How to measure the internal resistance of a battery using EIS?

I – INTRODUCTION
A battery is the association in series of a positive electrode, a separator (used here as a generic term, which includes the electrolyte) and a negative electrode. The impedance of a battery writes:

\[ Z = Z_+ + Z_- + R_Ω \]  

(1)

where \( Z_+ \) and \( Z_- \) are the impedance of the positive electrode and the negative electrode, respectively, and \( R_Ω \) is the sum of the resistance of the separator, the current collectors and the connections. It depends on the ionic conductivity of the electrolyte contained in the separator and on the electronic conductivity of the current collectors.

During discharge, the positive electrode works as a cathode and the negative electrode as an anode. During charge, the positive electrode works as an anode and the negative electrode as a cathode.

During battery discharge, charge and ageing, the composition of the electrodes and the electrolyte can change and lead to a change of \( R_Ω \). The formation or dissolution of resistive layers, parasitic reactions or the degradation of the various battery elements can also lead to a change of \( R_Ω \), which we will refer to as internal resistance of the battery.

The aim of this note is to present different methods to measure the internal resistance using impedance measurements. It will also be explained that performing impedance measurements at several frequencies and fitting the impedance graph will reduce the incercntainty in internal resistance measurement.

II – MANY WAYS TO MEASURE \( R_Ω \)
Several methods are proposed in the literature to measure the internal resistance. A dozen of methods are described in [1]. Temporal and frequential methods have been compared in EC-Lab® application notes 27, 28 and 38 [2, 3, 4]. The two most common methods are presented below.

II - 1 CURRENT INTERRUPT
The principle of the current interrupt method, or potential-decay method, is that an ohmic contribution appears when an electrical contact is established and a non-zero current is flowing. The reverse phenomenon happens when the electrical contact is switched off: the ohmic contribution disappears almost instantaneously. In EC-Lab® the sampling rate is 200 µs, which limits the temporal methods. This limitation does not apply in EIS because under-sampling is used to measure frequencies that are over the sampling rate allowed by the instrument.

II - 2 EIS
Measuring the internal resistance by EIS is quite an old method. We can for example mention the measurement of the separator resistance of a battery [5] or the internal resistance of lead-acid batteries [6] or NiCd batteries [7] (Fig. 1). The measurement details are not always given. Some patents describe batteries with a very small internal resistance or show a charge-discharge control device using the rate of change of internal resistance as an indicator [8, 9].
III - HIGH FREQUENCIES (HF) BEHAVIOUR OF THE IMPEDANCE OF A BATTERY

The principles of impedance measurements for batteries and their analysis are presented in the White Paper named “Studying batteries with Electrochemical Impedance Spectroscopy (EIS)”. Low frequency data interpretation is given in the application note “How to interpret lower frequencies impedance in batteries?” [10].

The behaviour of a battery separator or an electrolyte is, a priori, only resistive. It is only at very high frequencies that the dielectric behaviour of ionic conductors is visible [11].

An example of an impedance graph of a Li-ion battery is shown in Fig. 2. The HF limit is not resistive but is characteristic of an inductive behaviour related to the battery size, the battery connectors and the power leads. In this case, how can we measure the internal resistance? One obvious method is to choose a particular data point.

III - 1 SINGLE POINT DETERMINATION
Several methods of internal resistance using one impedance measurement point are used to approximate the measurement of $R_0$ (Fig. 3).

![Figure 1: Top: Change in internal resistance of a 6 V, 2.6 Ah lead-acid battery with SoC. Impedance measured at OCV. Figures taken from [6]. Bottom: internal resistance change vs. State of Charge (SoC) for a Mazda Ni-Cd type NCR6, 0.65 Ah battery through a 30 Ω constant load. Figure taken from [7].](image1.png)

![Figure 2: Example of an impedance diagram of Li-ion battery. HF High Frequencies, MF Medium Frequencies, LF Low Frequencies.](image2.png)
**III - 2 Determination by Fitting an Impedance Graph Obtained at Several Frequencies**

In this part we will present the limitations of the single point measurement, why it cannot lead to an accurate determination of the internal resistance and why the only way to get an accurate value of the internal resistance is to perform an impedance measurement at various frequencies and perform fitting of all or part of the data. This can be performed using EC-Lab® fitting tool ZFit.

An important step in the fitting process is the choice of the equivalent circuit. It can be useful to simulate impedance graphs to qualitatively validate the possible shapes of the impedance graphs of equivalent circuits (Fig. 4). Such a simulation can be performed using ZSim available in EC-Lab®.

**a. Accounting for the battery changes**

For single point measurements, the choice of the frequency is crucial. It is never certain that a correct frequency at a given state of charge or state of health will still be correct during battery operation and/or ageing.

