Drift correction in electrochemical impedance measurements

I- Introduction

Several conditions are required to measure the electrochemical impedance of a system. Its behaviour must be linear, invariant *vs.* time, and the system should be in a steady-state. Indeed, if the steady-state is not reached by the system, the electrochemical impedance signal used to calculate the Fourier Transform is not periodic. Moreover, the presence of a transient period due to the excitation step implies in the result spectrum a contribution to the response of the imposed sinusoid (Fig. 1).

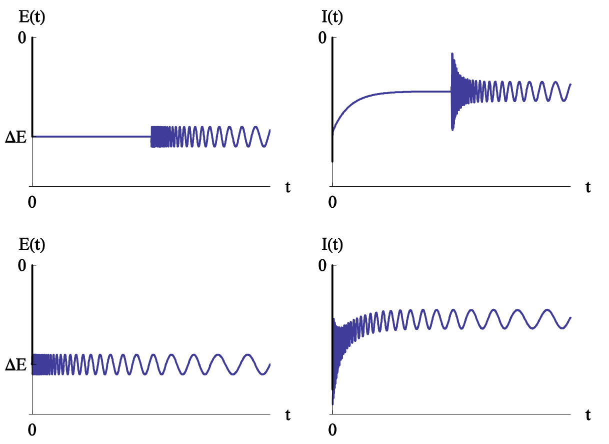

Fig. 1: Example of a current response to an excitation by a sum of a potential step (amplitude: Δ*E*) and a series of sinusoids (amplitude: δ*E*). Left: sinusoids series starting when the steady state is reached. Right: sinusoid series starting at the beginning of the potential step.

This application note deals with a drift correction method in impedance measurements when it is done in drift conditions just toward the steady-state. Fourier Transform of the input and output signals are used to do the drift correction. In the first part, a measurement error example is given for an electrical circuit, and the second part gives the comparison of measurements done for a lithium-ion battery with and without using drift correction.

II-Experimental part

All the impedance measurements shown in this application note were obtained with the EIS technique of EC-Lab® Express software (cf. Fig. 2), generally with a potential step amplitude of ΔE = 10 mV. Different cycles are done for each measurement (measurements were done successively).

Note: drift correction tool is also available in EC-Lab® software.

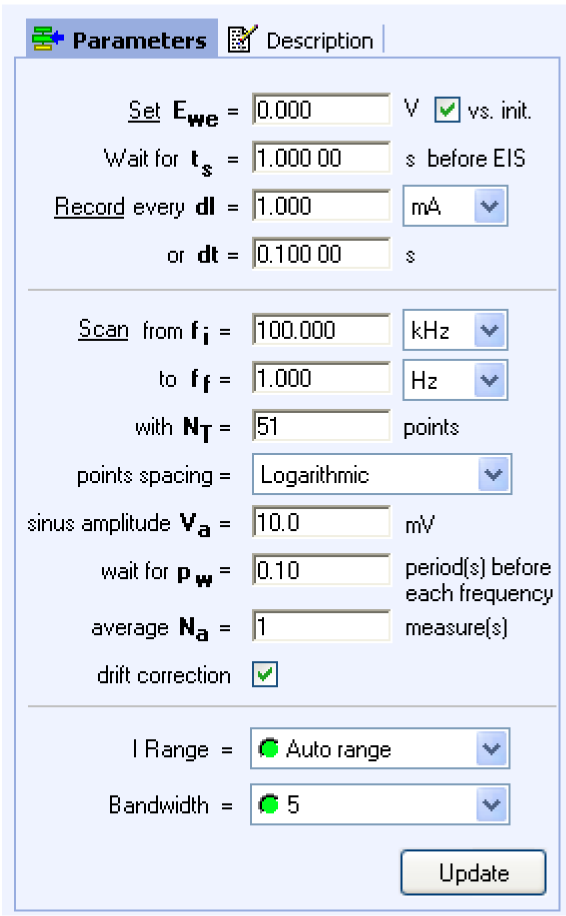

Fig. 2: PEIS technique diagram in the EC-Lab® Express software with the drift correction box ticked.

