

Application Note AN-BAT-013

Simultaneous EIS measurements of a Li-ion battery cathode and anode

Second Sense (S2) for concurrent measurements at both electrodes in battery research applications

In battery research, electrochemical impedance spectroscopy (EIS) is a necessary tool to investigate the processes occurring at the electrodes. With a common three-electrode battery, EIS can be performed sequentially first at one electrode and then at the other electrode.

However, thanks to the Second Sense (S2) functionality available in VIONIC powered by INTELLO, EIS can be performed simultaneously on both electrodes.

In this Application Note, EIS is performed simultaneously at the cathode and anode of a Li-ion battery. This study provides a measurement example for researchers who need to investigate the electrochemical processes occurring simultaneously on the poles of a battery.

INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is one of the most important technical tools for battery characterization. One limitation of analyzing two-electrode EIS data is that it can often be difficult to deconvolute impedance components that have similar time constants. Half-cell measurements can be used to study the impedance associated with the two electrodes separately, but may not reflect the processes occurring in the full cell at different states of charge and discharge [1].

If a reference electrode is introduced that does not interfere with the cell cycling, the impedance of the cathode and anode relative to the reference electrode can be measured after charging and discharging the cell as usual.

With VIONIC powered by INTELLO, the current is measured at the cathode (working electrode). The potential between the cathode and reference electrodes is also measured by connecting the S1 lead to the cathode and the RE lead to the reference electrode. Also, the potential between the anode and the reference electrode can be measured by connecting the S2 lead to the anode of the battery.

In this way, the electrochemical impedance data of the cathode (positive) and anode (negative) can be measured simultaneously.

EXPERIMENTAL SETUP

A battery pouch cell equipped with an internal reference electrode was used. The experiment consisted of a potentiostatic EIS measurement at a DC potential set to the open circuit potential (OCP), from 100 kHz to 100 mHz, 10 frequencies per decade, and 30 mV amplitude top.

The OCP was 3.71 V vs. reference.

The experiment was performed with VIONIC powered by INTELLO, while the data analysis was performed with NOVA 2.

RESULTS AND DISCUSSION

In Figure 1, the Nyquist plot of EIS measurement performed simultaneously on the cathode (blue) and anode (orange) is shown.

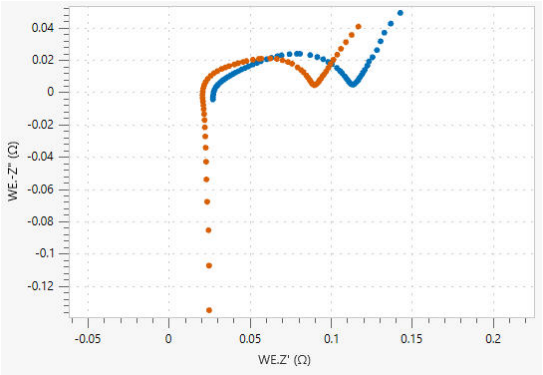

Figure 1. Nyquist plot of cathode (in blue) and anode (in orange).

Here, it is noticeable how the overall impedance of the cathode is higher than the impedance of the anode.

Similar information is gathered from the Bode modulus plot (Figure 2) and Bode phase plot (Figure 3) of the cathode and anode.

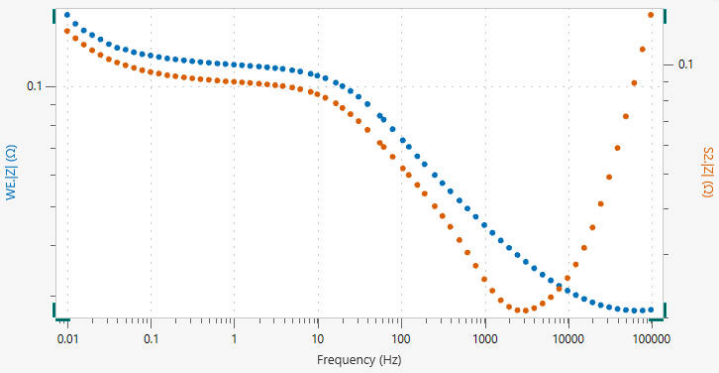

Figure 2. Bode modulus plot of cathode (in blue) and anode (in orange).

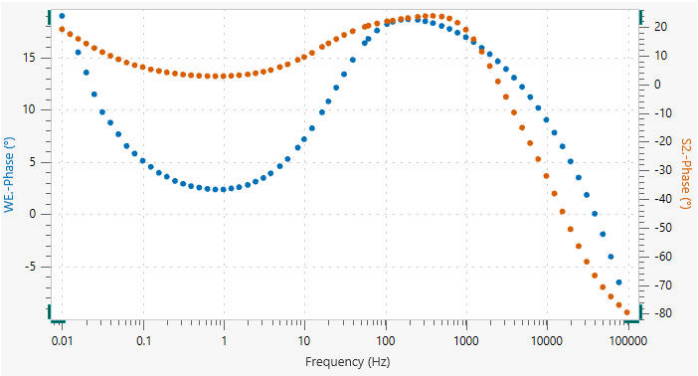

Figure 3. Bode phase plot of cathode (in blue) and anode (in orange).

