

Ohmic Drop

Part III: Suitable use of the ZIR techniques

I – INTRODUCTION

As shown in Application note #28 [1], EIS measurements are a good way to determine the electrolyte resistance R_{Ω} (or R_u for uncompensated resistance [2]). R_{Ω} is defined as the solution resistance between the working electrode and the reference electrode plus any resistances in the working electrode itself, wires, etc. [2, 3].

ZFit tool of EC-Lab® or EC-Lab® Express software allows the user to calculate this R_{Ω} value. Nevertheless ZFit tool implies that the equivalent electrical circuit is known, which is sometimes not obvious.

The aim of this note is to present the IR determination and compensation by impedance measurement technique (ZIR) and then how to determine R_{Ω} value without using the ZFit tool. A part of this note will be dedicated to enlighten the limits of this technique for some systems.

II – ZIR TECHNIQUES

The IR determination and compensation by impedance measurement technique (ZIR) is very close to the PEIS technique. Nevertheless, the EIS measurement is only done for one frequency f_{ZIR} . Then it is possible to write the following relationship:

$$R_{\Omega} \approx \text{Re } Z(f_{ZIR}) \quad (1)$$

With this technique, the resistance of the solution can be determined doing only one EIS measurement at high frequency, by default 100 kHz as shown in Figure 1 [4].

ZIR technique is available in EC-Lab® software, whereas potentiostatic and galvanostatic techniques – respectively GZIR and PZIR –

based on the same principle are available in EC-Lab® Express software.

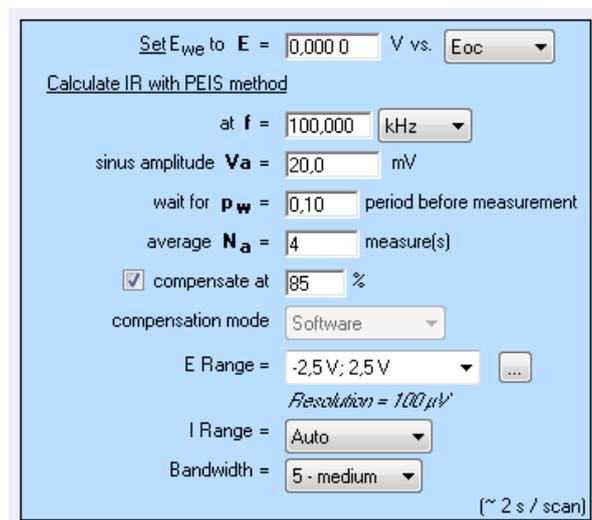


Figure 1: “Parameters Settings” window of ZIR experiment.

III – HIGH FREQUENCY EQUIVALENT CIRCUIT OF AN ELECTROCHEMICAL IMPEDANCE

III - 1 EQUIVALENT CIRCUIT OF AN ELECTROCHEMICAL IMPEDANCE

The equivalent circuit of an electrochemical impedance is given in Figure 2.

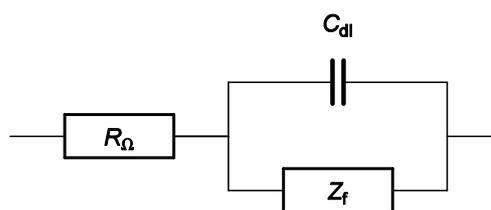


Figure 2: Equivalent circuit of an electrochemical impedance. C_{dl} is the double layer capacitance.

The equivalent circuit of the faradaic impedance Z_f depends on the electrochemical reaction involved.

As an example, the equivalent circuit of a redox reaction is shown in Figure 3 [5].

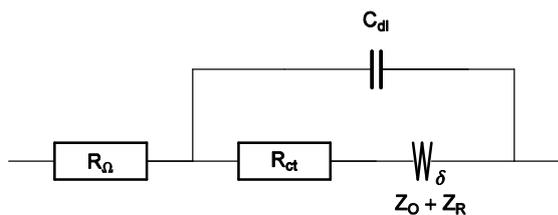


Figure 3: Equivalent circuit of a redox reaction.

III - 2 HIGH FREQUENCY EQUIVALENT CIRCUIT OF AN ELECTROCHEMICAL FARADAIC IMPEDANCE

Let us consider the high frequency equivalent circuit of an electrochemical reaction shown in Figure 4. Z_f is given by:

$$Z_f = R_\Omega + \frac{R_{ct}}{1 + R_{ct} C_{dl} i 2\pi f} \quad (2)$$

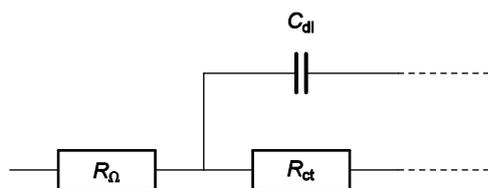


Figure 4: High frequency part of equivalent circuit shown in Figure 2.

