

Application Note AN-BAT-016

采用INTELLO系统进行不同荷电状态下的电化学阻抗谱分析

Study the internal components of battery at a range of conditions with electrochemical impedance spectroscopy (EIS)

A battery's state of charge (SOC) represents the percentage of available charge relative to its full capacity, with 100% SOC indicating a fully charged state and 0% SOC a fully discharged one. The SOC is usually estimated by measuring the voltage of the battery, for example 4.2 V might indicate 100% SOC, and 3 V, 0%. Along with a number of other parameters, the internal resistance of a battery varies with SOC, making electrochemical impedance spectroscopy (EIS) a powerful tool for characterizing this relationship. By monitoring resistance across different SOC levels, EIS enables the optimization of material design as well as the tracking of battery aging mechanisms to enhance performance and longevity. This Application Note provides a detailed guide to performing EIS measurements at different states of charge with INTELLO. The fitting and analysis of EIS measurements was done within the fit and simulation tool of NOVA.

INTRODUCTION

EIS is a powerful nondestructive investigative tool for explaining a range of phenomena that can cause damage and premature aging of a battery. One of its key uses is estimating the state of health (SOH) of a battery, which aids in the prediction of the lifetime of that battery.

In **Figure 1**, the typical impedance response of a battery in the form of a Nyquist plot is displayed. The insert shows the equivalent circuit that describes such a response. The high-frequency region of the plot corresponds to the ohmic resistance and often contains an inductive component as well. The mid-frequency region of the plot usually contains at least two semi-circles. They often contain contributions from the two electrodes or processes occurring at the interfaces. There is a significant amount of detail in this region that is difficult to unravel as the semi-circles often overlap each other.

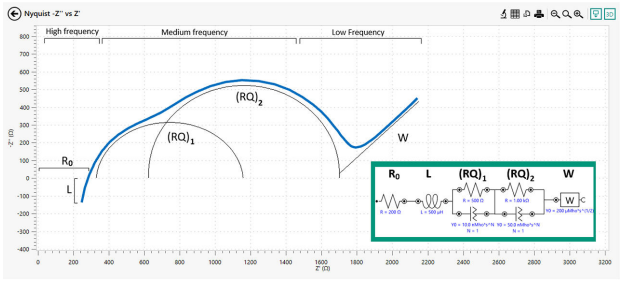


Figure 1. Typical Nyquist plot of a battery. The inset shows the corresponding equivalent circuit that describes the response.

In recent years, DRT (distribution of relaxation times) has become a more popular and convenient tool for deconvoluting the information in this region [1]. The low-frequency region mainly contains information about the diffusion of ions.

EIS is most regularly used diagnostically by measuring and examining the Nyquist and Bode plots at regular intervals during what's known as a calendar aging test. Changes in these plots can indicate a number of things. For example, depressions in the first semi-circle can indicate loss of anode material (i.e., graphite degradation) [2]. On the other hand, rising ohmic resistance can indicate growth of the SEI layer on the anode [3].

One of the drawbacks of EIS is that the data interpretation can be quite complex. It is also important to realize that the impedance of a battery changes with its SOC. This is another reason why it is useful to conduct EIS at a range of different SOC values to ensure that the right conclusions are made.

SAMPLE AND MEASUREMENT DETAILS

The sample in this Application Note was a Li-ion 2450-coin cell battery with a capacity of 120 mAh. The EIS was measured using the Autolab Duo Coin-cell holder which allows for 4-point contact with the battery. The Application Note AN-BAT-008 describes the benefits of the 4-point contact mode for measuring accurate EIS data on batteries [4].

In INTELLO, there is a default procedure which can be used for conducting EIS at different states of charge. There are several measurement parameters in the procedure that can be adjusted – it can also be modified further to suit the user needs (for example, to add break-in cycles). The measurement procedure is constructed from repeat loops, with each repeat consisting of a (dis)charge step or pulse, a rest step, and the actual EIS measurement. In this way, EIS can be measured with each step corresponding to a different SOC. Note that in this procedure the EIS measurement is configured for galvanostatic mode.

Besides the number of repeats, the main parameters relevant here are the C-rate, constant current (dis)charge duration per step, the (dis)charge potential limits, and the rest duration. The number of repeats should always be more than the expected number of steps to take the battery from the maximum SOC under study to the minimum, and vice versa. The number of steps this takes can be estimated from the capacity, the C-rate, and the (dis)charge duration. If the following parameters are set (capacity is 120 mAh, the (dis)charge C-rate is 1C, and the (dis)charge duration is 6 minutes), then we can calculate that 12 mAh of charge are added per step (120 mA × 0.1 h), or 10% of the battery per step.

