

## 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  $R_{\Omega}$  (or  $R_u$  for uncompensated resistance [2]).  $R_{\Omega}$  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<sup>®</sup> or EC-Lab<sup>®</sup> Express software allows the user to calculate this  $R_{\Omega}$  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  $R_{\Omega}$  value without using the ZFit tool. A part of this note will be dedicated to enlighten the limits of this technique for some systems.

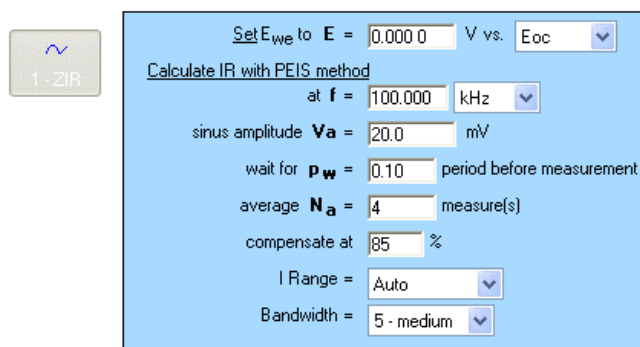
#### II-ZIR technique

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:

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

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 Fig. 1 [4].

ZIR technique is available in EC-Lab<sup>®</sup> software, whereas potentiostatic and galvanostatic techniques – respectively GZIR and PZIR – based on the same principle are available in EC-Lab<sup>®</sup> Express software.



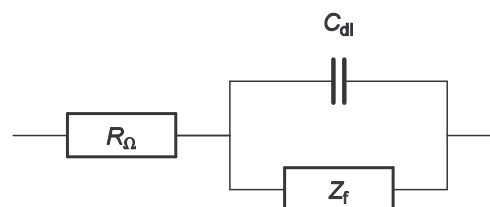
(~ 164  $\mu$ s / scan)

**Fig. 1: “Parameters Settings” window of ZIR experiment.**

#### III-High frequency equivalent circuit of an electrochemical impedance

##### III-1-Equivalent circuit of an electrochemical impedance

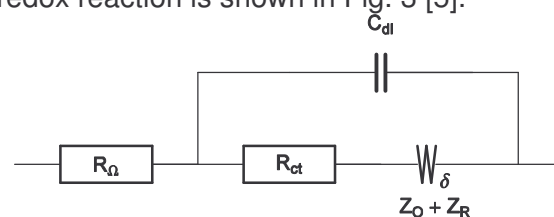
The equivalent circuit of an electrochemical impedance is given in Fig. 2.



**Fig. 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 Fig. 3 [5].



**Fig. 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 Fig. 4.  $Z_f$  is given by:

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

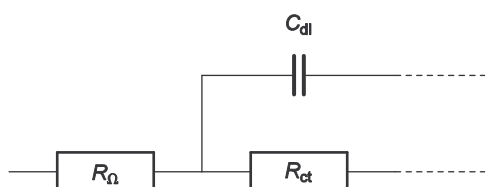


Fig. 4: High frequency part of equivalent circuit shown in Fig. 2.

The real part of  $Z_f$  is given by

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

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

Therefore, the real part of the impedance  $Z_f$  tends towards  $R_\Omega$  as frequency tends towards infinite as shown in Fig. 5.

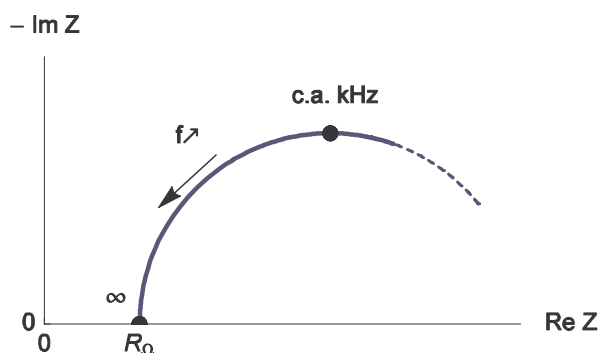


Fig. 5: High frequency Nyquist diagram of the equivalent circuit of an electrochemical impedance.

