

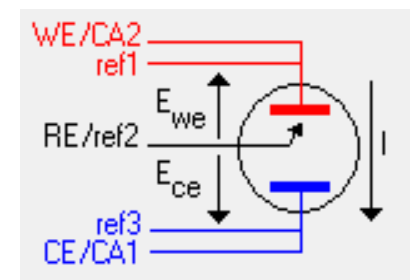
How to use Bio-Logic products to test batteries ?

N. Murer

- 1. Configuration**
2. DC techniques
3. Impedance spectroscopy
4. Processing data

Configuration

- **REF1** : Red – for the control and the measurement of the working electrode potential.
- **REF2** : White – for the control and the measurement of the reference electrode potential.
- **REF3** : Blue – for the control and the measurement of the counter electrode potential.
- **CA2** (Control amplifier): Red – for the control and the measurement of the working electrode current (standard mode).
- **CA1**: Blue – for the control and the measurement of the counter electrode current (standard mode).
- **GND** (Ground): Black



Two points connection

$$+ WE = CA2 + REF1$$

$$- CE = CA1 + REF2 + REF3$$

Four points connection

$$+ WE = CA2 \text{ (for current)}$$

$$REF1 \text{ (for potential)}$$

$$- CE = CA1 \text{ (for current)}$$

$$REF2 + REF3 \text{ (for potential)}$$

Three points connection

$$+ WE = CA2 \text{ (for current)}$$

$$REF1 \text{ (for potential)}$$

$$- CE = CA1 \text{ (for current)}$$

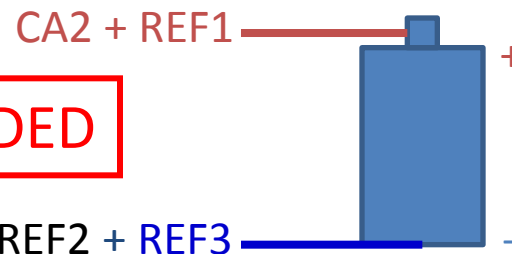
$$REF3 \text{ (for potential)}$$

$$REF = REF2$$

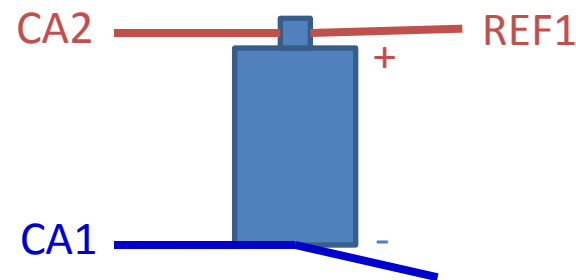
TO BE AVOIDED

$$CA1 + REF2 + REF3$$

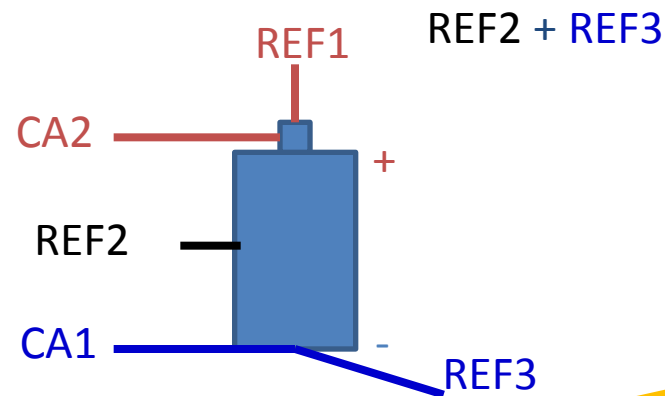
Configuration



OK



OK



Cell description

Cell Description

Electrode material
Initial state
Electrolyte
Comments

Additional recording conditions

Record

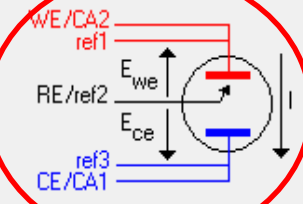
Ece/V
 Ewe-Ece/V
 P/W
 Analog IN 1/V
 Analog IN 2/V

[Record external devices on Analog IN#](#)

Parameters for the intercalation coefficient

Mass of active material [0,001] mg at x = [0,000]
Molecular weight of active material (at x = 0) : [0,001] g/mol
Atomic weight of intercalated ion : [0,001] g/mol
Acquisition started at: x₀ = [0,000]
Number of e⁻ transferred per intercalated ions : [1]
for Δx = 1, ΔQ = [26,802] mA.h

Cell connection mode



Reference electrode

Reference electrode

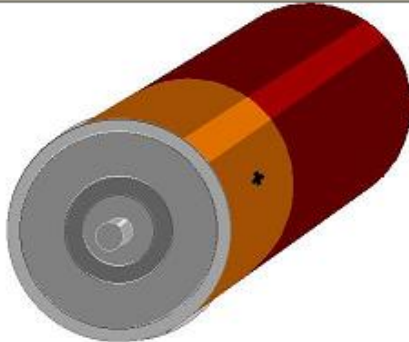
(unspecified)

Offset potential vs. Normal Hydrogen Electrode: 0,000 V

Batteries Testing Applications

Insert Techniques

- AC Voltammetry - ACV
- Impedance Spectroscopy
- Pulsed Techniques
- Technique Builder
- Ohmic Drop Determination
- Electrochemical Applications**
 - Batteries Testing**
 - Potentiodynamic Cycling with Galvanostatic Acceleration - PCGA
 - Galvanostatic Cycling with Potential Limitation - GCPL
 - Galvanostatic Cycling with Potential Limitation 2 - GCPL2
 - Galvanostatic Cycling with Potential Limitation 3 - GCPL3
 - Galvanostatic Cycling with Potential Limitation 4 - GCPL4
 - Galvanostatic Cycling with Potential Limitation 5 - GCPL5
 - Galvanostatic Cycling with Potential Limitation 6 - GCPL6
 - Galvanostatic Cycling with Potential Limitation 7 - GCPL7
 - Constant Load Discharge - CLD
 - Constant Power - CPW
 - Alternate Pulse Galvano Cycling - APGC
 - Potential Profile Importation - PPI
 - Galvano Profile Importation - GPI
 - Resistance Profile Importation - RPI
 - Power Profile Importation - PWPI
 - Photovoltaic/Fuel Cells
 - Corrosion



Insert Technique
 Before
 After

Load from default
 Advanced setting External devices
 Cell characteristics

Custom Applications

Outline

1. Configuration
- 2. DC techniques**
3. Impedance spectroscopy
4. Processing data

The most basic technique to characterize batteries is CP (ChronoPotentiometry). It consists in applying a positive or negative constant current and recording the evolution of the cell voltage with time.

