

Pseudo capacitance calculation

I- Introduction

It can sometimes be useful to substitute a RQ circuit by a RC circuit (Fig. 1).

This calculation is only available for a circuit (R/Q). It corresponds to the determination of a capacitance value C at an angular frequency $\omega_c = 2\pi f_c$ corresponding to the maximum imaginary part on the Nyquist circle obtained by fitting with the circuit (R/Q). Then, this value is the solution of the following equation

$$\frac{1}{2\pi(RQ)^{1/\alpha}} = \frac{1}{2\pi RC} \Rightarrow C = Q^{1/\alpha} R^{(1/\alpha)-1}$$

with α and Q as the CPE parameters [1,2].

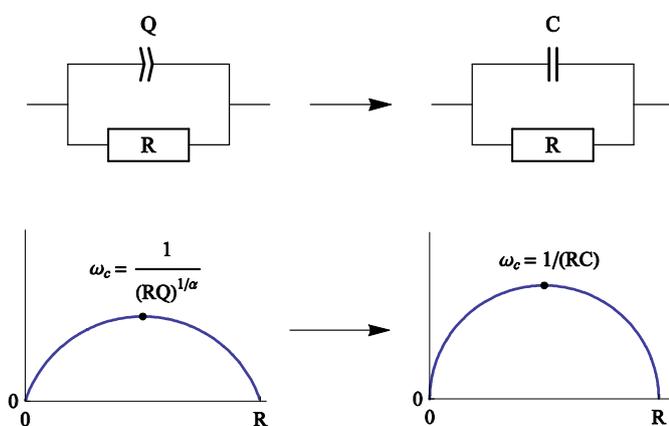


Fig. 1: Equivalent electrical circuit RQ and RC with the corresponding impedance diagram.

II-Experimental part

A lithium-ion battery, with LiFePO_4 as the positive electrode, was studied in this application note. The impedance diagram was recorded considering the setting described in the Fig. 2, *i.e.* in the 10 kHz – 10 mHz range with $V_a = 10$ mV, $p_w = 1$, $N_a = 1$, and the drift correction button ticked. The impedance diagram obtained is given in Fig. 3.

The ZFit tool was used to fit data with the equivalent circuit $L1+R1+Q2/R2+Q3$ (Fig. 4).

This circuit is not present in the electrical circuits list already in the ZFit tool, so the user must add this circuit using to the Edit menu.

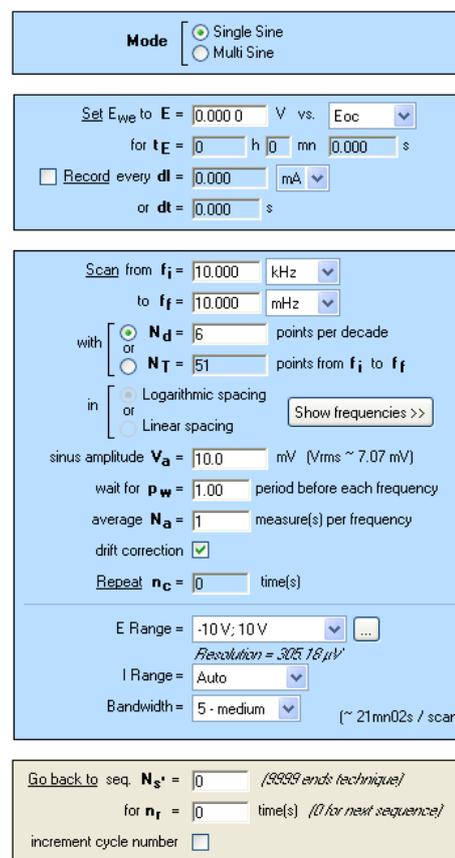


Figure 2 displays the PEIS "Parameters Settings" window. The window is divided into several sections:

