

Ohmic Drop

II- Introduction to Ohmic Drop measurement techniques

I-Introduction

As explained in ref [1], ohmic drop can have a large influence on the result of some experiments. It is then interesting to know how to determine the value of this resistance.

Various techniques can be used such as electrochemical impedance spectroscopy or current interrupt method. The aim of this application note is to compare these two methods.

II-EIS measurements

In the first part of this note, Electrochemical Impedance Spectroscopy measurement was done on circuit #1 of the Test Box 3. The behavior of this electrical circuit is linear as shown in ref [2]. This measurement was done with the PEIS technique at 0 V, with a frequency scan between 500 kHz and 1 Hz, a sinus amplitude of 10 mV and the drift correction box ticked.

Nyquist diagram of the impedance for circuit #1 is shown Fig. 1.

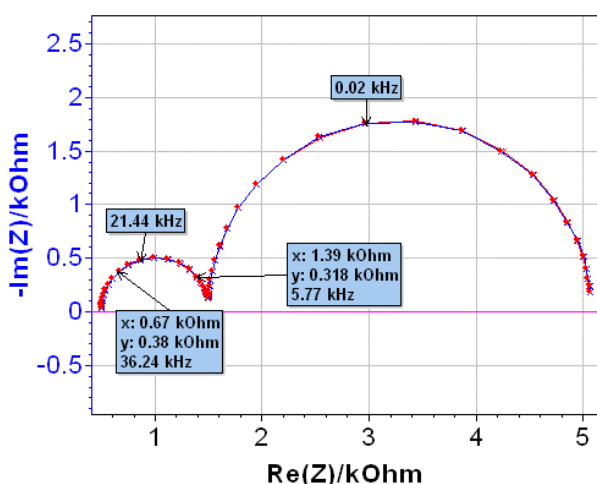


Fig. 1: Nyquist diagram of the impedance of circuit #1-Test Box 3 (blue), resulting fit obtained with ZFit for the R1+C2/R2+C3/R3 equivalent circuit (red).

The electrical circuit #1 of the Test Box 3 is equivalent to the circuit given in Fig. 2. In this circuit R_1 mimics the ohmic drop resistance R_Ω .

Thus an analysis with ZFit tool of EC-Lab® or EC-Lab® Express software allows the user to

determine the value of each parameters. Obtained results are:

- $R_1 = R_\Omega = 499 \Omega$,
- $C_2 = 6.68 \times 10^{-9} \text{ F}$,
- $R_2 = 1002 \Omega$,
- $C_3 = 2.30 \times 10^{-6} \text{ F}$,
- $R_3 = 3569 \Omega$

and ZFit parameters are given in Fig. 3.

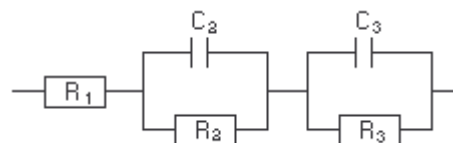


Fig. 2: Equivalent circuit of the electrical circuit #1 of the Test Box 3.

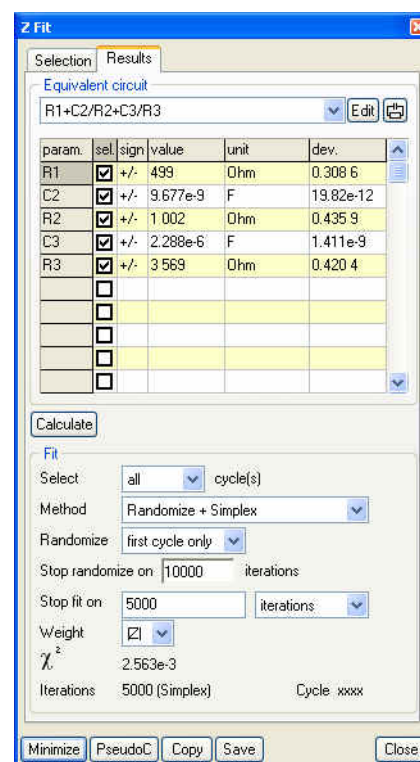


Fig. 3: ZFit parameters.

The results obtained by EIS are in good agreement with the components values. Result of this measurement will help us to calculate the voltage step response to a current step for the circuit #1 of the Test Box 3.

III-Current interrupt method

The principle of the current interrupt method is an ohmic contribution appearance when an electrical contact is established. The reverse phenomenon happens: when the electrical contact is switched off, the ohmic contribution disappears instantaneously. Illustration describing the principle of this method is given in Fig. 4 for a current step.