It is important to also include charge and discharge potential limits. Once these are reached, the corresponding repeat loop will be exited. For example, once 4.2 V is reached, the charge loop will be exited and the discharge loop will begin. Then, when 2.8 V is reached, the discharge loop will be exited and the measurement finished. The rest duration is also important, as the EIS measurement should be conducted only once a new steady-state voltage is reached after the charge has been extracted or injected. The parameters of the EIS measurement itself can also be adjusted from the main parameters window. The amplitude and the frequency range are of utmost interest. The amplitude should be chosen well for the

RESULTS AND DISCUSSION

Note: In the case below, the procedure was adjusted such that the battery was fully charged by a pre-conditioning cycle before being discharged from 100% SOC in steps of 10% and then charged again in steps of 10%. The analysis and discussion will be focused on the discharge.

The Nyquist plot measured during the discharge steps is shown in **Figure 2**. The expected features from a battery are seen, including three semi-circles in the mid-frequency region. The situation where the SOC is estimated to be 100% is shown in purple, and where the SOC is expected to be around 10% is shown in orange, with the intermediate plots showing SOC from between these extremes.

It should be noted that Li-ion batteries are not supposed be discharged regularly to 0% SOC, as over time this can prematurely age the battery. Therefore, most specifications list a discharge cutoff voltage that corresponds to about 10% SOC rather than 0%.

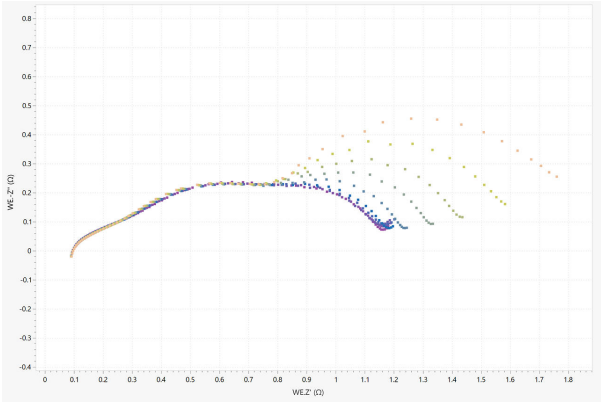


Figure 2. Nyquist plot during the discharge of a battery from 100% SOC (purple) to 10% SOC (orange).

The corresponding Bode plot is shown below in **Figure 3**. Both plots seem to indicate that only one of the RC time constants is primarily affected by the changing SOC, with the impedance rising as the battery discharges. Based on sources from the literature, it's likely that this lowest-frequency semi-circle corresponds to a slower charge transfer process at the cathode [6,7]. It is logical that the resistance of this process rises as a result of more lithium moving from the anode to be inserted into the cathode. There appears to be either no or very limited change in the contribution to the impedance from the other components in the battery as it is discharged. During the charge portion of the measurement, the opposite effect is seen, with the impedance decreasing as the battery is recharged. Eventually the original Nyquist/Bode plot that was measured at 100% SOC is recovered.

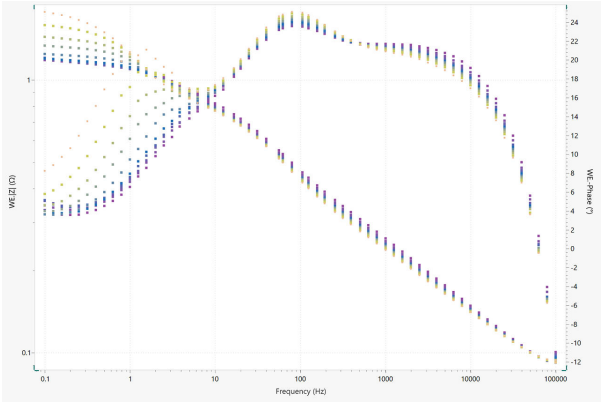


Figure 3. Bode plot during the discharge of a battery from 100% SOC (purple) to 10% SOC (orange).