- Mode:** Radio buttons for "Single Sine" (selected) and "Multi Sine".
- Set E_{we} to E :** Input field for voltage (0.0000 V vs. E_{oc}).
- for t_E :** Input fields for time in hours (0), minutes (0), and seconds (0.000).
- Record every dI :** Input field for current (0.000 mA).
- or dt :** Input field for time (0.000 s).
- Scan from f_i :** Input field for start frequency (10.000 kHz).
- to f_f :** Input field for end frequency (10.000 mHz).
- with:** Radio buttons for N_d (6 points per decade) or N_T (51 points from f_i to f_f).
- in:** Radio buttons for "Logarithmic spacing" (selected) or "Linear spacing".
- sinus amplitude V_a :** Input field (10.0 mV, $V_{rms} \sim 7.07$ mV).
- wait for p_w :** Input field (1.00 period before each frequency).
- average N_a :** Input field (1 measure(s) per frequency).
- drift correction:** Checked checkbox.
- Repeat n_c :** Input field (0 time(s)).
- E Range:** Dropdown menu (-10 V; 10 V).
- I Range:** Dropdown menu (Auto).
- Bandwidth:** Dropdown menu (5 - medium, $\sim 21mn02s / scan$).
- Resolution:** 3025.18 μV .
- Go back to seq. N_s :** Input field (0, *3025 ends technique*).
- for n_f :** Input field (0, *0 for next sequence*).
- increment cycle number:** Unchecked checkbox.

Fig. 2: PEIS "Parameters Settings" window.

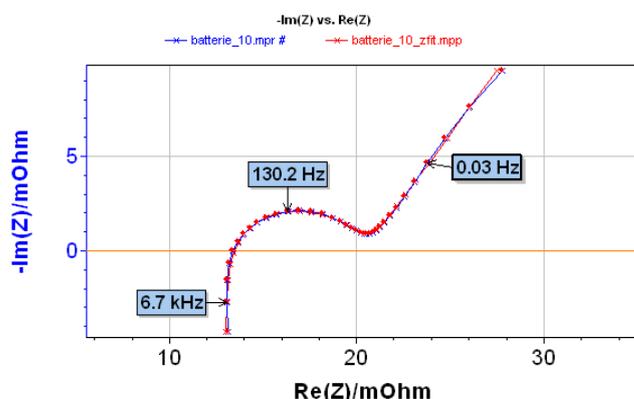


Fig. 3: Nyquist impedance diagram (blue) and ZFit analysis (red) of a Li-ion battery with a $L1+R1+Q2/R2+Q3$ equivalent circuit.

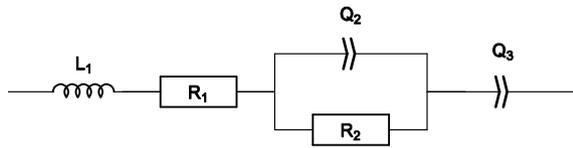


Fig. 4: $L_1+R_1+Q_2/R_2+Q_3$ equivalent electrical circuit.

In the Equivalent Circuit Edition, the $L_1+R_1+Q_2/R_2+Q_3$ circuit has to be defined and added with the Add button, as described in Fig. 5. The new circuit is then displayed in blue.

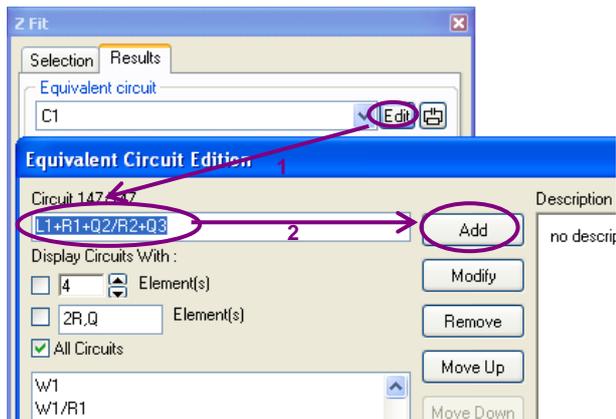


Fig. 5: How to add a new electrical equivalent circuit in the ZFit analysis tool.

Results of the ZFit analysis are given in Fig. 6. A good agreement is observed between the experimental diagram and the ZFit diagram as shown in Fig. 3.

