

Pseudo capacitance calculation

I-Introduction

It could be sometimes 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 the CPE parameters [1,2].

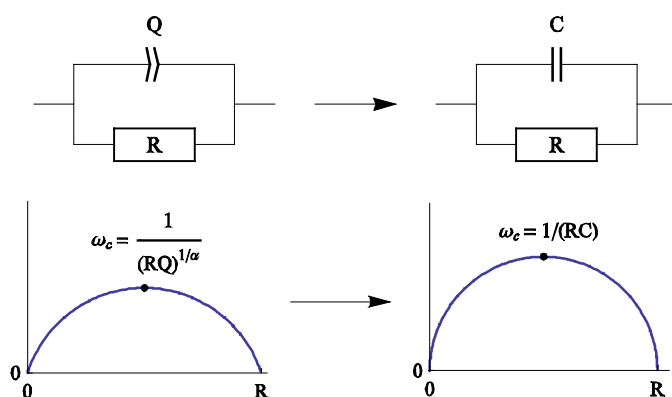


Fig. 1: Equivalent electrical circuit RQ and RC with the corresponding impedance diagram.

II-Experimental part

A lithium-ion battery, with LiFePO_4 as positive electrode, was studied in this application note. Impedance diagram was recorded considering the setting described in the Fig. 2, i.e. in the 10 kHz – 10 mHz range with $V_{pp} = 20$ mV, $p_w = 1$, $N_a = 1$ and the drift correction button ticked. The impedance diagram obtained is given in Fig. 3.

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 and the user has to add this circuit thank to the Edit menu.

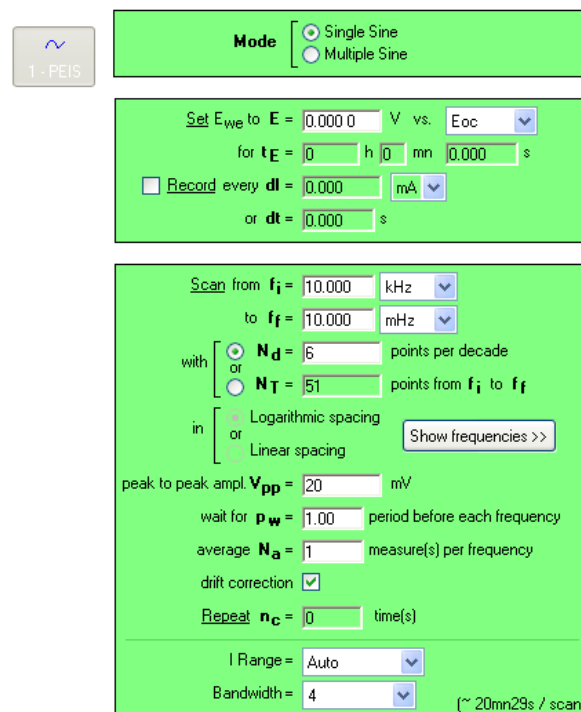


Fig. 2: PEIS "Parameters Settings" window.

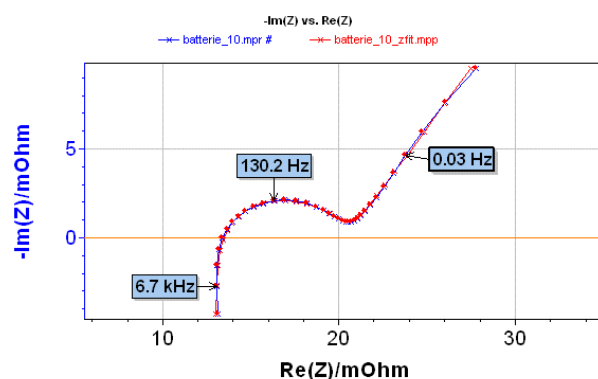


Fig. 3: Nyquist impedance diagram (blue) and ZFit analysis (red) of a Li-ion battery with a $L1+R1+Q2/R2+Q3$ equivalent circuit.

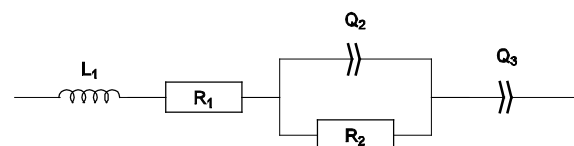


Fig. 4: $L1+R1+Q2/R2+Q3$ equivalent electrical circuit.

