Battery Cycling - 2

DC cycling script with EIS

(Complete battery stack characterization)

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SCIENTIFIC INSTRUMENTS

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1 Introduction

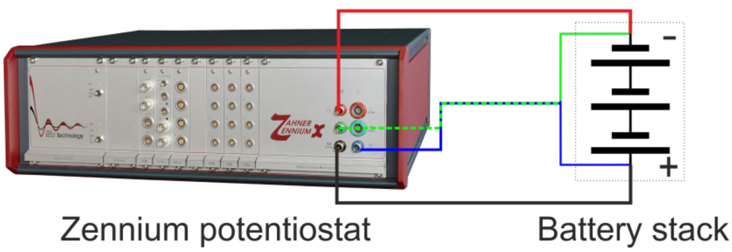
The battery cycling 2 software allows to combine DC cycling of a cell/battery with EIS measurements at different state of health (SOC) and state of charge (SOC). The EIS measurements can be recorded during the charging/discharging cycles and/or at the end of the charging/discharging cycles.

The battery cycling 2 program can also be used for segmented cells and cells with reference electrodes (with PAD4 card). A maximum run time of up to 1,000 hours is possible.

High capacitive system or high voltage batteries can be dangerous if not properly handled. The user is advised to read the Zahner's risk assessment document and take relevant precautions for the safety of the personnel and to avoid any property damage.

2 Experimental setup

The image on right shows a simple experimental setup, where the Zennium series potentiostat is connected with a cell stack.



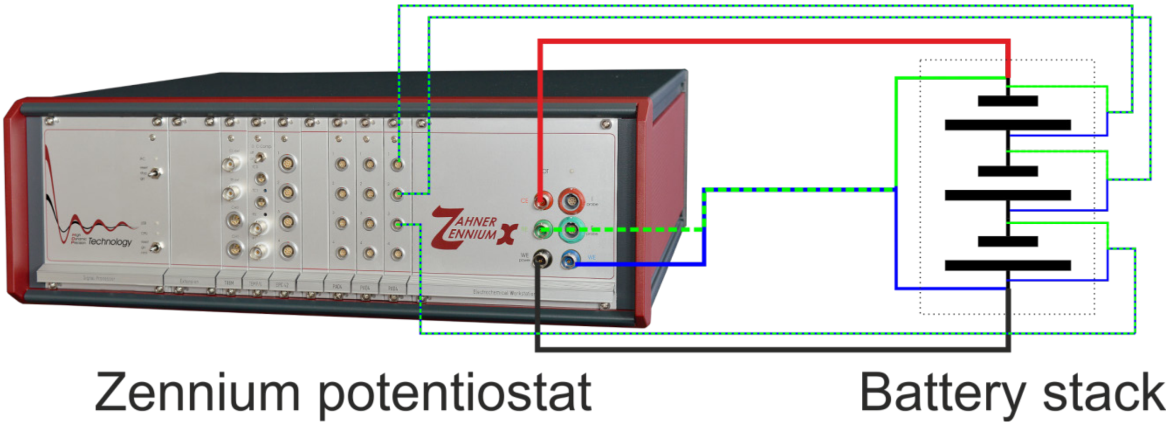
To mitigate the effect of induction in EIS measurements, please twist the voltage sense cables (blue and green) and the current-carrying cables (red and black). The twisting of the current-carrying cables is not shown in the image.

When starting up the Zennium series potentiostat, please allow up to 30 minutes of **warm-up time** for optimum accuracy in the measurements.

2.1 Zennium potentiostat with PAD4 cards

2.1.1 Hardware setup

For the characterization of the individual cells in a battery, PAD4 cards can be used in the Zennium series potentiostat. The PAD4 cards provide additional voltage channels which allow DC and EIS measurements on individual cells. The image on the next page illustrates an experimental setup of Zennium series potentiostat equipped with the PAD4 cards. The voltage of the total stack is measured with the Zennium series potentiostat and the individual cells are measured with the PAD4 channels.



Likewise, the PAD4 can be implemented in battery setups with reference electrode. One should take into account, that the PAD4 card has an entry impedance of 100 kΩ, hence the device under test (DUT) should not have an impedance value higher than 100 Ω for a voltage accuracy of 99.9%. Further information is provided in the application note: characterization of a 3-electrode cell.

