

EIS measurements on Li-ion batteries EC-Lab[®] software parameters adjustment

I-Introduction

To obtain significant EIS plots, without noise or trouble, experimental parameters should be chosen carefully. Then user has to pay attention of the definition of each parameter and to test the effect of each one on the result.

Moreover, each electrochemistry software is conceived differently and user has to adapt parameters depending on the software.

The aim of this note is to help the user to obtain good experimental results with EC-Lab[®] software. For this a detailed description of some key points (connection, cable length, experimental parameters, ...) is given in the following.

II-Experimental part

In the following, experiments were done on a Li-ion battery with a nominal capacity of 10 Ah. Experiments were carried out at the E_{oc} potential, *i.e.* 3.3 V.

Note:

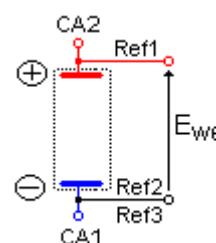
- experiments were obtained with EC-Lab[®] software in potentiostatic mode,
- initial potential has to be defined as a function of OCV potential. Indeed definition of this initial potential as a function of the Ref is equivalent to put the battery at 0 V,
- if another experiment is defined before, then it is possible to define the initial potential as a function of E_{ctrl} and E_{meas} (previous potential controlled and previous potential measured, respectively). If there is no experiment before it is not possible to use E_{ctrl} and E_{meas} .

N.B.: All settings and raw data files presented hereafter are available in the Data Sample folder of EC-Lab[®] software as "battery 10Ah_Va=xmV_pw=x_Na=x_drift?_connection?_repetition?_12.mpr". The file to consider is given on the graphic display.

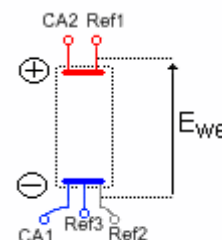
II-1 Connection

Two kinds of two electrodes connection can be considered:

- (1) "two-points" connection with CA2+Ref1 together on the positive electrode and CA1+Ref2+Ref3 together on the negative electrode:



- (2) "five-points" connection by separating each cable on each electrode, *i.e.* CA2 and Ref1 on the positive electrode and CA1, Ref2 and Ref3 on the negative electrode:



This connection is also recommended for accurate potential measurement.

As shown in Fig. 1, we can notice a shift of + 2.5 mΩ between EIS diagram obtained with the banana plugs connected together (1) comparing with the banana plugs connected separately (2).

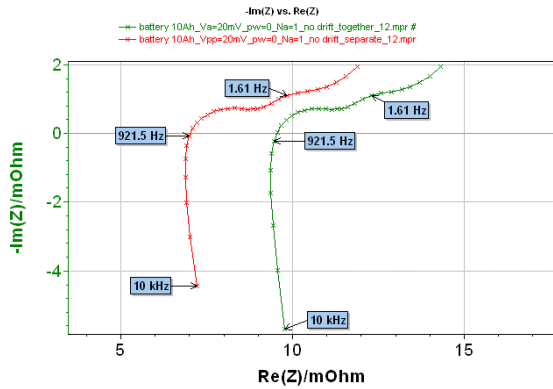


Fig. 1: Comparison of EIS diagrams obtained considering banana plug connected together (1) (green line and markers) and separately (2) (red line and markers).

This example shows that for systems with a small resistance, the connection is very important and can have a large influence on the results. That is why it is necessary to minimize the value of stray inductance or resistance [1] generated by the connection. Then connection of the banana plugs separately as close as possible of the electrochemical system is a good way to reduce the intrinsic connection influence.

II-2 Cable length

Use of lengthened cables can sometimes be required to well fit with laboratory configuration. Nevertheless, even with precaution long cables can induce non-significant results.

The following experiments were done with a standard cable (red EIS curve) and with cable of 10 m length (blue EIS curve). Note that to avoid oscillations of the potentiostat, resistances were added to the reference plugs on the 10 m cable.

As shown in Fig. 2, a slight difference can be noticed between the EIS curves obtained with standard or long cable. Nevertheless depending on the studied system, EIS measurements with long cables have to be analyzed with caution.