In the Equivalent Circuit Edition, the $L1+R1+Q2/R2+Q3$ circuit has to be defined and added with the Add button, as described

in Fig. 5. The new circuit is then displayed in blue.

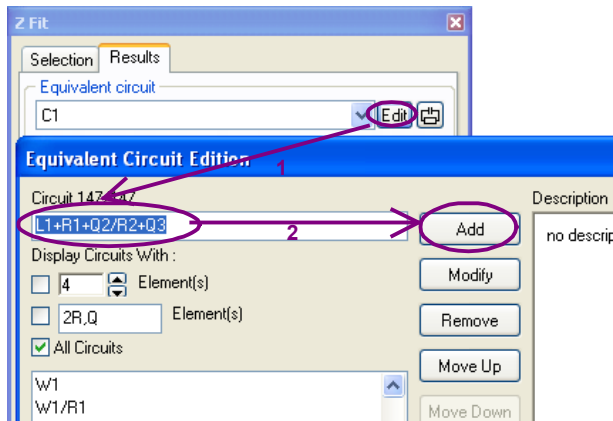


Fig. 5: How to add a new electrical equivalent circuit in the ZFit analysis tool.

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

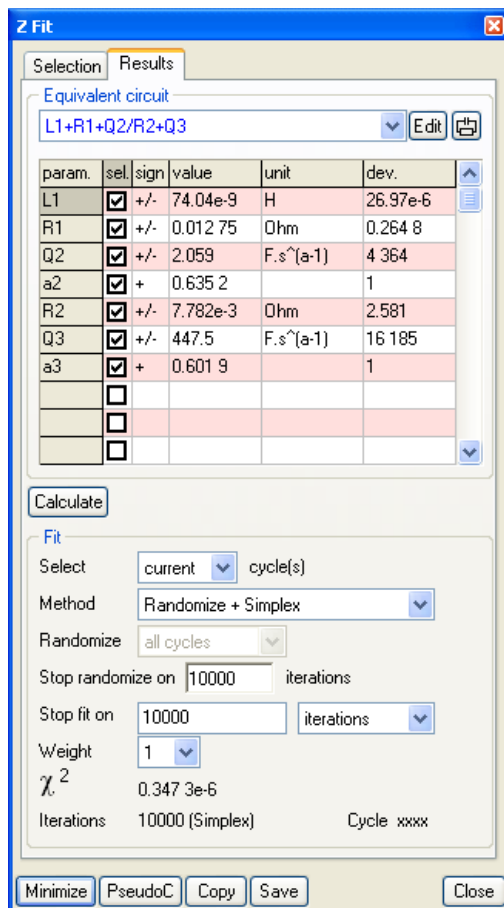


Fig. 6: ZFit analysis window obtained with the L1+R1+Q2/R2+Q3 equivalent circuit.

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 is displayed. This means that with the ZFit analysis tool of EC-Lab[®] and EC-Lab[®] Express, calculation of pseudo-capacitance is done automatically.

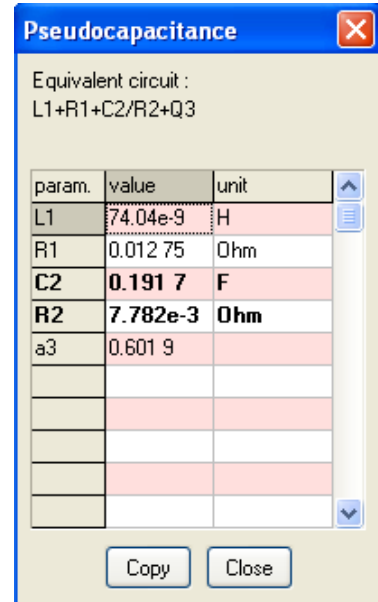


Fig. 7: Pseudocapacitance calculation in the ZFit window obtained with the L1+R1+Q2/R2+Q3 equivalent circuit.

However, the following equivalent circuit $L1+R1+Q2/(R2+Q3)$ (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. Nevertheless, even clicking on the PseudoC button, it is not possible to calculate a pseudo-capacitance value as displayed in Fig. 11. Indeed, the pattern in the equivalent circuit is $Q/(R+Q)$ and not the required one (R/Q).

