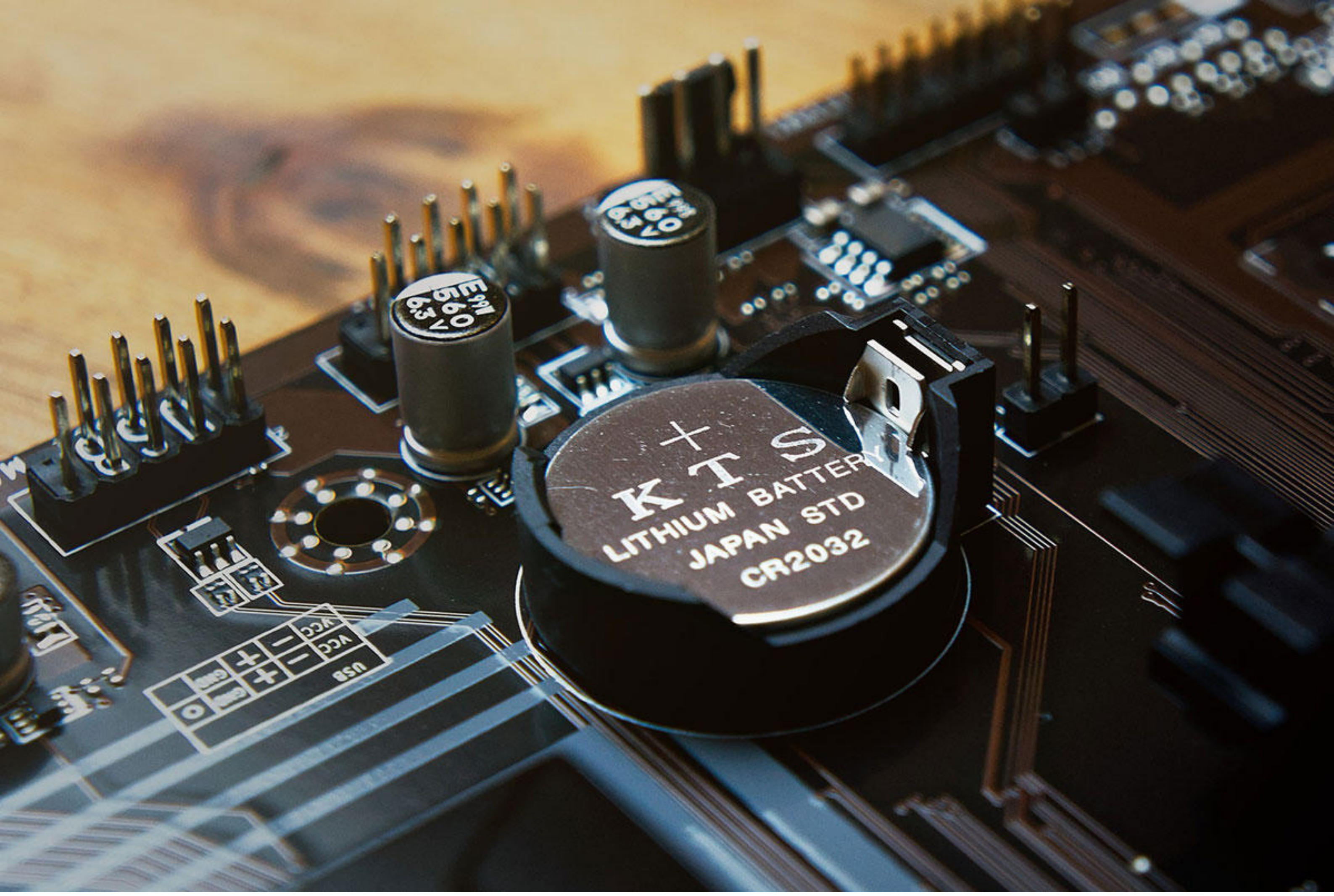

Application Note AN-BAT-014

Constant current constant voltage (CCCV) cycling with INTELLO

Intuitive battery analysis solutions from Metrohm Autolab

Charge/discharge cycling, or cycle testing, is perhaps one of the most fundamental techniques in battery research. This technique involves repeatedly charging and discharging a battery under controlled conditions in order to simulate real-world usage. From this, one can gather a wealth of data about the battery itself and the material inside.

