EC-Lab® Software: Techniques and Applications

Version 10.1x – February 2011

Equipment installation

WARNING !: The instrument is safety ground to the Earth through the protective conductor of the AC power cable.

Use only the power cord supplied with the instrument and designed for the good current rating (10 Amax) and be sure to connect it to a power source provided with protective earth contact.

Any interruption of the protective earth (grounding) conductor outside the instrument could result in personal injury.

Please consult the installation manual for details on the installation of the instrument.

General description

The equipment described in this manual has been designed in accordance with EN61010 and EN61326 and has been supplied in a safe condition. The equipment is intended for electrical measurements only. It should be used for no other purpose.

Intended use of the equipment

This equipment is an electrical laboratory equipment intended for professional and intended to be used in laboratories, commercial and light-industrial environments. Instrumentation and accessories shall not be connected to humans.

Instructions for use

To avoid injury to an operator the safety precautions given below, and throughout the manual, must be strictly adhered to, whenever the equipment is operated. Only advanced user can use the instrument.
Bio-Logic SAS accepts no responsibility for accidents or damage resulting from any failure to comply with these precautions.

GROUNDING

To minimize the hazard of electrical shock, it is essential that the equipment be connected to a protective ground through the AC supply cable. The continuity of the ground connection should be checked periodically.

ATMOSPHERE

You must never operate the equipment in corrosive atmosphere. Moreover if the equipment is exposed to a highly corrosive atmosphere, the components and the metallic parts can be corroded and can involve malfunction of the instrument.
The user must also be careful that the ventilation grids are not obstructed. An external cleaning can be made with a vacuum cleaner if necessary.
Please consult our specialists to discuss the best location in your lab for the instrument (avoid glove box, hood, chemical products, …).

AVOID UNSAFE EQUIPMENT

The equipment may be unsafe if any of the following statements apply:

- Equipment shows visible damage,
- Equipment has failed to perform an intended operation,
- Equipment has been stored in unfavourable conditions,
- Equipment has been subjected to physical stress.

In case of doubt as to the serviceability of the equipment, don't use it. Get it properly checked out by a qualified service technician.

LIVE CONDUCTORS

When the equipment is connected to its measurement inputs or supply, the opening of covers or removal of parts could expose live conductors. Only qualified personnel, who should refer to the relevant maintenance documentation, must do adjustments, maintenance or repair

EQUIPMENT MODIFICATION

To avoid introducing safety hazards, never install non-standard parts in the equipment, or make any unauthorised modification. To maintain safety, always return the equipment to Bio-Logic SAS for service and repair.

GUARANTEE

Guarantee and liability claims in the event of injury or material damage are excluded when they are the result of one of the following.

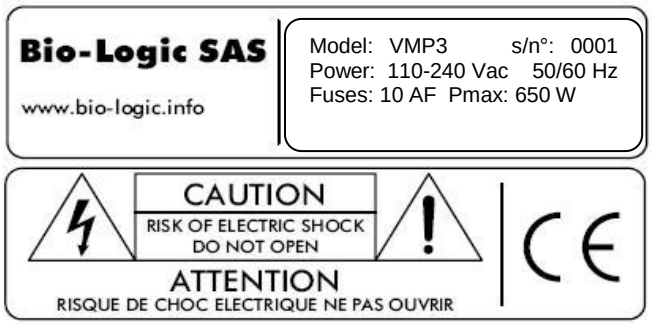
- Improper use of the device,
- Improper installation, operation or maintenance of the device,
- Operating the device when the safety and protective devices are defective and/or inoperable,
- Non-observance of the instructions in the manual with regard to transport, storage, installation,
- Unauthorized structural alterations to the device,
- Unauthorized modifications to the system settings,
- Inadequate monitoring of device components subject to wear,
- Improperly executed and unauthorized repairs,
- Unauthorized opening of the device or its components,
- Catastrophic events due to the effect of foreign bodies.

IN CASE OF PROBLEM

Information on your hardware and software configuration is necessary to analyze and finally solve the problem you encounter.

If you have any questions or if any problem occurs that is not mentioned in this document, please contact your local retailer (list available following the link **Erreur ! Référence de lien hypertexte non valide.**). The highly qualified staff will be glad to help you.
Please keep information on the following at hand:

- Description of the error (the error message, mpr file, picture of setting or any other useful information) and of the context in which the error occurred. Try to remember all steps you had performed immediately before the error occurred. The more information on the actual situation you can provide, the easier it is to track the problem.
- The serial number of the device located on the rear panel device.



- The software and hardware version you are currently using. On the Help menu, click About. The displayed dialog box shows the version numbers.
- The operating system on the connected computer.
- The connection mode (Ethernet, LAN, USB) between computer and instrument.

General safety considerations

Class I

The instrument is safety ground to the Earth through the protective conductor of the AC power cable.

Use only the power cord supplied with the instrument and designed for the good current rating (10 A max) and be sure to connect it to a power source provided with protective earth contact.

Any interruption of the protective earth (grounding) conductor outside the instrument could result in personal injury.

Guarantee and liability claims in the event of injury or material damage are excluded when they are the result of one of the following.

- Improper use of the device,
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- Inadequate monitoring of device components subject to wear,
- Improperly executed and unauthorised repairs,
- Unauthorised opening of the device or its components,
- Catastrophic events due to the effect of foreign bodies.

ONLY QUALIFIED PERSONNEL should operate (or service) this equipment.

Table of contents

1. Introduction

EC-Lab® software has been designed and built to control all of our potentiostats (single or multichannel: SP-50 SP-150, SP-200 and SP-300, MPG, MPG2, VMP, VMP2(Z), BiStat, VMP3, VSP, HCP-803, HCP-1005, CLB-500, EPP-400 and EPP-4000). Each channel board of our multichannel instruments is an independent potentiostat/galvanostat that can be controlled by EC-Lab® software.

Each channel can be set, run, paused or stopped, independently of each other, using identical or different techniques. Any settings of any channel can be modified during a run, without interrupt the experiment. The channels can be interconnected and run synchronously, for example to perform multi-pitting experiments using a common counter-electrode in a single bath.

One computer (or several for multichannel instruments) connected to the instrument monitor the system. The computer connects to the instrument through an Ethernet connection or with an USB connection. With the Ethernet connection, each one of the users is able to monitor his own channel from his computer. More than multipotentiostats, our instruments are modular, versatile and flexible multi-user instruments.

Once the techniques have been loaded and started from the PC, the experiments are entirely controlled by the instrument's on-board firmware. Data are temporarily buffered in the instrument and regularly transferred to the PC, which is used for data storage, on-line visualization, and off-line data analysis and display. This architecture ensures a very safe operation since a shut down of the monitoring PC does not affect the experiments in progress.

The application software package provides useful techniques separated into two categories **Electrochemical Techniques** and **Electrochemical Applications.** The techniques contain general voltamperometric (Cyclic Voltammetry, Chronopotentiometry), differential techniques, impedance techniques, and a technique builder including modular potentio and galvano, triggers, wait, and loop options. The applications are made of techniques more dedicated to specific fields of electrochemistry such as battery, fuel cells, super-capacitors testing, corrosion study, and custom applications. Electrochemical techniques and applications are obtained by associations of elementary sequences (blocks) and appear as flow diagrams combining these sequences. The settings can also be displayed as column setup.

Conditional tests can be performed at various levels of any sequence on either the working electrode potential, current, or on the counter electrode potential, or on the external parameters. These conditional tests force the experiment to go to the next step, loop to a previous sequence or end the sequence.

The aim of this manual is to describe every technique and application available in the EC-Lab® software. This manual composed of several chapters. The first is an introduction. The second section describes electrochemical techniques, and the third explains electrochemical applications. The fourth part details how to build complex experiments as linked techniques.

It is assumed that the user is familiar with Microsoft Windows© and knows how to use the mouse and keyboard to access the drop-down menus.

WHEN A USER RECEIVES A NEW UNIT FROM THE FACTORY, THE SOFTWARE AND FIRMWARE ARE INSTALLED AND UPGRADED. THE INSTRUMENT IS READY TO BE USED. IT DOES NOT NEED TO BE UPGRADED. WE ADVISE THE USERS TO READ AT LEAST THE SECOND AND THIRD CHAPTERS OF THIS DOCUMENT BEFORE STARTING AN EXPERIMENT.

2. Electrochemical Techniques

2.1 Voltamperometric techniques

2.1.1 OCV: Open Circuit Voltage

The Open Circuit Voltage (OCV) consists of a period during which no potential or current is applied to the working electrode. The cell is disconnected from the power amplifier. On the cell, the potential measurement is available. Therefore the evolution of the rest potential can be recorded. This period is commonly used as preconditioning time or for equilibration of the electrochemical cell.

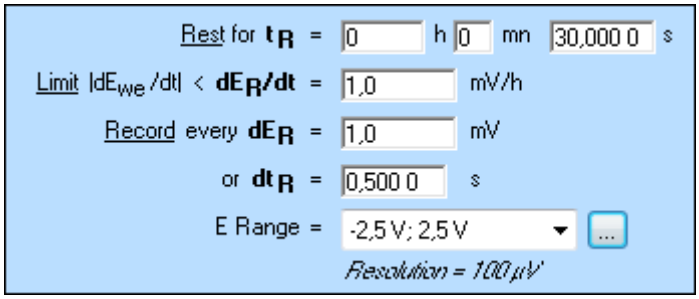


Fig. 1: Open Circuit Voltage Technique.

Rest for t_R = h mn s
fixes a defined time duration t_R for recording the rest potential.
or until $|dE_{we}/dt| < |dE_R/dt|$ = mV/h
stops the rest sequence when the slope of the open circuit potential with time, $|dE_R/dt|$ becomes lower than the set value (value 0 invalidates the condition).

Record E_{we} every dE_R = mV resolution and at least every dt_R = s
allows the user to record the working electrode potential whenever the change in the potential is $\geq dE_R$ with a minimum recording period in time dt_R.

Data recording with dE_R resolution can reduce the number of experimental points without loosing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded but if there is a sharp peak in potential, the rate of recording increases.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

2.1.2 CV: Cyclic Voltammetry

Cyclic voltammetry (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions. CV provides information on redox processes, heterogeneous electron-transfer reactions and adsorption processes. It offers a rapid location of redox potential of the electroactive species.

CV consists of linearly scanning the potential of a stationary working electrode using a triangular potential waveform. During the potential sweep, the potentiostat measures the current resulting from electrochemical reactions (consecutive to the applied potential). The cyclic voltammogram is a current response as a function of the applied potential.
Traditionally, this technique is performed using a straight analog ramp. Due to the digital nature of the potentiostat, however, the actual ramp applied consists of a series of small potential steps that approximate the linear ramp desired (see the control potential resolution part in the EC-Lab® software manual)

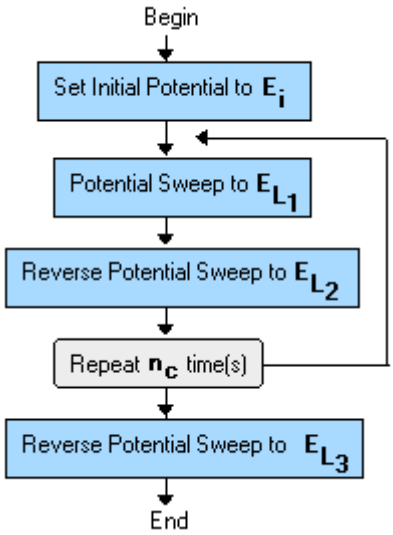


Fig. 2: General diagram for Cyclic Voltammetry.

The "Cyclic Voltammetry" technique has been briefly detailed in the EC-Lab® software manual. This technique corresponds to normal cyclic voltammetry, using a digital potential staircase *i.e*. it runs defined potential increment regular in time. The software adjusts the potential step to be as small as possible.

The technique is composed of:
- a starting potential setting block,
- a 1st potential sweep with a final limit E_1,
- a 2nd potential sweep in the opposite direction with a final limit E_2,
- the possibility to repeat n_c times the 1st and the 2nd potential sweeps,
- a final conditional scan reverse to the previous one, with its own limit E_F.

Note that all the different sweeps have the same scan rate (absolute value).

The detailed flow diagram (on the following figure) is made of five blocks (it is also possible to display the column diagram Fig. 4):

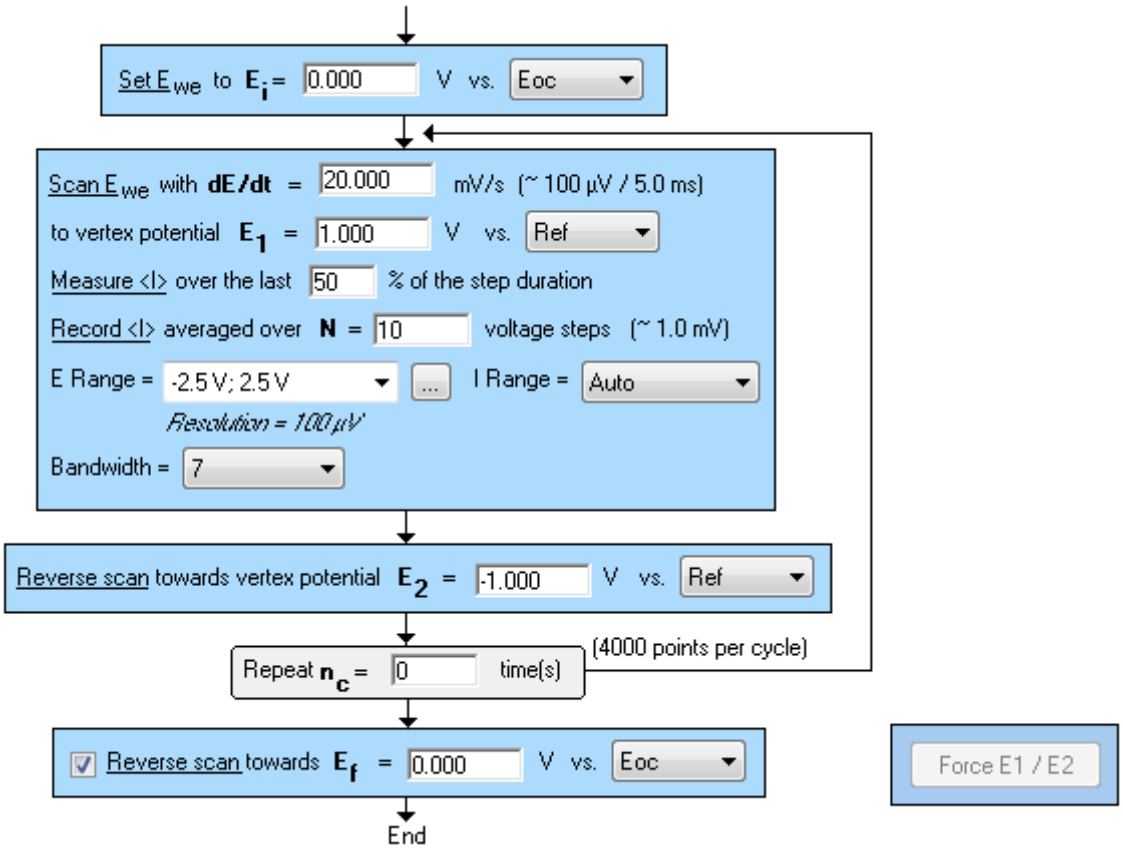


Fig. 3: Cyclic Voltammetry detailed flow diagram.

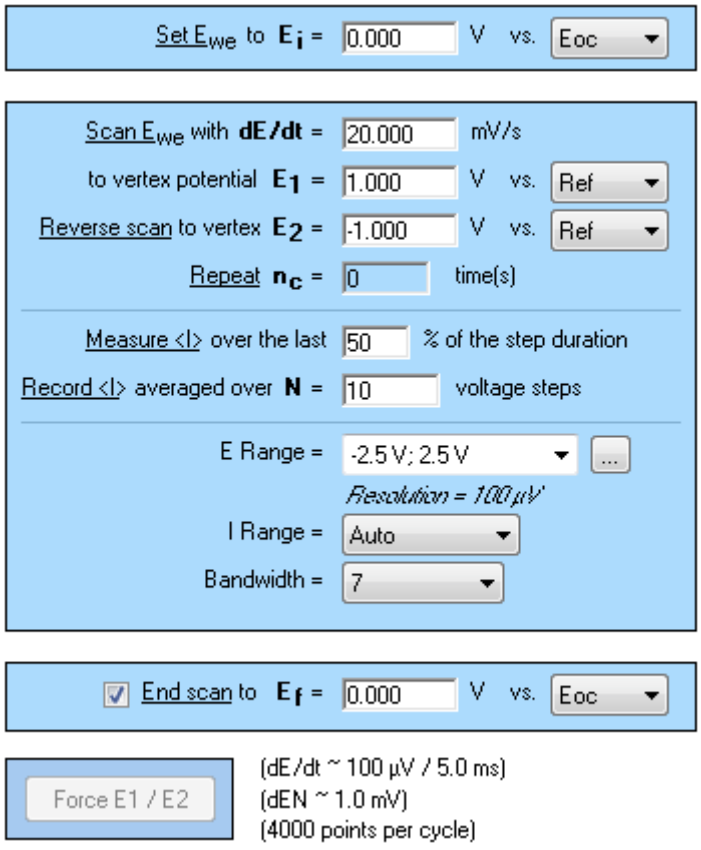


Fig. 4: Cyclic Voltammetry detailed column diagram.

- **Starting potential**

Set E_{we} to E_i = …….. V vs Ref/Eoc/Ectrl/Emeas
sets the starting potential in absolute (vs. Ref, the reference electrode potential in the cell) or according to the previous open circuit potential (E_{oc}) or controlled potential (E_{ctrl}) or Measured potential (E_{meas}).

- **First potential sweep with measurement and data recording conditions**

Scan E_{we} with dE/dt = ……. mV/s (≈ 300 µV/15 ms)
allows the user to set the scan rate in mV/s The potential step height and its duration are optimized by the software in order to be as close as possible to an analogic scan. Between brackets the potential step height and the duration are displayed according to the potential resolution defined by the user in the "**Advanced Settings**" window (see the corresponding section in the EC-Lab® software manual).

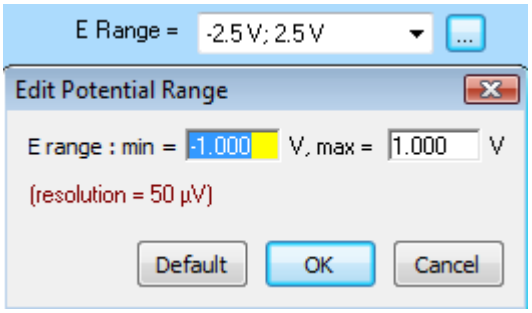
to vertex potential E_1 = ……. V vs Ref/Eoc/Ei.
fixes the first vertex potential value in absolute (vs. Ref) or according to the previous open circuit potential (E_{oc}), or according to the potential of the previous experiment (E_i).

Measure <I> over the last ……. % of the step duration
selects the end part of the potential step (from 1 to 100%) for the current average (<I>) calculation, to possibly exclude the first points where the current may be disturbed by the step establishment.
Note that the current average (<I>) is recorded at the end of the potential step to the data file.

Record <I> averaged over N = ……. voltage step(s)
averages N current values on N potential steps, in order to reduce the data file size and smooth the trace. The potential step between two recording points is indicated between brackets.
Once selected, an estimation of the number of points per cycle is displayed in the diagram.

E range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)



Some potential ranges are defined by default, but the user can customize the E Range in agreement of his system by clicking on ... .
Information on the resolution is given simultaneously to the change of minimum and maximum potentials.

I range = ……. bandwidth = …… .
enables the user to select the current range and the bandwidth (damping factor) of the potentiostat regulation.

- **Reverse scan**

Reverse scan towards vertex potential E_2 = …….. V vs Ref/Eoc/Ei.

runs the reverse sweep towards a 2nd limit potential. The vertex potential value can be set in absolute (Ref) or according to the previous open circuit potential (E_{oc}), or according to the potential of the previous experiment (E_i).

- **Repeat option for cycling**

Repeat n_c = …….. times
repeats the whole sequence n_c time(s). Note that the number of repeat does not count the first sequence: if $n_c = 0$ then the sequence will be done 1 time, $n_c = 1$ the sequence will be done 2 times, $n_c = 2$, the sequence will be 3 times...

- **Final potential**

Reverse scan (yes or no) towards E_F = …… V vs Ref/Eoc/Ei.
gives the possibility to end the potential sweep or to run a final sweep with a limit E_F.

Option: Force E_1 / E_2

While the experiment is running, clicking on this button allows the user to stop the potential scan, to set the instantaneous running potential E_{we} to E_{L1} or E_{L2} (according to the scan direction) and to start the reverse scan. Thus E_{L1} or (and) E_{L2} are modified and adjusted in order to reduce the potential range.
Clicking on this button is equivalent to click on the "Modify" button, enter the running potential as E_{L1} or E_{L2} and validate the changed parameters with the accept button. This button allows the user to perform the operation in a faster way when the limit potentials have not been properly estimated and to continue the scan without damage for the cell.

Note: it is highly recommended to adjust the potential resolution according to the experiment potential limit. This will considerably reduce the noise level and increase the plot quality.

Graph tool: Process data to Generate cycles

Since version 9.20 of EC-Lab® software it is no necessary to process the data file to generate the cycle number anymore. Now the software is autonomous to generate the cycle number by itself. For data files recorded before with older versions, the user must process the file to generate the cycle number.

Note: the automatic cycle number generation is available only with the CV and the CVA techniques.

Let's consider a data file made with an old software version. If the CV experiment is made of several cycles, the user can highlight the desired cycles. The way to do that is:

1) In the main menu bar, click on "Analysis / General Electrochemistry / Process data". The following window appears:

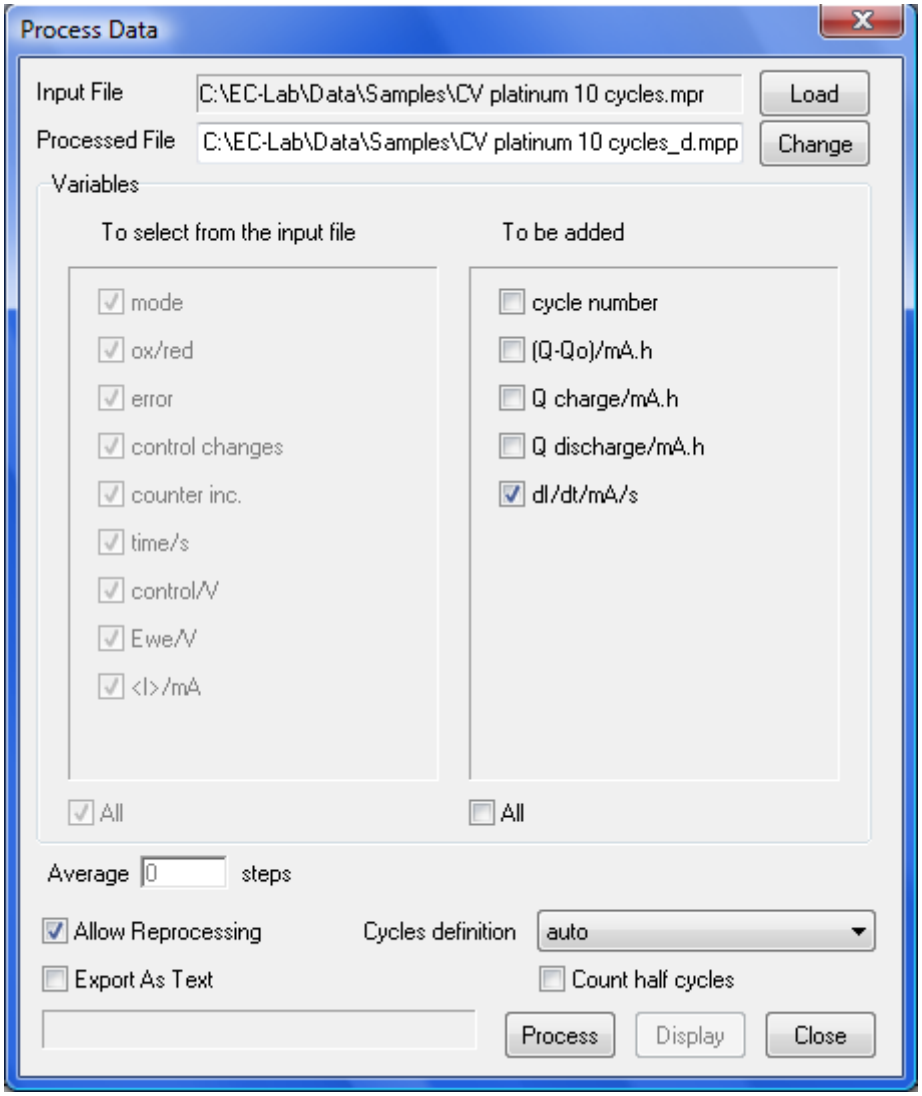


Fig. 5: Cyclic Voltammetry process window.

2) Select on the variables to process.
3) The process is finished when DONE appears.
4) Click on "**Display**" to plot the processed file

"n" has been added to the name of the processed file as an extension for the cycle number. The other variables that can be processed in a CV experiment are the charge exchanged during the oxidation step (Q charge) and during the reduction step (Q discharge) and the total charge exchanged since the beginning of the experiment ($Q-Q_0$).

2.1.3 CVA: Cyclic Voltammetry Advanced

The Cyclic Voltammetry Advanced (CVA) is an advanced version of the standard CV technique (report to the CV description part for more details about the technique). This technique has been implemented to offer the user all the extended capabilities that can be required during a potential sweep. In particular, a table has been added to the CVA to link potential sweeps with different scan rates. A vertex delay is possible at the beginning potential, at both vertex potentials and the final potential. For each of these delays, the current and the potential can be recorded at the user's convenience. A recording condition on cycles offers the possibility to not store every cycle. A reverse button can be used to reverse the potential sweep when necessary without modifying the vertex potentials (different from the Force button).

The technique is composed of:

- starting potential setting block,
- 1^{st} potential sweep with a vertex limit E_1,
- 2^{nd} potential sweep in the opposite direction with a vertex limit E_2,
- possibility to repeat n_c times the 1^{st} and the 2^{nd} potential sweeps,
- final conditional scan in the reverse direction to the previous one, with its own limit E_F.

Note that all the different sweeps have the same scan rate (absolute value). But it is possible to add sequences allowing to use different rates for each sequence.

The detailed diagram (the following figure) is made of three blocks:

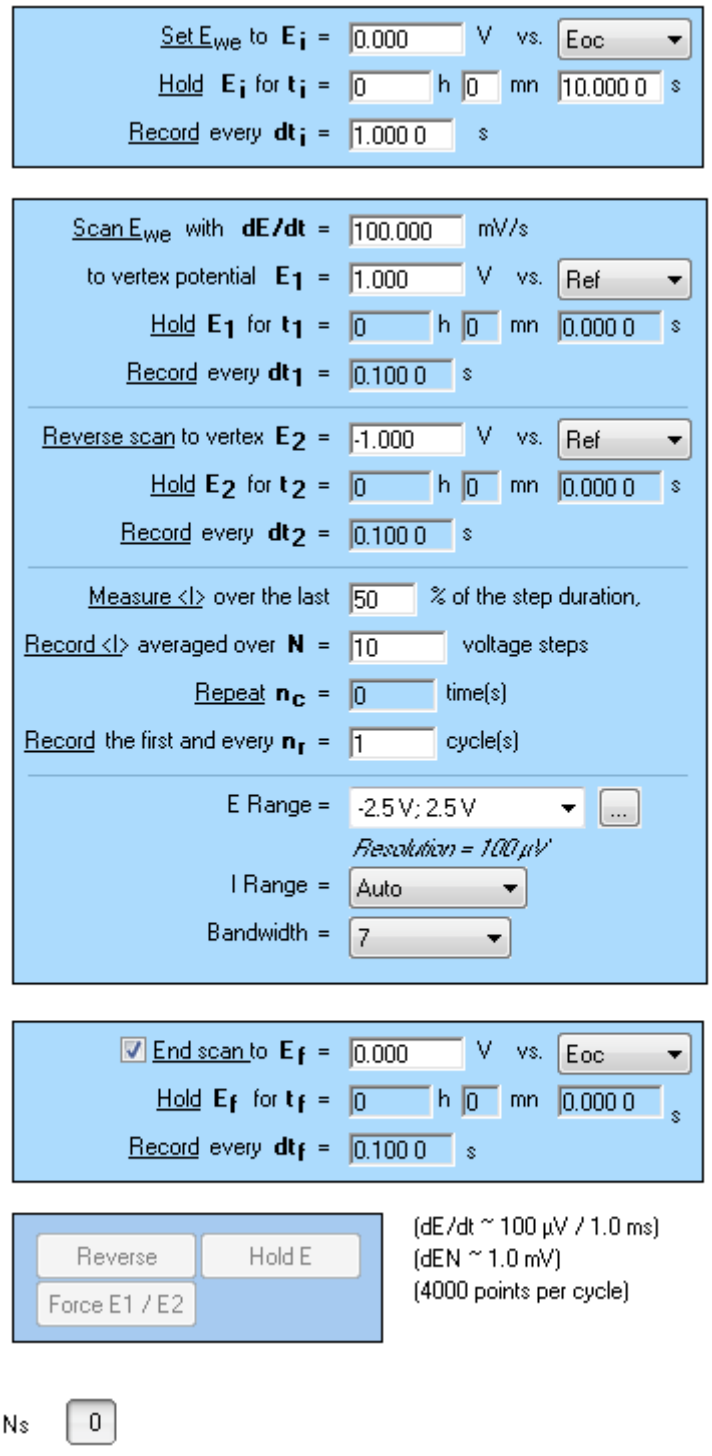


Fig. 6: Cyclic Voltammetry Advanced detailed diagram.

- **Starting potential:**

Set E_{we} to E_i = …….. V vs Ref/Eoc/Ectrl/Emeas
sets the starting potential in absolute (vs. Ref the reference electrode potential in the cell) or according to the previous open circuit potential (E_{oc}) or controlled potential (E_{ctrl}) or Measured potential (E_{meas}).

Hold E_i for t_i = ….. h ….. mn ….. s and record every dt_i = ….. s
offers the possibility to hold the initial potential for a given time and record data points during this holding period.

Note: This function can correspond to a preconditioning capability in an anodic stripping voltammetry experiment.

- **First potential sweep with measurement and data recording conditions:**

Scan E_{we} with dE/dt = ……. mV/s
allows the user to set the scan rate in mV/s The potential step height and its duration are optimized by the software in order to be as close as possible to an analogic scan. Between brackets the potential step height and the duration are displayed according to the potential resolution defined on the top of the window (in the "**Advanced**" tool bar**)**.

to vertex potential E_1 = ……. V vs Ref/Eoc/Ei.
fixes the first vertex potential value in absolute (Vs. Ref) or according to the previous open circuit potential (E_{oc}), or according to the potential of the previous experiment (E_i).

Hold E_1 for t_1 = ….. h ….. mn ….. s and record every dt_1 = ….. s
offers the ability to hold the first vertex potential for a given time and record data points during this holding period.

Measure <I> over the last ……. % of the step duration
selects the end part of the potential step (from 1 to 100%) for the current average (<I>) calculation, to possibly exclude the first points where the current may be disturbed by the step establishment.
Note that the current average (<I>) is recorded at the end of the potential step into the data file.

Record <I> averaged over N = ……. voltage step(s)
averages N current values on N potential steps, in order to reduce the data file size and smooth the trace. The potential step between two recording points is indicated between brackets.
Once selected, an estimation of the number of points per cycle is displayed into the diagram.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = ……. bandwidth = …… .
enables the user to select the current range and the bandwidth (damping factor) of the potentiostat regulation.

- **Reverse scan:**

Reverse scan towards vertex potential E_2 = …….. V vs Ref/Eoc/Ei.
runs the reverse sweep towards a 2nd limit potential. The vertex potential value can be set in absolute (vs. Ref) or according to the previous open circuit potential (E_{oc}) or according to the potential of the previous experiment (E_i).

Hold E_2 for t_2 = ….. h ….. mn ….. s and record every dt_2 = ….. s
offers the ability to hold the second vertex potential for a given time and to record data points during this holding period.

- **Repeat option for cycling:**

Repeat n_c = …….. times

repeats the whole sequence n_c time(s). Note that the number of repeat does not count the first sequence: if $n_c = 0$ then the sequence will be done 1 time, $n_c = 1$ the sequence will be done 2 times, $n_c = 2$, the sequence will be 3 times...

Record the first cycle and every n_r = ….. cycle(s)
offers the ability for the user to store only one cycle every n_r cycle in case of many cycles in the experiment. The first cycle is always stored.

- **Final potential:**

Reverse scan (yes or no) towards E_F = …… V vs Ref/Eoc/Ei.
gives the ability to end the potential sweep or to run a final sweep with a limit E_F.

Hold E_f for t_f = ….. h ….. mn ….. s and record every dt_f = ….. s
offers the possibility to hold the final potential for a given time and record data points during this holding period.

Options:

1- Reverse

While the experiment is running, clicking on this button allows the user to reverse the potential scan direction instantaneously. Contrary to the **Force** button, the vertex potential is not replaced by the current potential value. E_1 and E_2 are kept.

2- Force E_1 / E_2

While the experiment is running, clicking on this button allows the user to stop the potential scan, set the instantaneous running potential value E_{we} to E_1 or E_2 (according to the scan direction), and start the reverse scan. Thus E_1 or (and) E_2 are modified and adjusted in order to reduce the potential range.
Clicking on this button is equivalent to click on the "Modify" button. Enter the running potential as E_1 or E_2 and validate the changed parameters with the accept button. This button enables the user to perform the operation faster when the limit potentials have not been properly estimated and continue the scan without damaging the cell.

Note: it is highly recommended that the user adjusts the potential resolution (from 300 µV for 20 V amplitude to 5 µV for 0.2 V amplitude with a SP-150, VSP or VMP3) according to the experiment potential limit. This will considerably reduce the noise level and increase the plot quality.

3- Hold E

While the experiment is running, clicking in this button allows the user to hold the actual potential. Clicking again on this button the experiment will continue in the same direction.

4- Table/Sequence

The CVA technique is equipped with a table, the ability to add sequences. This allows the user to link several sequences of CVA with different scan rates or different vertex potentials.

Graph tool: Process Data
When the CVA experiment is made, the user can extract the charge quantities exchanged during the anodic step (Q charge), the cathodic step (Q discharge), and the total charge exchanged since the beginning of the experiment ($Q-Q_0$).

2.1.4 Linear Sweep Voltammetry: LSV

The linear sweep voltammetry technique is a standard electrochemical protocol. Unlike the CV, no backward scan is done, only the forward scan is applied. This technique is specially dedicated to RDE (Rotating Disk Electrode) or RRDE (Rotating Ring Disk Electrode) investigations which allows user to carry out steady-state measurements. This leads to the determination of redox potential and kinetic parameters. *The "External Device Configuration" of EC-Lab menu makes easy to control and measure the rotating rate of the R(R)DE device.*

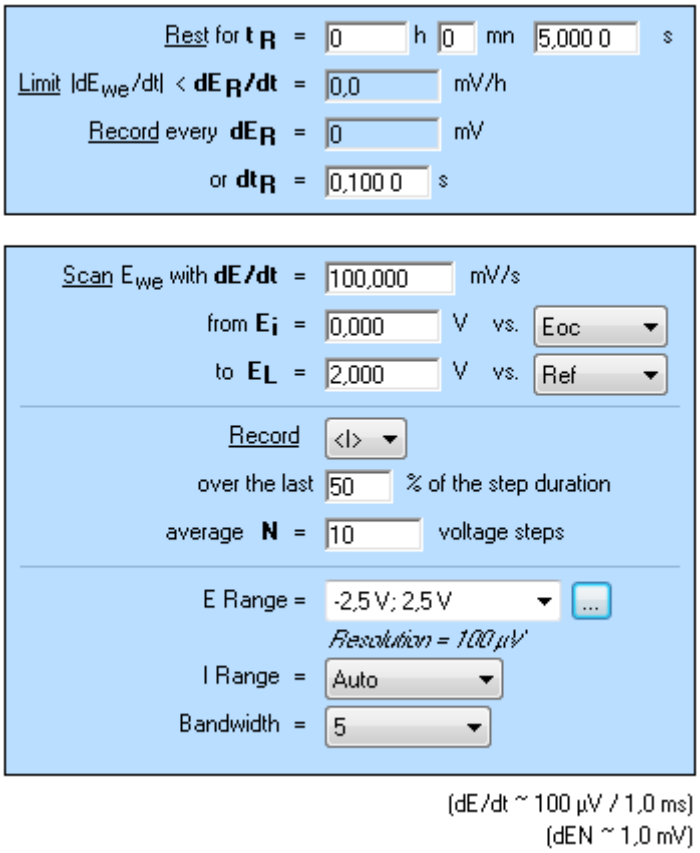


Fig. 7: Linear Sweep Voltammetry detailed diagram.

- **Rest period**

Rest for t_R = h mn s
fixes a defined time duration t_R for recording the rest potential.
or until $|dE_{we}/dt| < |dE_R/dt|$ = mV/h
stops the rest sequence when the slope of the open circuit potential with time, $|dE_R/dt|$ becomes lower than the set value (value 0 invalidates the condition).

Record E_{we} every dE_R = mV or dt_R = s
allows the user to record the working electrode potential whenever the change in the potential is ≥ dE_R with a minimum recording period in time dt_R.

- **Potential sweep with measurement and data recording conditions:**

Scan E_{we} with dE/dt = ……. mV/s
allows the user to set the scan rate in mV/s The potential step height and its duration are optimized by the software in order to be as close as possible to an analogic scan. Between

brackets the potential step height and the duration are displayed according to the potential resolution defined on the top of the window (in the "**Advanced**" tool bar**)**.

From Ei = ...V vs. Ref/Eoc/Ei.
fixes the intial potential value in absolute (Vs. Ref) or according to the previous open circuit potential (E_{oc}), or according to the potential of the previous experiment (E_i).

to E_L = ……. V vs Ref/Eoc/Ei.
fixes the limit potential value in absolute (Vs. Ref) or according to the previous open circuit potential (E_{oc}), or according to the potential of the previous experiment (E_i).

Hold E_1 for t_1 = ….. h ….. mn ….. s and record every dt_1 = ….. s
offers the ability to hold the first vertex potential for a given time and record data points during this holding period.

Record <I> over the last ……. % of the step duration
selects the end part of the potential step (from 1 to 100%) for the current average (<I>) calculation, to possibly exclude the first points where the current may be disturbed by the step establishment.
Note that the current average (<I>) is recorded at the end of the potential step into the data file.

averaged over N = ……. voltage step(s)
averages N current values on N potential steps, in order to reduce the data file size and smooth the trace. The potential step between two recording points is indicated between brackets.
Once selected, an estimation of the number of points per cycle is displayed into the diagram.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = ……. bandwidth = …… .
enables the user to select the current range and the bandwidth (damping factor) of the potentiostat regulation.

2.1.5 Chrono I/Q: Chronoamperometry / Chronocoulometry

The basis of the controlled-potential techniques is the measurement of the current response to an applied potential step.
Chronoamperometry involves stepping the potential of the working electrode from an initial potential, at which no faradic reaction generally occurs, to a potential E_i at which no electroactive species exist (at the beginning of the experiment). The current-time response reflects the change in the concentration gradient in the vicinity of the surface. Chronoamperometry is often used for measuring the diffusion coefficient of electroactive species or the surface area of the working electrode. This technique can also be applied to the study of electrode processes mechanisms.
An alternative and very useful mode for recording the electrochemical response is to integrate the current, so that one obtains the charge passed as a function of time. This is the chronocoulometric mode that is particularly used for measuring the quantity of adsorbed reactants.
The potential steps can be set to a fixed value (E_i) or relatively to the last rest potential ($E_{<oc>}$) or the last controlled potential (E_{pc}).

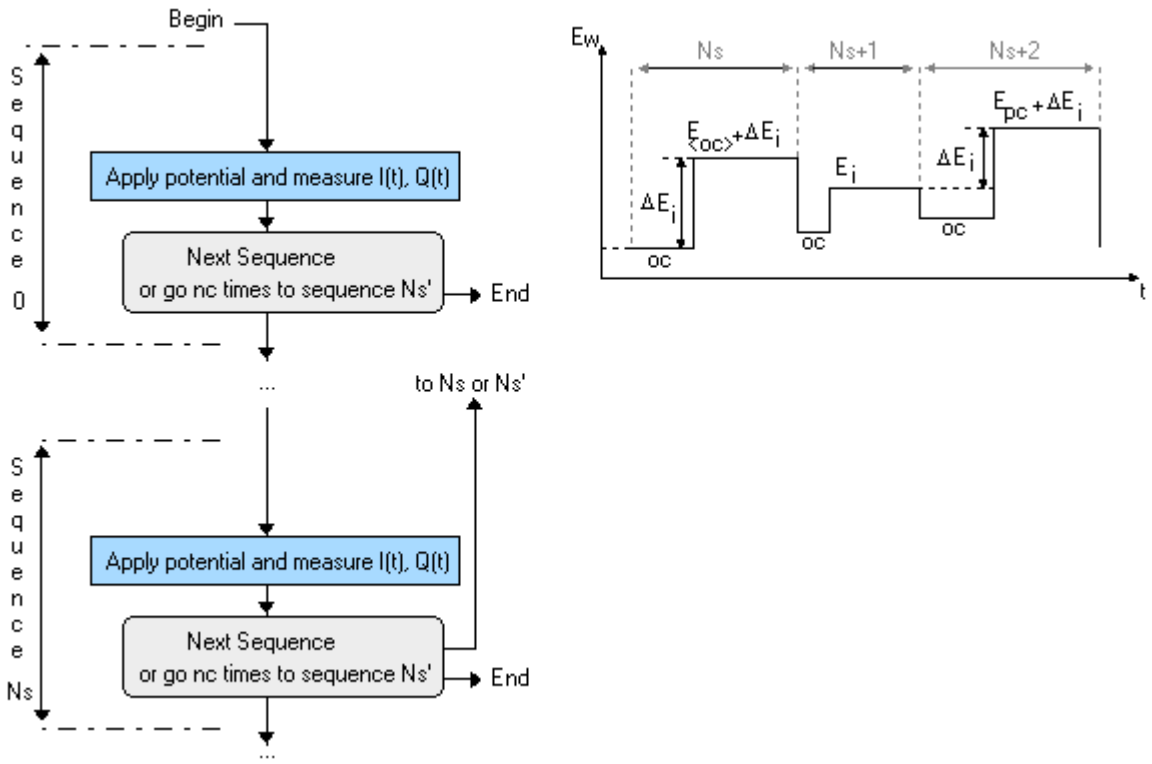


Fig. 8: Chronoamperometry / Chronocoulometry general diagram.

The detailed diagram is composed of two blocks:

- potential step,
- loop.

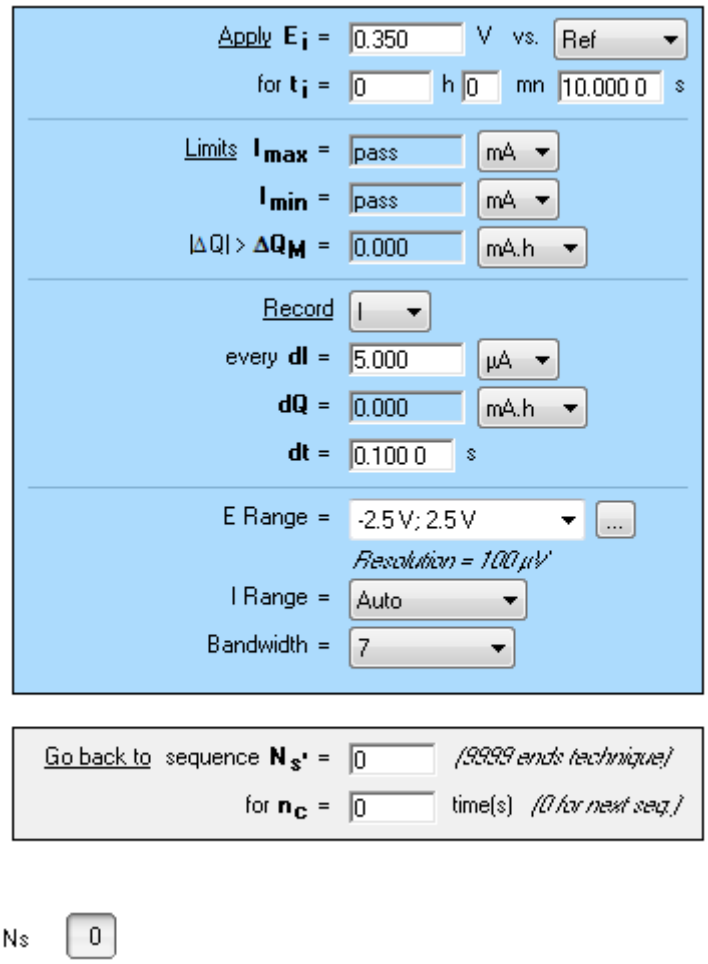


Fig. 9: Chronoamperometry / Chronocoulometry detailed diagram and table.

- **Potential step with data recording conditions:**

1) Potential step

Apply E_i = …… V vs Ref/Eoc/Ectrl/Emeas.
the potential step is defined in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}), controlled potential (E_{ctrl}) or measured potential (E_{meas}).

for t_i = …….. h …… mn …….. s
fixes the potential step duration.

limit |I| to I_{Max} = ….. pA/…/A and $|\Delta Q| < \Delta Q_M$ = fA.h/…/A.h/pC/…/kC.

I_{min} = …… pA/…/A
curtails the step duration if the current or charge limit is reached. If the limit is reached, the loop condition (go to $N_{s'}$ for n_c times), if set, is not used, and the program continues to the next sequence (N_s + 1).
The $|\Delta Q|$ value is the integral charge for the current sequence. This value is not reset if there is a loop on the same sequence ($N_{s'} = N_s$).
0 values disable the tests.

2) Recording conditions

Record I every dI_p = …. pA/…/A, dQ_p = …… fA.h/…/A.h/pC/…/kC and dt_p = …. S

<I> every dts = …….. s

you can record either an instantaneous current value I or an averaged current value <I>. The recording conditions during the potential step depend on the chosen current variable. For the instantaneous current the recording values can be entered simultaneously. Then it is the first condition reached that determines the recording. A zero value disables the recording for each criterion. For the averaged current the user defines the time for the average calculation. In that case the data points are recorded in the channel board memory every 200 µs for the VMP2, VMP3, VSP, SP-150, SP-50, BiStat and the SP-300, SP-200, HCPs and CLB-500 and 20 ms for the VMP and the MPG.
Leave dI alone for Chronoamperometry experiments, and dQ for Chronocoulometry experiments.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I range = ……. bandwidth = …… .
enables the user to select the current range and the bandwidth (damping factor) of the potentiostat regulation.

- **Loop**

goto Ns' = for nc = time(s)
allows the experiment to loop to a previous line $N_{s'}$ (<= N_s) for n_c times. The number of loops starts while the loop block is reached. For example, on N_s = 3, if one enters goto $N_{s'}$ = 2 for n_c = 1 time, the sequence N_s = 2, N_s = 3 will be executed 2 times.
n_c = 0 disables the loop and the execution continue to the next line ($N_{s'} = N_s + 1$). If there is no next line, the execution stops.
Report to the battery techniques section (3.1, page 83) for more details on loop conditions.
Here, it is possible to loop to the first instruction (N_s = 0) and the current instruction ($N_{s'} = N_s$). This is different from battery experiments (GCPL and PCGA) where the first instruction has a special meaning and there is still a loop on the current instruction.
This technique uses a sequence table. Sequences of the Chronoamperometry / Chronocoulometry technique can be chained using the "Table" frame. The first sequence is N_s = 0. Each line of the table (N_s) corresponds to a rest and potential step sequence. The sequences lines are executed one after the other, and it is possible to loop to a previous sequence line ($N_{s'}$).

Example: Setting $E_i = E_{oc} + \Delta E_{i0}$ on the first sequence (N_s = 0) and $E_i = E_{pc} + \Delta E_{i1}$ on the next sequence (N_s = 1), with a loop on the same sequence (goto $N_{s'}$ = 1), will perform the next recording:

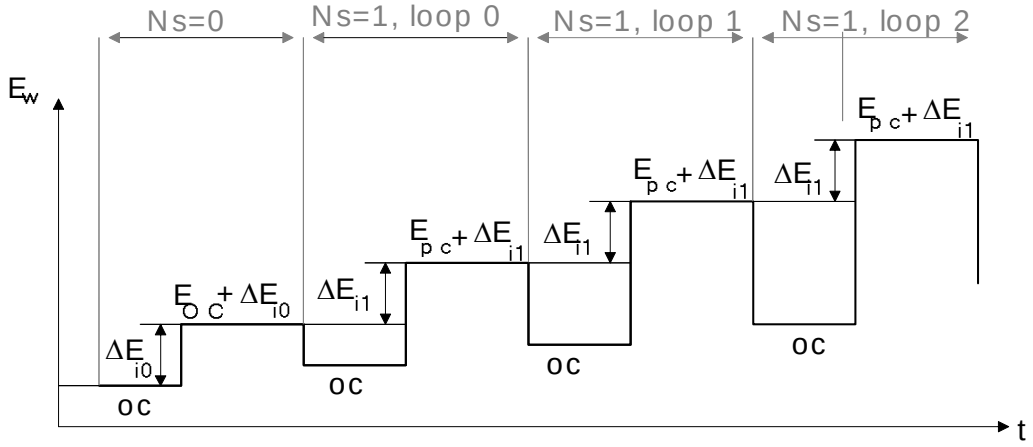


Fig. 10: Chronoamperometry / Chronocoulometry example.

Process: chronocoulometry

A process is associated with chronoamperometry / chronocoulometry technique (see figure below). The variables that can be processed are the same as for the CV technique and the charge variation dQ (chronocoulometry).

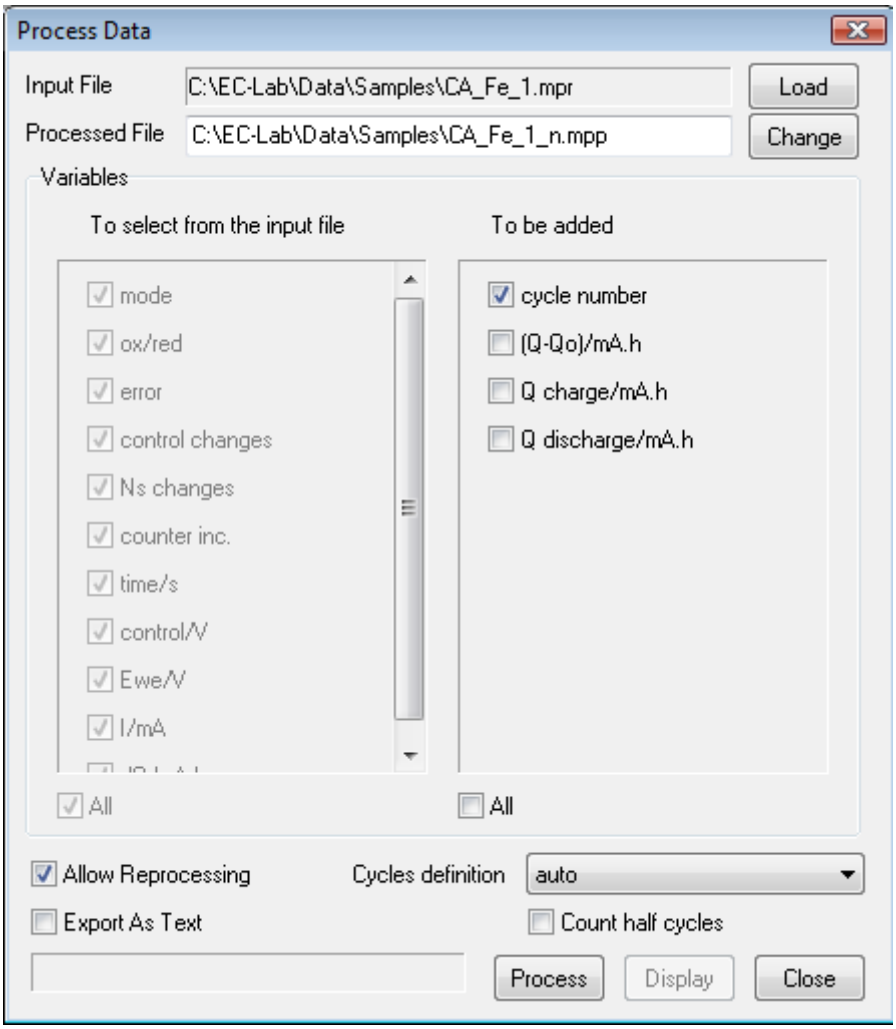


Fig. 11: Chronoamperometry/chronocoulometry processing window.

Note: In this technique the first and last data points of each potential steps are not recorded automatically.

2.1.6 CP: Chronopotentiometry

The Chronopotentiometry is a controlled current technique. The current is controlled and the potential is the variable determined as a function of time. The chronopotentiometry technique is similar to the Chronoamperometry / Chronocoulometry technique, potential steps being replaced by current steps. The constant current is applied between the working and the counter electrode.

This technique can be used for different kinds of analysis or to investigate electrode kinetics. But, it is considered less sensitive than voltammetric techniques for analytical uses. Generally, the curves $E_{we} = f(t)$ contain plateaus that correspond to the redox potential of the electroactive species.

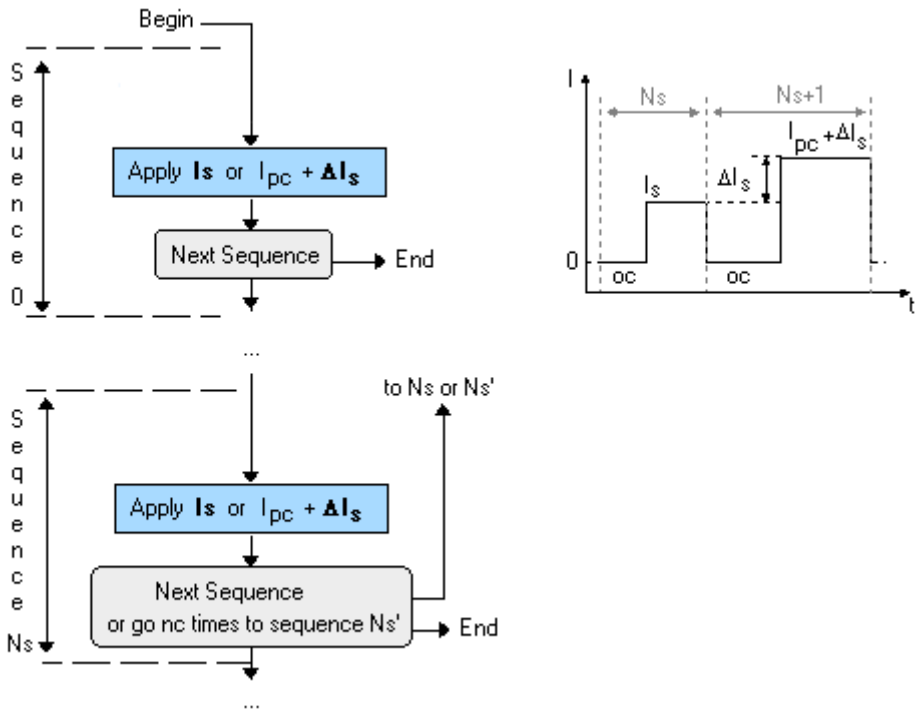


Fig. 12: Chronopotentiometry general diagram.

This technique uses a sequence table also. Each line of the table (N_s) corresponds to a rest and current step sequence.

The detailed diagram is made of two blocks:

- current step,
- loop.

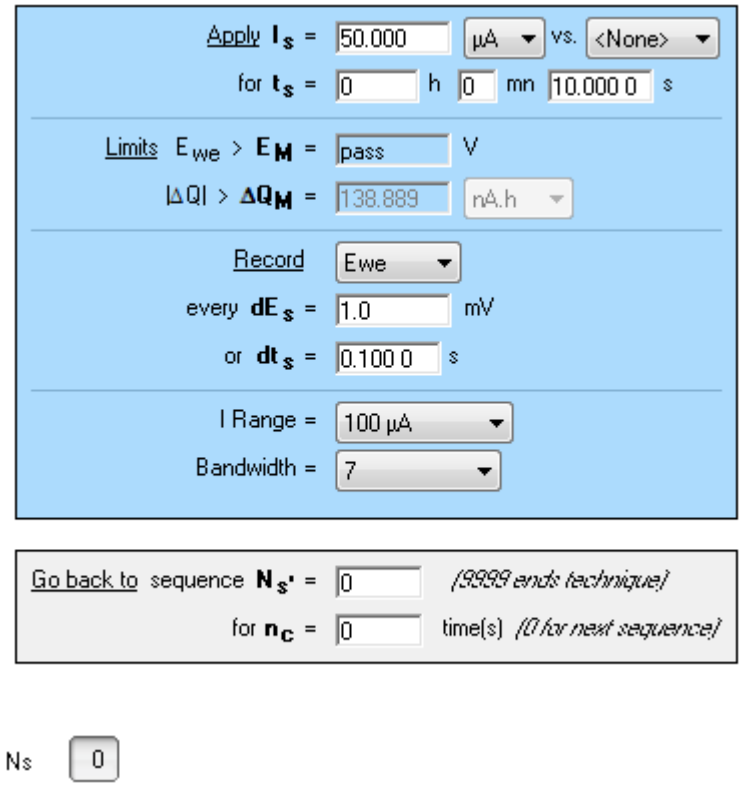


Fig. 13: Chronopotentiometry detailed diagram.

- **Current step**

Apply I_s = ……. pA/…/A vs. <none>/Ictrl/Imeas.
the current step is set to a fixed value or relatively to the previous controlled current I_{ctrl}, that is the current of the previous sequence current step block or to the previous measured current I_{meas}. This option is not available on the first sequence (N_s = 0).
To select the current step type, check the option box.

for t_s = …… h …… mn …… s
fixes the current step duration.

limit $|E_{we}| < E_M$ = …….. mV and $|\Delta Q| < \Delta Q_M$ = ……. fA.h/…/A.h/pC/…/kC
curtails the step duration if the potential or charge limit is reached. If the limit is reached, the loop condition (go to $N_{s'}$ for n_c times), if set, is not used, and the program continues to the next sequence (N_s + 1).
The $|\Delta Q|$ value is the integral charge for the current sequence. This value is not reset if there is a loop on the same sequence ($N_{s'} = N_s$).
0 values disable the tests.

Record E_{we} or <E_{we}> every dE_s = …… mV, and at least every dt_s = …….. s
defines the recording conditions during the potential step. 0 values disable the recording condition, and the corresponding box stays green. These values can be entered simultaneously, and this is the first condition that is reached that determines the recording.

I Range, Bandwidth
selects the current range and bandwidth values for the whole sequences.

- **Loop**

goto sequence Ns' = ……. for nc = …… time(s)

gives the ability to loop to a previous sequence $N_{s'}$ (<= N_s) for n_c times. Sequences of the chronopotentiometry technique can be chained using the "Table" frame. The first sequence is $N_s = 0$.
The number of loops starts while the loop block is reached. For example, on $N_s = 3$, if one enters goto $N_{s'} = 2$ for $n_c = 1$ time, the sequence $N_s = 2$, $N_s = 3$ will be executed 2 times.
$n_c = 0$ disables the loop and the execution continue to the next line ($N_{s'} = N_s + 1$). If there is no next line, the execution stops.
Report to the battery techniques section (3.1, page 83) for more details on loop conditions.
Thus, it is possible to loop to the first instruction ($N_s = 0$) and the current instruction ($N_{s'} = N_s$). That is different from the battery experiments (GCPL and PCGA) where the first instruction has a special meaning and where there is still a loop on the current instruction.

Process:

A process function is associated with chronopotentiometry technique. The variables that can be processed are the same as for the CV technique. For more details about CP process see the previous CV part.

Note: In this technique the first and last data points of each current steps are not recorded automatically.

2.1.7 SV: Staircase Voltammetry

Staircase voltammetry (SV) is one of the most widely used techniques for acquiring qualitative information about electrochemical reactions. SV like cyclic voltammetry provides information on redox processes, heterogeneous electron-transfer reactions and adsorption processes. It offers a rapid location of redox potential of the electroactive species.
SV consists of linearly scanning the potential of a stationary working electrode using a triangular potential waveform with a potential step amplitude and duration defined by the user. During the potential sweep, the potentiostat measures the current resulting from electrochemical reactions (consecutive to the applied potential). The cyclic voltammogram is a current response as a function of the applied potential.
Contrary to the cyclic voltammetry, the potential steps are not as small as possible but adjusted exactly to the user's convenience.

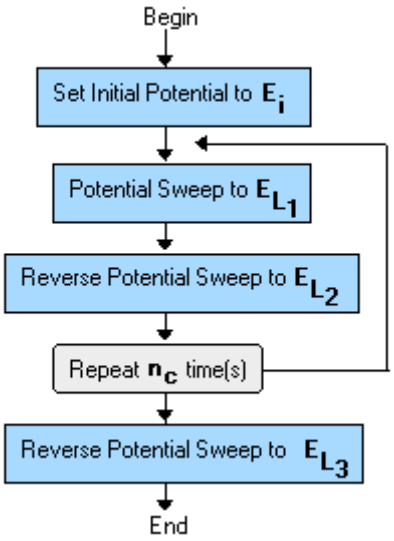


Fig. 14: General diagram for Staircase Voltammetry.

This technique is similar to the usual cyclic voltammetry, but using significant digital potential staircase (i.e. it runs defined potential increment regular in time).

The technique is composed of:
- a starting potential setting block,
- a 1st potential sweep with a final limit E_1,
- a 2nd potential sweep in the opposite direction with a final limit E_2,
- the possibility to repeat n_c times the 1st and the 2nd potential sweeps,
- a final conditional scan reverse to the previous one, with its own limit E_F.

Note that all the different sweeps have the same scan rate (absolute value).

The detailed diagram (on the following figure) is made of three blocks:

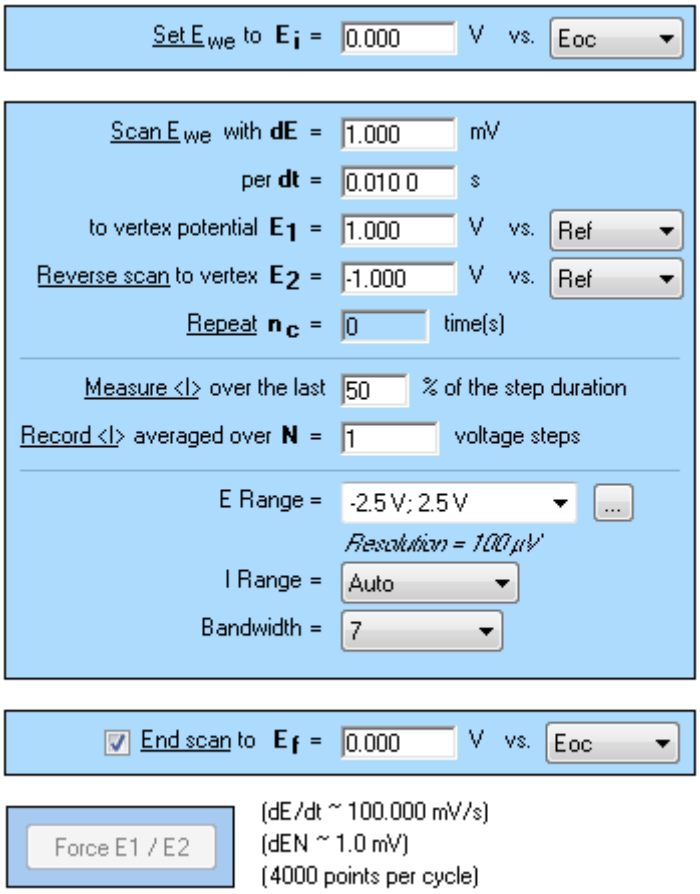


Fig. 15: Staircase Voltammetry detailed diagram.

- **Starting potential:**

Set E_{we} to E_i = …….. V vs Ref/Eoc/Ectrl/Emeas
sets the starting potential in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}), controlled potential (E_{ctrl}) or measured potential (E_{meas}).

