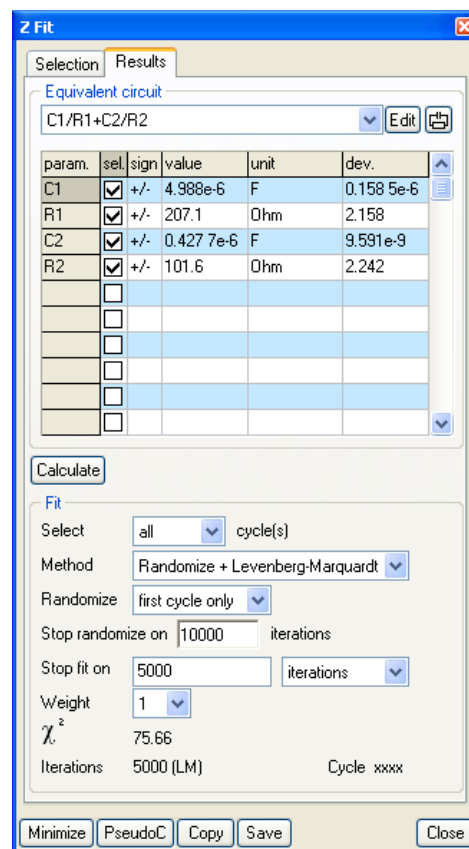


Fig. 6: Zfit window for circuit #2: Voigt circuit $C1/R1+C2/R2$.

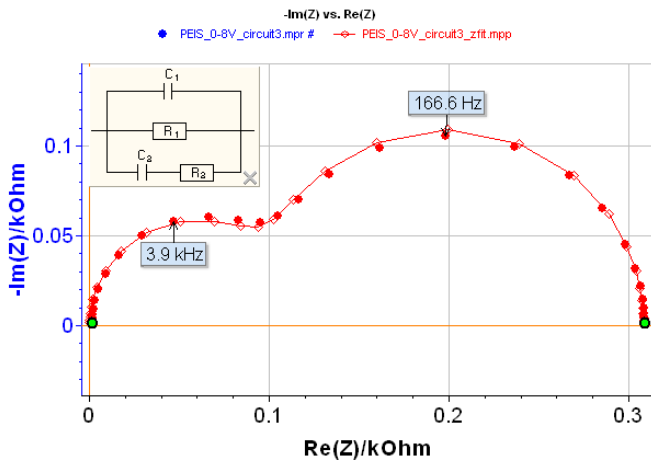
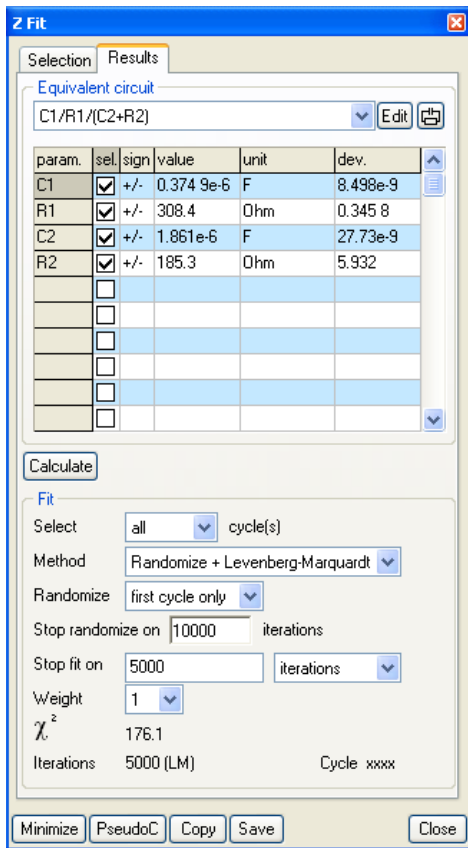


Fig. 7: Zfit window for circuit #3: Maxwell circuit $C1/R1/(C2/R2)$.