The data was exported to NOVA 2 for further analysis. Since the composition of the electrodes was not available, a generic equivalent circuit was used for the fit. The same equivalent circuit was used for both the cathode and the anode [2].

The fit results are shown as values of the equivalent circuit elements together with the equivalent circuit for the cathode (Figure 4) and the anode (Figure 5).

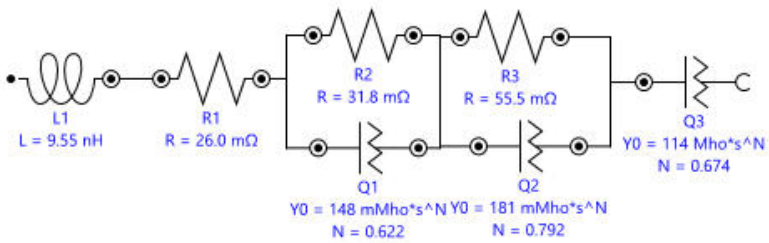

Figure 4. Equivalent circuit used to fit the data of cathode, with the fit results per electrical element.

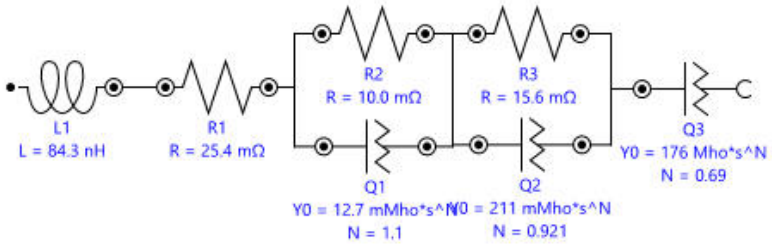

Figure 5. Equivalent circuit used to fit the data of anode, with the fit results per electrical element.

The fitting of the EIS data measured from the cathode resulted in a χ^2 value of 0.0010057, and a χ^2 value of 0.029497 for the anode.

The fit results should be taken only as an example since the electrodes' composition and the electrolyte chemistry were not fully known and/or available which is fundamental to build an accurate equivalent circuit for the electrode interfaces.

CONCLUSION

The EIS data of both the anode and cathode of a three-electrode battery can be obtained in a single measurement by individually sensing the potential between the cathode and reference electrode, and between the anode and the reference electrode.

BIBLIOGRAPHY

1. Anthony R. West; Laurence A.Middlemiss; Anthony J.R. Rennie; Ruth Sayers. Characterisation of Batteries by Electrochemical Impedance Spectroscopy. *Energy Rep.* 2020, *6* (5), 232–241.
2. Wen Liu; Yong Wang; Yong Li; Rui Guo; Haijuan Pei; Ying Luo; Jingying Xie. Lithium/Sodium Storage Behavior of an Amorphous Carbon Derived from the Used Acticarbon for Rechargeable Batteries. *J. Electrochem. Soc.* 2019, *166*, A1585.

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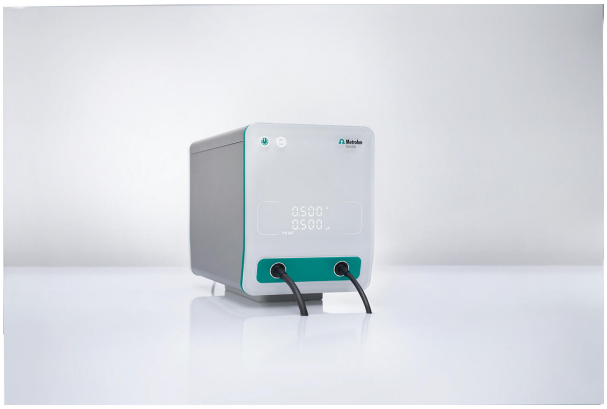
CONFIGURATION



VIONIC

VIONIC is our new-generation potentiostat/galvanostat that is powered by Autolab's new INTELLO software.

VIONIC offers the **most versatile combined specifications of any single instrument** currently on the market.

- Compliance voltage: ± 50 V
- Standard current ± 6 A
- EIS frequency: up to 10 MHz
- Sampling interval: down to 1 µs

Also included in VIONIC's price are features that would usually carry an additional cost with most other instruments such as:

- Electrochemical Impedance Spectroscopy (EIS)
- Selectable Floating
- Second Sense (S2)
- Analog Scan