- **First potential sweep with measurement and data recording conditions:**

Scan E_{we} with dE = ……. mV per dt = ……. s (≈ 300 µV/15 ms)

allows the user to set the potential step height in mV and the step duration in s. Between brackets the scan rate is displayed according to the potential resolution defined by the user in the "**Advanced Settings**" window (see the corresponding section in the EC-Lab® software manual for more details).

to vertex potential E_1 = ……. V vs Ref/Eoc/Ei.
fixes the first vertex potential value in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}), or to the initial potential (E_i).

- **Reverse scan**

Reverse scan towards vertex potential E_2 = …….. V vs Ref/Eoc/Ei.

runs the reverse sweep towards a 2nd limit potential. The vertex potential value can be set in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}) or to the initial potential (E_i).

- **Repeat option for cycling**

Repeat n_c = …….. times

repeats the whole sequence n_c time(s). Note that the number of repeat does not count the first sequence: if $n_c = 0$ then the sequence will be done 1 time, $n_c = 1$ the sequence will be done 2 times, $n_c = 2$, the sequence will be 3 times...

Measure <I> over the last ……. % of the step duration
selects the end part of the potential step (from 1 to 100%) for the current average (<I>) calculation, to possibly exclude the first points where the current may be disturbed by the step establishment.
Note that the current average (<I>) is recorded at the end of the potential step in the data file.

Record <I> averaged over N = ……. voltage step(s)
averages N current values on N potential steps, in order to reduce the data file size and smooth the trace. The potential step between two recording points is indicated between brackets.
Once selected, an estimation of the number of points per cycle is displayed in the diagram.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I range = ……. bandwidth = …… .
enables the user to select the current range and the bandwidth (damping factor) of the potentiostat regulation.

- **Final potential**

Reverse scan (yes or no) towards E_F = …… V vs Ref/Eoc/Ei.
give the possibility to end the potential sweep or to run a final sweep with a limit E_F.

Option: Force E_1 / E_2

While the experiment is running, clicking on this button allows the user to stop the potential scan, set the instantaneous running potential E_{we} to E_1 or E_2 (according to the scan direction), and start the reverse scan. Thus E_{L1} and/or E_{L2} are modified and adjusted in order to reduce the potential range.
Clicking on this button is equivalent to click on the "Modify" button. Enter the running potential as E_1 or E_2 and validate the changed parameters with the accept button. This button

allows the user to perform the operation faster when the limit potentials have not been properly estimated and to continue the scan without damage to the cell.

Note: it is highly recommended to adjust the potential resolution according to the experiment potential limit. This will considerably reduce the noise level and increase the plot quality.

Graph tool: Generate cycles

See the cyclic voltammetry technique for more details.

2.1.8 LASV: Large Amplitude Sinusoidal Voltammetry

Large Amplitude Sinusoidal Voltammetry (LASV) is an electrochemical technique where the potential excitation of the working electrode is a large amplitude sinusoidal waveform. Similar to the cyclic voltammetry (CV) technique, it gives qualitative and quantitative information on the redox processes. In contrast to the CV, the double layer capacitive current is not subject to sharp transitionsat reverse potentials. As the electrochemical systems are non-linear the current response exhibits higher order harmonics at large sinusoidal amplitudes. Valuable information can be found from data analysis in the frequency domain.

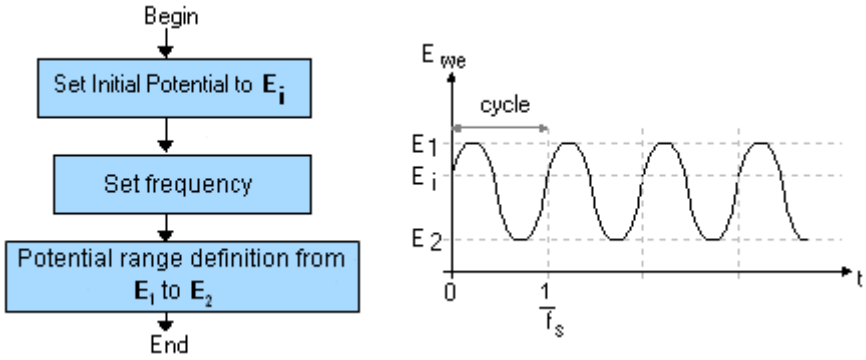


Fig. 16: General diagram for Large Amplitude Sinusoidal Voltammetry.

This technique is similar to usual cyclic voltammetry, but using a frequency to define the scan speed. The curve of the potential excitation can be compared to a large amplitude sinusoidal waveform.

The technique is composed of:
- a starting potential setting block,
- a frequency definition f_s,
- a potential range definition from E_1 to E_2,
- the possibility to repeat n_c times potential scan.

The detailed diagram (on the following figure) is made of two blocks:

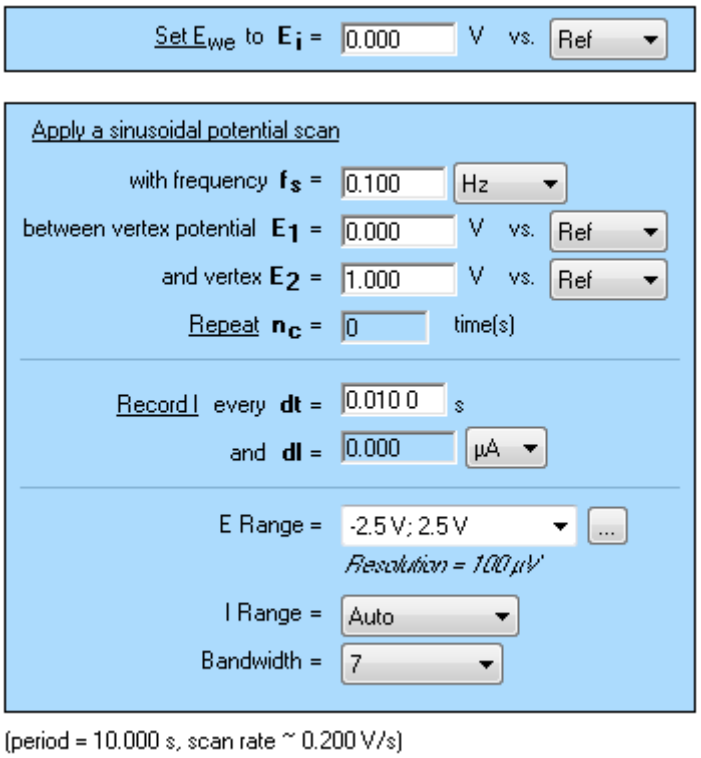


Fig. 17: Staircase Voltammetry detailed diagram.

- **Starting potential:**

Set E_{we} to E_i = …….. V vs Ref/Eoc/Ectrl/Emeas
sets the starting potential in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}) or controlled potential (E_{ctrl}) or Measured potential (E_{meas}).

- **Frequency and Potential range definition with measurement and data recording conditions:**

Apply a sinusoidal potential scan
With frequency fs = ….. kHz/Hz/mHz/µHz
Allows the user to set the value of frequency which will define the scan rate.

Between vertex potential E1 = ….. V vs Ref/Eoc/Ei
Fixes the first vertex potential value in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}) or previous potential (E_i).

And vertex E2 = …V vs vs Ref/Eoc/Ei
Fixes the second vertex potential value in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}) or previous potential (E_i).

Repeat n_c = …….. times
repeats the whole sequence n_c time(s). Note that the number of repeat does not count the first sequence: if n_c = 0 then the sequence will be done 1 time, n_c = 1 the sequence will be done 2 times, n_c = 2, the sequence will be 3 times...

Record every dt = ….. s and dI = ….. nA/µA/mA/A

offers the possibility to record I with two conditions on the current variation dI and (or) on time variation.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I range = ……. bandwidth = …… .
enables the user to select the current range and the bandwidth (damping factor) of the potentiostat regulation.

Note: this technique includes sequences to link sines with different amplitude for example.

2.1.9 Alternating Current Voltammetry (ACV)

Alternating Current Voltammetry (ACV) is assimilated to a faradaic impedance technique. On this technique a sinusoidal voltage of small amplitude (A) with a constant frequency (f_s) is superimposed on a linear ramp between two vertex potentials (E_1, E_2). The potential sweep is defined as follow $E(t) = E_{1,2} \pm \frac{dE}{dt} t + A\sin(2.\pi.f_s.t)$. Typically, the linear ramp varies on a long time scale compared to the superimposed AC variation.
Like the pulsed techniques, ACV discriminates the faradaic current from the capacitive one. Consequently, ACV can be used for analytical purpose. Moreover this technique can also be used for investigating electrochemical mechanism, for instance superimposition of forward and backward scan characterize a reversible redox system.

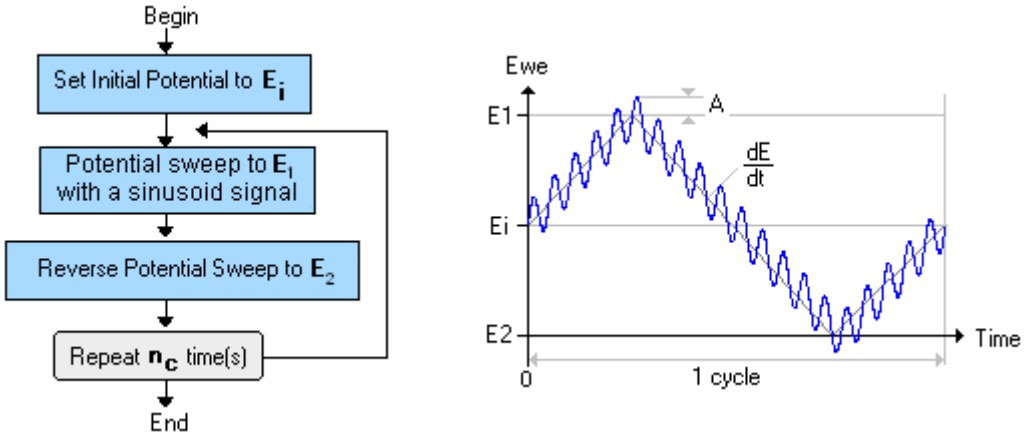


Fig. 18: General diagram for Alternating Current Voltammetry.

This technique corresponds to usual cyclic voltammetry with a superimposition of a sinusoid.

The technique is composed of:
- a starting potential setting block,
- a 1st potential sweep with a final limit E_1 and a sinusoid superimposed,
- a 2nd potential sweep in the opposite direction with a final limit E_2 (option),
- the possibility to repeat n_c times the 1st and the 2nd potential sweeps.

Note that all the different sweeps have the same scan rate (absolute value).

The detailed flow diagram (on the following figure) is made of three blocks (Fig. 17):

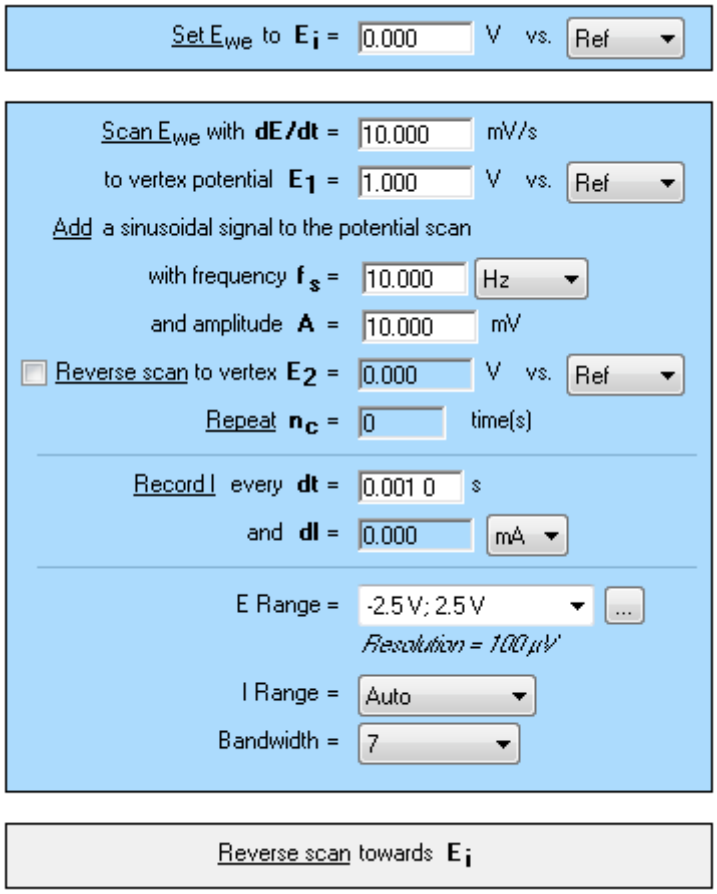


Fig. 19: Alternating Current Voltammetry detailed diagram.

- **Starting potential**

Set E_{we} to E_i = …….. V vs Ref/Eoc/Ectrl/Emeas
sets the starting potential in absolute (vs. Ref, the reference electrode potential in the cell) or according to the previous open circuit potential (E_{oc}) or controlled potential (E_{ctrl}) or Measured potential (E_{meas}).

- **Potential sweep with superimposition of sinusoid signal and measurement and data recording conditions**

Scan E_{we} with dE/dt = ……. mV/s
allows the user to set the scan rate in mV/s The potential step height and its duration are optimized by the software in order to be as close as possible from an analogic scan.

to vertex potential E_1 = ……. V vs Ref/Eoc/Ei
fixes the first vertex potential value in absolute (vs. Ref) or according to the previous open circuit potential (E_{oc}) or previous potential (E_i).

Add a sinusoidal signal to the potential scan
With frequency fs = …….. kHz/Hz/mHz/µHz
And amplitude A = … mV
defines the properties (frequency and amplitude) of the sinusoidal signal.

[] Reverse scan to vertex E_2 = … V vs Ref/Eoc/Ei

offers the possibility to do a reverse scan and to fixe the value of the vertex potential value in absolute (vs. Ref) or according to the previous open circuit potential (E_{oc}) or previous potential (E_i).

Repeat n_c = …….. times
repeats the whole sequence n_c time(s). Note that the number of repeat does not count the first sequence: if $n_c = 0$ then the sequence will be done 1 time, $n_c = 1$ the sequence will be done 2 times, $n_c = 2$, the sequence will be 3 times...

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I range = ……. bandwidth = …… .
enables the user to select the current range and the bandwidth (damping factor) of the potentiostat regulation.

Reverse scan towards E_i
offers the possibility to do a reverse scan towards E_i.

2.2 Electrochemical Impedance Spectroscopy

Methods employing excitation of an electrochemical cell by a sinusoidal signal were first employed as a way of measuring the rate constant of fast electron transfer reactions at short times. Now the interest rests on the complete analysis of what are often complicated processes involving surface and solution reactions (electrode and electrolyte). Among the modern computational techniques, the Electrochemical Impedance spectroscopy (EIS) is now a powerful tool for examining many chemical and physical processes in solution as well as in solids. EIS has uses in corrosion, battery, fuel cell development, sensors and physical electrochemistry and can provide information on reaction parameters, corrosion rates, electrode surfaces porosity, coating, mass transport, and interfacial capacitance measurements.
The VMP2/Z / VMP3 / VSP / SP-150 boards are designed to perform impedance measurements independently or simultaneously, from 10 µHz to 1 MHz (200 kHz for channel boards delivered before July 2005). For SP-300 and SP-200, the maximum frequency is 7 MHz.

Since the EC-Lab® version 9.50, a multisinus measurement was introduced for the impedance measurement techniques.

2.2.1 Principles of multisine measurements

To spare time during impedance measurements especially in low frequencies range but also to avoid the measurement drifts - if the system changes quickly with time - it may be useful to use a multisine excitation signal.
Indeed, to get information at different frequencies with an excitation signal, the system has to be excited successively by one frequency at the time, resulting in a very long experiment. Indeed, the total time taken for the complete analysis is the sum of the individual measurement times. This is the case for the single sine measurement.
In multisine measurement, all the frequencies are analyzed at the same time. Then, the use of Schroeder multisine, simultaneous application of several sinewave, allows the user to save a lot of time, especially for measurement at low frequency.

The multisine signal is thus defined as the sum of sinusoids at different frequencies having the same programmable amplitudes *A* - resulting in a time signal - and different phases Φ, with the following formula [1]:

$$u(t) = A\sum_{k=1}^{N}\cos(2\Pi f_k t + \Phi_k) \text{ with the phase } \Phi_k = \Phi_1 - 2\Pi\sum_{n=1}^{k-1}\frac{(k-n)}{N} \text{ [1].}$$

The EIS multisine measurement developed in EC-Lab® software is defined in order to minimize the crest factor defined by:

$$Cr(u) = \frac{u_M - u_m}{2u_{eff}} \text{ with } u_{eff} = A\sqrt{\frac{N}{2}} \text{ [2]}$$

With multisine calculation defined in EC-Lab® software, the crest factor values are included between 2 and 3.

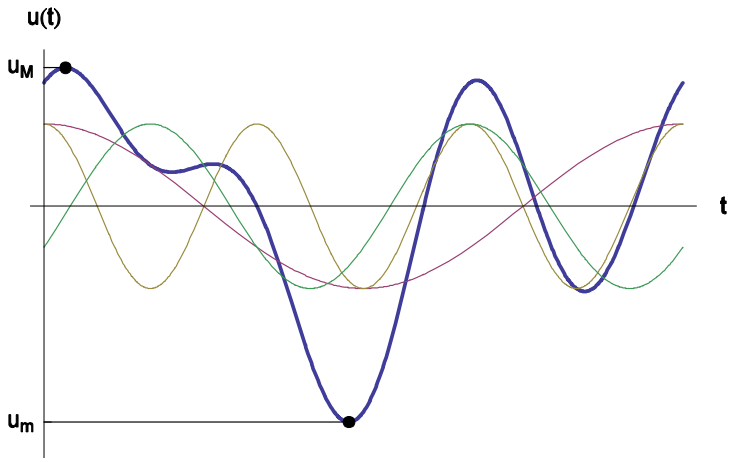


Fig. 20: Scheme of multisine signal.

To avoid a large excitation at the sine origin that could damage the electrochemical cell, all the sine are out of phase the ones compared to the others. Indeed, in multisine measurement a multiplicative factor can be applied on the signal amplitude – which can reach U_M or U_m values. Generally, it is better to not exceed 50 mV of sinus amplitude. Indeed, if the excitation – which is the sum of the maximum amplitude of all the applied frequencies – is too large, this might result in a measurement in the non-linear response domain of the electrochemical cell. Then, the sine amplitude values need to be minimized and accordingly the non-linear response of the system is minimized.

Obviously, the number of frequencies summed depends on the user needs, defined in the settings of the electrochemical impedance spectroscopy technique. In EC-Lab® software, multisine measurement is done simultaneously on a maximum of two decades. If the experiment is defined with more than two decades of twenty sine, the cutting out is automatically done by set of twenty sine.

To avoid noisier or non-linear results user has to define carefully the experimental conditions. An appropriate level of excitation has to be defined. Indeed, since a lot of frequencies are stimulated in the same time, there is less signal level at each frequency and then impedance measurement results tend to be noisier. However, increasing the level of excitation can bring to do impedance measurements in a non-linear condition and then impedance results are not good.
To define the right excitation conditions, the user has to know that in EC-Lab® software, the maximum amplitude of the signal is defined as 0.5 V and half of the I Range, for

potentiostatic or galvanostatic mode measurement, respectively. Multisine measurements are done only for frequencies smaller that 1 Hz, in the remainder of the frequency range only single sine measurement is available. Note that if the frequency range defined by the user is included in the two kinds of measurement (single sine and multisine), the measurement will be done in continuity with first a single sine measurement and afterwards a multisine measurement.

Then with EC-Lab® software, multisine measurements are faster than single sine ones (by an order of 3), that is very interesting for systems with a rapid change. Nevertheless, definition of measurement conditions, especially value of the excitation of the electrochemical cell, has to be done in agreement with the preservation of a steady-state regime of the system.

References:
- Van Gheem E., Vereecken J., Schoukens J., Pintelon R., Guillaume P., Verboven P. and Pauwels L., Electrochim. Acta 49 (2004) 2919-2925.
- Pintelon R. and Schoukens J., System identification – A frequency Domain approach, Ed. IEEE Press, 2001.
- Van der Ouderaa E., Schoukens J., Renneboog J., IEEE Trans. Instrum. Meas. 37(1) (1988) 145-147.
- Schoeder M. R., Pintelon R., Rolain Y., IEEE Trans. Instrum. Meas. IM-49 (2000) 275.

2.2.2 PEIS: Potentiostatic Impedance

2.2.2.1 Description

The PEIS experiment performs impedance measurements into potentiostatic mode by applying a sinus around a potential E that can be set to a fixed value or relatively to the cell equilibrium potential.

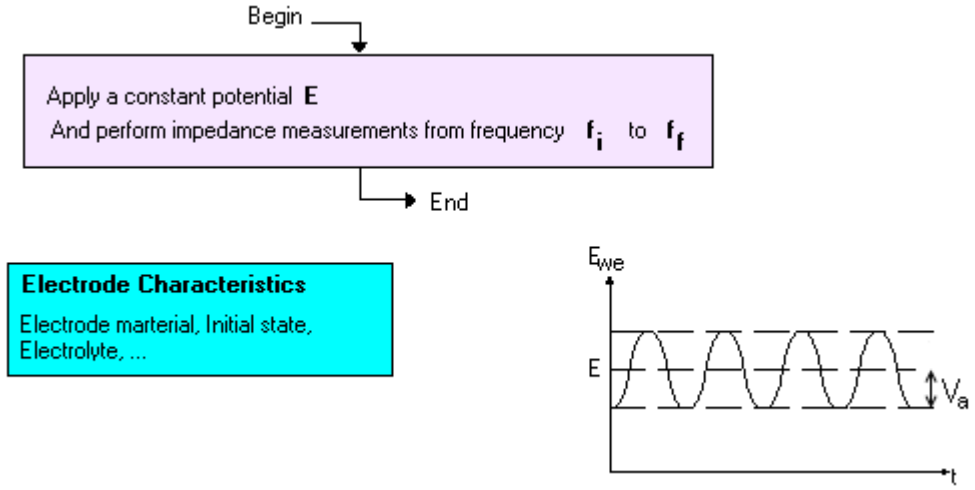


Fig. 21: PEIS general diagram.

The potential of the working electrode follows the equation:

$$E_{we} = E + V_a \sin(2 \pi f t)$$

The detailed flow diagram is made of four blocks that can be separated into four parts:

- single or multi sine mode,
- initial potential,
- frequency scan with recording conditions,
- repeat sequence.

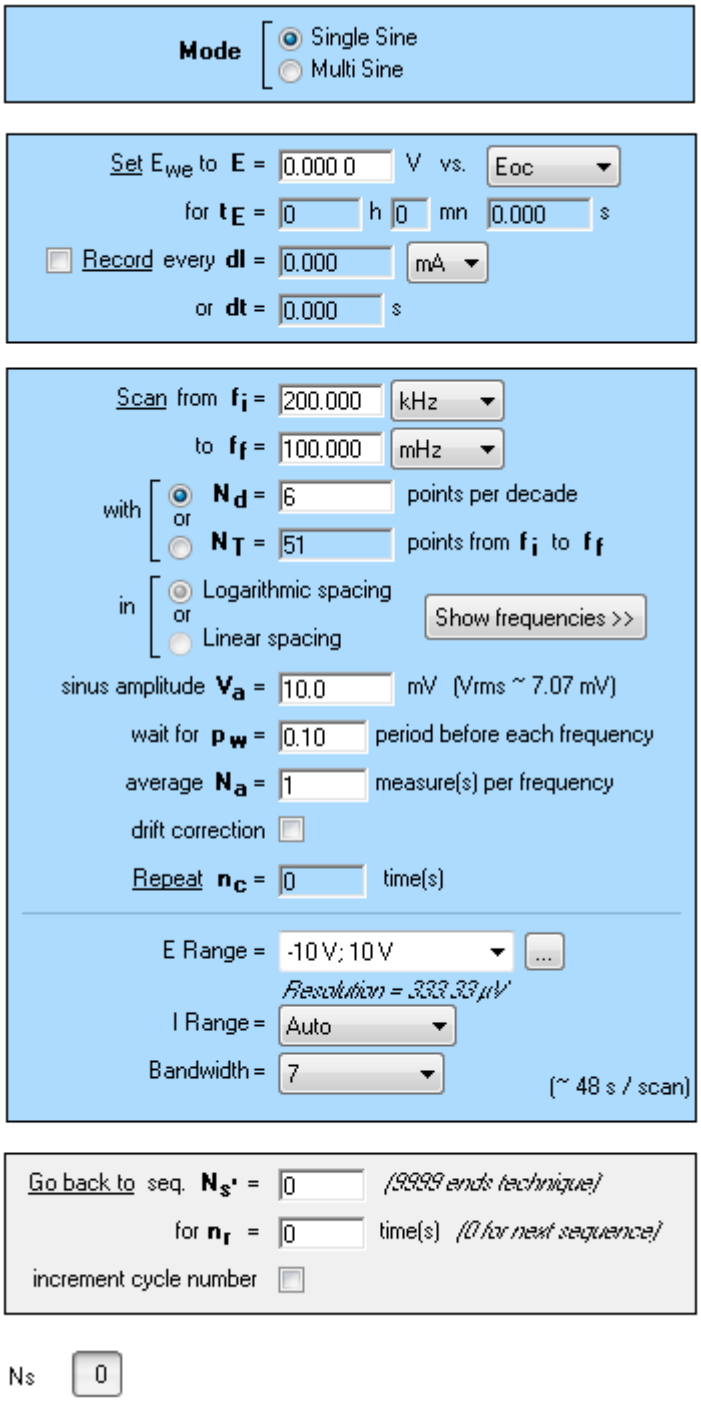


Fig. 22: PEIS detailed diagram.

- **Initial potential**

Set E_{we} to E = …….. V vs. Ref/Eoc/Ectrl/Emeas
for t_E = …… h ……. mn …… s

sets the potential to a fixed value E (vs. Ref, the reference electrode potential) or relatively to the previous:

- OCV potential (E_{oc}),
- controlled potential (E_{ctrl}),

- measured potential (E_{meas}),

for a t_E duration. Sets t_E large enough to wait for the cell current stabilization, if the applied potential is different from the open circuit potential. During this period, no impedance measurement is done.

Note: if another experiment is defined before, then it is possible to define the initial potential as a function of E_{ctrl} and E_{meas} (previous potential controlled and previous potential measured, respectively). If there is no experiment before it is not possible to use E_{ctrl} and E_{meas}.

□ Record every dI = ….. nA/µA/mA/A and dt = ….. s
offers the possibility to record E_{we} and I during the DC period before the AC simulation with two conditions on the current variation dI and (or) on time variation.

- **Impedance scan**

Scan from f_i = …… MHz/kHz/Hz/mHz/µHz to f_f = …… MHz/kHz/Hz/mHz/µHz
defines the initial (f_i) and final (f_f) frequencies of the scan. To have the first measured point more rapidly, it is recommended to scan from the highest frequencies to the lowest ones, but it is possible to reverse the frequencies scan order.

with N_d = …… points per decade in Logarithm spacing
N_t = …… points from fi to ff in Linear spacing
defines the frequencies distribution between the scan bounds f_i and f_f. It is possible to select the number of points per decade N_d or the total number of points N_t, in linear or logarithm spacing.
For example, a scan from f_i = 100 kHz to f_f = 1 kHz with N_d = 5 points per decade in logarithm spacing, will perform measures at the following frequencies (in kHz):
100, 63.1, 39.8, 25.1, 15.8, 10, 6.31, 3.98, 2.51, 1.58, 1
and a scan from f_i = 100 kHz to f_f = 1 kHz with N_t = 11 total number of points in linear spacing, will make measures at these following frequencies (Hz):
100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 1
Click on the **Show frequencies >>** button to display the list of the scanned frequencies.
Note: it is not possible to select N_d points per decade in linear spacing.

with an amplitude V_a = …… mV
sets the sinus amplitude to V_a. Equivalence with V_{RMS} is also given.
Note the following relationships between V_a, V_{pp} and V_{RMS} $V_a = V_{pp/2}$ and $V_{RMS} = V_{pp}/(2\sqrt{2})$.

Wait for p_w = …… period before each frequency measurement
offers the possibility to add a delay before the measurement at each frequency. This delay is defined as a part of the period. Of course for low frequencies the delay may be long.

average N_a = …… mesure(s) per frequency
repeats N_a measure(s) and average the values for each frequency.

Non stationary correction: drift correction

corrects the drift of the system. This feature is more specially dedicated to low frequencies.

Note:
1- If this option is selected, the sinus frequencies are evaluated over 2 periods (instead of 1), increasing the acquisition time by a factor of 2.
2- In the bottom right corner of the block, the approximate experiment duration is indicated as information for the user.

During the Run, several parameters remain accessible for modification such as the min and max frequencies and the number of points per decade.

- **Repeat**

Repeat for n_c = …… time(s)

allows for repeating PEIS measurements in order to represent Z evolution vs. time (see below).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = ……. Bandwidth = …….
Sets the current range and bandwidth values for the whole experiment.

- **Sequence repetition**

The last part of this technique is dedicated to repeat sequences when many sequences are done. Indeed since the version 9.9 of EC-Lab® software it is possible to add sequence in impedance measurements. This tool is convenient to spare time, indeed during the same experiment it is possible to work in single sine mode at high frequencies and in mutisine mode at low frequencies or to change the sinus amplitude.
When the box Increment cycle number is ticked, each sequence will be considered as a cycle. This tool is useful to fit EIS data files with ZFit.

2.2.2.2 Additional features:

- It is possible to add sequences. This could be very useful to do a first part of the high frequencies experiment with single sine measurement and the second part of the experiment at low frequencies with multisine measurement. This will allow the user to spare time.
- It is possible to modify on-line the settings of an impedance measurement during the experiment. The user can Modify, Pause, Resume or Stop the experiment while running.
- The counter electrode potential can be recorded in EIS techniques. So the EIS measurement is done simultaneously on the working electrode and on the counter electrode. To do that, select "**Record Ece**" in the Cell characteristics tab. Nyquist and Bode diagrams can be plotted for both the WE and the CE electrodes. The working and counter electrode variables are displayed respectively as follows with the additional extension Re (Z) and Re (Z_{CE}), -Im (Z) and –Im (Z_{CE}).

2.2.3 GEIS: Galvanostatic Impedance

This technique is very close to the Potentiostastic Impedance technique (PEIS), except that the current is controlled instead of the potential. So report to the PEIS experiment section for more details.

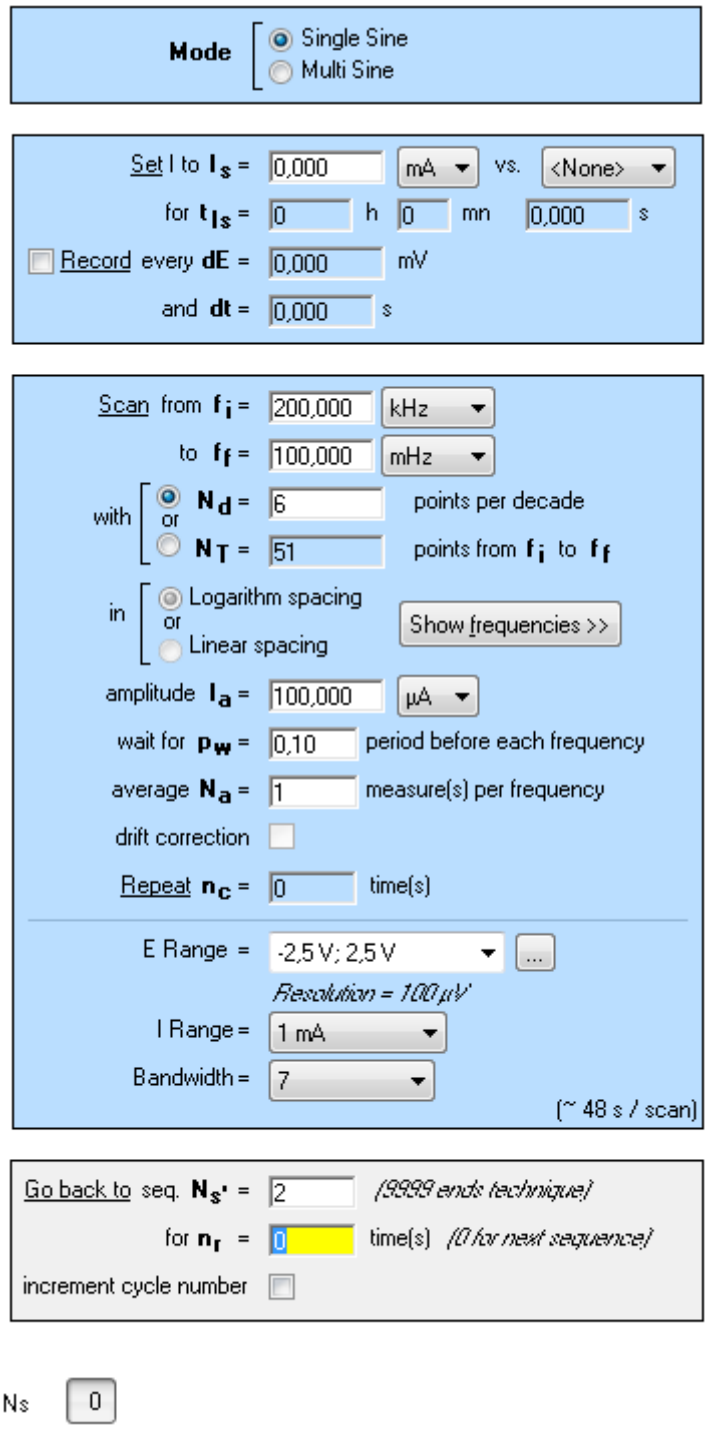


Fig. 23: GEIS diagram.

Note that the current can be applied vs. the previous control current or the previous measured current (previous sequence of a linked technique).

Instead of I_a, one can consider the current peak to peak amplitude (I_{pp}) related to I_a with $I_{pp}=2*I_a$ or the Root Mean Square (RMS) voltage related to I_a with $I_{RMS} = I_a/\sqrt{2}$.

2.2.4 Visualisation of impedance data files

2.2.4.1 Standard visualisation modes

EC-Lab® software provides a full range of variables and visualisation modes defined by default. When an impedance data file is displayed, click on “Selector” to show all the variables and visualisation modes available with impedance data files:

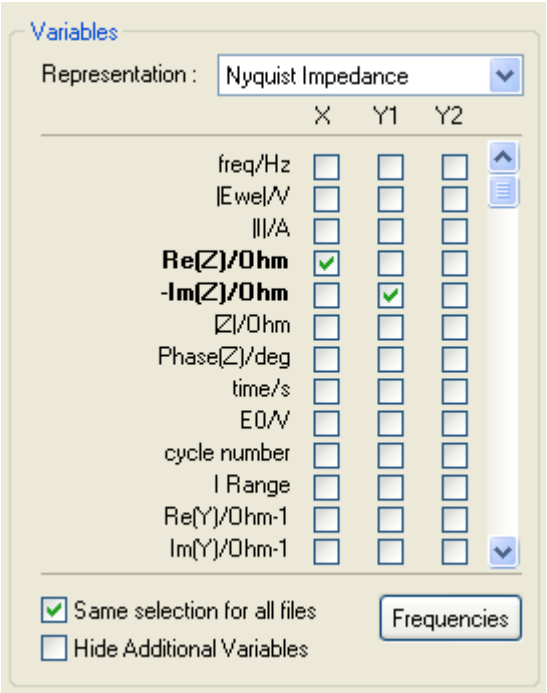


Fig. 24: Impedance data file selector.

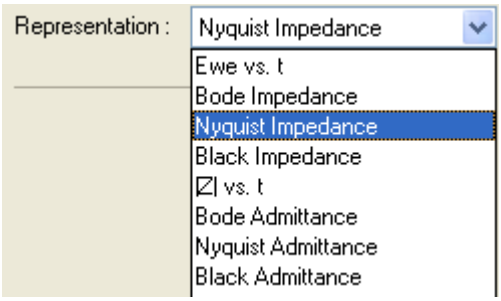


Fig. 25: Impedance graph plot selector.

Among the available variables the Impedance Z is calculated using Fast Fourier Transform function and the admittance Y is determined as Y=1/Z. For both variables Bode, Nyquist and Black diagrams can be plotted according to the EC-Lab® software’s predefined graph visualization modes.

- Bode diagram (for both impedance and admittance)

The Bode diagram is the plot of:

- log|Z| versus log(f) and Z-phase versus log(f) for the impedance
- log|Y| versus log(f) and Y-phase versus log(f) for the admittance.

On the first figure log |Z| and log |Y| have been overlaid on the same graph. On the second one Phase(Z) and Phase(Y) have been overlaid.

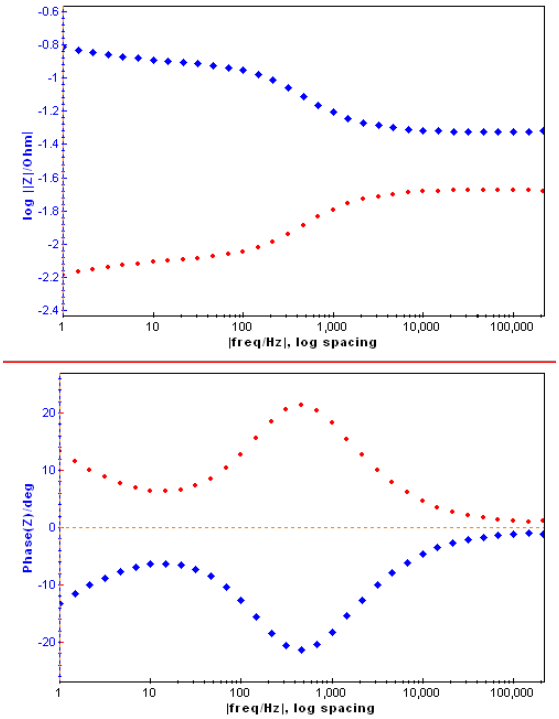


Fig. 26: BODE diagrams for both impedance (blue) and admittance (red).

- Nyquist diagram

The Nyquist diagram is the plot of:

- –Im(Z) versus Re(Z) for impedance
- Im(Y) versus Re(Y) for admittance.

The main difference between both visualizations is that the admittance diagram better shows the high frequency semi-circle.

With the Nyquist visualization, the axes are automatically displayed proportionally.

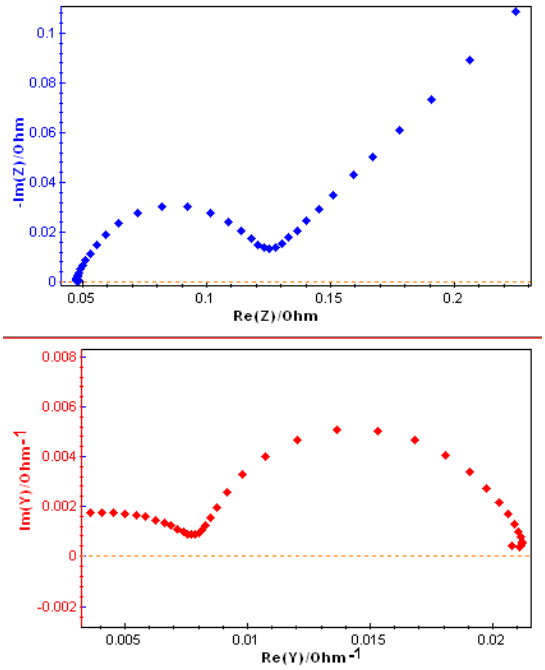


Fig. 27: NYQUIST diagrams for both impedance (blue) and admittance (red).

- Black Diagram

The Black diagram is the plot of
- log|Z| versus phase(Z) for impedance
- log|Y| versus phase(Y) for admittance.

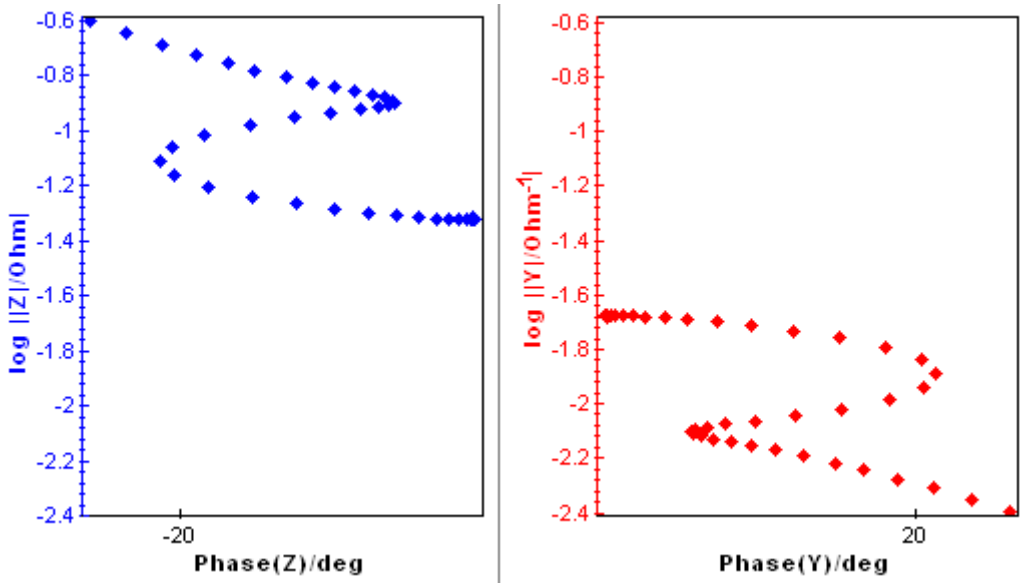


Fig. 28: BLACK diagrams for both impedance (blue) and admittance (red).

2.2.4.2 Counter electrode EIS data plot

When the user selects “Record Ece” in the Cell characteristics window, EIS measurement of the counter electrode is done and can be displayed.

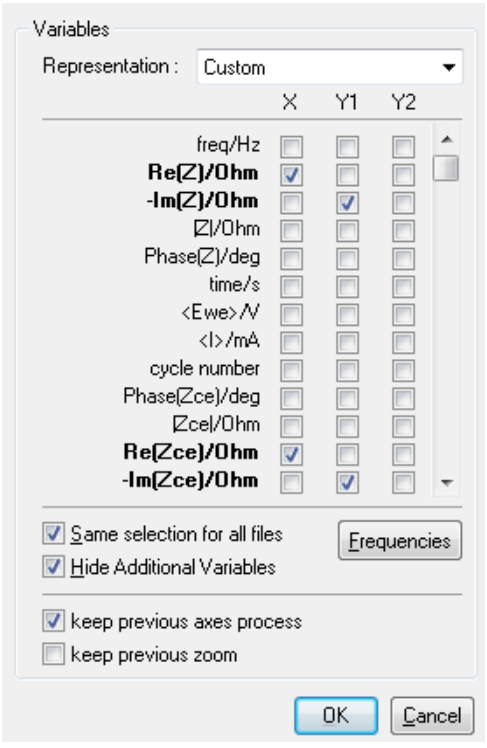


Fig. 29: EIS variable selection window with WE and CE.

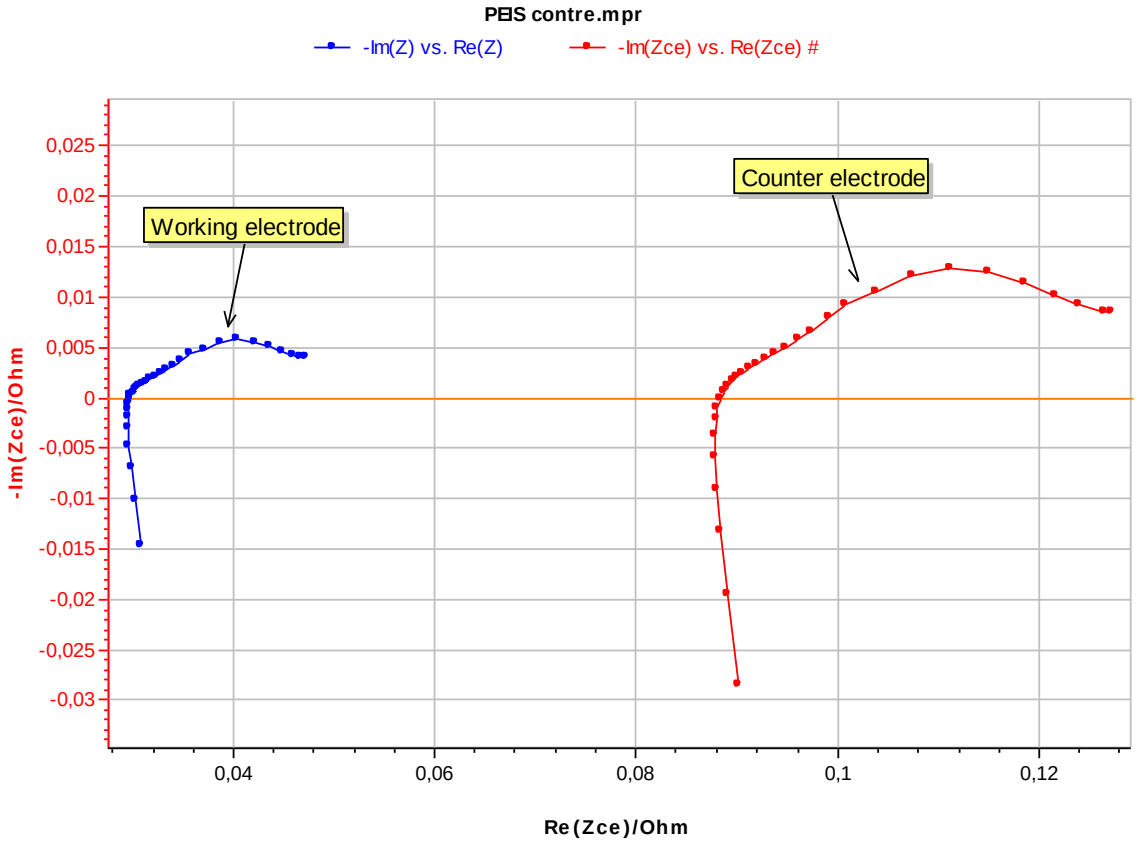


Fig. 30: PEIS data curves with WE and CE recording.

2.2.4.3 Frequency vs. time plot

It is possible to perform impedance measurements at different time intervals, to follow the evolution of |Z| (or Im(Z), Re(Z), phase(Z)) versus time for each frequency value.

The user can repeat a PEIS impedance experiment where the potential E is fixed for a given time t_E (for example 30 min).

After a run, open the impedance file in a graphic window, click on **Selector**, and the "file selection" window appears (figure below). Then select **time/s** for the X-axis and choose the parameter you want to represent on Y1-axis (|Z| in our example).
Note: for a Z vs. time plot the time variable must be plotted on X-axis.

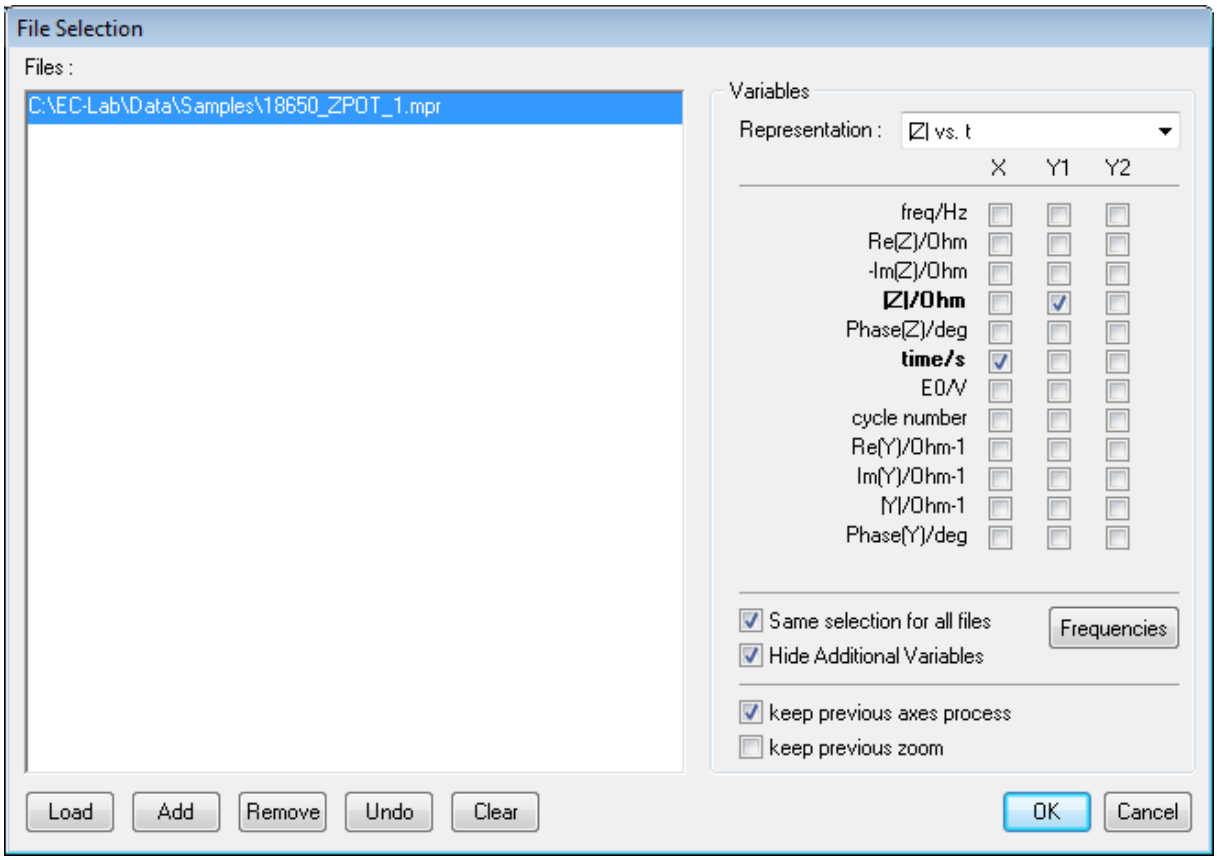


Fig. 31: File selection display.

Select Z(t) plot in the scroll menu. Then the following window is displayed to select frequencies to plot.

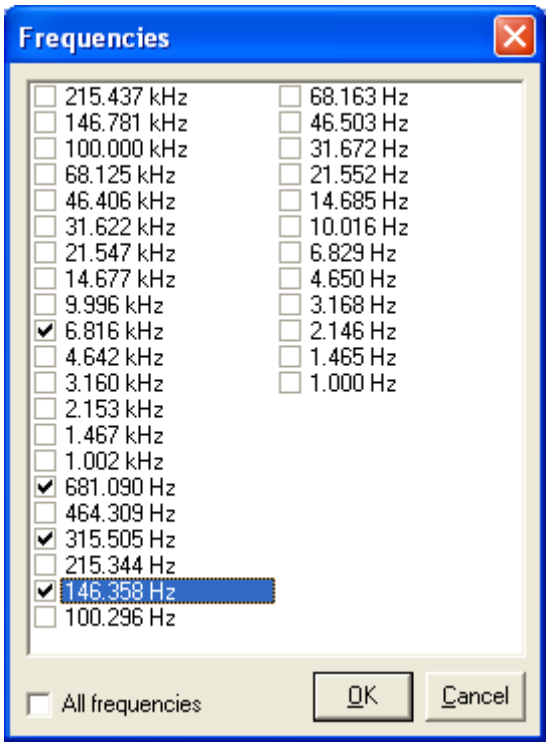


Fig. 32: Z vs. time display used to select frequencies.

Choose the desired frequencies and click **Ok.** The graphic representation will automatically display one trace for each chosen frequency. In the graphic display, |Z| = f(t) is represented for the four different frequencies selected before.

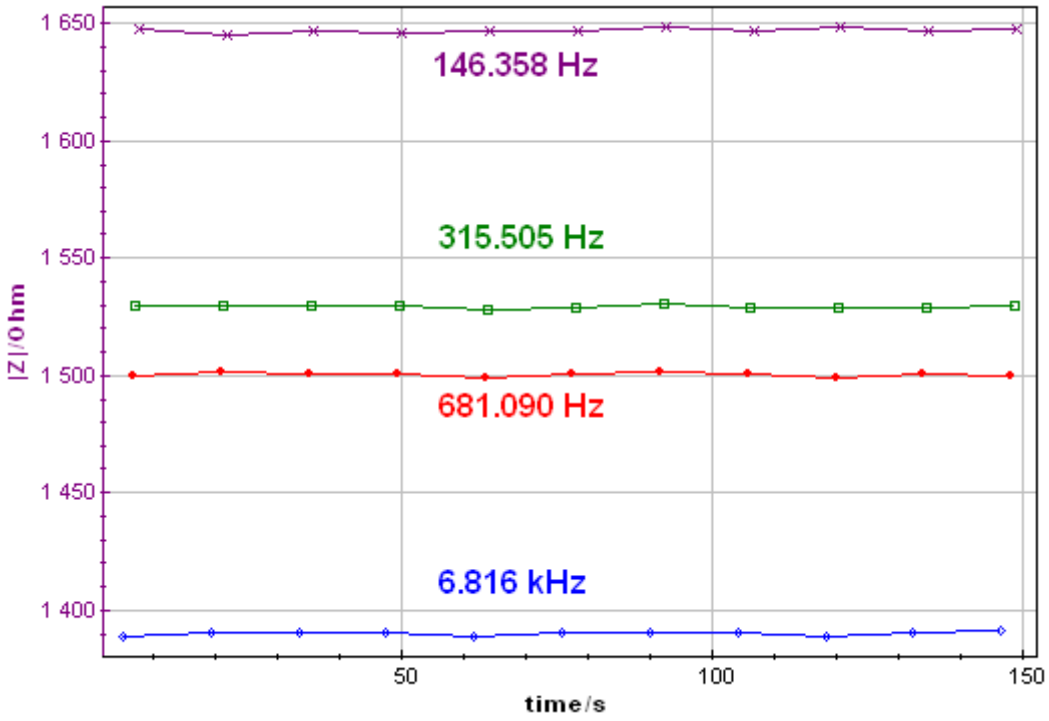


Fig. 33: Graphic display for four different frequencies.

2.2.5 Staircase Electrochemical Impedance Spectroscopy

The SPEIS and SGEIS powerful techniques are designed to perform successive impedance measurements (on a whole frequency range) during a potential sweep (SPEIS) or during a current sweep (SGEIS). The main application of these techniques is to study electrochemical reaction kinetics along voltamperometric (I(E)) curves in analytical electrochemistry. Thus these techniques find all their interest in studying the complexity of non-stationary interfaces with faradic processes where the total AC response (whole frequency range) is required.
Another common application of such techniques is semi-conductor materials study. For these stationary systems only two or three frequencies for each potential step are required to determine the donor density and the flat band potential.

2.2.5.1 SGEIS: Staircase Galvano Electrochemical Impedance Spectroscopy

With the SGEIS technique, the potentiostat works as a galvanostat and applies a current sweep (staircase shape). An impedance measurement (whole frequency range) can be performed on each current step. The user can also select several frequencies.
The SGEIS experiment performs impedance measurements in galvano mode by applying a sinus around a current I. The impedance measurement is repeated on each current step

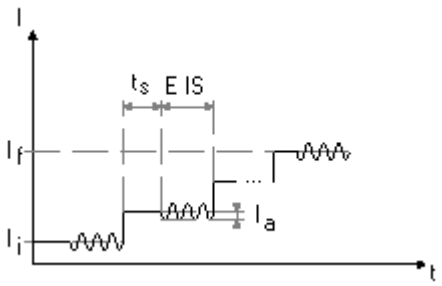


Fig. 34: SGEIS description diagram.

The detailed diagram is made of three blocks that can be separated into five parts:

- single or multi sine mode,
- initial current,
- waiting period before EIS, frequency scan with recording conditions and current scan with number of current steps definition.

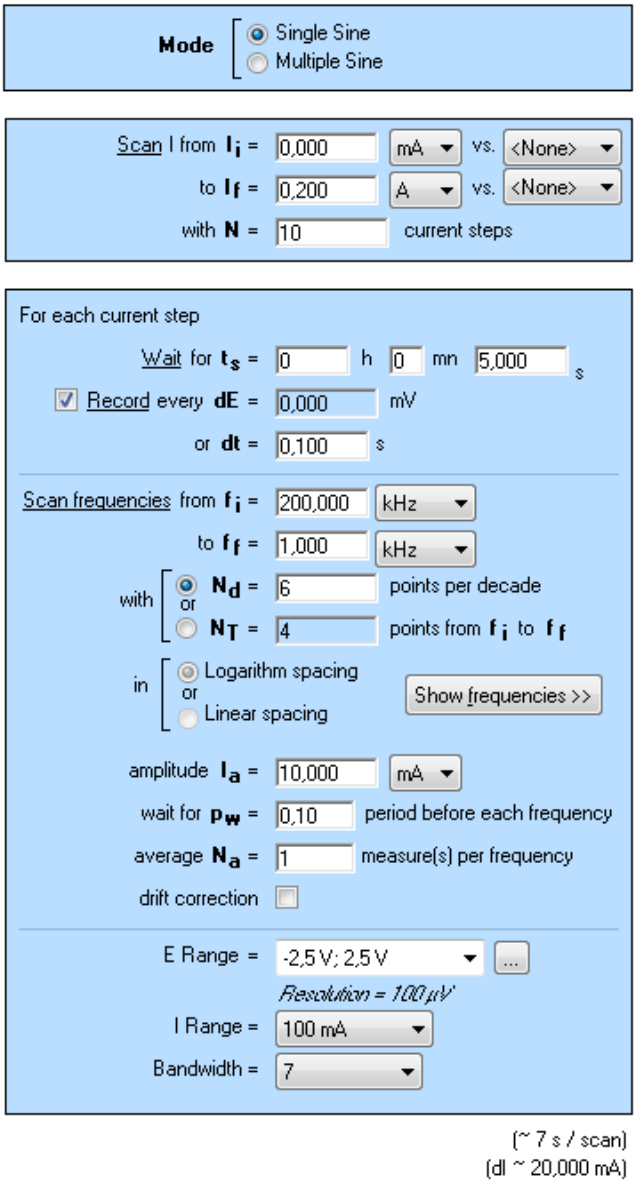


Fig. 35: SGEIS detailed diagram.

- **Initial current**

Scan I from I_i = …….. A vs. <None>/Ictrl/Imeas to I_f = …….. A vs. <None>/Ii
With N = ... current steps
sets the initial current to a fixed value I (<none>) or relatively to the previous:
- controlled current (I_{ctrl}),
- measured current (I_{meas}).

sets the final current to a fixed value I (<none>) or relatively to the previous current.
User defines the number of steps between I_i and I_f.

- **Waiting period before EIS**

Before EIS, wait for t_s = …….. h …….. mn …….. s
□ Record every dE = …….. mV and dt = ……. s

before the EIS measurement the user can apply an equilibration period with the ability to record the current. During this period, no impedance measurement is done.

- **Impedance scan**

Scan from f_i = …… MHz/kHz/Hz/mHz/µHz to f_f = …… MHz/kHz/Hz/mHz/µHz
defines the initial (f_i) and final (f_f) frequencies of the scan. To have results more rapidly, it is better to scan from the highest frequencies to the slowest ones, but it is possible to reverse the frequencies scan order.

with N_d = …… points per decade in Logarithm spacing
N_t = …… points from fi to ff in Linear spacing
defines the frequencies distribution between the scan bounds f_i and f_f. It is possible to select the number of points per decade N_d or the total number of points N_t, in linear or logarithm spacing.
For example, a scan from f_i = 100 kHz to f_f = 1 kHz with N_d = 5 points per decade in logarithm spacing, will perform measures at the following frequencies (in kHz):
100, 63.1, 39.8, 25.1, 15.8, 10, 6.31, 3.98, 2.51, 1.58, 1
and a scan from f_i = 100 kHz to f_f = 1 kHz with N_t = 11 total number of points in linear spacing, will make measures at the following frequencies (Hz):
100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 1
Click on the "**Show frequencies >>**" button, to display the list of scanned frequencies.
Note: it is not possible to select N_d points per decade in linear spacing.

with a sinus amplitude I_a = …… mA
sets the sinus amplitude to I_a.

average N_a = …… mesure(s) per frequency
repeats N_a measure(s) and average values for each frequency.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = ……. Bandwidth = …….
sets the current range and bandwidth values for the whole experiment.

Non stationary correction: drift correction
corrects the drift of the system. This feature is more especially dedicated to low frequencies.
Note: if this option is selected, the sinus frequencies are evaluated over 2 periods (instead of 1), increasing the acquisition time by a factor of 2.

- **Current scan with number of current steps definition**

Scan I to I_f = …… A vs. <none>/Ictrl/Imeas
With N = …….. current steps (dI = …..… mA)

defines the current scan limit to I_f in either absolute or versus the previous controlled or measured current. The user selects the number of current steps from I_i to I_f and the step amplitude dI is displayed as information.

Note:

- It is possible to modify on-line the settings of an impedance measurement during the experiment. The user can Modify, Pause, Resume or Stop the experiment while it's running.

2.2.5.2 SPEIS: Staircase Potentio Electrochemical Impedance Spectroscopy

2.2.5.2.1 Description

The SPEIS technique consists of a staircase potential sweep (potential limits and number of steps defined by the user). An impedance measurement (with an adjustable number of frequencies) is performed on each potential step. For all these applications a Mott-Schottky plot ($1/C^2$ vs. E_{we} or 1/C vs. E_{we}) can be displayed and a special linear fit is applied to extract the semi-conductor parameters.

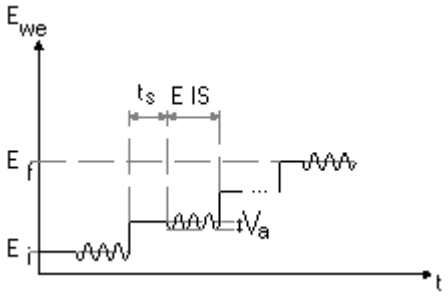


Fig. 36: SPEIS description diagram.

The potential of the working electrode follows the equation:

$$E_{we} = E + V_a \sin(2 \pi f t)$$

The detailed diagram is made of three blocks that can be separated into five parts:

- single or multi sine mode,
- initial potential,
- waiting period before EIS, frequency scan with recording conditions and potential sweep with definition of the number of potential steps.

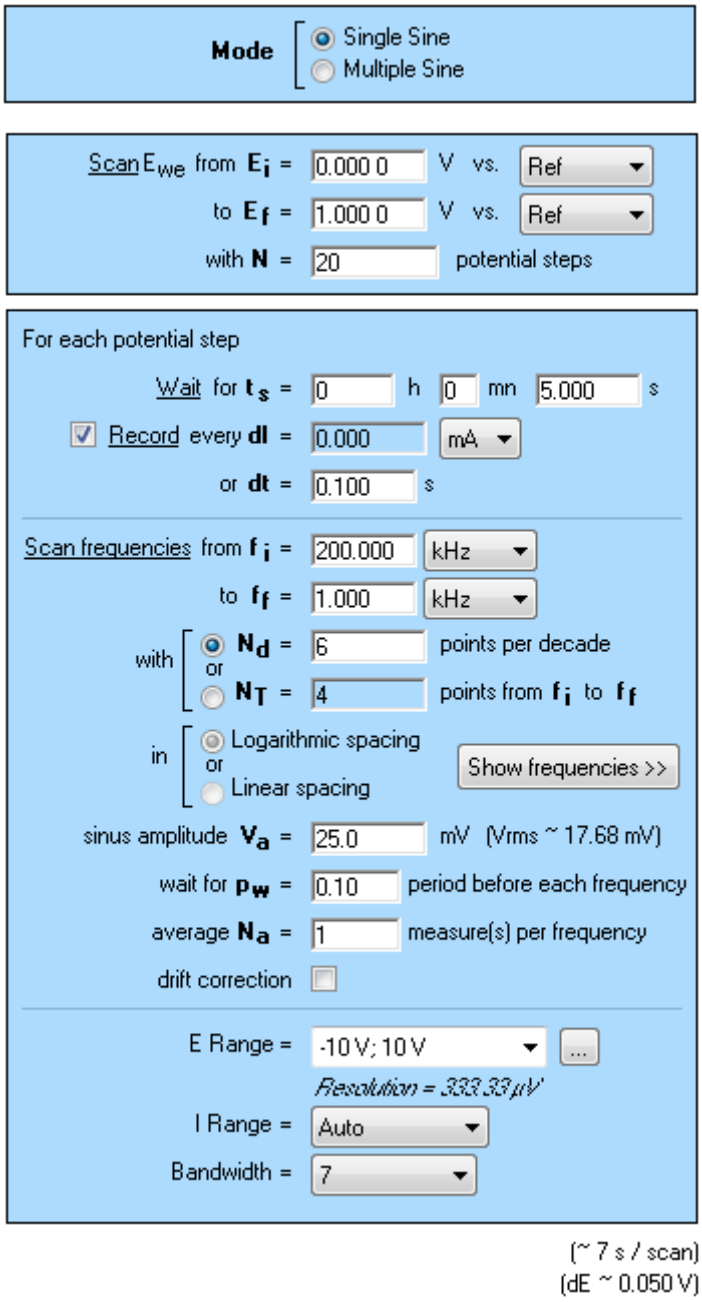


Fig. 37: SPEIS detailed diagram.