Among the most important parameters are the actual (experimental) capacity, the coulombic efficiency, and the rate capability. Important insight into the underlying chemistry and potential failure mechanisms can also be obtained from analysis of the curves from cycle testing batteries.

This Application Note introduces the cycling tools which energy researchers can use in INTELLO, as well as the steps to obtain the recommended plots.

TERMINOLOGY AND ABBREVIATIONS

A number of terms and parameters are specific to battery research; the ones which are used in INTELLO are presented below. Where appropriate, the unit is also displayed in parentheses.

Voltage, E (V): Potential in volts that is applied to or measured from the battery or cell. The voltage should be positive when measured as the potential difference between the anode and the cathode.

Current, i (A): Current in amps that is applied to or measured from the battery or cell. The sign can be positive or negative depending on whether the battery is being charged or discharged.

Capacity (mAh or Ah): Theoretical or nominal capacity is the measure of electric charge which can be stored in or delivered by a fully charged battery. The *theoretical capacity* is calculated based on the type and amount of active material used, while the *nominal capacity* is the experimental capacity measured under certain conditions. In INTELLO, either theoretical or nominal capacity can be entered in the cell properties section of the main parameters window.

C-rate, ×C: This is another way to represent the (dis)charging current, but it is relative to the battery's theoretical or nominal capacity and (dis)charging time. 1C is the current required to (dis)charge a battery fully in one hour, whereas 2C is the current required to (dis)charge the battery in 30 minutes. For example, to charge a battery with a capacity of 2000 mAh at 1C, 2 A has to be applied. To charge the same battery at 2C, 4 A must be applied. At 0.5C, apply 1 A, and so on. In INTELLO it is also possible to set current limits in the form of the C-rate, as well as the charging/discharging current.

Cycle: Typically refers to one complete sequence of commands which charges and then discharges the battery at a specified C-rate. Usually, the sequence in a cycle is repeated for a fixed number of times or until a parameter reaches a certain value (e.g., the coulombic efficiency drops below 90%).

Charge Capacity, Q+ (Ah): The charge capacity (t × charge current) is measured at the end of every charge step in the cycle. When there are multiple charge steps in a cycle, the capacity is accumulated over all of them. It is also possible in INTELLO to normalize this value to the mass or surface area of active material in order to give the *specific capacity*.

Discharge Capacity, Q- (Ah): The discharge capacity (t × discharge current) is measured at the end of every discharge step in the cycle. When there are multiple discharge steps in a cycle, the capacity is accumulated over all of them. It is possible in INTELLO to normalize this value to the mass or surface area of the active material to give the *specific capacity*.

BUILDING A CYCLE

Within INTELLO, it is easy to build a charge/discharge procedure. The dedicated cycle command is essentially a «Repeat for n times» command, with the actual charge/discharge sequence being nested within. In the detailed view of the cycle command, only the number of times the sequence should be repeated needs definition, as well as any end conditions which are required. Currently, it is also possible to end the cycle early if the coulombic efficiency falls below a certain level, if the total duration of all cycles together exceeds a given (set) time, or if the cycle duration of one of the repetitions exceeds a set time.

Only certain commands are able to be nested within a cycle, and therefore make up the charge/discharge sequence. These are:

CC (Dis)Charge: A command which either charges or discharges the battery at a constant current.
CV (Dis)Charge: A command which will charge or discharge the battery at a constant voltage.
Rest: A command where the cell is switched off and the open circuit potential (OCP) is measured.
EIS (frequency scan or single frequency): A command which allows an EIS (electrochemical impedance spectroscopy) measurement to be done at any point in the sequence.

The simplest sequence which can be built consists of just two commands – a CC Charge and a CC Discharge (**Figure 1**). This procedure will cycle a battery for three times at a C-rate of 0.5 C. For a 2000 mAh battery, this means that the CC Charge command will apply +1 A and the CC Discharge command will apply -1 A. The C-rate is a critical parameter as some batteries are not designed to be charged/discharged at high C-rates and can be damaged by doing so. Often, multiple C-rates will be tested to identify the rate capability – the maximum C-rate a battery can handle without being damaged. Another important safety feature to note is the charge E and discharge E limits. This will prevent the battery from being overcharged or discharged too deeply, which can also damage the battery.