Advanced Settings

Cell Characteristics

Parameters Settings

1 - CP

Turn to OCV between techniques

0

Apply $I_s = 50,000$ A vs. <None>

for $t_s = 0$ h 0 mn $10,000.0$ s

Limits $E_{we} > E_M =$ pass V

$|\Delta Q| > \Delta Q_M = 138,889$ mA.h

Record E_{we}

every $dE_s = 1,0$ mV

or $dt_s = 0,100.0$ s

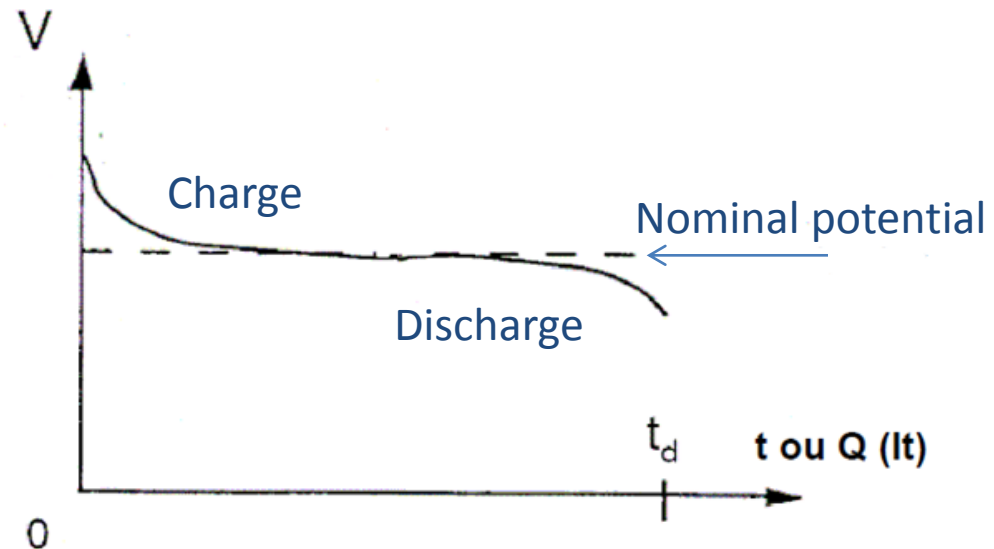
E Range = 0 V; 5 V
Resolution = 5 μ V

I Range = 100 μ A

Bandwidth = 5 - medium

Go back to sequence $N_s = 0$ (9999 ends technique)

for $n_c = 0$ time(s) (0 for next sequence)



Potentiodynamic Cycling with Galvanostatic Acceleration

Turn to OCV between techniques J[1]

0 1

① Scan E_{we} with $dE_s = 5,000$ mV
 per $dt_s = 12$ h 0 mn 0,000 0 s
 from $E_i = 0,000$ V vs. Eoc
 to $E_f = 4,200$ V vs. Ref
 Curtail step duration if $|I| < I_f = 10,000$ mA

Limit $|ΔQ| > ΔQ_M = 1,054,315$ mA.h
 $\Leftrightarrow Δx_M = 0,550$

Record every $dQ = 0,500$ mA.h
 or $dt_q = 120,000$ 0 s

E Range = 0 V; 5 V
Resolution = 100 μV

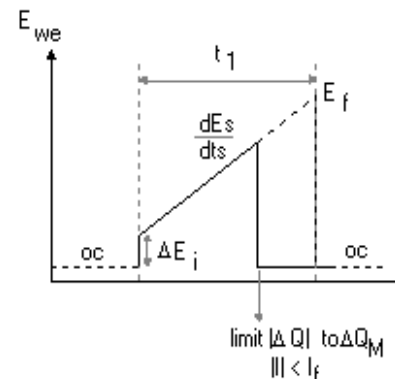
I Range = 1 A

Bandwidth = 5 - medium

② Rest for $t_R = 6$ h 0 mn 0,000 0 s
 Limit $|dE_{we}/dt| < dE_R/dt = 0,1$ mV/h
 Record every $dE_R = 5,0$ mV
 or $dt_R = 120,000$ 0 s
(if $t_R = 0$ or $|ΔQ| > ΔQ_M$ go to ④)

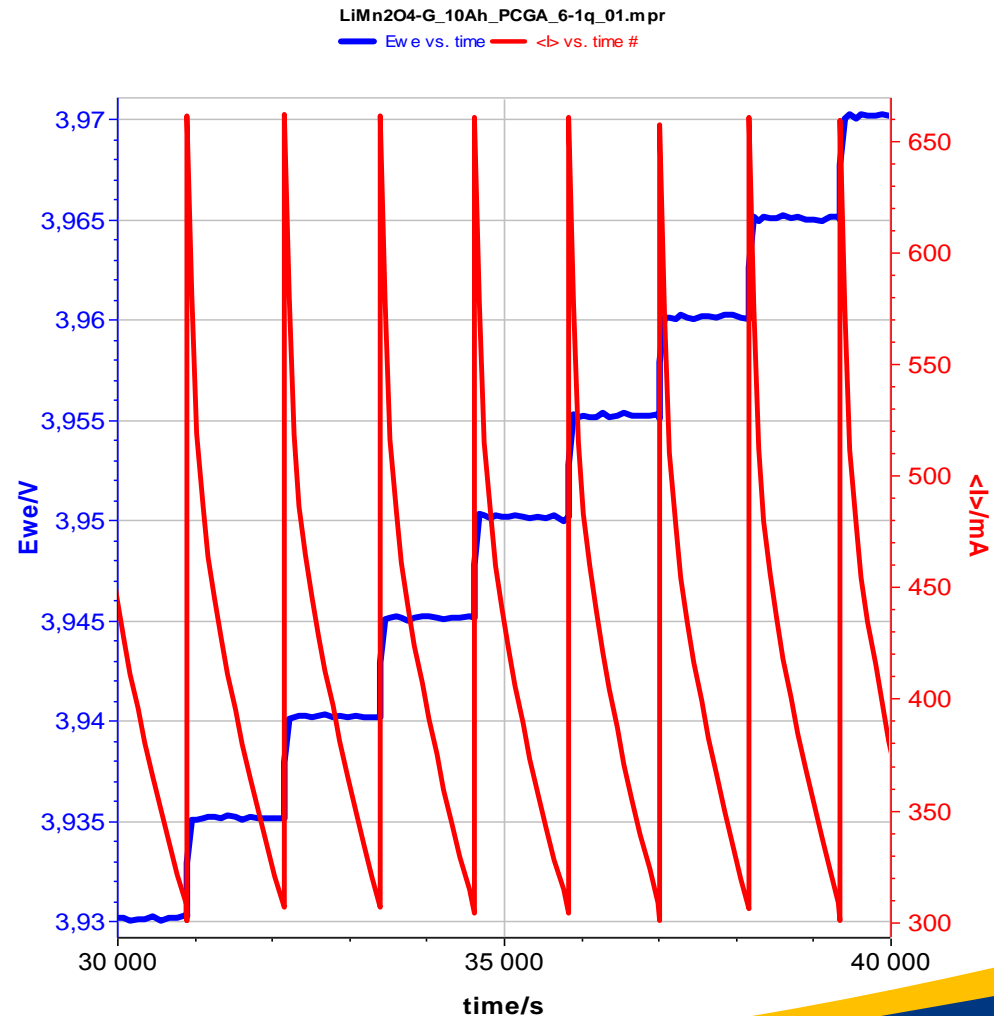
③ Test E_{we} vs. $E_L =$ pass V vs. Ref
 go to ①

④ Go back to seq. $N_s = 0$ *(9999 ends technique)*
 for $n_c = 0$ time(s) *(0 for next seq.)*



- Cycling under stepwise potentiodynamic mode.
- Potential sweep defined by setting the potential step amplitude and duration.
- Possible limit of the step duration on the charge or discharge currents value.
- Can be used for PITT (Potentiostatic Intermittent Titration Technique)¹ experiments.