The equivalent circuit used to do the fit on the experimental data contains the pattern (R/Q) . It is then possible to calculate the pseudo-capacitance. In the ZFit window, select the PseudoC button, and the window given in Fig. 7 appears. This means that with the ZFit analysis tool of EC-Lab[®] and EC-Lab[®] Express, calculation of pseudo-capacitance is done automatically.

However, the following equivalent circuit $L_1+R_1+Q_2/(R_2+Q_3)$ (Fig. 8) can also be considered to fit the diagram. As shown in Fig. 9, the obtained fit (red) is in good agreement with experimental data (blue). The parameters are displayed in the ZFit window given in Fig. 10.

However, even by clicking on the PseudoC button, it is not possible to calculate a pseudo-capacitance value as displayed in Fig. 11. The pattern in the equivalent circuit is $Q/(R+Q)$ and not the required one (R/Q) .

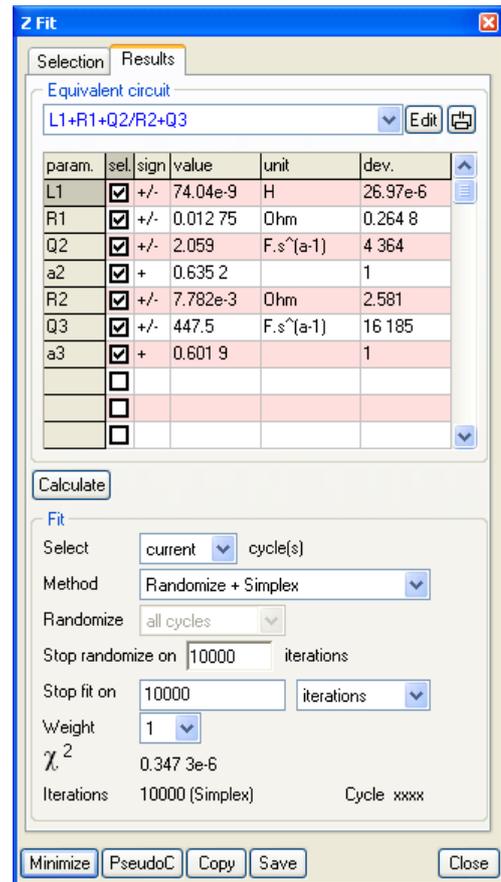


Fig. 6: ZFit analysis window obtained with the $L_1+R_1+Q_2/R_2+Q_3$ equivalent circuit.

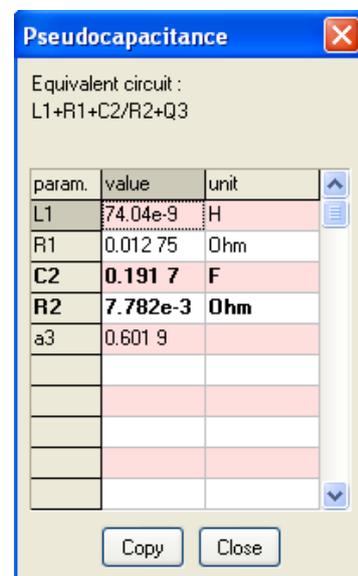


Fig. 7: Pseudocapacitance calculation in the ZFit window obtained with the $L_1+R_1+Q_2/R_2+Q_3$ equivalent circuit.

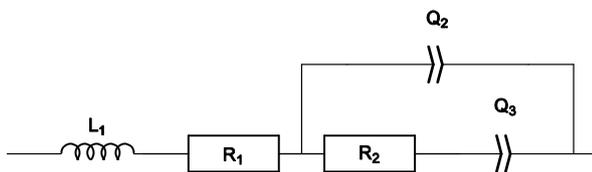


Fig. 8: $L1+R1+Q2/(R2+Q3)$ equivalent electrical circuit.