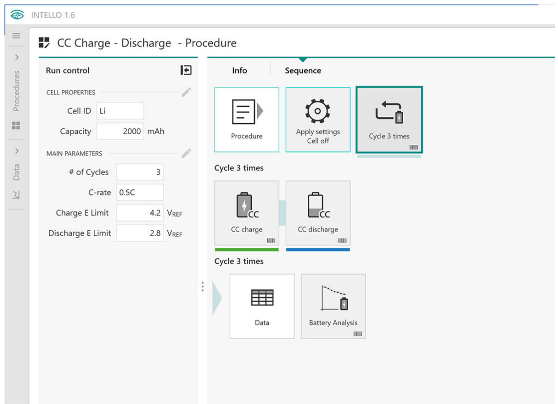

Figure 1. A simple CC Charge/Discharge procedure written in INTELLO 1.6.

One of the most common charging methods for commercial batteries is CCCV or constant current constant voltage charging. Following the constant current charging step above, the battery is switched to potentiostatic control, and a voltage (usually the end voltage limit of the CC step) is applied while the current drops. Once the current drops below a certain value or after a defined amount of time has passed, the charging sequence is considered complete, and the battery can be discharged.
CCCV charging is often the preferred method because it allows the battery to be fully charged while preventing an overcharge, providing a balance between safety and speed. It is easy to set up a CCCV charging sequence in INTELLO simply by placing a CV Charge command and setting the appropriate limits.

Figure 2 shows a cycling procedure where a CCCV Charge step has been implemented. In this example, the CV step will apply 4.2 V, and this is applied until either the current drops below 10 mA or the duration reaches 120 min. The parameters of the other steps remain the same.

It is easy to build even more complex sequences by combining commands, for example to pre-program a rest any time the charging or discharging is complete or to measure EIS at different states of charges (Note: these examples will be covered in another Application Note).

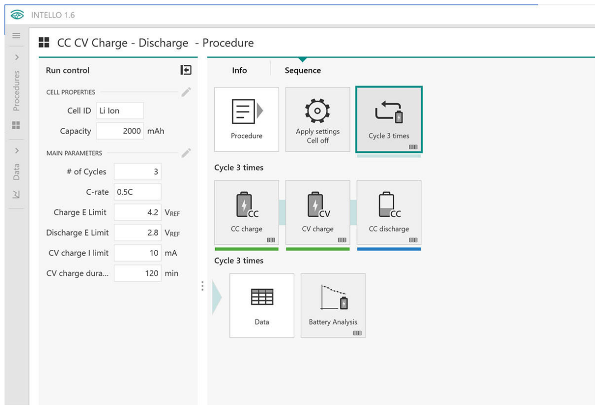

Figure 2. A simple CCCV Charge and CC Discharge procedure implemented in INTELLO 1.6.

RESULTS

Once the cycling test is completed, a number of plots are available to researchers hoping to learn more about the battery under study. The most important plots are suggested by INTELLO, but the user also has the option to add their own custom plots, depending on the sampled signals. Most often, the measured parameters are plotted as a function of either time, voltage, or cycle number.

Note: All plots presented hereafter were collected on a commercial LIR2450 coin cell battery with a 120 mAh capacity, using the Metrohm Autolab duo coin cell holder. The cell was charged using the CCCV method: first the cell was charged to 4.2 V at a rate of 1C and then the voltage was held at 4.2 V until the current dropped below 6 mA or until 30 min had passed. The cell was then rested for 30 min, discharged at a rate of 1C, and rested again for 30 min before the sequence was repeated.

Voltage/Current vs Time, E & i vs T. This is also known as the voltage and current profile of the cell/battery (Figure 3). This profile mainly shows how the voltage of the battery changes as the charge/discharge sequence is executed. It can provide more clarity about the dynamics of the charging/discharging process. For example, irregularities in the voltage are easily detectable in this plot. Irregularities could mean dips or unexpected plateaus which can indicate problems like electrolyte degradation.