- Successive potential steps with a conditional limit on the minimum current
- Current measured as a function of time, which allows determination of the incremental capacity dx/dV more precisely than CP.
- No relaxation period.
- The magnitude of the current transient can be used to provide a measure of the chemical diffusion flux of the mobile species as a function of time $t^{1/2}$.
- The main drawback is that the ohmic drop across the cell is not eliminated.



Galvanostatic Cycling with Potential Limitation

Turn to OCV between techniques \mathcal{P} [

0 1 2

①

Set I to $I_s = 130,000$ mA vs. <None>

for at most $t_1 = 10$ h 0 mn 0,000 0 s

Limit $E_{we} > E_M = 4,500$ V

Record every $dE_1 = 5,0$ mV

or $dt_1 = 60,000 0$ s

Hold E_M for $t_M = 1$ h 0 mn 0,000 0 s

Limit $|I| < I_m = 0,000$ mA

Record every $dQ = 1,000$ mA.h

or $dt_q = 120,000 0$ s

Limit $|\Delta Q| > \Delta Q_M = 0,000$ mA.h

$\Leftrightarrow \Delta x_M = 0,000$

E Range = 0 V; 5 V Resolution = 100 μ V

I Range = 1 A

Bandwidth = 5 - medium

②

Rest for $t_R = 0$ h 15 mn 0,000 0 s

Limit $|dE_{we}/dt| < dE_R/dt = 0,1$ mV/h

Record every $dE_R = 5,0$ mV

or $dt_R = 120,000 0$ s

(if $t_R = 0$ or $|\Delta Q| > \Delta Q_M$ go to ④)

③

If $E_{we} < E_L = 4,200$ V go to ①

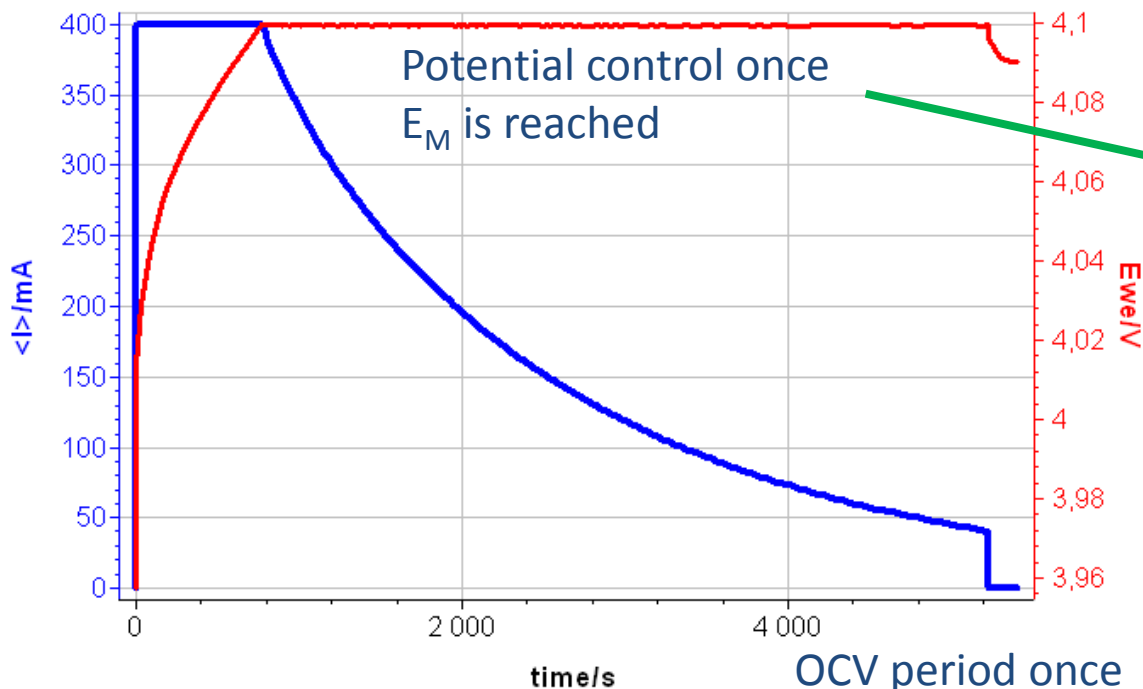
- Battery cycling under galvanostatic mode i.e. with an imposed current
- Possible voltage limitations under current for both charge (positive current) and discharge (negative current)
- GCPL can be used to perform GITT (Galvanostatic Intermittent Titration Technique)² experiments.
- Similarly to PITT, GCPL can be used to have the chemical diffusion coefficient of the mobile species in the electrode.

Charge sequence

Current control

18650_linked_1_GCPL_1corr.mpr

<I> vs. time E_{we} vs. time



If E_{we} is below E_L after OCV, the charge starts again.