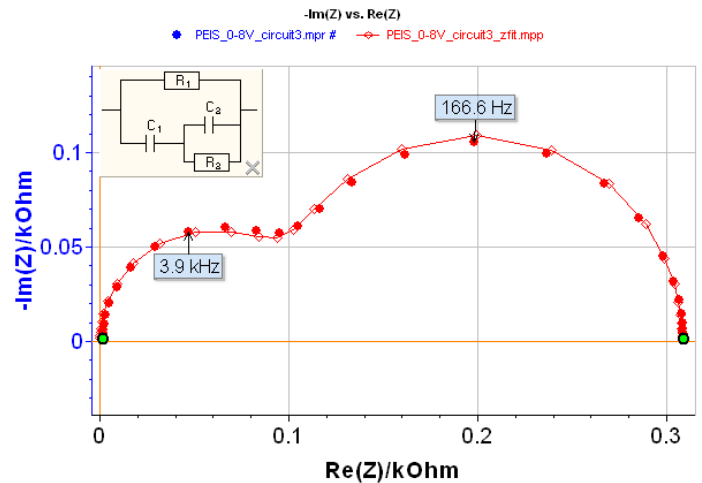
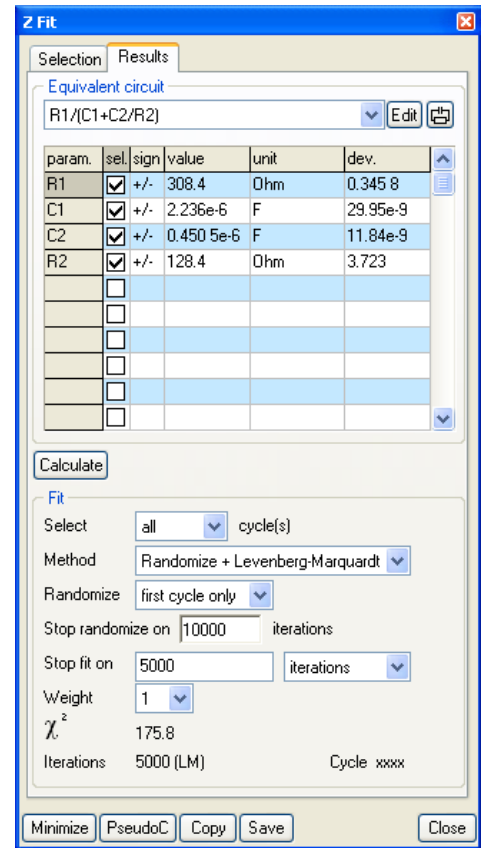


Fig. 8: Zfit window for circuit #4: ladder circuit $R1/(C1+C2/R2)$.

IV- Transformation formulae

The common structure of the impedance circuits #1-4 is written as:

$$Z(f) = \frac{K(1 + \tau_1 j2\pi f)}{(1 + \tau_2 j2\pi f + (\tau_3 j2\pi f)^2)}$$

It is therefore possible to write algebraic relationships used to determine transformation formulae. As an example, the simplest transformation formulae are obtained for circuit #1 and #3 [4]:

$$C_{13} = C_{11}, R_{13} = R_{11} + R_{21}$$

$$C_{23} = \frac{C_{21}R_{21}^2}{(R_{11} + R_{21})^2}$$

$$R_{23} = \frac{R_{11}^2}{R_{21}} + R_{11}$$

where the second subscripts denote the rank of the circuit. Using these transformation formulae with best fit parameter values obtained for circuit #1 (Fig. 4) and calculating value for circuit #3, it is obtained:

$$C_{13} = 3.85 \cdot 10^{-7} \text{ F}, R_{13} = 308.3 \text{ } \Omega$$

$$R_{23} = 185.2 \text{ } \Omega, C_{23} = 1.86 \cdot 10^{-6} \text{ F}$$

These parameter values are very close to the best fit parameters value obtained using Zfit for circuit #3 (Fig. 7):

$$C_{13} = 3.85 \cdot 10^{-7} \text{ F}, R_{13} = 308.4 \text{ } \Omega$$

$$R_{23} = 185.3 \text{ } \Omega, C_{23} = 1.90 \cdot 10^{-6} \text{ F}$$

Analogous relationships can be obtained with the others circuits [4].

References:

- [1] I. M. Novosel'skii, N. N. Gudina, Y. I. Fetistov, *Elektrokhimiya* 8 (1972) 565.
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- [3] S. Fletcher, *J. Electrochem. Soc.*, 141 (1994) 1823.
- [4] F. Berthier, J.-P. Diard, R. Michel, *J. Electroanal. Chem.*, 510 (2001) 1.
- [5] Bio-Logic Application Note #9 (<http://www.bio-logic.info>)