- **Initial potential**

Scan E_{we} from E = …….. V vs. previous Ref/Eoc/Ectrl/Emeas to E = …….. V vs. previous Ref/Eoc/Ei
With N = ... potential steps

sets the initial potential to a fixed value E (vs. Ref the reference electrode potential) or relatively to the previous:

- OCV potential (E_{oc}),
- controlled potential (E_{ctrl}),
- measured potential (E_{meas}),

sets final potential to a fixed value E (vs. Ref the reference electrode potential) or relatively to the previous:

- OCV potential (E_{oc}),

- initial potential (E_i).

The number of potential steps is defined by user with the N value.

- **Waiting period before EIS**

Before EIS, wait for t_s = …….. h …….. mn …….. s
□ Record every dI = …….. mV and dt = ……. s

before the EIS measurement the user can apply an equilibration period with the ability to record the potential. During this period, no impedance measurement is done.

- **Impedance scan**

Scan from f_i = …… kHz/Hz/mHz/µHz to f_f = …… kHz/Hz/mHz/µHz
defines the initial (f_i) and final (f_f) frequencies of the scan. To have results more rapidly, it is better to choice to scan from the highest frequencies to the lowest ones, but it is possible to reverse the frequencies scan order.

with N_d = …… points per decade in Logarithm spacing
N_t = …… points from fi to ff in Linear spacing
defines the frequencies distribution between the scan bounds f_i and f_f. It is possible to select the number of points per decade N_d or the total number of points N_t, in linear or logarithm spacing.
Click on the "**Show frequencies >>**" button, to display the list of scanned frequencies.
Note: it is not possible to select N_d points per decade in linear spacing.

with amplitude V_a = …… mV
sets sinus amplitude to V_a. Equivalence with V_{RMS} is also given.
Note the following relationships between V_a, V_{pp} and V_{RMS} $V_a = V_{pp/2}$ and $V_{RMS} = V_{pp}/(2\sqrt{2})$.

average N_a = …… mesure(s) per frequency
repeats N_a measure(s) and average values for each frequency.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = ……. Bandwidth = …….
sets the current range and bandwidth values for the entire experiment.

Non stationary correction: drift correction

corrects the drift of the system. This feature is more especially dedicated to low frequencies.
Note: if this option is selected, the sinus frequencies are evaluated over 2 periods (instead of 1), increasing the acquisition time by a factor of 2.

- **Potential scan with definition of the number of potential steps**

Scan Ewe to E_f = …… V vs. Ref/Eoc/Ectrl/Emeas
With N = …….. potential steps (dE = ……… mV)

define the potential sweep limit to E_f in either absolute or versus the open circuit potential, the previous controlled or measured potential. The user selects the number of potential steps from E_i to E_f and the step amplitude dE is displayed as information.

Graph tool: Mott-Schottky plot

For the SPEIS technique particularly used in semi-conductor materials study (Mott-Schottky experiments), it is possible to display the "$1/C^2$ vs. E_{we}" plot when selecting "**Mott-Schottky**" in the rapid selection scroll menu. This graphic display is available during the run because the capacitance values are automatically calculated during the experiment. When the Mott-Schottky plot is selected, the user must choose several frequencies among all the recorded frequencies. Moreover, a special fit, "**Mott-Schottky fit**", has been built to determine the semi-conductor parameters (flatband potential, donor density). For more details about this plot, refer to the EC-Lab® software manual.

Note:

- It is possible to modify the settings of an impedance measurement during the experiment. The user can Modify, Pause, Resume or Stop the experiment it's while running.

2.2.5.2.2 Application

The SPEIS technique is applied in this example to circuit #3 of Test Box 3. A potential sweep is made from E_i = 0 V to E_f = 2.1 V with 100 mV potential steps. On each step an impedance measurement is performed for a whole frequency range (200 kHz to 1 Hz).

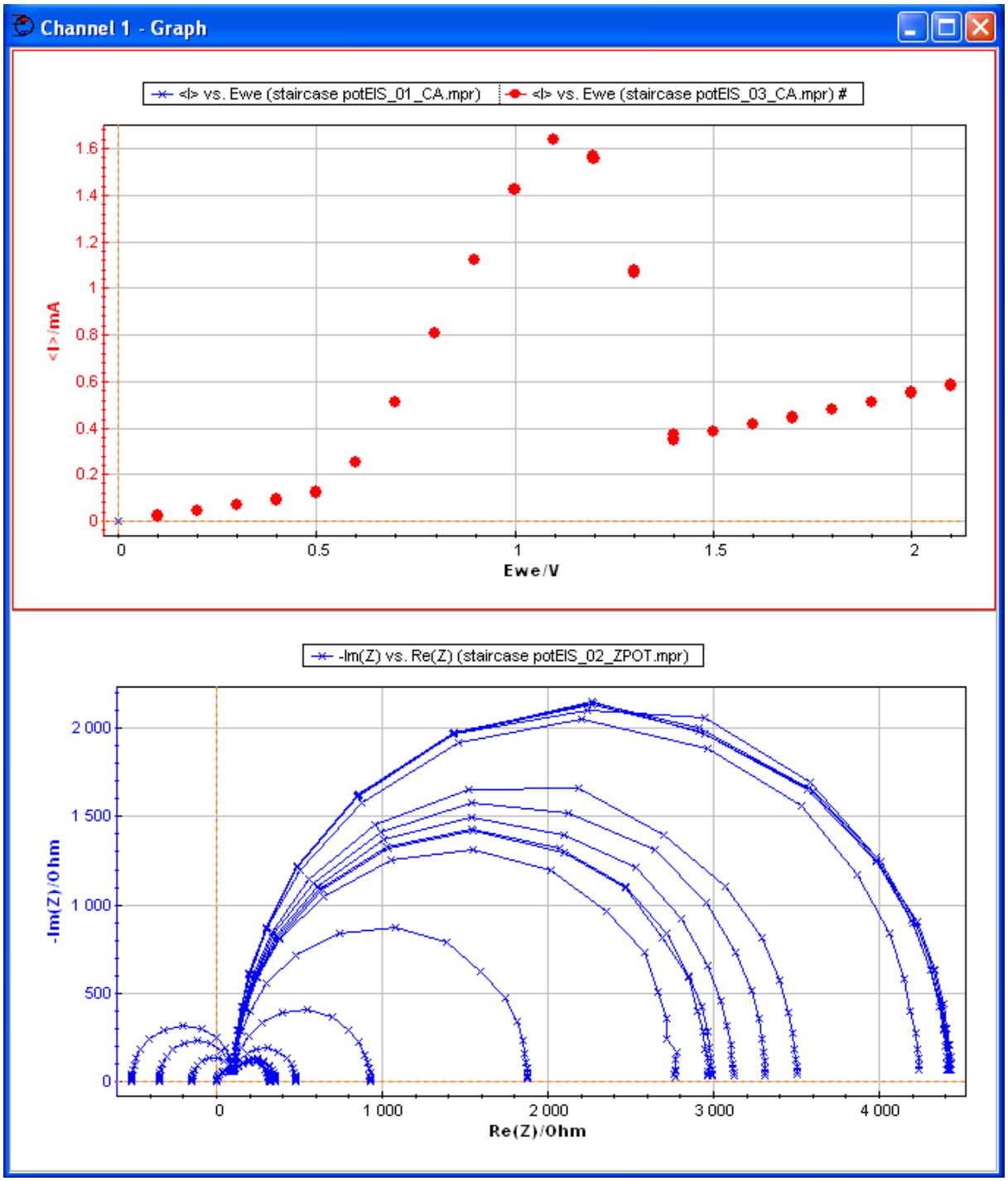


Fig. 38: Application of the SPEIS technique.

The user can plot $1/C^2$ vs. E_{we} of this data file either for few frequencies or the whole frequency range.

2.3 Pulses

2.3.1 DPV: Differential Pulse Voltammetry

DPV is very useful for analytical determination (for example, metal ion quantification in a sample). The differential measurements discriminate a faradic current from a capacitive one. In this technique, the applied waveform is the sum of a pulse train and a staircase from the initial potential (E_i) to a limit potential (E_V), or to the final potential (E_f) if the scan is reversed. The current is sampled just before the pulse and near the end of the pulse. The resulting current is the difference between these two currents. It has a relatively flat baseline. The current peak height is directly related to the concentration of the electroactive species in the electrochemical cell.

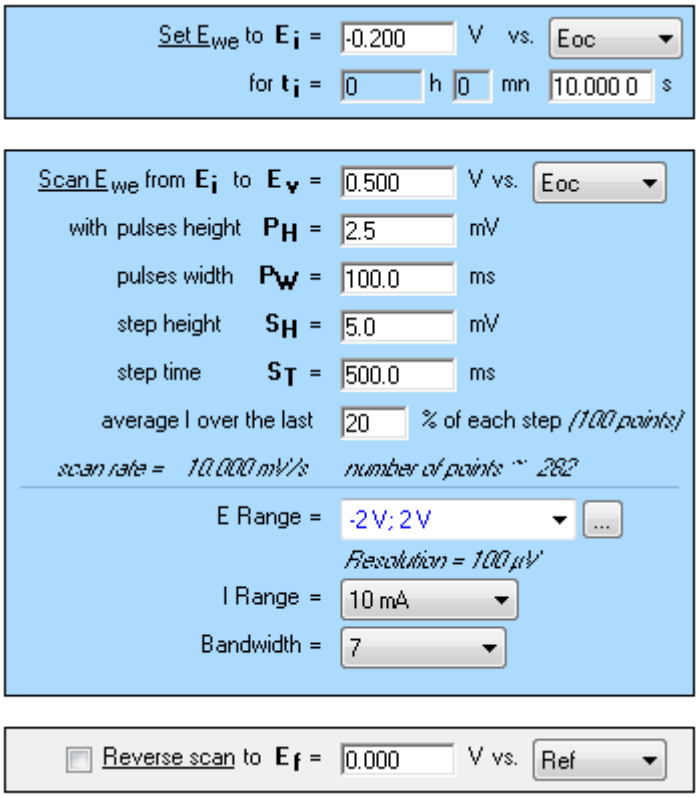


Fig. 39: DPV detailed diagram.

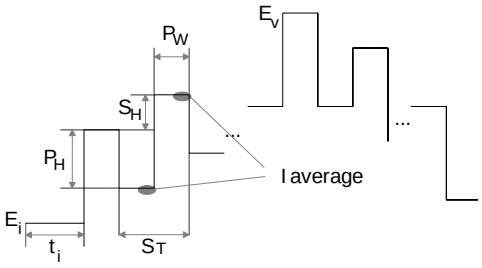


Fig. 40: DPV waveform.

Description:

- **Initial potential**

Set E_{we} to E_i = …… V vs. Ref/Eoc/Ectrl/Emeas for t_i = …… h …… mn …… s
sets E_{we} to the initial potential E_i. This potential value can be set in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}), controlled potential (E_{ctrl}) or eeasured potential (E_{meas}).
Notice that only the last point of this period is recorded at the time 0.

- **Pulse waveform**

Scan E_{we} from E_i to E_v = ……. V vs. Ref/Eoc/Ei

defines the vertex potential as E_v, either in absolute (vs. Ref the reference electrode potential) or versus E_{oc} or E_i.

with pulses height P_H = mV
pulses width P_W = ms
step height S_H = mV
step time S_T = ms

The pulse train is made of pulses with, pulse height P_H amplitude and pulse width P_W duration. Superimposed with a staircase of step height amplitude S_H and step time S_T duration.
Notice that only one point is recorded at the end of the potential pulse and one point before, making two points during the S_T period.
The example above (Fig. 41) is given for a positive scan. To perform a negative scan set E_v inferior to E_i and S_H to a negative value.

Scan rate = …… mV/s ….. number of points ~

these values are given as an indication and are calculated in the PC. The scan rate is directly given by S_H / (0.001S_T) and the number of points is roughly 2(E_v - E_i) / S_H for the forward scan.

average I over the last …… % of each step *(…… points)*
selects the end part of the potential step for the current average (<I>) calculus, to exclude the first points where the current may be perturbed by the step establishment. A value of 100 % will take all the step points for the average and a value of 0 % will take only the last point.
Note that the current average (<I>) is recorded at the end of the potential step to the data file.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range …….. Bandwidth …….
sets the current range and bandwidth values for the whole experiment.

Note: It is highly recommended to not use the automatic current range with pulsed techniques. The resolution of each range is different and dynamic current range changes may lead to spikes on the plot.

- **Reverse scan definition**

Reverse scan towards E_f = …….. V vs. Ref/Eoc/Ei
checks Reverse scan to perform a scan towards E_f either in absolute (<None>) or versus E_{oc} or E_i.

Running the settings defined into Fig. 39 will result in the following output:

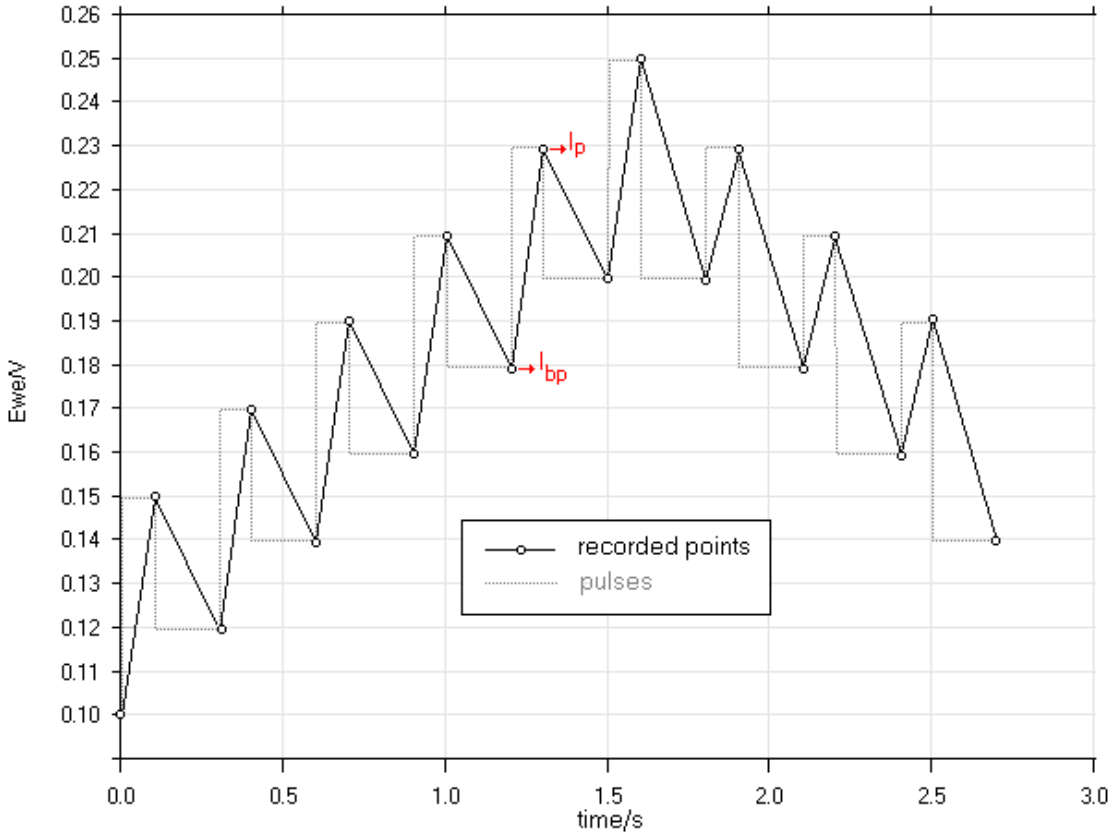


Fig. 41: DPV output (E_{we} vs. time).

These variables are stored in the DPV raw files (*.mpr):

- state byte,
- time/s,
- control/V,
- <I>/mA,
- $Q-Q_0$/mA.h.

And the next variables are calculated from <I> (to save size on disk):

- I forward/mA: <I> values at the end of the pulses (I_p, on Fig. 41),
- I reverse/mA: <I> values before the pulses (I_{bp}),
- I delta/µA: difference between <I> values before and at the end of the pulse (I_p - I_{bp}).

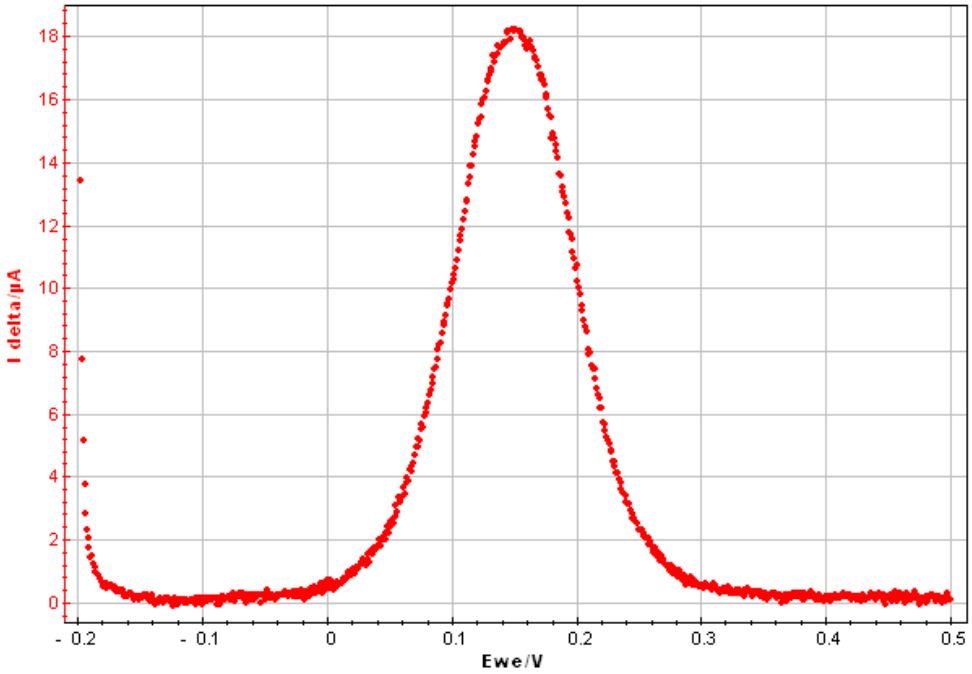


Fig. 42: DPV measurement in a Fe(II) solution.

2.3.2 SWV: Square Wave Voltammetry

Among the electroanalytical techniques, the Square Wave Voltammetry (SWV) combines the background suppression, the sensitivity of DPV and the diagnostic value of NPV. The SWV is a large amplitude differential technique in which a waveform of a symmetrical square wave (with one pulse in the forward direction and one in the reverse), superimposed on a base staircase potential, is applied to the working electrode. The square wave is characterized by a pulse height (P_H) and a pulse width (P_W). The pulse width can be expressed in terms of square wave frequency $f = 1/(2P_W)$. The scan rate is $v = P_H/(2P_W)$. The current is sampled twice during each square wave cycle, once at the end of the forward pulse and once at the end of the reverse pulse. The difference between the two measurements is plotted versus the base staircase potential. The resulting peak-shaped voltammogram is symmetrical around the half-wave potential and the peak current is proportional to the concentration. Excellent sensitivity accrues from the fact that the net current is larger than either the forward or reverse components (since it is the difference between them).

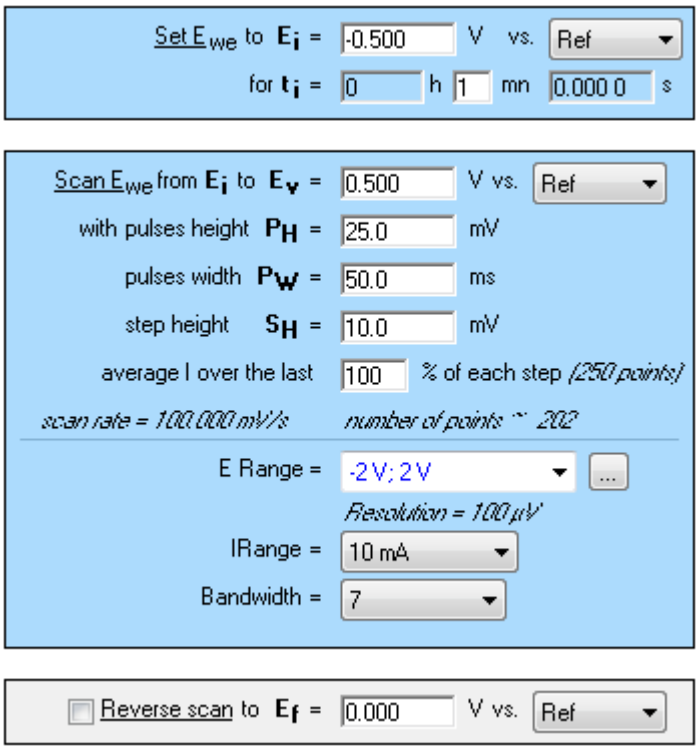


Fig. 43: SWV detailed diagram.

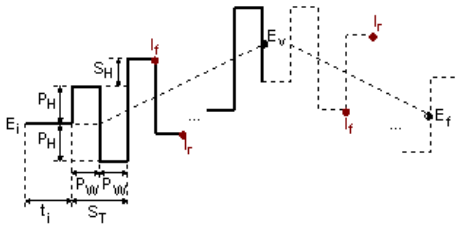


Fig. 44: SWV waveform.

Description:

- **Initial potential**

Set E_{we} to E_i = …… V vs. Ref/Eoc/Ectrl/Emeas for t_i = …… h …… mn …… s
sets E_{we} to the initial potential E_i. This potential value can be set in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}) or controlled potential (E_{ctrl}) or measured potential (E_{meas}).
Notice that only the last point of this period is recorded at the time 0.

- **Pulse waveform**

Scan E_{we} from E_i to E_v = ……. V vs. Ref/Eoc/Ei
defines the vertex potential as E_v, either in absolute (vs. Ref) or versus E_{oc} or E_i.

with pulses height P_H = mV
pulses width P_W = ms
step height S_H = mV
The pulse train is made of pulses with, pulse height P_H amplitude and pulse width P_W duration around the averaged potential scan. The scan increment is defined by staircases of step height amplitude S_H and step time S_T duration.
Notice that only one point is recorded at the end of the potential forward pulse and one point at the end of the potential reverse pulse, making two points during the S_T period.
The settings above (Fig. 43) are given for a positive scan. To perform a negative scan set E_v inferior to E_i and S_H to a negative value.

Scan rate = …… mV/s ….. number of points ~
These values are given as an indication and are calculated in the PC. The scan rate is directly given by S_H / (0.001S_T), and the number of points is roughly 2(E_v - E_i) / S_H for the forward scan.

average I over the last …… % of each step *(…… points)*

Selects the end part of the potential step for the current average (<I>) calculation, to exclude the first points where the current may be disturbed by the step establishment. A value of 100 % will take all the step points for the average, and a value of 0 % will take only the last point.
Note that the current average (<I>) is recorded at the end of the potential step into the data file.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

IRange …….. Bandwidth …….
sets the current range and bandwidth values for the whole experiment.

- **Reverse scan definition**

☐ Reverse scan towards E_f = …….. V vs. Ref/Eoc/Ei
Checks the Reverse scan box to perform a scan towards E_f either in absolute (vs. Ref) or versus E_{oc} or E_i.

Note: It is highly recommended to not use the automatic current range with pulsed techniques. The resolution of each range is different and dynamic current range changes may lead to spikes on the plot.

SWV recorded and calculated variables:

The variables below are stored into the SWV raw files (*.mpr):
- state byte,
- time/s,
- control/V,
- E_{we}/V,
- <I>/mA,
- Q-Q_0/mA.h.

And the next variables are calculated from <I> or the potential (to save size on disk):
- I forward /mA: <I> values at the end of the pulses (I_p)
- I reverse /mA: <I> values before the pulses (I_{bp})
- I delta /µA: difference between <I> values before and at the end of the pulse (I_p - I_{bp})
- E step /V: step potential value resulting from the potential sweep and used to plot the current.

2.3.3 DNPV: Differential Normal Pulse Voltammetry

Originally introduced as a polarographic technique (performed at a DME), the Differential Normal Pulse Voltammetry is a sensitive electroanalytical technique very similar to the DPV technique with a pulsed potential sweep. The potential pulse is swept from an initial potential E_i to a final potential E_v. There are two main differences with the DPV technique: first the pulse waveform is made with a prepulse (S_H amplitude with PP_W duration) before the pulse (P_H amplitude with P_W duration) and second the potential always comes back to the initial potential (E_i) after the pulsed sequence. E_i is assumed to be the potential where no faradic reaction occurs. The plotted current is the difference of both currents measured at the end of the pulse (I forward) and the end of the prepulse (I reverse).

This technique is often used in polarography and by biologists to define the most appropriate potential for the electrochemical detection to a fixed potential with the DPA technique.

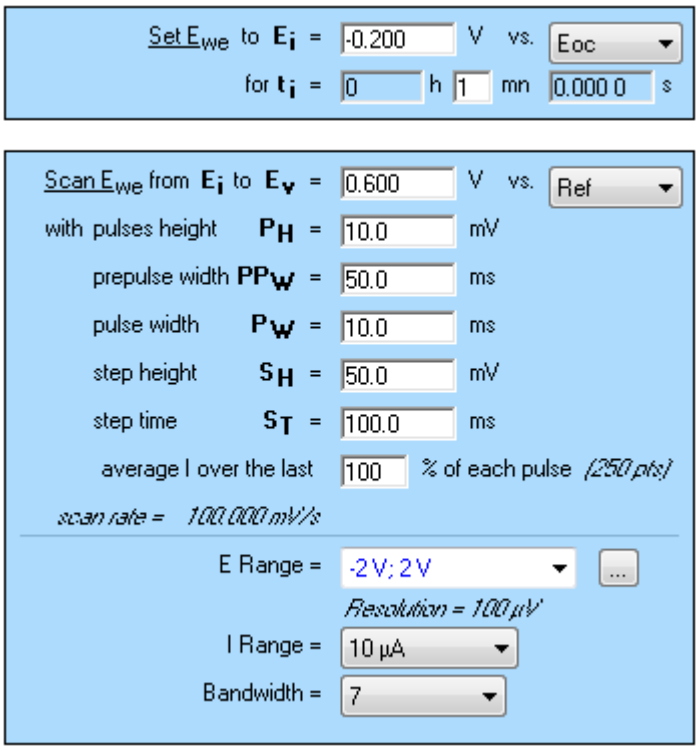


Fig. 45: DNPV detailed diagram.

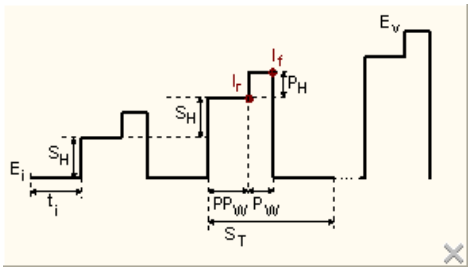


Fig. 46: DNPV waveform.

Description:

- **Initial potential**

Set E_{we} to E_i = …… V vs. Ref/Eoc/Ectrl/Emeas for t_i = …… h …… mn …… s
sets E_{we} to the initial potential E_i. This potential value can be set in absolute (vs. Ref the reference electrode potential), or according to the previous open circuit potential (E_{oc}), controlled potential (E_{ctrl}) or measured potential (E_{meas}).
Notice that only the last point of this period is recorded at the time 0.

- **Pulse waveform**

Scan E_{we} from E_i to E_v = ……. V vs. Ref/Eoc/Ei
defines the vertex potential as E_v, either in absolute (vs. Ref) or versus E_{oc} or E_i.

with **pulses height P_H = mV**
Prepulse width PP_W = ms
pulse width P_W = ms
step height S_H = mV
step time S_T = ms

The scan increment is defined by a pseudo staircase made of steps with amplitude P_H and duration S_T.
Notice that only one point is recorded at the end of the potential forward pulse and one point at the end of the potential reverse pulse, making two points during the S_T period.
The settings above (Fig. 45) are given for a positive scan. To perform a negative scan set E_v inferior to E_i and S_H to a negative value.

Scan rate = …… mV/s ….. number of points ~

These values are given as an indication and are calculated in the PC. The scan rate is directly given by $S_H / (0.001S_T)$ and the number of points is roughly $2(E_v - E_i)/S_T$ for the forward scan.

average I over the last …… % of each step *(…… points)*

Selects the end part of the potential step for the current average (<I>) calculation, to exclude the first points where the current may be disturbed by the step establishment. A value of 100 % will take all the step points for the average and a value of 0 % will take only the last point.

Note that the current average (<I>) is recorded at the end of the potential step into the data file.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

IRange …….. Bandwidth …….

sets the current range and bandwidth values for the entire experiment.

Note: It is highly recommended to not use the automatic current range with pulsed techniques. The resolution of each range is different and dynamic current range changes may lead to spikes on the plot.

DNPV recorded and calculated variables:

The variables below are stored in the DNPV raw files (*.MPR):

- state byte,
- time/s,
- control/V,
- E_{we}/V,
- <I>/mA,
- $Q-Q_0$/mA.h.

And the next variables are calculated from <I> or the potential (to save size on disk):

- I forward /mA: <I> values at the end of the pulses (I_p),
- I reverse /mA: <I> values before the pulses (I_{bp}),
- I delta /µA: difference between <I> values before and at the end of the pulse ($I_p - I_{bp}$),
- E step /V: step potential value resulting from the potential sweep and used to plot the current.

2.3.4 NPV: Normal Pulse Voltammetry

Pulsed techniques have been introduced to increase the ratio between the faradic and nonfaradic currents in order to permit a quantification of a species to very low concentration levels. The Normal Pulse Voltammetry is one of the first pulsed techniques elaborated for polarography needs. An essential idea behind the NPV is the cyclic renewal of the diffusion layer. With a DME, this is achieved by the stirring accompanying the fall of the mercury drop. But at other electrodes, renewal may not be so easily accomplished.

NPV consists of a series of pulses of linear increasing amplitude (from E_i to E_v). The potential pulse is ended by a return to the base value E_i. The usual practice is to select E_i in a region where the electroactive species of interest does not react at the electrode. The current is sampled at a time t near the end of the pulse and at a time t' before the pulse. The plotted

current is the difference of both currents measured at the end of the pulse (forward) and at the end of the period previous to the pulse (reverse).

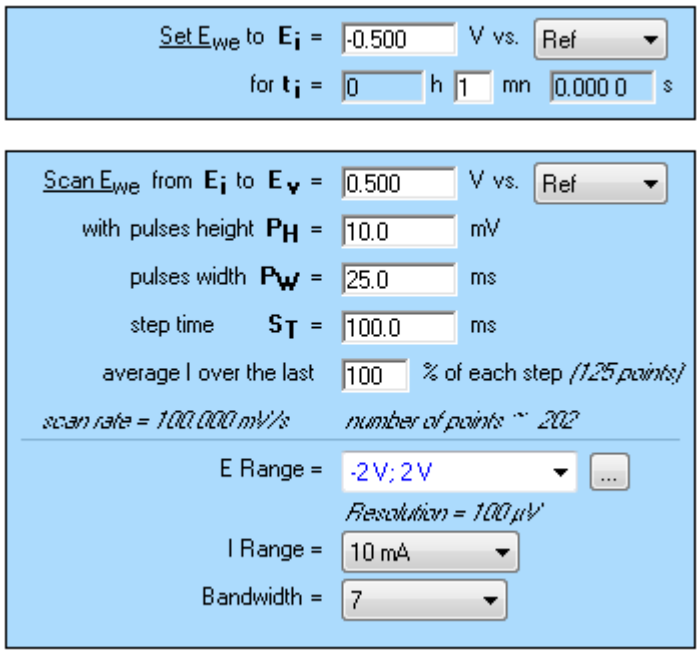


Fig. 47: NPV detailed diagram.

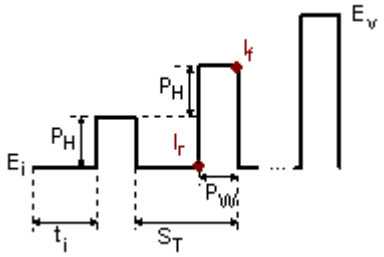


Fig. 48: NPV waveform.

Description:

- **Initial potential**

Set E_{we} to E_i = …… V vs. Ref/Eoc/Ectrl/Emeas for t_i = …… h …… mn …… s
sets E_{we} to the initial potential E_i. This potential value can be set in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}), controlled potential (E_{ctrl}), or measured potential (E_{meas}).
Notice that only the last point of this period is recorded at the time 0.

- **Pulse waveform**

Scan E_{we} from E_i to E_v = ……. V vs. Ref/Eoc/Ei
defines the vertex potential as E_v, either in absolute (vs. Ref) or versus E_{oc} or E_i.

with pulses height P_H = mV
pulses width P_W = ms
step time S_T = ms
The pulse train is made of pulses with a pulse height P_H amplitude that is added to the pulse height of the previous pulse and a pulse width P_W duration. After each pulse the potential always comes back to the initial potential. The scan increment is defined by a pseudo staircase composed of steps with amplitude P_H and duration S_T.
Notice that only one point is recorded at the end of the potential forward pulse and one point at the end of the potential reverse pulse, making two points during the S_T period.
The settings above (Fig. 47) are given for a positive scan. To perform a negative scan set E_v inferior to E_i and S_H to a negative value.

Scan rate = …… mV/s ….. number of points ~
these values are given as an indication and are calculated in the PC. The scan rate is directly given by $P_H / (0.001 S_T)$ and the number of points is roughly $2(E_v - E_i) / S_T$ for the forward scan.

average I over the last …… % of each step *(…… points)*
selects the end part of the potential step for the current average (<I>) calculation, to exclude the first points where the current may be disturbed by the step establishment. A value of 100 % will take all the step points for the average and a value of 0 % will take only the last point.
Note that the current average (<I>) is recorded at the end of the potential step to the data file.

E Range = …….
enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

IRange …….. Bandwidth …….
sets the current range and bandwidth values for the whole experiment.

Note: It is highly recommended to not use the automatic current range with pulsed techniques. The resolution of each range is different, and dynamic current range changes may lead to have spikes on the plot.

NPV recorded and calculated variables:

The variables below are stored into the NPV raw files (*.mpr):
- state byte,
- time/s,
- control/V,
- E_{we}/V,
- <I>/mA,
- Q-Q_0/mA.h.

And the next variables are calculated from <I> or from the potential (to save size on disk):
- I forward /mA: <I> values at the end of the pulses (I_p),
- I reverse /mA: <I> values before the pulses (I_{bp}),
- I delta /µA: difference between <I> values before and at the end of the pulse (I_p - I_{bp}),
- E step /V: step potential value resulting from the potential sweep and used to plot the current.

2.3.5 RNPV: Reverse Normal Pulse Voltammetry

The Reverse Normal Pulse Voltammetry is a derivative technique from the NPV. The main difference is that the initial (base) potential E_i is placed in the diffusion-limited region for electrolysis of the species present in the bulk solution. The pulses are made through the region where the species in solution is not electroactive. The RPV experiment involves a significant faradic current. This method is a reversal experiment because of the detection of the product from a prior electrolysis.

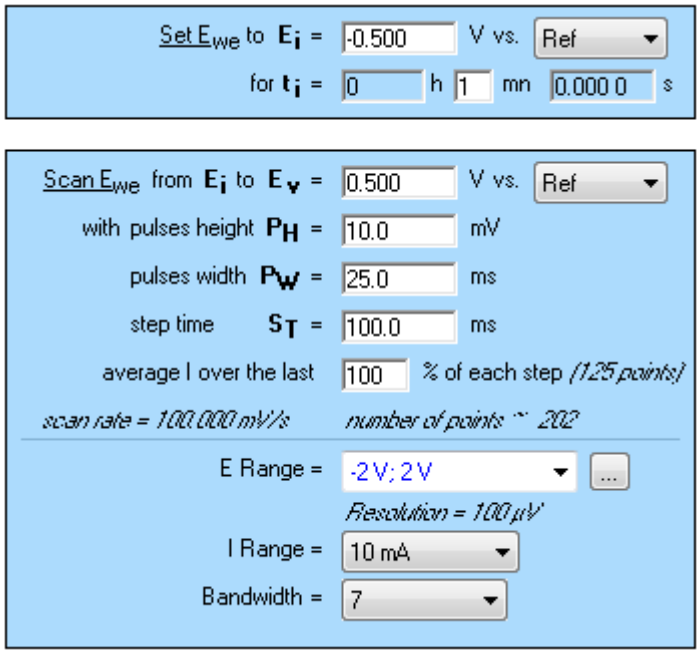


Fig. 49: RNPV detailed diagram.

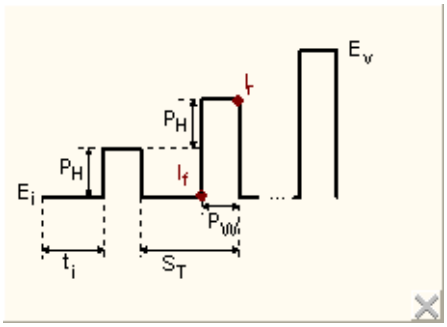


Fig. 50: RNPV waveform.

Description:

- **Initial potential**

Set E_{we} to E_i = …… V vs. Ref/Eoc/Ectrl/Emeas for t_i = …… h …… mn …… s
sets E_{we} to the initial potential E_i. This potential value can be set in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}), controlled potential (E_{ctrl}), or measured potential (E_{meas}).
Notice that only the last point of this period is recorded at the time 0.

- **Pulse waveform**

Scan E_{we} from E_i to E_v = ……. V vs. Ref/Eoc/Ei
defines the vertex potential as E_v, either in absolute (vs. Ref) or versus E_{oc} or E_i.

with pulses height P_H = mV
pulses width P_W = ms
step time S_T = ms
The pulse train is made of pulses with a pulse height P_H amplitude that is added to the pulse height of the previous pulse and a pulse width P_W duration. After each pulse the potential always comes back to the initial potential. The scan increment is defined by a pseudo staircase made with steps of amplitude P_H and duration S_T.
Notice that only one point is recorded at the end of the potential forward pulse and one point at the end of the potential reverse pulse, making two points during the S_T period.
The settings above (Fig. 49) are given for a positive scan. To perform a negative scan set E_v inferior to E_i and S_H to a negative value.

Scan rate = …… mV/s ….. number of points ~
these values are given as an indication and are calculated in the PC. The scan rate is directly given by P_H / (0.001S_T) and the number of points is roughly 2(E_v - E_i) / S_T for the forward scan.

average I over the last …… % of each step *(…… points)*
selects the end part of the potential step for the current average (<I>) calculation, to exclude the first points where the current may be disturbed by the step establishment. A value of

100 % will take all the step points for the average, and a value of 0 % will take only the last point.
Note that the current average (<I>) is recorded at the end of the potential step into the data file.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range …….. Bandwidth …….
sets the current range and bandwidth values for the entire experiment.

Note: It is highly recommended to not use the automatic current range with pulsed techniques. The resolution of each range is different, and dynamic current range changes may lead to have spikes on the plot.

RNPV recorded and calculated variables:

The variables below are stored into the RNPV raw files (*.mpr):
- state byte,
- time/s,
- control/V,
- E_{we}/V,
- <I>/mA,
- Q-Q_0/mA.h.

And the next variables are calculated from <I> or from the potential (to save size on disk):
- I forward /mA: <I> values at the end of the pulses (I_p),
- I reverse /mA: <I> values before the pulses (I_{bp}),
- I delta /µA: difference between <I> values before and at the end of the pulse (I_p - I_{bp}),
- E step /V: step potential value resulting from the potential sweep and used to plot the current.

2.3.6 DPA: Differential Pulse Amperometry

The Differential Pulse Amperometry results from the DNPV technique without increasing pulse steps. The potential waveform and the current sampling are the same as for DNPV. A DPA experiment is often used as a sensitive method for the quantification of electrochemical species at a defined potential (E_s). This potential value is often determined with a DNPV experiment (using a potential sweep with the same waveform) previously performed. This technique is dedicated to the quantification of biological electroactive species.

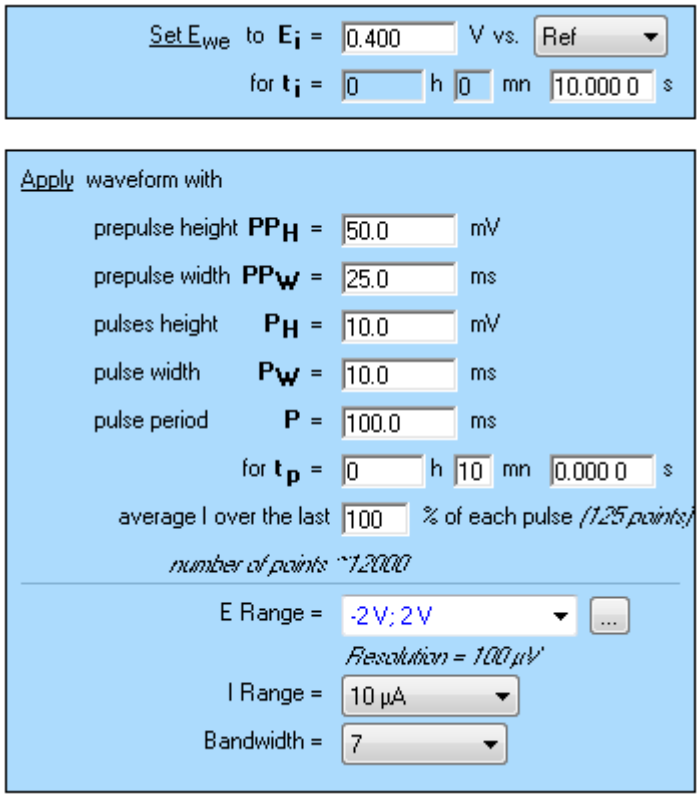


Fig. 51: DPA detailed diagram.

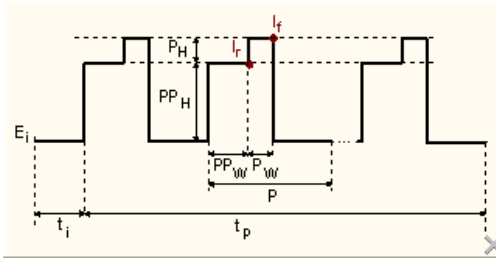


Fig. 52: DPA waveform.

Description:

- **Initial potential**

Set E_{we} to E_i = …… V vs. Ref/Eoc/Ectrl/Emeas for t_i = …… h …… mn …… s
sets E_{we} to the initial potential E_i. This potential value can be set in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}), controlled potential (E_{ctrl}), or measured potential (E_{meas}).
Notice that only the last point of this period is recorded at the time 0.

- **Pulse waveform**

Apply a waveform with the following characteristics

Prepulse height	**PP_H =**	**mV**
Prepulse width	**PP_W =**	**ms**
Pulses height	**P_H =**	**mV**
Pulse width	**P_W =**	**ms**
Period	**P=**	**ms**
Time period	**t_P =**	**ms**

Noticed that only one point is recorded at the end of the potential forward pulse and one point at the end of the potential reverse pulse, making two points during the P period.

number of points ~
This value is given as an indication and is calculated in the PC. The number of points is roughly 2(t_p) / P for the forward scan.

average I over the last …… % of each step *(…… points)*
selects the end part of the potential step for the current average (<I>) calculation, to exclude the first points where the current may be disturbed by the step establishment. A value of

100 % will take all the step points for the average, and a value of 0 % will take only the last point.
Note that the current average (<I>) is recorded at the end of the potential step into the data file.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range …….. Bandwidth …….
sets the current range and bandwidth values for the whole experiment.

Note: It is highly recommended to not use the automatic current range with pulsed techniques. The resolution of each range is different and dynamic current range changes may lead to have spikes on the plot.

DPA recorded and calculated variables:

The variables below are stored into the DPA raw files (*.MPR):

- state byte,
- time/s,
- control/V,
- E_{we}/V,
- <I>/mA,
- Q-Q_0/mA.h.

And the next variables are calculated from <I> or from the potential (to save size on disk):

- I forward /mA: <I> values at the end of the pulses (I_p),
- I reverse /mA: <I> values before the pulses (I_{bp}),
- I delta /µA: difference between <I> values before and at the end of the pulse (I_p - I_{bp}),
- E step /V: step potential value resulting from the potential sweep and used to plot the current.

2.4 Technique Builder

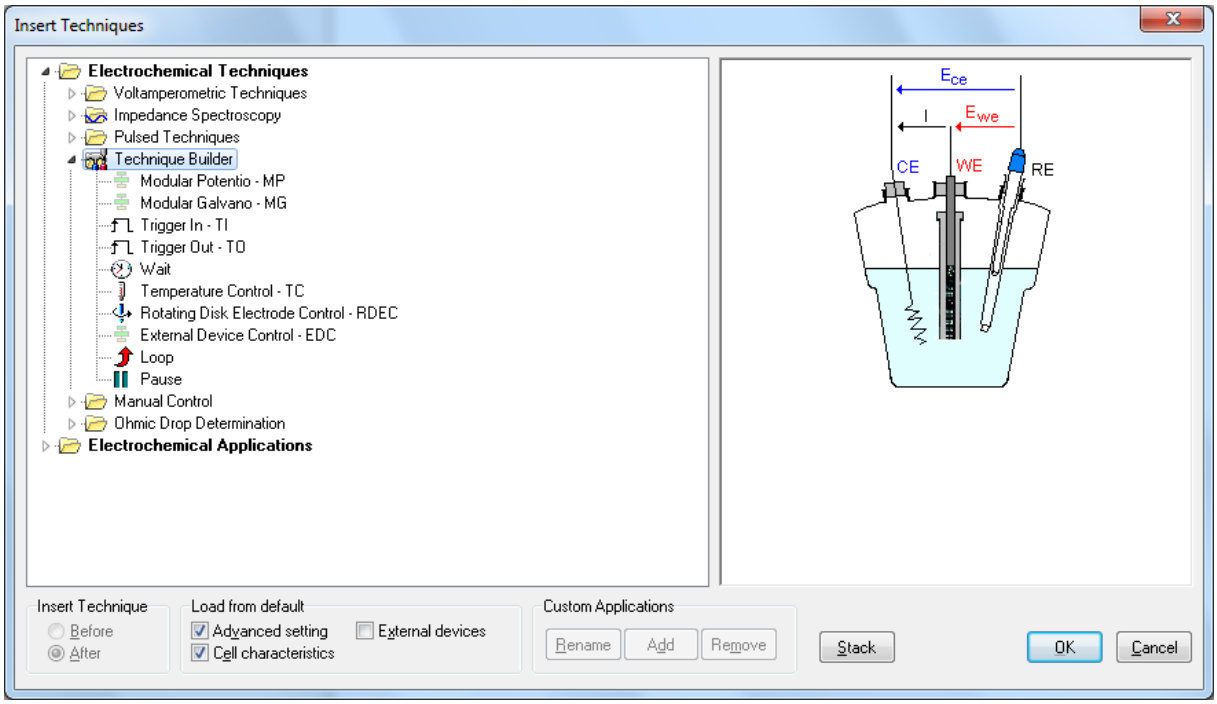


Fig. 53: Technique builder selection window.

This section is dedicated to experiment building. With the techniques and tools described in this section the user has the ability to easily create his own application with linked techniques and eventually to save the created experiment in the custom applications. The **Modular Galvano** and **Modular Potentio** techniques have been designed to cover all the electrochemical fields and experiments thanks top a modular approach. Linked with **Triggers**, **Wait** periods, external device control methods, and **loops**, these techniques become powerful enough to build complex settings.

2.4.1 MG: Modular Galvano

The Modular Galvano technique enables the user to perform combinations of OCV, galvanostatic, and galvanodynamic periods. It is possible to chain these periods in any order and to perform loops. It gives a lot of flexibility in creating galvano techniques. The galvanodymamic mode can be used to study stepwise electron-transfer reactions and multicomponent systems.

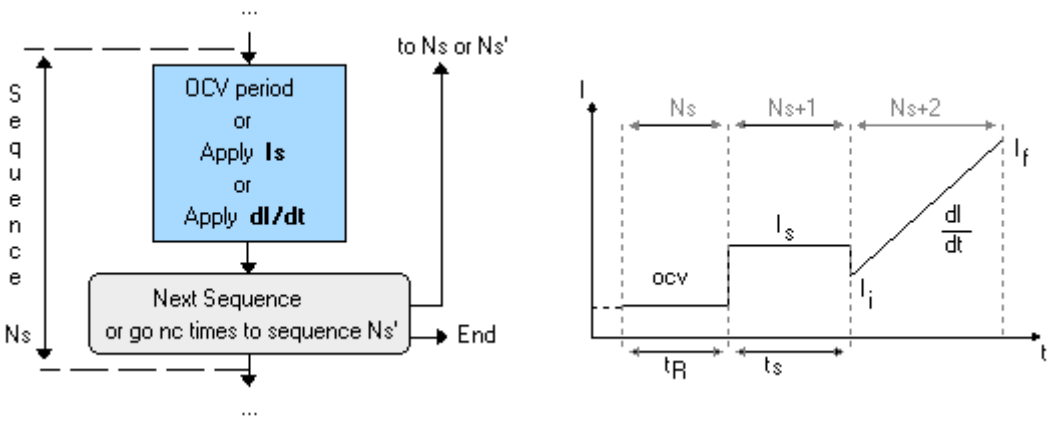


Fig. 54: Modular Galvano general diagram.

- **Mode selection:**

Click on **Mode** = OCV(0), Potentiostatic(1) or Potentiodynamic(2) to select the corresponding mode. Then the detailed diagram appears.
To select the second sequence ($N_s = 1$), click on the corresponding row in the Modular galvano table (see below).

2.4.1.1 Open Circuit Voltage (Mode = 0)

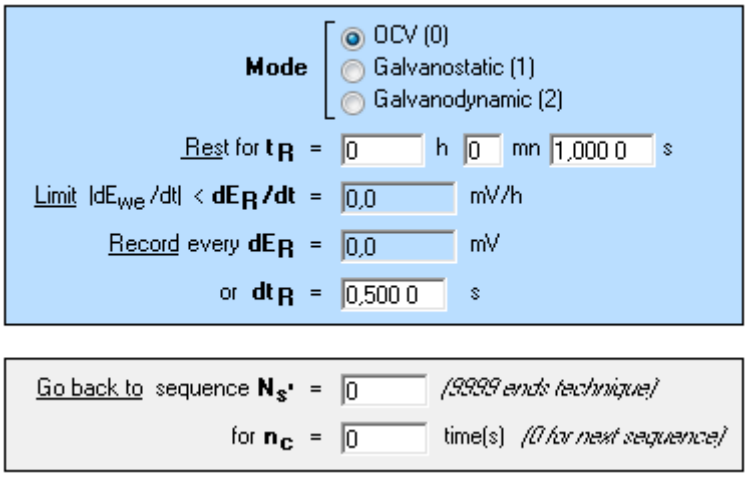


Fig. 55: MG OCV detailed diagram.

The open circuit voltage is the standard block. So report to the OCV technique section 2.1.1, page 5 for more details.

- **Loop:**

Go back to Ns' = …….. for nc = ……. time(s)
each one of the OCV, potentiostatic and potentiodynamic periods is represented by a single line in the grid parameters. If n_c is set to 0, the sequence lines are executed one after another. Then an OCV, potentiodynamic and OCV sequence for example will be programmed by 3 lines in the parameters table. Setting $n_c > 0$ will loop to a previous line $N_{s'}$ ($< N_s$) for n_c times.

Go to the battery protocols section (3.1, page 83) for more details on loops conditions. It is possible to loop to $N_{s'} = 0$, but $N_{s'}$ must be < N_s (current sequence line number).

2.4.1.2 Galvanostatic (Mode = 1)

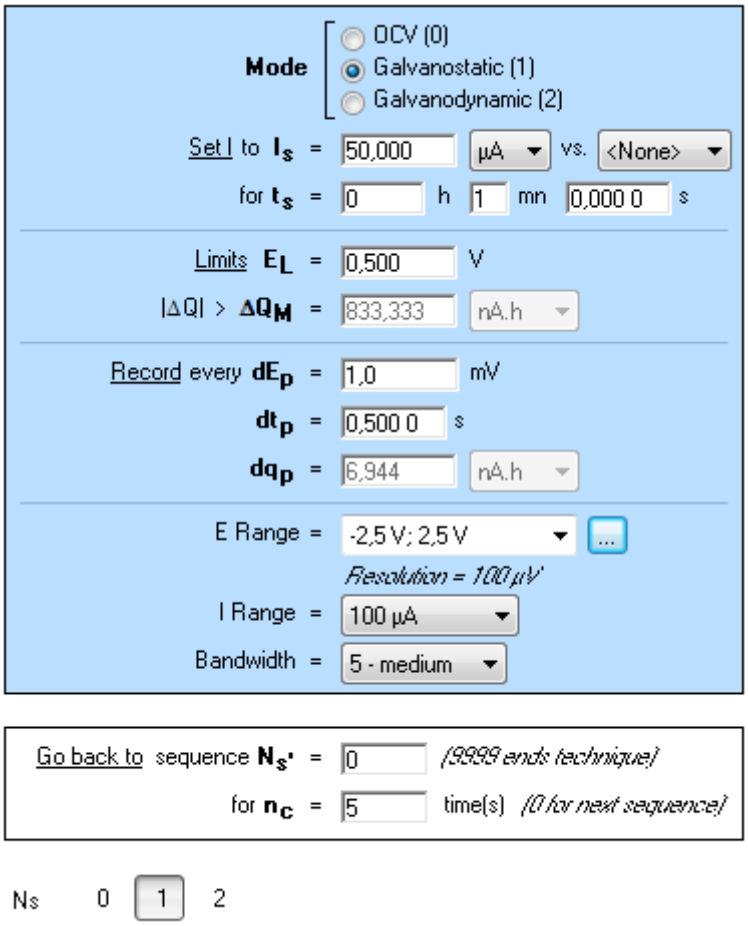


Fig. 56: Modular Galvano, Galvanostatic detailed diagram.

Set I to I_s = …….. pA/…/A vs.<None>/Ictrl/Imeas for t_s = …… h ….. mn ….. s
sets the current to a fixed value I_s for t_s time. The current value can be defined in absolute or versus a previous controlled current or measured current.

Limit E_{we} to E_L = ……. V and |ΔQ| to ΔQ_M = ……. fA.h/…/A.h/pC/…/kC
defines the potential and sequence charge limits. The E_L limit is dependent on the charge sign, the limit is:

$E_{we} > E_L$ if $I_s > 0$
$E_{we} < E_L$ else

To cancel the limits type "p" for "pass" in the E_L edition box and zero for ΔQ_M.
For the galvanostatic mode ΔQ_M is not accessible and is calculated from I_s and t_s ($\Delta Q_M = I_s \cdot t_s$).

Record every dE_p = …… mV, dt_p = ….. s and dQ_p = …… fA.h/…/A.h/pC/…/kC
defines the recording conditions. A zero value cancels the corresponding recording criterion. These values can be entered simultaneously. If so the first condition that is reached determines the recording. For the galvanostatic mode dQ_p is not accessible and is calculated from I_s and dt_p ($dQ_p = I_s \cdot dt_p$).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

With I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

2.4.1.3 Galvanodynamic (Mode = 2)

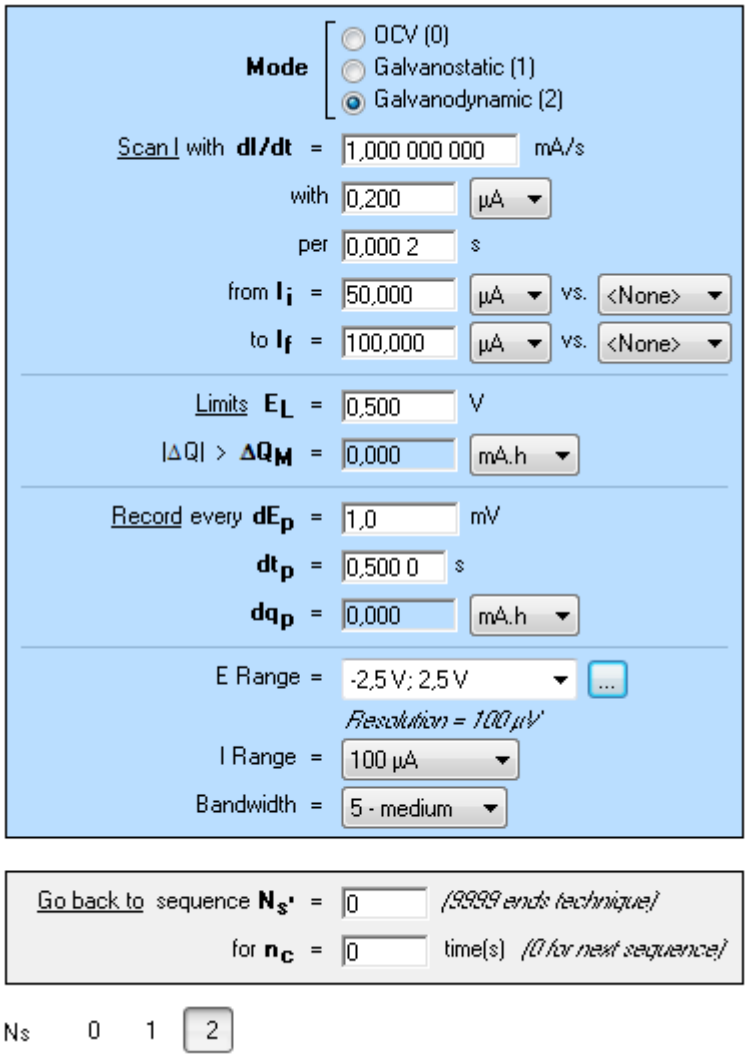


Fig. 57: Modular Galvano, Galvanodynamic detailed diagram.

Scan I with dI/dt = ……. mA/s, with …….. pA/…/A / …… s
defines the scan rate. The same as for the Modular Potentio technique, entering the dI/dt value will automatically calculate the dI and dt values in order to minimize the current steps dI. Nevertheless, one can enter dI and dt directly.

from I_i = …… pA/…/A vs. <None>/Ictrl/Imeas to I_f = pA/…/A vs. <None>/Ii.
defines the initial I_i and final I_f current of the scan.

Limit E_{we} to E_L = ……. V and |ΔQ| to ΔQ_M = ……. fA.h/…/A.h/pC/…/kC

defines the potential and sequence charge limits. The E_L limit is dependent on the charge sign, the limit is:

$E_{we} > E_L$ if $I_s > 0$

$E_{we} < E_L$ else

To cancel the limits type "p" for "pass" in the E_L edition box and zero for ΔQ_M.

For the galvanostatic mode ΔQ_M is not accessible and is calculated from I_s and t_s ($\Delta Q_M = I_s \cdot t_s$).

Record every dE_p = …… mV, dt_p = ….. s and dQ_p = …… fA.h/…/A.h/pC/…/kC
defines the recording conditions. A zero value cancels the corresponding recording criterion. These values can be entered simultaneously. If so the first condition that is reached determines the recording. For the galvanostatic mode dQ_p is not accessible and is calculated from I_s and dt_p ($dQ_p = I_s \cdot dt_p$).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

2.4.1.4 Sequences with the Modular galvano technique

The three modes of the Modular Galvano technique can be chained as sequences in the table in any order that the user requires. Each of the parameters can be modified in its box. However parameters like I Range or Bandwidth must keep the same value for all the sequences.
Note that the first sequence has the number $N_s = 0$. To switch from one sequence to another, click on the desired row in the table.
For more details about the Table frame see the chronoamperometry technique p.19.

Management of the various steps can be done thanks to sequence or table (Fig. 58).

Ns	Mode	tR (h:m:s)	dER/dt (mV/h)	dER (mV)	dtR (s)	Is	unit Is	vs.	ts (h:m:s)
0	0	0:00:1.0000	0.0	0.00	0.5000	0.000	mA	<None>	0:00:0.00
1	1	0:00:0.0000	0.0	0.00	0.0000	50.000	µA	<None>	0:01:0.00
2	2	0:00:0.0000	0.0	0.00	0.0000	0.000	mA	<None>	0:00:0.00
3							mA	<None>	
4							mA	<None>	

Fig. 58: Modular Galvano table.

Note: In this technique, the first and last data points of each current steps are not automatically recorded.

2.4.2 MP: Modular Potentio

The Modular Potentio technique performs OCV, potentiostatic and potentiodynamic periods. It is possible to chain these periods in any order and perform loops that provide great flexibility. This technique is very useful because it allows coupling potential sweep detections with preconditioning steps either in OCV or at a particular potential (preconcentration).

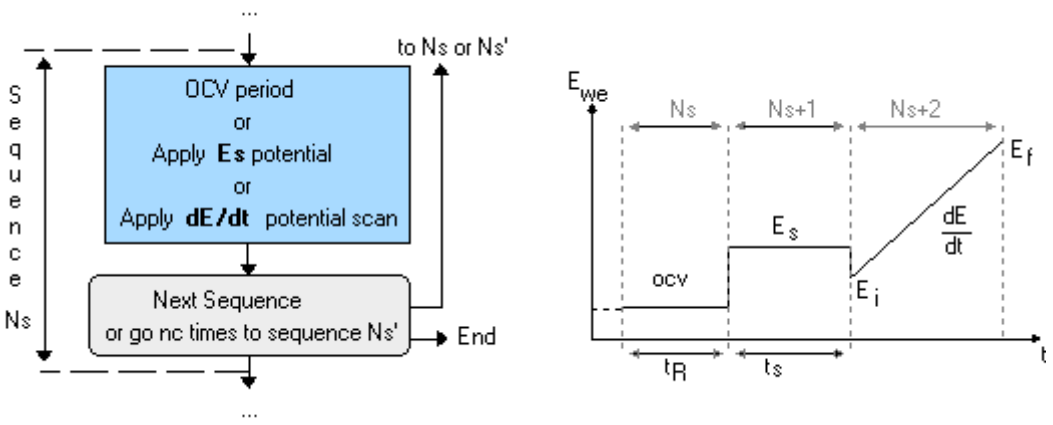


Fig. 59: Modular Potentio general diagram.

- **Mode selection:**

Click on **Mode** = OCV(0), Potentiostatic(1) or Potentiodynamic(2) to select the corresponding mode.

2.4.2.1 Open Circuit Voltage (Mode = 0)

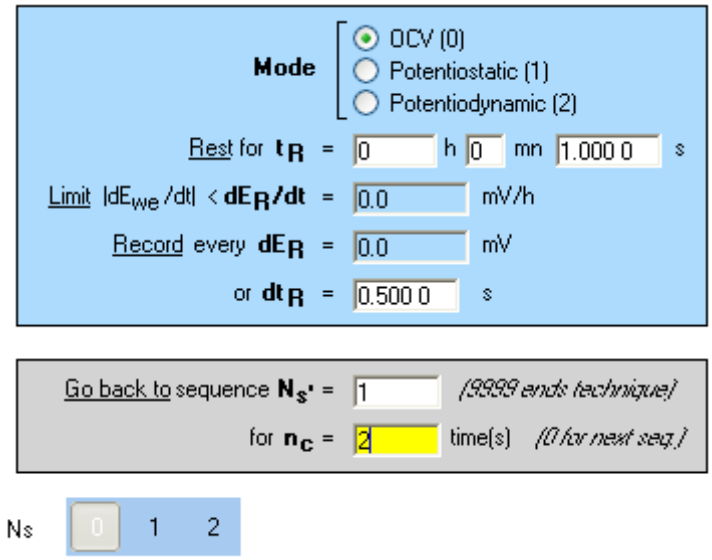


Fig. 60: Modular Potentio, OCV detailed diagram.