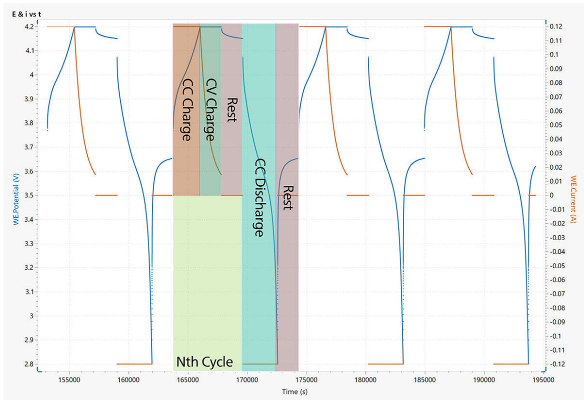

Figure 3. Example of an E & i vs T plot from the charging and discharging of a Li-ion coin cell battery. For clarity, a limited number of cycles are shown. One of the cycles is annotated to show the response from each section of the charge/discharge sequence.

Voltage vs (Dis)charge Capacity, E vs Q+/Q- is shown in Figure 4. These are also known as charge and discharge curves, and they also plot the voltage but now as a function of capacity instead of time. This alternative way of representing the same information is quite popular as it is easier to see more details about the electrochemical reaction.

The plateaus in this plot indicate phase changes within the active material. The slope of the curves can provide information about the kinetics of the reaction as well information about the resistive components in the battery. Other important uses include monitoring the health of the battery. As the cycle test continues, the capacity can begin to fade leading to curve shortening, which can give insights into potential failure mechanisms. The discharge capacity curve is shrinking, indicating that the capacity is fading in this case (Figure 4).

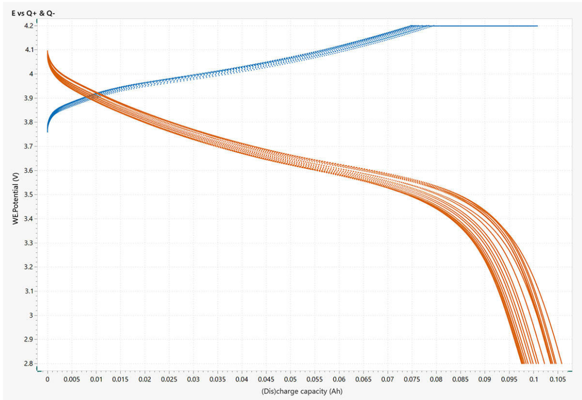

Figure 4. Example of an E vs Q+/Q- plot from the charging and discharging of a Li-ion coin cell battery.

Voltage vs Σ Capacity, E vs |Q|. In Figure 5, the voltage vs Σ Capacity plot is shown, which is a different way of representing the information in Figure 4. Changes in this plot can also give indications regarding possible failure mechanisms. Ideally, if no degradation occurs, each cycle should start at zero while a displacement to the right (positive) indicates a loss of capacity.

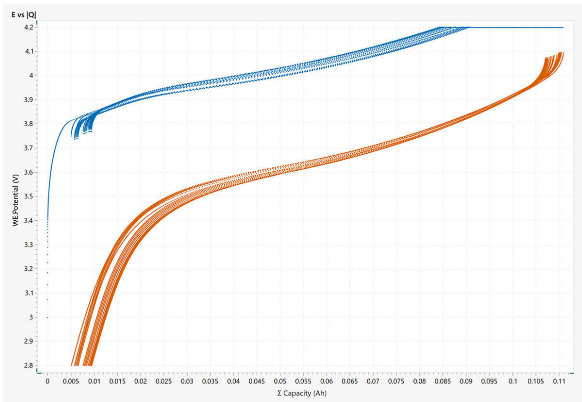

Figure 5. Example of an E vs |Q| plot from the charging and discharging of a Li-ion coin cell battery.

Capacity vs Cycle, Q+ & Q- vs Cycle. In **Figure 6**, a plot of the last measured Q+ and Q- per cycle is shown. This plot can sometimes be combined with the plot in **Figure 7** (CE vs cycle). Monitoring the capacity with respect to the cycle number gives researchers another way to check if the capacity is dropping as the cycling continues.