### IV- $R_\Omega$ measurement in the simplest case

Real part of  $Z_f$  changes with frequency according to Eq. (2). Then the measurement relative error  $\epsilon(f)$  can be defined as follow:

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

Changes of the measurement relative error with various values of ratio  $R_{ct} / R_\Omega$  are given in Fig. 6.

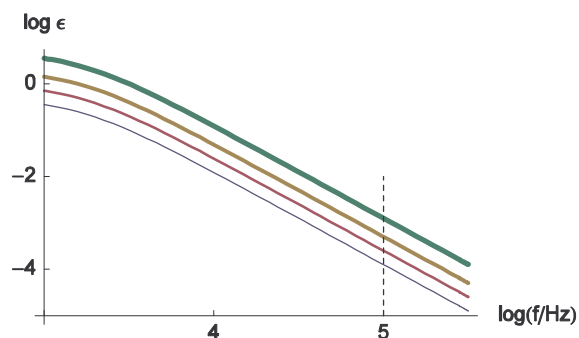


Fig. 6: Change of the measurement relative error of  $R_\Omega$  with frequency plotted for  $R_{ct} / R_\Omega = 0.5, 1, 2, 5$  and  $\tau = R_{ct} C_{dl} = 10^{-4}$  s. The line thickness increases with increasing  $R_{ct} / R_\Omega$  ratio values.

Generally, characteristics 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  $R_\Omega$  measurement is correct.

### V- $R_\Omega$ 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 Fig. 7. The inductive part could be related to the connection or to the inductive behavior of the battery's container.

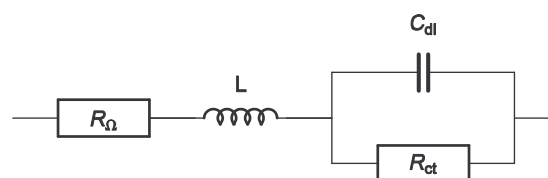
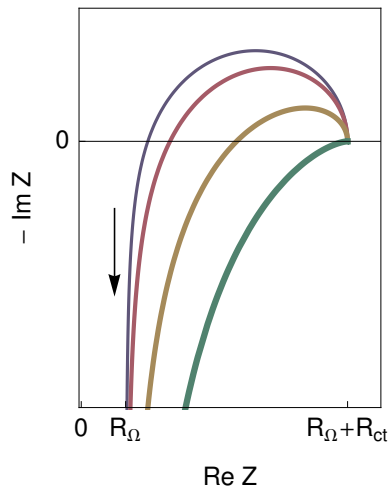


Fig. 7: High frequency equivalent circuit of a faradaic impedance considering an inductance in series.

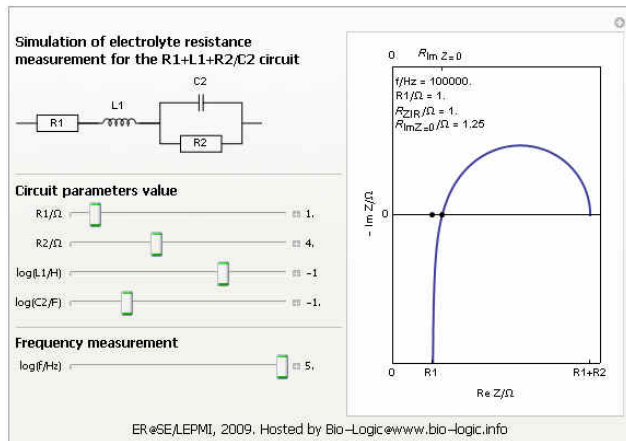
Impedance of the circuit given Fig. 7 can be written as follows:

$$Z_f = R_\Omega + L i 2\pi f + \frac{R_{ct}}{1 + R_{ct} C_{dl} i 2\pi f} \quad (3)$$

Depending of  $L$  value, the shape of the impedance diagrams can change. Fig. 8 gives an example of the various shapes of impedance diagrams that can be observed with an inductance in series. Curves displayed in Fig. 8 can be reproduced with ZSim (EC-Lab<sup>®</sup> software) or with the Equivalent Circuit Library available on the Bio-Logic website (Fig. 9) [5].