The data above was transferred to and fitted in NOVA, using the equivalent circuit in **Figure 4**. To obtain a better fit, the non-ideal capacitance was modelled using constant phase elements (CPE). The CDC code for this equivalent circuit is [LR(RQ)(RQ)([RW]Q)], and consists of an inductor element, a series resistance element, and three RQ parallel circuits, with the last also containing a Warburg element in parallel [8].
In order to fit the data properly, here are some practical tips. The first is to start from realistic values for the RQ circuits. These were obtained by first doing an electrochemical circuit fit and then pasting the resulting values into the fit and simulation tool. For the inductor, the value was set to 100 nH. The serial resistance was set by reading from the Nyquist plot; in this case it was 60 mOhm. The next tip is to adjust the boundaries (minimum and maximum values) of the fitting to realistic values. For example, for the resistors the boundaries were set to 1 × 10^{-5} to 5 Ohm. It can also be helpful to fix all three RQ circuits and then release each one in turn. The process of fitting the data allows changes in the Nyquist plot to be made quantifiable.

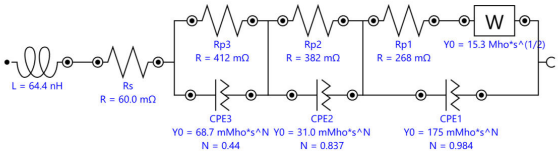


Figure 4. Equivalent circuit used in the fitting of the EIS data.

In **Figure 5**, the serial (ohmic) resistance as a function of the SOC is shown. The ohmic resistance isn't affected that much, only rising very slightly over the course of the measurement.

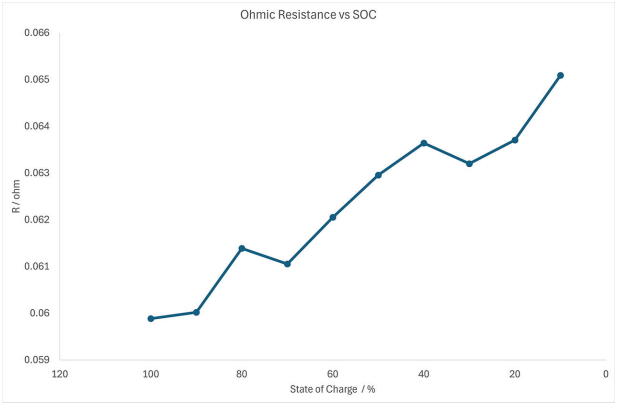


Figure 5. Ohmic (serial) resistance vs. the SOC of the battery.

In **Figure 6**, Y_0 (a term containing information on the capacitance) vs. SOC is shown. Only the Y_0 of CPE1 rises as the SOC decreases – the remaining two CPEs are unaffected.

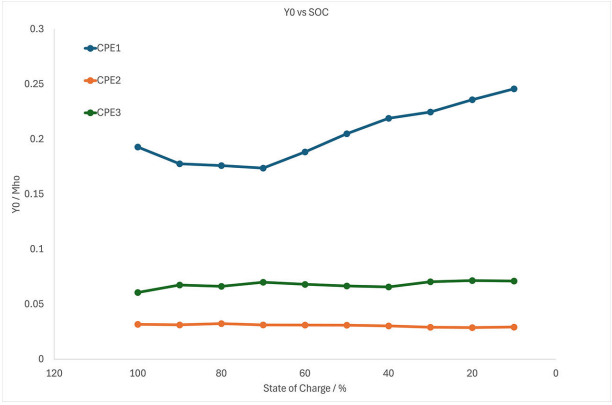


Figure 6 The values of the capacitance term from each of the three CPE elements used in the fitting vs. the SOC of the battery.

In **Figure 7**, the corresponding resistances from each RQ circuit are shown. Like **Figure 6**, R_p1 is the only resistance term to be strongly affected by the changing state of charge, also rising as the SOC decreases.

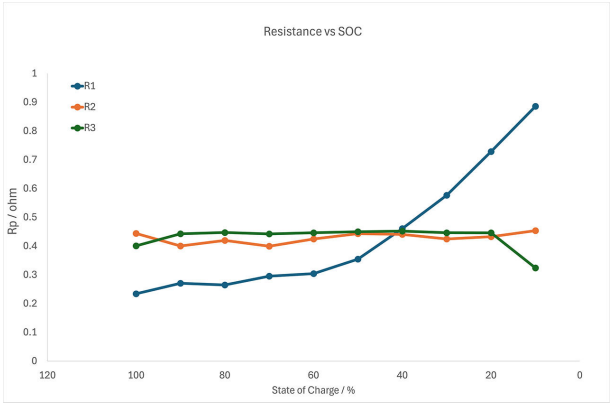


Figure 7. The resistance values from each of the three R elements used in the fitting are plotted vs. the SOC of the battery

The values from fitting the data measured at 100% and 10% SOC are summarized below in **Table 1**.

Table 1. Values from selected circuit elements obtained from fitting data at 100% and 10% SOC.