OCV period once the current limit I_m is reached

Turn to OCV between techniques

0 1 2

①

Set I to I_s = 130,000 mA vs. <None>

for at most t₁ = 10 h 0 mn 0,000 0 s

Limit E_{we} > E_M = 4,500 V

Record every dE₁ = 5,0 mV
or dt₁ = 60,000 0 s

Hold E_M for t_M = 1 h 0 mn 0,000 0 s

Limit |I| < I_m = 0,000 mA

Record every dQ = 1,000 mA.h
or dt_q = 120,000 0 s

Limit |ΔQ| > ΔQ_M = 0,000 mA.h

<=> Δx_M = 0,000

E Range = 0 V; 5 V
Resolution = 100 μV

I Range = 1 A

Bandwidth = 5 - medium

②

Rest for t_R = 0 h 15 mn 0,000 0 s

Limit |dE_{we}/dt| < dE_R/dt = 0,1 mV/h

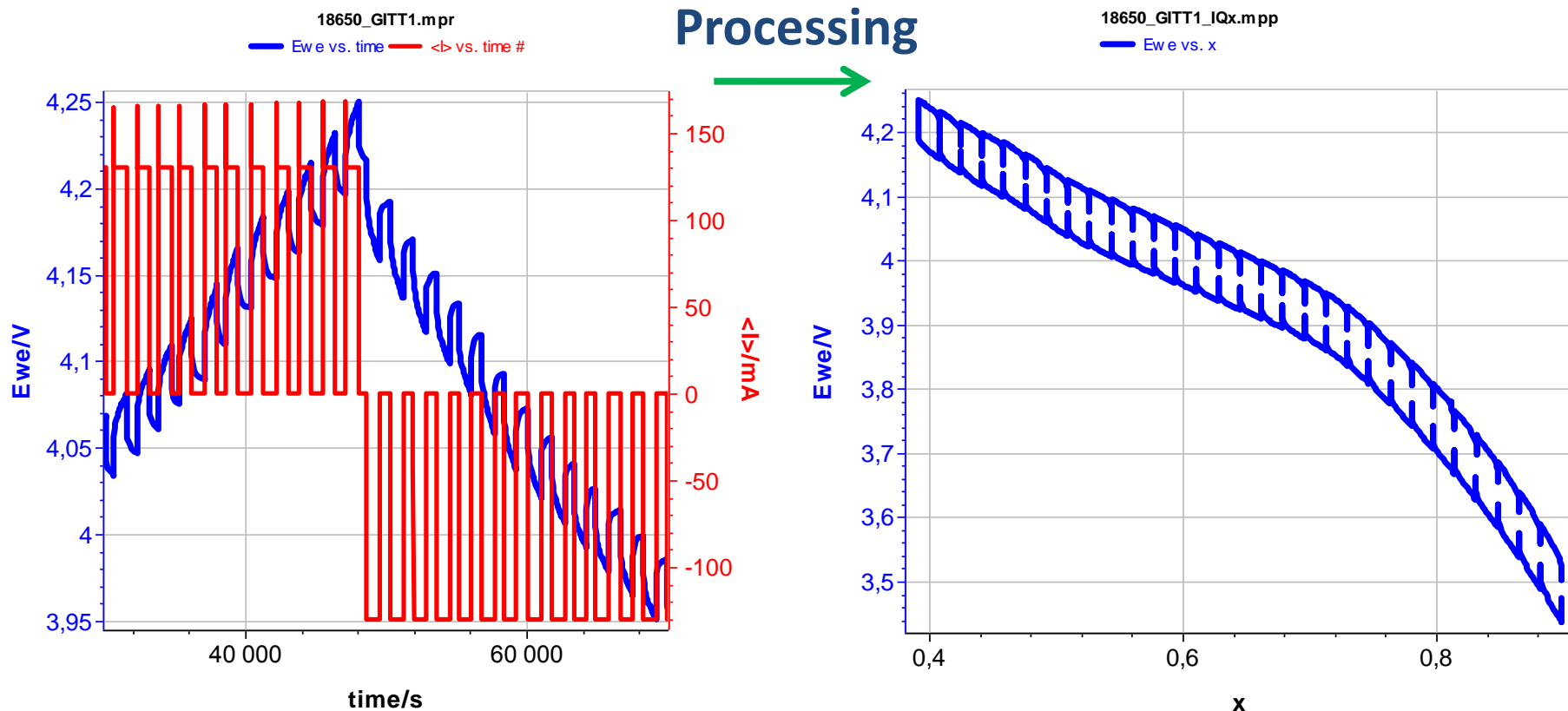
Record every dE_R = 5,0 mV
or dt_R = 120,000 0 s

(if t_R = 0 or |ΔQ| > ΔQ_M go to ④)

③

If E_{we} < E_L = 4,200 V go to ①

In case of a sluggish process, the charge/discharge is performed until E_L is reached.



It is now possible after processing to see the evolution of E vs x , which is the number of moles of inserted mobile species (Li^+ , OH^- ...).

Other GCPL techniques

GCPL2 : GCPL with a limitation on the voltage of the working electrode and of the counter electrode.

GCPL3 : GCPL2 with the possibility to hold potential after charge or discharge.

GCPL4 : GCPL with the possibility to set the global time of the charge/discharge period.

GCPL5: GCPL with the possibility to calculate the dynamic resistance at different time .

GCPL6 : GCPL with a voltage control and limit on WE-CE.

GCPL7 : GCPL but the holding period is performed with a current control.

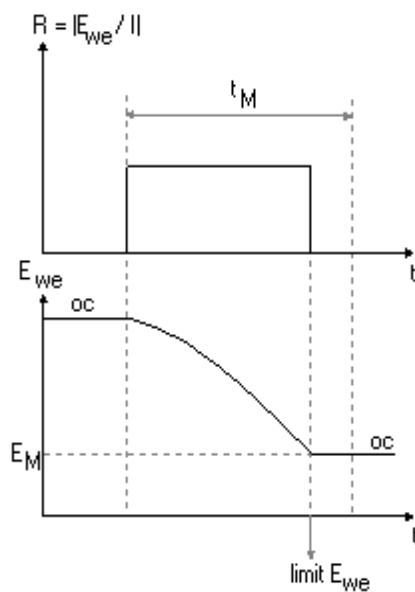
SGCPL : GCPL with a limitation on the external input/output

See Application Note #1, 2, 3

<http://bio-logic.info/potentiostat/notesan.html>

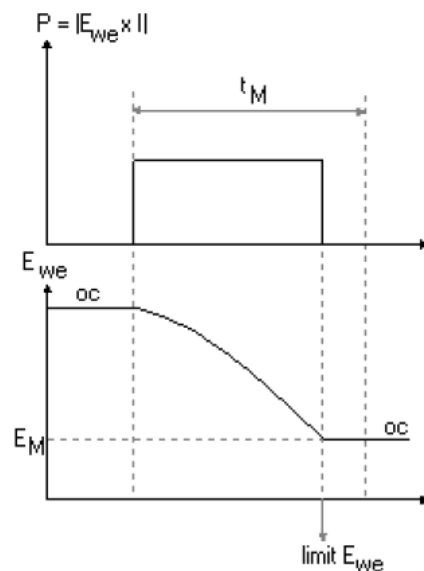
CLD: Constant Load Discharge

- Discharge of a battery at a constant resistance.
- Potentiostat seen as a constant resistor by the battery.



CPW: Constant Power

- The current is controlled to hold $E \cdot I$ constant.
- Used for determination of Ragone plot (power vs. energy).