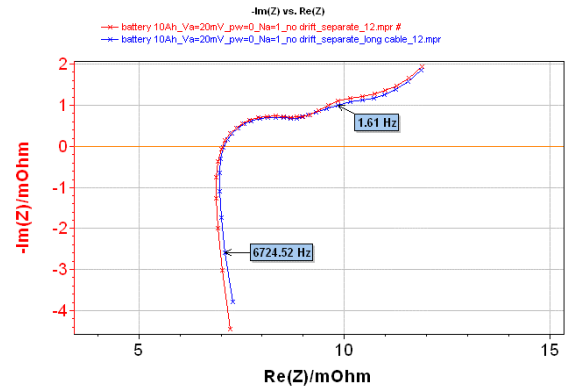


Fig. 2: Comparison of EIS curves obtained with a standard cable (red curve and markers) and with a 10 m cable (blue curve and markers).

II-3 Experimental parameters

Experiments were done with PEIS technique (Fig. 3).

II-3-a Excitation amplitude

The first parameter to determine is the value of the potential excitation V_a . Note that before the 9.56 EC-Lab[®] version, excitation amplitude was defined as V_{pp} (peak-to-peak amplitude). Equivalence between V_a , V_{pp} and V_{RMS} is defined by the relationship:

$$V_a = \frac{1}{2} V_{pp} = \sqrt{2} V_{RMS}$$

This parameter value has to be chosen considering the current amplitude I/I and the potential amplitude $|E|$ values. I/I and $|E|$ are the amplitude applied around the DC level of current or around the DC level of potential. It is the AC amplitude. In EC-Lab[®] software DC levels of current or of potential are called $\langle I \rangle$ and $\langle E \rangle$. V_a value has to be determined in such a way that the system would be in a linear part to obtain significant EIS results [2].

Ns 0 1

Fig. 3: "Parameters Settings" window of PEIS experiment.

Firstly, a V_a value of 0.5 mV was chosen. Obtained EIS diagram is given in Fig. 4.

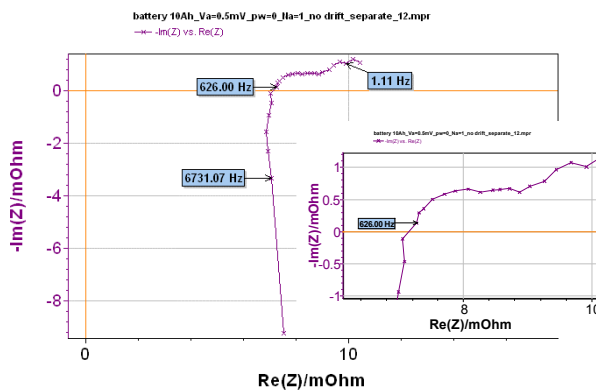


Fig. 4: EIS diagram obtained with the following experimental conditions: $V_a = 0.5$ mV, $p_w = 0$, $N_a = 1$ and no drift correction.

Considering the poor quality of this EIS diagram, we have to analyze current and potential amplitude values, which are significant for EIS measurement (Fig. 5 & Fig. 6).

Indeed $\langle E_{we} \rangle$ value which is the open circuit potential of the battery is not significant for the EIS measurement but as expected this value is maintained during the measurement.

Value of $|E|$ is very small, only few microvolt (Fig. 5). Considering the specifications of the instrument in impedance, signals smaller than

1 mV present the same level that the noise. Then in this measurement the value of potential amplitude ($|E_{we}|$) is included in the measurement noise that explains the poor quality of the EIS diagram.

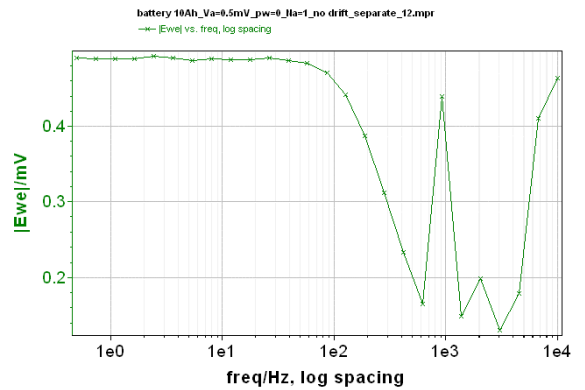


Fig. 5: Change of potential amplitude $|E_{we}|$ with frequency.

