

Dynamic resistance determination. A relation between AC and DC measurements?

I – INTRODUCTION

Currently, several types of batteries are investigated (Li-ion, LiFePO₄, ...). Each type has its own specifications such as nominal voltage (V), capacity (A.h), power (W), energy (Wh), cyclability... The apparent resistance $R_{\Delta t}$ of the battery is also a relevant parameter.

This resistance can be determined by a simple current interrupt technique. In this technique, a current pulse is applied to the battery and the voltage shift is measured after a certain period of time Δt (Fig. 1). The *ratio* of the voltage shift ΔE and the current difference ΔI yields to a resistance, R:

$$R_{\Delta t} = \frac{\Delta E}{\Delta I} = \frac{E_2 - E_1}{I_2 - I_1} \quad (1)$$

The duration Δt may be different depending on the procedure used. For example, this period is 30 s in the procedure of the United States Advanced Battery Consortium (USABC) [1].

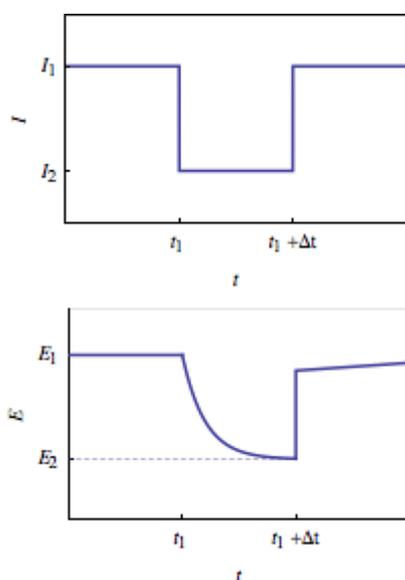


Fig. 1: Current and voltage change versus time after current pulse applied at t_1 .

This apparent resistance is called dynamic resistance when it is measured while the device is in operation [2-4]. For a battery, this value depends on the Δt , ΔI , Depth-Of-

Discharge (DOD), State-Of-Charge (SOC), State-Of-Health (SOH)...

In this application note, we will show how to determine the dynamic resistance by a DC technique. In the second part, the relationship between the dynamic resistance and the impedance will be discussed. During the discharge, the dynamic resistance and the impedance are determined by DC measurement or by AC measurement (Electrochemical Impedance Spectroscopy; EIS), respectively.

II – EXPERIMENTAL

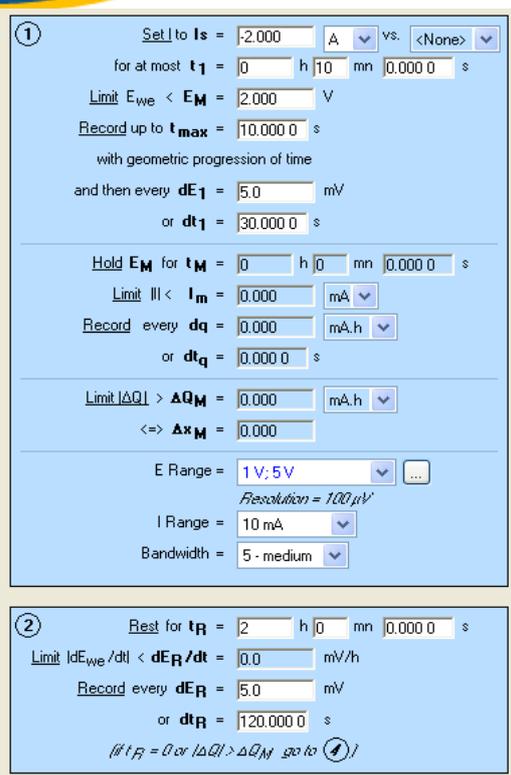
The measurements discussed hereafter were carried out on a LiFePO₄ battery with capacity of 3.2 A.h (initially charged).

EC-Lab[®] software is used to monitor a VSP, equipped with a 4A internal booster. EC-Lab[®] is also used to process the resulting data.

Note: All settings and raw data files presented hereafter are available in the Data Sample folder of EC-Lab[®] Software as filename_DR.mpr.