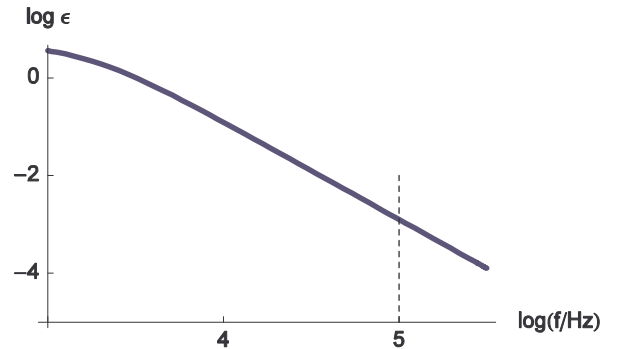
**Fig. 8: Nyquist impedance diagrams for the  $R+L+(R/C)$  circuit (Fig. 7, (Eq. 3)).  $R_{\Omega} = 0.2 \Omega$ ;  $R_{ct} = 1 \Omega$ ;  $C_{dl} = 10^{-4} F$ ,  $L = 10^{-5}$ ;  $2 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $10^{-4} H$ . The line thickness increases with increasing  $L$  values.**



**Fig. 9: Equivalent Circuit Library available on the Bio-Logic website [5].**

Fortunately, the real part of the impedance is unchanged comparing to the previous example ( $R_{\Omega}$  measurement in the simplest case) even with the add of the inductance  $L$  (eq(3)). Then the real part of  $Z_f$  for the  $R+L+(R/C)$  circuit is still given by Eq. (2). Moreover the relative error curves on  $R$  are independent of the inductance ( $L$ ) value. Then

values displayed on the Fig. 10 are the same than those given in Fig. 6.



**Fig. 10: Change of the measurement relative error of  $R_{\Omega}$  with frequency. The parameters values are the same that the ones given in Fig. 8.**

### V-2-(R/L) circuit in series

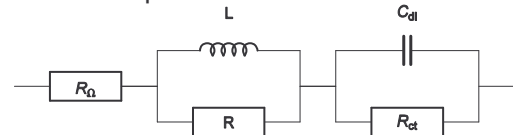
The high frequency behavior can be the one of an inductance in series but sometimes the behavior is the one of a (R/L) circuit in series (Fig. 11). Impedance of this circuit is given by

$$Z_f = R_{\Omega} + \frac{LRi2\pi f}{R + Li2\pi f} + \frac{R_{ct}}{1 + R_{ct} C_{dl} i 2\pi f} \quad (4)$$

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

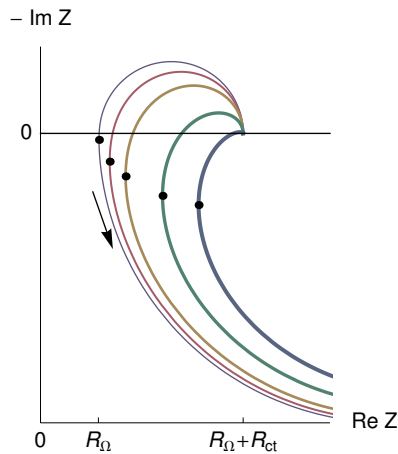
$$Re Z_f = \frac{R_{ct}}{4\pi^2 f^2 C_{dl}^2 R_{ct}^2 + 1} + \frac{4\pi^2 f^2 L^2 R}{4\pi^2 f^2 L^2 + R^2} + R_{\Omega}$$

This value depends of  $L$  and  $R$ .



