Dynamic resistance determination: Is there a link between EIS and DC measurements?

Aymeric Pellissier, Jean-Paul Diard, Sébastien Benoit,
Bio-Logic Science Instruments

INTRODUCTION

Currently, several types of batteries are investigated (Li-ion, $LiFePO_4$, ….). Each type has its own specifications such as nominal voltage (V), capacity (A.h), power (W), energy (W.h), cyclability... The dynamic resistance $R_{\Delta t}$ of a 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 to the current difference ΔI yields to a resistance, $R_{\Delta t}$:

$$R_{\Delta t} = \Delta E(t)/\ \Delta I(t) \qquad [1]$$

The duration Δt may be different depending on the used procedure and the instrument. For example, this period is 30 s in the procedure of the United States Advanced Battery Consortium (USABC).
The aim of this poster is to compare the resistance measured by Electrochemical Impedance Spectroscopy (EIS) and DC measurements.

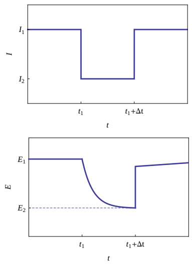


Fig. 1: Current and voltage change versus time after current pulse applied at t_1. $\Delta E(t) = E_2 - E_1$; $\Delta I(t) = I_2 - I_1$

DYNAMIC RESISTANCE DETERMINATION…

During a discharge (Fig. 2), the dynamic resistance is determined by DC method and EIS measurement. The DC and EIS measurements are shown in Figs. 3 and 4, respectively

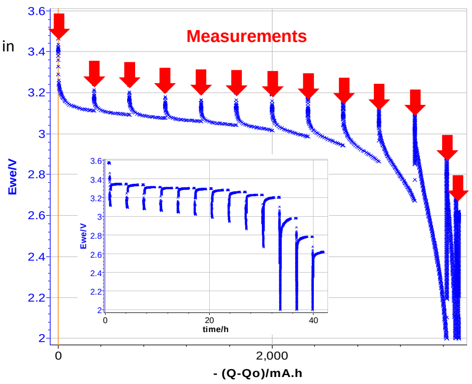


Fig. 2: Voltage evolution versus charge. The EIS and DC measurements are indicated by the red arrows. (Inset: Voltage *vs.* time).

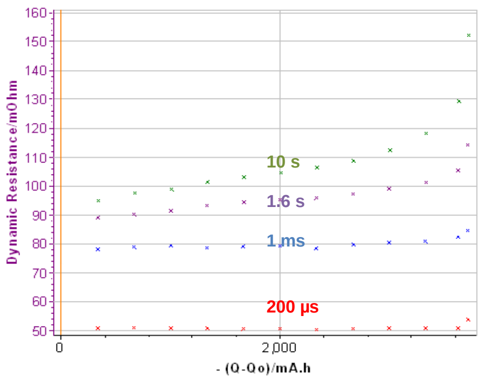


Fig. 3: Dynamic resistance change at certain period after the current pulse: Δt: 200 µs, 1 ms; 1.6 s and 10 s.

DC measurement
EIS measurement

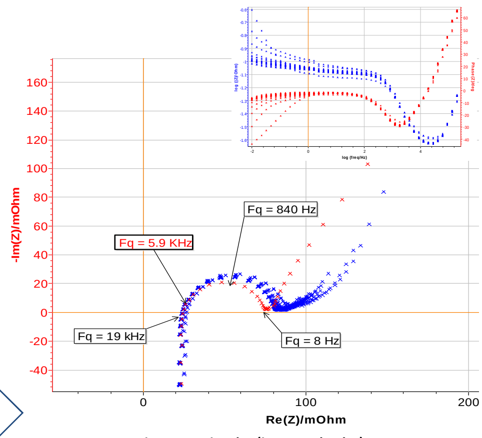


Fig. 4: Nyquist plot (inset: Bode plot).

… AND COMPARISON

To compare the data obtained with DC or EIS experiments, the dynamic resistance and impedance after each discharge step are plotted versus time (Fig. 5). Both DC and AC data have to be given in terms of frequency.
The DC data conversion is done by ω = 1/Δt where ω is the pulsation in rad.s^{-1}.
So if Δt = 200 µs, the corresponding frequency is 5 kHz.
It is noteworthy that the impedance is not a pure resistance at 5 kHz (not only real part). The phase at this frequency is -20° (Fig. 4).

- **similar trends (small increase)**
- **same magnitude (between 25-50 mOhm).**

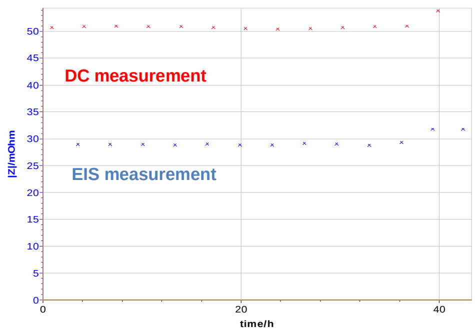
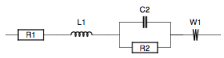


Fig. 5: Dynamic resistance and impedance plots resulting from DC (200 µs) and Dynamic resistance AC (~5 kHz) investigations, respectively.

FURTHER INTO THE THEORY

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  (typical for a battery):

The impedance is given by:

$$Z(s) = R_1 + L_1 s + R_2/(1+R_2C_2 s) + \sigma/s^{1/2} \qquad [2]$$

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

$$E(t) = L^{-1}[(\Delta I/s)Z(s)] =$$
$$= \Delta I\ (R_1 + L_1\ \delta(t) + R_2[1-\exp(-t/(R_2C_2)) + 2\sigma t^{1/2}/\pi^{1/2}]) \qquad [3]$$

Where δ(t) is the Dirac delta function.

The *ratio* E(t)/ΔI(t) and modulus are given by the Eqs. (3) and (4), respectively.

$$|Z(\omega)| = [(R_1 + \sigma/\omega^{1/2} + R_2/(1+R_2^2C_2^2\omega^2))^2 + (R_1 + \sigma/\omega^{1/2} + R_2/(1+R_2^2C_2^2\omega^2))^2]^{1/2} \qquad [4]$$

Modulus *versus* angular frequency (from AC measurement) and *ratio* E(t)/ΔI(t) *versus* the inverse of Δt (from DC measurement) are plotted in Fig. 6. The superimposition of both plots show that data coming from AC and DC measurement are in good agreement.

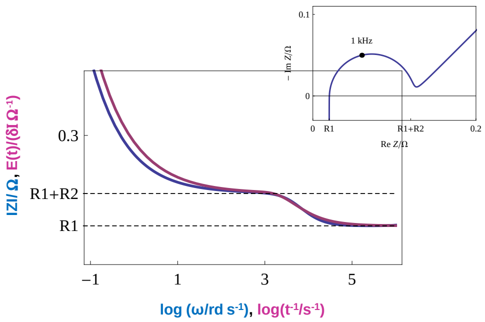


Fig. 6: |Z| and Dynamic resistance (DC simulation) plot versus logarithm of ω or Δt ,respectively (inset: The corresponding Nyquist plot).

CONCLUSION

The dynamic resistance determined by DC method, for instance GITT 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 *via* Eq. (3) and lead to similar trends.

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

More info on:
http://www.bio-logic.info/potentiostat/notesan.html