The open circuit voltage is the standard block, so report to the OCV technique section for more information.

- **Loop:**

goto N_s' = …… for n_c = …… time(s)
each one of the OCV, potentiostatic and potentiodynamic periods is represented by a single line in the grid parameters. If n_c is set to 0, the sequence lines are executed one after another. Then an OCV, potentiodynamic and OCV sequence for example will be programmed by 3 lines in the parameters table. Setting $n_c > 0$ will loop to a previous line $N_{s'}$ ($< N_s$) for n_c times.

Report to the battery techniques section (3.1, page 83) for more details on loop conditions.
It is possible to loop to $N_{s'} = 0$, but $N_{s'}$ must be < N_s (current sequence line number).

2.4.2.2 Potentiostatic (Mode = 1)

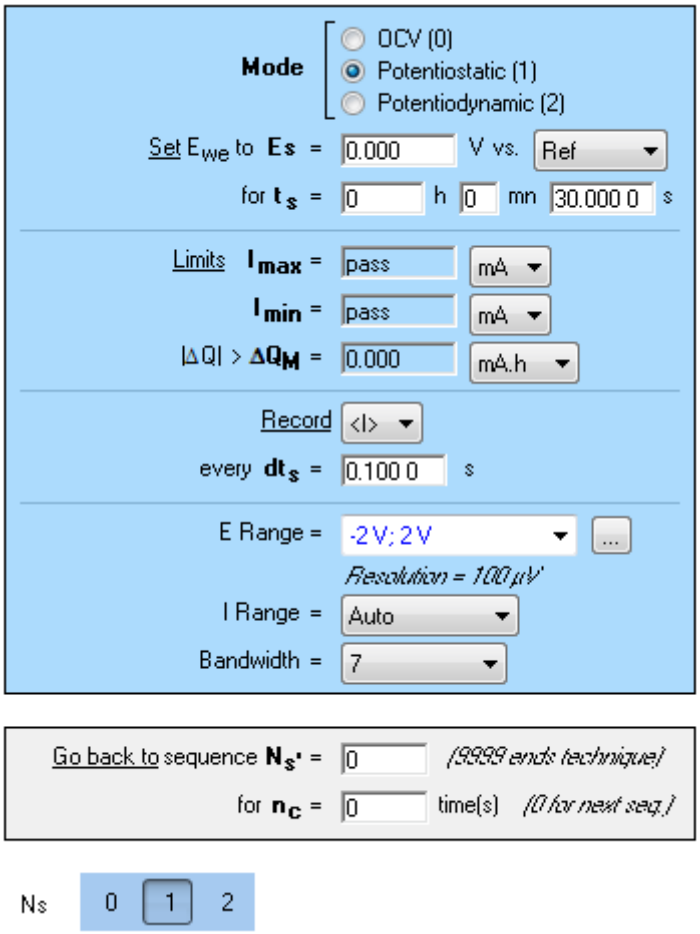


Fig. 61: Modular Potentio, potentiostatic detailed diagram.

Set E_{we} to Es = …….. V vs.Ref/Eoc/Ectrl/Emeas
sets the potential to a FIXED value (vs. Ref the reference electrode potential) or RELATIVELY to the previous open circuit potential (E_{oc}) or to the previous controlled (E_{ctrl}) or measured (E_{meas}) potential (in linked experiments or linked sequences).

for t_s = ……. h ……. mn ……. s
defines the potential step duration (if not stopped on limits)

Limit I to I_{max} = ….. pA/…A and to I_{min} = ….. pA/…/A. And |ΔQ| to ΔQ_M = ….. fA.h/…/A.h/pC/…/kC
sets limits for the potential step. If one limit is reached ($I > I_{max}$ or $I < I_{min}$ $|\Delta Q| > \Delta Q_M$) before the end of the step duration (t_s), then the program proceeds to the next sequence. A zero value disables the ΔQ_M limit, and typing "p" to enter "pass" disables the I_{max} and I_{min} limits.
Note: the ΔQ value tested here versus ΔQ_M is the current sequence (N_s) integral charge.

Record I every dI_p = …. pA/…/A, dQ_p = …… fA.h/…/A.h/pC/…/kC and dt_p = …. S

<I> every dts = …….. s

You can record either an instantaneous current value I or an averaged current value <I>. The recording conditions during the potential step depend on the chosen current variable. For the instantaneous current the recording values can be entered simultaneously. The first condition reached determines the recording. A zero value disables the recording for each criterion. For the averaged current, the user defines the time for the average calculation. In that case the data points are recorded in the channel board memory every 200 µs for the VMP2, VMP3, MPG2, VSP, SP series and the BiStat and 20 ms for the VMP and the MPG.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

2.4.2.3 Potentiodynamic (Mode = 2)

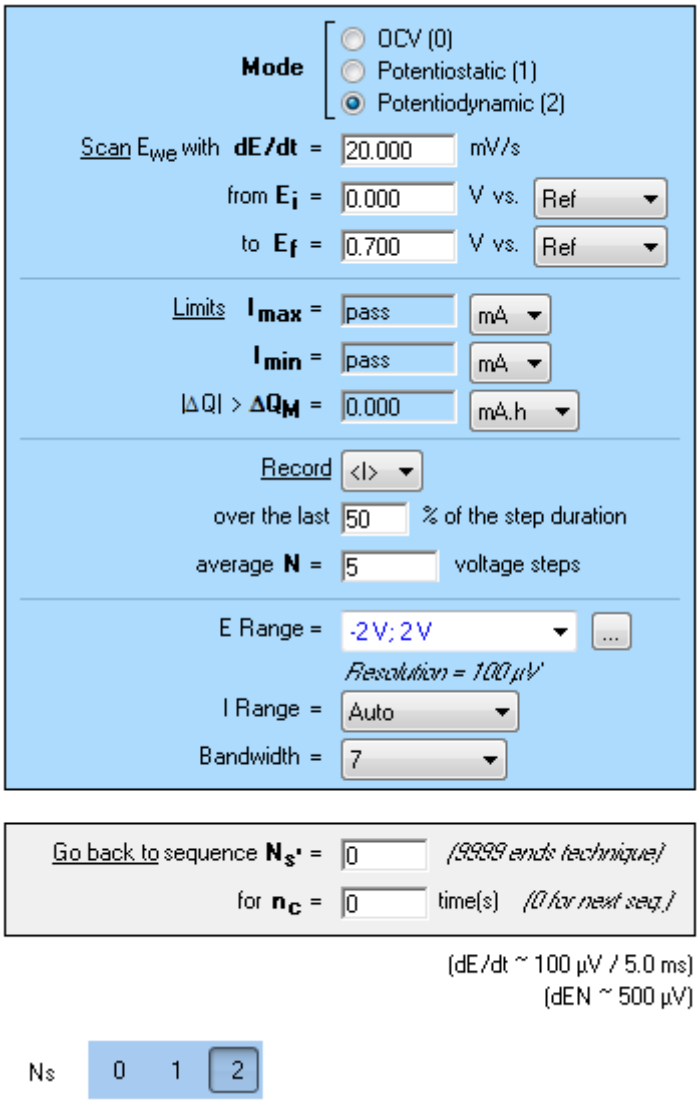


Fig. 62: Modular Potentio, potentiodynamic detailed diagram.

Scan E_{we} with dE/dt = …… mV/s
defines the potential scan speed. One can enter dE/dt, the software will automatically calculate the corresponding staircase values dE and dt that minimise the potential steps dE. However, it is possible to directly set the dE and dt values.

from E_i = …….. V vs. Ref/Eoc/Ectrl/Emeas
defines the initial potential E_i to a FIXED value (vs. Ref the reference electrode potential) or RELATIVELY to the previous sequence final open circuit potential (E_{oc}) or controlled potential (E_{ctrl}) or measured potential (E_{meas}).

to E_f = …… V vs. Ref/Eoc/E_i.
defines the final potential E_f in absolute (vs. Ref the reference electrode potential) or relatively to the open circuit potential (E_{oc}) or to the initial potential E_i.

Limit I to I_{max} = ….. pA/…A and to I_{min} = ….. pA/…/A. And |ΔQ| to ΔQ_M = ….. fA.h/…/A.h/pC/…/kC
sets limits for the potential step. If one limit is reached ($I > I_{max}$ or $I < I_{min}$ $|\Delta Q| > \Delta Q_M$) before the end of the step duration (t_s), then the program proceeds to the next sequence. A zero value disables the ΔQ_M limit, and typing "p" to enter "pass" disables the I_{max} and I_{min} limits.
Note: the ΔQ value tested here versus ΔQ_M is the current sequence (N_s) integral charge.

Record <I> over the last …… % of the step duration averaged N = ……. voltage steps
I every dI_p = …….. µA or dt_p = …… s
two different recording conditions on the current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
fixe the current range and bandwidth for this experiment.

The three modes of the Modular Potentio technique can be chained as sequences in the table in any order the user requires. Each of the parameters can be modified in its box. But parameters like I Range or Bandwidth must keep the same value for all the sequences.
Note that the first sequence has the number $N_s = 0$.

Ns	Mode	tR (h:m:s)	dER/dt (mV/h	dER (mV)	dtR (s)	Es (V)	vs.	ts (h:m:s)	dE/dt (mV
0	0	0:00:1.0000	0.0	0.00	0.5000	0.0000	<None>	0:00:0.0000	0.000
1	1	0:00:0.0000	0.0	0.00	0.0000	0.0000	<None>	0:00:30.0000	0.000
2	2	0:00:0.0000	0.0	0.00	0.0000	0.0000	<None>	0:00:0.0000	20.000
3							<None>		
4							<None>		

Fig. 63: Modular Potentio table.

Note: in this technique the first and last data points of each potential steps are not recorded automatically.

2.4.3 Triggers

Selecting the triggers option allows the user to insert a trigger command before or after a technique. The procedure is the same as for linked techniques. Two options are available:

trigger in and trigger out. The next table summarizes the different possibilities for trigger in and out:

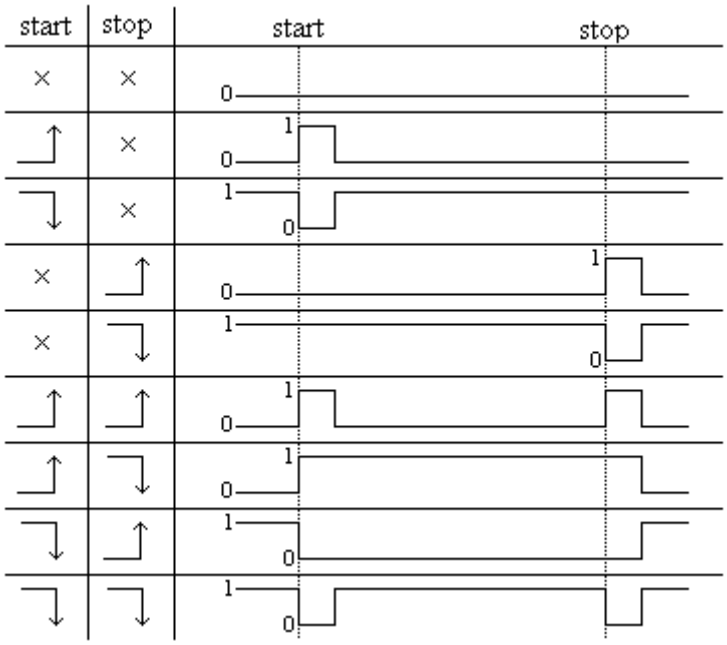


Table 1: Triggers in and out.

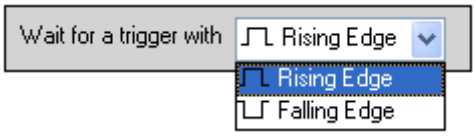


Fig. 64: Trigger In and Out.

The trigger In option puts the instrument in a waiting configuration until it receives a trigger with rising edge (or falling edge) depending on the instrument that generates the trigger signal. The trigger Out option sends a trigger to an external instrument with a rising edge (or falling edge) before or after a technique. It is possible to select the duration of the Trigger Out. Inserting the trigger before or after the technique will start or stop the run. These features can be set for every technique of the experiment.

The triggers are available on the DB9 connector as described below:

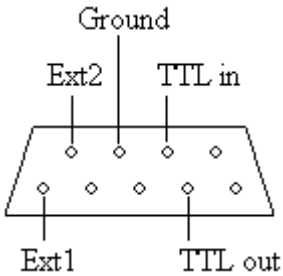


Fig. 65: DB9 Pin assignment.

A special cable made with a DB9 connector on one side and 8 BNC plugs on the other side is provided with the instrument upon request.

2.4.4 The Wait Option

The Wait option has been designed for linked experiments. This technique can be loaded only once another technique has been previously loaded.

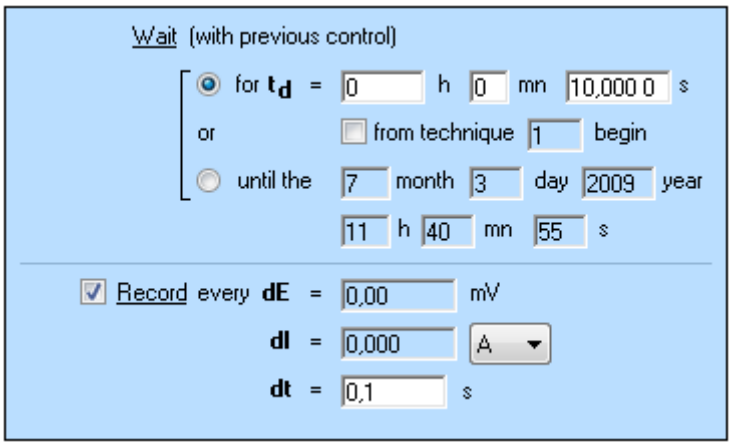


Fig. 66: Wait.

Wait (with previous control)

For t_d = ….. h ….. mn …… s □ from technique …… begin

It is possible to choose the wait duration (t_d). In that case the duration can start at the end of the previous technique or the beginning of a particular technique.

Until the ….. month ….. day …… year …. h ……mn ….. s

The user can define the date of the end of the wait technique (**until …**).

Record every dE = …… mV dI = …. pA/…/A and dt = …. s

choose one or several recording conditions.

2.4.5 Temperature Control – TC

The Temperature Control (TC) technique allows the user to control a temperature, and change it during the experiment. A direct link to the External Device window is done by clicking on the underlined words.

The TC technique contains a table, then the user can link several TC sequences (row Ns = 0 to n). Only one row of the table is executed at each loop of the experiment (beginning to Ns = 0) and is incremented with the following loops. This tool allows the user to have, for example, an increase of the temperature values and to maintain during a defined duration this temperature value before each step.

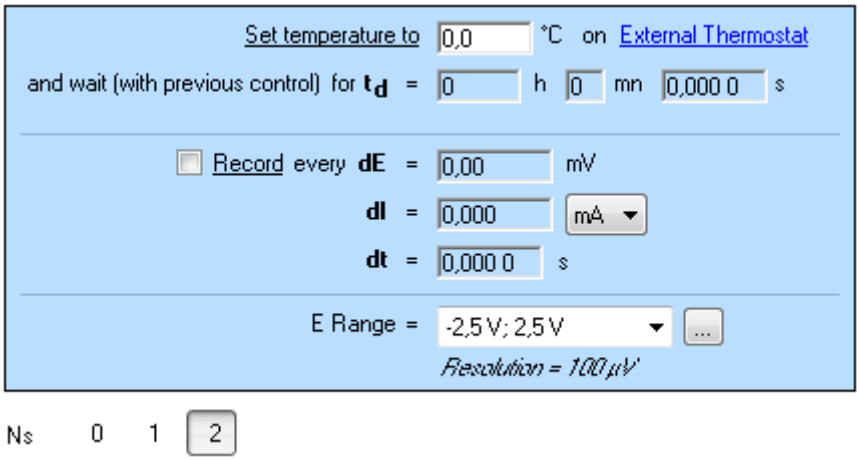


Fig. 67: Temparature control.

□ **Set temperature to ……. Rpm on** External Thermostat
one can set a temperature and configure the temperature recording using the External thermostat link (menu **Config, External Devices**, see the Critical Pitting Temperature for the VMP only...).

Record every dE = …… mV dI = …. pA/…/A and dt = …. s
chooses one or several optional recording conditions.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

Caution: The TC technique has a parameters table in the "parameters settings" window which can be related to the sequences selection. The user can link several TC sequences (N_s = 0 to n). These sequences are linked differently from the other techniques. In other standard technique one sequence is executed directly after the other. For the TC technique each sequence corresponds to a loop of a linked technique (see after). Therefore only one sequence of the wait technique is executed at each loop of the linked experiment. The sequences are considered successively at each loop. This allows the user to increase temperature values at each sequence/loop.
If more experiment loops than the number of sequences are set in the TC experiment table, then the TC technique is restarted from the beginning.

2.4.6 Rotating Disk Electrode Control – RDEC

The Rotating Disk Electrode Control (RDEC) technique allows the user to control a rotating speed, and change it during the experiment. A direct link to the External Device window is done by clicking on the underlined words.
The RDEC technique contains a table, then the user can link several RDEC sequences (row Ns = 0 to n). Only one row of the table is executed at each loop of the experiment (beginning to Ns = 0). This tool allows the user to have, for example, an increase of the rotating speed and to maintain during a defined duration this rotating speed before each step.

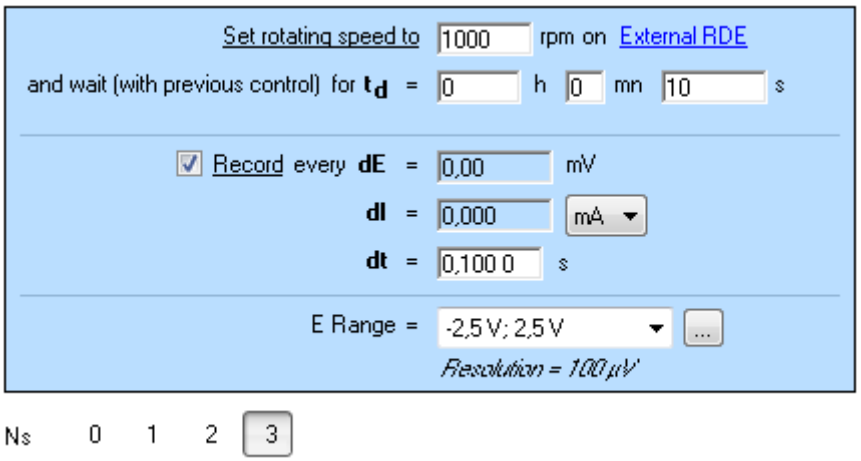


Fig. 68: Rotating Disk Electrode Control.

□ Set rotating speed to ……. rpm
one can set a temperature or the rotating electrodes speed if configured (menu **Config, External devices**,...). The recordings are optional.

Record every dE = …… mV dI = …. pA/…/A and dt = …. s
chooses one or several optional recording conditions.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)
The RDEC technique has a parameters table in the "parameters settings" window which can be related to the sequences selection.

Ns	Apply control	Control/°C/rpm	select td	td (h:m:s)	from prot. num.	prot. num.	date (m/d/y)	date (h:m:s)
0	1	1000.0	1	0:00:1.0000	0	1	10/15/20	14:44:42
1	1	2000.0	1	0:00:1.0000	0	0	01/01/20	00:00:00
2	1	3000.0	1	0:00:1.0000	0	0	01/01/20	00:00:00
3	1	4000.0	1	0:00:1.0000	0	0	01/01/20	00:00:00
4	1	5000.0	1	0:00:1.0000	0	0	01/01/20	00:00:00

Fig. 69: Wait table.

Caution: The RDEC technique has a parameters table in the "parameters settings" window which can be related to the sequences selection. The user can link several RDEC sequences (N_s = 0 to n). These sequences are linked differently from the other techniques. In other standard technique one sequence is executed directly after the other. For the RDEC technique each sequence corresponds to a loop of a linked technique (see after). Therefore only one sequence of the wait technique is executed at each loop of the linked experiment. The sequences are considered successively at each loop. This allows the user to increase temperature values at each sequence/loop.
If more experiment loops than the number of sequences are set in the RDEC experiment table, then the RDEC technique is restarted from the beginning.

2.4.7 External Device Control –EDC

The External Device Control (EDC) technique allows the user to control an external device, and change external device parameters during the experiment. A direct link to the External Device window is done by clicking on the underlined words.
The EDC technique contains a table, then the user can link several EDC sequences (row Ns = 0 to n). Only one row of the table is executed at each loop of the experiment (beginning to Ns = 0). The external device parameters can be hold during a defined duration before each step.

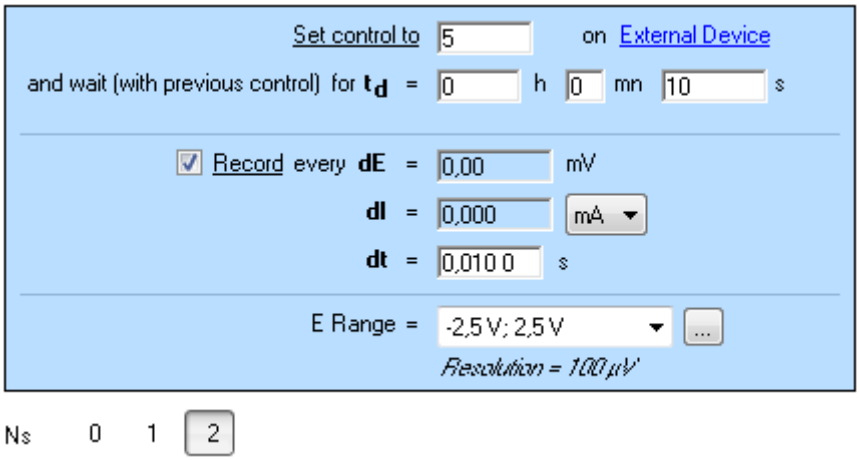


Fig. 70: External Device Control parameters.

□ Set control to …….
one can configure the external device using the link External devices (menu **Config, External devices**). The recordings are optional.

Record every dE = …… mV dI = …. pA/…/A and dt = …. s
chooses one or several optional recording conditions.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)
The EDC technique has a parameters table in the "parameters settings" window which can be related to the sequences selection.

2.4.8 The Loop option

As with the Wait option, the loop option has been designed for linked experiments. This technique can be loaded only when another technique has been previously loaded.

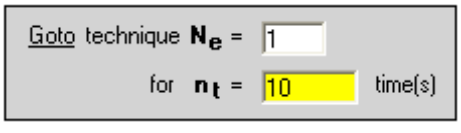


Fig. 71: Loop technique.

This option goes to a previous technique loaded in the experiment and can repeat this operation several times

Note that it is possible to apply a 50 ms OCV period between two techniques with linked techniques (reduced to 0.6 ms if the previous technique is an OCV). The user just has to activate **"Turn to OCV between techniques"** in the Advanced Settings window.

2.4.9 The Pause technique

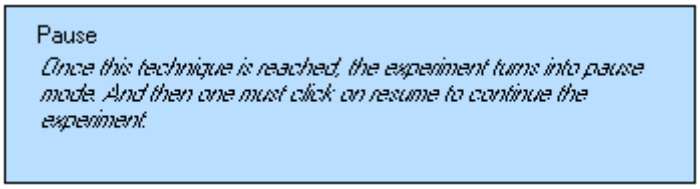


Fig. 72: Pause technique.

Once this technique is reached the experiment is turns into Pause mode. The user must click on the resume button to continue the experiment. In this case the instrument is in the OCV mode.

2.5 Manual Control

2.5.1 Potential Manual Control

This application enables the user to directly control the working electrode potential using the mouse to move a sliding index.

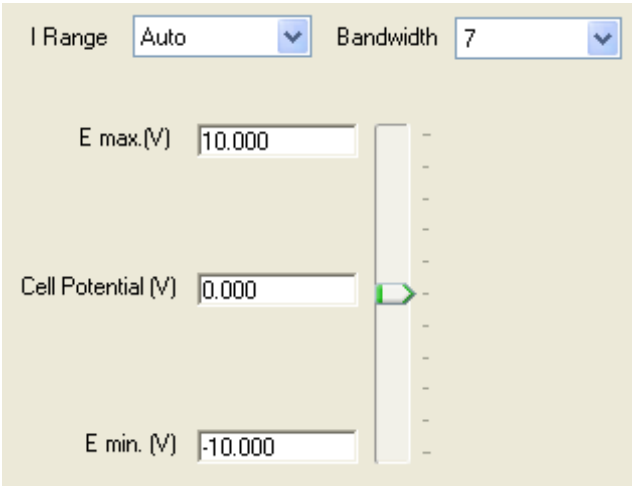


Fig. 73: Manual Potential Control.

It contains a sliding index, 2 boxes for setting the lower and upper limits of the potential, one box for the current potential value, and the possibility to select the bandwidth.

Potential setting: once you have selected this menu, you can fix the potential limits and the controlled potential. Then accept the settings.

Application of the potential to the cell: this is performed by using the **Run** button. If you have already set a potential in the intermediate box, this potential is applied to the cell. If not, it will be the value corresponding to the index position.
Moving the sliding index acts on the potential value in the given limits. You can also change the potential value in the intermediate box. It is applied when you hit enter.

The cell is turned off by using the **Stop** button.

You can always read the applied potential and the current running in the cell in the potential and current panels on the right.

2.5.2 Current Manual Control

This menu proposes the same features as the Potential Manual Control by replacing the potential control by the current control. Therefore report to the Potential Manual Control section previously described for more details.

2.6 Ohmic Drop Determination

The ohmic drop is defined by the solution resistance between the working electrode and the reference electrode. It is a critical parameter that can be significant when experiments are made in nonaqueous media. It may lead to severe distortion of the voltammetric response. The best way to determine the uncompensated resistance (R_u) is to perform an impedance measurement at high frequencies before to run other experiments.

2.6.1 MIR: manual IR compensation

If the user knows the value of Ru, he should set the value in the box and define the compensation percentage. The value of compensate R_u can be used for IR compensation in linked techniques.

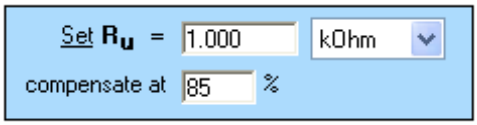


Fig. 74: MIR diagram.

2.6.2 ZIR: IR compensation with EIS

The ZIR technique offers the possibility to determine the solution resistance R_u for one high frequency value. The user can select the percentage of compensation. It is highly recommended to not exceed 85% of the R_u measured value to avoid oscillations of the instrument. To compensate the solution resistance, the user has to put this ZIR technique before other experiments in a linked experiments series; by this way R_u value will be automatically considered before each experiment of the series.
This technique is very close to the Potentiostastic Impedance technique (PEIS), except that the EIS measurement is made for only one frequency. So report to the PEIS experiment section for more details.

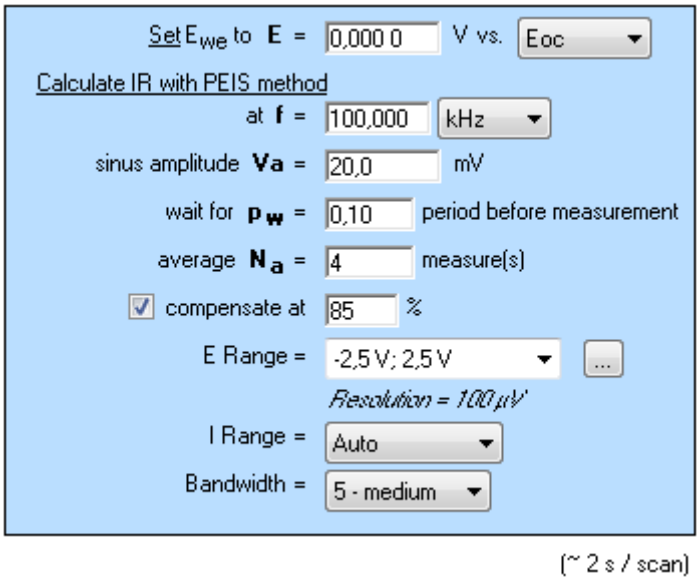


Fig. 75: ZIR diagram.

- **Impedance scan**

Set Ewe to E = …. V vs. Ref/Eoc/Ectrl/Emeas
sets the potential to a fixed value E (vs. Ref, the reference electrode potential) or relatively to the previous:

- OCV potential (E_{oc}),
- controlled potential (E_{ctrl}),
- measured potential (E_{meas}).

Calculate IR with PEIS method at f = ….. MHz/kHz/Hz/mHz/µHz
defines the frequency to measure the resistance.

with an amplitude V_a = …… mV
sets the sinus amplitude to V_a.

Wait for p_w = …… period before each frequency measurement
offers the possibility to add a delay before the measurement at each frequency. This delay is defined as a part of the period. Of course for low frequencies the delay may be long.

average N_a = …… measure(s) per frequency
repeats N_a measure(s) and average values.

□ **Compensate at ….. %**
defines the level of the measured uncompensated resistance R_u that will be compensated to define IR. The user can check the box to consider the compensated resistance in the following technique or not.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = ……. Bandwidth = …….
sets the current range and bandwidth values for the whole experiment.

2.6.3 CI: Current Interrupt

Some set-up induces ohmic drop, iRu. In that case, ohmic drop can be significant and then affects the measurement. A method to determine/estimate the resulting uncompensated resistance (Ru) is to perform the Current Interrupt (CI) method. A current step is applied and the Ru value is determined by the ratio between the measured voltage and the measured current. The CI technique enables the user to determine the resistance when the current step is applied ((E2 - E1) / (I2 - I1)) and/or interrupted ((E4 - E3) / (I4 - I3)). Then an averaged correcting Ru value is calculated. Averaged values can be determined on several cycles. The user can select the percentage of compensation. It is highly recommended to not exceed 85% of the Ru measured value in order to avoid oscillations of the instrument.

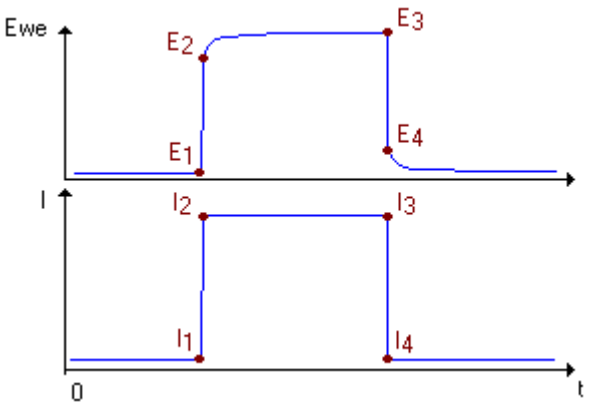


Fig. 76: Current Interrupt principle.

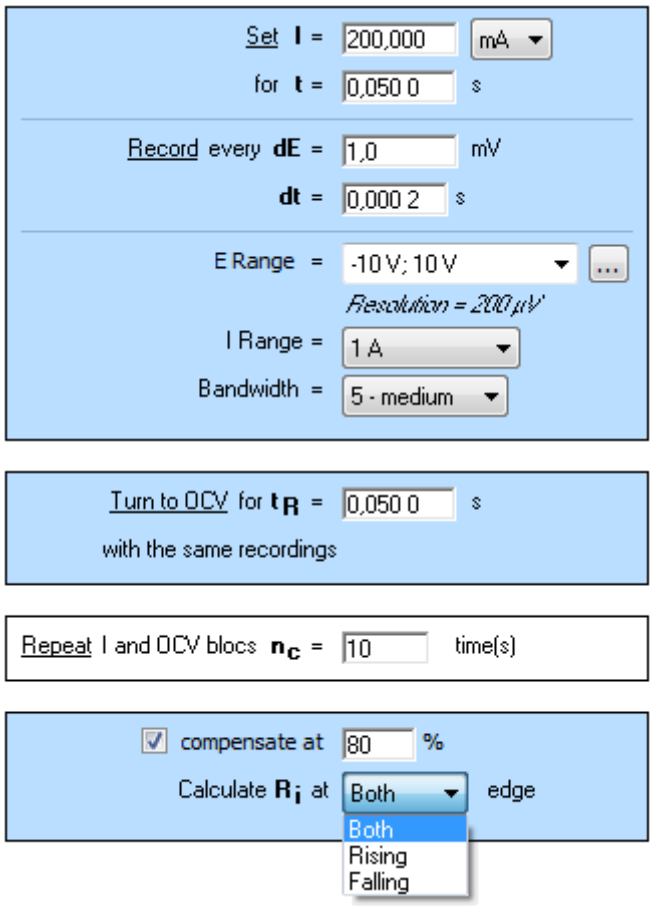


Fig. 77: Current Interrupt detailed diagram.

Set I = …. pA/…/A for t = ... s
sets the current to a fixed value I

Record every dE = …… mV and dt = …. s
chooses one or several optional recording conditions.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = ……. Bandwidth = …….
sets the current range and bandwidth values for the whole experiment.

Turn to OCV for t_R = ... s with the same recordings
Turn to the OCV mode for a given time with the same recording conditions as the galvanostatic block

Repeat I and OCV blocks nc = ... times
Repeat the previous two sequences to calculate an averaged resistance value.

□ **Compensate at ….. %**
defines the level of the measured uncompensated resistance R_u that will be compensated to define IR. The user can check the box to consider the compensated resistance in the following technique or not.

Calculate Ri at Both/Rising/Falling edge
Do the resistance calculation for either the rising edge, or the falling edge or both of them.

3. Electrochemical applications

3.1 Battery

In this application domain, it is usual to run a succession of charge and discharge sequences with possible open circuit periods, varying the conditions for the cycles.

The techniques are defined on the basis of controlled mode and open circuit mode. The controlled variable is either the potential or the current. A controlled current event is called a sequence whereas a controlled potential is labelled as a sweep. Such a sweep or sequence appears as a line in the parameter value table associated with the technique. The user can set the variable values directly in the table or can set them in the diagram.

After a first specific sequence (or sweep), $N_S = 0$, which enables the user to perform an open circuit period while recording only the potential (no controlled value can be set in this first sequence/sweep), the technique executes the successive $N_{S'}$ sequences/sweeps of the table lines.

It is possible to run partial cycling before changing cycling conditions. To do so, the user must loop to a previous sequence/sweep $N_{S'}$ ($N_{S'} < N_S$) and repeat the loop n_c times (note that the number of such cycles will be $n_c + 1$).

Skipping to the next sequence/sweep (or line) is obtained by setting n_c to 0.

A usual technique consists of a first sequence/sweep ($N_S = 0$) of open circuit potential, then a second sequence/sweep ($N_S = 1$) of charge, then a third sequence/sweep ($N_S = 2$) of discharge and finally a loop on the second sequence/sweep ($N_S = 1$) for a given time.

To skip directly from a controlled current/potential period mode to the next sequence, without an open circuit period, the user must set the open circuit period to 0 ($t_r = 0$).

The end of the technique is obtained when $N_{S'}$ and n_c take 0 values in the last sequence/sweep. It is also possible to force the end of the technique by setting $N_{S'}$ to 9999 at any sequence/sweep.

3.1.1 PCGA: Potentiodynamic Cycling with Galvanostatic Acceleration

This application corresponds to electrode cycling under stepwise potentiodynamic mode. The user is allowed to define the potential sweep by setting the potential step amplitude and duration. It is also possible to go to the next potential step before the duration which has ended if the charge or discharge currents are lower than a given value, while stille cycling with a minimum galvanostatic rate.

This is a direct technique for determination of the incremental capacities, - dx/dV, of insertion electrode materials while using the compacting function (report to the end of this section). The quality of the determination is usually better than that obtained by derivation of a titration curve made with chronopotentiometry under galvanostatic mode (because of the significant noise on the potential derivative with respect to the charge, i.e time).

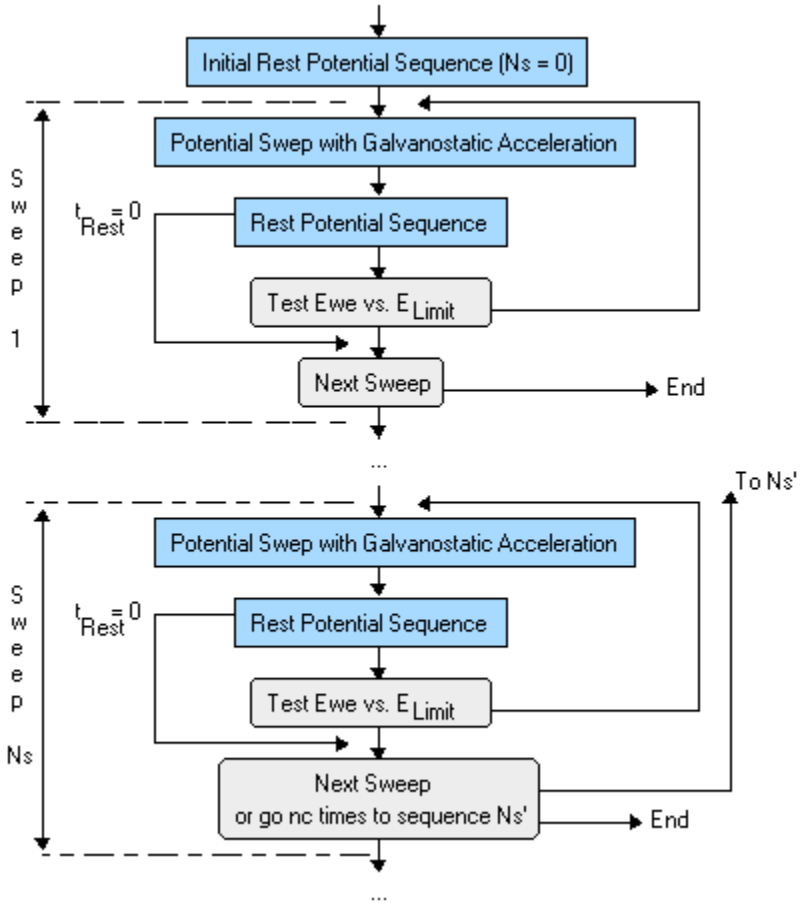


Fig. 78: General diagram of the PCGA application.

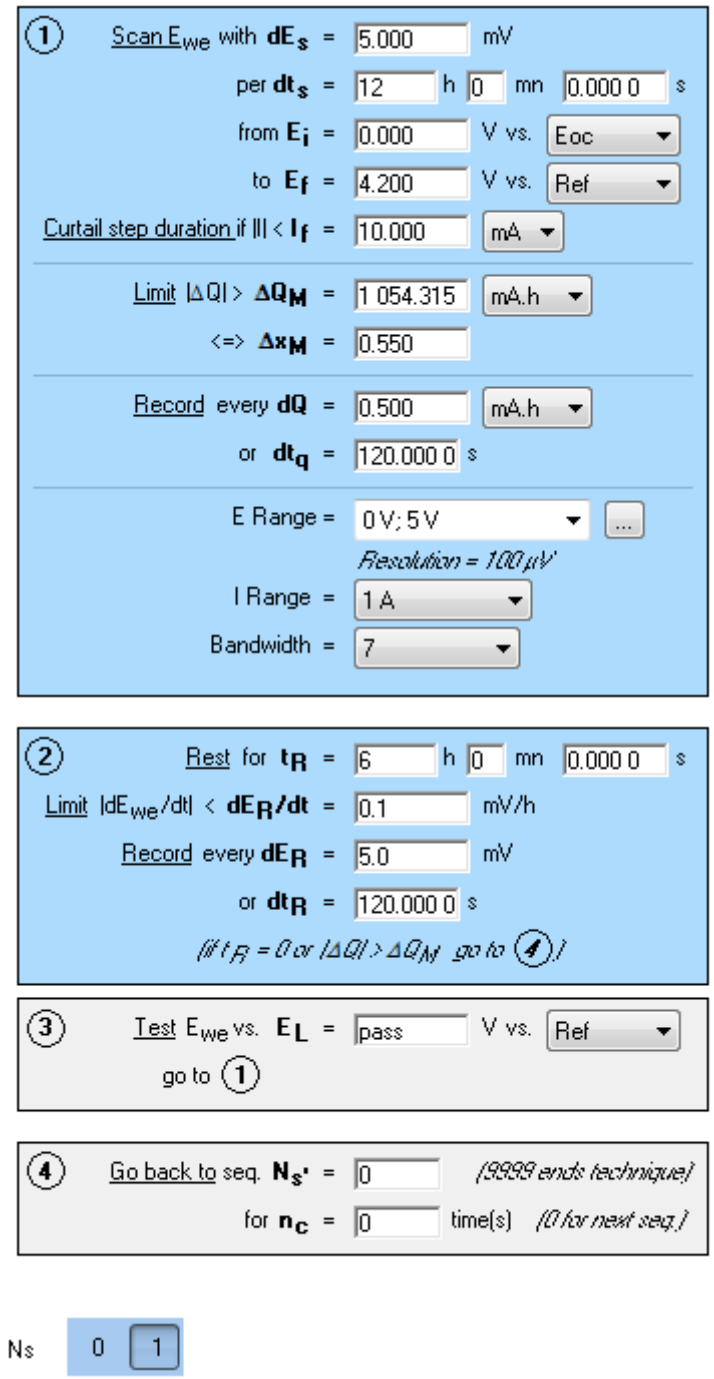


Fig. 79: Detailed diagram of a PCGA sweep.

3.1.1.1 Description of a potentiodynamic sequence

See Fig. 79.

- **First step: stepwise potentiodynamic sweep.**

Scan E_{we} with dE_s= ……. mV per dt_s = ……. h ……. mn ….. s
fixes the potential scan rate, choosing the step amplitude dE_s and its duration dt_s independently. According to the control potential resolution, it might be necessary to adjust the experiment limit to have exactly the desired potential step amplitude. The default resolution is near 300 µV for the SP-150, VSp, VMP3 technology and 333µV for the SP-200/300 technology. For example this resolution cannot lead to exact 5 mV steps (because

5/0.3 = 16.67 is not a integer). In that case the user will receive the following warning message:

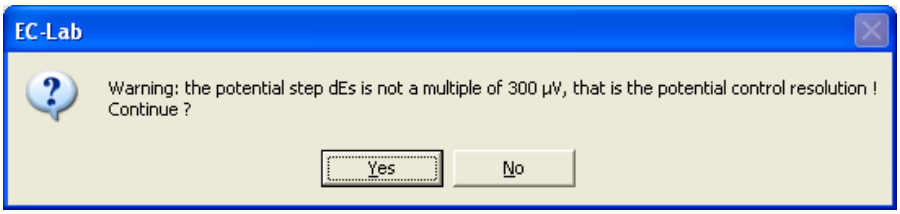


Fig. 80: PCGA warning message for the step amplitude.

If the user answers Yes the step will automatically be adjusted to 5.1 mV instead of 5 mV. To perform exact 5 mV steps, the potential control resolution must be adjusted (report to the corresponding section in the EC-Lab® software manual for more details).

From E_i = …….. V vs. Ref/Eoc/Ectrl/Emeas
sets the starting potential in absolute (vs. Ref the reference electrode potential) or with respect to the final open circuit potential value of the previous sequence E_{oc} or the previous controlled potential value (E_{ctrl}) or the previous measured potential value (E_{meas}). It allows the experiment to start at the open circuit potential of the battery.

to E_f = …….. V vs. Ref/Eoc/Ei
sets the final potential in absolute (vs. Ref the reference electrode potential or versus the previous open circuit potential or previous the initial potential).

Curtail step duration if |I| < I_f = …….. pA/…/A
fixes a minimum value for the current. As soon as the measured current value is lower than I_f, the next potential step is performed. This is the "galvanostatic" acceleration.

Record ΔQ every dQ = ……. mA.h and at least every dt_q = …… s
in the constant potential mode the system acts as a coulometer and a recording is performed every time the charge increment/decrement since the previous recording is ≥ dQ and/or every dt_q time interval.

Limit ΔQ to ΔQ_M = ……. mA.h <=> Δx_M = ……
fixes the maximum charge change from the beginning of this sequence during the sequence. This charge is equivalent to a Δx_M quantity, which corresponds to a normalized charge (related to intercalation electrodes).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

- **Second step: open circuit period as in the GCPL technique.**

turn to Rest for t_R = h mn s
or until $|dE_{we}/dt| < |dE_R/dt|$ = mV/h
Record E_{we} every dE_R = mV and at least every dt_R = s
reports to the OCV technique description for more details (section 2.1.1, page 5).

- **Third step: test on the open circuit final potential, as in the GCPL technique too.**

test E_{we} vs. **E_L = ……. V vs. Ref/Eoc/Ei.**

the test is performed according to the conditional value either > if the open circuit sequence occurs after a charge (I > 0) or < in the case of a discharge (I < 0).
As seen previously, the above 3 steps will be repeated until the working electrode potential reaches the limiting condition $E_{we} \geq E_L$ after a charge or $E_{we} \leq E_L$ after a discharge.

Note: the user is allowed to bypass this test by entering p (= pass) instead of a voltage value.

- **Fourth step: repeat sequences**

The fourth step fixes the next sweep by filling the $N_{S'}$ and n_c variables as seen in tutorial 2 for the GCPL technique: setting $N_{S'}$ to a previous sweep and n_c to the number of repeats will loop n_c times to $N_{S'}$. Setting n_c to 0 will go to the next sweep (or will end the technique on the last sweep). Setting $N_{S'}$ to 9999 will stop the technique at the end of this sweep.

A sweep corresponds to a line in the table. The columns represent the successive values for variables of the diagram, the current range, the bandwidth settings, and the loop conditions. The current range and bandwidth settings are obtained either with a double click on any cell of the corresponding columns or directly in the cell characteristics window.

Warning (see also GCPL - Warnings 1 and 2): when running a charge cycle (positive potential sweep), the value of the electrode potential for the test, E_L, must be set at a lower value than the sweep limit value, E_f.
Similarly, when running a discharge cycle (negative potential sweep), E_L, must be set at a more positive value than the sweep limit value, E_f.

The cell characteristics window for battery testing applications has been previously described.

3.1.1.2 Description of the cell characteristics window for batteries

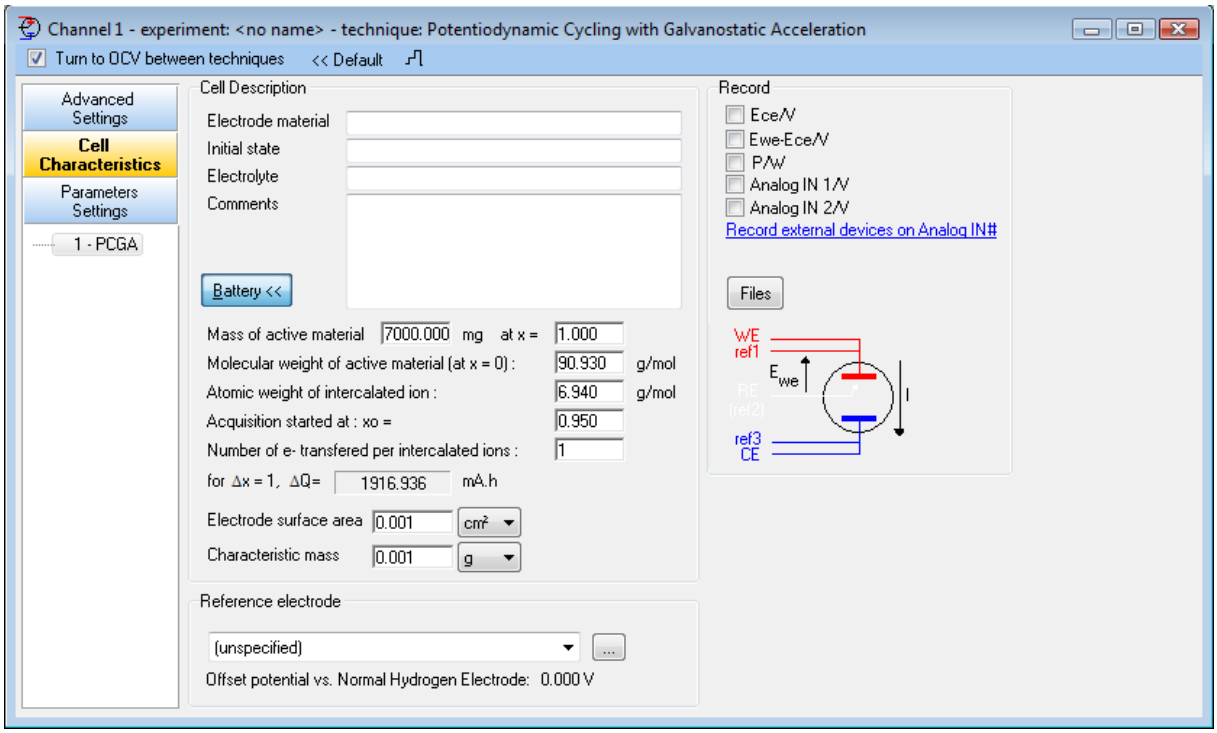


Fig. 81: Cell characteristics window for battery applications.

This window has been designed for battery electrode materials acting as intercalation electrode, which is the case of several primary and secondary batteries. It allows you to:

- Enter the physical characteristics corresponding to the active material of the working electrode. This makes on-line monitoring of the redox processes possible in term of normalized units (molar amounts of intercalation).
- Select the recording of the counter electrode potential.
- Select the recording of external signals (pH, T, P,...) using auxiliary inputs 1, 2 and 3.

3.1.1.3 PCGA Data processing

3.1.1.3.1 Compact function

The **Compact** function is very useful in representing the incremental capacity of a battery. The user has to represent dQ = f(E_{we}) in the graphic display (see the application note # 2 on our web site for more details). Using the compact function a new variable can be created: dQ which is the charge calculated every potential step.

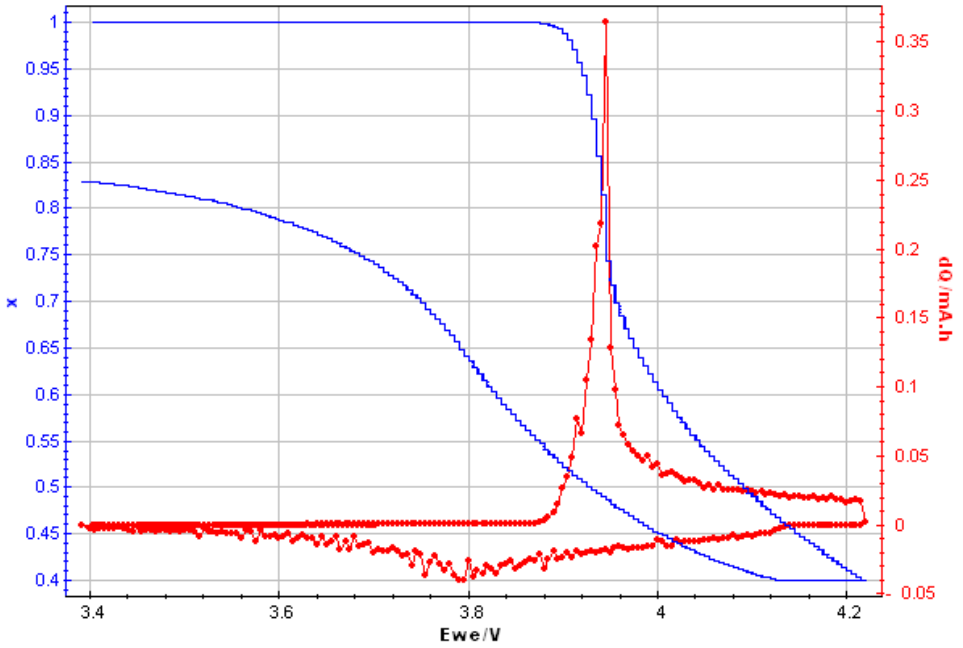


Fig. 82: Incremental capacity (dQ vs Ewe) graph (red circles) and X vs. Ewe plot (blue lines) of a Li button cell.

3.1.1.3.2 Intercalation coefficient determination

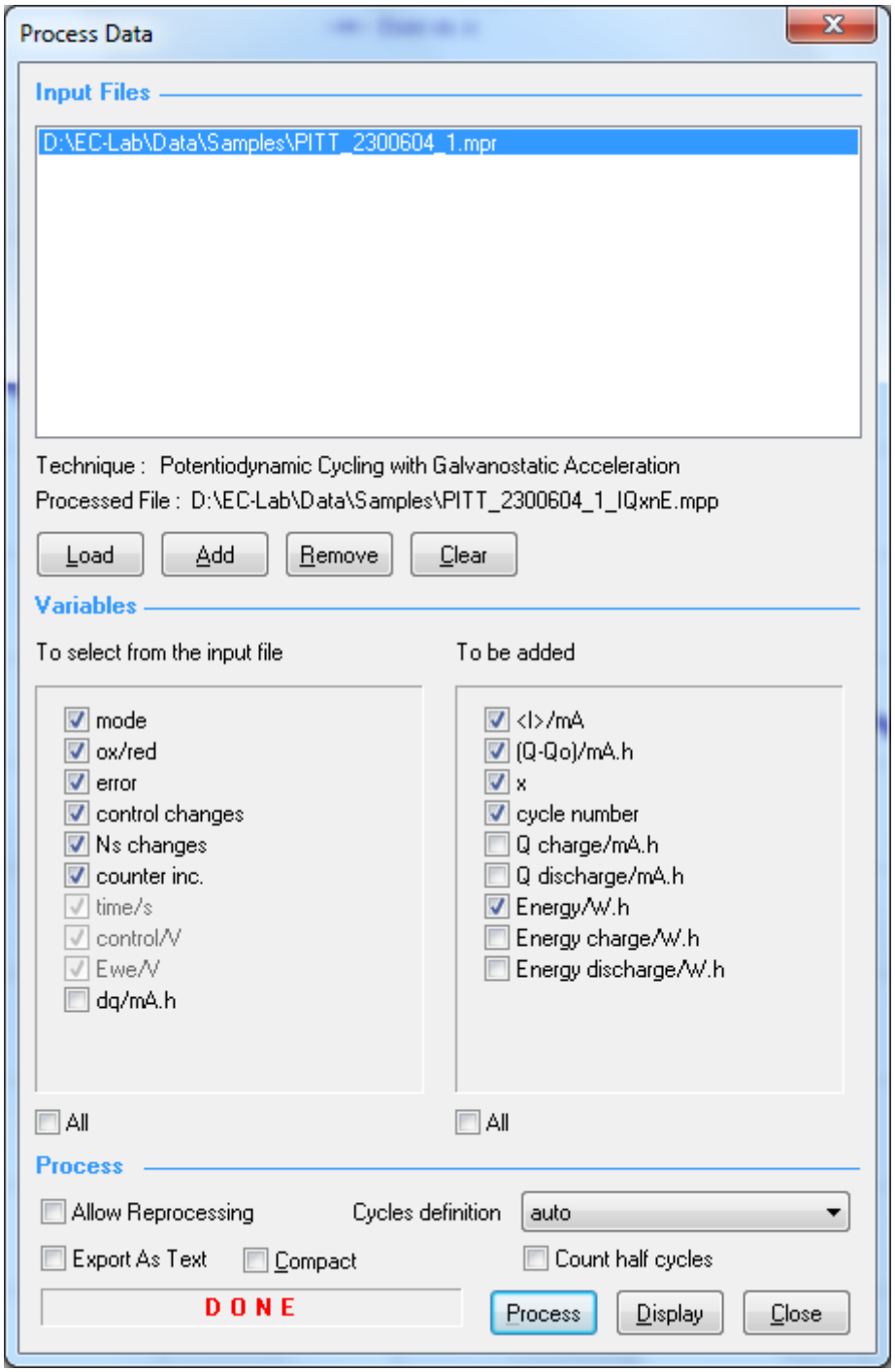


Fig. 83: Process window for PCGA technique.

The X variable is obtained by processing the PCGA raw data file but without compacting it. X can be processed if the user has previously defined the cell characteristics. If the user has forgotten it, it is still possible to modify the cell characteristics after the experiment in the raw data file. In the **Tools** menu, select "**Modify cell characteristics…**". Open the desired raw data file and the cell characteristics window appears. Once the characteristics are changed, click on **Save**.

3.1.2 GCPL: Galvanostatic Cycling with Potential Limitation

This technique corresponds to battery cycling under galvanostatic mode (essentially), i.e. with an imposed current, but with possible potential limitations under current for both charge and discharge and tests on potential values during open circuit period.

.

At the user's convenience the potential limitations can lead to different options:

- Skipping to an open circuit potential period or to the next imposed current sequence.
- Switching from imposed current mode to imposed potential mode by maintaining for a given time the potential of the working electrode at the limit potential, once it is reached.

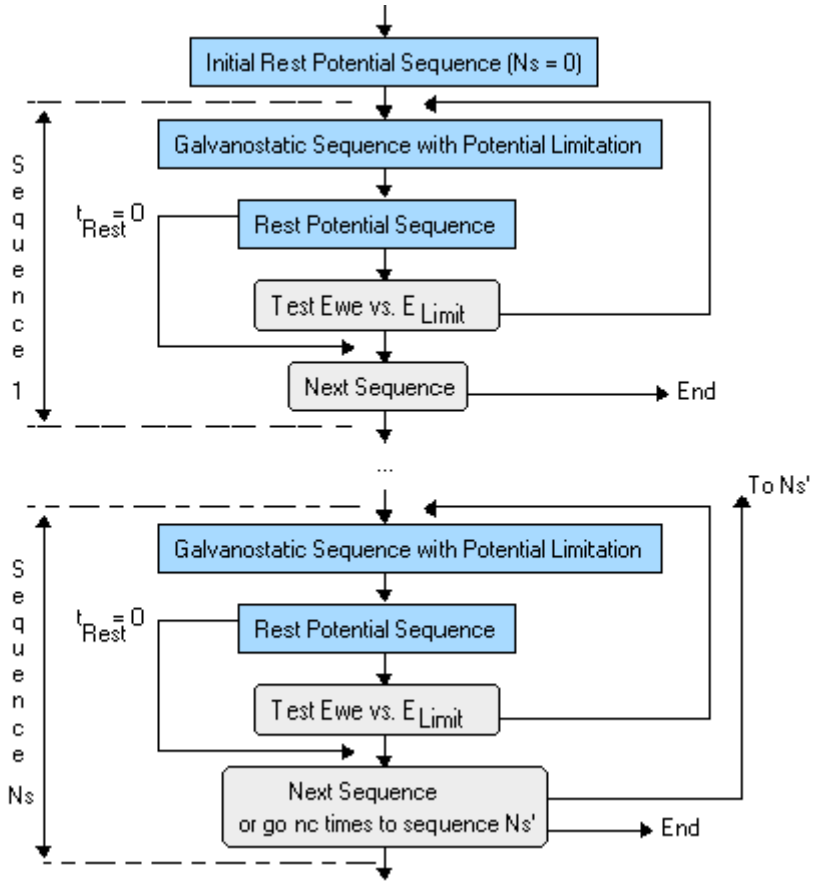


Fig. 84: General diagram of the GCPL application.

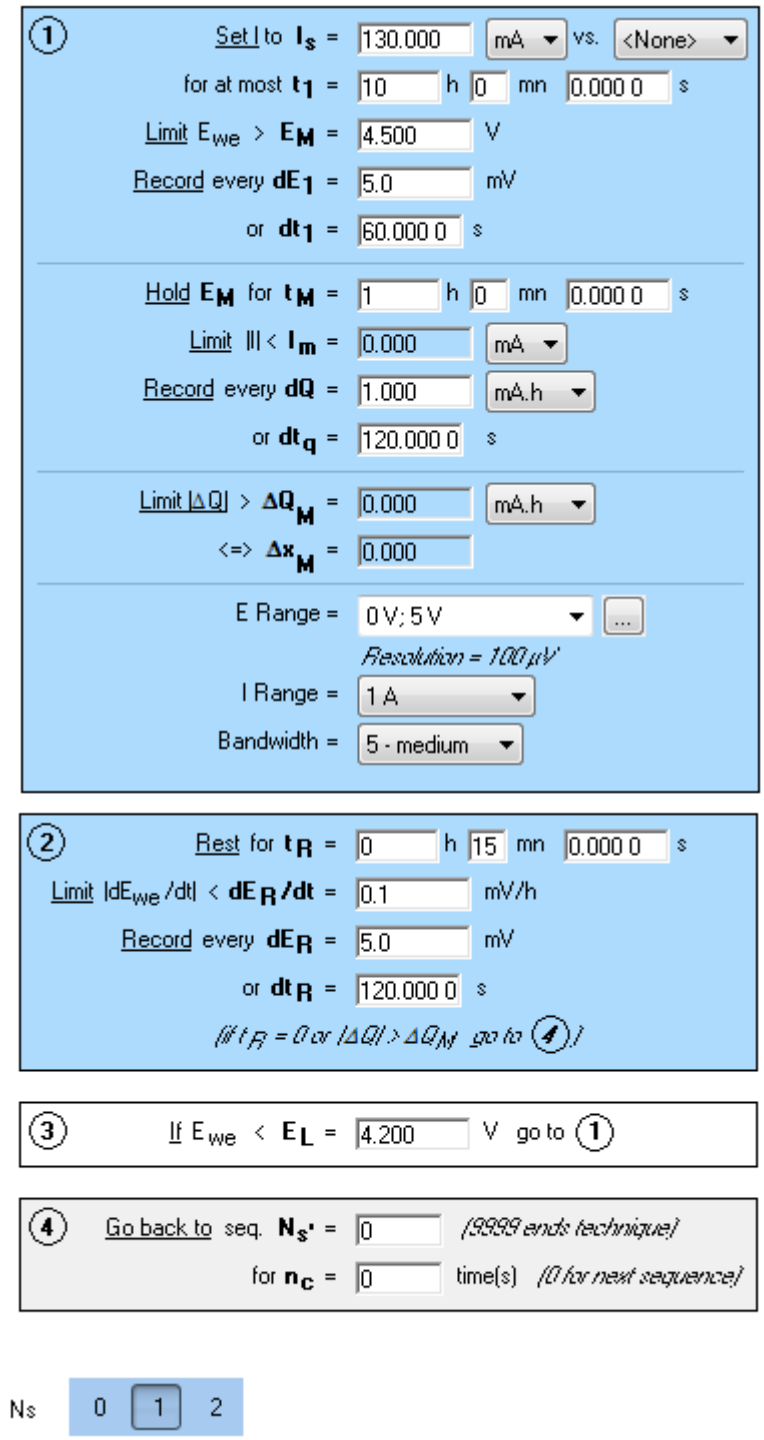


Fig. 85: Detailed diagram of one GCPL sequence.

In the battery applications, the current values panel displays additional information:
Q - Q_0 and x – x_0 are the total charge and the normalized charge since the beginning of the experiment respectively.
N_s is the current sequence number in case of a technique using several sequences. It corresponds to the line number in the associated table. The first sequence number is 0.
n_{c1}…n_{c5} are the current values of the 5 loop counters.

3.1.2.1 Description of a galvanostatic sequence

See Fig. 85.

- **First step: galvanostatic period that can be followed by a potentiostatic period.**

1) Galvanostatic period

Set I to Is = …. pA/…/A vs. <None>/Ictrl/Imeas, for at most t_1 = ….. h …… mn …… s
fixes the current value in absolute, versus the previous controlled current (previous sequence) or versus the previous measured current and the maximum duration of the imposed current period. The sign of the current value is "-" for a discharge and "+" for a charge when the positive electrode of the cell is connected to the working electrode cable (red).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

Record E_{we} every dE_1 = ……. mV and at least every dt_1 = ……. s
allows the user to record the working electrode potential with a given potential resolution (whenever the change in the working electrode potential is $\geq dE_1$) or/and at least every dt_1 time interval .

2) Potentiostatic period

Limit E_{we} < E_M = ……. V
fixes the limit of the working electrode potential under charge/discharge (see warning 1).
and stand for t_M = …… h ……. mn …… s or until $|I| < I_m$ = …… pA/…/A
allows the user to stand at the potential E_M for a given time or until the current reaches a low limit value I_M.
If the limit potential E_M is not reached within the time t_1, or if t_M is set to 0, the system skips to the next step.