III- DYNAMIC RESISTANCE DETERMINATION

As described above, to determine the dynamic resistance of the battery, a galvanostatic pulse has to be applied to the battery. As the voltage change does not follow a linear evolution (Fig. 1), a sampling rate with geometric progression is of interest. GCPL5 technique offers this sampling rate with a common *ratio* of 2 during t_{max} . All the other parameters of the GCPL5 technique are similar to the GCPL technique which is shown in a previous application note [5]. A discharge of 2 A is applied to the cell and the dynamic resistance determination is performed periodically. The settings of GCPL5 are displayed in Fig. 2.



①

Set I to $I_s = -2.000$ A vs. <None>

for at most $t_1 = 0$ h 10 mn 0.000 0 s

Limit $E_{we} < E_M = 2.000$ V

Record up to $t_{max} = 10.000 0$ s

with geometric progression of time

and then every $dE_1 = 5.0$ mV

or $dt_1 = 30.000 0$ s

Hold E_M for $t_M = 0$ h 0 mn 0.000 0 s

Limit $I < I_m = 0.000$ mA

Record every $dQ = 0.000$ mA.h

or $dt_Q = 0.000 0$ s

Limit $|\Delta Q| > \Delta Q_M = 0.000$ mA.h

<=> $\Delta x_M = 0.000$

E Range = 1 V; 5 V Resolution = 100 μ V

I Range = 10 mA

Bandwidth = 5 - medium

②

Rest for $t_R = 2$ h 0 mn 0.000 0 s

Limit $|dE_{we}/dt| < dE_R/dt = 0.0$ mV/h

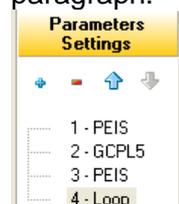
Record every $dE_R = 5.0$ mV

or $dt_R = 120.000 0$ s

(if $t_R = 0$ or $|\Delta Q| > \Delta Q_M$ go to ⚡)

Fig. 2: GCPL5 settings.

To complete the dynamic resistance determination, an EIS measurement is done after each sequence of discharge. The setting of the experiment, which is a series of linked techniques, is shown in Fig. 3. EIS measurements are shown in green arrow in Fig. 4. It will be discussed in the next paragraph.



Parameters Settings

- 1 - PEIS
- 2 - GCPL5
- 3 - PEIS
- 4 - Loop

Fig. 3: GCPL5 and EIS linked techniques.

A typical behavior of the LiFePO₄ battery is observed (Fig. 4) *i.e.* slow voltage decreases down to the capacity of the cell and then a deep voltage drop.

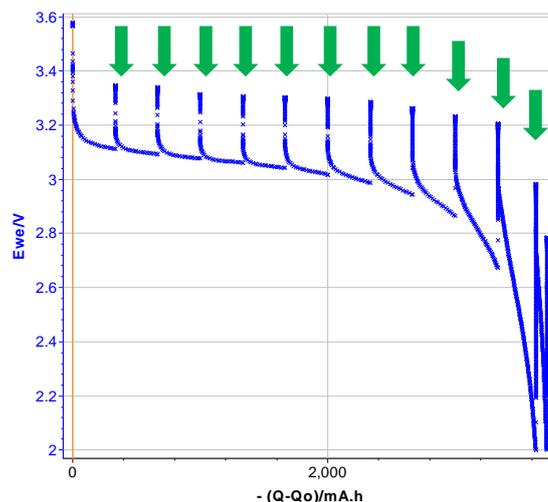
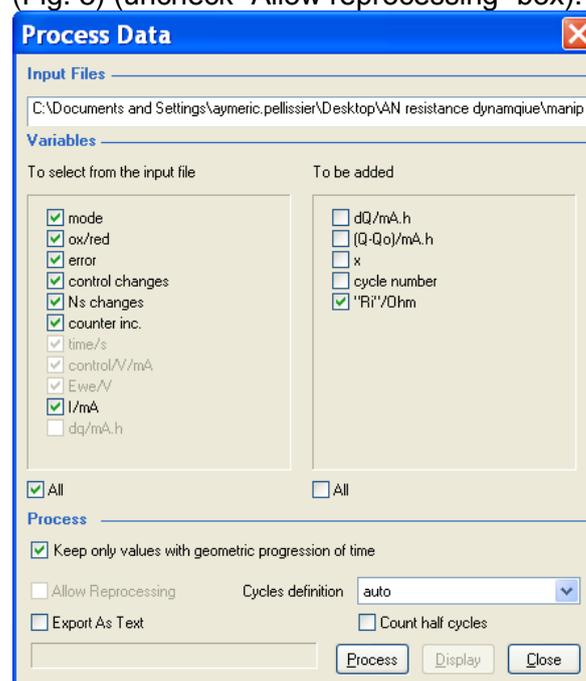