The real part of Z_f is given by

$$\text{Re } Z_f = R_\Omega + \frac{R_{ct}}{1 + 4\pi^2 f^2 (R_{ct} C_{dl})^2} \quad (3)$$

with $\lim_{f \rightarrow \infty} \text{Re } Z_f = R_\Omega$.

Therefore, the real part of the impedance Z_f tends towards R_Ω as frequency tends towards infinite as shown in Figure 5.

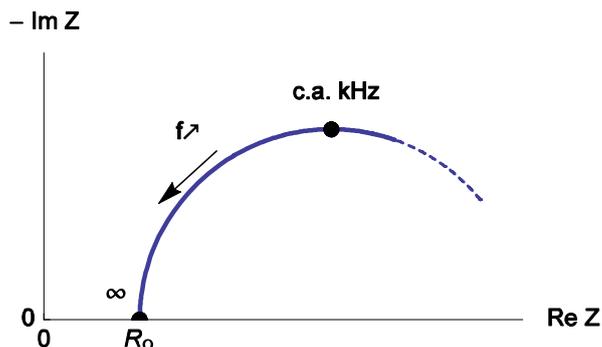


Figure 5: High frequency Nyquist diagram of the equivalent circuit of an electrochemical impedance.

IV – R_Ω MEASUREMENT IN THE SIMPLEST CASE

Real part of Z_f changes with frequency according to Eq. (3). Then the measurement relative error $\epsilon(f)$ can be defined as follow:

$$\epsilon(f) = \frac{\text{Re } Z_f - R_\Omega}{R_\Omega} = \frac{R_{ct}}{R_\Omega} \frac{1}{1 + 4\pi^2 \tau^2 f^2} \quad (4)$$

Changes of the measurement relative error with various values of ratio R_{ct} / R_Ω are given in Figure 6.

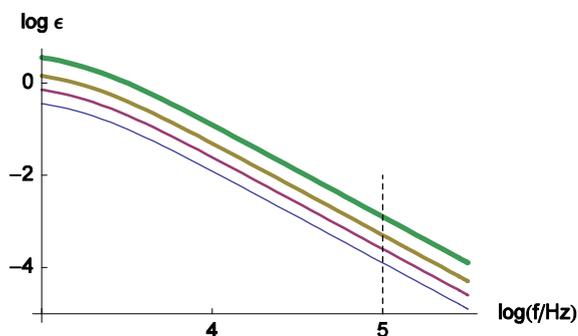


Figure 6: Change of the measurement relative error of R_Ω with frequency plotted for $R_{ct} / R_\Omega = 0.5, 1, 2, 5$ and $\tau = R_{ct} C_{dl} = 10^{-4}$ s. The line thickness increases with increasing R_{ct} / R_Ω ratio values.

Generally, characteristic frequencies for the high frequency loop are around kHz. The frequency value used by default for the ZIR techniques is 100 kHz. In the previous figure, we can see that the relative error at 100 kHz is small and can be neglected; in this case the R_Ω measurement is correct.

V – R_{Ω} MEASUREMENT WITH AN INDUCTANCE IN SERIES

V - 1 INDUCTANCE IN SERIES

An inductive behavior can be observed at high frequencies for some electrochemical systems – batteries for example. Equivalent electrical circuit for this kind of systems is given in Figure 7. The inductive part could be related to the connection or to the inductive behavior of the battery's container.

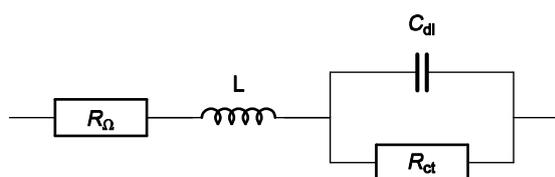


Figure 7: High frequency equivalent circuit of a faradaic impedance considering an inductance in series.

Impedance of the circuit given Figure 7 can be written as follows:

$$Z_f = R_{\Omega} + L i 2\pi f + \frac{R_{ct}}{1 + R_{ct} C_{dl} i 2\pi f} \quad (5)$$

Depending of L value, the shape of the impedance diagrams can change. Figure 8 gives an example of the various shapes of impedance diagrams that can be observed with an inductance in series. Curves displayed in Figure 8 can be reproduced with ZSim (EC-Lab® software).