Record ΔQ every dQ = ……. mA.h and at least every dt_q = ……. s
in the constant potential mode the system acts as a coulometer, and a recording is performed every time the charge increment/decrement since the previous recording is $\geq$ dQ and/or every dt_q time interval.
Limit ΔQ to ΔQ_M = ……. mA.h <=> Δx_M = ……
fixes the maximum charge change from the beginning of this sequence during the sequence. This charge is equivalent to a Δx_M quantity, which corresponds to a normalized charge (related to intercalation electrodes).

- **Second step: open circuit period with monitoring of the electrode potentials.**

turn to Rest for t_R = ……. h ……. mn ……. s
fixes a maximum time t_R to stay in open circuit mode.
or until $|dE_{we}/dt| < |dE_R/dt|$ = ……. mV/h
gives the user the ability to shorten the open circuit period when the decay of the potential is lower than a given value.

Record E_{we} every dE_R = ……. mV and at least every dt_R = ……. s
allows the user to record the working electrode potential with a given potential resolution (whenever the change in the working electrode potential is $\geq dE_R$) or/and at least every dt_R time interval .

Note the conditional test, if $t_R = 0$ which bypasses the open circuit period.

- **Third step: test on the final open circuit potential.**

test E_{we} >(<) E_L = …….. V.

The test is performed with the conditional value > if the open circuit period (just before the test) occurs after a charge (I > 0) and with the conditional value < after a discharge (I < 0).

If the condition is not fulfilled, the above 3 steps will be repeated until the working electrode potential reaches the final open circuit condition $E_{we} \geq E_L$ after a charge, or $E_{we} \leq E_L$ after a discharge.

Note: the user is allowed to bypass this test by entering p (= pass) instead of a voltage value.

- **Fourth step: conditional test which proposes to go to the next sequence or to loop on a previous sequence $N_{S'}$ ($N_{S'} < N_S$).**

If n_c is set to 0, then the technique executes the next sequence.
If the user wants to loop to a previous sequence (line), he has to fill the 2 last columns of the table "**Go to $N_{S'}$**" and " **n_c cycles**".

The end of the technique is obtained by setting $N_{S'}$ and n_c to 0 in the last sequence, or setting **Goto** sequence $N_{S'}$ = 9999 at any sequence, which then will be the last one executed even if the next sequence has its settings.

Such a complete sequence corresponds to one line of the table. This line is composed of the columns which represent the successive variables encountered when setting the diagram, the current range, and the loop conditions; all parameters which must be set by the user (see Warning 2).

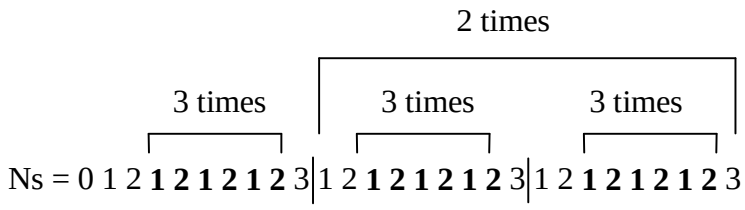
Note that it is always possible to force the end of a technique while it is running, at any sequence/sweep, using the **Modify** button and setting **Goto** sequence **$N_{S'}$** = 9999 at the sequence one wants to stop.

The following table setting gives an example of the use of the loop conditions:

Ns	dUr (mV)	dtr (s)	UL (V)	goto Ns'	nc cycles
0	1.000	1.0	3.000	0	0
1	1.000	1.0	2.000	0	0
2	1.000	1.0	3.500	1	3
3	1.000	1.0	2.500	1	2

Fig. 86: Example of loop conditions.

With these loop conditions the technique will do the following set of sequences:



Thus, after the initial sequence 0, there will be 4 cycles on steps 1-2, repeated 3 times

Warning 1: When running a charge sequence (I > 0), the final value of the working electrode potential, E_L, must be set at a lower value than the first limit value, E_M. This is due to the fact that at the end of the current-on period charge, the working electrode potential reaches a maximum and decreases during the open circuit period which follows. If E_L is set at a higher value than E_M, the experiment will never reach the limiting condition (test $E_{we} > E_L$) and the technique will always loop on the first step.
Similarly, when running a discharge sequence (I < 0), the final value of the working electrode potential, E_L, must be set at a higher value than the first limit value, E_M. At the end of the discharge the working electrode potential reaches a minimum, and increases during the rest potential period. If E_L is set at a lower value than E_M, the experiment will never reach the limiting condition (test $E_{we} < E_L$) and the technique will always loop on the first step.

Warning 2: When setting values in the diagram or the table's line, the user must set variables to 0 if he requires this particular value. Otherwise the program will detect an empty cell and will end the technique.

Note 1: For the 1st sequence/sweep ($N_S = 0$), the galvanostatic block is ignored. This allows the user to run a 1st open circuit period before starting a charge or discharge sequence.

Note 2: If the ΔQ_M limit is reached, the E_{we} vs. E_L test is ignored and the next sequence is executed.

Note 3: The choice of the operating current range which is usually done in the "I Range" menu of the "Parameter settings" window can also be obtained by double-clicking on any cell of the corresponding column in the table associated to the detailed diagram window.

3.1.2.2 Application

The following figure shows the result of a GCPL experiment obtained with a Li-ion battery (10 A.h) in an intermittent charge discharge cycling (GITT mode).

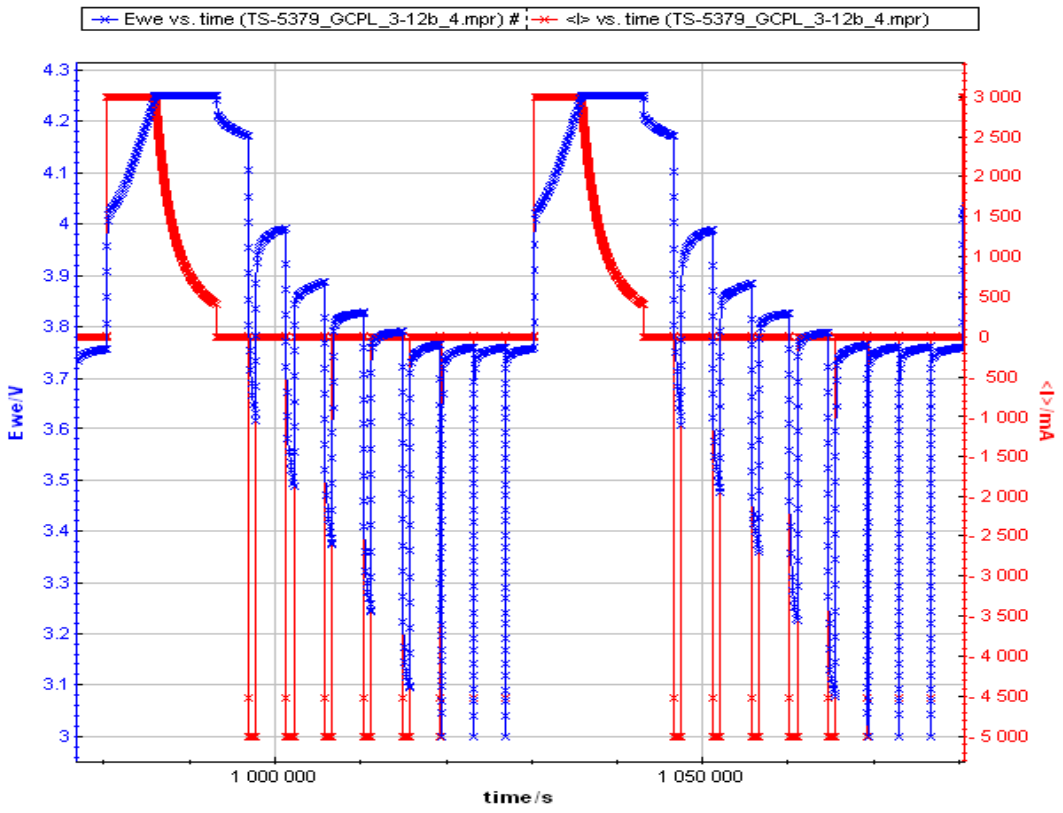


Fig. 87: Example of GCPL experiment obtained with a Li-ion battery (10 A.h).

3.1.2.3 GCPL Data processing:

3.1.2.3.1 Compacting process for the apparent resistance determination

Selecting **Keep only values at the end of every (open circuit period / I on period)** compresses the data resulting from the raw data file by keeping only one point for the whole open circuit period or the whole galvanostatic sequence. This point is taken at the time corresponding to the end of the period/sequence.
Once selected, it calculates the ohmic drop ("Ri") at the end of the galvanostatic sequences and the ohmic drop at the end of the rest periods. Then the name of the compacted processed file is [filename]_channel_cR.mpp in the case where Ri is the only one processed variable.

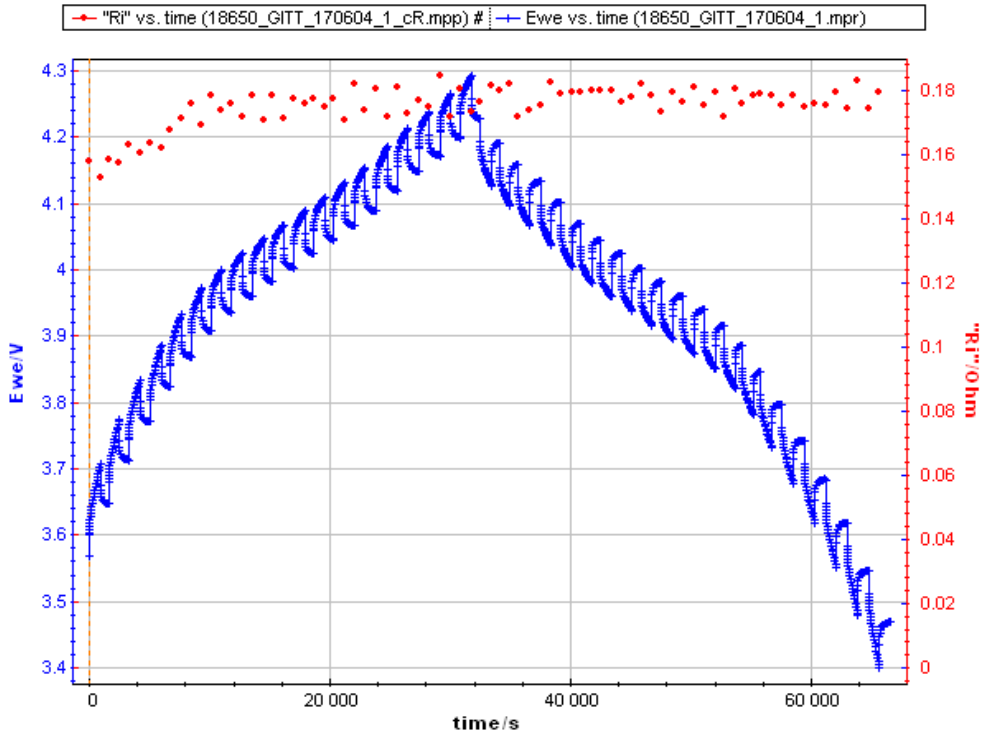


Fig. 88: Ri determination (red circles) after a GITT experiment (blue crosses) obtained with an 18650 Li-ion battery.

3.1.3 GCPL2: Galvanostatic Cycling with Potential Limitation 2

The GCPL2 application is similar to the GCPL one, but has been designed to limit both the working electrode (WE) and the counter electrode (CE) potential, and it does not hold the cell potential after the current charge/discharge.

The GCPL2 technique is made of 4 blocks:

- Galvanostatic,
- OCV,
- Potential test,
- Loop.

This is detailed below:

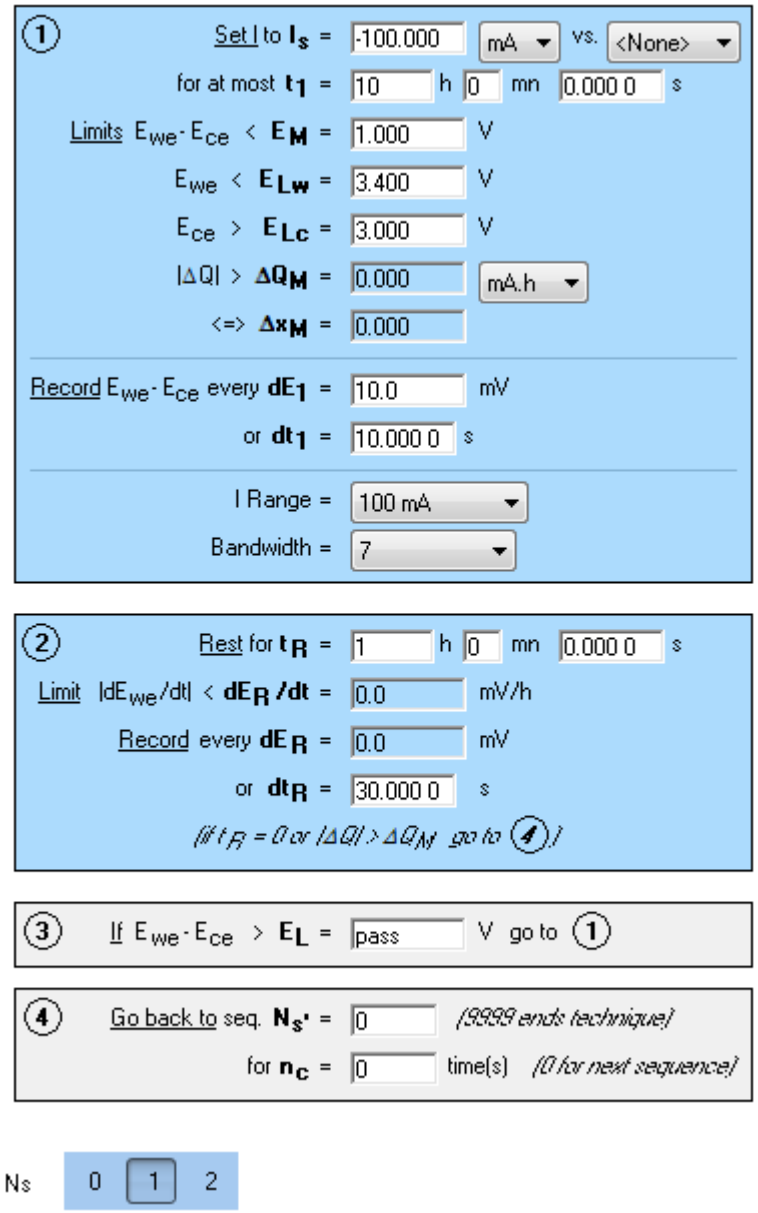


Fig. 89: GCPL2 detailed diagram.

- **Galvanostatic period**

Set I to Is = …. pA/…/A vs. <None>/Ictrl/Imeas, for at most t_1 = ….. h …… mn …… s
fixes the current value in absolute, versus the previous controlled current (previous sequence) or versus the previous measured current and the maximum duration of the imposed current period. The sign of the current value is "-" for a discharge and "+" for a charge when the positive electrode of the cell is connected to the working electrode cable (red).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

Record E_{we}-E_{ce} every dE_1 = …… mV and at least every dt_1
records one point each time E_{we} - E_{ce} variation $\geq dE_1$ and time $\geq dt_1$. These recording conditions can be set separately or together. The first condition that is reached decides the recording. A zero value cancels the recording condition.

Until E_{we} - E_{ce} > E_M = ……. V
Limit E_{we} < E_{Lw} = …… V
Limit E_{ce} > E_{Lc} = ……. V
Go to the next block if one condition is reached. The tests depend on the I_s sign:
. if $I_s \geq 0$ and (E_{we} - E_{ce} > E_M or E_{we} > E_{Lw} or E_{ce} < E_{Lc}) then go to the next block (OCV),
. if $I_s < 0$ and (E_{we} - E_{ce} < E_M or E_{we} < E_{Lw} or E_{ce} > E_{Lc}) then go to the next block (OCV),
Note the E_{ce} test is reversed because the E_{ce} potential has the opposite sign of E_{we}.

Limit |ΔQ| to ΔQ_M = ……. mA.h <=> Δx_M = …….
Fixes the maximum charge change from the beginning of this sequence. This charge is equivalent to a Δx_M quantity, which corresponds to a normalized charge (related to intercalation electrodes).

- **Open Circuit Voltage**

The open circuit voltage is the standard block, so report to the OCV or GCPL techniques sections for more information.

- **Potential test**

Test E_{we} - E_{ce} vs. E_L ……. V
The third step is the test on the open circuit final potential. <u>This test is skipped if there is no OCV period (t_R = 0)</u>.
The test performed takes the conditional value > or <, depending on in the open circuit sequence occurs after a charge (I > 0) or a discharge (I < 0).
And the above 2 steps will be repeated until the working electrode potential reaches the limiting condition $E_{we} \geq E_L$ after a charge or $E_{we} \leq E_L$ after a discharge.
<u>Note:</u> the user can bypass this test by entering p (= pass) instead of a voltage value.

- **Loop**

Next sequence or goto sequence $N_{s'}$ = …… n_c = …… time(s)
loops to a previous sequence $N_{s'}$ (< N_s), n_c time(s). Set n_c = 0 to cancel the loop and go to the next sequence (N_s + 1).

<u>Note</u>: E_{ce} and E_{we}-E_{ce} recording are forced into the GCPL2 data files.

3.1.4 GCPL3: Galvanostatic Cycling with Potential Limitation 3

The GCPL3 application is the same as the GCPL2 technique with the ability to hold the potential after the galvanostatic phase. Report to the GCPL2 application section for a description of this application.

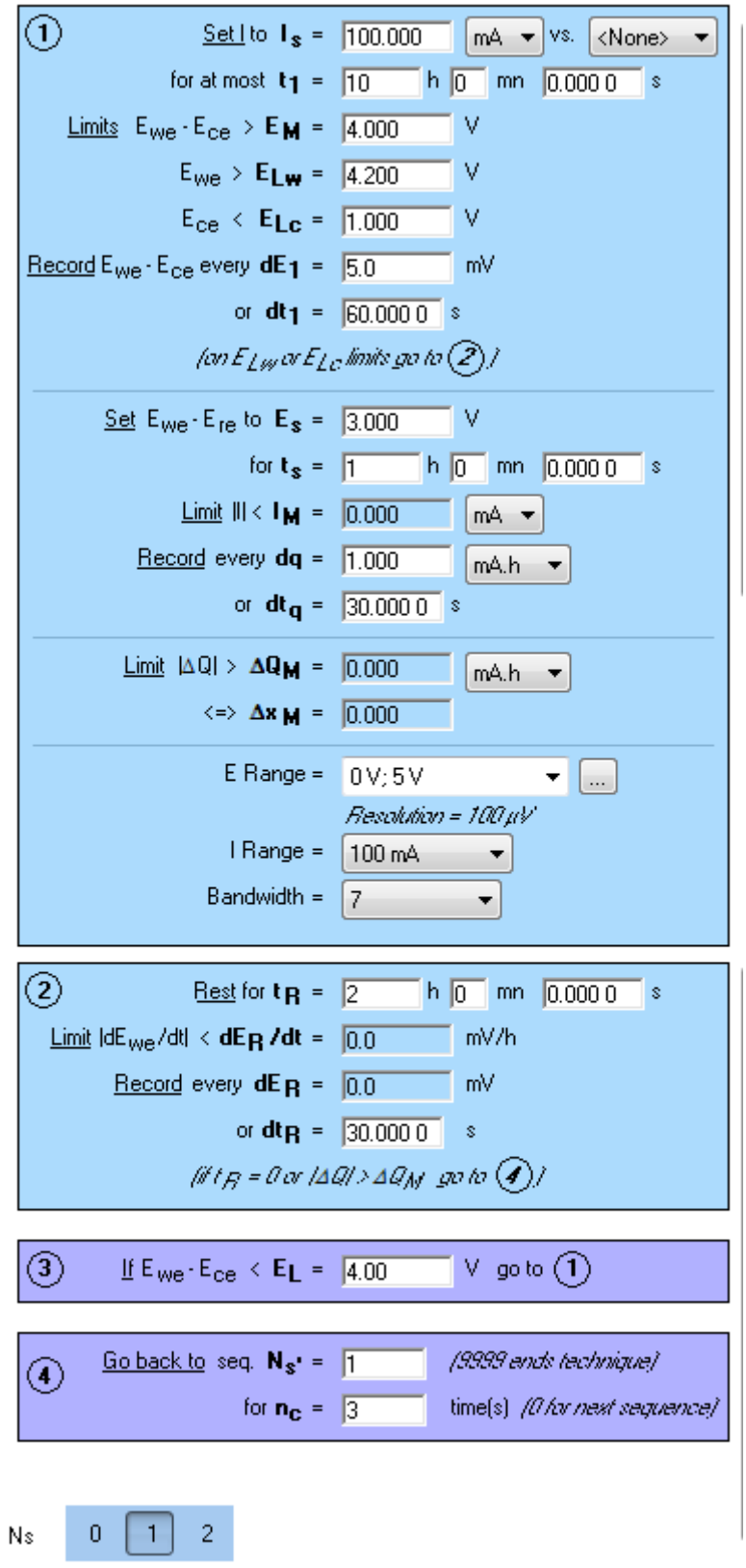


Fig. 90: GCPL3 detailed diagram.

3.1.5 GCPL4: Galvanostatic Cycling with Potential Limitation 4

The GCPL4 application is similar to the GCPL application, but with the global time limitation for the charge/discharge period.

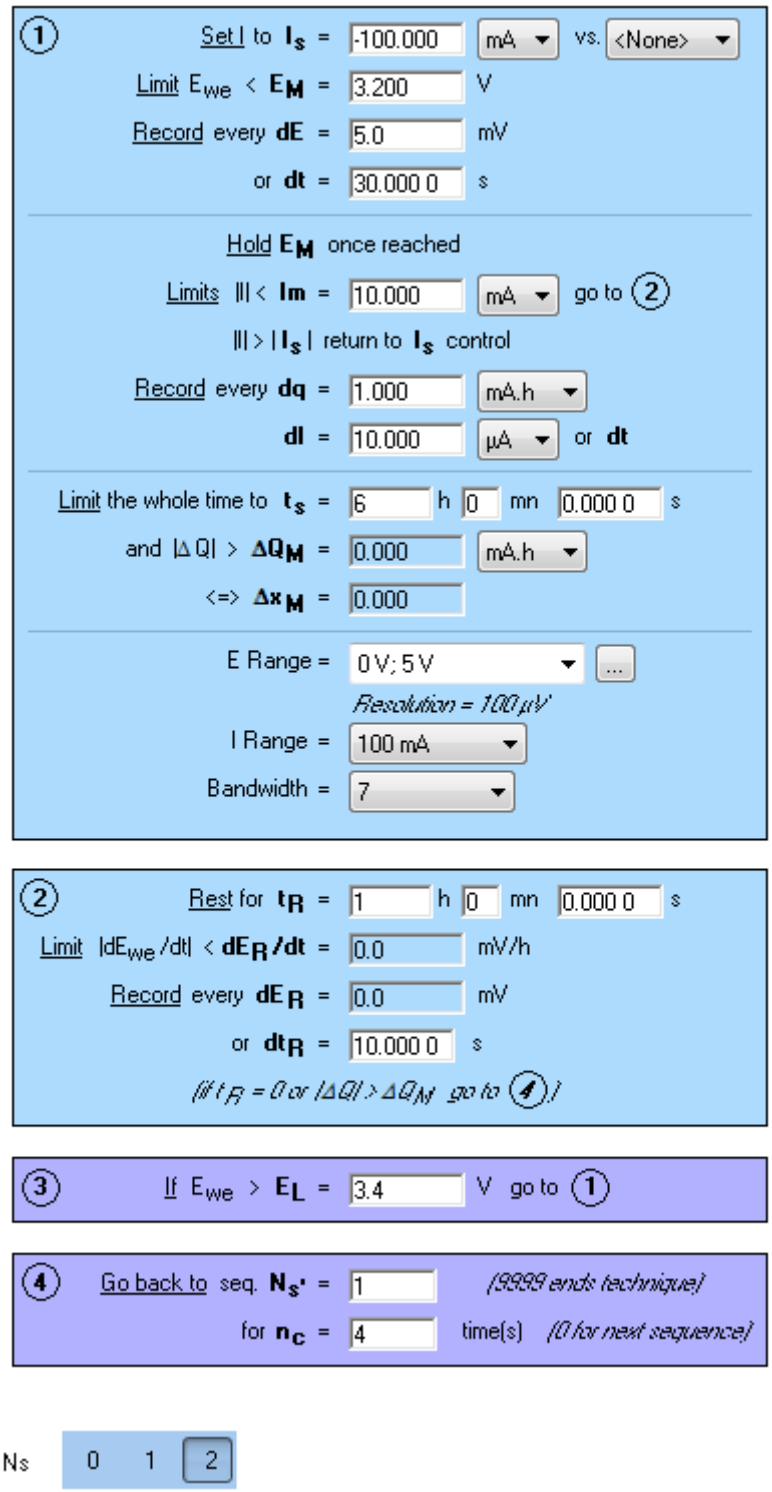


Fig. 91: GCPL4 detailed diagram.

- **first step (galvanostatic period):**

Set I to Is = …. pA/…/A vs <None>/Ictrl/Imeas with I Range = ….. and Bandwidth = ….. fixes the current value in absolute, versus the previous controlled current (previous sequence) or versus the previous measured current. The sign of the current value is "-" for a discharge and "+" for a charge when the positive electrode of the cell is connected to the working electrode cable (red).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

Irange = …….. and Bandwidth = …….
defines the current range and bandwidth for this experiment.

Record every dE = ……. mV and dt = …… s
defines the recording conditions during the galvano period. These values can be entered simultaneously. The first condition that is reached determines the recording. A zero value disables the recording for each criterion.

Limit E_{we} < E_M = ……. V
fixes the limit of the working electrode potential under charge/discharge (see warning 1 of GCPL technique). This limit could be disabled by entering "pass" (type "p") in the control.

Hold E_M once reached, until $|I| < I_m$ = …… pA/…/A (next block on limit)
allows the user to stand at the potential E_M until the end of the sequence or until the current reaches a low limit value I_m. The limit I_m could be disabled by entering "pass" (type "p") in the control.

Record every dq = ……. mA.h, dI = ……. pA/…/A and dt
defines the recording conditions during the potential period. These values can be entered simultaneously. The first condition that is reached determines the recording. A zero value disables the recording for each criterion.

Limit $|I|$ to $|Is|$ when holding E_M (return to Is on limit)
if the current $|I|$ overhaul $|I_s|$ in constant potential mode, the system returns to constant current mode in order to protect the cell.

Limit the whole time to t_s = …… h …… mn …… s
defines the total sequence duration (if not stopped on limits).

Limit $|\Delta Q|$ to ΔQ_M = ……. mA.h <=> Δx_M = ……
fixe the maximum charge change from the beginning of this sequence during the sequence. This charge is equivalent to a Δx_M quantity, which corresponds to a normalized charge (related to intercalation electrodes).

Report to the GCPL application section for more information on the other blocks.
The process option is the same as for the GCPL application.

3.1.6 GCPL5: Galvanostatic Cycling with Potential Limitation 5

A parameter commonly used by industrial battery manufacturers is the "**Apparent Resistance**" of the cell. This parameter called "R_i", is considered by each manufacturer like an internal characteristic for their cell. The R_i value is determined by the ratio dE/dI when a current step is done. The manufacturers determine R_i values at different time after the current step depending on their instrument's time base. So it becomes difficult to compare Ri values between different manufacturers. R_i determination is now available in EC-Lab® software using a GCPL application (refer to the process data section in EC-Lab® software manual and to the GCPL application section 3.1.2 page 90 for more details). In fact, Ri values are determined just after the current step according to the time. Current and potential values are recorded with geometric progression of time in order to have a good distribution of points versus time. Report to the GCPL section for more details.

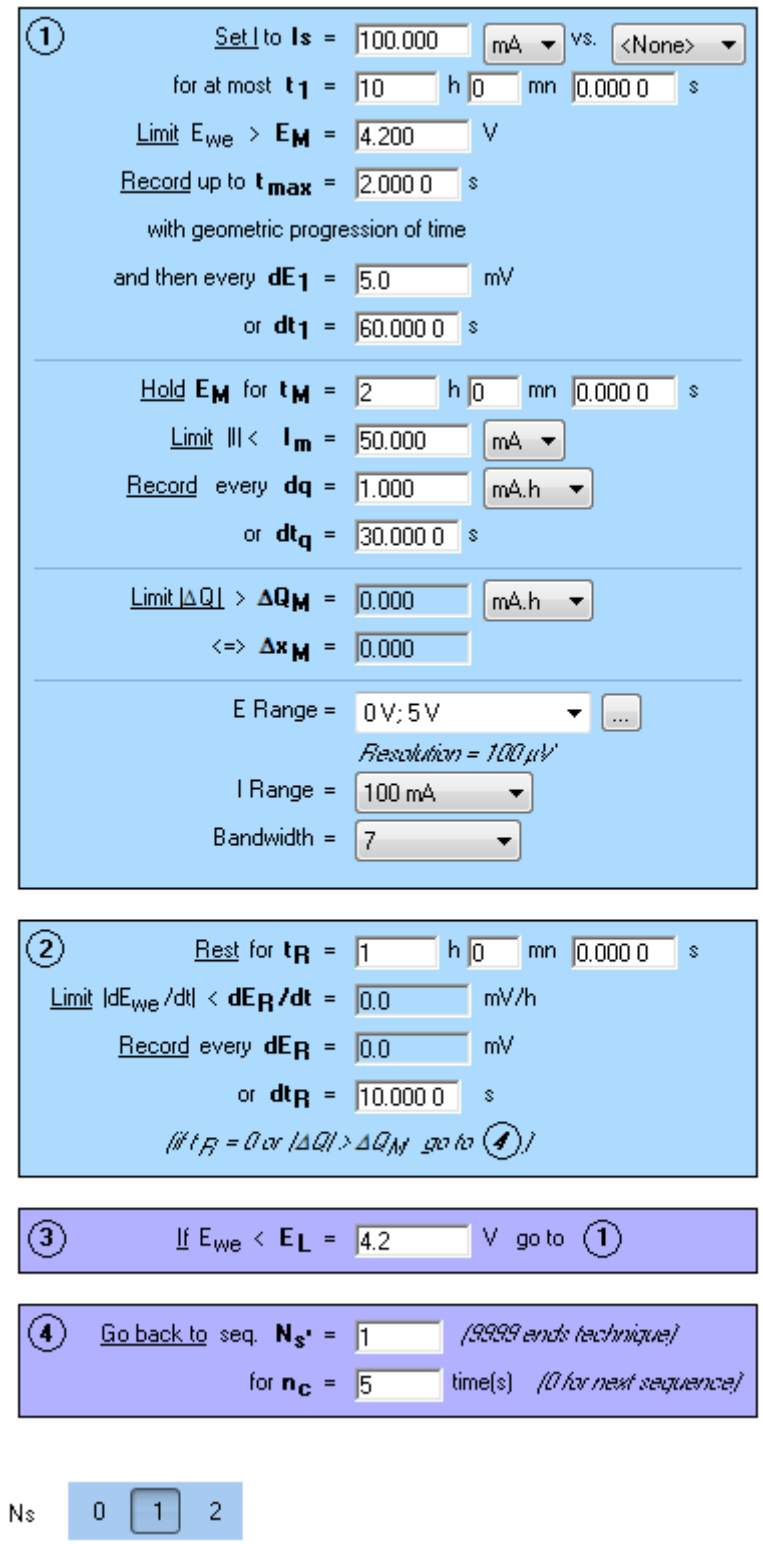


Fig. 92: Detailed diagram of one GCPL 5 sequence.

3.1.6.1 Description of a galvanostatic sequence

(Fig. 92)

- **first step: galvanostatic period that can be followed by a potentiostatic period.**

1) <u>Galvanostatic period</u>

Set I to Is = …….. pA/…/A vs. <None>/Ictrl/Imeas for at most t_1 = …… h …… mn …... s
fixes the current value in absolute or versus the previous controlled current or previous measured current, the sign (- for reduction and + for oxidation) and the maximum duration of the imposed current period.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

Irange = ……... and Bandwidth = …….
defines the current range and bandwidth for this experiment.

Record E_{we} up to tmax = ……s with geometric progression of time
and then every dE_1 = …… mV and at least every dt_1 = …… s
allows the user to record the working electrode potential with two successive resolutions. First, the potential is recorded with a geometric time resolution in order to determine the apparent resistance with a process. Secondly, the potential is recorded with a given potential resolution (whenever the change in the working electrode potential is $\geq dE_1$) or/and at least every dt_1 time interval.

2) <u>Potentiostatic period (possible)</u>

Limit E_{we} < E_M = …… V
fixes the limit of the working electrode potential under charge/discharge (see warning 1).
and stand for t_M = …… h …… mn …… s or until $|I|$ < I_m = …… pA/…/A
allows the user to stand at the potential E_M for a given time or until the current reaches a low limit value I_M.
If the limit potential E_M is not reached within the time t_1, or if t_M is set to 0, the system skips to the next step.

Record ΔQ every dQ = ……. mA.h and at least every dt_q = ……. s
In the constant potential mode the system acts as a coulometer and a recording is performed every time the charge increment/decrement since the previous recording is $\geq$ dQ and/or every dt_q time interval.

3) <u>Safety limit for the cell</u>

Limit ΔQ to ΔQ_M = ……. mA.h <=> Δx_M = ……..
fixes the maximum charge change from the beginning of this sequence during the sequence. This charge is equivalent to a Δx_M quantity, which corresponds to a normalized charge (related to intercalation electrodes).

- Report to the GCPL section for the description of the second, third and fourth part of this technique.

In order to plot the apparent resistance variation versus logarithmic time, the user must process the raw file after the experiment.

3.1.6.2 GCPL5 Data processing

(see the data processing section in the EC-Lab® software manual).

Selecting **Keep only values with geometric progression of time** allows the user to keep data recorded with geometric time spacing in a processed file. Once selected, it calculates the ohmic drop ("Ri") at different times recorded with geometric time spacing.
Then the name of the compacted processed file is [filename]_channel_cR.mpp in the case where Ri is the only processed variable.

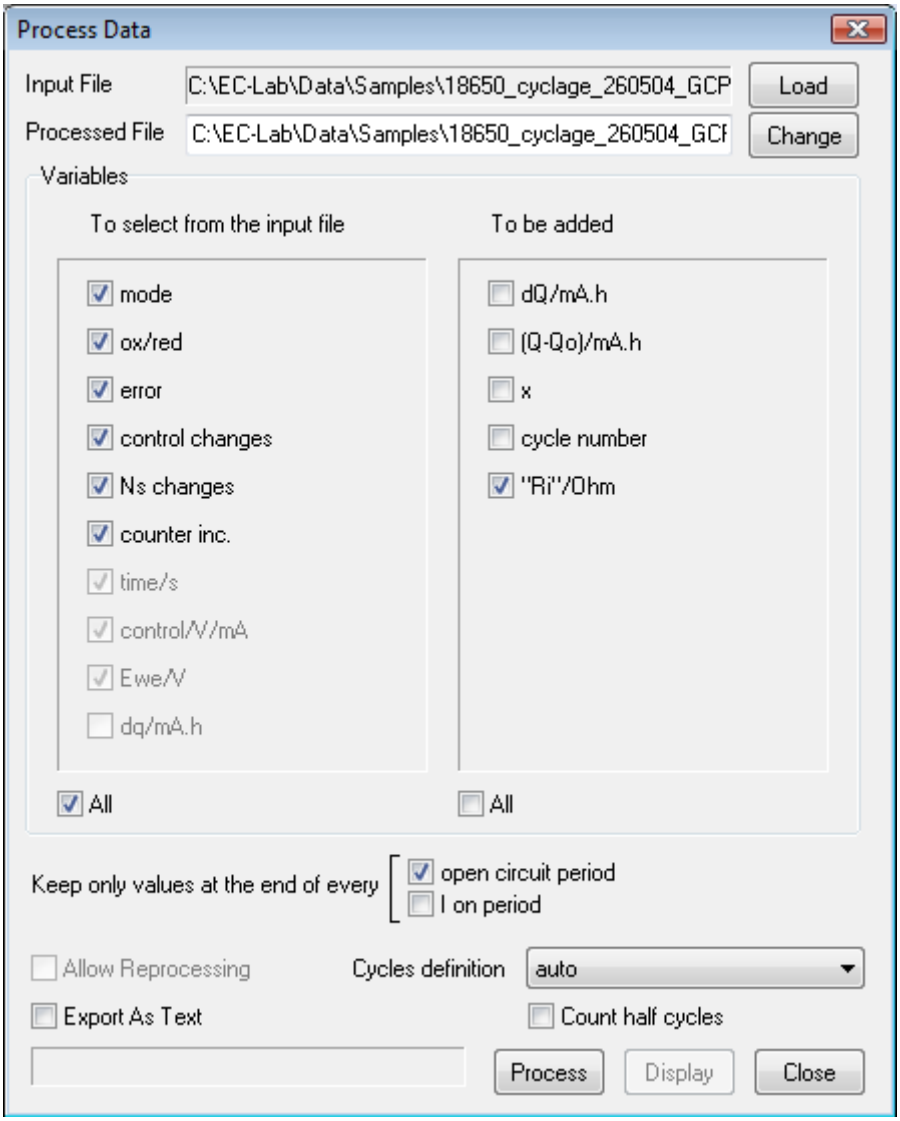


Fig. 93: GCPL 5 Process window.

Other processed values such as dQ, I, Q-Q_0, X and cycle number are also available as with other GCPL applications. For more detail see the GCPL application.

3.1.6.3 Application:

One classical application of this technique can be to follow the ohmic drop "Ri" evolution with aging of a Li-ion cell after several charge/discharge cycles. Another application can be to determine the internal resistance of the battery versus time.

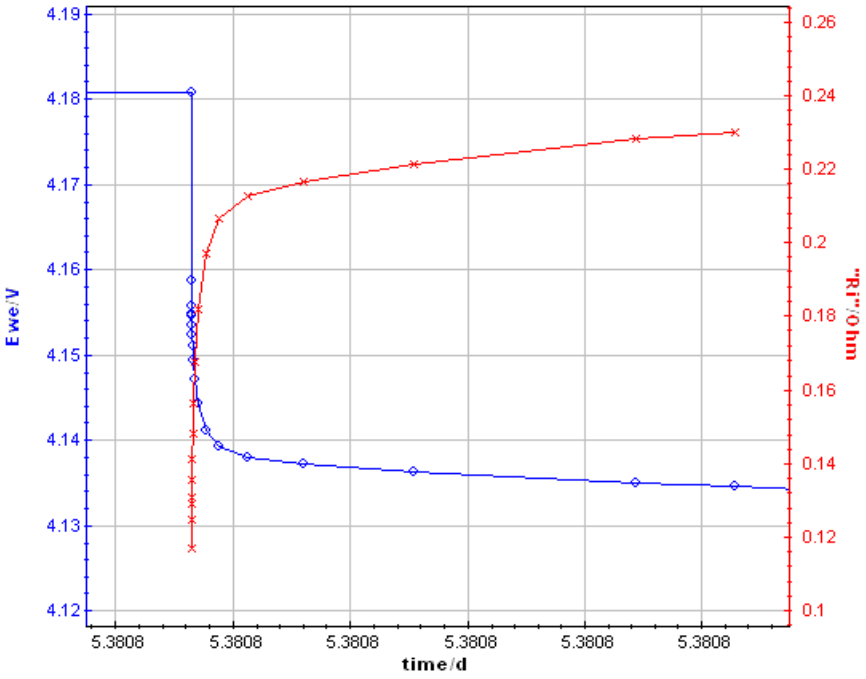


Fig. 94: GCPL 5 processed file display for Ri determination.

3.1.7 GCPL6: Galvanostatic Cycling with Potential Limitation 6

This technique corresponds to battery cycling under galvanostatic mode (essentially), i.e. with an imposed current, but with possible potential limitations under current for both charge and discharge and tests on potential values during open circuit period.

.

At the user's convenience the potential limitations can lead to different options:

- Skipping to an open circuit potential period or to the next imposed current sequence.
- Switching from imposed current mode to imposed potential mode by maintaining for a given time the potential of the working electrode at the limit potential, once it is reached.

At the opposite of the GCPL1 technique, the floating mode (potential control and hold at a given value) is not done between Ref1 and Ref2 cables but between Ref1 and Ref3 cable. This technique offers the user the possibility to follow the voltage of each electrode versus a reference electrode in the battery.

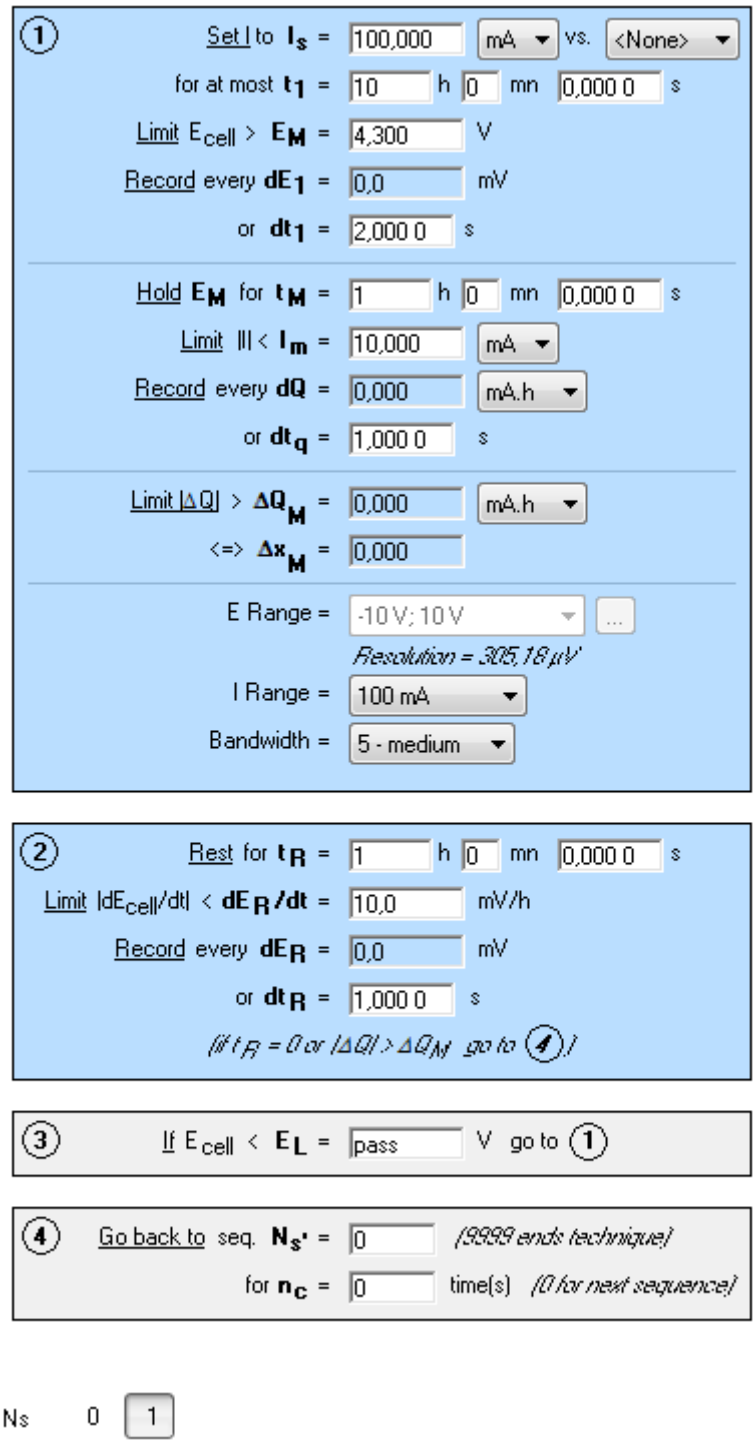


Fig. 95: Detailed diagram of one GCPL6 sequence.

3.1.7.1 Description of a galvanostatic sequence

- **First step: galvanostatic period that can be followed by a potentiostatic period.**

1) <u>Galvanostatic period</u>

Set I to Is = …. pA/…/A vs. <None>/Ictrl/Imeas, for at most t_1 = ….. h …… mn …… s fixes the current value in absolute, versus the previous controlled current (previous sequence) or versus the previous measured current and the maximum duration of the imposed current period. The sign of the current value is "-" for a discharge and "+" for a

charge when the positive electrode of the cell is connected to the working electrode cable (red).

Limit E_{cell} > E_M = ……. V
fixes the limit of the working electrode potential under charge/discharge (see warning 1).

Record E_{cell} every dE_1 = ……. mV and at least every dt_1 = ……. s
allows the user to record the working electrode potential with a given potential resolution (whenever the change in the working electrode potential is ≥ dE_1) or/and at least every dt_1 time interval .

2) Potentiostatic period

Hold E_M for t_M = …… h ……. mn …… s and limit $|I| < I_m$ = …… pA/…/A
allows the user to stand at the potential E_M for a given time or until the current reaches a low limit value I_M.
If the limit potential E_M is not reached within the time t_1, or if t_M is set to 0, the system skips to the next step.

Record ΔQ every dQ = ……. mA.h and at least every dt_q = ……. s
in the constant potential mode the system acts as a coulometer, and a recording is performed every time the charge increment/decrement since the previous recording is ≥ dQ and/or every dt_q time interval.
Limit ΔQ to ΔQ_M = ……. mA.h <=> Δx_M = ……

fixes the maximum charge change from the beginning of this sequence during the sequence. This charge is equivalent to a Δx_M quantity, which corresponds to a normalized charge (related to intercalation electrodes).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

- **Second step: open circuit period with monitoring of the electrode potentials.**

turn to Rest for t_R = ……. h ……. mn ……. s
fixes a maximum time t_R to stay in open circuit mode.
or until $|dE_{cell}/dt| < |dE_R/dt|$ = ……. mV/h
gives the user the ability to shorten the open circuit period when the decay of the potential is lower than a given value.

Record every dE_R = ……. mV and at least every dt_R = ……. s
allows the user to record the working electrode potential with a given potential resolution (whenever the change in the working electrode potential is ≥ dE_R) or/and at least every dt_R time interval .

Note the conditional test, if t_R = 0 which bypasses the open circuit period.

- **Third step: test on the final open circuit potential.**

test E_{cell} >(<) E_L = …….. V.

The test is performed with the conditional value > if the open circuit period (just before the test) occurs after a charge (I > 0) and with the conditional value < after a discharge (I < 0).

If the condition is not fulfilled, the above 3 steps will be repeated until the working electrode potential reaches the final open circuit condition $E_{we} \geq E_L$ after a charge, or $E_{we} \leq E_L$ after a discharge.

Note: the user is allowed to bypass this test by entering p (= pass) instead of a voltage value.

- **Fourth step: conditional test which proposes to go to the next sequence or to loop on a previous sequence $N_{S'}$ ($N_{S'} < N_S$).**

If n_c is set to 0, then the technique executes the next sequence.
If the user wants to loop to a previous sequence (line), he has to fill the 2 last columns of the table "**Go to $N_{S'}$**" and " **n_c cycles**".

The end of the technique is obtained by setting $N_{S'}$ and n_c to 0 in the last sequence, or setting **Goto** sequence $N_{S'}$ = 9999 at any sequence, which then will be the last one executed even if the next sequence has its settings.

Such a complete sequence corresponds to one line of the table. This line is composed of the columns which represent the successive variables encountered when setting the diagram, the current range, and the loop conditions; all parameters which must be set by the user (see Warning 2).

Note that it is always possible to force the end of a technique while it is running, at any sequence/sweep, using the **Modify** button and setting **Goto** sequence **$N_{S'}$** = 9999 at the sequence one wants to stop.

3.1.8 CLD: Constant Load Discharge

The Constant Load Discharge application has been designed to discharge a battery at a constant resistance. The potentiostat is seen as a constant resistor by the battery.

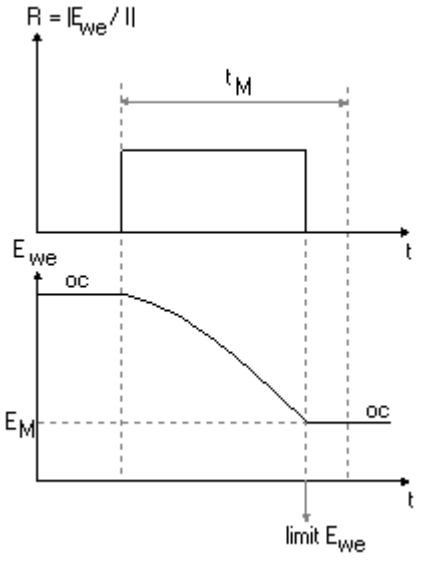


Fig. 96: CLD control (I) and measure (E_{we}) sample vs. time.

The constant resistance control is made by controlling the current to maintain the constant ratio E/I.

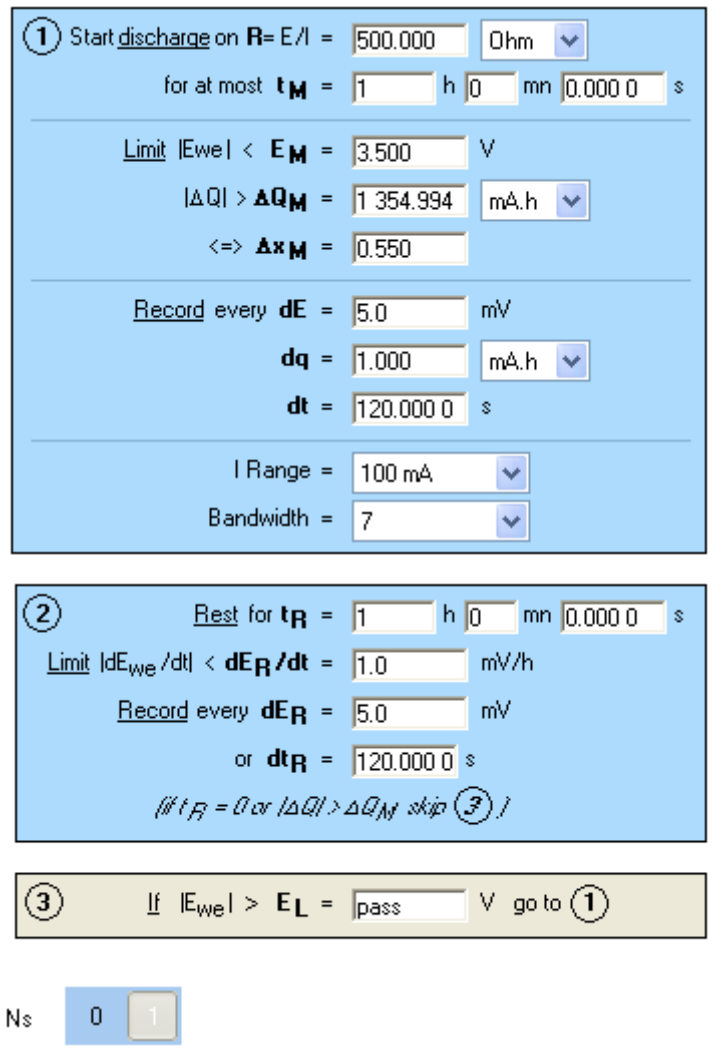


Fig. 97: CLD detailed diagram.

- **first step: definition of the resistance and choice of recording conditions**

Start Discharge on R=E/I= …… Ohm/kOhm/Mohm for at most t_M = ….. h ….. mn ….. s
sets the cell resistance to R = E/I for t_M duration.

With I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

Record every dE = …… mV, dq = …… mA.h and dt = …… s
defines the recording conditions. These values can be entered simultaneously, the first condition that is reached determines the recording. A zero value disables the recording for each criterion.

Until $|E_{we}| < E_M$ = …… V, $|\Delta Q| > \Delta Q_M$ = …….. mA.h <=> Δx_M = ……
Fixes the limit of the working electrode potential (E_{we}) and the charge from the beginning of the sequence ($|\Delta Q|$, $|\Delta x|$), for the whole step. The maximum charge can be entered into mA.h (ΔQ_M) or as a normalized charge (related to intercalation electrodes: Δx_M). Once a limit is reached, the experiment proceeds to the next step (Rest), even if the programmed time t_M is not terminated. These limits can be bypassed by entering 0 values into the controls.

Note: when the ΔQ_M (Δx_M) limit is reached, the E_L test is skipped. This is due to the fact that the ΔQ_M limit is considered as the maximal charge that can be applied to the battery during the discharge. Once reached, the experiment must go to the next sequence.

- Report to the GCPL technique chapter for more information on the other blocks.

3.1.9 CPW: Constant Power

3.1.9.1 Description

The Constant Power application is designed to study the discharge (eventually the charge) of a cell at constant power. The following figure presents the working electrode potential evolution vs. time when the power stays constant.

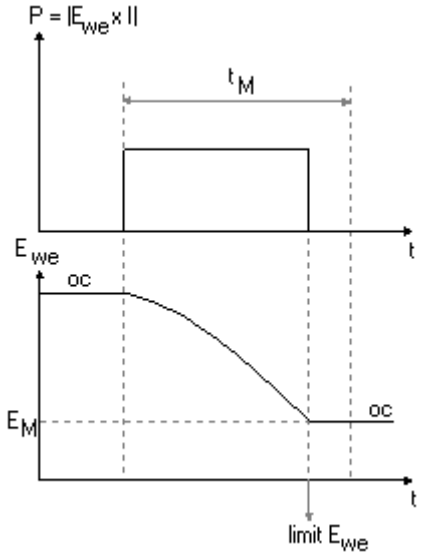


Fig. 98: CPW discharge control (P) and measure (E_{we}) sample vs. time

The constant power control is made by checking the current to maintain the E*I constant. The current increases when E_{we} decreases.

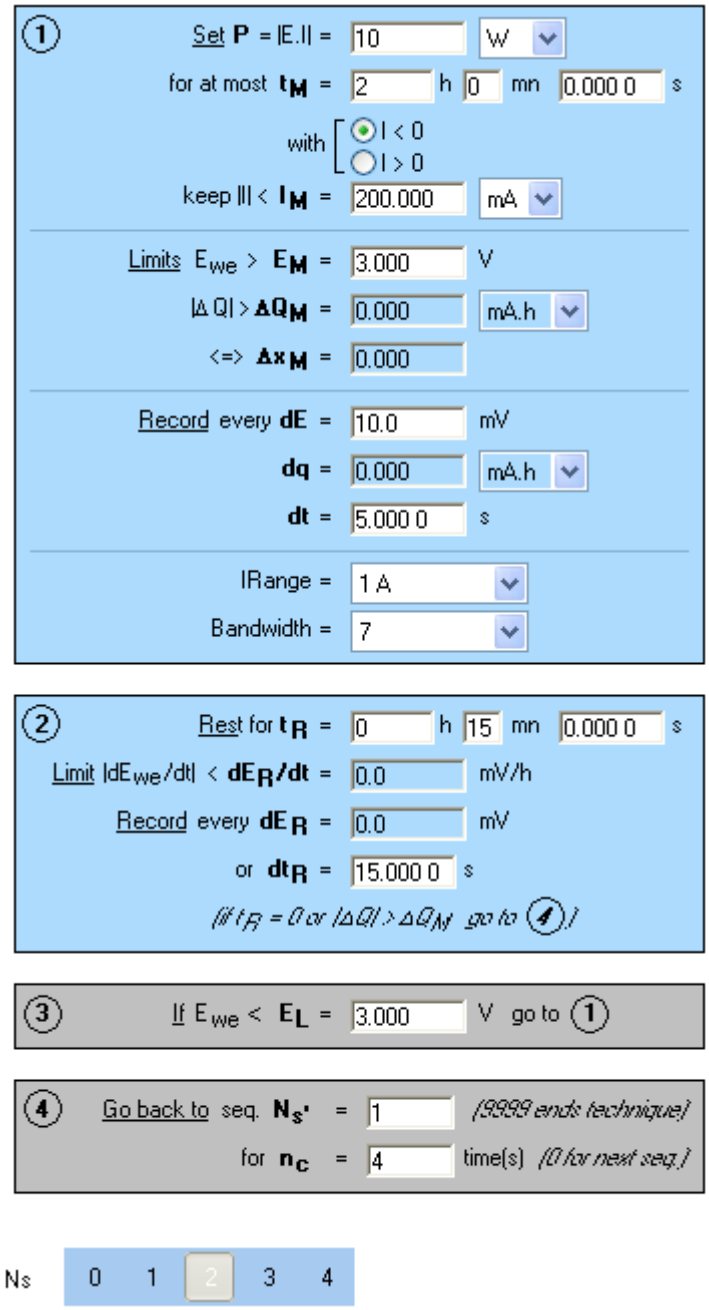


Fig. 99: CPW detailed diagram.

- **first step: choice of the power value**

Set P=E*I= …… µW/mW/W for at most t_M = …… h …… mn …… s
sets the cell power to P = E*I for t_M duration.

With I > 0 or I < 0 and keep I < I_M = …… pA/…/A
defines the charge (I > 0**)** or discharge (I < 0**)** mode and limits the current to a maximum value I_M in order to preserve the cell and/or the instrument.

With I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

Record every dE = …….. mV, dq = ……. mA.h and dt = …… s

Defines the recording conditions. These values can be entered simultaneously. The first condition that is reached determines the recording. A zero value disables the recording for each criterion.

Until E_{we} < E_M = ……. V, $|\Delta Q|$ to ΔQ_M = …… mA.h <=> Δx_M = ……
fixes the limit of the working electrode potential (E_{we}) to a maximum value if I>0 or to a minimum value if I<0 and the charge from the beginning of the sequence ($|\Delta Q|$, $|\Delta x|$), for the whole step. The maximum charge can be entered into mA.h (ΔQ_M) or as a normalized charge (related to intercalation electrodes : Δx_M). Once a limit is reached the experiment proceeds to the next step (Rest), even if the programmed time t_M is not terminated. These limits can be bypassed by entering 0 values into the controls.

Note: when the ΔQ_M (Δx_M) limit is reached, the E_L test is skipped. This is due to the fact that the ΔQ_M limit is considered as the maximal charge that can be applied to the battery during the discharge. Once reached the experiment must go to the next sequence.

- Report to the GCPL technique chapter for more information on the other blocks.

Caution:

Applying a constant power during a discharge experiment corresponds to an increase of the current (in absolute) when the potential decreases. The user must be careful to note the final current of the first constant power step. For example, let's consider a 30 watts power discharge applied to a battery with a 10 A booster. We suppose that the potential limits of this experiment are 4 V and 2.5 V. The initial current will be 7.5 A but the final current will be 12 A (overload in current). It will not be possible to go to the final current.

3.1.9.2 Application of the CPW technique

The constant power technique is commonly used for a Ragone plot representation (power vs. energy). The usual technique consists of successive sequences made with:

- discharge to $P/2^n$ watts with n the number of the sequence ($n_0 = 0$).
- Open circuit period after the discharge.

The discharge step is stopped when a minimum potential value is reached.
One can see the change of current and potential during a CPW experiment versus energy on the figure below. For a constant power discharge, the current decreases in the negative direction but it increases in absolute to compensate the fall of potential.

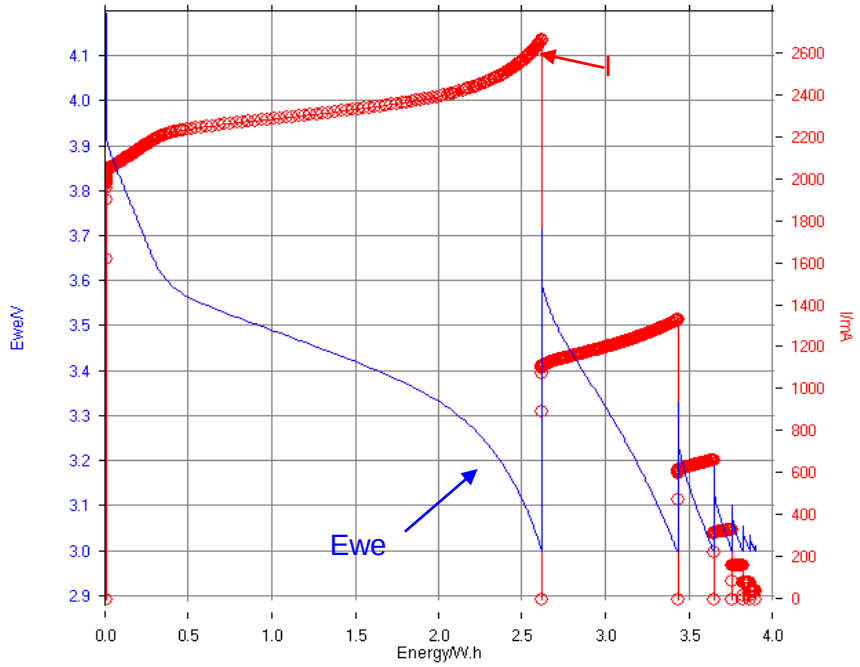


Fig. 100: E measured (---blue line) and I adjusted (red circles) evolution vs. energy during a CPW experiment on a Li-ion battery (1.35 A.h). P = 8 W.

The plotted current values are absolute values (negative in reality). In order to have a constant power, the working electrode potential decreases when the current increases (in absolute). The power vs. energy plot for a Li-ion (1.35 A.h) battery is presented on the figure below. Each constant power is separated with an OCV period limited with a potential variation dE_R/dt = 2 mV/h.

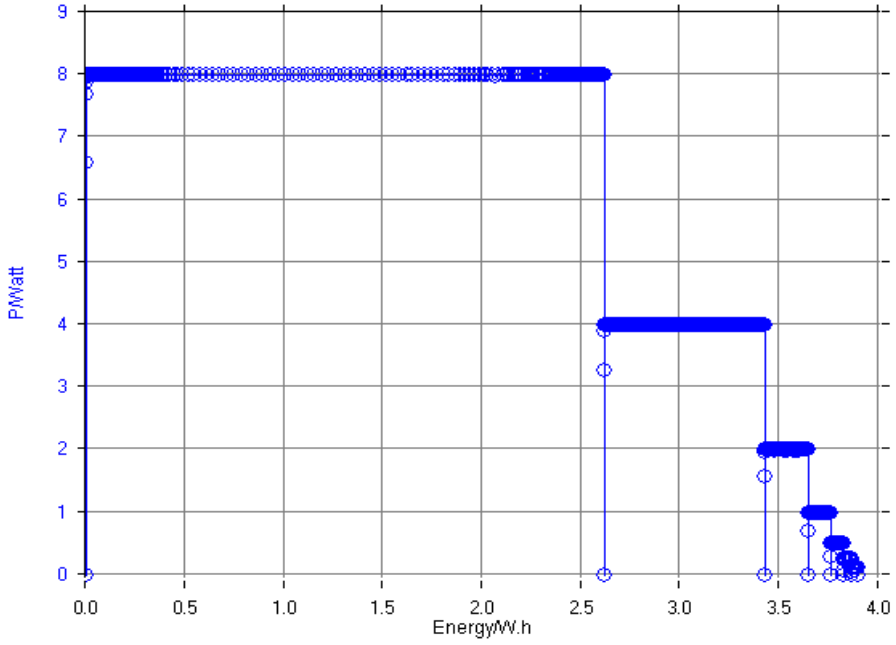
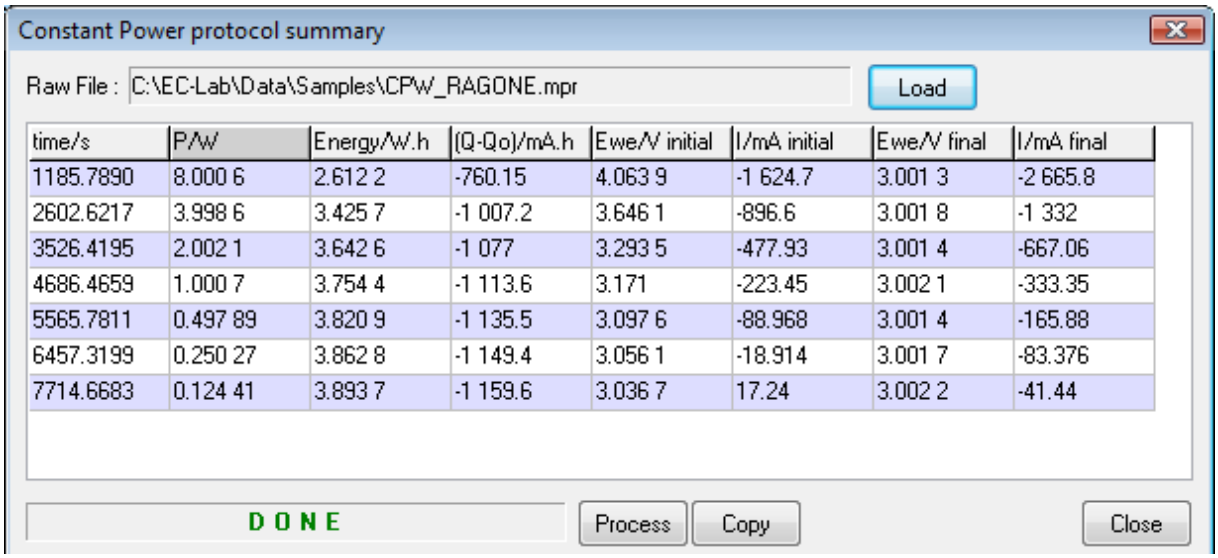


Fig. 101: Power vs. energy plot for a Li-ion cell (1.35 A.h). P = 8 W.