The PAD4 card in combination with an external shunt can also be used in current mode (see PAD4 manual). This allows the current measurement on individual electrodes in a battery/cell stack. IM6e, IM6ex, Zennium, and Zennium-pro can measure up to 4 additional channels, IM6 and Zennium-X can measure up to 16 additional channels if equipped with PAD4 cards.

2.1.2 Software settings

For the DC measurements (charging/discharging routine) using the PAD4 cards, the PAD4 channels must be set up in the *Thales Signal Acquisition*.

For EIS measurements, the PAD4 channels must be activated in the “check cell connections” in the *EIS Test-Sampling* window. Once the PAD4 channels are properly set up for the DC and EIS measurements then the channels can be used in the battery cycling-2 software. Further information on setting up the PAD4 channels for DC and EIS measurements is provided in the PAD4 manual.

3 Battery cycling 2 software

To start the battery cycling 2 software, click on the EXE icon in the Thales software (classic mode) and then load the battcycling2.rtm file from the **c:\thales\examples\applications**. This starts the "Battery Cycling 2" software.

Alternatively, the battery cycling 2 software can also be started by clicking the *Z-icon* on the top left corner of the Thales software then click on *Optional Methods → Battery Cycling*.

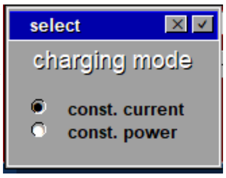
The basic idea of the battery cycling 2 software is to enable detailed investigation of batteries at various SOC and SOH with EIS. Therefore, the software distinguishes between four different states of the cycling procedure: the charging and discharging ramp and the reversing potential after the charge and discharge phases. It gives the possibility to measure at different SOC during the ramps and offers sophisticated options to reach steady-state conditions with various EIS options.

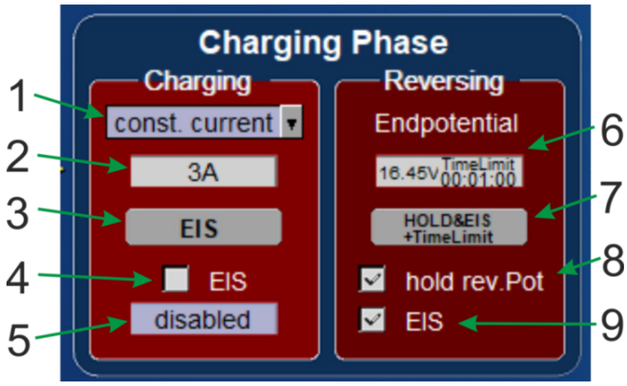
The different sections of the battery cycling 2 software are discussed below.

3.1 Charging phase

The charging phase includes

1. Charging at constant current or constant power.
2. Charging current (in *A*) or charging power (in *W*).
3. EIS settings (during the charging phase).
4. Enable "EIS" (during the charging phase).
5. EIS status (during the charging phase).
6. End potential or time limit.
7. Hold at reverse potential and EIS setting.
8. Enable "Hold reverse potential".
9. Enable "EIS" (at reverse potential).

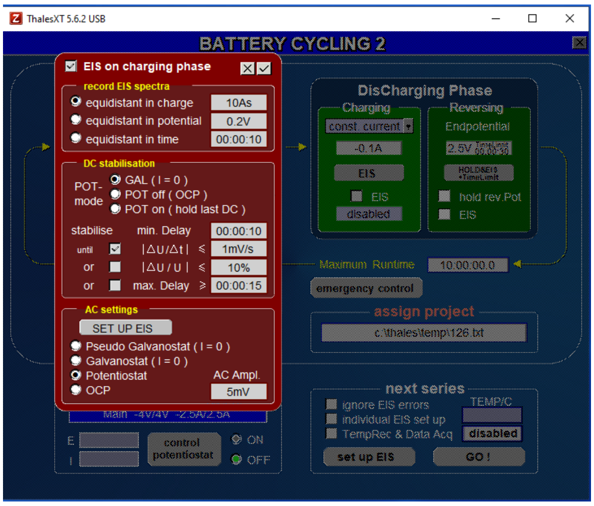




If the time limit is activated in the reversing section (point 7) then the EIS during the charging phase (point 3) is be deactivated.