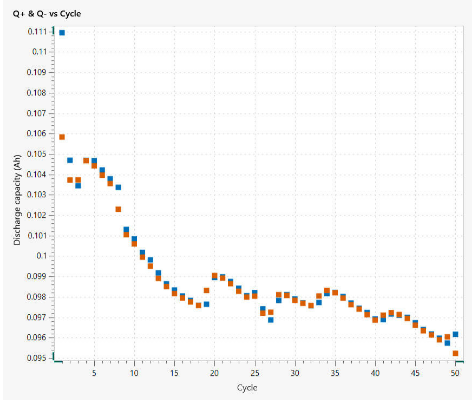

Figure 6. An example of a Q+/Q- vs cycle plot from the charging and discharging of a Li-ion coin cell battery.

Coulombic Efficiency, CE vs Cycle. A plot of the coulombic efficiency as a function of the cycle number is shown in **Figure 7**. This indicates how efficiently the electrons are being transferred during the charge-discharge process. Over time, this efficiency can fall due to side reactions or material degradation. Inefficiencies in the process might mean the battery has to be charged more frequently, further reducing its lifetime. In extreme cases, the inefficiency can lead to higher heat generation and safety concerns. In INTELLO, it is possible to end a cycling procedure once the CE falls below an acceptable value.

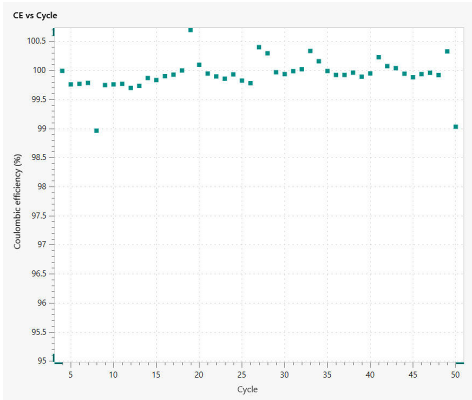

Figure 7. Example of a CE vs cycle plot, from the charge-discharge of a Li-ion coin cell battery.

Relative Capacity, RC vs Cycle. This is also known as the capacity retention plot (**Figure 8**). It is designed to monitor the relative capacity (i.e., the discharge capacity divided by the theoretical capacity) as a function of cycle number. Its main purpose is to check if the capacity of the battery is reducing over the cycles, and to therefore determine how many times a battery can be cycled before its capacity falls below an unacceptable level. In this case, the relative capacity is falling rather quickly (**Figure 8**), possibly indicating that the high C-rate is damaging this battery.

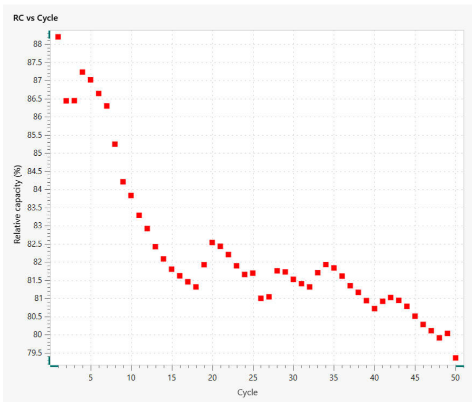

Figure 8. Example of the RC vs cycle plot from the cycling of a Li ion coin cell battery.

Other plots Besides the previously mentioned plots, it is also possible to plot, among others:

Differential Capacity vs Voltage (dQ/dE vs V): This is an important plot for inspecting the electrochemical processes within the battery. This plot and the corresponding analysis will be discussed in more detail in a separate Application Note.

Temperature vs time: It is possible to measure the temperature of the battery during the charge/discharge process. Temperature is an important parameter that must be considered in battery research.

CONCLUSIONS

Within the battery cycling environment of INTELLO, batteries of different geometries and sizes can undergo cycle testing. Cycling procedures can be made quickly and conveniently in INTELLO, and the plots needed to understand the battery chemistry and behavior can be produced and analyzed with ease.

CONTACT

Metrohm Brasil
Rua Minerva, 161
05007-030 São Paulo

metrohm@metrohm.com.br

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