Value of $|I|$ is small but in good agreement with the accuracy of the instrument (Fig. 6).

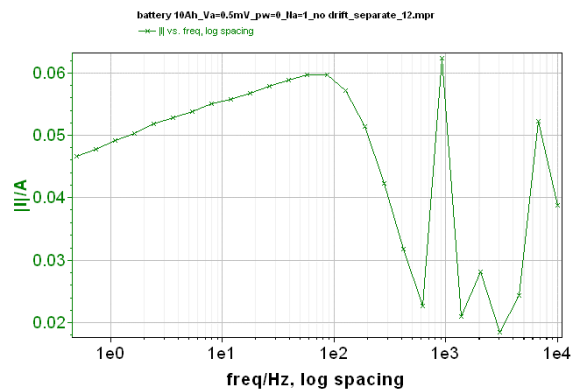


Fig. 6: Change of current amplitude $|I|$ with frequency.

In this experiment the critical parameter is the amplitude of potential value. Note nevertheless that current and/or potential can be critical parameters depending on the studied system.

To improve EIS diagram, V_a value has to be changed. Considering the previous results it seems that an increase of the V_a value could help to obtain good quality EIS diagram.

Fig. 7 gives the EIS diagram obtained with 10 mV as V_a value.

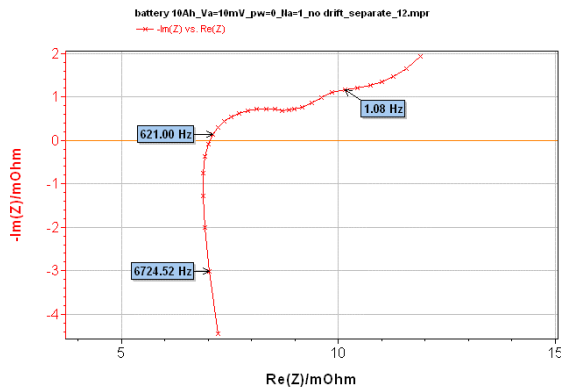


Fig. 7: EIS diagram obtained with the following experimental conditions: $V_a = 10$ mV, $p_w = 0$, $N_a = 1$ and no drift correction.

This time, value of potential amplitude ($|E_{we}|$) is significant and in agreement with the accuracy of the instrument.

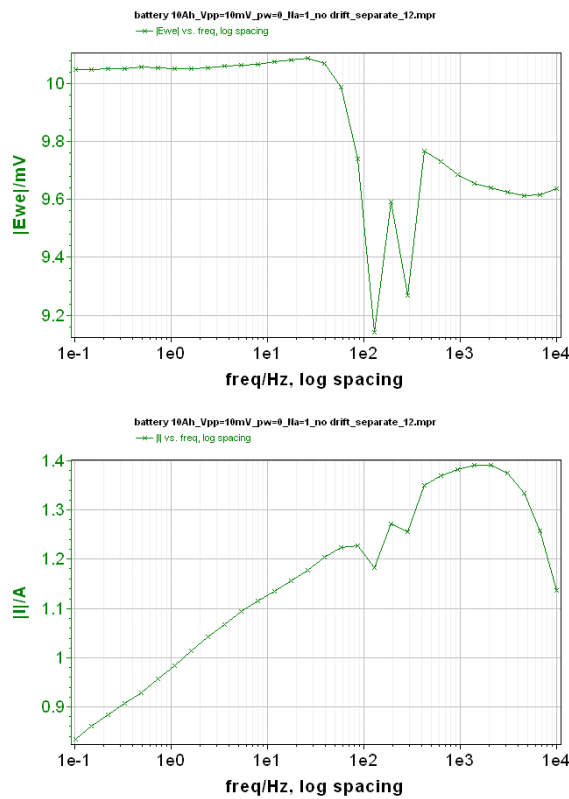


Fig. 8: Top: Change of potential amplitude $|E_{we}|$ with frequency. Bottom: Change of current amplitude $|I|$ with frequency.

Influence of the increase of the V_a value can clearly be noticed on the comparison between EIS diagrams obtained with $V_a = 0.5$ mV and with $V_a = 10$ mV as shown in Fig. 9.