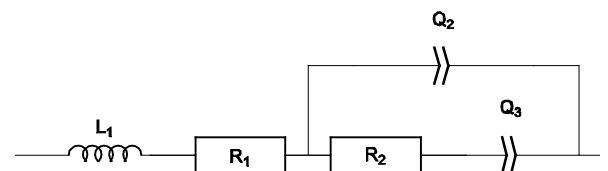


Fig. 8: L1+R1+Q2/(R2+Q3) equivalent electrical circuit.

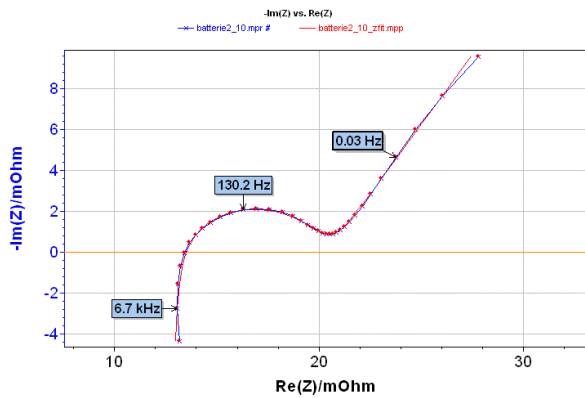


Fig. 9: Nyquist impedance diagram (blue) and ZFit analysis (red) of a Li-ion battery with a $L1+R1+Q2/(R2+Q3)$ equivalent circuit.

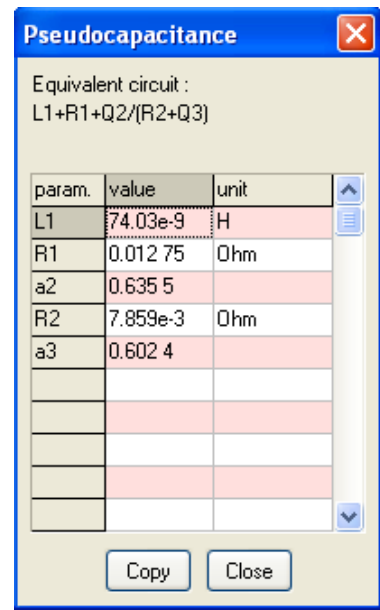


Fig. 11: Pseudocapacitance calculation in the ZFit window obtained with the $L1+R1+Q2/(R2+Q3)$ equivalent circuit.

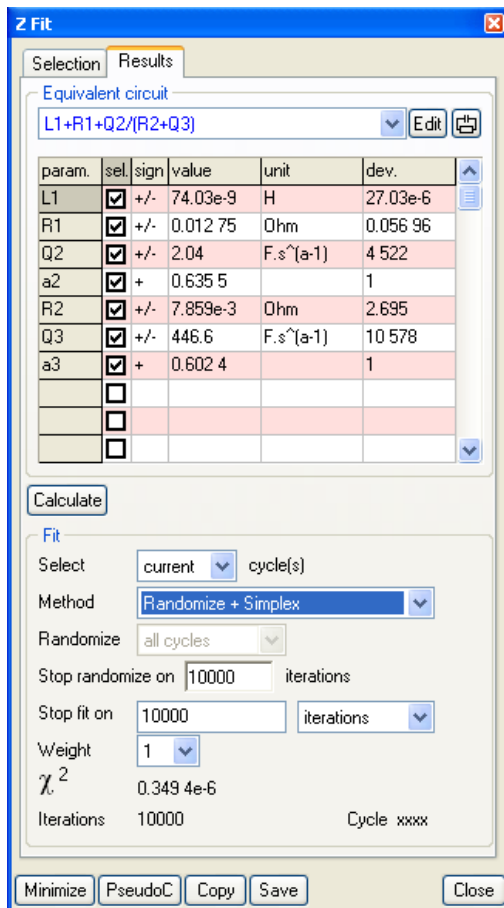


Fig. 10: ZFit analysis window obtained with the $L1+R1+Q2/(R2+Q3)$ equivalent circuit.

It is not possible to distinguish between the two fits considering χ^2 value which are very close. In the same way, values of 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 two following 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