3.1.1 EIS setting during charging

Clicking on *EIS* (point 3) in the charging phase opens a sub-window, where the EIS measurements can be set up.



Record EIS spectra:

The EIS measurements can be recorded at

- Equidistant charge or
- Equidistant potential or
- Equidistant time.

AC settings:

"SET UP EIS" leads to the *EIS* window, where the *frequency range*, *steps per decades,* and *measure periods* can be defined for the EIS measurements. EIS can be measured in potentiostatic, galvanostatic, pseudo-galvanostatic mode, or at open circuit potential (OCP) conditions. The input box at the bottom right can be used to define the AC amplitude for the EIS measurements (for a description of the different EIS options, please refer to the EIS manual).

DC stabilisation:

The EIS measurements require stabilisation conditions, so the user can define the stabilisation conditions in terms of "DC stabilisation". Before starting the EIS measurement, the potentiostat measures the **voltage change per time (*ΔU/Δt*)** and/or the **voltage change per total voltage (*ΔU/U*)** if activated and specified in the stabilisation indicators. When any of the active stabilisation indicators fall below the user-defined limits then the EIS measurement is started. If the stabilisation indicators are not reached in the specified time or are not activated then the EIS measurement starts when the maximum delay time is reached (if *max. Delay* is activated).

During the "DC stabilisation" phase, the battery can be held at

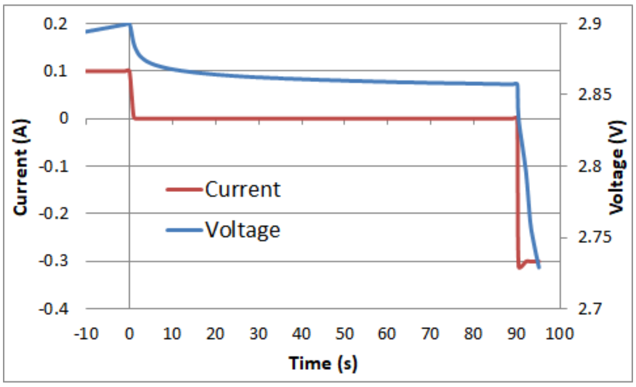
- Galvanostatic mode (potentiostat ON, with *I=0*)
- Open circuit potential mode (potentiostat OFF, at OCP conditions)
- Potentiostatic mode (potentiostat ON, voltage held at the last DC voltage).

In the following 3 subsections,

1. a small battery is charged to a voltage of 2.9 V with a charging current of 0.1 A,
2. held at *i*) galvanostatic mode (I=0), *ii*) open-circuit condition, and *iii*) potentiostatic mode for 30 seconds,
3. relaxation (at open circuit conditions) is carried out for 60 seconds.

3.1.1.1 DC stabilisation - galvanostatic mode

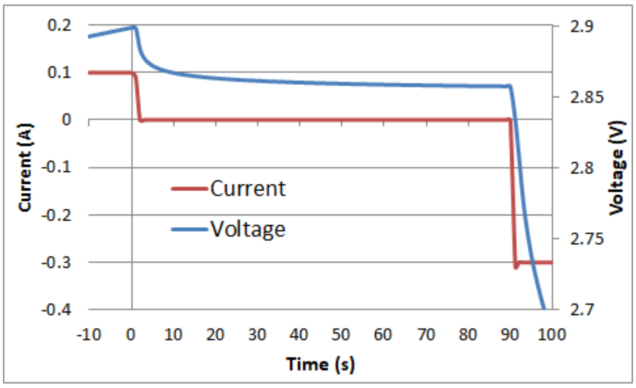
In the graph, a battery is charged to a voltage of *2.9 V* with a charging current of *0.1 A*. At time *0 s*, the DC stabilisation process (*Gal I=0*) is started for *30 s*. No stabilisation conditions like *ΔU/U* or *ΔU/t* are activated. After *30 s* the relaxation phase is activated which kept the battery at open-circuit conditions for *60 s*.



After the above-mentioned stabilisation process, the EIS can be started (not started here in graph, but discharging cycle at *-0.3 A* is started).