See Application Note #6, 33, 34

<http://bio-logic.info/potentiostat/notesan.html>

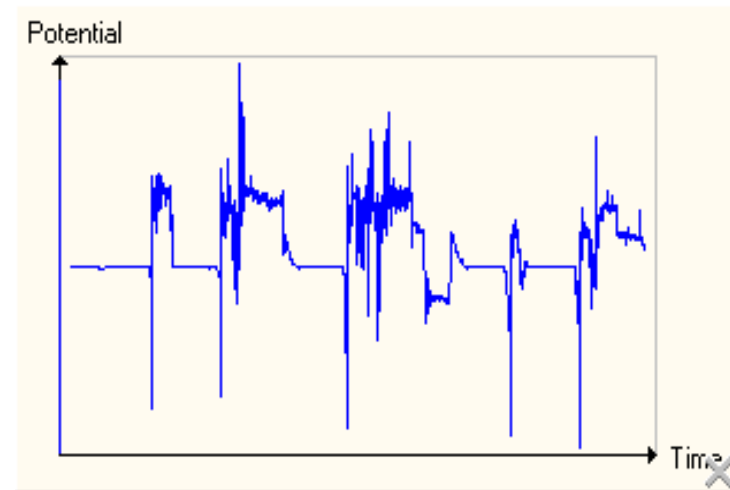
Urban profile importation

GPI Galvano: I control

PPI Potentio: E control

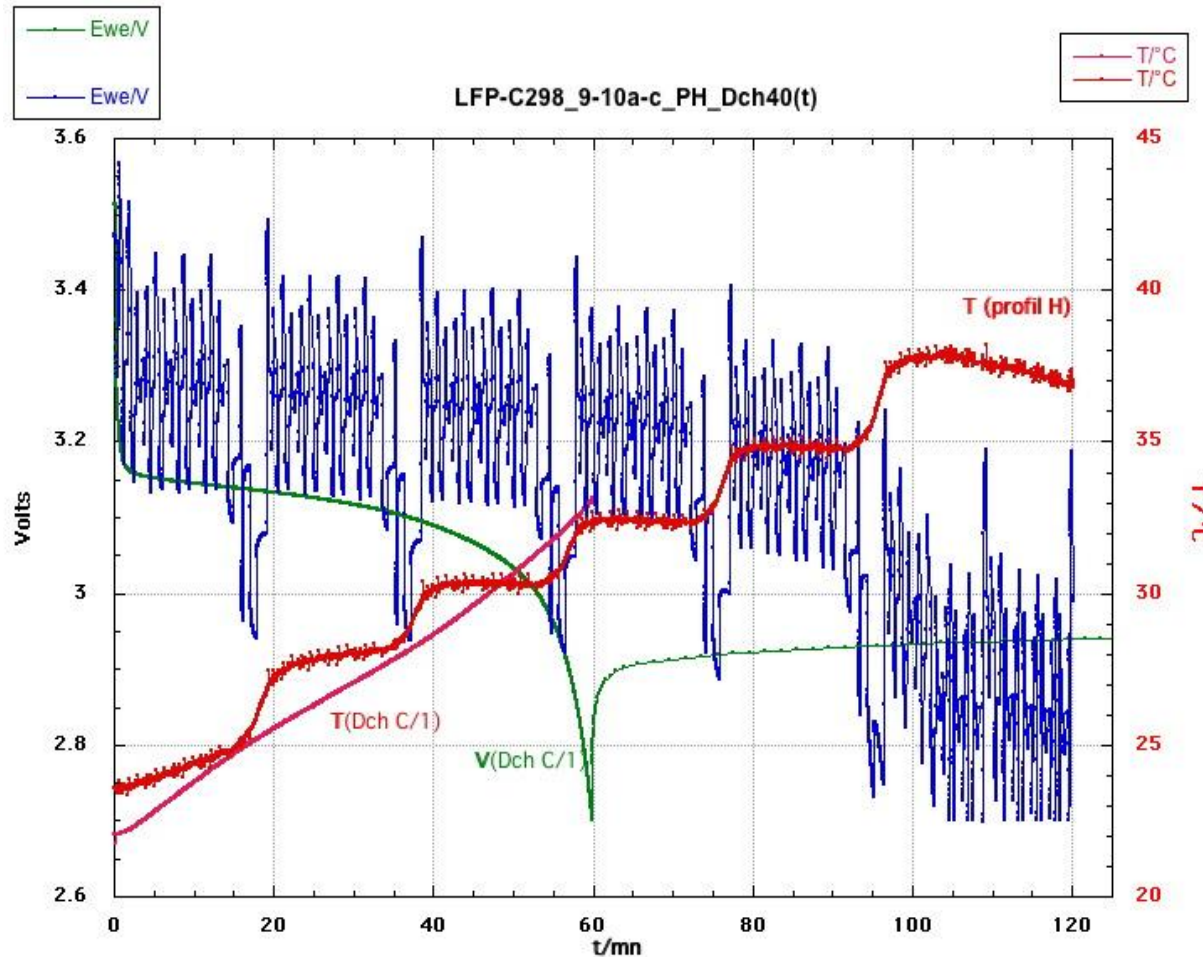
RPI Resistance: R control

PWPI Power: P control



- Up to 3000 sequences in the same technique
- Possibility to repeat one or several sequences
- Profile created step by step or imported from an ASCII file

GPI: European standard profile NEDCL on a 40 A.h LFP cell



- Green: discharge at a constant rate C/1
- Red: Temperature change during the constant discharge C/1
- Blue: discharge profile with 4 urban cycles and 1 extra urban cycle
- Repeated 6 times
- Red: Temperature change during the urban cycles

Outline

1. Configuration
2. DC techniques
- 3. Impedance spectroscopy**
4. Processing data

Impedance Spectroscopy

- It can be performed either with an applied current (GEIS) or potential (PEIS) mode.
- It can be performed automatically at different states of charge by linking PEIS to GCPL.
- It is used to study the electrode-electrolyte interfaces.
- It can be used to evaluate the dependence of the impedance with the state of charge (SOC).
- It can be used to study aging of the battery (state of health = SOH).

See Application Note #5, 8, 9, 14, 15, 16, 17, 18, 19, 23

<http://bio-logic.info/potentiostat/notesan.html>

See Impedance tutorial

Impedance Spectroscopy

Potentiostatic EIS / Galvanostatic EIS techniques

Mode Single Sine
 Multi Sine

Set E_{we} to $E = 0,000\ 0$ V vs. E_{oc}
for $t_E = 0$ h 0 mn $0,000$ s
 Record every $dI = 0,000$ mA
or $dt = 0,000$ s

Scan from $f_i = 200,000$ kHz
to $f_f = 100,000$ mHz
with $N_d = 6$ points per decade
or $N_T = 51$ points from f_i to f_f
in Logarithmic spacing Linear spacing

sinus amplitude $V_a = 10,0$ mV ($V_{rms} \sim 7,07$ mV)
wait for $p_w = 0,10$ period before each frequency
average $N_a = 1$ measure(s) per frequency
drift correction
Repeat $n_c = 0$ time(s)

E Range = 0 V: 5 V
Resolution = 100 μ V
I Range = Auto
Bandwidth = 5 - medium (~ 48 s / scan)

Go back to seq. $N_s^* = 0$ (9999 ends technique)
for $n_f = 0$ time(s) (0 for next sequence)
increment cycle number

- EIS can be performed with an increasing DC bias voltage and current.
- A patented drift correction can be applied to the battery if the steady state is not reached.
- There is a possibility to set sequences with different sinus amplitudes.
- A multisine mode can be used to reduce the measurement duration.