III- Impedance measurement in drift conditions toward a steady state

III-1 Electrical test circuit

Fig. 3 shows an electrical circuit made of 3 capacitors and 2 resistors.

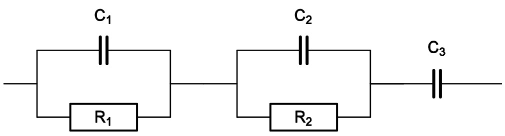

Fig. 3: Electrical test circuit.

Impedance of this linear circuit is well known when a potential step with a ΔE amplitude is applied [1]. Nevertheless, studying this circuit can give an example of the drift correction method. Fig. 4 shows the measured transient current corresponding to the electrical circuit response to a potential step. Let's consider that the current value is close to zero after ~ 2 minutes. Thus, to measure the impedance of this steady state circuit, it is necessary to wait 2 minutes before measurement.

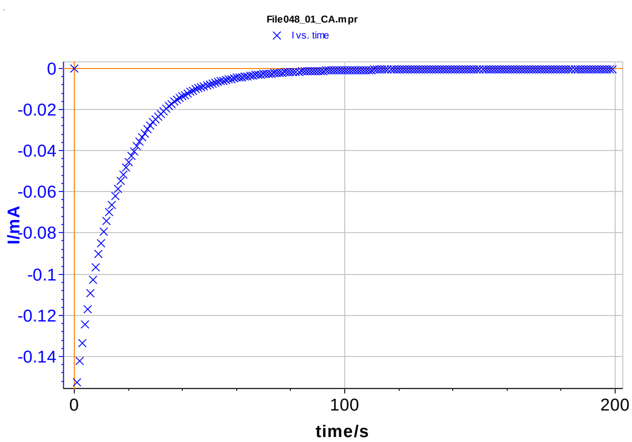

Fig. 4: Current response of the electrical circuit (Fig. 3) to a potential step.

Three impedance Nyquist graphs – corresponding to cycles - of the electrical circuit (cf. Fig. 3) measured successively without waiting for the steady state are given in Fig. 5.

A difference in the middle frequency range for the second arc of circle (intermediate frequencies) can be noticed. The second and third cycles are close to each other and correspond to the graph obtained at the open circuit potential. The measurement duration is around 8 min, and the second and third cycles are plotted in steady-state conditions. It is not the case for the first graph.

Reaching the steady state can take a long time that is not convenient for doing measurements series. Thus it is useful to gain time.