Fig. 4: GCPL5 data.

The resulting data are processed via the “Process Data” window. For Dynamic resistance determination, “Keep only values with geometric progression of time” and “R_i” (dynamic resistance) boxes have to be ticked (Fig. 5) (uncheck “Allow reprocessing” box).



Process Data

Input Files: C:\Documents and Settings\aymeric.pellissier\Desktop\AN resistance dynamique\marip

Variables

To select from the input file:

- mode
- ox/red
- error
- control changes
- Ns changes
- counter inc.
- time/s
- control/V/mA
- Ewe/V
- I/mA
- dq/mA.h

To be added:

- dq/mA.h
- (Q-Qo)/mA.h
- x
- cycle number
- "R_i"/Ohm

All All

Process

Keep only values with geometric progression of time

Allow Reprocessing Cycles definition: auto

Export As Text Count half cycles

Buttons: Process, Display, Close

Fig. 5: Dynamic resistance process.

Fig. 6 shows that the dynamic resistance increases when the battery is discharged. Data resulting from GCPL investigation can be processed and it is possible to determine the dynamic resistance for several Δt (Fig. 6B).

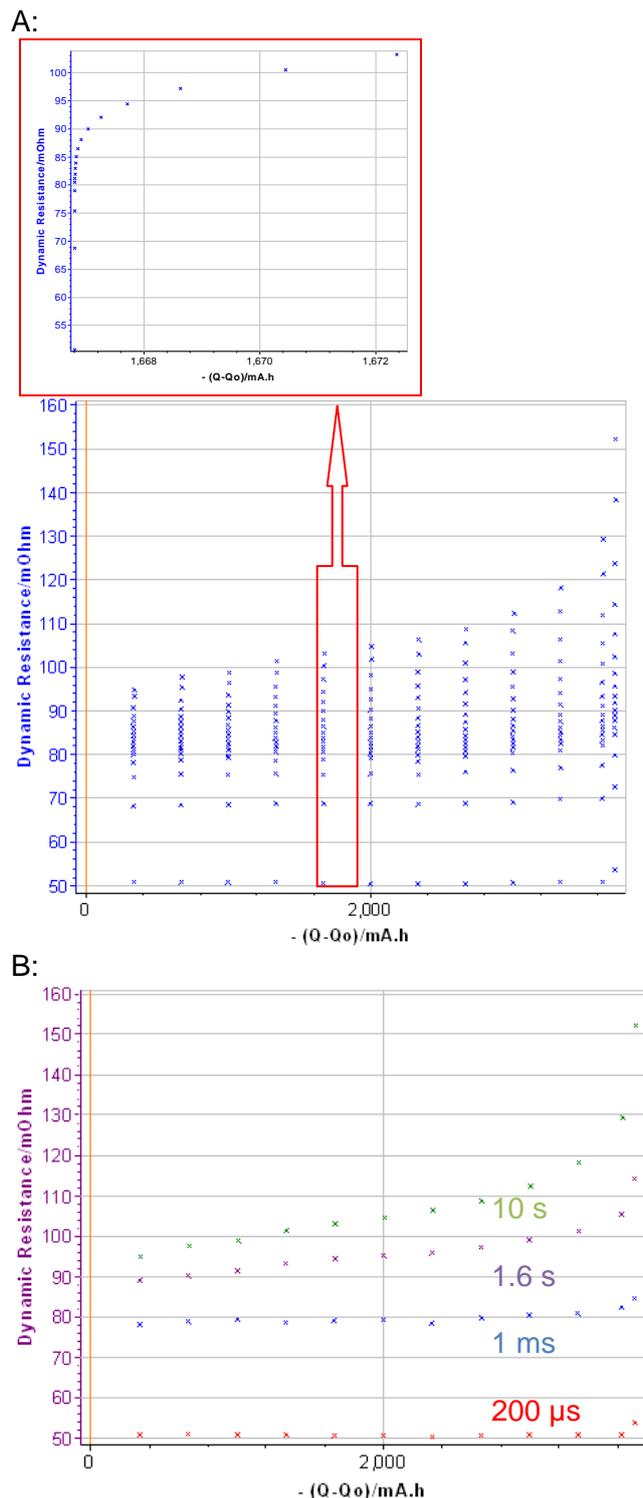


Fig. 6: Dynamic resistance change. A) during the whole discharge (inset: zoom of the 6th discharge step); B) at certain period after the pulse: 200 μs , 1 ms, 1.6 s and 10 s.

IV- EIS MEASUREMENT