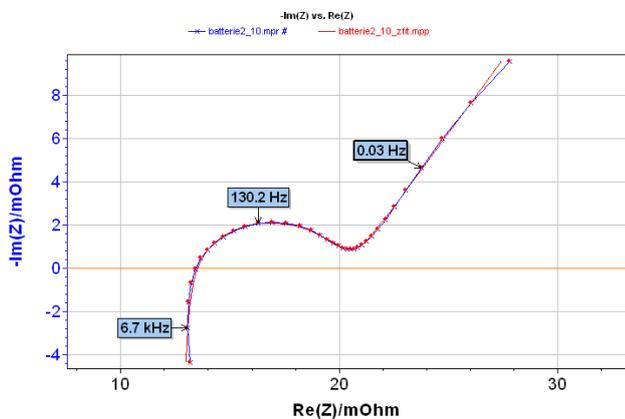


Fig. 9: Nyquist impedance diagram (blue) and ZFit analysis (red) of a Li-ion battery with a $L1+R1+Q2/(R2+Q3)$ equivalent circuit.

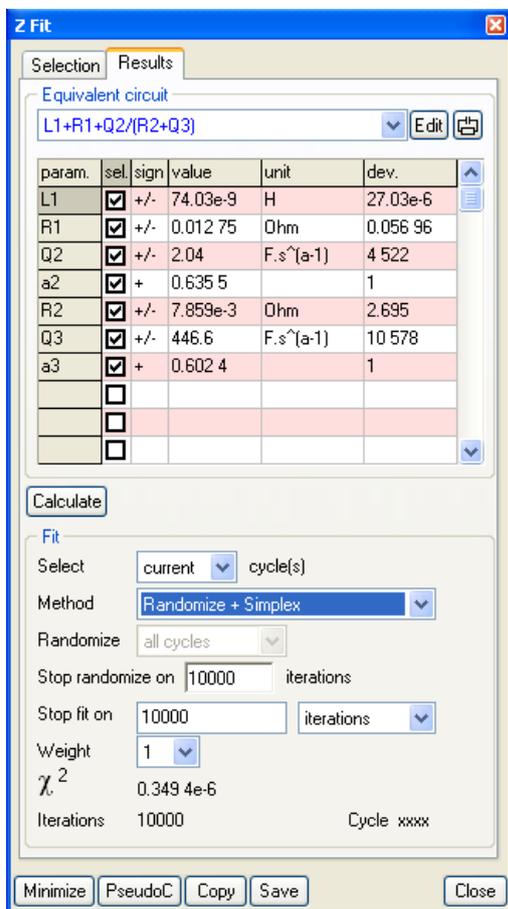


Fig. 10: ZFit analysis window obtained with the $L1+R1+Q2/(R2+Q3)$ equivalent circuit.

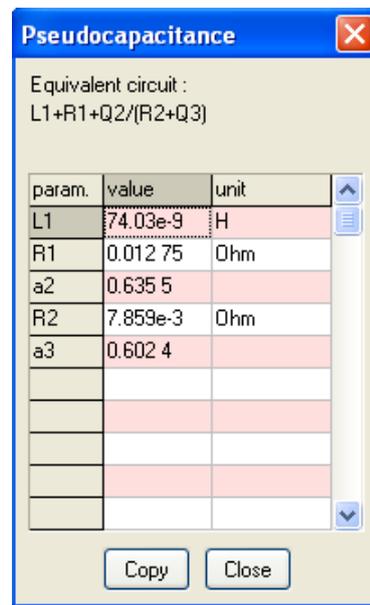


Fig. 11: Pseudocapacitance calculation in the ZFit window obtained with the $L1+R1+Q2/(R2+Q3)$ equivalent circuit.

It is not possible to distinguish between the two fits considering the χ^2 values, which are very close. In the same way, the values of the fit parameters obtained for the two circuits (Fig. 6 and Fig. 10) are very close.

Note that in some peculiar cases, it is possible to establish equivalence between the following two electrical circuits $L1+R1+Q2/R2+Q3$ and $L1+R1+Q2/(R2+Q3)$.

References

- [1] Electrical circuits containing CPEs, Bio-Logic website, <http://www.bio-logic.info/potentiostat/notes>
- [2] Impedance spectroscopy, 2nd Edition, ed. Barsoukov E., Ross Mac Donald J., 2005