3.1.1.2 DC stabilisation - open circuit potential mode

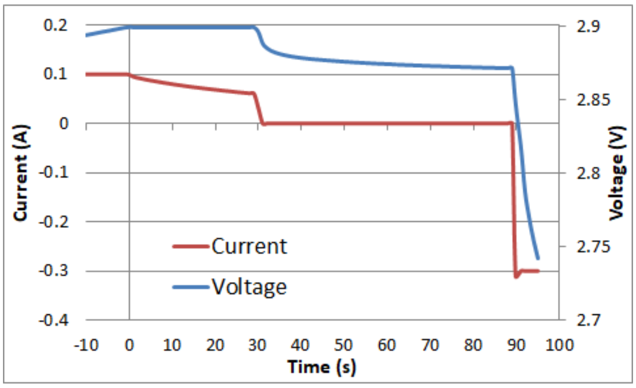
In the graph, a battery is charged to a voltage of *2.9 V* with a charging current of *0.1 A*. At time *0 s*, the DC stabilisation process (hold at open circuit potential) is started for *30 s*. No stabilisation conditions like *ΔU/U* or *ΔU/t* are activated. After *30 s*, the relaxation phase is activated which kept the battery at open-circuit conditions for *60 s*.



After the above-mentioned stabilisation process, the EIS can be started (not started here in graph, but discharging cycle at *-0.3 A* is started)

3.1.1.3 DC stabilisation - potentiostatic mode

In the graph, a battery is charged to a voltage of *2.9 V* with a charging current of *0.1 A*. At time *0 s*, the DC stabilisation process (POT-ON: hold last DC) is started for *30 s*. No stabilisation conditions like |*I*| or *ΔI/t* are activated. After *30 s*, the relaxation phase is activated which kept the battery at open-circuit conditions for *60 s*.



After the above-mentioned stabilisation process, the EIS can be started (not started here in graph, but discharging cycle at *-0.3 A* is started).

Here the stabilization is not carried out for long enough time. In a real experiment, the stabilization phase should be long enough that during the stabilization the current reaches zero.

3.1.2 Hold potential and EIS setting

Hold end state:

In the “Hold and EIS settings”, the stabilisation indicators are the same as explained in the EIS setting (section 3.1.1).

Relaxation phase:

At the end of the charging scan, the user can define a relaxation phase. This relaxation is carried out at the open circuit conditions. The relaxation phase starts after the “hold end state” phase. The EIS measurement starts after the relaxation phase.

EIS after each phase:

In default settings, the EIS is disabled. Here, the user can choose after how many charging phases the EIS should be measured. In the image, EIS after each charging phase is chosen. EIS measurement conditions (operation mode, AC amplitude, and frequency range) can be set up similar to what is explained in section 3.1.1.

Max charging time:

The battery cycling 2 software allows users to define a maximum charging time. If the end potential is not reached in the defined time then the charging routine is terminated.

This function can also be used as a safety precaution, as in the case of a defective battery the end potential is never obtained irrespective of how long the battery is charged and all the charging current ends up heating the battery.

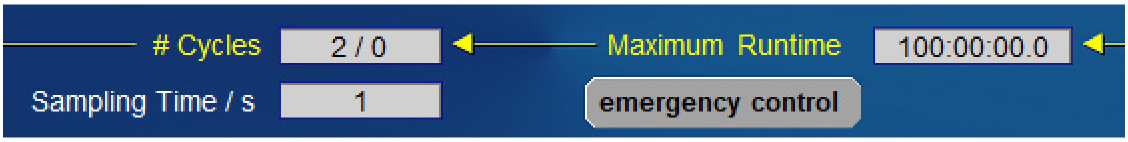
Using the *max charging time* as reversing condition, the user cannot measure the EIS spectra during the ramping phase. EIS is only allowed at the end of the charging/discharging phase.

3.2 Discharging Phase

The discharging phase can also be carried out at constant current or constant power. The end potential defines the endpoint of the discharging phase. The complete discharging phase can be set up similar to the charging phase.

3.3 Charging/Discharging routine

The complete charging/discharging routine can be defined in the image shown below.



Maximum Runtime: Time limit of the measurement (allowed up to 1000 hours).

Cycles: Number of cycles (*Total cycles*, *Last half cycle*).
Last half cycle → 1 (yes), 0 (no)

If a cycle is started with charging then at the end of all the cycles the battery is discharged. Herewith *Last half cycle*=1, the battery can be charged at the end of the measurement.