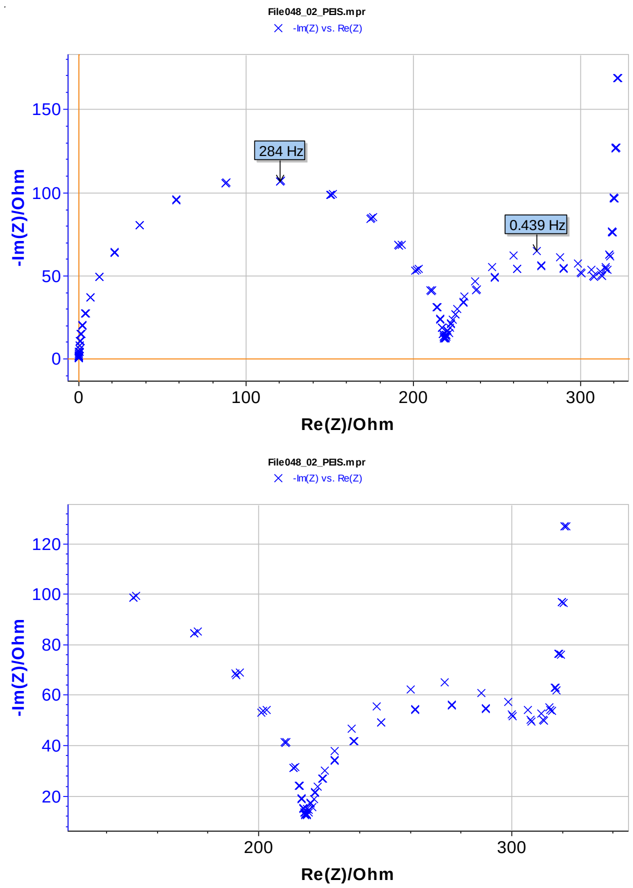

Fig. 5: Three impedance Nyquist graphs of the electrical circuit (Fig. 3) measured successively from the potential step application. Enlargement of the low frequencies area is also given. (f_{min} = 20 mHz, f_{max} = 100 kHz (51 measured points), ΔE = 50 mV, ΔE = 10 mV).

III-2 Principle of the drift correction method toward a steady state

Several methods are available to define the drift correction [2,3]. Another very easy method was proposed recently [4 - 7]. The method given in this paper is based on the Fourier transform impedance measurement. This method consists of the calculation of discrete potential and current Fourier transforms. Correction is done by compensation using the f_{m-1} and f_{m+1} adjacent frequencies of f_m in the Fourier spectrum, with the following equations:

$$\mathrm{Re}\, I_{cor} = \mathrm{Re}\, I(f_m) - \frac{\mathrm{Re}\, I(f_{m+1}) + \mathrm{Re}\, I(f_{m-1})}{2} \quad (1)$$

$$\mathrm{Im}\, I_{cor} = \mathrm{Im}\, I(f_m) - \frac{\mathrm{Im}\, I(f_{m+1}) + \mathrm{Im}\, I(f_{m-1})}{2} \quad (2)$$

The principle of this correction is shown in Fig. 6. Without drift, $\mathrm{Re}\, I(f_{m+1})$, $\mathrm{Re}\, I(f_{m-1})$, $\mathrm{Im}\, I(f_{m+1})$, and $\mathrm{Im}\, I(f_{m-1})$ are null and drift correction does not modify the measurement.

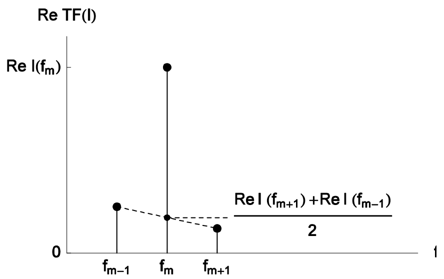

Fig. 6: Principle of drift correction method for an imposed potential. (Real part of the Fourier spectrum).

An example of the drift correction is given in Fig. 7 for the Fig. 3 circuit. These measurements were obtained successively from the potential step application. The three graphs are close and in agreement with results obtained in open circuit.

The drift correction method used towards a steady-state reduces the impedance experiment's measurement time for an electrical circuit submitted to a potential step.