A process called "Constant Power technique summary" has been especially designed for Ragone plot representation. To use this data process, click on "process" in the graphic

window or choose "Process data\Constant Power technique summary" in the **File** menu. Then the following processing window will be displayed:



time/s	P/W	Energy/W.h	(Q-Qo)/mA.h	Ewe/V initial	I/mA initial	Ewe/V final	I/mA final
1185.7890	8.000 6	2.612 2	-760.15	4.063 9	-1 624.7	3.001 3	-2 665.8
2602.6217	3.998 6	3.425 7	-1 007.2	3.646 1	-896.6	3.001 8	-1 332
3526.4195	2.002 1	3.642 6	-1 077	3.293 5	-477.93	3.001 4	-667.06
4686.4659	1.000 7	3.754 4	-1 113.6	3.171	-223.45	3.002 1	-333.35
5565.7811	0.497 89	3.820 9	-1 135.5	3.097 6	-88.968	3.001 4	-165.88
6457.3199	0.250 27	3.862 8	-1 149.4	3.056 1	-18.914	3.001 7	-83.376
7714.6683	0.124 41	3.893 7	-1 159.6	3.036 7	17.24	3.002 2	-41.44

Fig. 102: CPW process window.

This process window is made of a table containing the characteristic variables of each power step, such as the time, the energy and charge of the end of the step, the working electrode potential and the current that crossed the cell at the beginning and the end of the step. The "Copy" tab allows the user to paste the values of the table in graphic software in order to have a Ragone plot (see figure below).

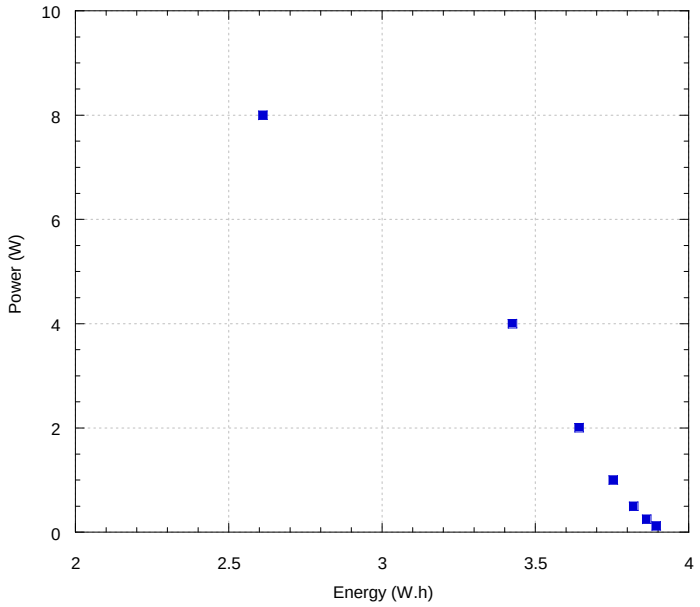


Fig. 103: Ragone plot for a Li-ion cell (1.35 A.h).

3.1.10 APGC: Alternate Pulse Galvano Cycling

The Alternate Pulse Galvano Cycling experiment has been designed to perform fast galvano steps between two values (I_1 and I_2), with special recording conditions. This gives the ability to follow fast phenomena on long periods.

The diagram is made of four blocks that can be linked with a parameters table:

- Pulsed Galvano Charge,
- Rest Potential Sequence,
- Test E_{we} vs. E_L,
- Next sequence.

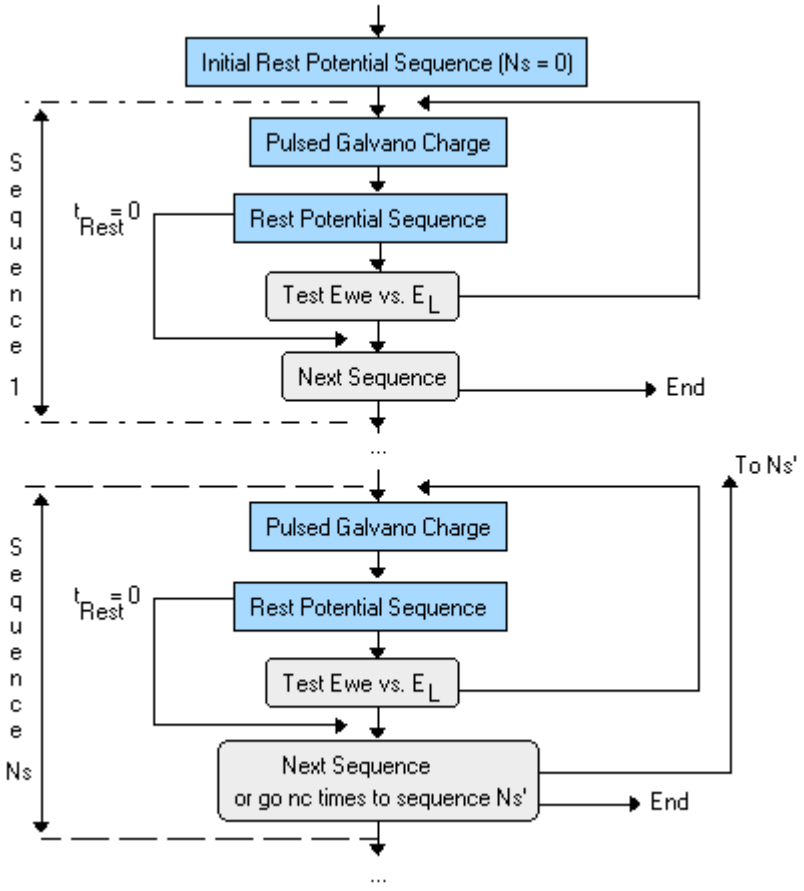


Fig. 104: APGC general diagram.

Similar to the other battery experiments, the first sequence ($N_s = 0$) is forced to OCV and the other sequences are executed one after one, with the possibility to loop to a previous experiment number from the third sequence ($N_s \geq 2$).

The detailed diagram is described below:

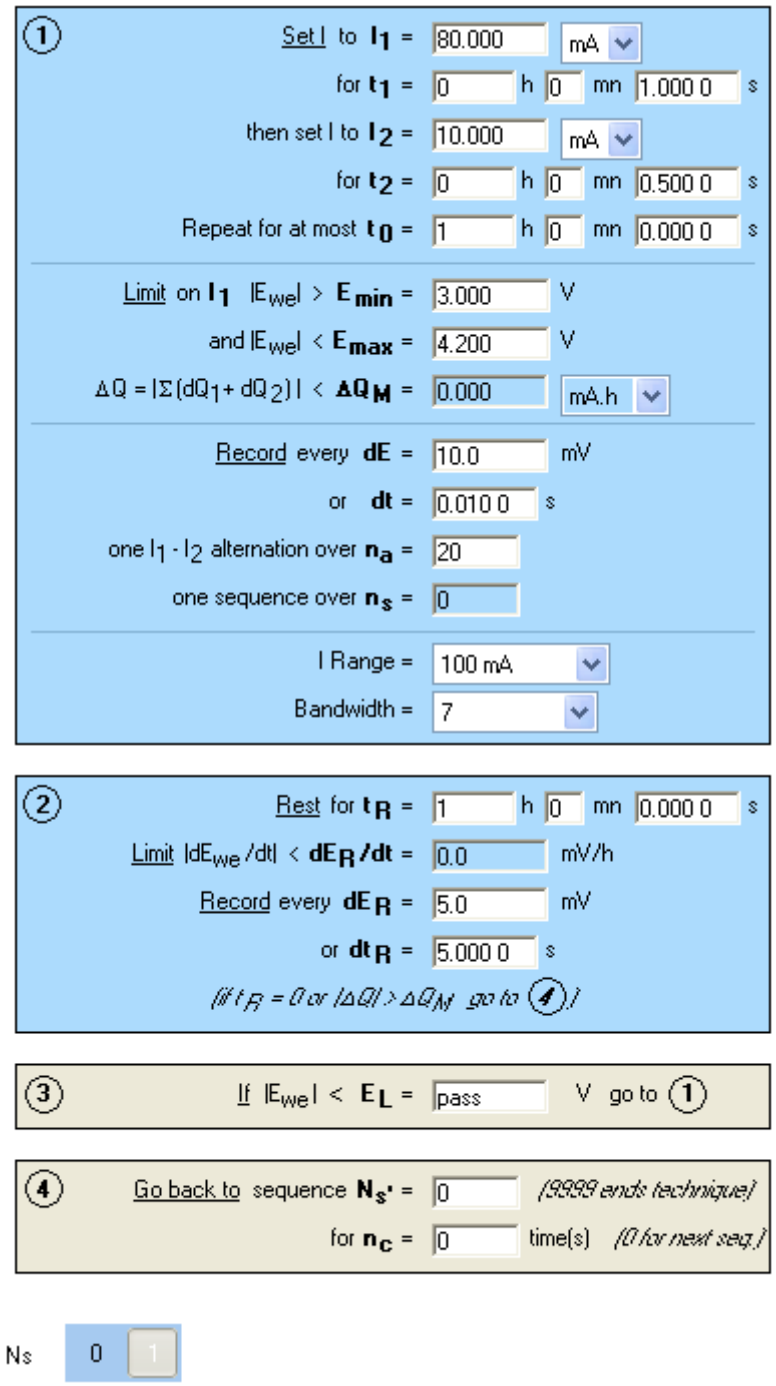


Fig. 105: APGC detailed diagram.

- **Pulsed Galvano Charge**

Set I_1 to ……. pA/…/A, for t_1 = …… h …… mn ……. s
Set I_2 to ……. pA/…/A, for t_2 = …… h …… mn ……. s
define the pulse currents values and durations.

With I Range = …… and Bandwidth = ……..
fixes the current range and the bandwidth for this experiment.

Repeat for at most t_0 = …… h …… mn …… s
sets the pulse period duration. If t_2 is set to zero, then I_2 and t_0 (and n_a) are not used and the current I_1 is applied for t_1 duration.

on I_1 Keep $|E_{we}|$ between E_{min} = …….. V and E_{max} = ……. V
limits the WE potential on I_1 current steps.

and limit $\Delta Q = |\Sigma(dQ_1 + dQ_2)|$ to ΔQ_M = …….. mA.h
limits the total charge of the galvano pulse (for current sequence) to ΔQ_M.

Record E_{we} once over n_a = ……. I_1 - I_2 alternances and over n_s = ……. sequences
limits the recordings (with dE and dt resolutions) one I_1-I_2 alternation for n_a (if $t_2 > 0$) and one sequence for n_s. Zero values bypass the n_a and n_s limitations.

with resolution dE = ……. mV and at least every dt = …….. s
On I_1 - I_2 alternation multiple of n_a and sequence multiple of n_s, record one point each time the potential variation (from previously recorded value) is superior to dE and time $\geq$ dt. These recording conditions can be set separately or together. The first condition reached determines the recording. A zero value cancels the recording condition.

- **Rest Potential Sequence**

The open circuit voltage is the standard block, so report to the OCV or GCPL techniques chapters for more information.

- **Test $E_{we} > E_L$**

Tests that the battery is charged or discharged. For a proper run of this test, one must ensure that $I_1 > I_2$, then:

. if $|I_1| \geq |I_2|$ $E_{we} \leq E_L$ (oxidation) then the galvano pulse is performed again else the execution continues to the next sequence,
. if $|I_1| \leq |I_2|$ $E_{we} < E_L$ (reduction) then the galvano pulse is performed again else the execution continues to the next sequence.

If the OCV period is canceled ($t_R = 0$) or the E_{min}, E_{max} or ΔQ_M limits have been reached, then the E_L test is not performed. If the user types the "p" character (for "pass") for E_L, then the test is skipped too.

- **Next sequence**

Next sequence or Goto sequence $N_{s'}$ = ……. , for n_c = ……. time(s)
loops to a previous sequence $N_{s'}$ (< N_s), n_c time(s). Set $n_c = 0$ to cancel the loop and go to the next sequence ($N_s + 1$).

Note: in this technique the first and last data points of each current steps are not recorded automatically.

3.1.11 PPI: Potentio Profile Importation

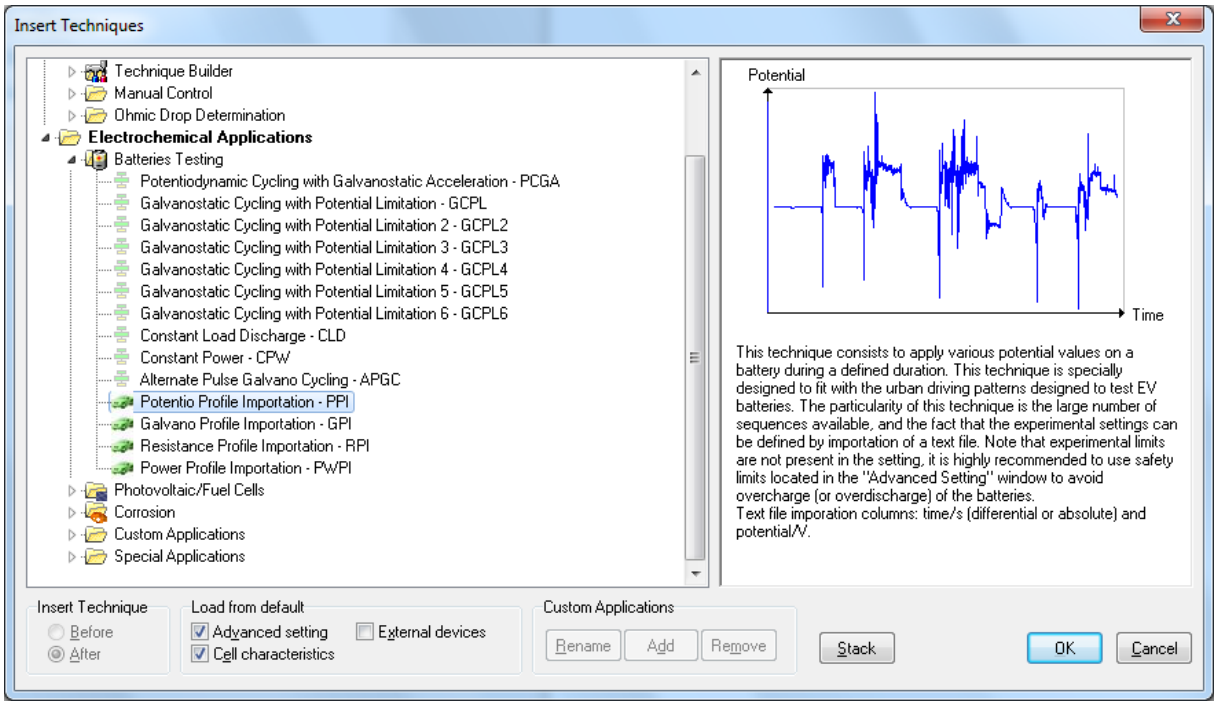


Fig. 106: Selection window for a profile importation.

Select the PPI application and click on OK. The following window is displayed:

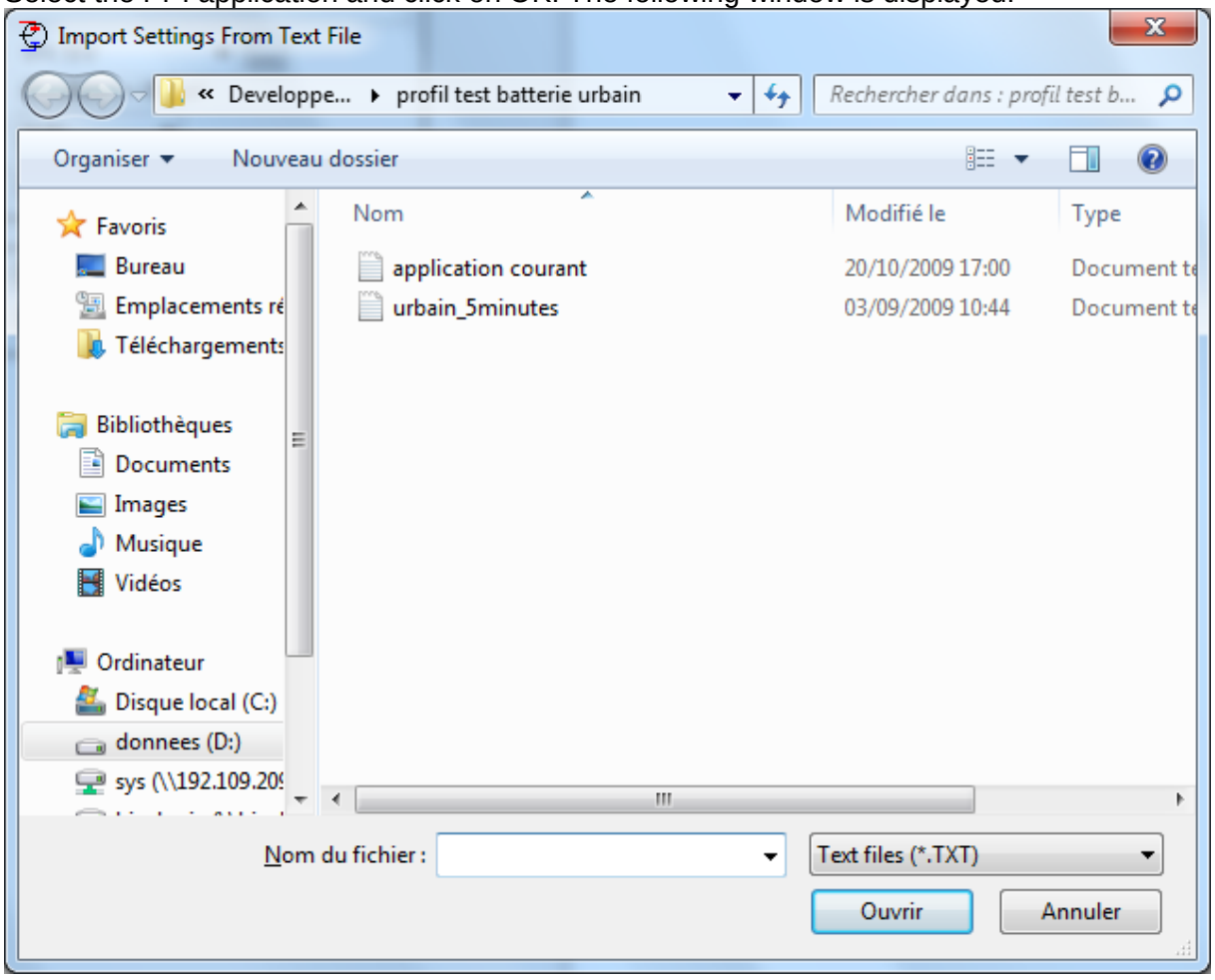


Fig. 107: Text Import window.

The user has to select the text file to import (with two columns: time and potential in this case).
This technique corresponds to battery cycling under galvanostatic mode. This technique is specially designed to fit with the urban driving patterns designed to test EV batteries. The particularity of this technique is the large number of sequences available and the fact that the experimental settings can be defined by importation of a text file. This technique can be used in charge and in discharge mode (depending on the sign of the current). Note that experimental limits are not present in the setting, it is highly recommended to use safety limits located in the "Advanced Setting" window to avoid overcharge (or overdischarge) of the batteries. The text file importation columns are time/s (differential or absolute) and current/A.

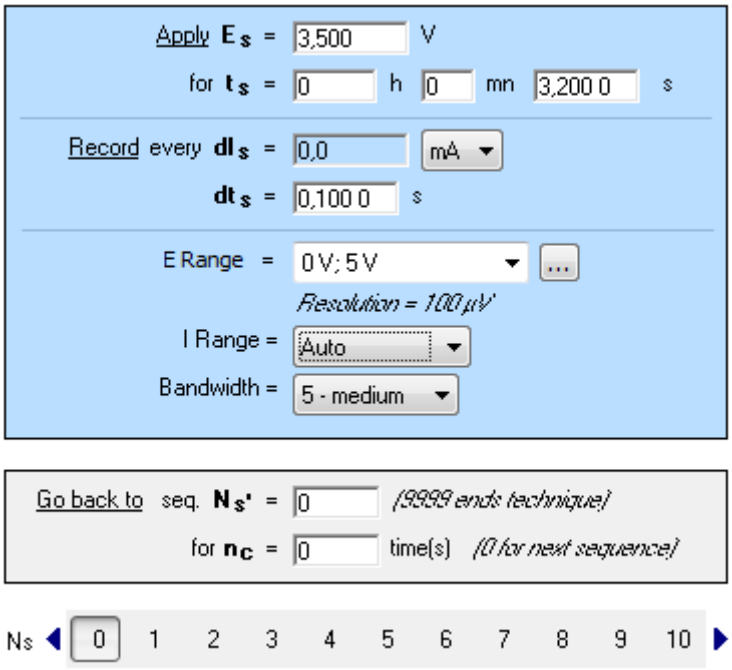


Fig. 108: PPI detailed diagram.

Automatically the number of sequences corresponding to the number of rows in the table is displayed. The maximum number of sequences is limited to 2500 on our standard boards (limited by the memory size).in the case that the software fnid two lines with teh same parameters, they will be merged in only one line to save memory. In the table to import the first column must the time and the second one must be the other variable such as potential or current.

- **Pulsed potentio Charge**

Apply E_s = ……. V, for t_1 = …… h …… mn ……. s
define the voltage pulse value and duration.

Record every dI_s = pA/…/A and/or dts = ……. s
limits the recordings conditions in current variuation and/or time variation

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

- **Conditional test which proposes to go to the next sequence or to loop on a previous sequence $N_{S'}$ ($N_{S'} < N_S$).**

If n_c is set to 0, then the technique executes the next sequence.
If the user wants to loop to a previous sequence (line), he has to fill the 2 last columns of the table "**Go to $N_{S'}$**" and " **n_c cycles**".

The end of the technique is obtained by setting $N_{S'}$ and n_c to 0 in the last sequence, or setting **Goto** sequence $N_{S'}$ = 9999 at any sequence, which then will be the last one executed even if the next sequence has its settings.

3.1.12 GPI: Galvano Profile Importation

This technique consists to apply various potential values on a battery during a defined duration. This technique is specially designed to fit with the urban driving patterns designed to test EV batteries. The particularity of this technique is the large number of sequences available, and the fact that the experimental settings can be defined by importation of a text file. Note that experimental limits are not present in the setting, it is highly recommended to use safety limits located in the "Advanced Setting" window to avoid overcharge (or overdischarge) of the batteries. The text file importation columns are time/s (differential or absolute) and potential/V.

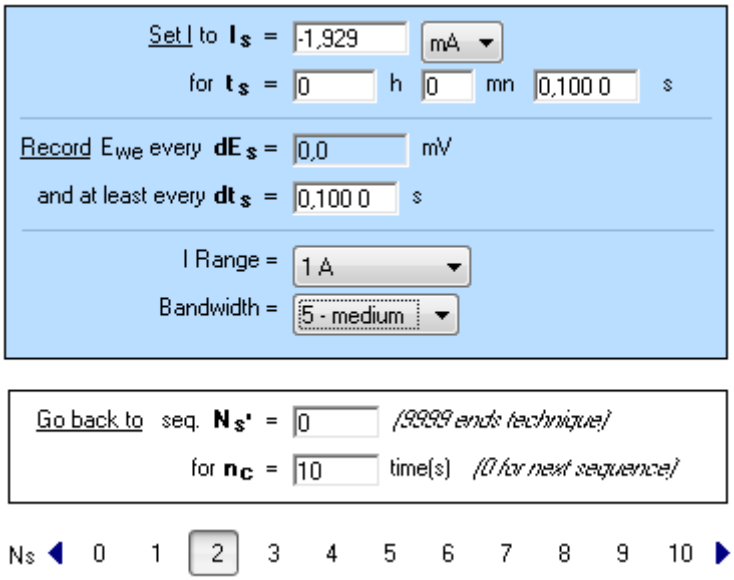


Fig. 109: GPI detailed diagram.

- **Pulsed galvano Charge**

Set I to I_s = ……. V, for t_s = …… h …… mn ……. s
define the current pulse value and duration.

Record E_{we} every dE_s = ... mV and at least every dts = ……. s
limits the recordings conditions in voltage variation and/or time variation

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

- **Conditional test**

which proposes to go to the next sequence or to loop on a previous sequence $N_{S'}$ ($N_{S'} < N_S$).

3.1.13 RPI: Resistance Profile Importation

This technique consists to apply various resistance values on a battery during a defined duration. This technique is specially designed to fit with the urban driving patterns designed to test EV batteries. The particularity of this technique is the large number of sequences available, and the fact that the experimental settings can be defined by importation of a text file. Note that experimental limits are not present in the setting, it is highly recommended to use safety limits located in the "Advanced Setting" window to avoid overcharge (or overdischarge) of the batteries. The text file importation columns are time/s (differential or absolute) and resistance/Ohm.

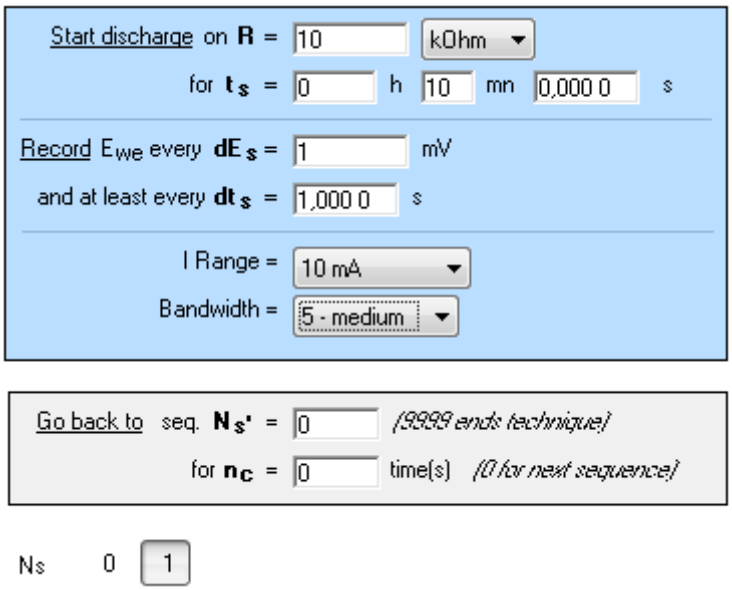


Fig. 110: RPI detailed diagram.

- **Pulsed Resistance discharge**

Start discharge on R = ……. mOhms/..../MOhms for t_s = …… h …… mn ……. s
define the restance pulse value and duration.

Record E_{we} every dE_s = ... mV and at least every dts = ……. s
limits the recordings conditions in voltage variation and/or time variation

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

- **Conditional test**

which proposes to go to the next sequence or to loop on a previous sequence $N_{S'}$ ($N_{S'} < N_S$).

3.1.14 PWPI: Power Profile Importation

This technique consists to apply various power values on a battery during a defined duration. This technique is specially designed to fit with the urban driving patterns designed to test EV batteries. The particularity of this technique is the large number of sequences available, and the fact that the experimental settings can be defined by importation of a text file. Note that experimental limits are not present in the setting, it is highly recommended to use safety limits located in the "Advanced Setting" window to avoid overcharge (or overdischarge) of the batteries. The text file importation columns are time/s (differential or absolute) and power/Watt.

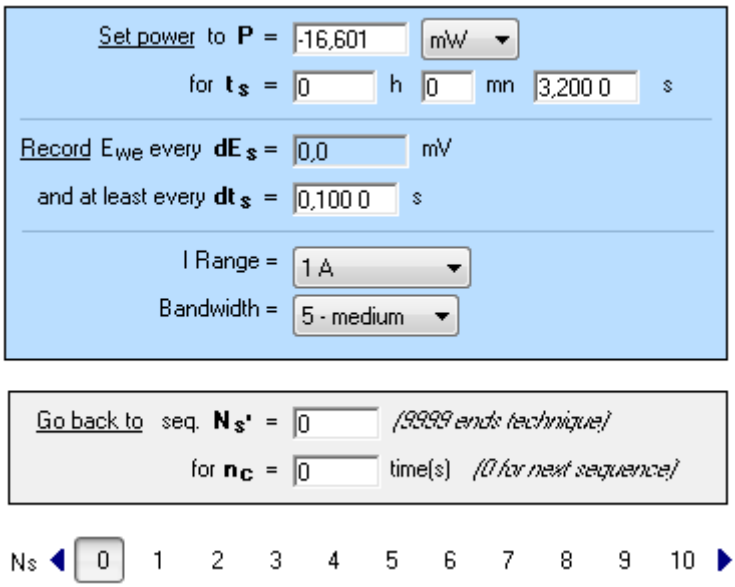


Fig. 111: PWPI detailed diagram.

- **Pulsed power discharge**

Set power to P = ……. mW/..../kW for t_s = …… h …… mn ……. s
define the restance pulse value and duration.

Record E_{we} every dE_s = ... mV and at least every dts = ……. s
limits the recordings conditions in voltage variation and/or time variation

I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

- **Conditional test**

which proposes to go to the next sequence or to loop on a previous sequence $N_{S'}$ ($N_{S'} < N_S$).

3.2 Photovoltaics / Fuel Cells

This section is especially dedicated to energy devices not requiring any charge sequence. They are studied only in the discharge mode, fuel being for these devices a gas or the sun light.
This section includes five different applications: the I – V characterization, the constant load discharge, the constant power, voltage and current.

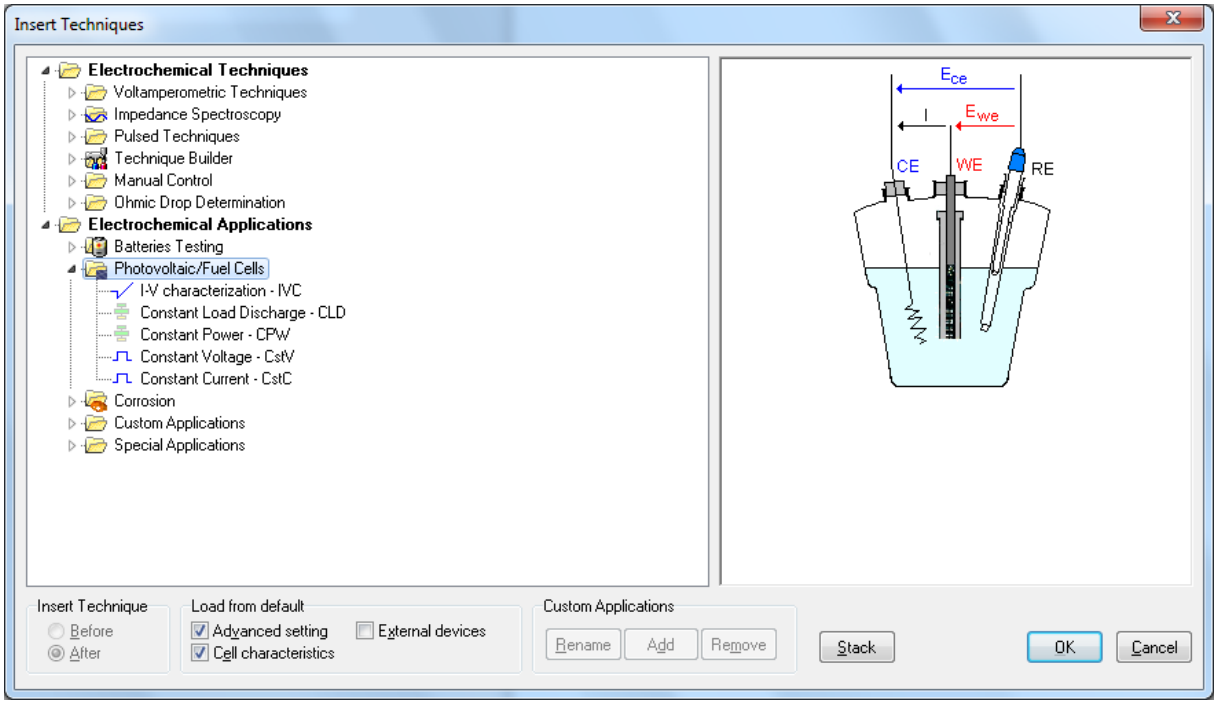


Fig. 112: Photovoltaic / fuel cell applications

3.2.1 I-V Characterization: IVC

I-V characterization is intensively used to carry out investigations on Photovoltaic or Fuel cells. The principle of this technique is to apply a linear potential sweep and to measure the corresponding current and power. Some characteristic parameters of the cell such as maximum current, maximum potential and maximum power can be determined.

3.2.1.1 Description

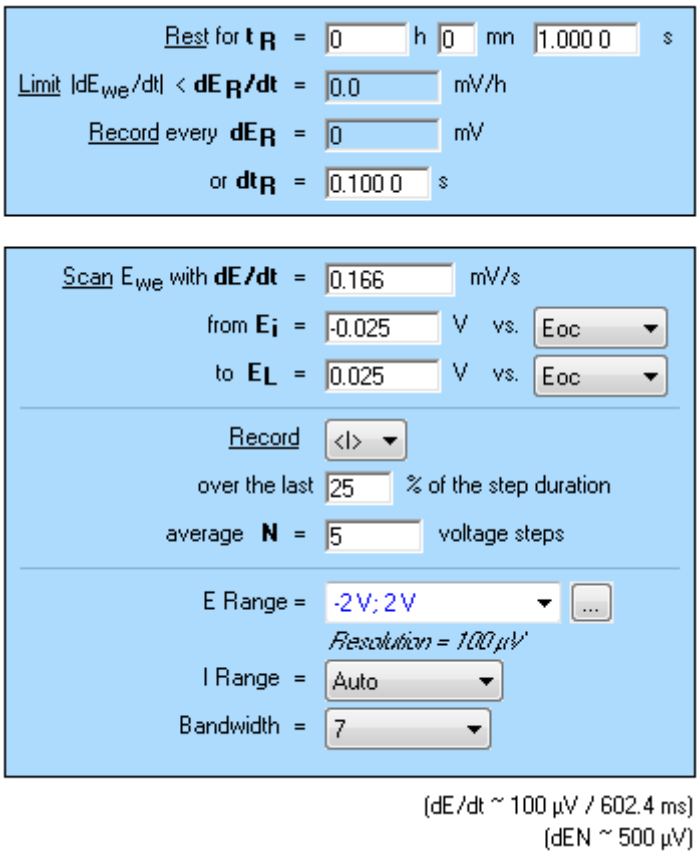


Fig. 113: Detailed diagram of the I-V Characterization.

- **First step: rest potential (or open circuit) sequence.**

Rest for t_R = ……. h …… mn …….. s
fixes a defined time duration t_R for recording the rest potential.

or until $|dE_{we}/dt| < dE_R/dt$ …… mV/h
gives the user the ability to shorten the open circuit period at the time when the decay of the potential is lower than a given value.

Record E_{we} with dE_R = …… mV resolution and at least every dt_R = …….. s
allows the user to record the working electrode potential whenever the change in the potential is ≥ dE_R or every dt_R time interval .
Data recording with dE_R resolution reduces the number of experimental points without losing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded but if there is a sharp peak in potential, the rate of the potential recording is governed by the potential recording resolution.

- **Second step: potential scan.**

Scan E_{we} with dE/dt ……. = mV/s
defines the potential scan. The software selects the smallest potential step according to the control potential resolution defined in the “Advanced settings” window (see the corresponding section in the EC-Lab® software manual for more details).

From Ei = ……. V vs. Ref/Eoc/Ectrl/Emeas to E_L = …… V vs. Ref/Eoc/Ei

from a potential E_i defined in absolute (vs. Ref the reference electrode potential) or versus a previous open circuit potential (E_{oc}), previous controlled potential (E_{ctrl}) or previous measured potential (E_{meas}) to E_p value defined in absolute or versus E_{oc} or E_i.

Record <I> over the last …… % of the step duration averaged N = ……. voltage steps
I every dI_p = …….. pA/nA/µA/mA/A or dt_p = …… s

Two different recording conditions on the current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……

Define the current range and the bandwidth for the whole experiment. I Range is automatically set according to I_t and I_c values.

3.2.1.2 Process

Associated with the I-V characterization, an analysis is available for this section offering the determaintaion of the following parameters:

- Short Circuit Current (I_{sc}), which corresponds to the maximum current when E = 0 V,
- the Open Circuit Voltage (E_{oc}), which is the potential when the current is equal to zero ampere,
- the theoretical power (P_T), which is defined by the following relationship $P_T = I_{sc} \times E_{oc}$,
- the maximum power
- the fill factor (FF), which is the ratio of P_{MAX} and P_T,
- the efficiency can also be calculated.

3.2.2 Constant load discharge

The Constant Load Discharge application has been designed to discharge a device at a constant resistance. The potentiostat is seen as a constant resistor by the energy device.
The constant resistance control is made by controlling the current to maintain the constant ratio E/I.

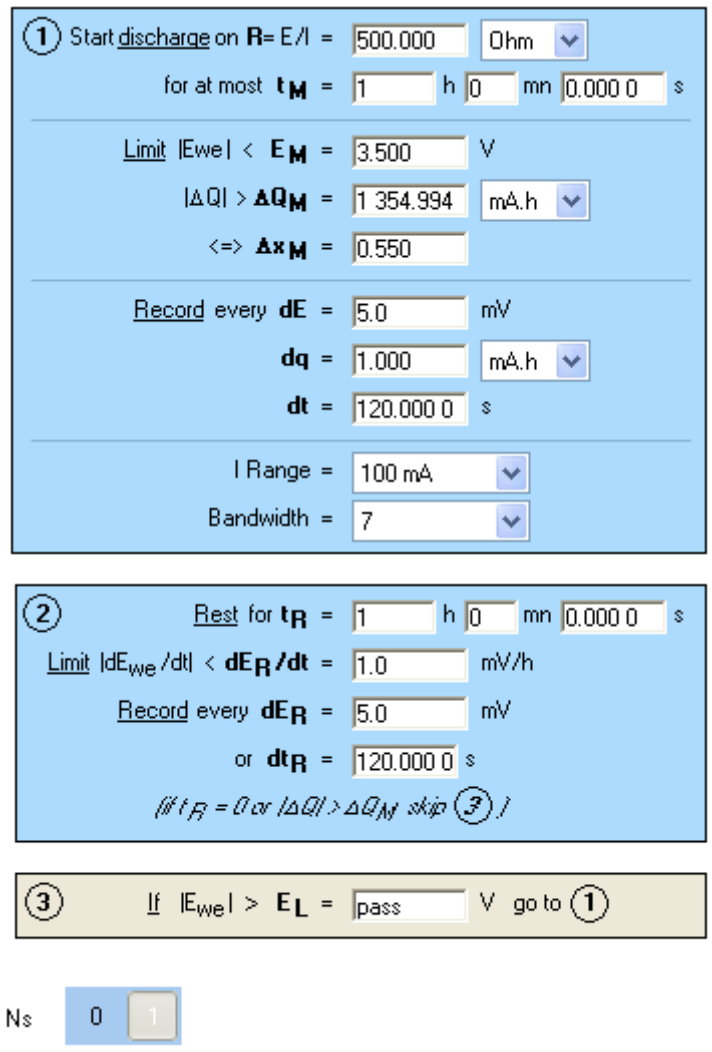


Fig. 114: CLD detailed diagram.

- **first step: definition of the resistance and choice of recording conditions**

Start Discharge on R=E/I= …… Ohm/kOhm/Mohm for at most t_M = ….. h ….. mn ….. s
sets the cell resistance to R = E/I for t_M duration.

With I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

Record every dE = …… mV, dq = …… mA.h and dt = …… s
defines the recording conditions. These values can be entered simultaneously, the first condition that is reached determines the recording. A zero value disables the recording for each criterion.

Until $|E_{we}| < E_M$ = …… V, $|\Delta Q| > \Delta Q_M$ = …….. mA.h <=> Δx_M = ……
Fixes the limit of the working electrode potential (E_{we}) and the charge from the beginning of the sequence ($|\Delta Q|$, $|\Delta x|$), for the whole step. The maximum charge can be entered into mA.h (ΔQ_M) or as a normalized charge (related to intercalation electrodes: Δx_M). Once a limit is reached, the experiment proceeds to the next step (Rest), even if the programmed time t_M is not terminated. These limits can be bypassed by entering 0 values into the controls.

Note: when the ΔQ_M (Δx_M) limit is reached, the E_L test is skipped. This is due to the fact that the ΔQ_M limit is considered as the maximal charge that can be applied to the energy device during the discharge. Once reached, the experiment must go to the next sequence.

3.2.3 CPW: Constant Power

The Constant Power application is designed to study the discharge of an energy device at constant power. The constant power control is made by checking the current to maintain the E*I constant. The current increases when E_{we} decreases.

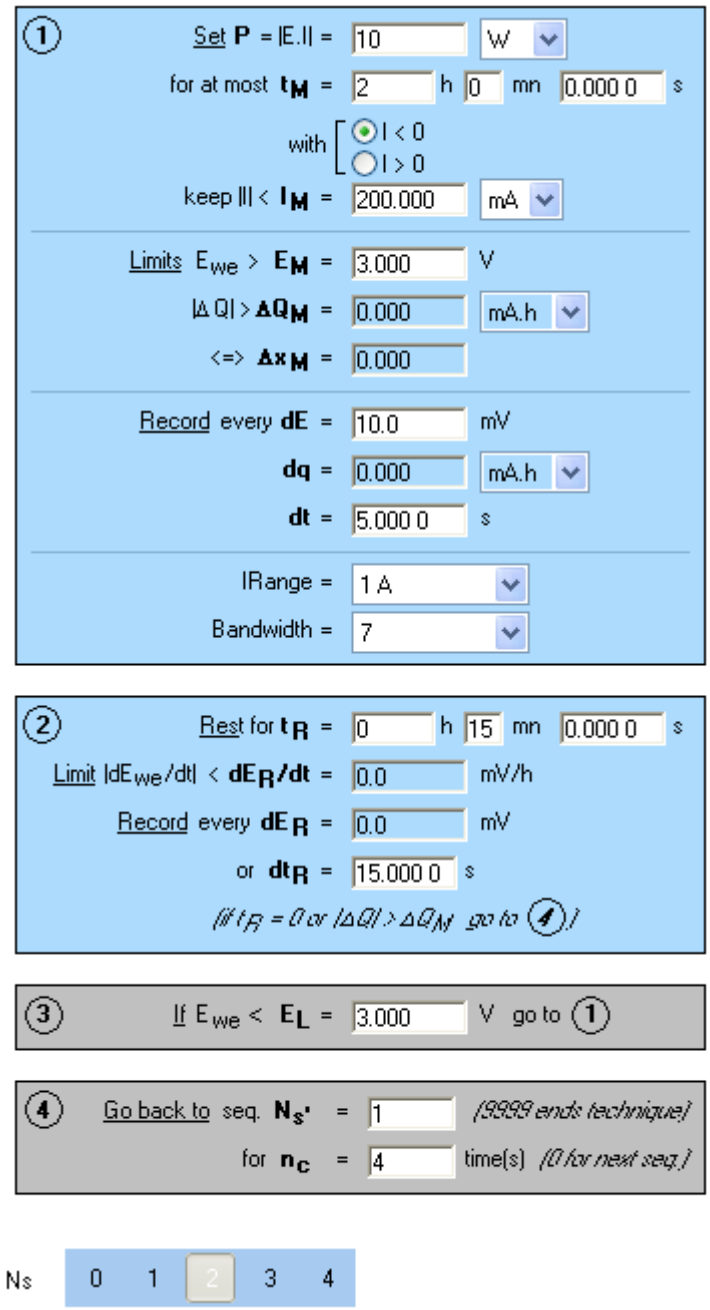


Fig. 115: CPW detailed diagram.

- **first step: choice of the power value**

Set P=E*I= …… µW/mW/W for at most t_M = …… h …… mn …… s
sets the cell power to P = E*I for t_M duration.

With I > 0 or I < 0 and keep I < I_M = …… pA/…/A
defines the charge (I > 0**)** or discharge (I < 0**)** mode and limits the current to a maximum value I_M in order to preserve the cell and/or the instrument.

With I Range = …… and Bandwidth = ……..
fixes the current range and bandwidth for this experiment.

Record every dE = …….. mV, dq = ……. mA.h and dt = …… s
Define the recording conditions. These values can be entered simultaneously. The first condition that is reached determines the recording. A zero value disables the recording for each criterion.

Until E_{we} < E_M = ……. V, $|\Delta Q|$ to ΔQ_M = …… mA.h <=> Δx_M = ……
fixes the limit of the working electrode potential (E_{we}) to a maximum value if I>0 or to a minimum value if I<0 and the charge from the beginning of the sequence ($|\Delta Q|$, $|\Delta x|$), for the whole step. The maximum charge can be entered into mA.h (ΔQ_M) or as a normalized charge (related to intercalation electrodes : Δx_M). Once a limit is reached the experiment proceeds to the next step (Rest), even if the programmed time t_M is not terminated. These limits can be bypassed by entering 0 values into the controls.

Caution:

Applying a constant power during a discharge experiment corresponds to an increase of the current (in absolute) when the potential decreases. The user must be careful to note the final current of the first constant power step. For example, let's consider a 30 watts power discharge applied to a battery with a 10 A booster. We suppose that the potential limits of this experiment are 4 V and 2.5 V. The initial current will be 7.5 A but the final current will be 12 A (overload in current). It will not be possible to go to the final current.

3.2.4 Constant Voltage : CstV

The constant voltage (CstV) technique is specially dedicated to fuel cell(s) or photovoltaic cell(s) testing. It is designed to apply successively several voltage steps to the cell(s). Between each voltage step, an open circuit voltage period can be added.

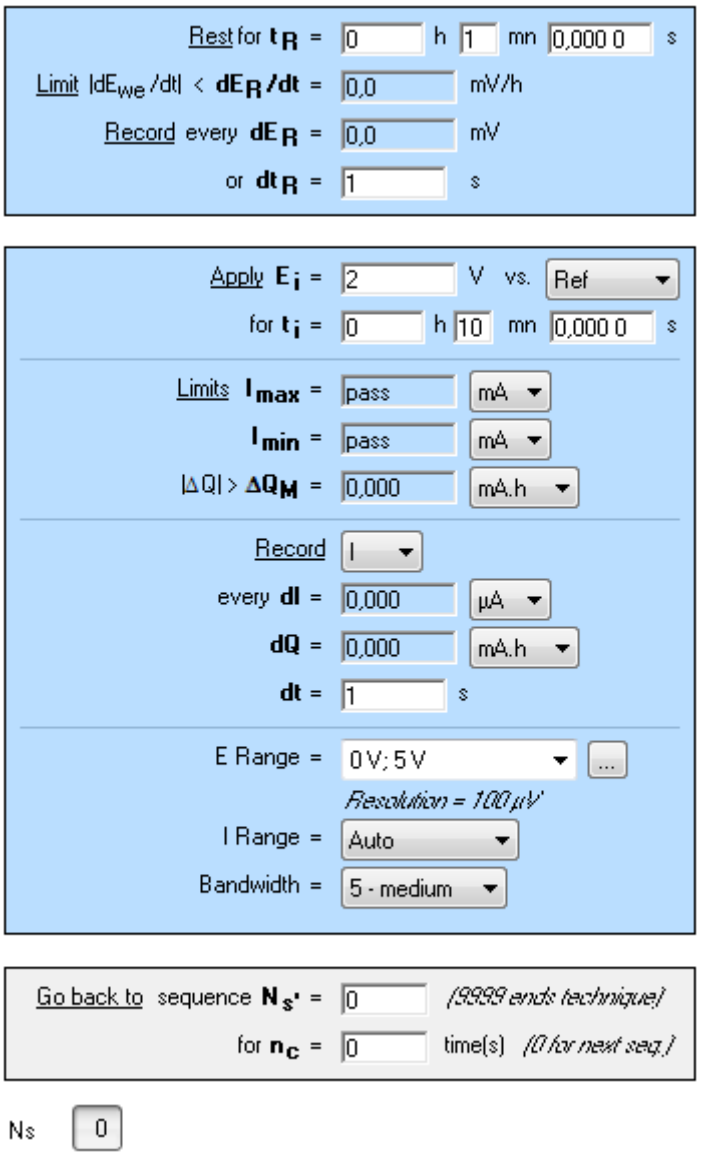


Fig. 116: Constant Voltage detailed diagram.

- **Rest period**

The rest period is an open circuit voltage period. Refer to the OCV description for more details

- **Potential step with data recording conditions:**

1) Potential step

Apply E_i = …… V vs Ref/Eoc/Ectrl/Emeas.
the potential step is defined in absolute (vs. Ref the reference electrode potential) or according to the previous open circuit potential (E_{oc}), controlled potential (E_{ctrl}) or measured potential (E_{meas}).

for t_i = …….. h …… mn …….. s
fixes the potential step duration.

limit |I| to I_{Max} = ….. pA/…/A and $|\Delta Q| < \Delta Q_M$ = fA.h/…/A.h/pC/…/kC.

I_{min} = …… pA/…/A

curtails the step duration if the current or charge limit is reached. If the limit is reached, the loop condition (go to $N_{s'}$ for n_c times), if set, is not used, and the program continues to the next sequence (N_s + 1).

The $|\Delta Q|$ value is the integral charge for the current sequence. This value is not reset if there is a loop on the same sequence ($N_{s'} = N_s$).

0 values disable the tests.

2) Recording conditions

Record I every dI_p = …. pA/…/A, dQ_p = …… fA.h/…/A.h/pC/…/kC and dt_p = …. S

<I> every dts = …….. s

you can record either an instantaneous current value I or an averaged current value <I>. The recording conditions during the potential step depend on the chosen current variable. For the instantaneous current the recording values can be entered simultaneously. Then it is the first condition reached that determines the recording. A zero value disables the recording for each criterion. For the averaged current the user defines the time for the average calculation. In that case the data points are recorded in the channel board memory every 200 µs for the VMP2, VMP3, VSP, SP-150, BiStat and the SP-300 and 20 ms for the VMP and the MPG.

Leave dI alone for Chronoamperometry experiments, and dQ for Chronocoulometry experiments.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I range = ……. bandwidth = …… .

enables the user to select the current range and the bandwidth (damping factor) of the potentiostat regulation.

- **Loop**

goto Ns' = for nc = time(s)

allows the experiment to loop to a previous line $N_{s'}$ (<= N_s) for n_c times. The number of loops starts while the loop block is reached. For example, on N_s = 3, if one enters goto $N_{s'}$ = 2 for n_c = 1 time, the sequence N_s = 2, N_s = 3 will be executed 2 times.

n_c = 0 disables the loop and the execution continue to the next line ($N_{s'} = N_s + 1$). If there is no next line, the execution stops.

Here, it is possible to loop to the first instruction (N_s = 0) and the current instruction ($N_{s'} = N_s$).

3.2.5 Constant Current : CstC

The constant current (CstC) technique is specially dedicated to fuel cell(s) or photovoltaic cell(s) testing. It is designed to apply successively several current steps to the cell(s). Between each current step, an open circuit voltage period can be added."

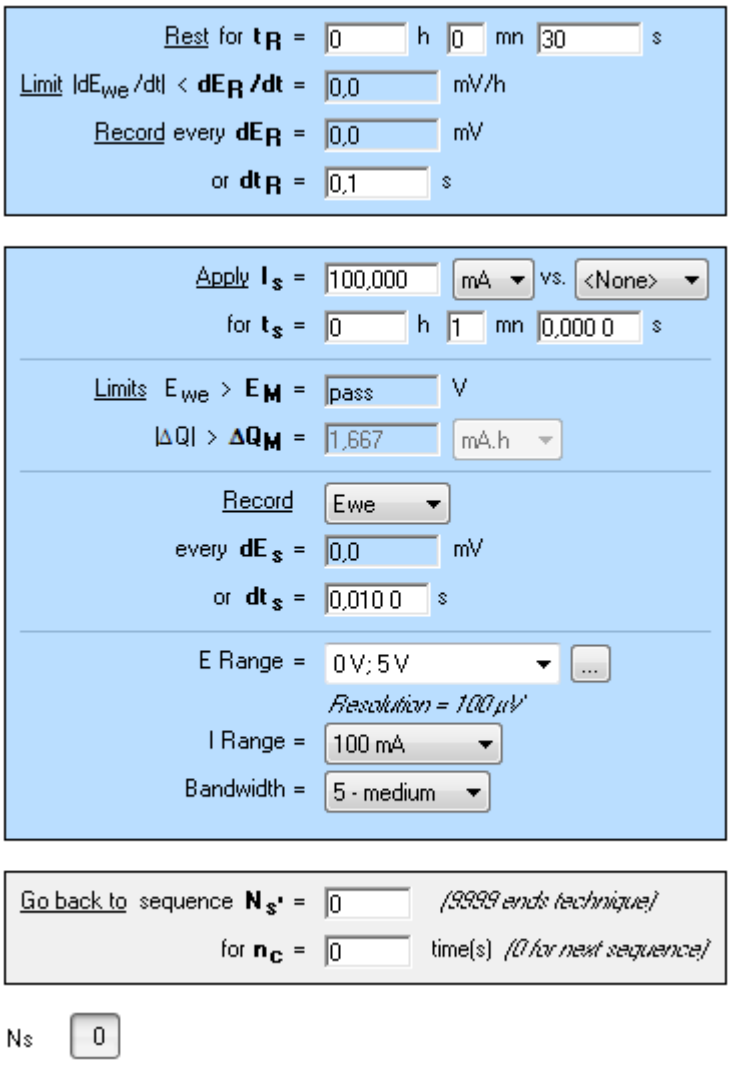


Fig. 117: Constant Current detailed diagram.

- **Rest period**

The rest period is an open circuit voltage period. Refer to the OCV description for more details

- **Current step**

Apply I_s = ……. pA/…/A vs. <none>/Ictrl/Imeas.
the current step is set to a fixed value or relatively to the previous controlled current I_{ctrl}, that is the current of the previous sequence current step block or to the previous measured current I_{meas}. This option is not available on the first sequence (N_s = 0).
To select the current step type, check the option box.

for t_s = …… h …… mn …… s
fixes the current step duration.

limit $|E_{we}| < E_M$ = …… mV and $|\Delta Q| < \Delta Q_M$ = ……. fA.h/…/A.h/pC/…/kC
curtails the step duration if the potential or charge limit is reached. If the limit is reached, the loop condition (go to $N_{s'}$ for n_c times), if set, is not used, and the program continues to the next sequence (N_s + 1).
The $|\Delta Q|$ value is the integral charge for the current sequence. This value is not reset if there is a loop on the same sequence ($N_{s'} = N_s$).
0 values disable the tests.

Record E_{we} or $<E_{we}>$ every dE_s = …… mV, and at least every dt_s = …….. s
defines the recording conditions during the potential step. 0 values disable the recording condition, and the corresponding box stays green. These values can be entered simultaneously, and this is the first condition that is reached that determines the recording.

I Range, Bandwidth
selects the current range and bandwidth values for the whole sequences.

- **Loop**

goto sequence Ns' = ……. for nc = …… time(s)
gives the ability to loop to a previous sequence $N_{s'}$ (<= N_s) for n_c times. Sequences of the chronopotentiometry technique can be chained using the "Table" frame. The first sequence is N_s = 0.
The number of loops starts while the loop block is reached. For example, on N_s = 3, if one enters goto $N_{s'}$ = 2 for n_c = 1 time, the sequence N_s = 2, N_s = 3 will be executed 2 times.
n_c = 0 disables the loop and the execution continue to the next line ($N_{s'} = N_s + 1$). If there is no next line, the execution stops.

3.3 Corrosion

Corrosion is the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the metal and its properties.

3.3.1 EVT: E_{corr} versus Time

This technique corresponds to the follow up of the corrosion potential (when the circuit is open) versus time. During the measurement no potential or current is applied to the cell.

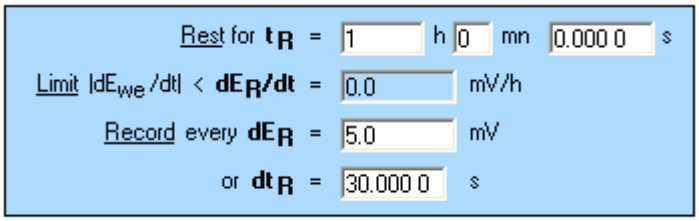


Fig. 118: E_{corr} vs. Time diagram.

Rest for t_R = h mn s
fixes a defined time duration t_R for recording the rest potential.
or until $|dE_{we}/dt| < |dE_R/dt|$ = mV/h
stops the rest sequence when the slope of the open circuit potential with time, $|dE_R/dt|$ becomes lower than the set value (value 0 invalidates the condition).

Record E_{we} every dE_R = mV resolution and at least every dt_R = s

allows the user to record the working electrode potential whenever the change in the potential is ≥ dE_R with a minimum recording period in time dt_R.

Data recording with dE_R resolution can reduce the number of experimental points without losing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded but if there is a sharp peak in potential, the rate of recording increases.

3.3.2 LP: Linear Polarization

The linear polarization technique is used in corrosion monitoring. This technique is especially designed for the determination of a polarization resistance R_p of a material and I_{corr} through potential steps around the corrosion potential. R_p is defined as the slope of the potential-current density curve at the free corrosion potential:

$$R_p = \frac{dE}{dI} \qquad dE \to 0$$

R_p is determined using the 'R_p Fit' graphic tool.
This technique is also used to plot polarization curves and determine corrosion rate and coefficients with Tafel Fit.

3.3.2.1 Description

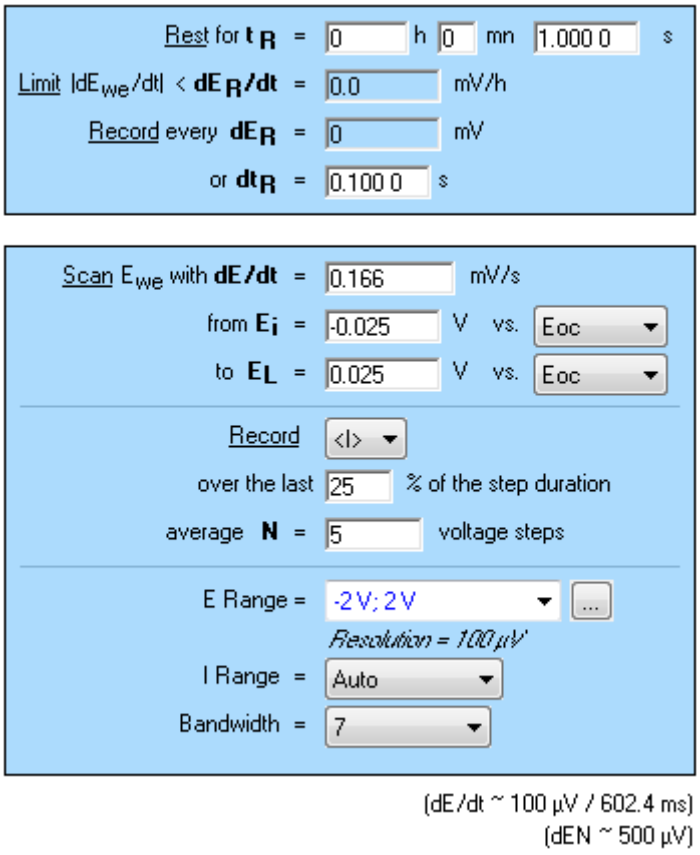


Fig. 119: Detailed diagram of the Linear Polarization application.

- **First step: rest potential (or open circuit) sequence.**

Rest for t_R = ……. h …… mn …….. s
fixes a defined time duration t_R for recording the rest potential.

or until |dE_{we}/dt| < dE_R/dt …… mV/h
gives the user the ability to shorten the open circuit period at the time when the decay of the potential is lower than a given value.

Record E_{we} with dE_R = …… mV resolution and at least every dt_R = …….. s
allows the user to record the working electrode potential whenever the change in the potential is $\geq dE_R$ or every dt_R time interval .
Data recording with dE_R resolution reduces the number of experimental points without losing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded but if there is a sharp peak in potential, the rate of the potential recording is governed by the potential recording resolution.

- **Second step: potential scan.**

Scan E_{we} with dE/dt ……. = mV/s
defines the potential scan. The software selects the smallest potential step according to the control potential resolution defined in the “Advanced settings” window (see the corresponding section in the EC-Lab® software manual for more details).

From Ei = ……. V vs. Ref/Eoc/Ectrl/Emeas to E_p = …… V vs. Ref/Eoc/Ei
from a potential E_i defined in absolute (vs. Ref the reference electrode potential) or versus a previous open circuit potential (E_{oc}), previous controlled potential (E_{ctrl}) or previous measured potential (E_{meas}) to E_p value defined in absolute or versus E_{oc} or E_i.

Record <I> over the last …… % of the step duration averaged N = ……. voltage steps I every dI_p = …….. pA/nA/µA/mA/A or dt_p = ……. s
Two different recording conditions on the current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user’s manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……
Defines the current range and the bandwidth for the whole experiment. I Range is automatically set according to I_t and I_c values.

Contrary to the MPP technique, no current limitation is available with the linear polarization application.

3.3.2.2 Process and fits related to LP

The LP application can be used for R_p and I_{corr} determination using the R_p fit (see EC-Lab® software manual for more details). It can also be used to determine the corrosion rate with the Tafel fit (see EC-Lab® software manual for more details).

3.3.3 CM: Corrosimetry (Rp vs. Time)

This application is advanced in corrosion tests. It is designed to follow the corrosion standard values (R_p, E_{corr}, I_{corr}) evolution versus time (for very a long time: several months). It consists of periodic linear potential sweeps around the corrosion potential (E_{corr}). The current is

measured during the potential scan. According to the recording conditions on the current, either one point is plotted as an average on each potential step or several points are plotted as instantaneous values. An automatic linear fit is performed around E_{corr} to determine the polarization resistance (R_p). One R_p value is obtained for each sweep, and the R_p evolution is plotted versus time on another graph. The user can define the anodic and cathodic corrosion constants in the settings for more accurate calculations.

3.3.3.1 Description

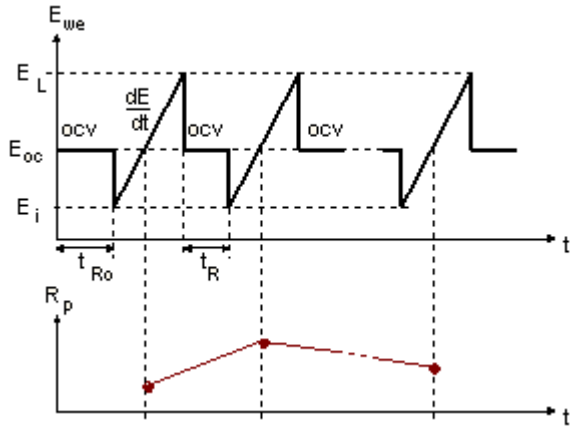


Fig. 120: Graphic description of the Corrosimetry application.