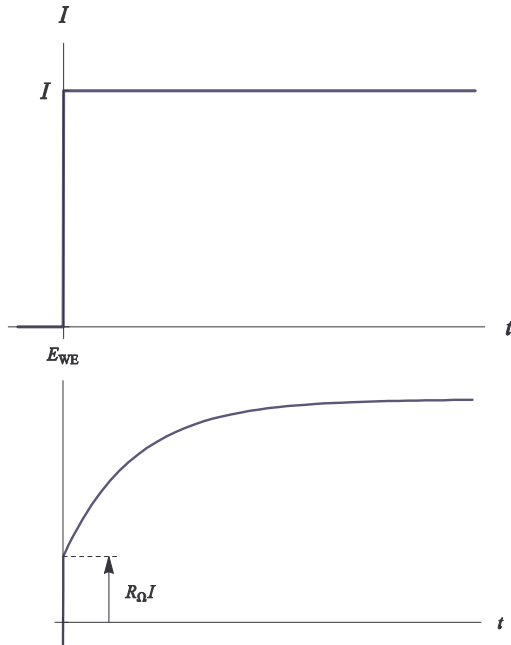


Fig. 4: Current interrupt method principle with a current step.

Considering the previous EIS measurement and the principle of the current interrupt method, one knows that impedance of circuit #1 is given by:

$$Z(s) = R_1 + \frac{R_2}{1 + R_2 C_2 s} + \frac{R_3}{1 + R_3 C_3 s}$$

where s is the Laplace variable.

It is thus possible to calculate the circuit response using the inverse Laplace transform to a current step with amplitude ΔI :

$$\begin{aligned} E_{WE}(t) &= L^{-1} \left[\frac{\Delta I}{p} Z(p) \right] \\ &= \Delta I \left(R_1 + R_2 \left(1 - \exp \left(-\frac{t}{R_2 C_2} \right) \right) + R_3 \left(1 - \exp \left(-\frac{t}{R_3 C_3} \right) \right) \right) \end{aligned}$$

Two time constants $\tau_2 = R_2 C_2 = 6.7 \times 10^{-6}$ s and $\tau_3 = R_3 C_3 = 8.2 \times 10^{-3}$ s can be defined and be calculated. These two values are significantly different and only the main constant τ_2 can be observed on the voltage step response with a linear time scale.

Considering the specifications of EC-Lab[®] and EC-Lab[®] Express software, respectively 200 μ s and 20 μ s acquisition time, and calculations done previously, it is possible to simulate the current interrupt method with a current step on the circuit #1 of the Test Box 3 and the measurement of the ohmic drop using the current interrupt method (Fig. 5).

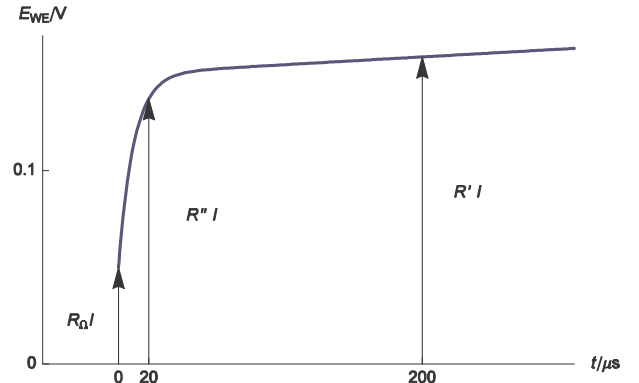


Fig. 5: Simulation of current interrupt method (0.1 mA) on the circuit #1 of the Test Box 3 considering EC-Lab[®] and EC-Lab[®] Express specifications. $R_\Omega I$ is the true ohmic drop. $R' I$ and $R'' I$ represent the ohmic drop measured respectively with EC-Lab[®] and EC-Lab[®] Express software.

With EC-Lab[®] software measurement is done every 200 μ s. Then the first measured potential is 0.15 V. Considering Ohm's law and the applied current (0.1 mA), it is then possible to calculate $R' I = 0.150$ V, then $R' = 1.5$ k Ω .

With EC-Lab[®] Express software, measurement is done every 20 μ s. In this case the first point is obtained at 0.074 V. It is then possible to calculate $R'' I = 0.074$ V, then $R'' = 1.1$ k Ω .

The two obtained values are not in agreement with the theoretical value of the ohmic drop resistance R_Ω , which is 499 Ω . Indeed depending of the software and consequently of the minimum acquisition time period, the value experimentally obtained is close to $R_1 + R_2$ for EC-Lab[®] software and between the value of R_1 and the value of $R_1 + R_2$ for EC-Lab[®] Express software.

V-Battery analysis

A 18650 lithium-ion battery, with a capacity of 1.2 Ah, was studied. The positive electrode is composed of LiFePO₄, the

negative one of graphite carbon and the electrolyte is a lithium salt.