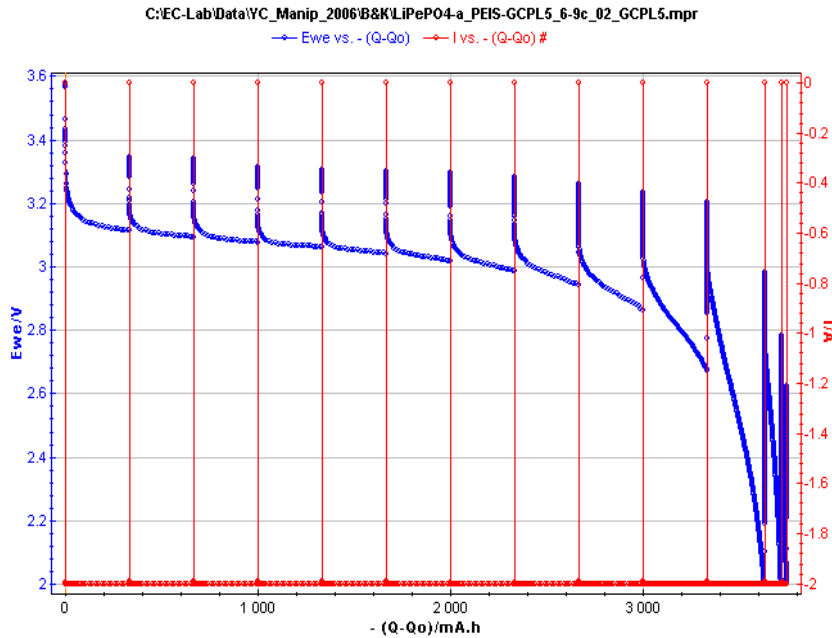
See Application Note #5, 8, 9, 14, 15, 16, 17, 18, 19, 23

<http://bio-logic.info/potentiostat/notesan.html>

See Impedance tutorial

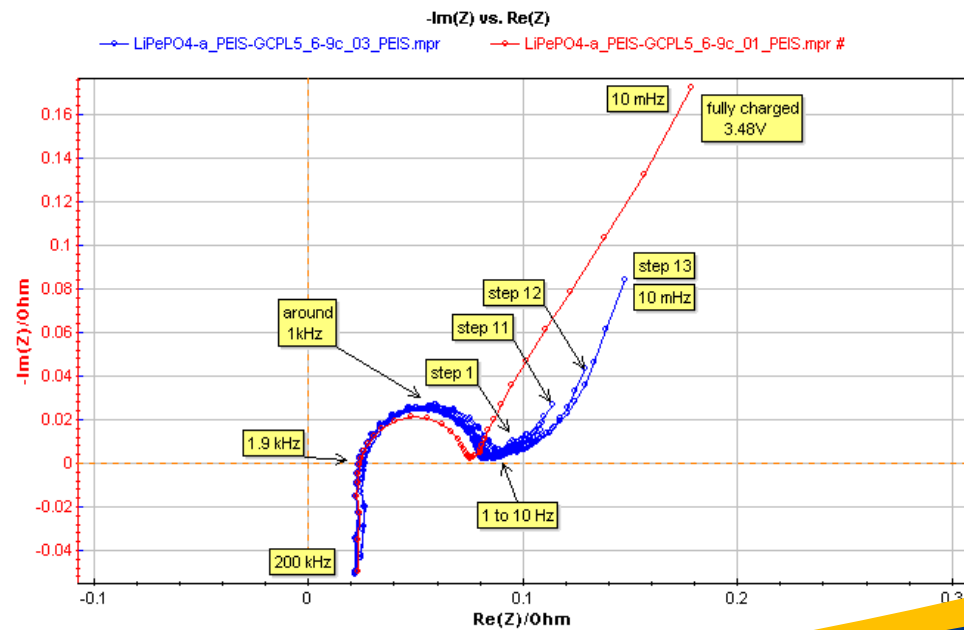
Impedance Spectroscopy

- Materials: Lithium Iron Phosphate
 LiFePO_4 / Graphite
- Nominal potential = 3,1V
- Structure: 3D

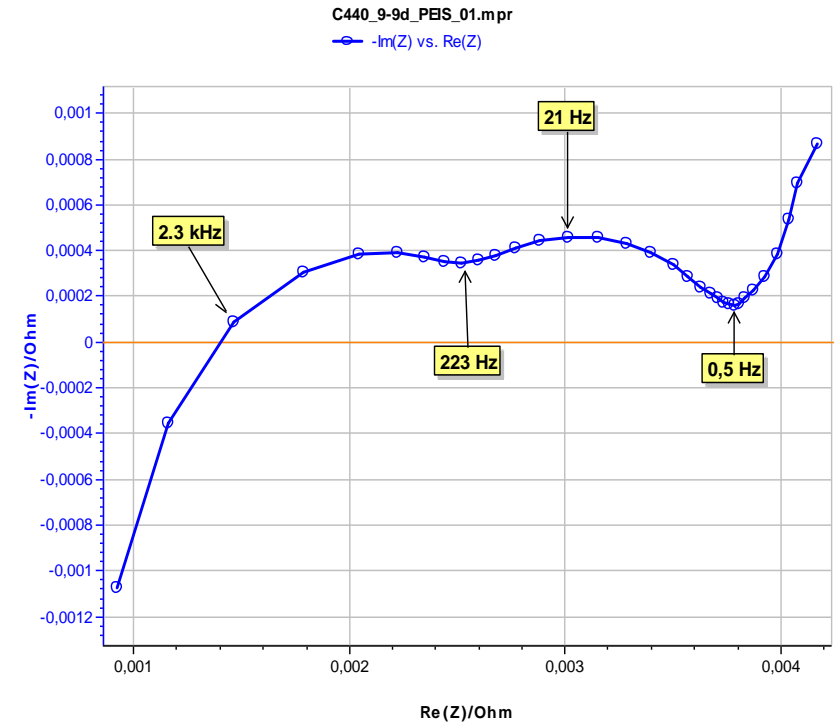
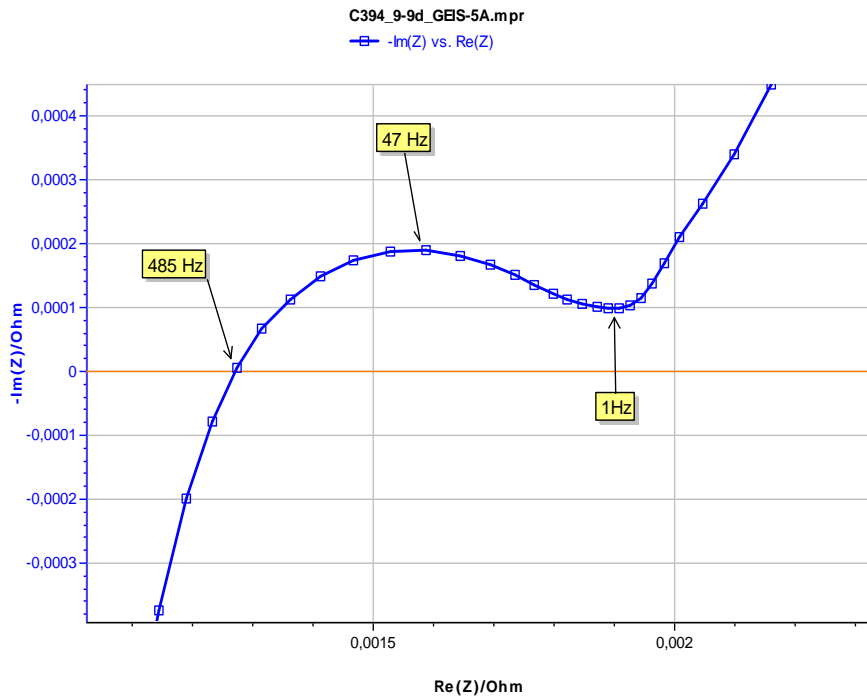


After each discharge step, an EIS measurement can be performed at OCV. The corresponding EIS spectrum is changing, highlighting changing electrode/electrolyte interfaces.