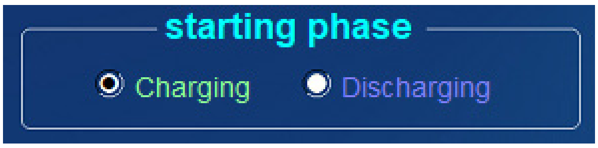
Sampling Time / s: Sampling time of I/E data during DC measurements

Emergency control: The user can set the charge or temperature limit as an emergency control.

The user must set up a temperature reader (i.e., a thermometer) with Thales software for the *emergency control* to work properly. To read temperature, the user must set up the temperature channel. Further information is provided in the Signal Acquisition manual.

3.3.1 Starting phase

The "starting phase" defines if the cycling routine should start with charging or discharging.

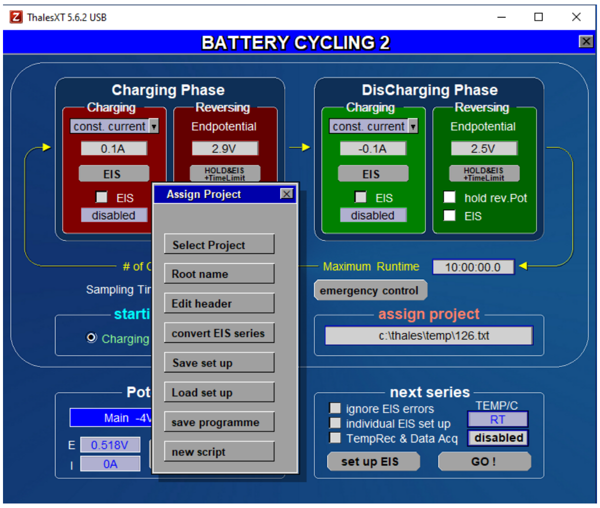


3.3.2 Saving the charging/discharging routine

The "assign project" section opens a sub-window, where the saving format can be defined.

Select project:

Select the folder where the files should be saved and then click *exit*.



Root name:

Root name defines the name of the files to be saved.

Edit Header:

Edit Header allows comments which are saved in the header of the saved files.

Convert EIS series:

With convert EIS series, the impedance data files can be configured in such a way that they also contain information about time and charge (for equidistant time and equidistant charge measurement during the charging/discharging phase). With this, the EIS spectra can be later on compared for different times or charges.

Save set up:

Save the settings of the battery cycling 2 software for future use.

Load set up:

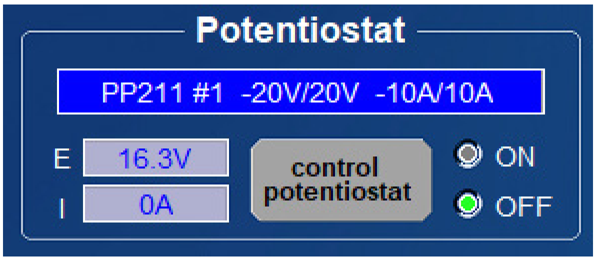
Load the saved settings of the battery cycling 2 software.

New script & Save programme:

"New script" and "Save programme" is for developers of the Thales software.

The battery cycling measurements can last for a very long time; hence the battery cycling 2 software saves the data continuously during the measurement in a predefined folder.

3.4 Potentiostat settings



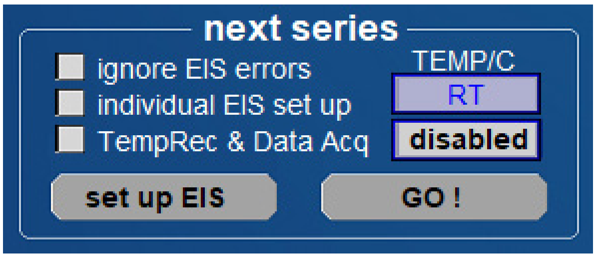
The "Potentiostat" section shows the settings of the active potentiostat and the current and voltage values of the potentiostat.

The "test sampling and control potentiostat" window can be accessed through the control potentiostat button.

The user can directly turn on and turn off the potentiostat from the battery cycling 2 software.