V-1-EIS measurements

Before impedance measurement, the system was maintained 30 s at 3.10 V, and the frequency scan was done between 50 kHz and 10 mHz, with an amplitude equal to 10 mV, one period wait before each frequency measurement and the drift correction method used. The Nyquist diagram is given in Fig. 6.

ZFit analysis was done in the [0.022 - 7.27] kHz frequency range (cf. Fig. 6). The equivalent circuit in the high frequencies domain is close to $L1+R1+Q2/R2$. The value of R_1 determined with the ZFit analysis tool is $\sim 9.13 \cdot 10^{-3} \Omega$. Summary of the obtained values is given Fig. 7.

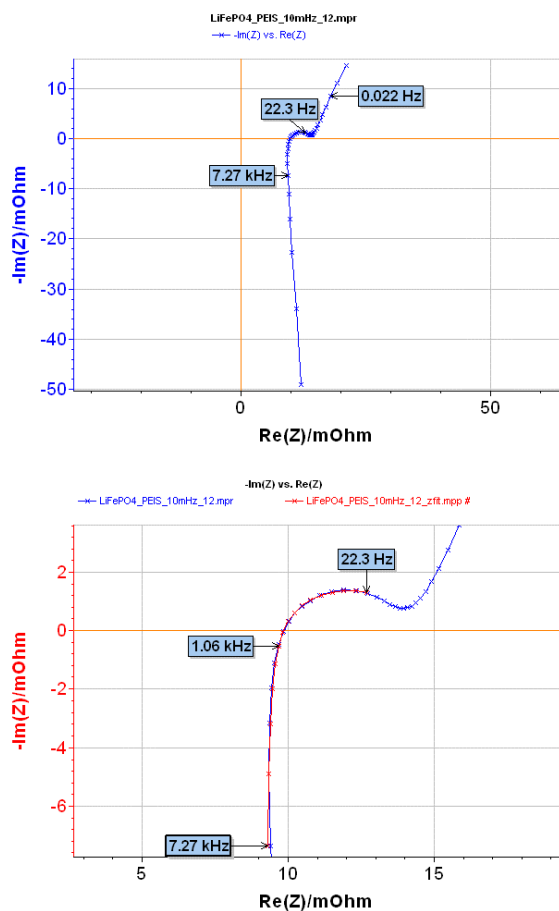


Fig. 6: Nyquist diagram of Lithium-ion battery (blue) and resulting fit (red) obtained with ZFit for the $L1+R1+Q2/R2$ equivalent circuit in the [0.022 - 7.27] kHz frequency range.

Note that sometimes it could be useful to estimate the value of the battery resistance by direct reading on the EIS diagram when $-Im(Z) = 0 \Omega$. Doing this approximation, an error can be encountered. Indeed in this

example a direct reading gives a value of $\sim 9.8 \cdot 10^{-3} \Omega$, whereas the ZFit calculated value is $\sim 9.13 \cdot 10^{-3} \Omega$, this means a difference of $\sim 10\%$ between these two values.

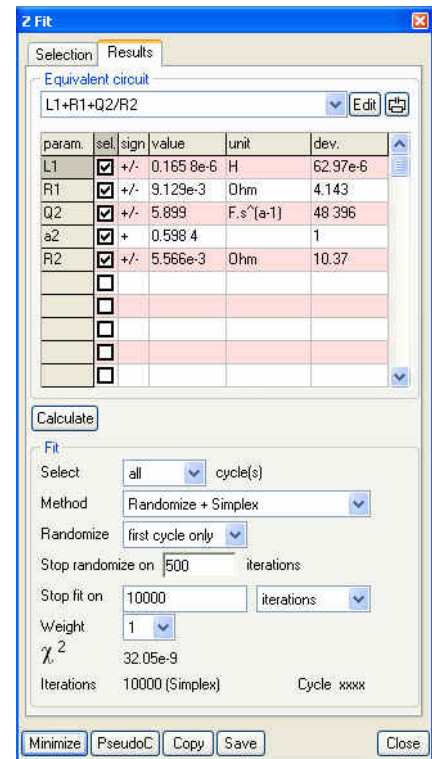


Fig. 7: ZFit analysis window.

V-2-Current interrupt method

As previously for the electrical circuit let us simulate the step response of the $L1+R1+Q2/R2$ circuit obtained with EIS measurements. Due to the real value of a_2 it is not possible to determine in a closed form the inverse Laplace transform of

$$E_{WE}(t) = L^{-1} \left[\frac{\Delta I}{p} Z(p) \right]$$

for the Lithium-ion battery. Fortunately, efficient algorithms are available for numerical inversion of Laplace Transform (NILT) [3,4].

It is then possible to simulate a current step of 400 mA applied on the battery. This simulation was done with the parameters related to EC-Lab[®] and EC-Lab[®] Express software. The result of the simulation done with the two software is shown in Fig. 8.