EIS after every discharge increment



Impedance Spectroscopy



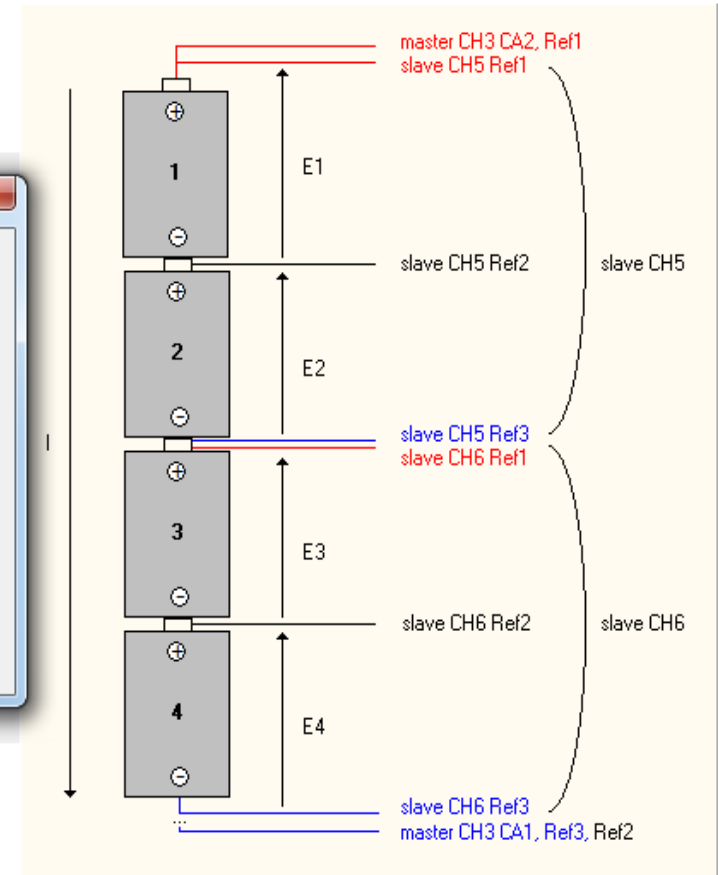
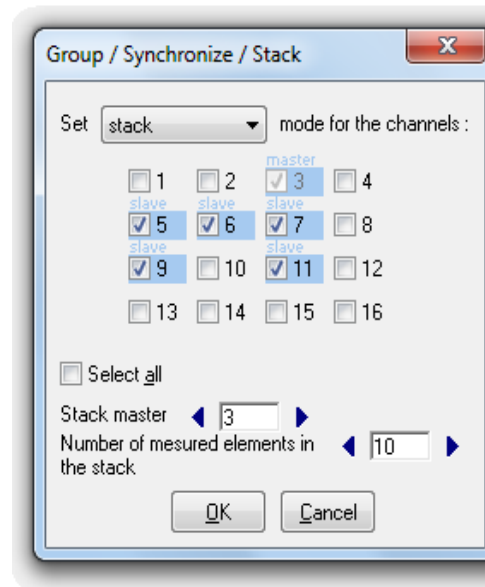
➔ Charged state

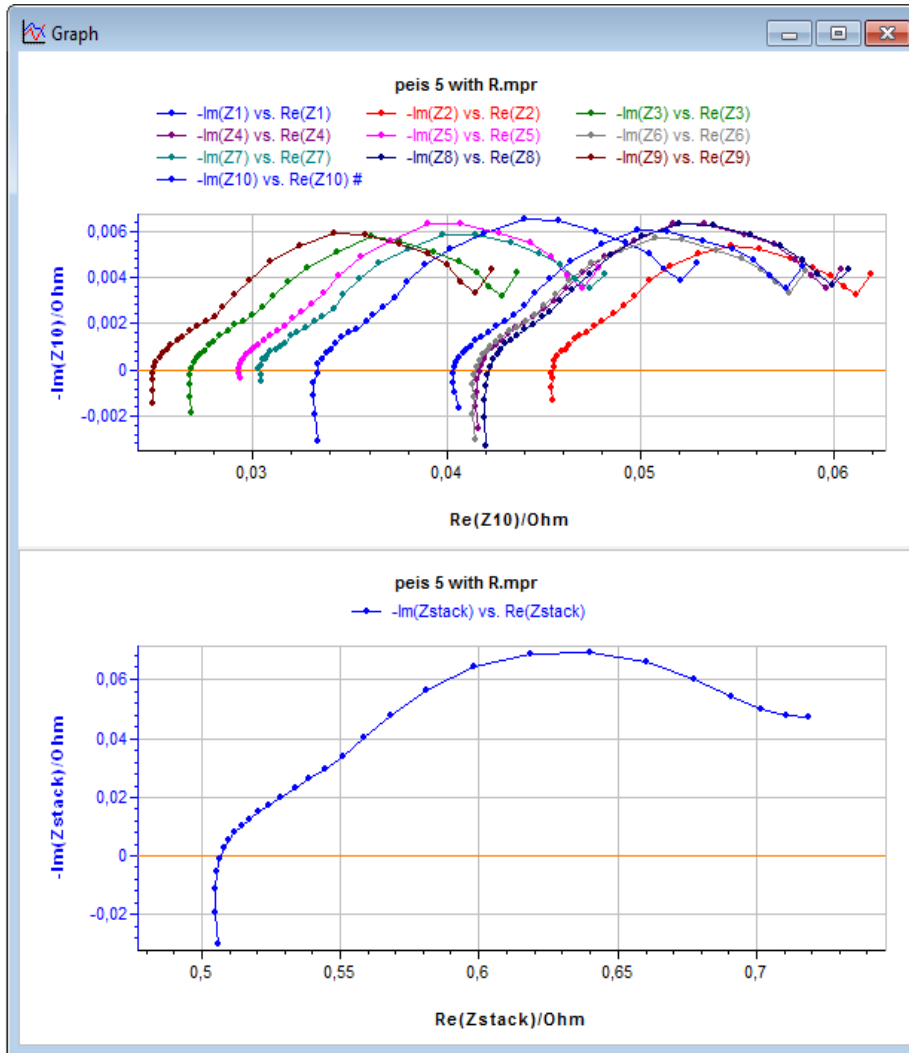
➔ Discharged state

The two impedance graphs can be fitted with an equivalent circuit using ZFit (see Impedance tutorial)

All the battery techniques are also available in stack mode.