3.5 Activating signal acquisition

Ignore EIS errors:



If the battery cycling 2 software encounters an error during the EIS measurement then it stops the EIS measurement and skips to the subsequent charging or discharging phase. By activating the *ignore EIS errors*, the battery cycling 2 software ignores such errors and continues with the EIS measurement and the cycling routine.

Individual EIS set up:

With *individual EIS set up* activated, the user can individually set up the EIS measurements during the charging/discharging scans and at the end of the charging/discharging scan.

Without the *individual EIS set up*, a single EIS setting is valid for all the EIS measurements during the charging/discharging routine and at reversing potentials.

TempRec & Data Acq:

The *TempRec & Data Acq* allows the battery cycling 2 software to acquire the active channels from the *Thales Signal Acquisition* software. With this, the battery cycling 2 also records data from the acquisition channels during the cycling routine (temperature measurements and/or additional voltage channels for EIS or charging/discharging phases).

The user must set up the acquisition channels in the *Signal Acquisition* window before they can be acquired in battery cycling 2 software.

4 Cycling routine with battery cycling-2 software

In this chapter, measurements with different stabilization settings and EIS settings are shown. These measurements provide insight into the effect of different settings on the battery. For the measurements, a Lithium Nickel Manganese Cobalt Oxide (NMC) battery is used.

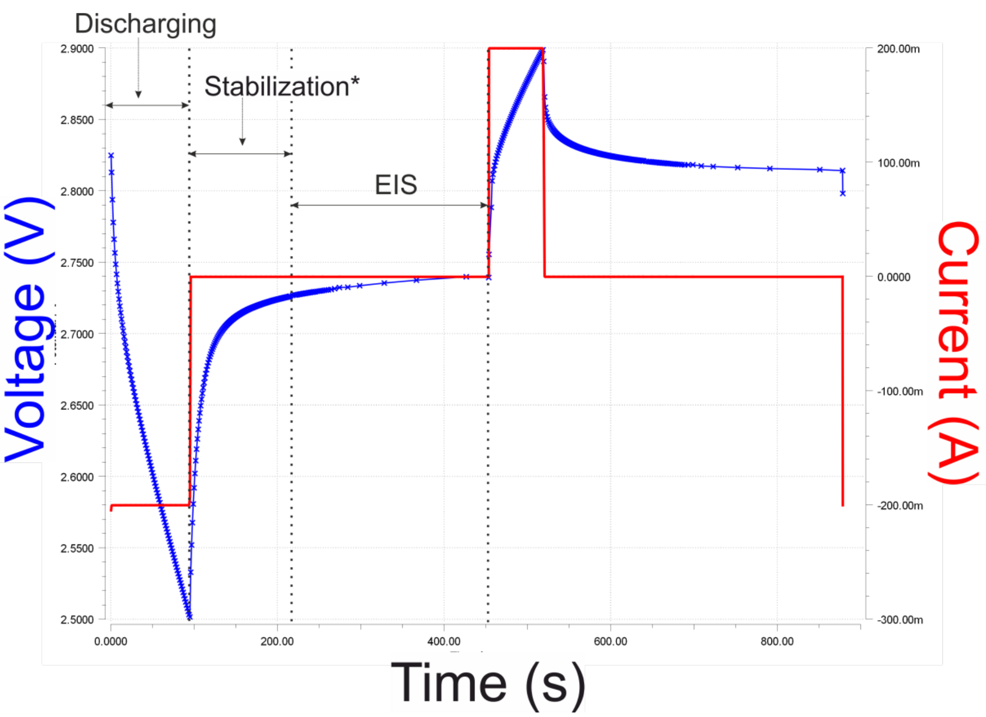
4.1 Measurement 1 – galvanostatic-mode

In the image below, the NMC battery is

1. discharged to a voltage of *2.5 V*,
2. stabilized at *Gal (I=0)*,
3. EIS measurement in galvanostatic mode (*I=0*) with Ampl=*10 mA*,
4. charged to a voltage of *2.9 V*,
5. stabilized at Gal (*I=0*),
6. EIS measurement in galvanostatic mode (*I=0*) with Ampl=*10 mA*.

In the measurement, the stabilization is not carried out for a long enough time that the battery reaches equilibrium. In real experiments, the stabilization should be carried out for a long enough time that the voltage (*V*) of the battery does not change with time.