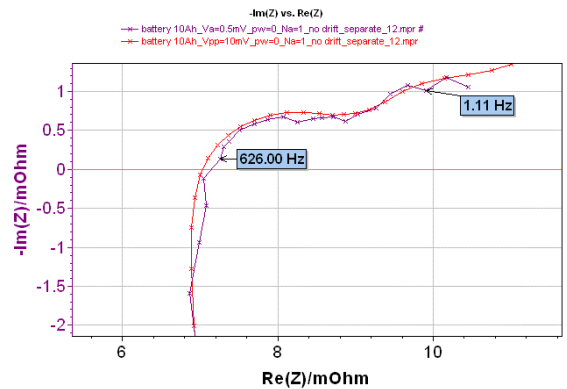


Fig. 9: Comparison of EIS diagrams obtained with a potential excitation V_a of 0.5 mV (purple curve) and of 10 mV (red curve).

II-3-b p_w value

P_w box offers to the user the possibility to add a delay before the measurement at each frequency. This delay is defined as a fraction of the period. In other words, this delay offers the possibility to let the system come back to a steady-state sinusoidal behavior and to be out of a transient period resulting from the frequency transition. This parameter is important especially for system with high time constant.

The aim of this part is to show the effect of p_w value on EIS diagram in comparison with well-defined diagram (for $V_a = 10$ mV). Fig. 10 shows a comparison between two EIS diagrams obtained with two values of p_w (0 and 1) and $V_a = 0.5$ mV and one diagram obtained with $V_a = 10$ mV and $p_w = 0$.

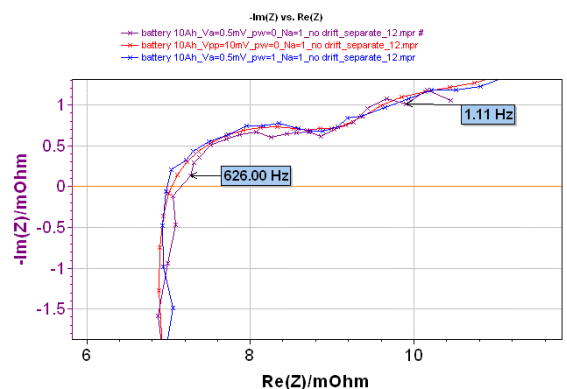


Fig. 10: Comparison of EIS diagrams obtained with $V_a = 0.5$ mV, $N_a = 1$ with no drift correction and a value of p_w equal to 0 (purple curve) or 1 (blue curve) with EIS diagram obtained with $V_a = 10$ mV ($p_w = 0$ red curve).

First, we can notice that the diagram obtained with the value of $p_w = 1$ is less

noisy than the one obtained with $p_w = 0$. Moreover this diagram obtained with $p_w = 1$ is almost superimposed with the “correct” EIS diagram obtained with $V_a = 10$ mV.

This result means that it is possible to slightly compensate a noisy shape of EIS diagram just by increasing the p_w value and without to disturb the cell a lot. This result is in agreement with high time constant of the system. Of course this increases the experiment time. For example in this experiment case for a value of p_w of 0, a time of 6 s is needed for one scan whereas when the value of p_w is 1 a time of 13 s is needed for one scan.

II-3-c N_a value

N_a is the number of repetition of measurement at each frequency, and then an average is done for each frequency. This means that the noise is reduced following the mathematical law $\sqrt{N_a}$.

In the following, two values of N_a were tested 1 and 36, the other parameters are equal: $V_a = 0.5$ mV, $p_w = 0$, no drift correction, separate connection. The full frequency sweep is repeated 15 times to show the data point dispersion.

Fig. 11 shows the result obtained with $N_a = 1$. It is possible to see that for each frequency the recorded points are not superimposed. It is clearly visible on the enlargement.

Fig. 12 shows the experiment done with $N_a = 36$. Obviously for each frequency, recorded points are superimposed meaning then that coordinates of each recorded point are not more affected by the surrounding noise.