- One master Z channel and up to 15 standard slave channels (= 30 cells) with VMP3.
- EIS or DC measurements on each element of the stack
- Possibility of linked experiments





- Stack of 10 elements.
- The impedance of the stack is the sum of the impedance of each element.
- It allows to make a quick comparison of the different charging state of the batteries.

Outline

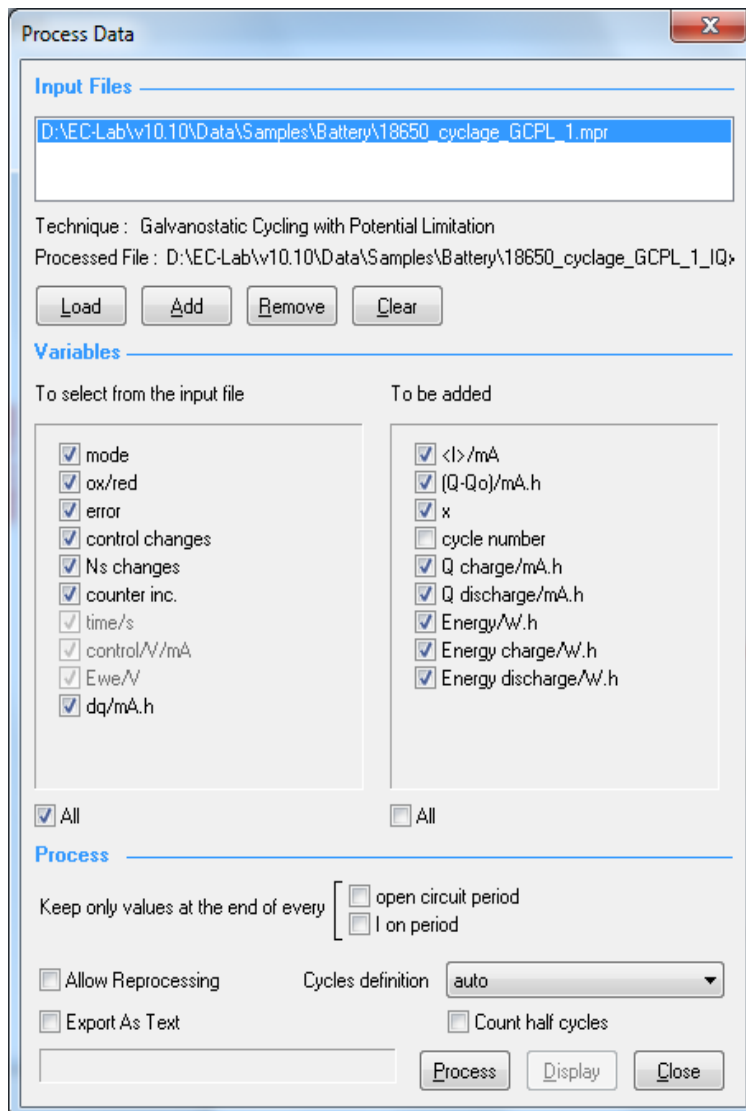
1. Configuration
2. DC techniques
3. Impedance spectroscopy
- 4. Processing data**

Process Data

Two processing modes: standard and compact depending on the technique used.

Standard processing mode creates a new .mpp file with additional variables as chosen:

- Energy (charge/discharge)
- Intercalation coefficient x
- $Q_{\text{charge}} / Q_{\text{discharge}}$
- Cycle number,
- The number of data points will be the same as in the initial data file



Process Data

Process Data [X]

Input Files

D:\EC-Lab\w10.10\Data\Samples\Battery\18650_cyclage_GCPL_1.mpr

Technique : Galvanostatic Cycling with Potential Limitation
 Processed File : D:\EC-Lab\w10.10\Data\Samples\Battery\18650_cyclage_GCPL_1.cR

[Load] [Add] [Remove] [Clear]

Variables

To select from the input file	To be added
<input type="checkbox"/> mode	<input type="checkbox"/> dQ/mA.h
<input type="checkbox"/> ox/red	<input type="checkbox"/> (Q-Qo)/mA.h
<input type="checkbox"/> error	<input type="checkbox"/> x
<input type="checkbox"/> control changes	<input type="checkbox"/> cycle number
<input type="checkbox"/> Ns changes	<input checked="" type="checkbox"/> "Ri"/Ohm
<input type="checkbox"/> counter inc.	
<input checked="" type="checkbox"/> time/s	
<input checked="" type="checkbox"/> control/V/mA	
<input checked="" type="checkbox"/> Ewe/V	
<input type="checkbox"/> dq/mA.h	

All All

Process

Keep only values at the end of every [open circuit period]
 [I on period]

Allow Reprocessing Cycles definition: auto

Export As Text Count half cycles

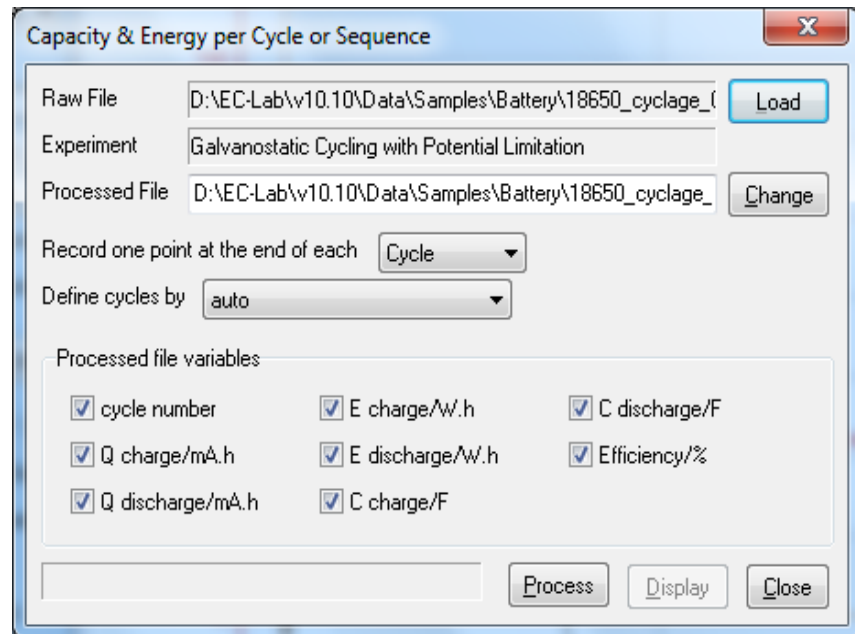
[Process] [Display] [Close]

Compact processing mode calculates an averaged or integrated variable on every step (current or voltage depending the technique)

- Determination of the dynamic resistance with the GCPL5 technique
- Determination of the incremental capacity with a PCGA

Processing to get capacity and energy per cycle

- Determination of energy, capacity and efficiency
- Separated for charge and discharge periods
- Stored in a .mpp file



Other applications

All these techniques are also available for the study of other energy devices :

- Fuel cells
- Supercapacitors
- Photovoltaic cells

**Thank you for your
attention**