During the EIS measurement, the battery cycling-2 software also measures the current and voltage of the battery with the impedance measurement at each frequency.



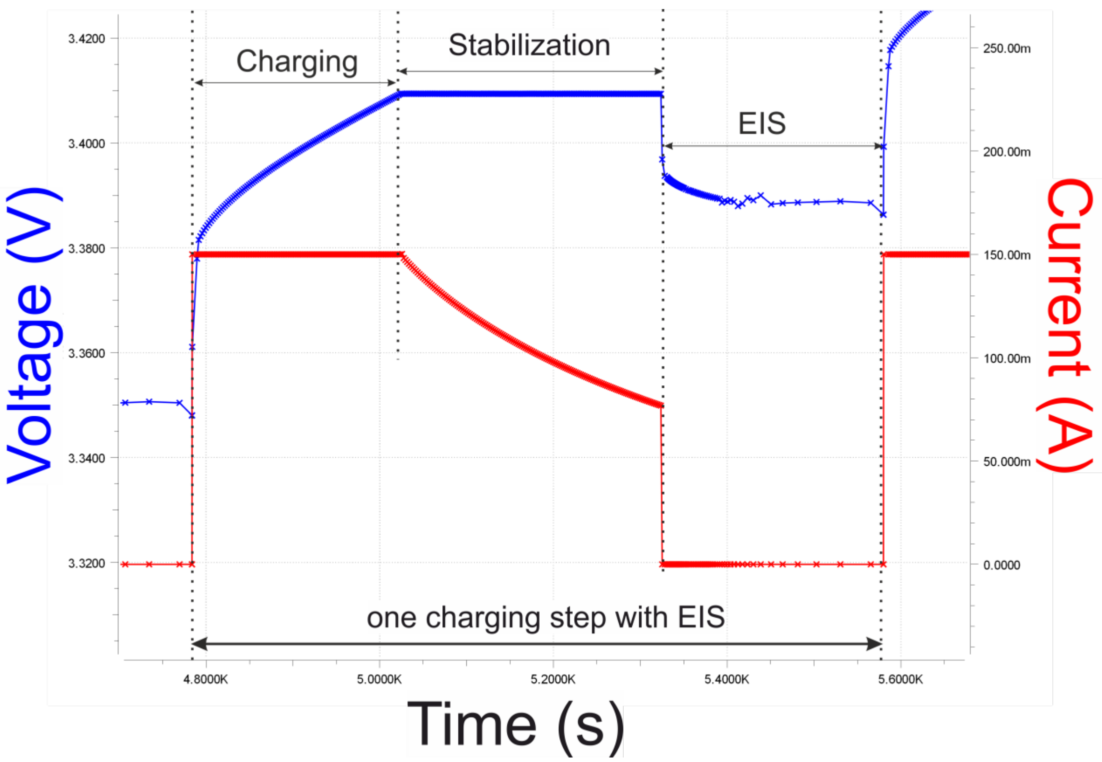
In the previous image, the transition between the stabilization process and EIS is smooth as both of the measurements are in galvanostatic mode.

For low ohmic objects, it is recommended to use galvanostatic mode for the EIS measurement.

4.2 Measurement 2 – Mixed mode

In the image below, the NMC battery is

1. charged with charging current of *150 mA*,
2. stabilization in potentiostatic mode (hold last DC),
3. EIS measurement in galvanostatic mode (*I=0*) with Ampl=*10 mA*.



In the image above starting EIS after stabilization caused a big change in current. This induces instability in the battery and artefacts in the EIS measurement. For optimum results, the stabilization should be carried over the duration of hours. In addition, it must be made sure that while starting the EIS the current/voltage parameter does not change drastically.

4.2.1 Complete charging/discharging cycle

The image below shows a charging-discharging routine for the NMC battery. The charging and discharging routine is carried out with

- EIS spectra measured during the charging/discharging routine.
  - Stabilisation via *holding at last DC potential*.
  - EIS measurement in galvanostatic mode (*I=0*) with Ampl=*10 mA*.
- EIS spectra measured at the end of the charging/discharging routine.
  - Stabilisation via *holding at last DC potential*.
  - Relaxation at *OCP* (*I=0*).
  - EIS measurement in galvanostatic mode (*I=0*) with Ampl=*10 mA*.