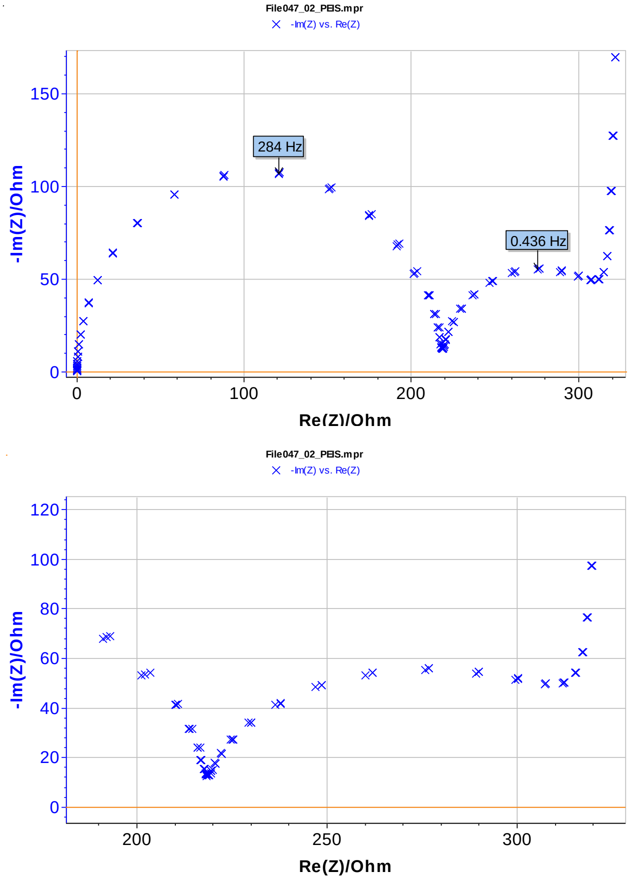

Fig. 7: Three impedance Nyquist graphs with drift correction of Fig. 3 circuit measured successively from the potential step imposition.

IV- Study of a lithium-ion battery

This drift correction method was applied on a 1.35 Ah Sony Energytec Li-Ion battery. Characterization of lithium-ion batteries is often done by series of partial charge/discharge with current or potential limitations, and an open circuit period. Duration of this relaxation period could be very long due to the slow diffusion coefficient of the intercalated species into the host material (~ 10^{-12} $mol.cm^{-2}$). Indeed, Fig. 8 shows the current response of this battery to a potential step and the time (~ 1 h 00) required to reach equilibrium state.

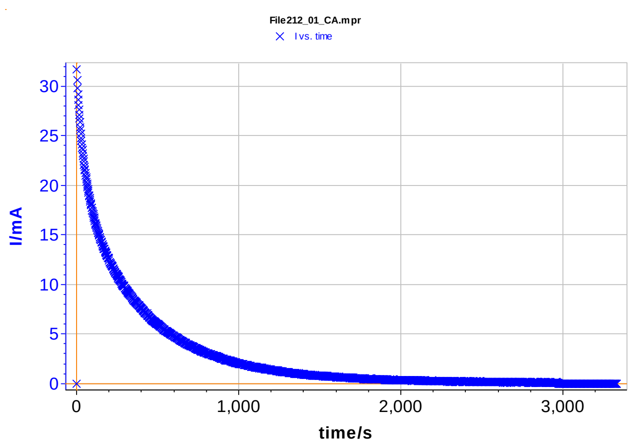

Fig. 8: Lithium-ion battery current response to a potential step (E_{OC} = 3.09 V).

IV-1 Measurement without drift correction

The two impedance graphs of the lithium-ion battery measured in potentiodynamic mode are given in Fig. 9. These graphs were recorded from the potential step application. Measurement total time is around 1 h 20 min. These two graphs – corresponding to different cycle - present significant differences mainly in the low frequencies range (cf. Fig. 9).

IV-2 Measurement with drift correction

Results obtained for lithium-ion battery impedance measurement with drift correction are given in Fig. 10. These two impedance graphs are very close as shown in the low frequency enlargement. The drift correction allows the user to save time for battery impedance measurement.

V-Conclusion

The drift correction method proposed in this note is very easy to use with only the measurements of two sinusoid periods. This method is a good way to do impedance measurements on systems with very long relaxation times. This method can be improved by increasing the number of points of the Fourier spectrum used to do the correction. It is also, for example, possible to model the baseline with a second (or more) degree polynomial function.

Numerous electrochemical systems are not stable in time such as:

- electrodes on which occurs a corrosion reaction,
- electrochemical generators during a charge or a discharge period on which a galvanodynamic impedance measurement is done.

Indeed non-steadiness of systems can induce a slight deviation on the obtained impedance graphs compared with the theoretical one.

