Autolab Application Note EC13

The importance of using four-terminal sensing for EIS measurements on low-impedance systems

Keywords

Low-impedance, four-terminal sensing, Kelvin sensing, batteries, fuel cells, Metrohm Autolab, electrochemical impedance spectroscopy, EIS, Nyquist plot.

Introduction

In this application note, electrochemical impedance spectroscopy (EIS) is used to test a commercial battery connected in two different ways. The differences in the impedance values are analyzed and discussed.

When low-impedance devices under test (DUTs) are investigated, certain best practices should be implemented. First, the leads sensing the potential difference should be separated from the leads carrying the current. Secondly, the potential leads should be connected as close as possible to the DUT; possibly avoiding extra wires, since they contribute to the overall impedance, and the effect is non negligible with low-impedance DUTs.

In the first EIS measurement, the battery is connected in a two-terminal sensing configuration. The RE and CE leads are joined together (short circuited) and connected to the negative terminal (black wire) of the battery. The WE and S leads are also joined together and connected to the positive terminal (red wire of the battery), Figure 1-A. In the second EIS measurement, the battery is connected in a four-terminal sensing (Kelvin sensing) configuration. The CE lead is connected to the negative terminal, the WE lead to the positive terminal, the RE lead to the junction between the negative terminal and the battery, and the S lead to the junction between the positive terminal and the battery

(Figure 1-B).

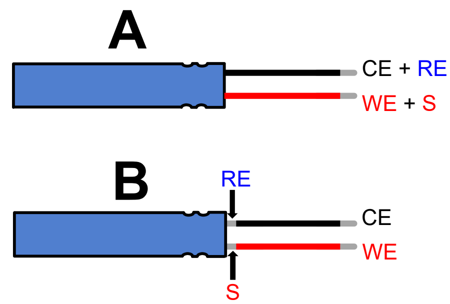

Figure 1 – Illustration of the two-terminal (A) and the four-terminal (B) sensing configurations.

The difference in how the leads are connected results in different measured impedance values for the battery. In order to explain this discrepancy, recall that the RE and S leads measure the potential difference $V_{RE\text{-}S}$, while the CE and WE leads carry the current $i_{CE\text{-}WE}$ necessary to overcome the potential drop V_{drop} across the cell.

The current value $i_{CE\text{-}WE}$ is the same in both measurements since the CE and WE leads are connected in the same way. The V_{drop} is also the same across the cell; V_{drop} is calculated as follows:

$$V_{drop} = i_{CE-WE} \cdot Z_{tot} = i_{CE-WE} \cdot (Z_{bat} + Z_{wires}) \qquad 1$$

The total impedance of the cell, Z_{tot}, is the sum of the battery impedance, Z_{bat}, and the impedance of the wires, Z_{wires}.

However, the potential difference $V_{RE\text{-}S}$ that is measured in the two-terminal sensing configuration (Figure 1-A) is not the same as the $V_{RE\text{-}S}$ measured in the four-terminal sensing configuration (Figure 1-B).

In the case of Figure 1-A, the RE and S measure a potential difference $V_{RE\text{-}S,\,A}$, given by the product of $i_{CE\text{-}WE}$ and the sum of Z_{bat} and Z_{wires}. Therefore, $V_{RE\text{-}S,\,A}$, coincides with the V_{drop} calculated from Equation 1

$$V_{RE-S,A} = V_{drop} = i_{CE-WE} \cdot (Z_{bat} + Z_{wires}) \qquad 2$$

In the case of Figure 1-B, the RE and S measure a potential difference given by the product of $i_{CE\text{-}WE}$ and Z_{bat}.

$$V_{RE-S,B} = i_{CE-WE} \cdot Z_{bat} \qquad 3$$

Consequently, EIS carried out on a DUT connected in a two-terminal sensing configuration is expected to result in the measurement of higher impedance values than EIS performed on a DUT connected in a four-terminal sensing configuration. The difference is given by Z_{wires}.

Experimental Setup

For the EIS measurements, a Metrohm Autolab PGSTAT204 equipped with a FRA32M module is used (Figure 2).