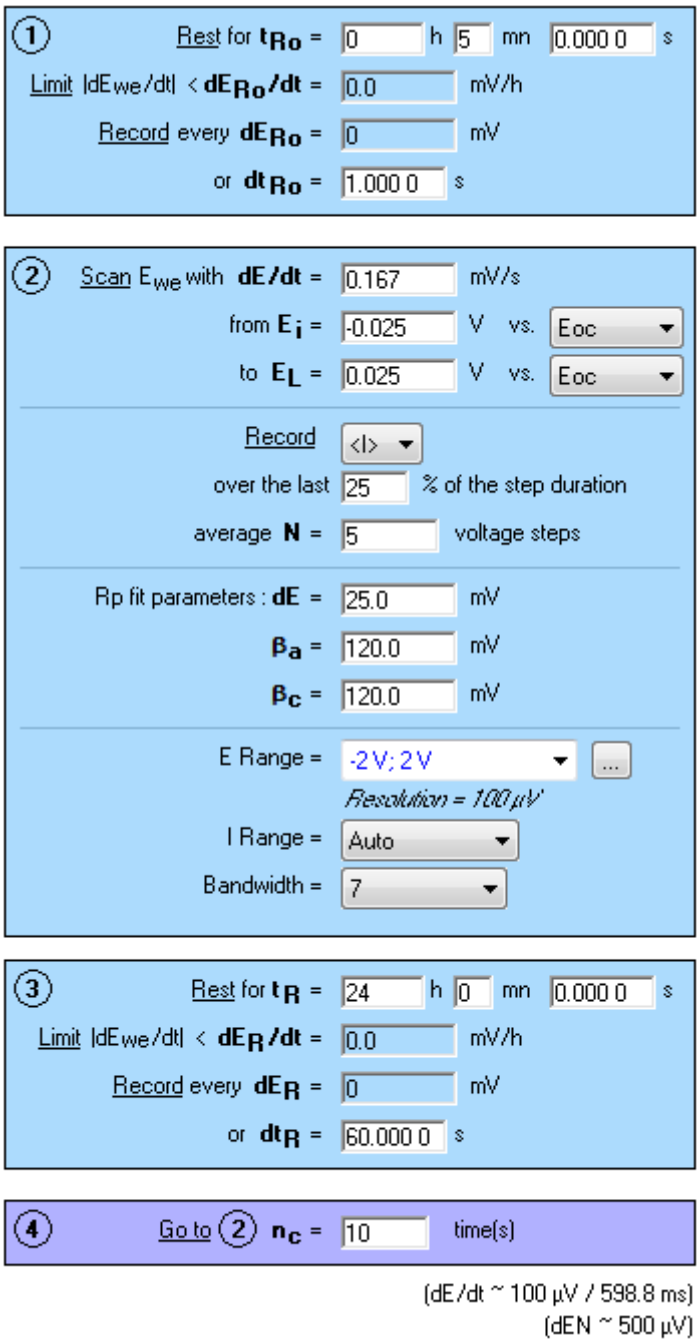


Fig. 121: Detailed diagram of the Corrosimetry application.

- **First step: rest potential (or open circuit) sequence.**

Rest for t_R = ……. h …… mn …….. s
fixes a defined time duration t_R for recording the rest potential.

or until $|dE_{we}/dt| < dE_R/dt$ …… mV/h
gives the user the ability to shorten the open circuit period at the time when the decay of the potential is lower than a given value.

Record E_{we} with dE_R = …… mV resolution and at least every dt_R = …….. s
allows the user to record the working electrode potential whenever the change in the potential is ≥ dE_R or every dt_R time interval.

Data recording with dE_R resolution reduces the number of experimental points without loosing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded but if there is a sharp peak in potential, the rate of the potential recording is governed by the potential recording resolution.

- **Second step: potential scan.**

Scan E_{we} with dE/dt ……. = mV/s
defines the potential scan. The software selects the smallest potential step according to the control potential resolution defined at the top of the “Parameter settings” window (see the corresponding section in the EC-Lab® software manual for more details).

From Ei = ……. V vs. Ref/Eoc/Ectrl/Emeas to E_p = …… V vs. Ref/Eoc/Ei
from a potential E_i defined in absolute or versus a previous open circuit potential (E_{oc}), or previous controlled potential (E_{ctrl}), or previous measured potential (E_{meas}) to E_p value defined in absolute or versus E_{oc} or E_i.

Record - <I> over the last …… % of the step duration averaged N = ……. voltage steps
- I every dI_p = …….. pA/nA/µA/mA/A or dt_p = …… s
Two different recording conditions on the current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user’s manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……
defines the current range and bandwidth for the whole experiment. I Range is automatically set according to I_t and I_c values.

Rp fit parameters : dE = ….. mV β_a = ….. mV β_c = ….. mV
allows the user to select the potential window around E_{corr} for the R_p fit and to set corrosion coefficients previously determined by a Tafel Fit.

- **Third step: rest potential (or open circuit) sequence.**

reports to the first step for more details about the OCV period.

- **Fourth step: repeat sequence.**

Repeat n_c = ….. time(s)
The potential sweep described in the second step will be repeated n_c times.

Contrary to the MPP technique, no current limitation is available with the linear polarization application.

3.3.3.2 Applications of the Corrosimetry application

When the experiment is running EC-Lab® software displays the polarization curve I vs. E_{we} on a first graph and the processed value R_p versus time on a second graph. I_{corr} and E_{corr} are also calculated in the processed file (.mpp) and can be displayed in real-time on the second graph.

3.3.4 VASP: Variable Amplitude Sinusoidal microPolarization

This technique is a non-linear EIS technique and can only be used for systems with “tafelian” behavior, it is used as a corrosion technique to determine the corrosion current and corrosion coefficients. In this technique a potential sinusoidal wave is applied around the corrosion potential (Ecorr) with N amplitudes increasing from Va min and Va max. At each amplitude, the polarization resistance (Rp) is determined and plotted versus sinus amplitude. A parametric identification is done on the curve to determine the corrosion current and corrosion coefficients. This technique is only available on channel board with EIS ability.

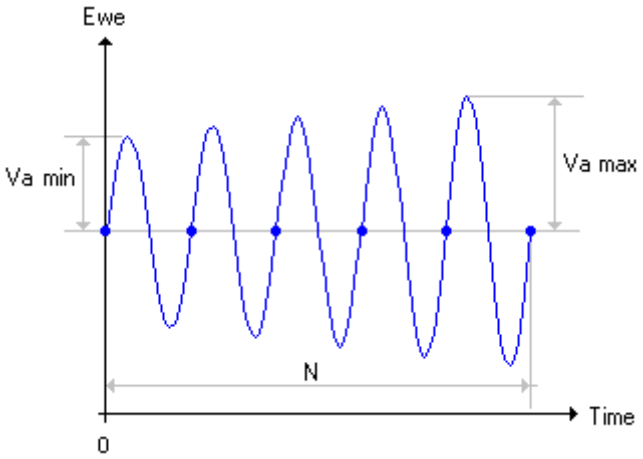


Fig. 122: Variable Amplitude Sinusoidal microPolarization technique.

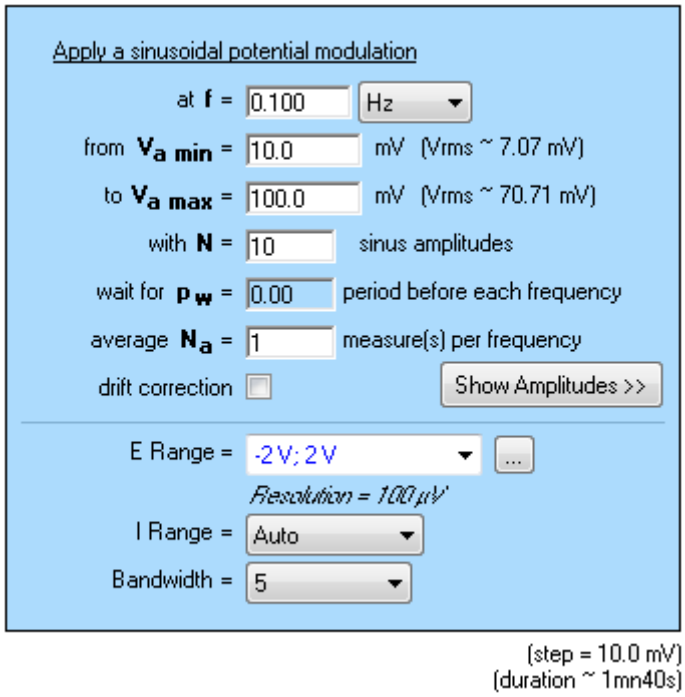


Fig. 123: Detailed diagram of the Variable Amplitude Sinusoidal microPolarization technique.

Description:

- **Apply a sinusoidal potential modulation**

at f = ... MHz/kHz/Hz/mHz/µHz
sets the frequency of the modulation applied to the cell.

From Va min = ... mV
to Va max = ... mV.
sets the range of the sinus. The equivalent value in mV_{RMS} is indicated.

With N = ... sinus amplitude
sets the number of the frequency applied between Va min and Va max.

Wait for Pw = ... period before each frequency
offers the possibility to add a delay before the measurement at each frequency. This delay is defined as a part of the period. At low frequencies the delay may be long.

Average Na = ... measure(s) per frequency
repeats Na measure(s) and average values for each frequency.

Drift Correction
corrects the drift of the system. This feature is more specially dedicated to low frequencies.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = ... Bandwidth = ...
Sets the current range and the bandwidth for the whole experiment.

3.3.5 CASP: Constant Amplitude Sinusoidal microPolarization

Constant Amplitude Sinusoidal microPolarization is used to determine the corrosion current and the corrosion coefficients of a "tafelian" system. A sinusoidal voltage is applied around the corrosion potential (Ecorr) with a small amplitude Va and a constant low frequency (fs). This technique is associated to a dedicated fir (CASP Fit), this analysis tool uses a direct Fourier transform and the amplitude of the harmonics are determined and used to calculate the corrosion parameters. This technique is faster than ther standard polarization technique and there is no need to know the corrosion coefficient values. This technique is available on channel board with and without EIS ability.

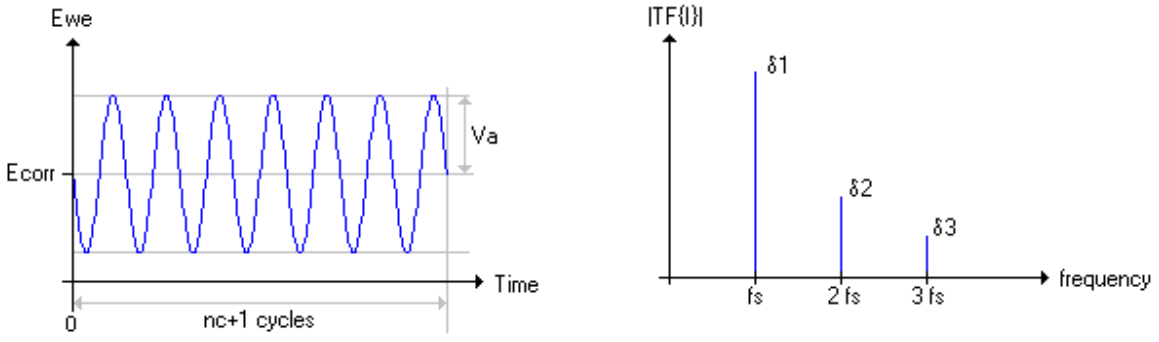


Fig. 124: Principle of the Constant Amplitude Sinusoidal microPolarization technique and its associated analysis.

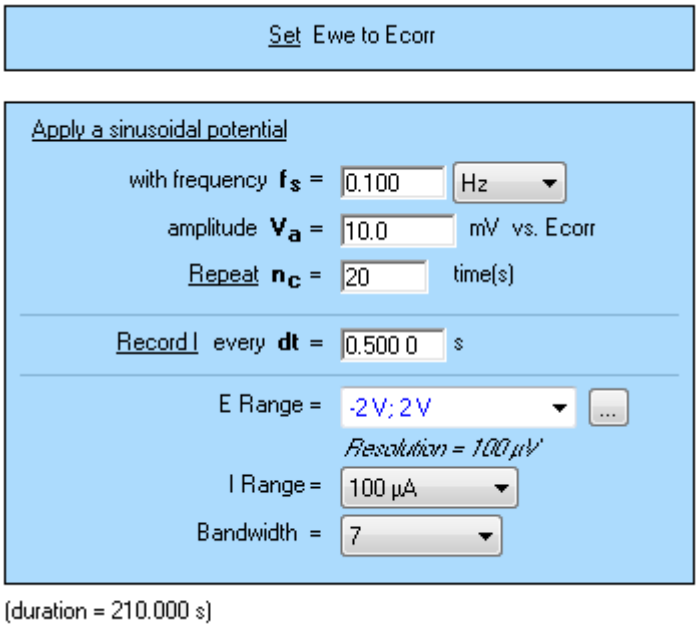


Fig. 125: Detailed diagram of the Constant Amplitude Sinusoidal microPolarization technique.

Description:

- **Apply a sinusoidal potential**

with frequency f_s = ... kHz/Hz/mHz/µHz
sets the frequency of the modulation applied to the cell. The maximum frequency is 500 Hz.

Amplitude Va = ... mV vs. **Ecorr**
Sets the amplitude the sinus.

Repeat n_c = ... time(s)
allows repeating sinusoidal period. Repetition leads to optimized results. It is recommend to perform 20 cycles at least.

Record every dt = ... s
sets the sampling rate of the measurement.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

Irange = ... Bandwidth = ...
Sets the current range and the bandwidth for the whole experiment.
Note it is recommend to adjust a fix current range in order to get constant sampling rate.

3.3.6 GC: Generalized Corrosion

The generalized corrosion technique is applied for general corrosion (sometimes called uniform corrosion) study. For this corrosion, anodic dissolution is uniformly distributed over the entire metallic surface. The corrosion rate is nearly constant at all locations. Microscopic anodes and cathodes are continuously changing their electrochemical behavior from anode to cathode cells for a uniform attack.

This technique corresponds to half a cycle or one cycle of usual cyclic voltammetry, with the particularity of a digital potential sweep i.e. it runs by potential steps (defined and periodic in amplitude and time). For the VMP3, VMP2, VSP SP-150, BiStat and the SP-300, the potential step and its duration are defined according to the potential control resolution (see the EC-Lab® software manual for more details). For the VMP, the minimum amplitude of the potential step is 100 µV and its minimum durations is 20 ms. Then the particular value for the scan rate is 300 mV/min (5 mV/s). Lower scan rates will be obtained with longer step duration whereas higher scan rates will be obtained with higher step amplitudes. If the user specifies a scan rate, the system proposes the closer value that can be obtained with adequate multiples of the potential and time resolutions (100 µV, 20 ms) or (100 µV, 10 ms).

In the present version of this application, the result file contains the mean value of the current measured for the whole potential step duration. This mean value is the result of measurements carried out every 2 ms.

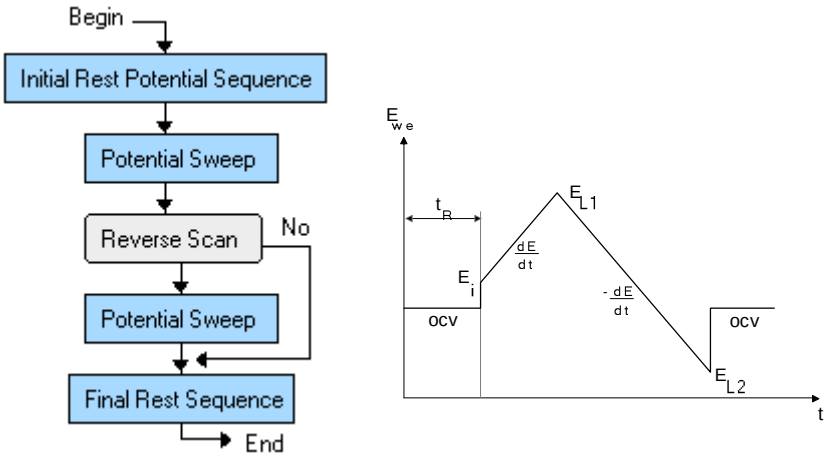


Fig. 126: General diagram of the Generalized Corrosion technique.

3.3.6.1 Description

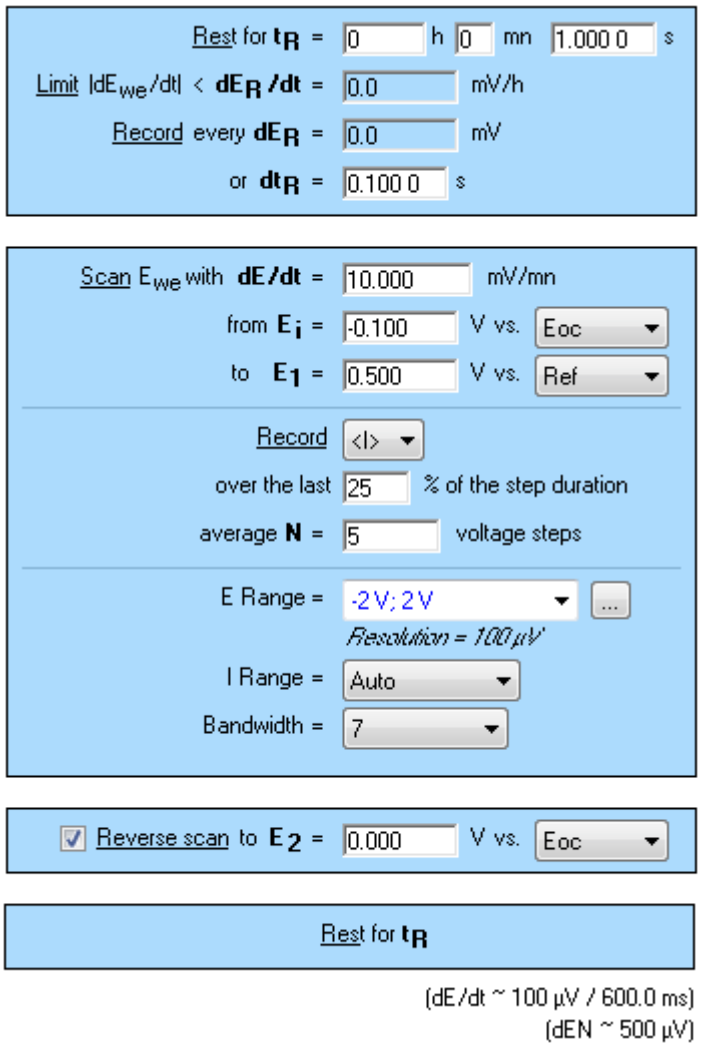


Fig. 127: Detailed diagram of the Generalized Corrosion technique.

- **First step: rest potential (or open circuit) sequence.**

Rest for t_R = ……. h …… mn …….. s
fixes a defined time duration t_R for recording the rest potential.

or until $|dE_{we}/dt| < dE_R/dt$ …… mV/h
gives the user the ability to shorten the open circuit period at the time when the decay of the potential is lower than a given value.

Record E_{we} with dE_R = …… mV resolution and at least every dt_R = …….. s
allows the user to record the working electrode potential whenever the change in the potential is ≥ dE_R or every dt_R time interval .
Data recording with dE_R resolution reduces the number of experimental points without loosing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded, but if there is a sharp peak in potential, the rate of the potential recording is governed by the potential recording resolution.

- **Second step: potential scan.**

Scan E_{we} with dE/dt ……. = mV/s

defines the potential scan. The software selects the smallest potential step according to the control potential resolution defined in the “Advanced settings” window (see the EC-Lab® software manual for more details).

From Ei = ……. V vs. Ref/Eoc/Ectrl/Emeas to E_1 = …… V vs. Ref/Eoc/Ei
from a potential E_i defined in absolute (vs. Ref the reference electrode potential) or versus a previous open circuit potential (E_{oc}), previous controlled potential (E_{ctrl}) or previous measured potential (E_{meas}) to E_1 vertex potential defined in absolute or versus E_{oc} or E_i.

Record <I> over the last …… % of the step duration averaged N = ……. voltage steps I every dI_p = …….. pA/nA/µA/mA/A or dt_p = …… s
two different recording conditions on the current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user’s manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……
defines the current range and bandwidth for the whole experiment. I Range is automatically set according to I_t and I_c values.

- **Third step: reverse scan**

□ Reverse scan with same scan rate, towards final limit E2 = ……. V vs. Ref/Eoc/Ei.
defines the reverse scan up to the final potential E_2. This potential can be defined in absolute or versus previous E_{oc} or E_i.

- **Fourth step: Rest**

Executes a rest potential period similar to the initial one. At the end, the working electrode is disconnected.

3.3.6.2 Process and fits related to GC

Like the LP, the GC application can be used for R_p and I_{corr} determination using the R_p Fit (see the EC-Lab® software manual for more details). It can also be used to determine the corrosion rate with the Tafel Fit (see the EC-Lab® software manual for more details).

3.3.7 CPP: Cyclic Potentiodynamic Polarization

The Cyclic Potentiodynamic Polarization is often used to evaluate pitting susceptibility. It is the most common electrochemical test for localized corrosion resistance. The potential is swept in a single cycle or slightly less than one cycle. The size of the hysteresis is examined along with the difference between the values of the starting open circuit corrosion potential and the return passivation potential. The existence of hysteresis is usually indicative of pitting, while the size of the loop is often related to the amount of pitting.
This application is based both on the MPP and MPSP techniques, except that the potentiodynamic phase is done before the potentiostatic one, some phases are optional and there is an additional potentiodynamic phase:

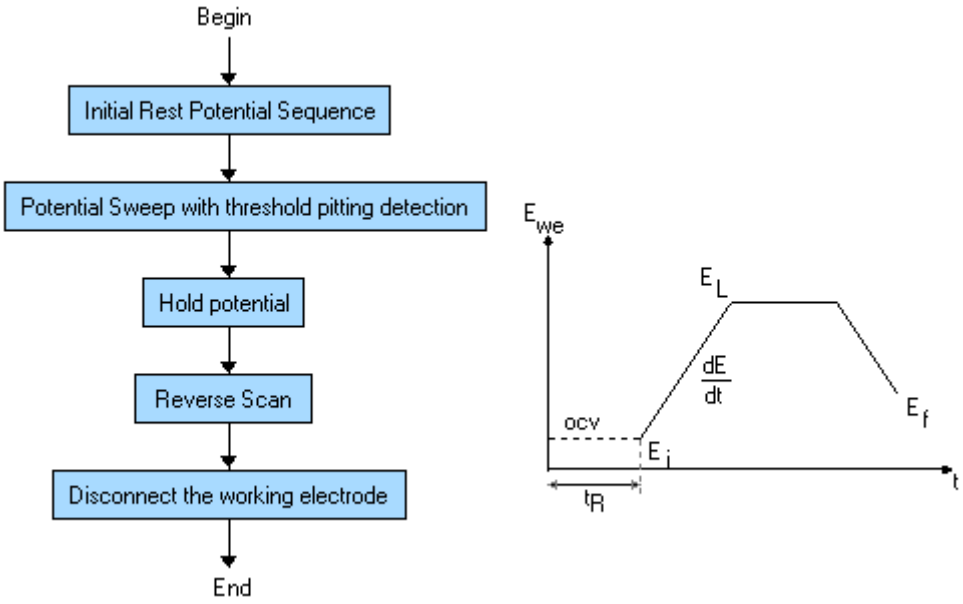


Fig. 128: CPP general diagram.

The detailed diagram is made of five blocks:

- Initial Rest Potential Sequence,
- Potential sweep with threshold pitting detection,
- Hold potential,
- Reverse scan.

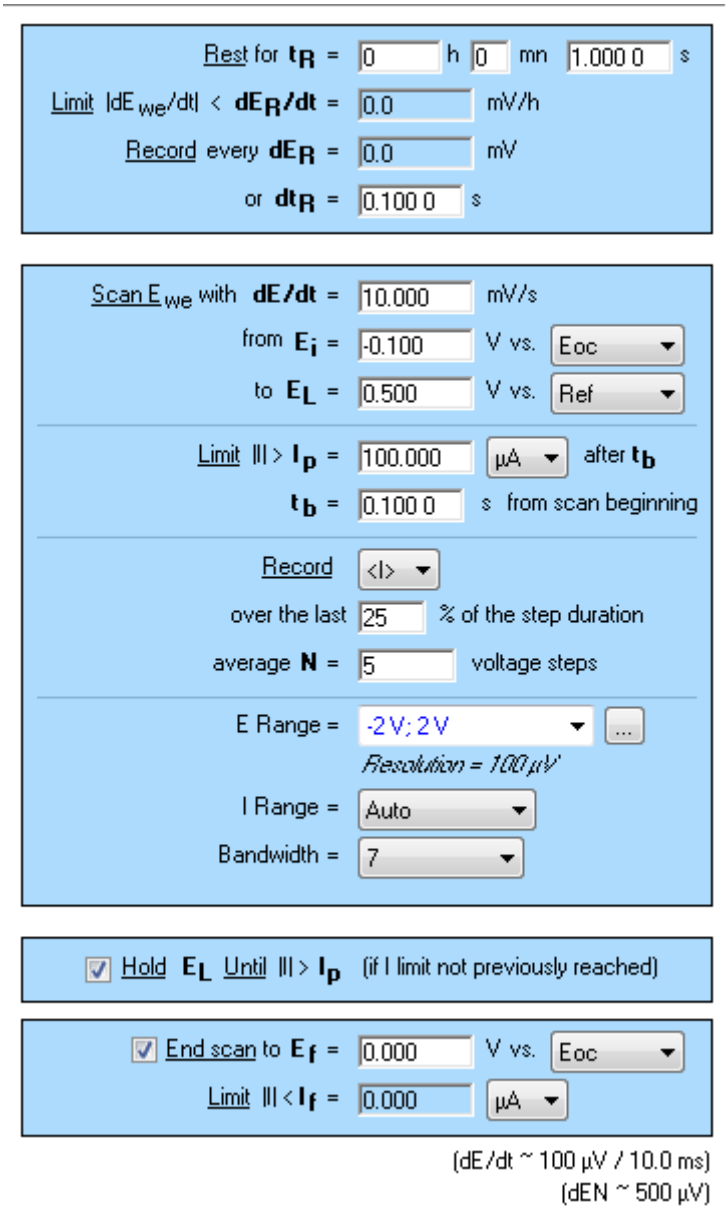


Fig. 129: CPP detailed diagram.

- **First step: rest potential (or open circuit) sequence.**

Rest for t_R = ……. h …… mn …….. s
fixes a defined time duration t_R for recording the rest potential.

or until $|dE_{we}/dt| < dE_R/dt$ …… mV/h
gives the user the ability to shorten the open circuit period at the time when the decay of the potential is lower than a given value.

Record E_{we} with dE_R = …… mV resolution and at least every dt_R = …….. s
allows the user to record the working electrode potential whenever the change in the potential is ≥ dE_R or every dt_R time interval .
Data recording with dE_R resolution reduces the number of experimental points without losing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded, but if there is a sharp peak in potential, the rate of the potential recording is governed by the potential recording resolution.

- **Second step: potential scan.**

Scan E_{we} with dE/dt ……. = mV/s
defines the potential scan. The software selects the smallest potential step according to the control potential resolution defined in the "Advanced settings" window (see the EC-Lab® software manual for more details).

From Ei = ……. V vs. Ref/Eoc/Ectrl/Emeas to E_1 = …… V vs. Ref/Eoc/Ei
from a potential E_i defined in absolute (vs. Ref the reference electrode potential) or versus a previous open circuit potential (E_{oc}), previous controlled potential (E_{ctrl}) or previous measured potential (E_{meas}) to E_1 vertex potential defined in absolute or versus E_{oc} or E_i.

Until |I| > I_P = pA/…/A, after t_b = s
fixes the threshold pitting current I_P to detect. Setting of a blanking time t_b permits to eliminate a possible large peak of current when just applying the initial potential step (in case of large ΔE_i value).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……
defines the current range and bandwidth for the entire experiment. I Range is automatically set according to I_t and I_c values.

Record <I> over the last …… % of the step duration averaged N = ……. voltage steps
I every dI_p = …….. pA/nA/µA/mA/A or dt_p = …… s
Two different recording conditions on the current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

- **Third step: Hold potential**

Hold E_L Until |I| > I_p
if the current limit has not been reached during the previous phase ($|I| \leq I_p$), then the final potential of the scan E_L is held until the current reaches the I_p limit.
If the current limit has been reached during the previous phase ($|I| > I_p$) then this block is skipped even if checked.

- **Fourth step: reverse scan**

Reverse scan towards E_f = V vs. Ref/Eoc/Ei
if checked then apply a potential scan from the current potential to E_f, that can be set to a fixed value (vs. Ref the reference electrode potential) or relatively to the previous potential E_i or E_{oc}.

or until |I| < I_f = pA/…/A
defines a current limit for the reverse scan. If $|I| < I_f$, then the scan is stopped before the E_L potential is reached. A zero value disables the test.

At the end, the working electrode is disconnected.

3.3.8 Dep. Pot.: Depassivation Potential

The Depassivation potential is the concatenation of the MPSP (without the |I| test) and MPP techniques (see figure below). First, the MPSP technique is used to depassivate the electrode metal while applying the appropriate potential. The MPSP technique can be considered as a pre-conditioning step where the electrode surface is cleaned. Secondly, the MPP technique is used to study the corrosion pitting.

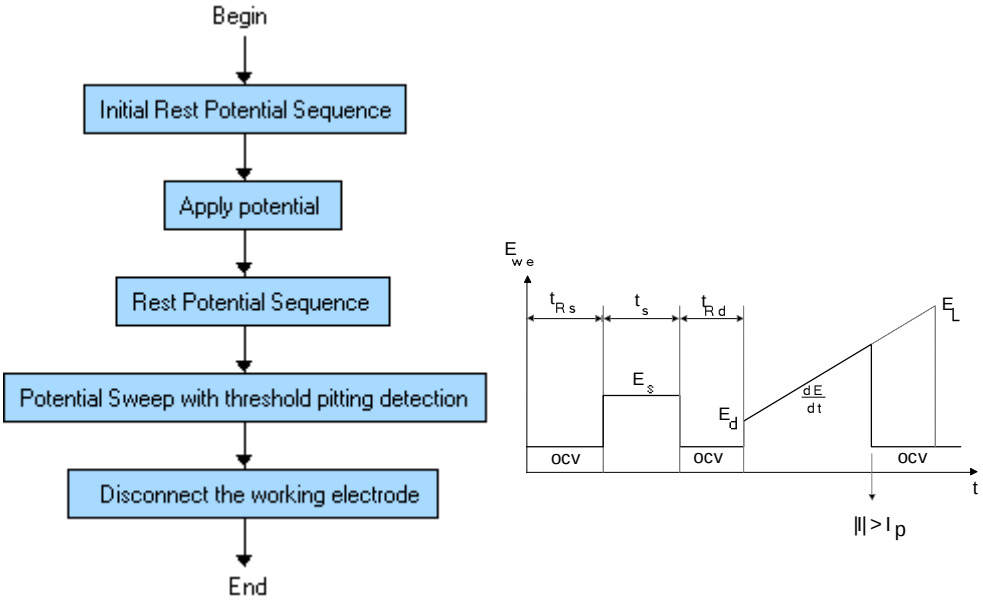


Fig. 130: General diagram of the Depassivation Potential application.

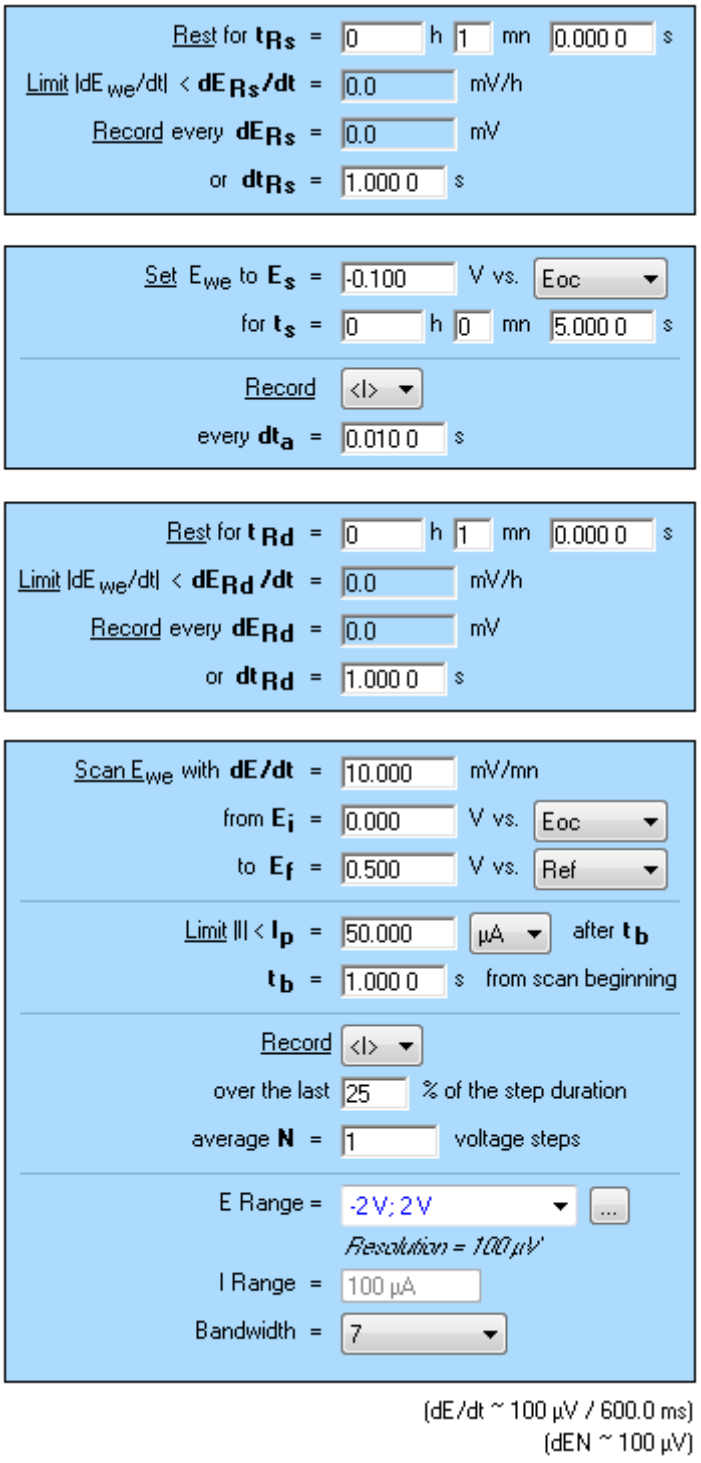


Fig. 131: Detailed diagram of the Depassivation Potential application.

- **First step: rest potential (or open circuit) sequence.**

Rest for t_R = ……. h …… mn …….. s
fixes a defined time duration t_R for recording the rest potential.

or until $|dE_{we}/dt| < dE_R/dt$ …… mV/h
gives the user the ability to shorten the open circuit period at the time when the decay of the potential is lower than a given value.

Record E_{we} with dE_R = …… mV resolution and at least every dt_R = …….. s
allows the user to record the working electrode potential whenever the change in the potential is $\geq dE_R$ or every dt_R time interval .
Data recording with dE_R resolution reduces the number of experimental points without loosing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded, but if there is a sharp peak in potential, the rate of the potential recording is governed by the potential recording resolution.

- **Second step: potentiostatic period with pitting limit for the current.**

Set Ewe = Es = ……. v vs. Ref/Eoc/Ectrl/Emeas for t_s = …….. h …….. mn ……. s
sets the potential directly (vs. Ref the reference electrode potential) or with respect to the final rest potential value E_{oc} or previous controlled potential (E_{ctrl}) or previous measured value (E_{meas}) for t_s duration.

Record • <I> every dt_a = ……. s.
• I every dI_p = …….. µA or dt_p = …… s
Two different recording conditions on a current are available with the potentiostatic mode: either recording an averaged current <I> on given time duration or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

Until |I| > I_P = …… pA/…/A, after t_b = …… s
fixes the threshold pitting current I_P to detect. Setting of a blanking time t_b eliminates a possible large peak of current when just applying the initial potential step (in case of large ΔU_i value).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …….; **bandwidth = …..**
The current range depends on the I_P value and is automatically fixed. The choice of the current range depends on the threshold pitting current value (I_P) and is automatically fixed. The bandwidth is selected by the user. The choice of the bandwidth is made by the user (see the EC-Lab® software manual).

Upon detection of the pitting limit in current, or if the time for the application of the potential has been reached, the working electrode is disconnected. In the case of a multi-pitting experiment the applied potential after the open circuit period will be the average potential of the working electrodes. These electrodes will be disconnected one by one as and when they reach their pitting current.

- **Third step: rest potential (or open circuit) sequence.**

See the first step for more details about the open circuit period

- **Fourth step: potential sweep with threshold pitting detection sequence.**

Scan E_{we} with dE/dt = mV/mn
Fixes the scan rate, dE/dt, in mV/mn. The software adjusts the potential step amplitude and its duration.

From Ei = ……. V vs. Ref/Eoc/Ectrl/Emeas to E_p = …… V vs. Ref/Eoc/Ei

from a potential E_i defined in absolute (vs. Ref the reference electrode potential) or versus a previous open circuit potential (E_{oc}), previous controlled potential (E_{ctrl}) or previous measured potential (E_{meas}) to E_p value defined in absolute or versus E_{oc} or E_i.

Record • <I> over the last …… % of the step duration averaged N = ……. voltage steps
• I every dI_p = …….. µA or dt_p = …… s

Two different recording conditions on current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

Until |I| > I_P = pA/…/A, after t_b = s

fixes the threshold pitting current I_P to detect. Setting of a blanking time t_b eliminates a possible large peak of current when just applying the initial potential step (in case of large ΔE_i value).

The cell is disconnected at the end of the experiment.

3.3.9 CPT: Critical Pitting Temperature

Available instruments with the CPT application

Instrument	*MPG*	*VMP*	*VMP2/Z*	*VMP3/ Z*	*BiStat/ Z*	*VS P*	*HCP-803*	*EPP 400/4000*	*SP-150*	*CLB-500*
4-20 mA		×								
-10, +10 V			×	×	×	×	×		×	×

The CPT technique can be performed by most of our instruments. The levels of automation in this technique are different according to the selected instrument. Historically designed for the VMP, the CPT technique was fully automated with a TCU (Temperature Control Unit) and any thermostatic bath controlled by a 4-20 mA analog input (Huber Ministat, Eurotherm 2408,…). This technique can be used with or without VMP boosters. It has been written originally to allow the VMP to perform the standard and extended ASTM G150 methods. It has been extended to the other instruments of our product range that are provided with – 10 to + 10 V analog inputs/output instead of the 4-20 mA of the VMP.

3.3.9.1 Differences in the CPT technique between the VMP and the other instruments

The following describes the main differences between the VMP and the other instruments of our range:

Features	VMP	Other
TCU	Yes	No
Multi corrosion cell	Yes	No
Master channel for temperature control	Yes	No
Analog input	Current 4-20 mA	Potential (–10 ;+10 V)
Temporization/synchronization	Yes	No

To use the CPT with the VMP3 or VSP, the user must have a temperature control unit equipped with potential analog inputs/outputs to receive the control in potential and to send the measured temperature to the instrument. We will give a detailed list of compatible TCU. Our instruments can be configured at the user's convenience to display and directly control the analog potentials as temperatures in the "External Device" configuration window.

3.3.9.2 MINISTAT Thermostat/Cryostat - circulating bath

Among the compatible TCU units on the market, most of them can be controlled with a 4-20 mA current. For example, The Ministat is a thermostatic bath with circulating fluid. It can be operated manually or under control of the VMP TCU unit. It reads and controls the temperature of the circulating liquid between -25°C and 120°C. It can be connected to several serially coupled jacketed electrochemical cells. The temperature of each individual cell is monitored by the TCU with a PT100 temperature sensor to provide accurate (± 0.15°C) temperature reading of the electrolyte inside the cell.

For the potential control, the compatible TCU unit with circulating fluid must be equipped with an analog card (not standard with the systems). Compatible units are:

- Julabo HL, SE, HE and SL series,
- Haake: Phoenix series,
- Neslab: EX series.

Fig. 132: Ministat Cryo/thermostat.

Fig. 133: PT 100 temperature sensor (∅ 7 mm – L 200 mm - cable 2 m).

The Ministat provides fast heating as well as cooling. Moreover, when the temperature rises above the requested temperature, the Ministat switches automatically to cooling to provide rapid stabilization at the requested temperature setting.
The Ministat provides a security temperature control (to be set manually) to prevent exceeding the requested level for any circumstance.
The Ministat has been selected for the first CPT application and its parameters are stored within the software (see next chapters), but if more cooling liquid volume is needed, one can provide a Cryo/thermostat with higher capacity. In the same way PT100 sensors can be provided with different diameter lengths and materials.

3.3.9.3 TCU: Temperature Control Unit (only for the VMP)

The TCU is designed as an interface between the VMP and the Ministat. The TCU generate a current signal that is calibrated for the temperature range of the Ministat (4 mA at - 25°C; 20 mA at 120°C). This same signal can also be used to setup thermostats other than the Ministat.
The TCU also provides the readings of the PT100 thermocouple sensor in each of the individual electrochemical cells. This data is then fed back into the proper VMP channel for further data processing. This is done by connecting the Auxiliary input/output connector from each VMP channel to the TCU input/output connector (seen in the picture below).

Fig. 134: VMP + TCU.

Connections

The TCU can control a thermostat per channel or grouped channels controlled by the same temperature controller as shown below:

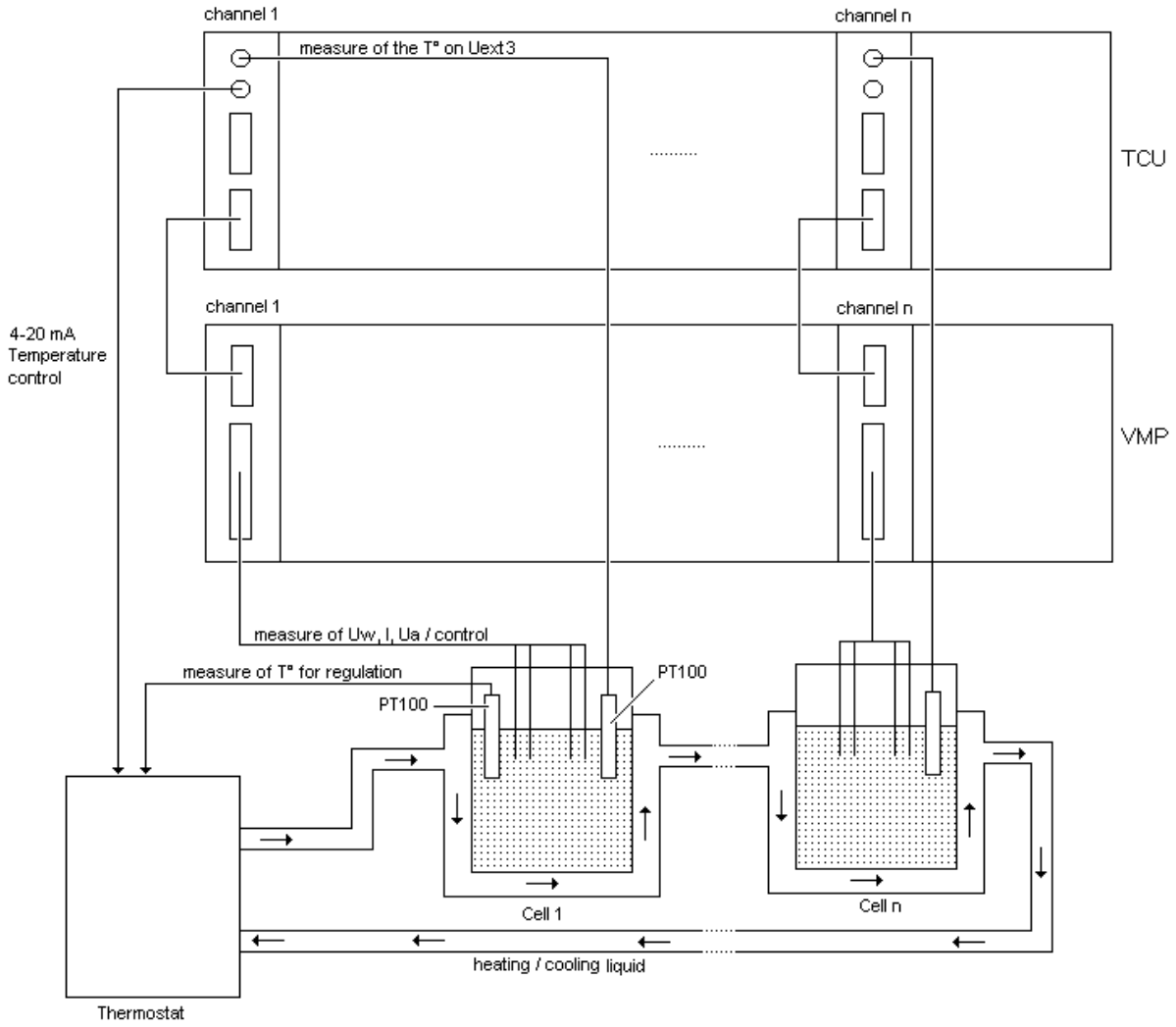


Fig. 135: Temperature control of several cells with a single thermostat.

3.3.9.4 CPT Technique

Before running any CPT experiment, one must first calibrate the temperature controls. Select **Config \ External Device (RDE…)** in the EC-Lab® main menu to load the next window:

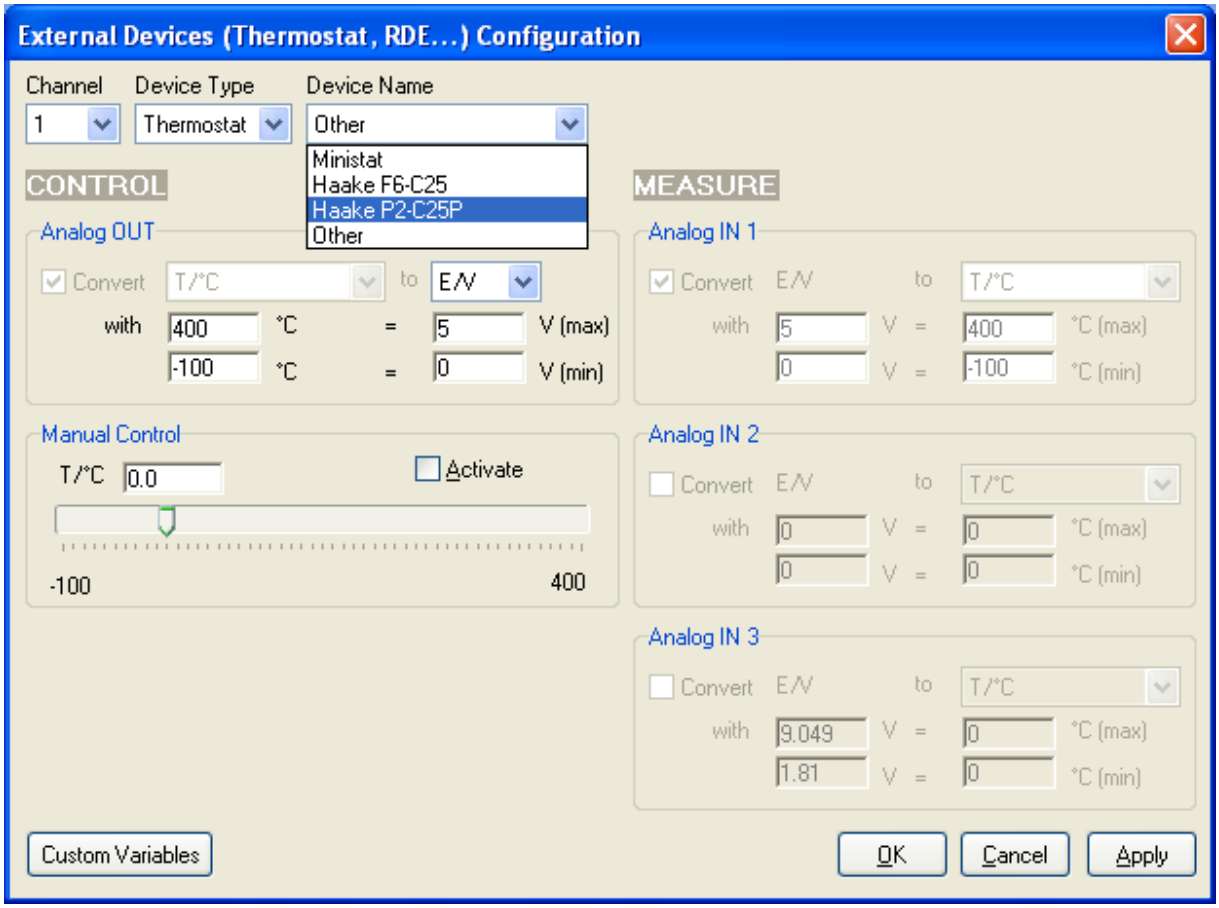


Fig. 136: Temperature configuration for the Ministat

First, select the channel to configure. In the Device Type, select "**Thermostat"** and the "**Device Name**" in the list. Either the standard supplied Ministat or an external thermostat can be selected. For the Ministat, the calibration parameters are factory set (4 mA at -25°C; 20 mA at 120°C). If external thermostats are used, the user needs to define the control calibration values (temperature range) corresponding to specific thermostat in use. Quite often (as with the Ministat and Eurotherm controllers), the temperature range can also be changed in the thermostat itself. Click on the **Apply** button to validate the settings.
Once this is done, the "Manual control" slidebar allows manual setting and activation of the temperature of the cell.
This menu can be activated without any TCU unit, but will only have effects for the VMP systems equipped with TCU unit.

Note: if the temperature is activated for a channel, all the experiments will record the temperature. This will be then possible to run the OCV and see the effects of manual changes of the temperature.
This menu can be used in the same way to control rotating electrode speed instead of temperature. In this case select **Device Type** = **RDE.** Then the Temperature / Rotating speed configuration window will allow the user to set manually the rotating speed. The "Wait" technique can be used to control the rotating speed in an experiment.

Once the thermostat has been configured, the CPT experiment can be loaded for a given channel the same way as the other experiments (the CPT technique is located into the Corrosion section of the EC-Lab® techniques). The next figures show the CPT diagram:

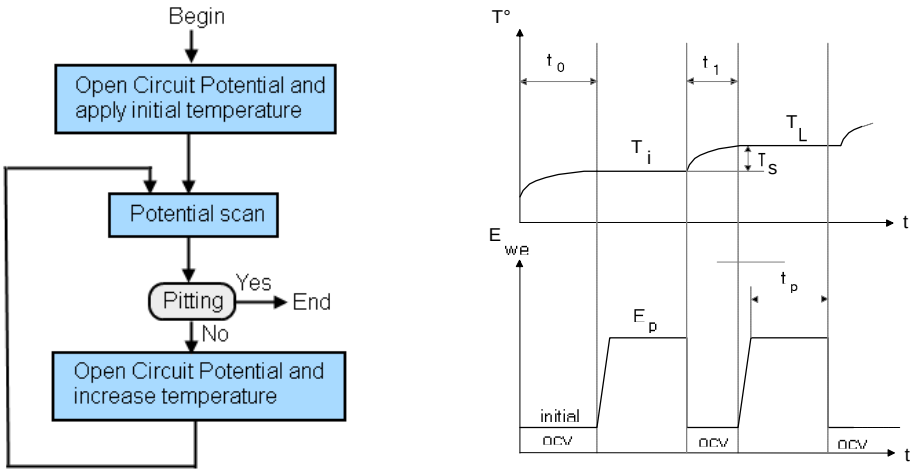


Fig. 137: General diagram of the CPT technique.

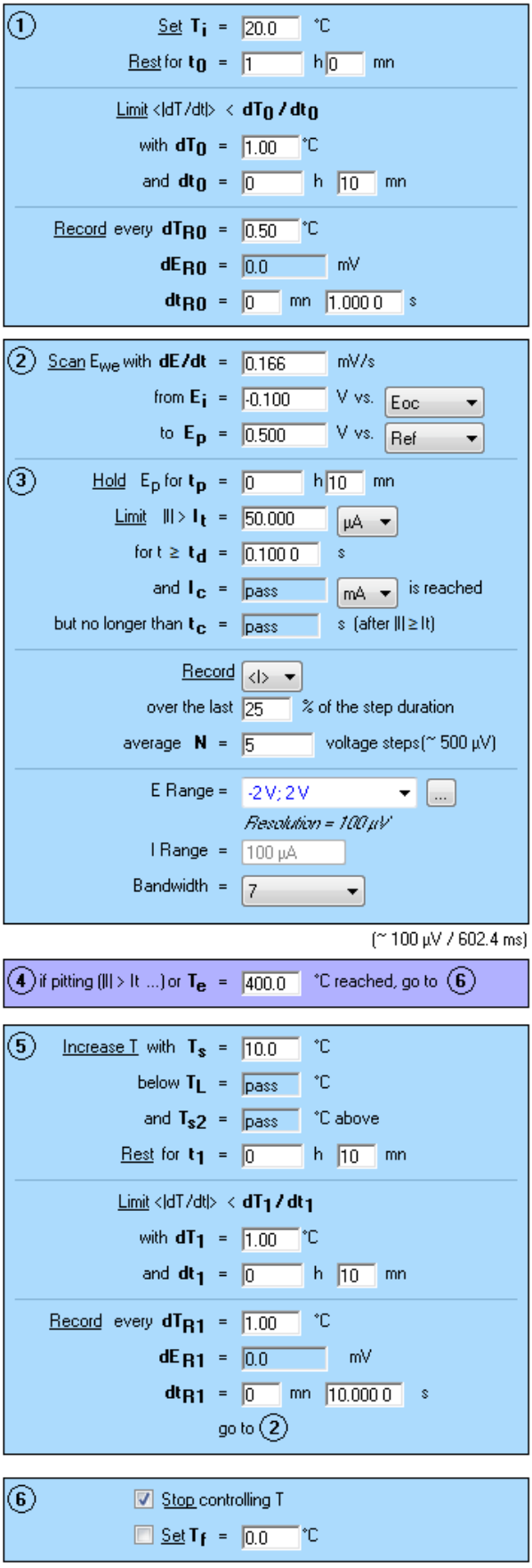


Fig. 138: Detailed diagram of the CPT technique.

The whole sequence can be described with the following figure:

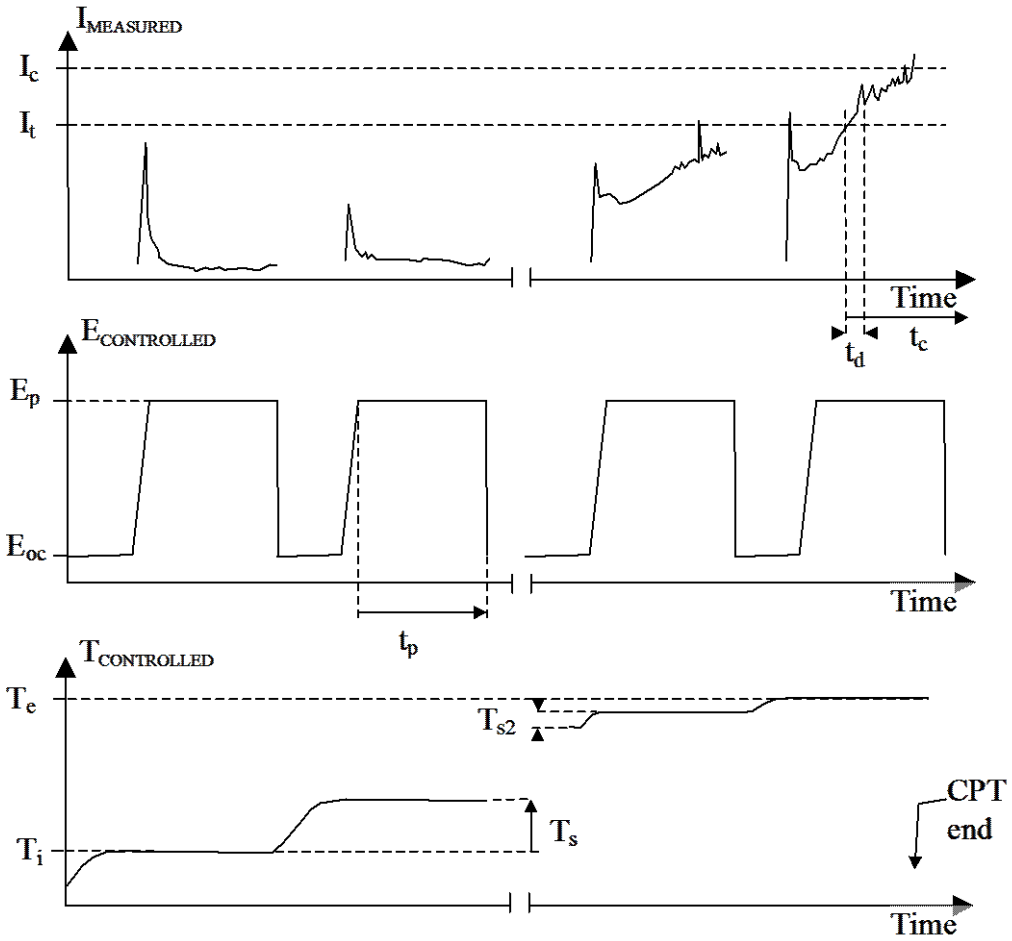


Fig. 139: I, E_{we} and T vs. time for the CPT experiment.

- **First step: set the initial temperature and turn to rest.**

Set T_i = …….. °C
sets the temperature T_i.

Rest Until <|dT/dt|> < dT_0 = …… °C / dt_0 = ….. h ….. mn or for t_0 = …… h ….. mn
turns to rest until the temperature is stabilized or during t_0 time. The first limit reached stops the rest period. A 0 value devalidates a limit. If $dT_0 = 0$ or $dt_0 = 0$ then the rest duration will be t_0. If only t_0 is null, the rest period will continue until the temperature is stabilized under dT_0/dt_0 limit. And if both dT_0/dt_0 and t_0 are null the rest is skipped (but the temperature is also set to T_i value).

Record every dT_{R0} = …… °C, dE_{R0} = ……. mV and dt_{R0} = ……. mn …… s.
records on temperature (dT_{R0}), potential (dE_{R0}) and time (dt_{R0}) resolutions. The first condition reached defines a recording. A zero value disables a recording condition.

- **Second step: potential scan.**

Scan E_{we} with dE/dt ……. = mV/s
Defines the potential scan. The software selects the smallest potential step according to the control potential resolution defined in the “Advanced settings” window (see the EC-Lab® software manual for more details).

From Ei = ……. V vs. Ref/Eoc/Ectrl/Emeas to E_p = …… V vs. Ref/Eoc/Ei
from a potential E_i defined in absolute (vs. Ref the reference electrode potential) or versus a previous open circuit potential (E_{oc}), previous controlled potential (E_{ctrl}) or previous measured potential (E_{meas}) to E_p value difined in absolute or versus E_{oc} or E_i.

Hold E_p for t_p = …… h …….. mn or until |I| > I_t = ……. mA for t ≥ t_d = …… s
And I_c = …… mA reached, but no longer than t_c …… = s (after |I| > I_t)
Hold the potential to E_p for t_p time or until the critical pitting condition is reached.
The condition is first defined by I_t and t_d: If the current remains higher than the preset value I_t during the time t_d, than the CPT is reached. If it doesn't, this condition can (but does not have to =pass) be followed by a second condition, set by I_c and t_c: If the current continues to rise and reaches the value of I_c within a time t_c (t_c includes t_d so must be >t_d) then again the condition for pitting is reached. Fig. 139 illustrate these conditions.

Record <I> over the last …… % of the step duration averaged N = ……. voltage steps
I every dI_p = …….. µA or dt_p = …… s
Two different recording conditions on a current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……
Defines the current range and bandwidth for the whole experiment. I Range is automatically set according to I_t and I_c values.

Pitting (|I| > I_t for t ≥ t_d …) or T_e = …… °C reached
☑ Stop Controlling T
☐ Set T_f …… °C
If pitting or temperature T_e is reached then it stops controlling temperature (TCU control = 0 mA) or applies a final temperature T_f and stops the experiment.
Otherwise, go to the third step.

- **Third step: increase temperature and turn to rest.**

Increase T with T_s = ….. °C below T_L = …… °C and T_{s2} = …… °C above
Increases the temperature with Ts or Ts2 according to the TL value. This allows for bigger steps in temperature with each cycle that pitting is not reached in order to speed up the experiment's total duration.

Rest Until <|dT/dt|> < dT_1 = …… °C / dt_1 = ….. h ….. mn or for t_1 = …… h …… mn
rest parameters (see first step).

Record every dT_{R1} = …… °C, dE_{R1} = …… mV and dt_{R1} = …… mn …… s.
IF dT_1, dt_1 and t_1 are set to 0, than the rest will not be executed (but the temperature will be increased) and the experiment will restart at the second step without the potential scan. This means that the potential E_P will be applied continuously for the rest of the duration of the pitting experiment.

3.3.9.5 CPT2 technique

The CPT2 technique is exclusively reserved to the VMP. Before running any CPT2 experiment, one must first calibrate the temperature controls. Select **Config | Temperature |**

Rotating electrodes... in the EC-Lab® main menu to load the next window. Report to the CPT technique for more information.

Once the thermostat has been configured, the CPT2 experiment can be loaded for a given channel in the same way as the other experiments (the CPT2 technique is located in the Corrosion section of the EC-Lab® techniques). The next figure shows the CPT2 diagram:

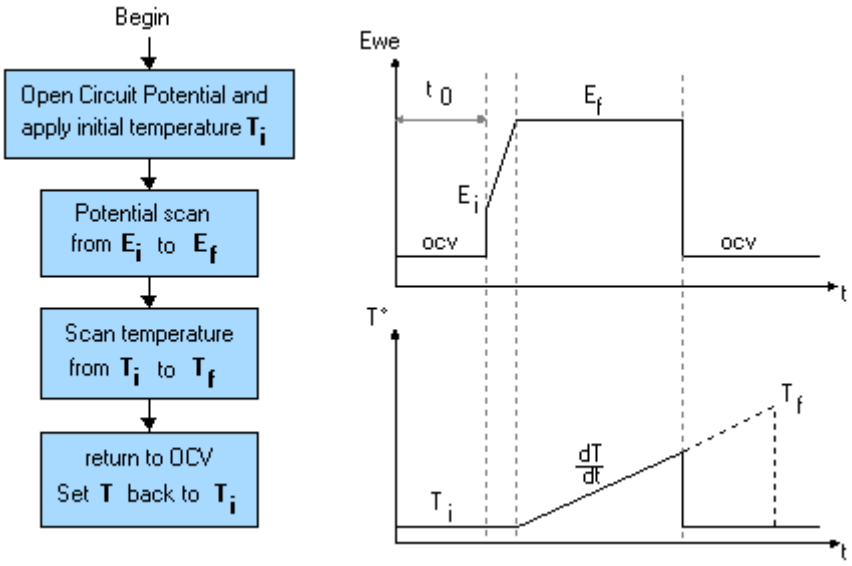


Fig. 140: General diagram of the CPT2 technique.

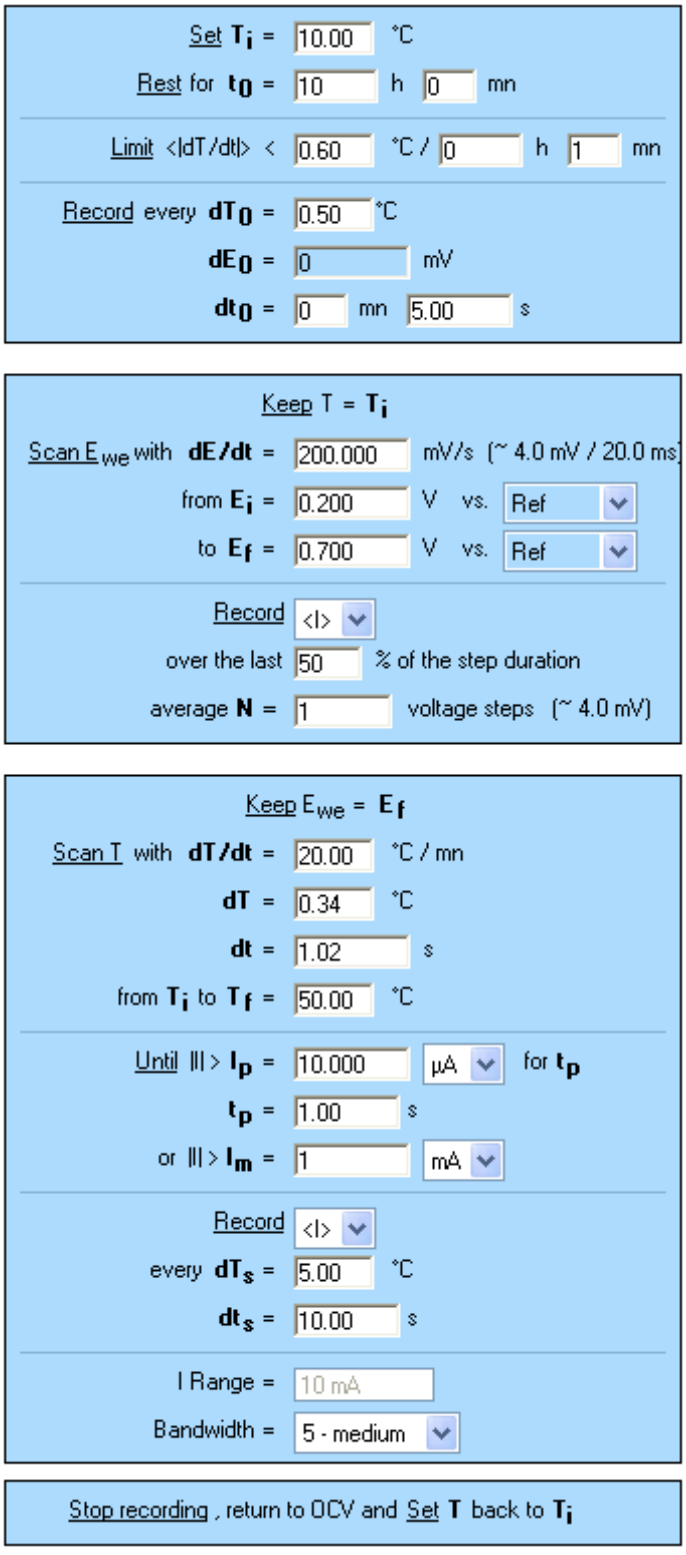


Fig. 141: Detailed diagram of the CPT2 technique.