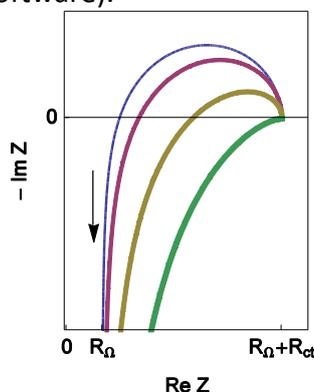


Figure 8: Nyquist impedance diagrams for the $R+L+(R/C)$ circuit (Figure 7, (Eq. 3)). $R_{\Omega} = 0.2 \Omega$; $R_{ct} = 1 \Omega$; $C_{dl} = 10^{-4} F$, $L = 10^{-5}$; 2×10^{-5} , 5×10^{-5} , $10^{-4} H$. The line thickness increases with increasing L values.

Fortunately, the real part of the impedance is unchanged comparing to the previous example (R_{Ω} measurement in the simplest case) even with the add of the inductance L (Eq. (5)). Then the real part of Z_f for the $R+L+(R/C)$ circuit is still given by Eq. (3). Moreover the relative error curves on R are independent of the inductance (L) value. Then values displayed on the **Error! Reference source not found.** are the same than those given in Figure 6.

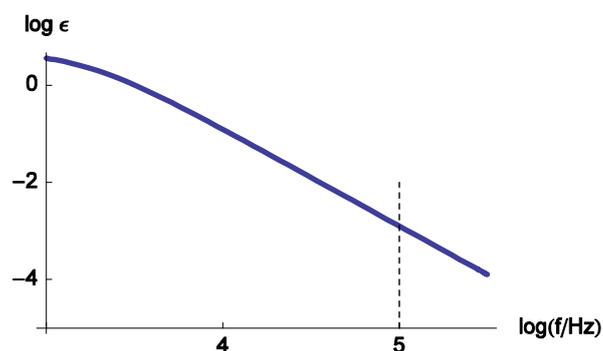


Figure 9: Change of the measurement relative error of R_{Ω} with frequency. The parameters values are the same that the ones given in Figure 8.

V - 2 (R/L) CIRCUIT IN SERIES

The high frequency behavior can be the one of an inductance in series but sometimes the behavior is the one of a (R/L) circuit in series (Fig. 10). Impedance of this circuit is given by

$$Z_f = R_{\Omega} + \frac{LR i 2\pi f}{R + L i 2\pi f} + \frac{R_{ct}}{1 + R_{ct} C_{dl} i 2\pi f} \quad (6)$$

Real part of Z_f (Eq. 4) is given by

$$\text{Re } Z_f = \frac{R_{ct}}{4\pi^2 f^2 C_{dl}^2 R_{ct}^2 + 1} + \frac{4\pi^2 f^2 L^2 R}{4\pi^2 f^2 L^2 + R^2} + R_{\Omega} \quad (7)$$

This value depends of L and R .

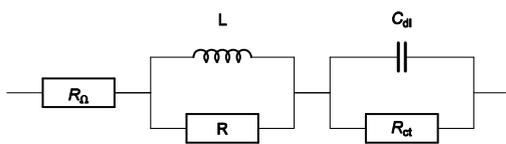


Fig. 10: High frequency equivalent circuit of a faradaic impedance taking account of a (R/L) circuit in series.

Figure 11 shows Nyquist impedance diagrams obtained for the system $R+(R/L)+(R/C)$. Note that different shapes for the Nyquist impedance diagrams can be obtained [5]. These kinds of Nyquist diagrams could be obtained with some batteries. An example of lead acid battery Nyquist diagrams can be found in the reference [6] or in Figure 12 for a LiFePO_4 battery.

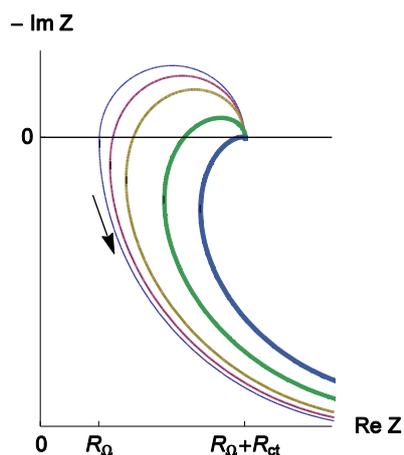


Figure 11: Nyquist impedance diagrams for the $R+(R/L)+(R/C)$ circuit (Fig. 11, (Eq. 4)). $R_\Omega = 0.2 \Omega$; $R_{ct} = 0.5 \Omega$, $R = 2 \Omega$; $C_{dl} = 10^{-4} \text{ F}$, $L = 10^{-7}, 2 \times 10^{-6}; 5 \times 10^{-6}, 1.3 \times 10^{-5}; 2.3 \times 10^{-5} \text{ (H)}$. The line thickness increases with increasing L . Dots: minima of the real part of the impedance.