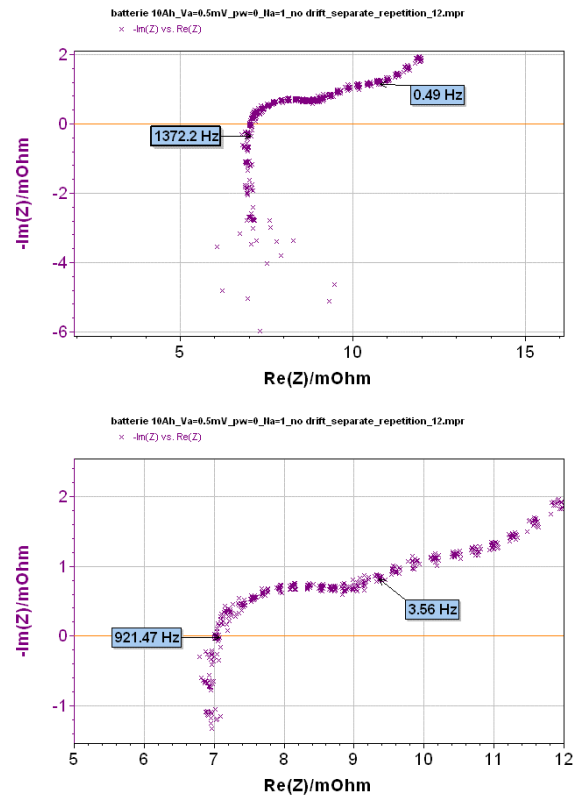


Fig. 11: Repetition of EIS diagrams obtained with the following experimental conditions: $V_a = 0.5$ mV, $p_w = 0$, $N_a = 1$ and no drift correction. Top: complete diagram, bottom: enlargement.

II-3-d Drift correction

Drift correction tool is specially dedicated to systems with very long relaxation time. Indeed non-steadiness of systems can induce a slight deviation on the obtained impedance graphs compared with theoretical one. This tool is extensively explained in reference [3].

III-Conclusion

To obtain optimized EIS results, cautions have to be considered. Indeed each parameter not well defined can have a huge influence on the final result as shown within this application note.

So before to do a measurement, experimental conditions have to be defined with care in agreement with the studied system and with the used software. A good compromise between significant results and acceptable experiment time has to be found.

This note gives an example on measurement done on Li-ion batteries;

nevertheless same precautions can be used with other systems.

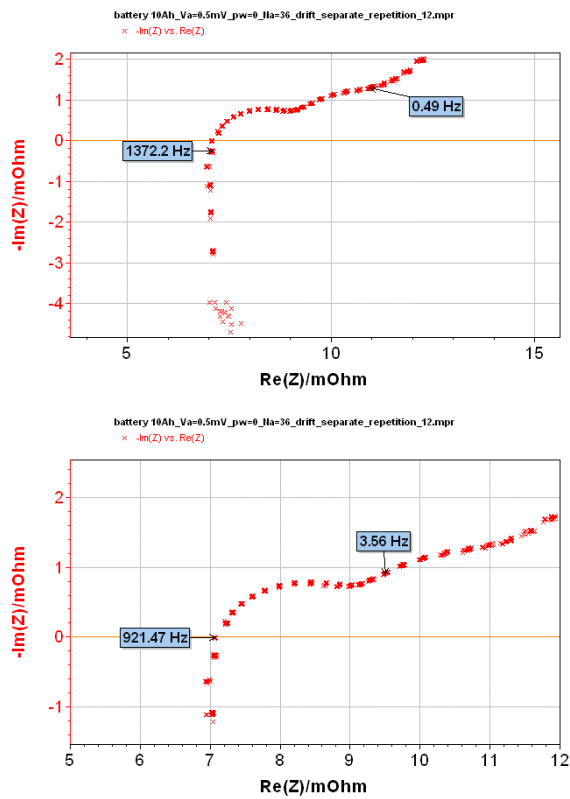


Fig. 12: Repetition of EIS diagrams obtained with the following experimental conditions: $V_a = 0.5 \text{ mV}$, $p_w = 0$, $N_a = 36$ and no drift correction. Top: complete diagram, bottom: enlargement.

References:

- [1] Application Note #5 (<http://www.biologic.info/potentiostat/notes>)
- [2] Application Note #9 (<http://www.biologic.info/potentiostat/notes>)
- [3] Application Note #17 (<http://www.biologic.info/potentiostat/notes>)