Figure 2 – The Metrohm Autolab PGSTAT204, equipped with the FRA32M module.

The battery used for the experiments is a rechargeable Li-ion, Ansmann 18650, with 2600 mAh of nominal capacity and a nominal voltage of 3.7 V.

EIS potentiostatic measurements are performed at open circuit potential (OCP), between 1 kHz and 100 mHz, 10 mV amplitude, with a rate of 10 frequencies per decade.

Results and Discussion

In Figure 3, the Nyquist plots corresponding to EIS measurements on the battery with four-terminal (black dots) and two-terminal (red dots) sensing configurations are shown.

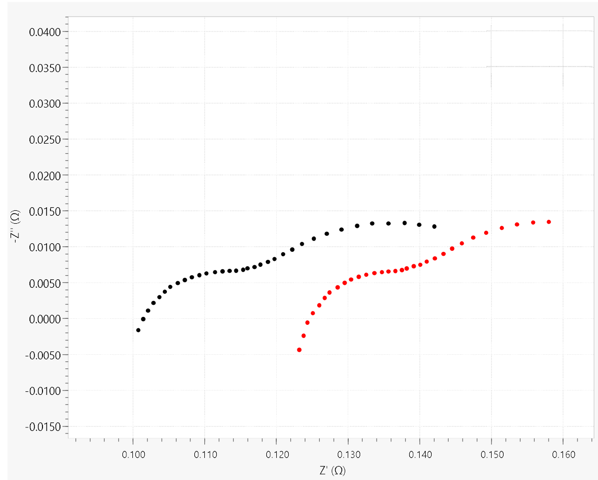

Figure 3 - Nyquist plots from EIS measurements performed on the Li-ion battery with four-terminal (black dots) and two-terminal (red dots) sensing configurations.

The Nyquist plot corresponding to the four-terminal sensing configuration is shifted towards lower impedance values, with respect to the Nyquist plot resulting from the two-terminal sensing configuration. The amount of the shift is related to the impedance of the wires in the two-terminal sensing configuration.

To estimate the amount of the shift, the impedance values where $-Z'' = 0$ i.e., where the impedance has only a resistive contribution, are calculated. The difference between the two values gives the resistive contribution of the wires to the overall impedance.

The Interpolate command present in the NOVA software allows such calculations to be performed easily, Figure 4.

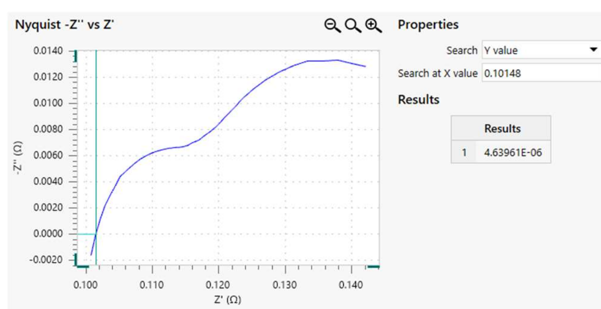

Figure 4 - The Interpolate command on the Nyquist plot related to the four-terminal sensing EIS measurement.

The results are shown in Table 1.

Table 1 - Values of the resistive contribution to the overall impedance for the two configurations.

Connections	R (mΩ)
Two-terminal sensing	124
Four-terminal sensing	101

The difference between the resistance values gives the resistive contribution of the wires in the two-terminal sensing experiment, i.e., R_{wires} = 23 mΩ.

In addition, the red plot shows a more pronounced tail towards negative values of the imaginary part of the impedance, $-Z''$ at high frequencies. This high-frequency feature is usually caused by the inductance of the wires. A deeper explanation of the results is beyond the scope of this application note.

Finally, it is worth noting that the use of the four-terminal sensing configuration is important only when low-impedance DUTs are under investigation, since the contribution of the wires to the overall impedance is low.

Conclusions

A commercial battery is used for EIS measurements in two sensing configurations. The importance of a four-terminal sensing configuration for low-impedance DUTs is examined. The contribution of the wires to the overall impedance measured in the two-terminal sensing measurement is determined and explained.

Date

05 January 2017