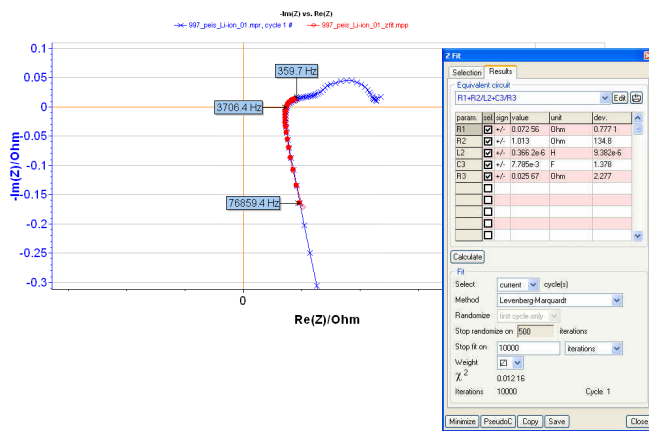
**Fig. 11: High frequency equivalent circuit of a faradaic impedance taking account of a (R/L) circuit in series.**

Fig. 12 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 Fig. 13 for a Li-ion battery.



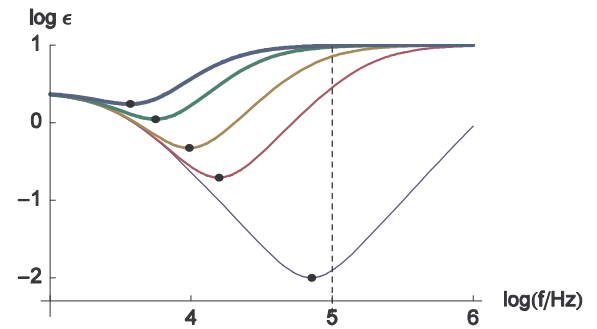
**Fig. 12: Nyquist impedance diagrams for the R+(R/L)+(R/C) circuit (Fig. 11, (Eq. 4)).  $R_{\Omega} = 0.2 \Omega$ ;  $R_{ct} = 0.5 \Omega$ ,  $R = 2 \Omega$ ;  $C_{dl} = 10^{-4} F$ ,  $L = 10^{-7}$ ,  $2 \times 10^{-6}$ ;  $5 \times 10^{-6}$ ,  $1.3 \times 10^{-5}$ ;  $2.3 \times 10^{-5}$  (H). The 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 Fig. 12 with ZSim tool (EC-Lab® software) or with the equivalent circuit library of the Bio-Logic website [5].



**Fig. 13: Nyquist diagram and ZFit analysis obtained on Li-ion batteries.**

Changes of the relative error measurement on  $R_{\Omega}$  are presented in Fig. 14. 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 Fig. 12.



**Fig. 14: Change of the relative error measurement of  $R_{\Omega}$  with frequency. The parameters values are the same than those used in Fig. 12. Dots: minima of the measurement relative error of  $R_{\Omega}$ .**

## VI-Conclusion

ZIR techniques allow the user to determine  $R_{\Omega}$  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. 11 - must be done.

This note was mainly dedicated to the determination of  $R_{\Omega}$  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.



**Fig. 15: Ohmic drop compensation in linked experiments.**

## References:

- [1] Bio-Logic Application Note #28 (<http://www.bio-logic.info>)
- [2] Electrochemical methods. Fundamentals and applications, A. J. Bard, L. R. Faulkner, ed. Wiley (Hoboken), 2001
- [3] Bio-Logic Application Note #27 (<http://www.bio-logic.info>)
- [4] Techniques and Applications Manual
- [5] Handbook of EIS (<http://www.bio-logic.info/potentiostat/notes.html#heis>)
- [6] Huet, F., Nogueira, R. P., Torcheux, L., and Lailier, P. Simultaneous real-time measurements of potential and high-frequency resistance of a lab cell. *J. Power Sources* 113 (2003), 414–421.