Element	100% SOC	10% SOC
R_s / Ohm	0.059	0.065
R_P1 / Ohm	0.23	0.89
Y_01 / Ohm^{-1}	0.19	0.24

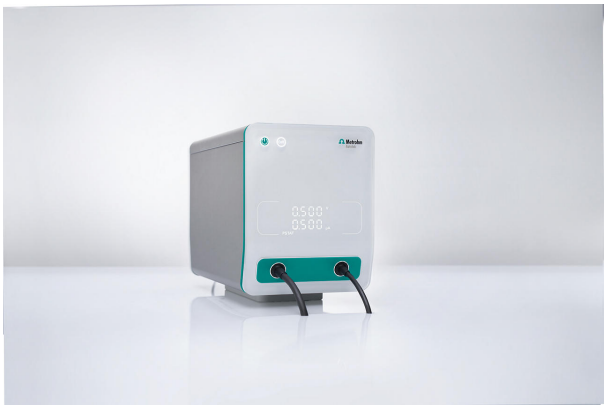
REFERENCES

1. Soni, R.; Robinson, J. B.; Shearing, P. R.; et al. Lithium-Sulfur Battery Diagnostics through Distribution of Relaxation Times Analysis. *Energy Storage Materials* **2022**, *51*, 97–107. DOI:10.1016/j.ensm.2022.06.016
2. Iurilli, P.; Brivio, C.; Wood, V. On the Use of Electrochemical Impedance Spectroscopy to Characterize and Model the Aging Phenomena of Lithium-Ion Batteries: A Critical Review. *Journal of Power Sources* **2021**, *505*, 229860. DOI:10.1016/j.jpowsour.2021.229860
3. Galeotti, M.; Cinà, L.; Giammanco, C.; et al. Performance Analysis and SOH (State of Health) Evaluation of Lithium Polymer Batteries through Electrochemical Impedance Spectroscopy. *Energy* **2015**, *89*, 678–686. DOI:10.1016/j.energy.2015.05.148
4. *Metrohm Autolab DuoCoin Cell Holder with EIS measurements on a commercial battery*. https://www.metrohm.com/en/applications/application-notes/autolab-applikationen-anautolab/an-bat-008.html (accessed 2025-06-17).
5. *High-frequency EIS: a powerful tool for the future of mobility*. https://www.metrohm.com/en/discover/blog/2024/hf-eis-for-ssbs.html (accessed 2025-06-17).
6. Schmidt, J. P.; Chrobak, T.; Ender, M.; et al. Studies on LiFePO4 as Cathode Material Using Impedance Spectroscopy. *Journal of Power Sources* **2011**, *196* (12), 5342–5348. DOI:10.1016/j.jpowsour.2010.09.121
7. Ovejas, V. J.; Cuadras, A. Impedance Characterization of an LCO-NMC/Graphite Cell: Ohmic Conduction, SEI Transport and Charge-Transfer Phenomenon. *Batteries* **2018**, *4* (3), 43. DOI:10.3390/batteries4030043
8. Orazem, M. E.; Ulgut, B. On the Proper Use of a Warburg Impedance. *J. Electrochem. Soc.* **2024**, *171* (4), 040526. DOI:10.1149/1945-7111/ad3b76

CONTACT

Metrohm Taiwan Ltd.
開封街二段 46 號 5 樓
108 台北市
info@metrohm.com.tw

CONFIGURATION



VIONIC

VIONIC 是我们的新一代恒电位仪/恒电流仪,由 Autolab 的新 INTELLO 软件提供动力。

相比目前市场上任何单一仪器,VIONIC 提供了**全面**的组合规格。

- 顺从电压:± 50 V
- 标准电流 ± 6 A
- EIS 频率:达 10 MHz
- 采样间隔:低至 1µs

VIONIC 的价格中通常还包括大多数其他仪器产生的额外费用,例如:

- 电化学阻抗谱 (EIS)
- 可选浮动配件
- 第二测量电极 (S2)
- 模拟扫描

NOVA 是设计为通过 USB 接口控制所有 Autolab 仪器的软件包。

由电化学家针对电化学而设计,集成了超过二十余年的用户体验和最新的 .NET 软件技术,NOVA 使您的 Autolab 恒电位仪/恒电流仪拥有更强性能和灵活性。

NOVA 提供了以下的独特功能:

- 功能强大且灵活的程序编辑器
- 重要实时数据一目了然
- 强大的数据分析和绘图工具
- 集成化控制外围仪器,诸如万通 LQH 液体处理设备

下载最新版本的 NOVA