This is the major problem when choosing a single frequency point or a single value to determine the internal resistance.
b. Accounting for the HF inductive behaviour

The influence of an inductance in series on the impedance graphs of batteries has been studied at least since 1987 [16] (Fig. 4(1)), but the HF behaviour of batteries does not always correspond to that of an inductor as is shown by the impedance graph in Fig. 2. The impedance element:

$$Z_{La} = L_a(i\omega)^\alpha$$

(2)

is available in ZFit [17]. Its impedance graph is a half-line making an $\alpha\pi/2$ angle with the real axis as recalled in Fig. 4(2).

The first two cases in 4 lead to an impedance graph, whose HF limit asymptotically tends to a half-line. The HF graph is not a line anymore in the case (3) of Fig. 4, which is closer to the behaviour shown in Fig. 2. Using Z Fit or interactive files [18, 19] allows the user to simulate curves shown in Fig. 4.

The visual comparison of impedance graphs shown in Fig. 4 and in Fig. 2 lead to choose circuits $R_1+L_2/R_2$ and $R_1+L_2/R_2+Q_3/R_3+Q_4/R_4+Q_5$ to account for the HF part of the diagram and the entire graph, respectively. Fitting results are shown in Fig. 5.

Figure 4: Change of impedance graphs of circuits $R_1+L_2+R_3/Q_3$ (1), $R_1+L_a+Q_3/R_3$ (2) et $R_1+L_2/R_2+Q_3/R_3$ (3) for various $L_1$ values. The thickness of the lines increases with $L_1$ and $L_a$ values. The black dot corresponds to $R_1$.

The value of $R_1$ obtained by fitting is shown in Fig. 5. Its value is lower than the values determined using a single point measurement or a single point on the impedance graph (Tab. I). For this system, the maximum difference can reach 4.26%. It could be much bigger for other systems.
Figure 5: HF inset of the impedance graph of Fig. 2. Line: fitting result. Comparison of the various internal resistances obtained by single point measurement methods and by fit.

Table I: Internal resistance value depending on the measurement method. \( R_{\text{fit}} = 0.0916 \Omega \).

<table>
<thead>
<tr>
<th>( R )</th>
<th>( R_{\text{mes}}/\Omega )</th>
<th>( R_{\text{mes}} - R_{\text{fit}}/% )</th>
<th>( R_{\Omega,\phi=0} )</th>
<th>( R_{\Omega,\phi=0}/\Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{\Omega,\phi=0} )</td>
<td>0.0955</td>
<td>4.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(</td>
<td>Z</td>
<td>_{\text{min}} )</td>
<td>0.0938</td>
<td>2.40</td>
</tr>
<tr>
<td>( R_{\Omega,\text{min}} )</td>
<td>0.0933</td>
<td>1.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

IV – CONCLUSION

Several methods can be used to measure the internal resistance of a battery using its impedance graph. It can be chosen to perform a single frequency point measurement and use the value of the real part of the impedance.

It can be chosen to perform impedance at several frequencies and to graphically choose a point on the graph for example the minimal impedance modulus or the real part of the impedance at a zero phase. This can be erroneous for two reasons:

- as the battery changes the correct frequency at a given battery state can be erroneous at a different state
- choosing a point on the impedance graph neglects the presence of an inductive behaviour.

Only impedance graphs made at different frequencies and subsequent fitting can prevent the user from favouring a particular point on the graph, allow the user to account for the change of the battery during operation or ageing, and finally remove the effect of the inductance which can dramatically affect the resistive HF behaviour of a battery.

\[ |Z|_{\text{min}}/\Omega = 9.38 \times 10^{-2} \]

\[ R_{\Omega,\text{min}}/\Omega = 9.33 \times 10^{-2} \]

\[ R_{\Omega,\phi=0}/\Omega = 9.55 \times 10^{-2} \]

\[ R_{1}/\Omega = 9.16 \times 10^{-2} \]

Data files can be found in:
C:\Users\xxx\Documents\EC-Lab\Data\Samples\Battery\ AN62_EIS_Fig_2

REFERENCES

2) Application note #27 “Ohmic drop. I-Effect on measurements.”
3) Application note #28 “Ohmic drop. II-Introduction to Ohmic Drop measurement techniques.”
4) Application note #38. Dynamic resistance de-termination. A relation between AC and DC measurements?
10) Application note #61 “How to interpret lower frequencies impedance in batteries?”
17) Application note #42 “ZFit : The modified inductance element La.”
18) Interactive equivalent circuit library: R1+L1+R1/C1 circuit.
19) Interactive equivalent circuit library: R1+L2/R2+R3/C31 circuit.

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