To complete the characterization, EIS investigations are performed after each pulse. The settings are shown in Fig. 2 and Fig. 7.

As the voltage of the cell changes during the measurement, it is recommended to check the patented “drift correction” [6].

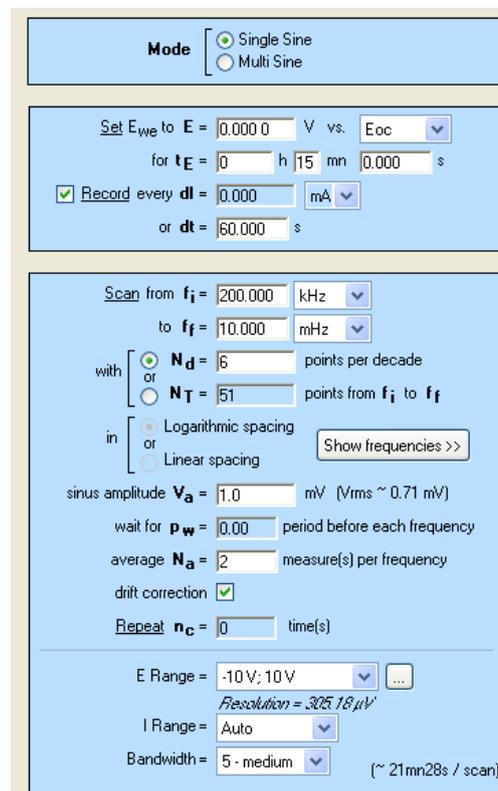


Figure 7 shows the software interface for setting up an EIS experiment. The 'Mode' is set to 'Single Sine'. The 'Set E_{We} to E' is 0.0000 V vs. Eoc. The time for t_E is 0 h 15 mn 0.000 s. The 'Record every dt' is 0.000 mA or 60.000 s. The scan range is from f_i = 200.000 kHz to f_f = 10.000 mHz. The number of points per decade (N_d) is 6, and the number of points from f_i to f_f (N_T) is 51. The spacing is set to 'Logarithmic spacing'. The sinus amplitude V_a is 1.0 mV (V_{rms} ~ 0.71 mV). The wait for p_w is 0.00 period before each frequency. The average N_a is 2 measure(s) per frequency. The drift correction is checked. The repeat n_c is 0 time(s). The E Range is -10 V; 10 V with a resolution of 305.18 μV . The I Range is Auto. The Bandwidth is 5 - medium (~ 21mn28s / scan).

Fig. 7: Setting of the experiment

The EIS plots (Fig. 8) show the typical behavior of the LiFePO₄ battery (display one semicircle at intermediary frequencies, a diffusion behavior at low frequencies and inductance behavior at high frequencies).