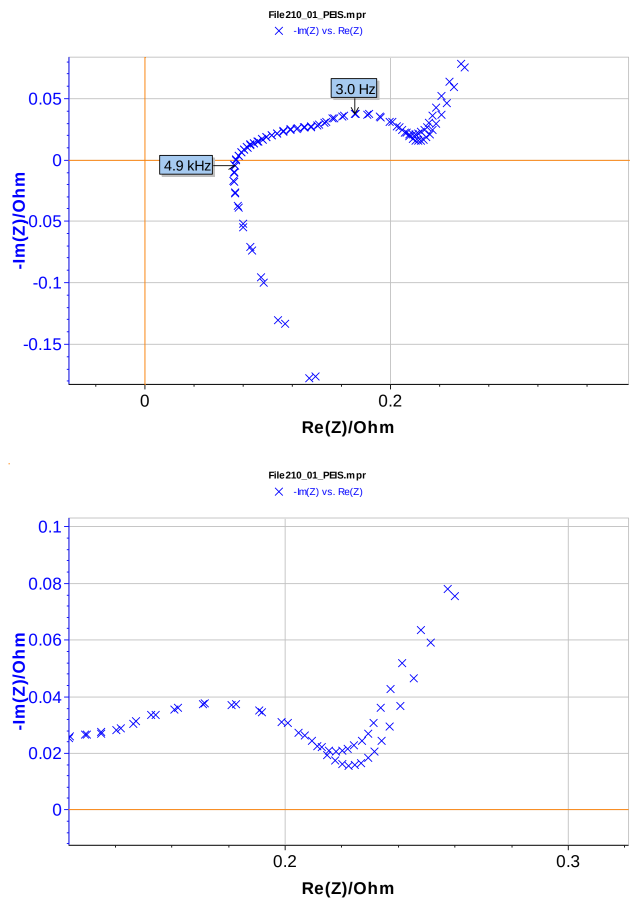

Fig. 9: Lithium-ion battery impedance Nyquist graphs successively measured and low frequency enlargement. (f_{min} = 5 mHz, f_{max} = 10 kHz, 51 measurement points, δE = 3 mV, E_{OCV} = 3.09 V).

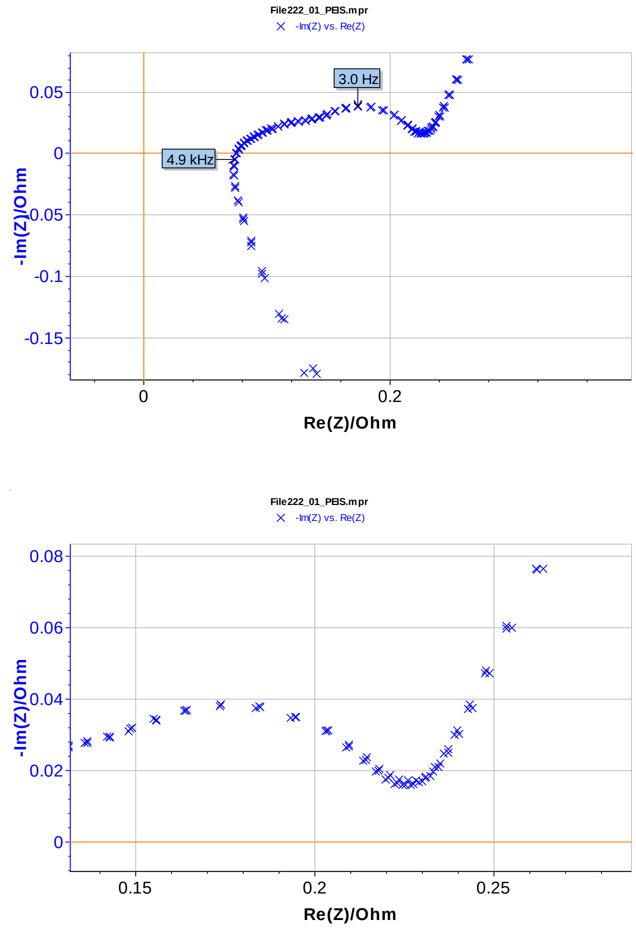

Fig. 10: Lithium-ion battery impedance Nyquist graphs successively measured and low frequency enlargement; measurements done with drift correction. Same conditions as those of Fig. 9.

References

[1] Bio-Logic Application Note #9 (http://www.bio-logic.info)

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