As previously, it is possible for the reader to obtain the curves displayed on Figure 11 with ZSim tool (EC-Lab® software) or with the equivalent circuit library of the Bio-Logic website [5].

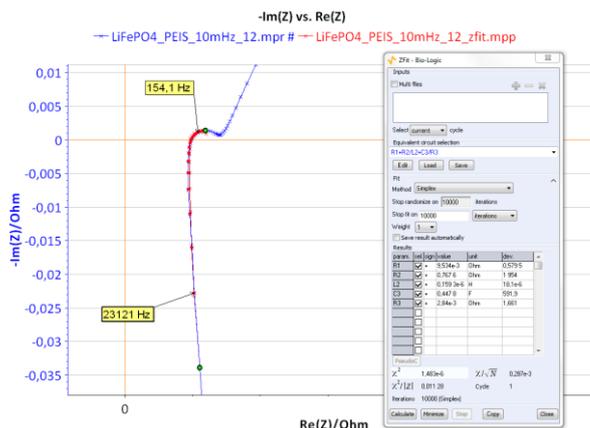


Figure 12: Nyquist diagram and ZFit analysis obtained on LiFePO_4 batteries.

Changes of the relative error measurement on R_Ω are presented in Figure 13. This relative error doesn't decrease monotonously when the frequency increases. In this case, the minimum of the relative error is obtained for the frequency corresponding to the impedance real part minimum, *i.e.* frequencies enlightened by dots on the Figure 11.

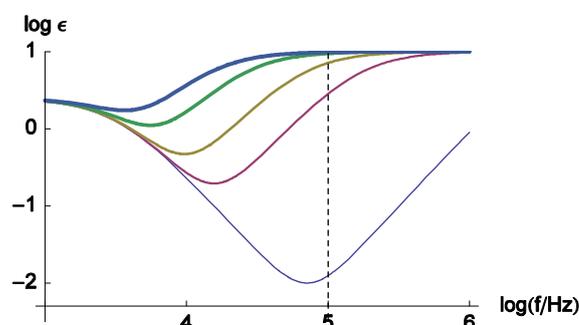


Figure 13: Change of the relative error measurement of R_Ω with frequency. The parameters values are the same than those used in Figure 11. Dots: minima of the measurement relative error of R_Ω .

VI – CONCLUSION

ZIR techniques allow the user to determine R_Ω without using ZFit. These ZIR techniques can be used systematically if the studied system doesn't present an inductive behavior. Nevertheless if the system contains an inductor L , some precautions have to be taken before to run a ZIR experiment. In this case, to

determine a reasonable frequency for the ZIR techniques, a preliminary impedance experiment and an analysis with ZFit - choosing the electrical circuit given in Fig. 10 - must be done.

This note was mainly dedicated to the determination of R_{Ω} value, nevertheless ZIR techniques are also dedicated to compensate the ohmic drop. For this, one of the ZIR techniques has to be located before the other techniques.

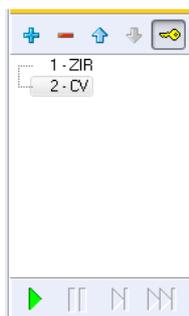


Figure 14: Ohmic drop compensation in linked experiments.

Data files can be found in :
C:\Users\xxx\Documents\EC-
Lab\Data\Samples\EIS\
LiFePO4_PEIS_10mHz_12

REFERENCES

- 1) [Application Note #28](#) "Ohmic Drop, Part II : Introduction to Ohmic Drop measurement techniques"
- 2) A. J. Bard, L. R. Faulkner, *Electrochemical methods. Fundamentals and applications*, Wiley, Hoboken, (2001).
- 3) [Application Note #27](#) "Ohmic Drop, Part I : Effect on measurements"
- 4) Techniques and Applications Manual
- 5) [Handbook of EIS](#)
- 6) Huet, F., Nogueira, R. P., Torcheux, L., and Lailier, *J. Power Sources*, 113 (2003), 414.

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