Considering this figure the first recorded point with EC-Lab[®] software is obtained for a potential of ~ 3.104 V. Indeed following

Ohm's law, we have the relationship $R' \Delta I = \Delta E$, where ΔE is the difference between initial potential of the battery (~ 3.098 V) and first recorded potential (~ 3.104 V), *i.e.* $\Delta E \sim 6.10^{-3}$ V. Then R' with EC-Lab[®] software is equal to 0.014Ω .

The same calculation can be done with EC-Lab[®] Express software considering the potential of the first recorded point (~ 3.104 V). Considering Ohm's law and ΔE , which is the difference between initial potential of the battery (~ 3.099 V) and first recorded potential (~ 3.104 V), *i.e.* $\Delta E = 5.10^{-3}$ V, R'' is equal to 0.012Ω .

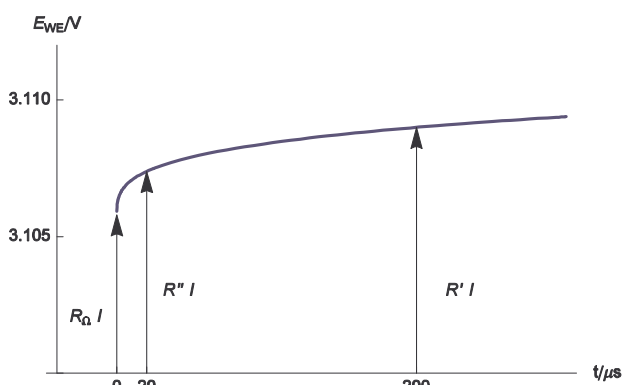


Fig. 8: Simulation of perfect current step (400 mA) on lithium-ion battery considering EC-Lab[®] specifications. $R_{\Omega} I$ is the real ohmic drop. $R' I$ and $R'' I$ represent the ohmic drop obtained respectively with EC-Lab[®] and EC-Lab[®] Express software.

Results obtained with EIS measurement and current interrupt method are close each other for this system with a low kinetics. Moreover these results are close to the theoretical value of ohmic drop resistance which was not the case for the measurements done on the electrical circuit.

VI-Conclusion

This note shows the limitations imposed by the current interrupt method. Indeed depending of the kinetics of the system, this method is more or less accurate. Note that the right value of ohmic drop resistance is never obtained. Impedance measurement is a well-adapted tool and gives the right value of the ohmic drop whatever the kinetics of the system.

Note that a special tool was developed in the EC-Lab[®] and EC-Lab[®] Express software which offers the possibility to measure by EIS and compensate the ohmic drop. This tool

allows the user to obtain an immediate value of the ohmic drop without need to know the electrical equivalent circuit. Note that by default this measurement is done for 100 kHz, but user can change this value according to the studied system.

For example, considering the previous studied systems, the determination of the ohmic drop was done with:

- the PZIR technique of EC-Lab[®] Express software. Obtained results are 502.6Ω at 500 kHz for the circuit and $9.77.10^{-3} \Omega$ at 800 Hz for the lithium-ion battery,
- the ZIR technique of EC-Lab[®] software. Obtained results are 501.3Ω at 500 kHz for the circuit and $9.76.10^{-3} \Omega$ at 800 Hz for the lithium-ion battery

Nevertheless, one can ask why such a difference of sampling between current interrupt and EIS methods. That is because in EIS we use the undersampling or Super-Nyquist sampling method. This is a well-known concept, which allows us to measure single tone frequencies over the sampling rate of the instrument.

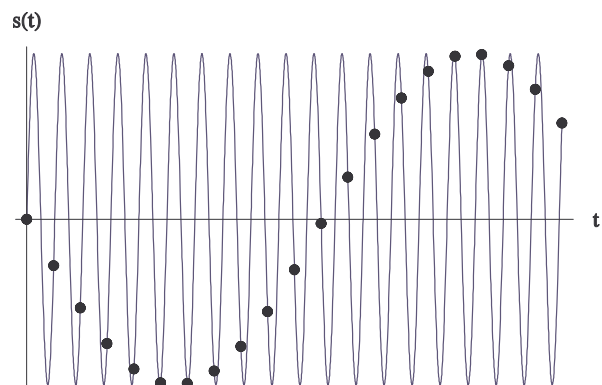


Fig. 9: Undersampling scheme.

References:

- [1] Bio-Logic Application Note #27 (<http://www.bio-logic.info>)
- [2] Bio-Logic Application Note #9 (<http://www.bio-logic.info>)
- [3] C. Montella, R. Michel, J.-P. Diard, J. Electroanal. Chem., 608 (2007) 37-46.
- [4] C. Montella, J.-P. Diard, J. Electroanal. Chem., 623 (2008) 29-40.