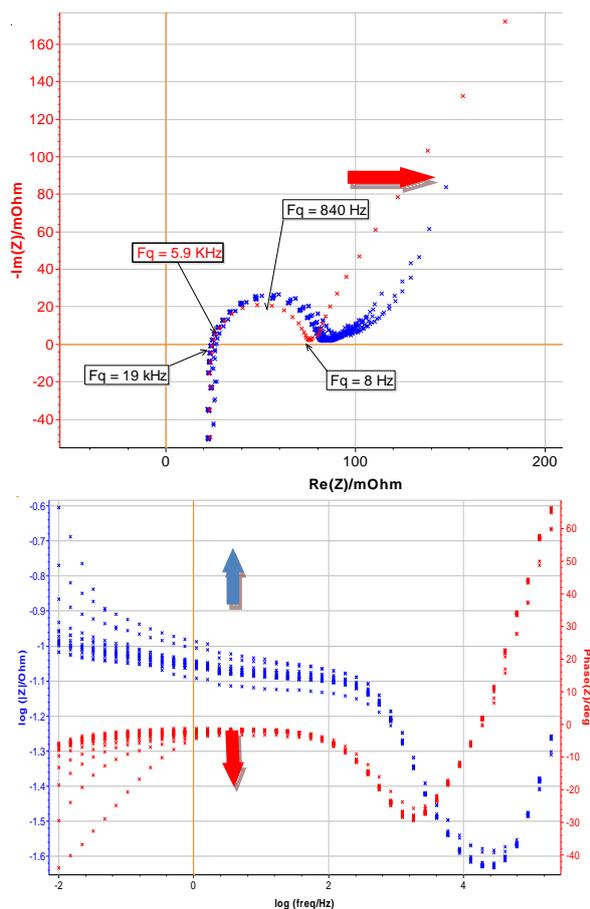


Fig. 8: Nyquist and Bode plots of the EIS data.

V- DC/AC DATA COMPARISON

The DC (time domain) and AC (frequency domain) data are compared at two levels. Firstly (part V-1), the dynamic resistance resulting from GCPL investigation is compared to the resistance fit from the EIS data. Secondly (part V-2), the step response (*i.e.* response of the system to a discrete potential step) of the system is calculated from GCPL data at several Δt (not only one point as it was done in the first part) and compared to the EIS data.

V - 1 ONE POINT COMPARISON

To compare the data between DC and AC experiments, the dynamic resistance and impedance after each discharge step are plotted versus time (Fig. 9). Both DC and AC data have to be given in terms of frequency. The DC data conversion is done by the relationship (2).

$$\omega = 1/\Delta t \quad (2)$$

where ω is the pulsation in rad.s^{-1} .

So if Δt of 200 μs is considered, the corresponding frequency is 5 kHz.

Fig. 9 shows that both dynamic resistance (DC measurement) and impedance (AC measurement) yield to similar trends (small increase) and have the same magnitude (between 25-50 mOhm).

It is noteworthy that the impedance is not a pure resistance at 5 kHz (Fig. 8). The phase at this frequency is -20° .

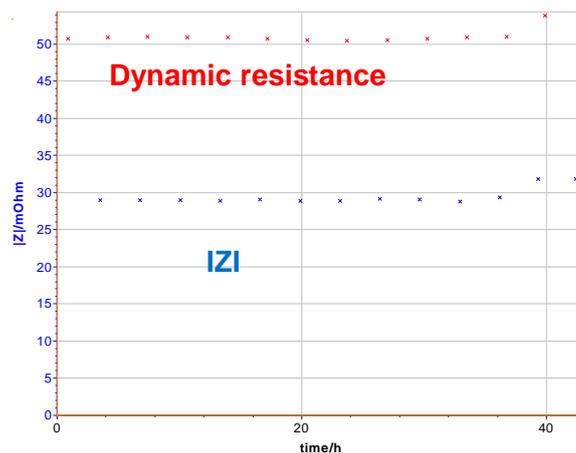
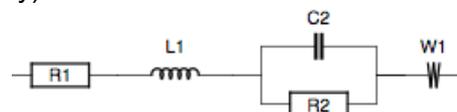


Fig. 9: Dynamic resistance and impedance plots resulting from DC (200 μs) and AC (~ 5 kHz) investigations, respectively.

V-2 STEP RESPONSE CALCULATION ON THE WHOLE FREQUENCY RANGE

In order to compare the time domain and the frequency domain measurement, it is possible to calculate the step response of the battery using the inverse of the Laplace Transform, L^{-1} .

For example, let us consider the equivalent circuit $R1 + L1 + R2/C2 + W1$ (typical for a battery):



The impedance is given by:

$$Z(s) = R1 + L1s + \frac{R2}{1 + R2C2s} + \frac{\sigma}{\sqrt{s}} \quad (3)$$

For a step of current, δI , the step response of the circuit is given by:

$$E(t) = L^{-1} \left[\frac{\delta I}{s} Z(s) \right] = \delta I (R1 + L1\delta(t) + R2(1 - \exp(-\frac{t}{R2C2}) + \frac{2\sigma\sqrt{t}}{\sqrt{\pi}})) \quad (4)$$

where $\delta(t)$ is the Dirac delta function.

The *ratio* $E(t)/I(t)$ and modulus are given by the equation (4) and (5), respectively.

$$|Z(\omega)| = \left(\left(R1 + \frac{\sigma}{\sqrt{\omega}} + \frac{R2}{1+R2^2C2^2\omega^2} \right)^2 + \left(R1 + \frac{\sigma}{\sqrt{\omega}} + \frac{R2}{1+R2^2C2^2\omega^2} \right)^2 \right)^{1/2} \quad (5)$$

Modulus *versus* angular frequency (from AC measurement) and *ratio* $E(t)/I(t)$ *versus* the inverse of Δt (from DC measurement) are plotted in Fig. 10. The superimposition of both plots show that data coming from AC and DC measurement are in good agreement.

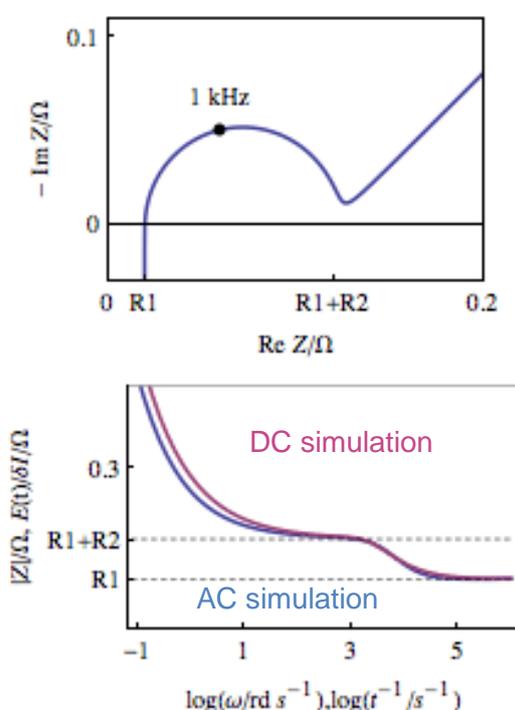


Fig. 10: **Dynamic resistance (DC simulation) and Z plot versus logarithm of Δt or ω , respectively (bottom).** For information, the corresponding Nyquist plot is given at the top.

VI-Conclusion

This note shows first how to compute a dynamic resistance thanks to EC-Lab form GCPL data.

The second part (paragraphs IV/V) shows that the dynamic resistance determined by DC method, for instance GCPL techniques, can be compared to impedance data. The conclusion of this comparison is that the dynamic resistance can be used as a rough approximation of the impedance measured by AC method. The values of the dynamic resistance or the modulus are theoretically linked together (equation 4) and lead to similar trends.

Nonetheless, to fully characterize the battery, an investigation on the whole frequency range by AC method is needed.

REFERENCES

1. Electric Vehicle Battery Test Procedures Manual, Rev2, 1996. Appendix I.
2. M. Safari, C. Delacourt, C. Journal of the Electrochemical Society, (2011), 158(10), A1123-A1135.
3. K. Taken, M. Ichimura, K. Takano, J. Yamaki, S. Okada, Journal of Power Sources (2004), 128, 67-75.
4. A. Tenno, R. Tenno, R. Suntio, IEEE (2002), 176-183.
5. [Application Note #5](#) "Protocols for studying intercalation electrodes materials: Part I: Galvanostatic cycling with potential limitation (GCPL)"
6. [Application Note #17](#) "Drift correction in electrochemical impedance measurements"