The whole sequence can be described with the following figure:

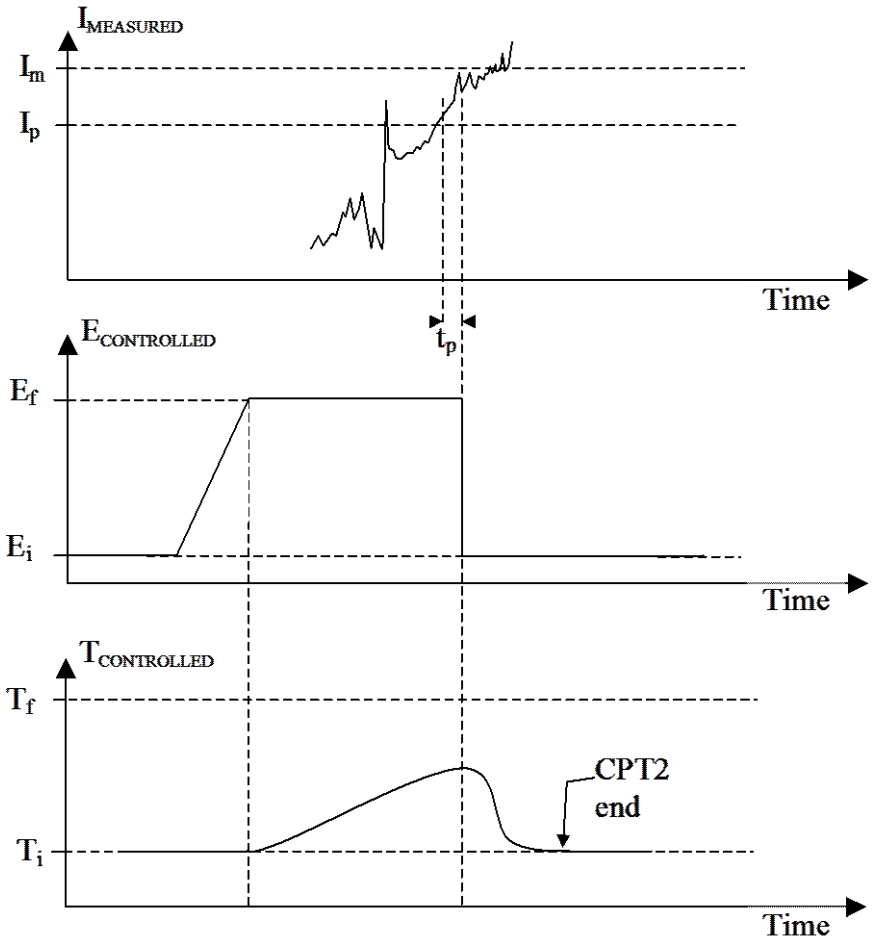


Fig. 142: I, E_{we} and T vs. time for the CPT2 experiment.

- **First step: set the initial temperature and turn to rest.**

The initial temperature block is identical to the CPT initial temperature block, so report to the CPT technique chapter for more information.

- **Second step: potential scan.**

Keep T = Ti
during this step, the temperature is maintained to the value defined in the first step.

Scan E_{we} with dE/dt = mV/s
fixes the scan rate, dE/dt, in mV/s. The software automatically adjusts the step amplitude and its duration. The potential and the time step values are multiples of 100 µV and 20 ms respectively. The minimum 100 µV step amplitude and 20 ms potential level duration gives a 5 mV/s scan rate.

From Ei = ……. V vs. Ref/Eoc/Ectrl/Emeas to E_p = …… V vs. Ref/Eoc/Ei
from a potential E_i defined in absolute (vs. Ref the reference electrode potential) or versus a previous open circuit potential (E_{oc}), previous controlled potential (E_{ctrl}) or previous measured potential (E_{meas}) to E_p value defined in absolute or versus E_{oc} or E_i.

Record • <I> over the last …… % of the step duration averaged N = ……. voltage steps
• I every dI_p = …….. µA or dt_p = …… s

two different recording conditions on the current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

- **Third step : temperature scan.**

Keep $E_{we} = E_F$
during this step, the potential is kept to E_F.

Scan T with dT/dt = ……. °C/mn, with …… °C/ …… s
fixes the scan rate, dT/dt, in °C/mn or at the user's convenience with the choice of the temperature increment (in °C) and step duration (in s). Default choice of the system proposes a scan rate as close as possible as the requested one and obtained with the smallest possible step amplitude. The temperature and the time step values are multiples of 0.01°C and 20 ms respectively. Due to the TCU, the minimum time value is 1 s.

from T_i to T_f = ……. °C
fixes the final temperature scan value T_f.

Or until |I| > I_P = …….. µA for t_P = …….. s or |I| > I_m = ……. mA
fixes the threshold pitting current I_P (during t_P) or I_m to detect.

Record • <I> over the last …… % of the step duration averaged N = ……. voltage steps
• I every dI_p = …….. µA or dt_p = …… s
two different recording conditions on the current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

I Range = …….. bandwidth = …….
The current range depends on I_P and I_m values and is automatically fixed.
The choice of the bandwidth is made by the user (see the EC-Lab® software manual).

Once the threshold pitting current or the maximum temperature value is reached, the working electrode is disconnected. Afterwards the temperature is set back to the initial temperature **T_i**.

Lock the CPT2 technique:

Parameters of the CPT2 technique can be locked to prevent any user modification. To proceed, one must create the CPT2 setting file *"CPT2_lock.mps"* in the same directory as the EC-Lab® software.

If the file *"CPT2_lock.mps"* does not exist, save your own set of CPT2 parameters into the file *"CPT2_lock.mps"* (button **Save Set**) in the same directory than EC-Lab®.
Then, the CPT2 technique will be locked when the next program starts.

To unlock the CPT2 technique, move or rename the *"CPT2_lock.mps"*, stop and restart EC-Lab® (this can be useful to modify the *"CPT2_lock.mps"* file, else the **Load Set** button is disabled).

3.3.10 MPP: Multielectrode Potentiodynamic Pitting

Pitting corrosion occurs when discrete areas of a material undergo rapid attack while the vast majority of the surface remains virtually unaffected. The basic requirement for pitting is the

existence of a passive state for the material in the environment of interest. Pitting of a given material depends strongly upon the presence of an aggressive species in the environment and a sufficiently oxidizing potential. This technique is designed to study pitting corrosion on one or several electrodes together in the electrochemical cell. This technique corresponds to the pitting potential determination of a material, using a potential sweep.

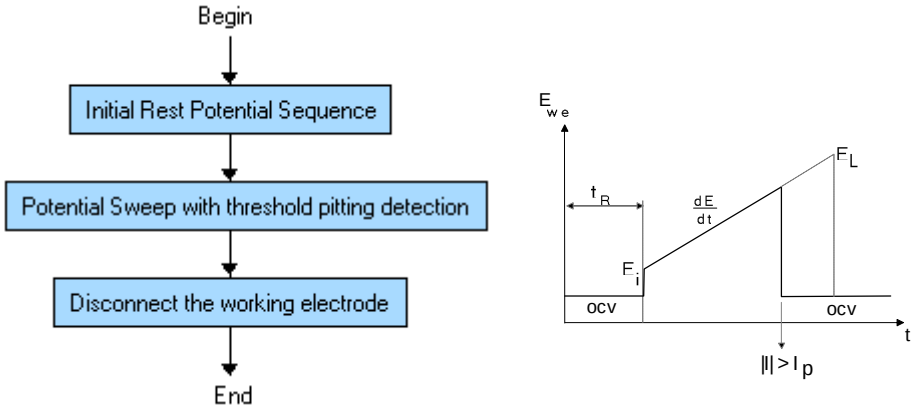


Fig. 143: General diagram of the Potentiodynamic Pitting technique.

First, there is an open circuit sequence with recording of the working electrode potential for a given time or until its variation vs. time is lower than a given limit.

Then, the instrument applies a potential sweep starting either from the potential reached at the end of the open circuit sequence plus a possible offset, or from a given value. The potential sweep goes on until its limit or until the current reaches a value defined as the limit pitting current, then the working electrode is disconnected.

For multi-pitting, i.e. if the same technique is applied on several channels in parallel, the open circuit potential taken into account for applying the initial potential will be the average open circuit potential of the working electrodes. The technique stops independently on each channel and the corresponding electrode is disconnected, as soon as the pitting limit value of the current is reached on the channel.

The EC-Lab® software uses a particular "Process Data" function, **Multi-Pitting Statistics**, which gives the mean values and the mean quadratic deviations of the final rest potentials and pitting potentials obtained from all the channels used in the experiment.

3.3.10.1 Description

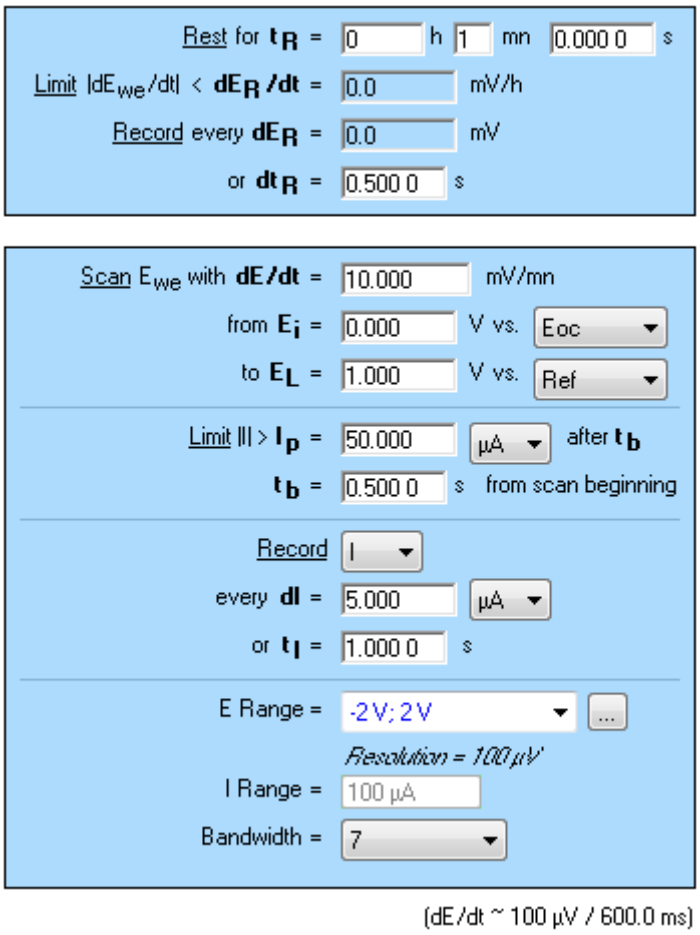


Fig. 144: Detailed diagram of the Potentiodynamic Pitting technique.

- **First step: a rest potential (or open circuit) sequence.**

Rest for t_R = ……. h …… mn …….. s
fixes a defined time duration t_R for recording the rest potential.

or until $|dE_{we}/dt| < dE_R/dt$ …… mV/h
gives the user the ability to shorten the open circuit period at the time when the decay of the potential is lower than a given value.

Record E_{we} with dE_R = …… mV resolution and at least every dt_R = …….. s
allows the user to record the working electrode potential whenever the change in the potential is ≥ dE_R or every dt_R time interval .
Data recording with dE_R resolution reduces the number of experimental points without loosing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded, but if there is a sharp peak in potential, the rate of the potential recording is governed by the potential recording resolution.

- **Second step: potential sweep with threshold pitting detection sequence.**

Scan E_{we} with dE/dt = mV/mn
fixes the scan rate, dE/dt, in mV/mn. The software adjusts the potential step amplitude and its duration..

From Ei = ……. V vs. Ref/Eoc/Ectrl/Emeas to E_p = …… V vs. Ref/Eoc/Ei
from a potential E_i defined in absolute (vs. Ref the reference electrode potential) or versus a previous open circuit potential (E_{oc}), previous controlled potential (E_{ctrl}) or previous measured potential (E_{meas}) to E_p value defined in absolute or versus E_{oc} or E_i.

Record • <I> over the last …… % of the step duration averaged N = ……. voltage steps
• I every dI_p = …….. µA or dt_p = …… s
Two different recording conditions on the current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

Until |I| > I_P = pA/…/A, after t_b = s
fixes the threshold pitting current I_P to detect. Setting of a blanking time t_b eliminates a possible large peak of current when just applying the initial potential step (in case of large ΔE_i value).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …….. , Bandwidth = ……
The choice of the current range depends on the threshold pitting current value (I_P) and is automatically fixed. The bandwidth is selected by the user.

Once the threshold pitting current is reached, the working electrode is disconnected.

The figure below (Fig. 145) shows the result of a potentiodynamic multi-pitting experiment performed on 8 passivated stainless steel electrodes.

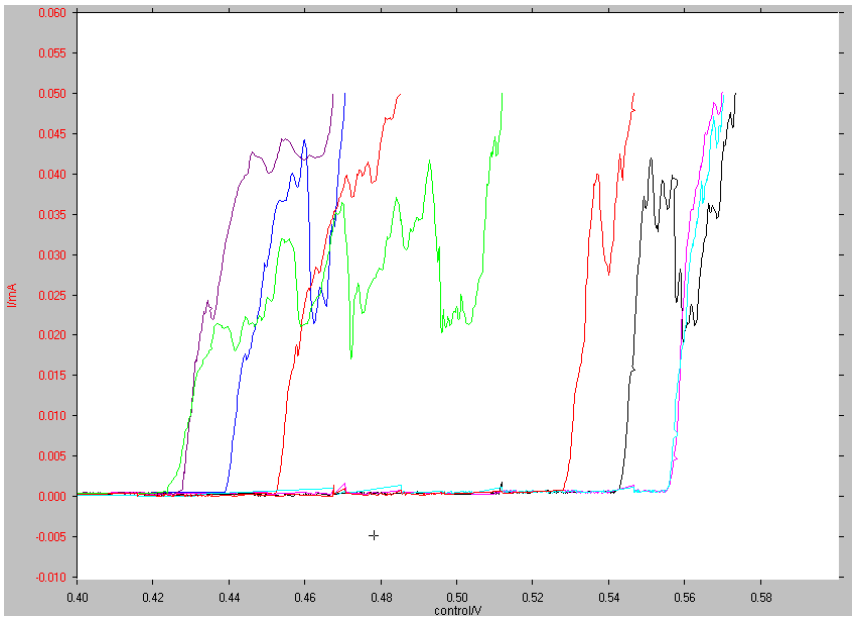


Fig. 145: 8 electrodes Potentiodynamic Pitting experiment. Electrode: Stainless steel in 0.02 M NaCl. Scan rate: 100 mV/mn. Recording resolution: 0.2 µA or 20 ms.

3.3.10.2 Data processing

Data processing using **Multi-Pitting Statistics** gives the mean values <E> and the mean quadratic deviations σ of the final rest potentials (E_{oc}) and pitting potentials (E_p) obtained from all the channels used in the experiment. Note that the E_p value corresponds to the potential measured for $I = I_p$.

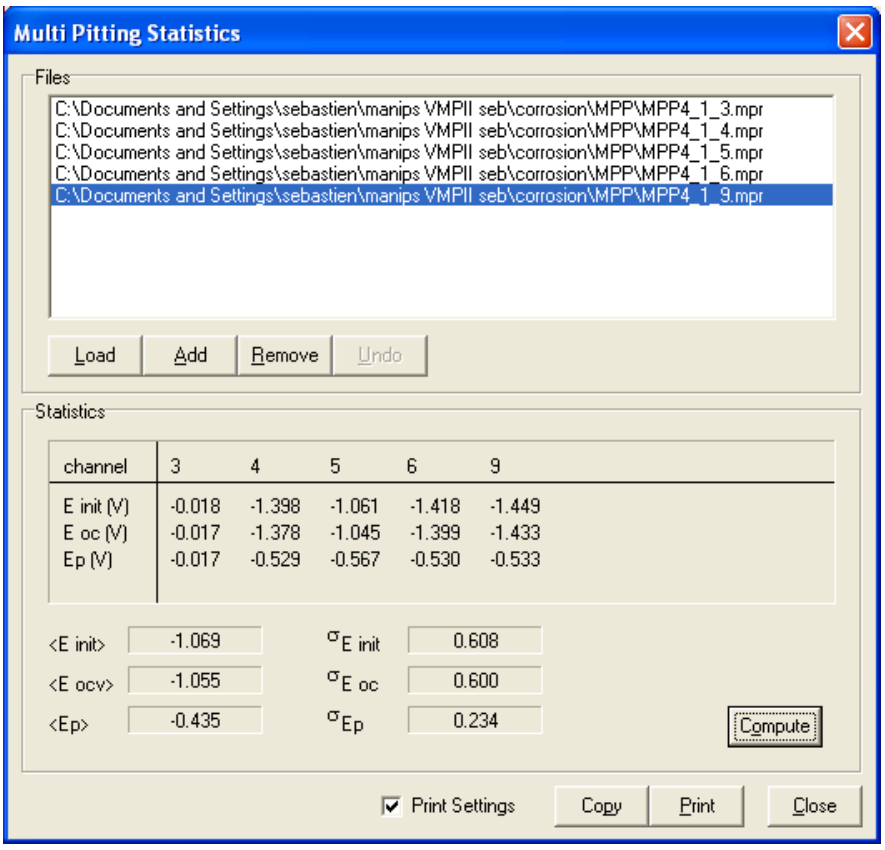


Fig. 146: Multi pitting statistics window.

Report to the multipitting statistics process for more details (in the EC-Lab® software manual).

3.3.11 MPSP: Multielectrode Potentiostatic Pitting

Pitting corrosion occurs when discrete areas of a material undergo rapid attack while the vast majority of the surface remains virtually unaffected.
The MPSP technique corresponds to studying pitting occurrence under applied constant potential. This technique is especially designed to study pitting on several electrodes in the same electrochemical cell.
First, there is an open circuit sequence where the working electrode potential is recorded for a given time or until its time variation is lower than a defined limit.
Then, the system applies a constant potential, which can be the potential value reached at the end of the open circuit period plus a given potential offset, or a defined value, until the current reaches a value defined as the pitting current. At the end of the technique, the working electrode is disconnected.

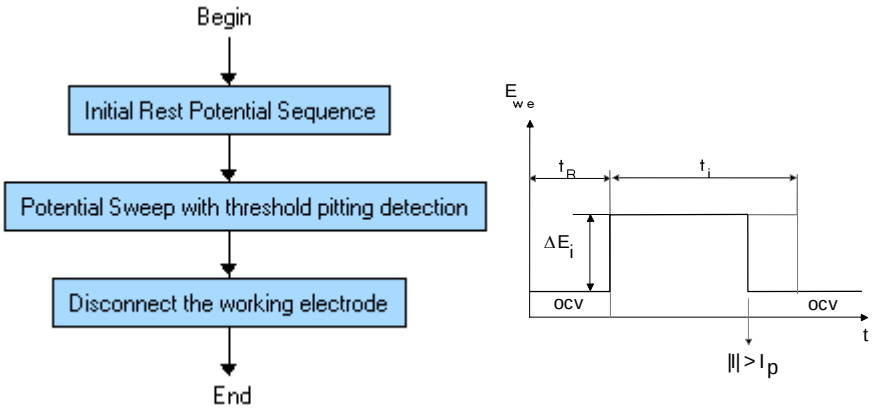


Fig. 147: General diagram of the Potentiostatic Pitting application.

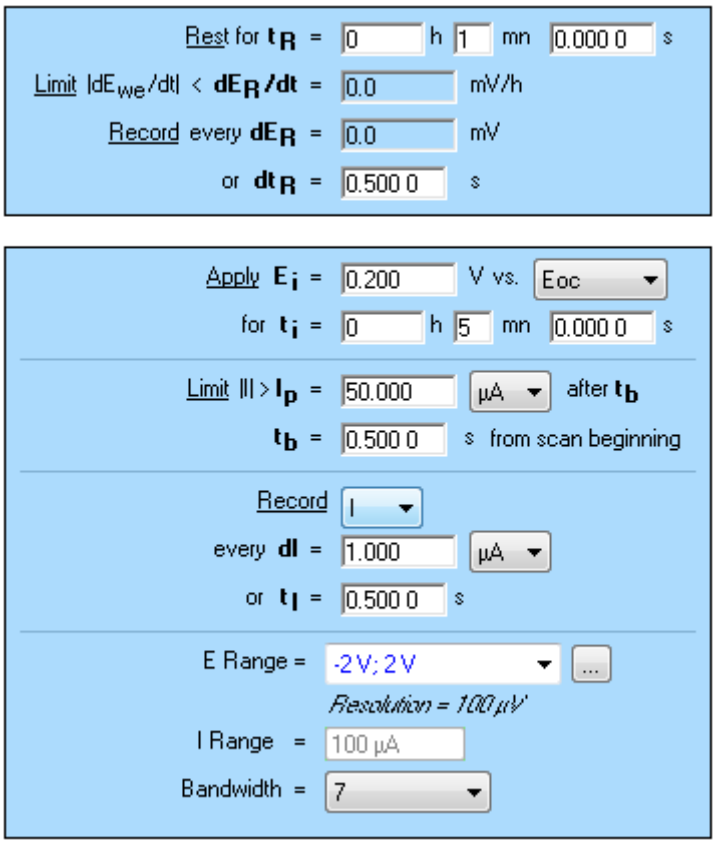


Fig. 148: Detailed diagram of the Potentiostatic Pitting application.

- **First step: "standard" open circuit sequence**

previously described, with conditional duration and choice of recording resolution.

- **Second step: potentiostatic period with pitting limit for the current.**

Apply E_i = ……. v vs. Ref/Eoc/Ectrl/Emeas during t_i = …….. h …….. mn ……. s
sets the potential directly (vs. Ref the reference electrode potential) or with respect to the final rest potential value E_{oc} or previous controlled potential (E_{ctrl}) or previous measured value (E_{meas}) for t_i duration.

Record • <I> every dt_a = ……. s.

- **I every dI_p = …….. µA or dt_p = …… s**

Two different recording conditions on the current are available with the potentiostatic mode: either recording an averaged current <I> on given time duration or recording an instantaneous current I with a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ).

Until |I| > I_P = …… pA/…/A, after t_b = …… s
fixes the threshold pitting current I_P to detect. Setting of a blanking time t_b eliminates a possible large peak of current when just applying the initial potential step (in case of large ΔU_i value).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …….; **bandwidth = ……..**
the current range depends on the I_P value and is automatically fixed.
The user makes the choice of the bandwidth.
Upon detection of the pitting limit in current, or if the time for application of the potential has been reached, the working electrode is disconnected. In the case of multi-pitting experiment, the applied potential after the open circuit period will be the average potential of the working electrodes. These electrodes will be disconnected one by one as and when they reach their pitting current.

Data processing

No data processing is available with the MPSP application.

3.3.12 ZRA: Zero Resistance Ammeter

The Zero Resistance Ammeter is an application for the measurement of galvanic coupling current of dissimilar metals. It is also made to perform some types of electrochemical noise measurement. It consists of applying zero volts between the working electrode (WE) and the counter electrode (CE) and then measuring the current and the potentials (E_{we}, E_{ce}) versus the reference electrode (REF). In most of the cases, the coupling current is measured between two identical electrodes. In real situations, the electrodes are slightly different resulting in anodic behavior for one of them and cathodic behavior for the other one.

The potential is controlled in this application between Ref1 and Ref3 in the standard connection mode. The first metal must be connected to Ref1+CA2 leads, and the other metal must be connected to Ref3+CA1 leads. Ref2 is connected to the reference electrode. It could be necessary to connect the ground lead if the signal is noisy.

Note 1: for the VMP, this technique is not available for channel board versions C0247XX03U_WC and C0247XX03W_GND (1997-1998 delivery).

Note 2: for the ZRA technique the recording of E_{ce} (vs. E_{ref}) is forced into the data file.

The ZRA technique is made of 4 blocks:

- Initial OCV,
- ZRA,
- OCV,
- Repeat.

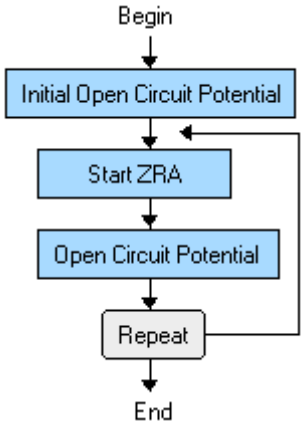


Fig. 149: ZRA general diagram.

They are detailed below:

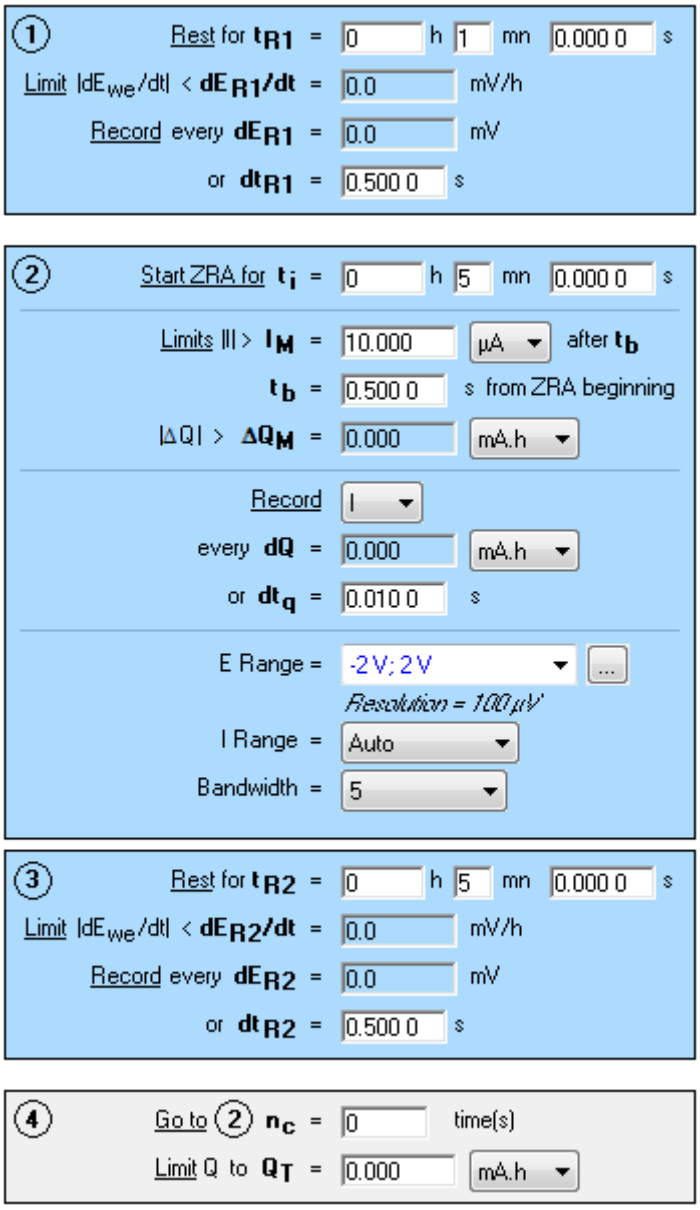


Fig. 150: ZRA detailed diagram.

- **Initial OCV**

The open circuit voltage is the standard block, so report to the OCV technique chapter for more information.

- **ZRA**

Start ZRA for t_i = …… h …….. mn ……. s
applies 0 V between the working electrode (WE) and the counter electrode (CE) for t_i time.

or until |I| > I_M = …… pA/…/A, after t_b = ……. s
limits the ZRA duration if the current becomes greater than I_M. This test is performed only t_b seconds after the beginning of the ZRA block to avoid exiting on the current perturbation that may occur when the 0 V potential is established.

Record <I> and Q every dQ = …….. mA.h and at least every dt_q = …… s
defines the recording conditions on the charge and time. Each one of these parameters can be entered simultaneously, but the first condition reached decides the recording. A zero value cancels the recording condition.

Limit |ΔQ| to ΔQ_M = …… mA.h
limits the charge per n_c loop to ΔQ_M. Setting ΔQ_M to 0 cancels the test.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… Bandwidth = ……
sets I range and bandwidth for the whole experiment.

- **OCV**

The open circuit voltage is the standard block, so report to the OCV technique chapter for more information.

- **Repeat**

Repeat n_c = ……. time(s)
repeats the ZRA and the OCV blocks n_c times. If n_c is set to 0 then these blocks will be done only once, n_c = 1 will execute the blocks twice....

Limit Q to Q_T = ……. mA.h
limits the total charge from the beginning of the experiment to Q_T. Setting Q_T to 0 cancel the test.

3.3.13 ZVC: Zero Voltage Current

The ZVC technique is the same as the ZRA technique except that the control (apply 0 V) is done between the working electrode (WE) and the reference electrode (REF) rather than between the working electrode (WE) and the counter electrode (CE).
Therefore report to the ZRA for more details on the ZVC technique.

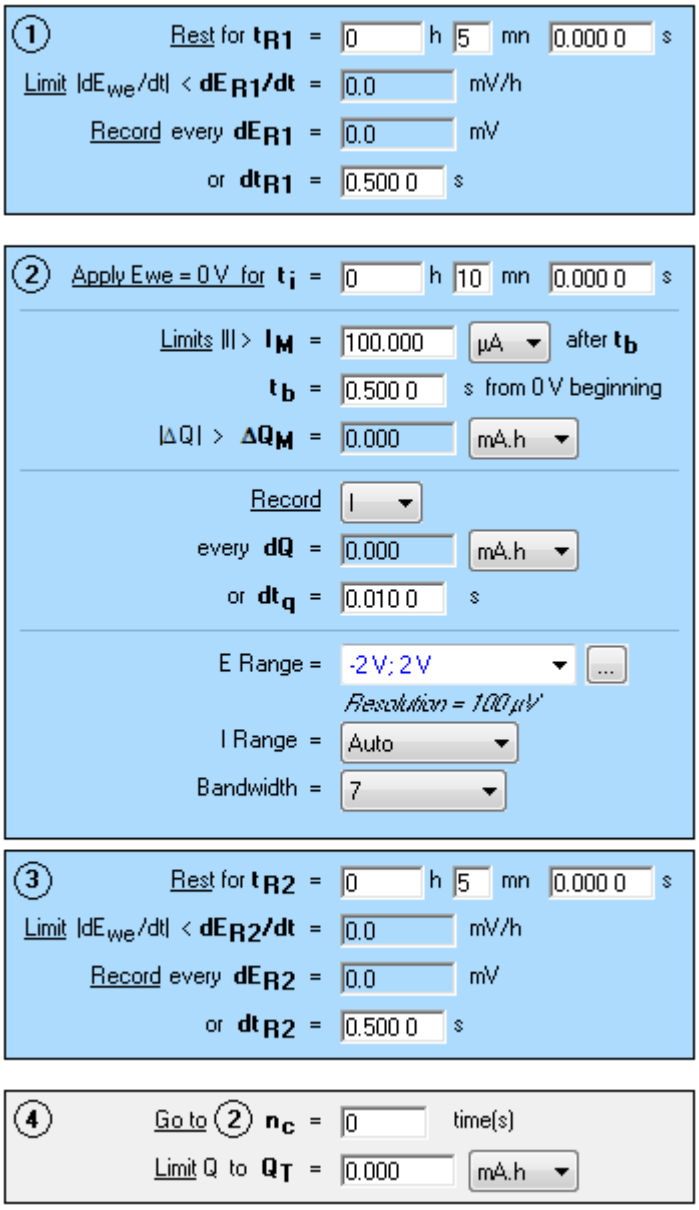


Fig. 151: ZVC detailed diagram.

3.4 Custom Applications

3.4.1 MUIC: Measurement of U-I Correlations

This technique is an example of a special application tailor-made for one of our customers.
It records the potential fluctuations of a working electrode *vs*. a reference electrode at the same time as the random current between the working electrode and the counter electrode which are connected through a low value resistor acting as the measurement shunt resistor.
Analysis of the correlation functions between E_{we} and I gives information on the type of corrosion attack. This technique takes advantage of synchronous measurement of E_{we} and I using the two ADC lines.

Operating this technique requires a specific VMP to cell cable, with the shunt resistance being placed at the cell connection.

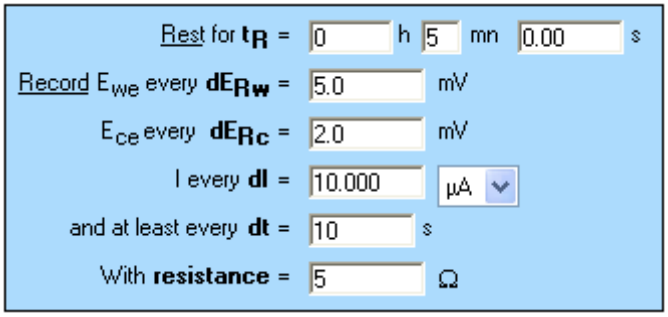


Fig. 152: Detailed diagram for U-I correlation measurement.

3.4.2 PR: Polarization Resistance

The polarization resistance can be used in several electrochemical techniques such as corrosion monitoring or general electrochemistry. This technique makes measurement of the polarization resistance R_p of a material and I_{corr} through potential steps around the corrosion potential or measurement of the charge transfer resistance (R_{ct}). R_p is defined as the slope of the potential-current density curve at the free corrosion potential: $R_p = (\Delta E/\Delta I)_{\Delta E->0}$. In this application the determination of R_p and I_{corr} is made only with three or four potential steps.

The detailed diagram is made of five blocks:

- Initial open circuit voltage,
- Potential step(s),
- Open circuit voltage,
- (Reverse) potential step(s),
- Repeat.

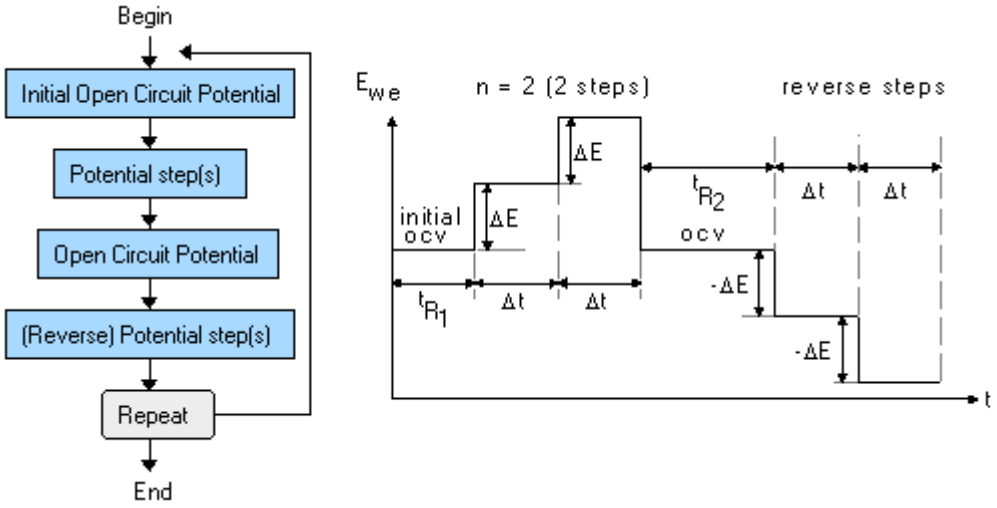


Fig. 153: Polarization Resistance general diagram.

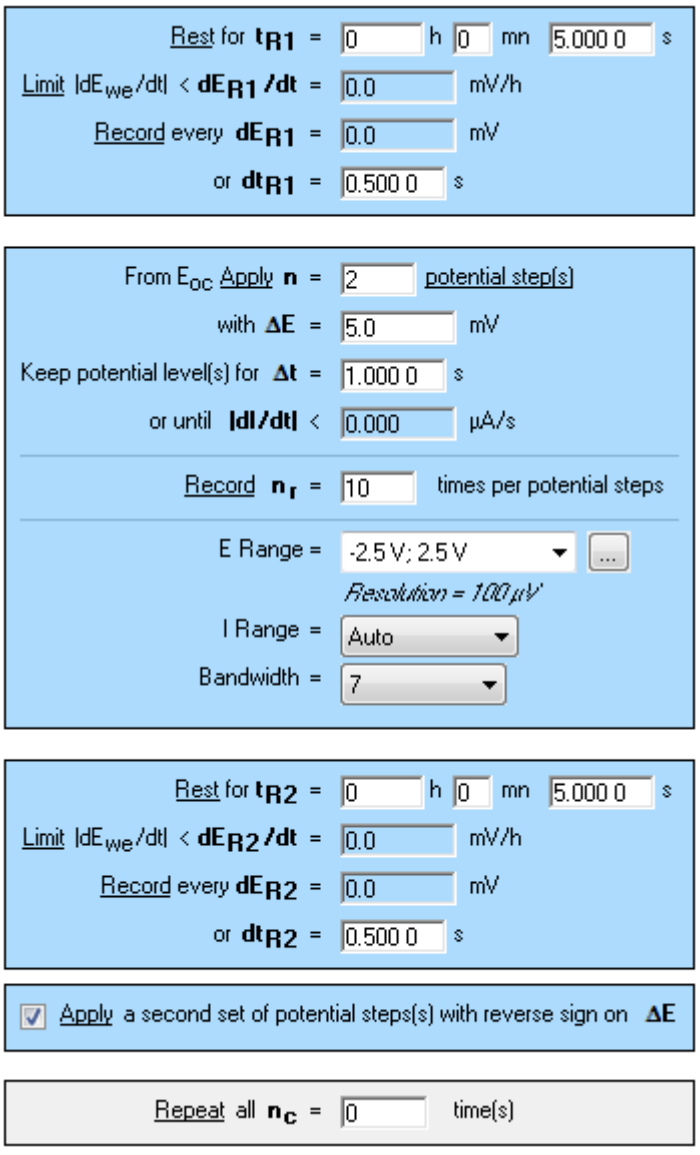


Fig. 154: Polarization Resistance detailed diagram.

- **Initial open circuit voltage**

The open circuit voltage is the standard block, so report to the OCV technique chapter for more information.

- **Potential step(s)**

From E_{oc} Apply n = ……. potential step(s), with ΔE = …….. mV
Keep potential level(s) for Δt = …….. s or until |dI/dt| < …….. µA/s
applies n potential steps with ΔE amplitude and Δt duration, from the potential of the previous OCV period (E_{oc}). If the current variation is small: |dI/dt| < dI/dt limit then the step is shortened. Set the dI/dt limit to 0 to cancel the test.

Do recording n_r = ……. times per potential level duration
defines the number of points recorded per potential steps (that will be recorded every Δt / n_r seconds). Note that <I> (average current between 2 recorded points) is stored into the data files for this technique. So if one sets n_r = 1 there will be only one point per potential step with the average current of the step. However it is recommended to record several points per step, because the associated process (described below) is able to skip the first points where the current may be perturbed by the potential step establishment.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …….. and Bandwidth = ……..
sets the I Range and Bandwidth for the whole experiment. Note that the bandwidth does not perform any action on the measures but acts on the instrument's control loop to establish the potential.

- **Open Circuit Voltage**

The open circuit voltage is the standard block, so report to the OCV technique chapter for more information.

- **Reverse potential step(s)**

Apply a second set of potential step(s) with reverse sign on ΔE
If checked, then it will perform the potential steps again then with -ΔE.

- **Repeat**

Repeat n_c = …… time(s)
repeats the whole sequence n_c time(s). Note that the number of repeats does not count the first sequence: if n_c = 0 then the sequence will be done 1 time n_c = 1 the sequence will be done 2 times n_c = 2, the sequence will be 3 times...

Process:

The polarization resistance files can be processed to calculate the R_p and I_{corr} values.
Select **Analysis, Polarization Resistance** to load the following window:

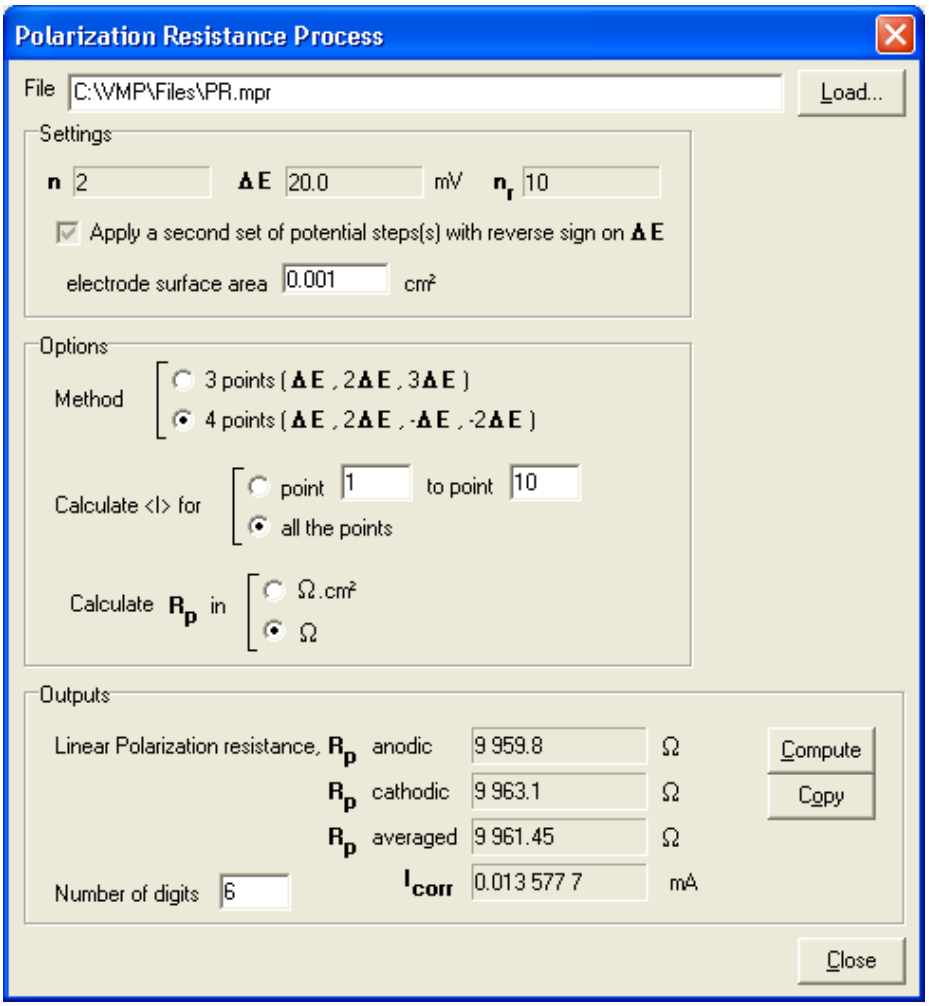


Fig. 155: Polarization Resistance process.

Click on the **Load...** button to select a polarization resistance file. Then a summary of the parameters will be displayed into the settings frame. Note that it is possible to modify the electrode surface area value (for R_p in $\Omega.cm^2$ calculus) here.

Then according to the experiment type, it is possible to select the 4 points or the 3 points methods that both correspond to specific settings:

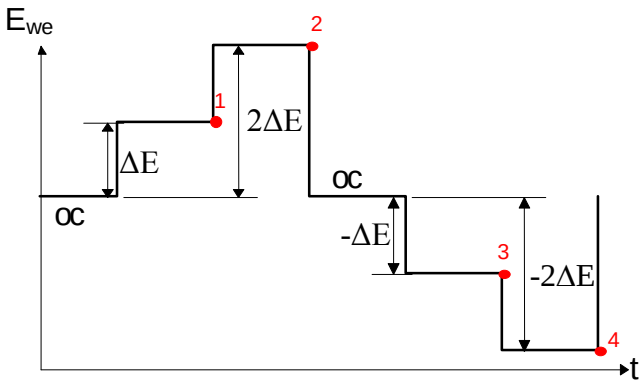


Fig. 156: 4 points method.

(n = 2, reverse steps)

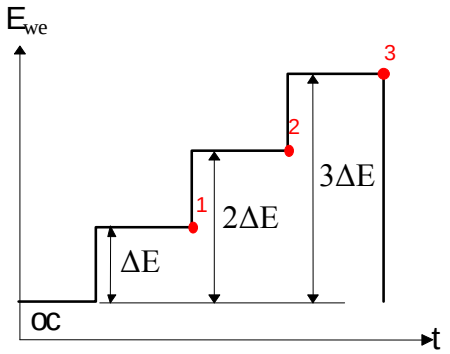


Fig. 157: 3 points method.

(n = 3, do not reverse steps)

The 4 points method gives more accuracy, so it is proposed by default. Nevertheless, it is not always possible to make a reduction after an oxidation, so then chose the 3 points method.
Note: one can perform more than the 4 points and 3 points method with the Polarization Resistance technique, but the process here accepts only these two.

If several points have been recorded per potential steps (n_r > 1), it is possible to exclude some points for the calculus. For example, selecting Calculate <I> for point 3 to 10 will exclude the first two points.

Chose the R_p unit ($\Omega.cm^2$ or Ω) and click on **Compute** to calculate the next values:

$$R_{p_{anodic}} = \frac{e_2 - e_1}{i_2 - i_1}, \ldots R_{p_{cathodic}} = \frac{e_4 - e_3}{i_4 - i_3} \ldots \text{ and } R_{p_{averaged}} = \frac{R_{p_{anodic}} + R_{p_{cathodic}}}{2}$$

3 points method: $I_{corr} = \frac{i_1}{\sqrt{\left|4r_2 - 3r_1^2\right|}}$ with $r_1 = \frac{i_2}{i_1}$, and $r_2 = \frac{i_3}{i_1}$

4 points method: $I_{corr} = \frac{i_1 i_3}{\sqrt{\left|i_2 i_4 - 4 i_1 i_3\right|}}$ with (e_1,i_1) being the potential and the average current (without excluded points) on the potential step ΔE, (e_2,i_2) on 2ΔE, (e_3,i_3) on -ΔE or 3ΔE (according to the selected method) and (e_4,i_4) -2ΔE
Note: if there are several loops (n_c > 0), then the (e_n,i_n) values are averaged on the different loops before the calculus.

3.4.3 SPFC: Stepwise Potential Fast Chronoamperometry

The Stepwise Potential Fast Chronoamperometry is a simple technique designed to loop on two potential steps.

The diagram is made of five blocks:

- Initial Open Circuit,
- Applied E_1 period,
- Applied E_2 period,
- Open Circuit,
- Repeat.

They are detailed below:

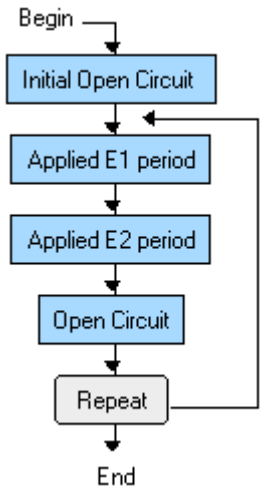


Fig. 158: SPFC general diagram.

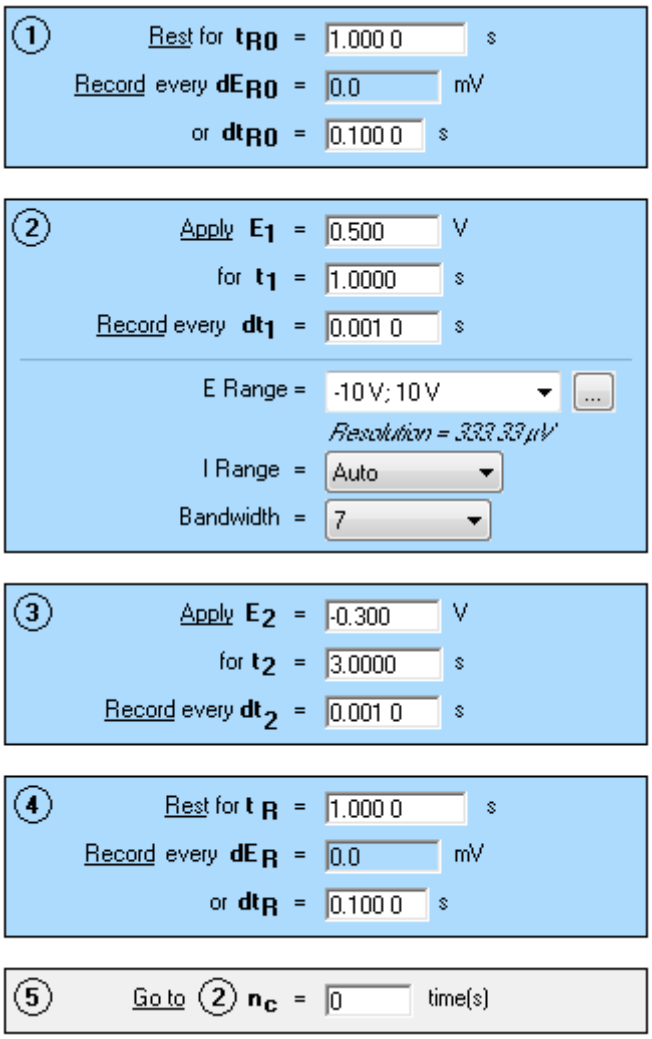


Fig. 159: SPFC detailed diagram.

- **Initial Open Circuit**

This is the standard OCV block without the dE_R/dt test. Therefore report to the OCV section for more details.

- **Applied E_1 period**

Apply E_1 = …… V, for t_1 = …….. s
sets the potential to E_1 for t_1 duration

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
sets the I Range and Bandwidth for the entire experiment.

Record <I> every dt_1 = …… s
records points every dt_1 time.

- **Applied E_2 period**

Apply E_2 = …… V, for t_2 = …….. s
applies a second potential step E_2 in the same way than the first step with different parameters

Record <I> every dt_2 = …… s
records points every dt_2 time.

- **Open Circuit**

reports to the OCV technique for more details.

- **Repeat**

Repeat n_c = ……. time(s)
repeats the E_1, E_2 and OCV blocks n_c times. A value of n_c = 0 cancels the loop.

3.4.4 PEISW: Potentio Electrochemical Impedance Spectroscopy Wait

The Potentio Electrochemical Impedance Spectroscopy Wait is a technique designed to do an impedance measurement at one frequency when the value of IZI has reached a defined value or after a time.

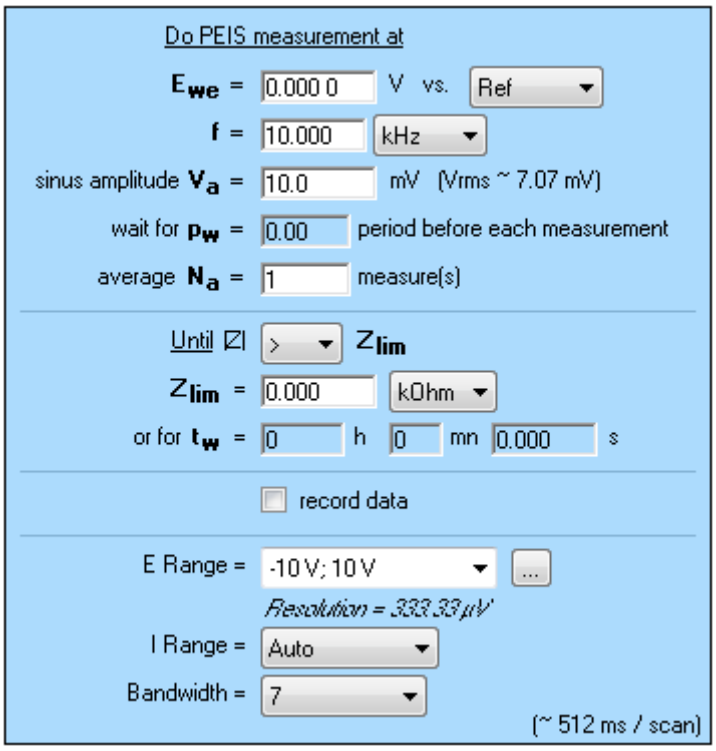


Fig. 160: PEISW detailed diagram.

- **Impedance scan**

Do PEIS measurement at Ewe = …….. V vs. Ref/Eoc/Ectrl/Emeas
defines at which potential the measurement will be done.

f_i = …… MHz/kHz/Hz/mHz/µHz
defines at which frequency the measurement will be done

with an amplitude V_a = …… mV
sets the sinus amplitude to V_a. Equivalence with V_{RMS} is also given.

Note the following relationships between V_a, V_{pp} and V_{RMS} $V_a = V_{pp/2}$ and $V_{RMS} = V_{pp}/(2\sqrt{2})$.

Wait for p_w = …… period before each frequency measurement
offers the possibility to add a delay before the measurement at each frequency. This delay is defined as a part of the period. Of course for low frequencies the delay may be long.

average N_a = …… mesure(s) per frequency
repeats N_a measure(s) and average values for each frequency.

- **Wait period**

Until IZI >/< Zlim
defines the duration of the wait as a function of a IZI value

Zlim = …… MΩ/kΩ/Ω/mΩ/µΩ
fixes the value of Zlim.

Or for tw = h mn s
Or as a function of the time.

□ **record data**
offers to the user the possibitlity to record the data before to reach the limit condition.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = ……. Bandwidth = …….
sets the current range and bandwidth values for the whole experiment.

3.4.5 How to add a homemade experiment to the custom applications

EC-Lab® software offers the user the ability to create his own applications and save it as a "Custom Application". This new application built by the user, is made with several linked techniques. The procedure to create linked experiments is described in the following section.
When the experiment is built, the user can save it in the custom applications. Right click on the mouse and select "**Save as Custom applications**" or in the experiment menu select "**Save as Custom applications**". An experiment saved as custom application appears now in the "custom application" section of the technique window in blue. The blue color is used (like for the user's reference electrode) to distinguish the standard EC-Lab® applications from the customer applications. The custom applications are available only for a new experiment (not when one or several techniques are already loaded).

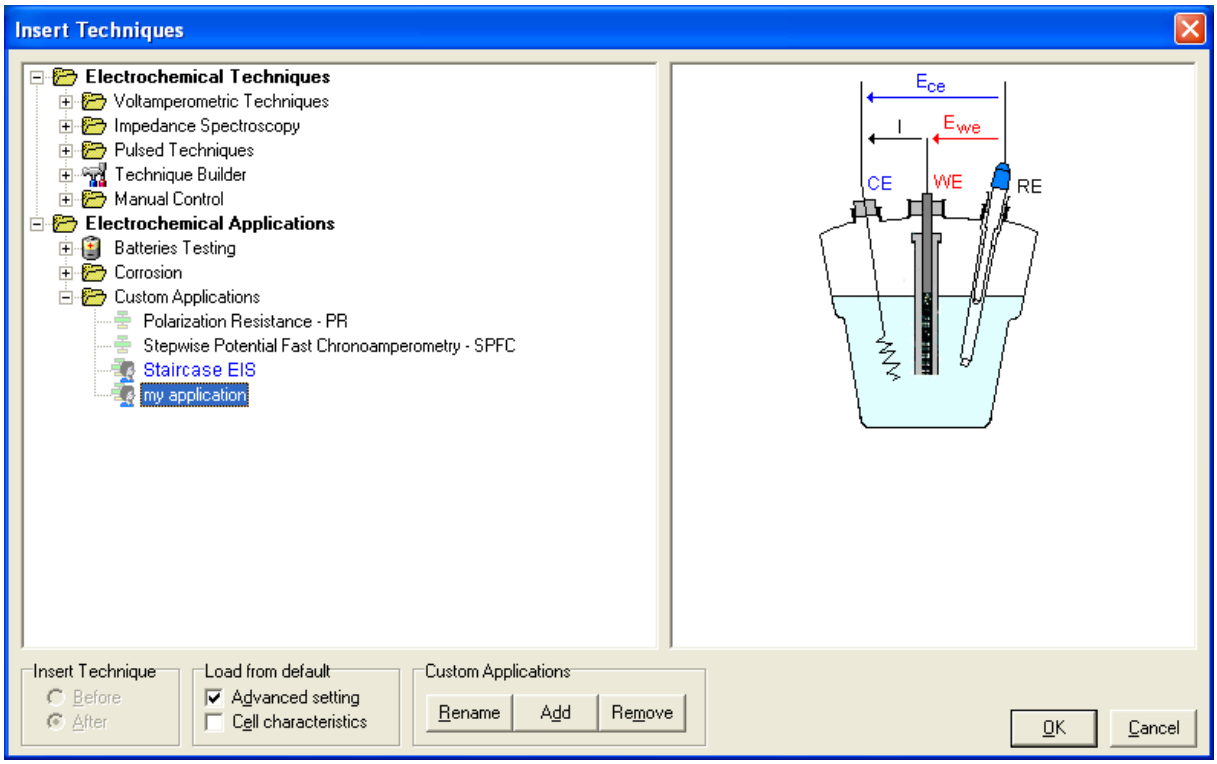


Fig. 161: Custom application section in the technique window.

In this example two custom applications have been created: Anodic stripping voltammetry and RDE rotating speed effect. In the bottom of the technique window a frame with three buttons is dedicated to the custom applications. The selected custom application can be renamed or removed. The user can also add a custom application with the "**Add**" button.

3.5 Special applications

For each special application, it is possible to stop the experiment with an external limit such as a temperature, a speed, …. In the "**Config**" menu select "**External Device**" and select Other in Device Type, this window is displayed in the Fig. 162. To record external analog signals through the auxiliary DB9 connector. The user has to configure Analog In1 and/or Analog In2 inputs to record external signals. Our instruments can control and record analog signals from – 10 to + 10 V. Most of the external devices work into a 0 to + 5 V range. The user has to define the conversion between the input voltage and the variable to plot in the activated frame. It is a direct linear conversion in the range defined by the user between the min and the max value.

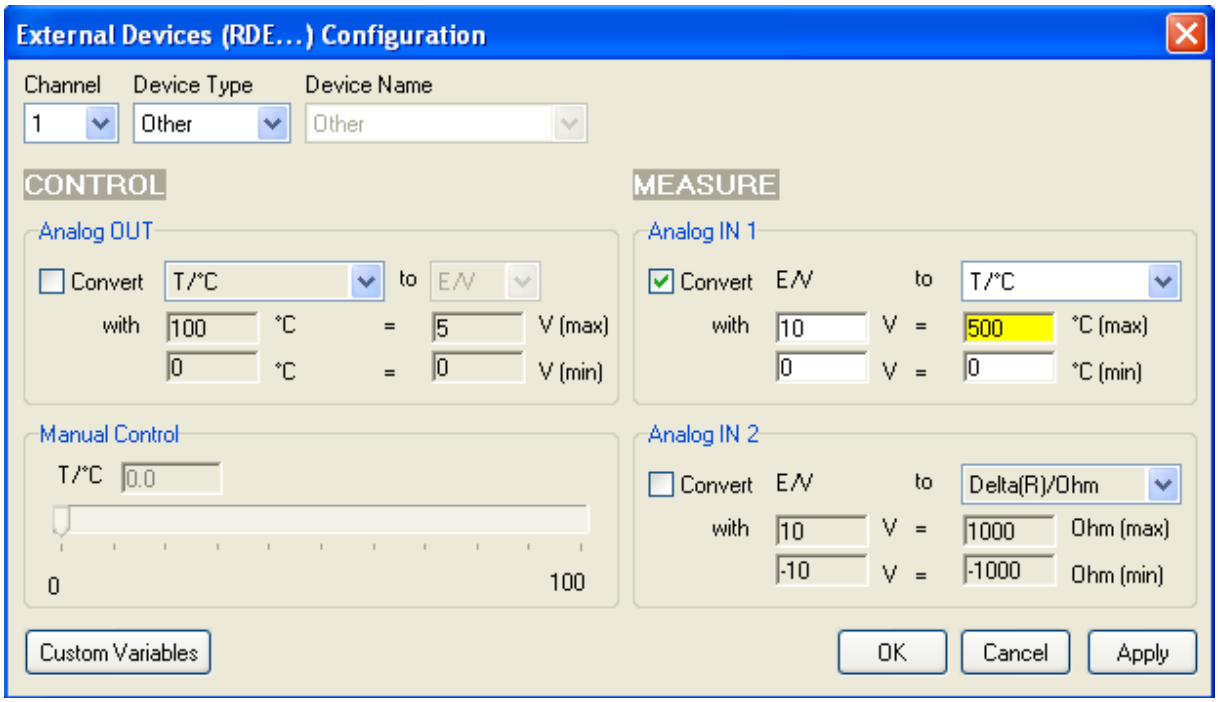


Fig. 162: External devices configuration window.

The user must define several parameters to configure the external to record/measure data via analog input 1 and 2 (right column). The way to proceed for the configuration is described below:

1- Choose the channel to configure. Each channel can be configured for a specific device. One channel can record one device and the other one another device.
2- Select the Device Type (in this case other).
3- The user must tick the box to activate the selected Analog input.
4- In the activated frame, the user must define the conversion between the input voltage and the variable to plot. This is a direct linear conversion in the range defined by the user between the min and the max value.
5- The user can also define the name and the unit of the variable he wants to display. Click on "**Custom Variables**". The figure below is displayed:

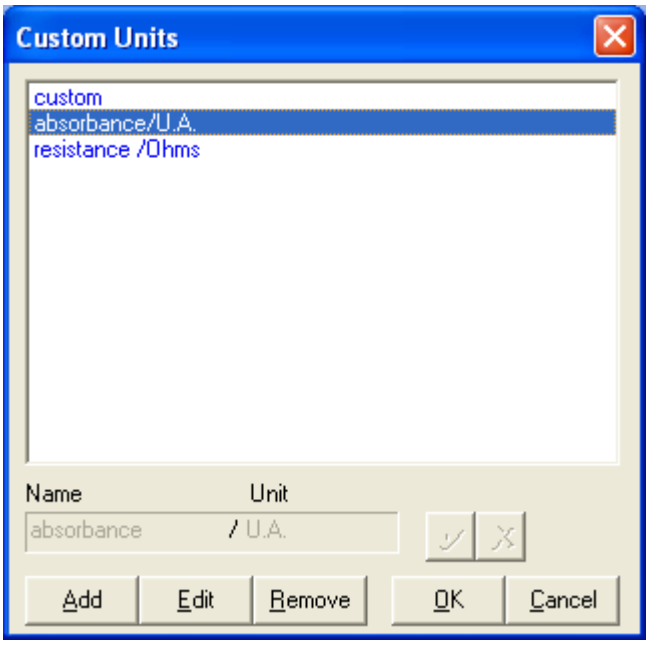


Fig. 163: Custom Units window to define new variables.

To create a new variable with its unit, click on "**Add**" and put the name and the unit of the new variable in the frame. Then click on  to validate. The new variable is displayed in the list in blue color (as a custom variable) and can now be selected as the recorded variable for the analog inputs.

6- Finally click on "**Configure**" to configure the selected channel to record the auxiliary input signal

The new selected variables for Analog In1 and for Analog In2 are automatically displayed on the "Cell characteristics" window and activated for recording. In the "**Selector**" the created variables are displayed and can be plotted. These auxiliary variables can be used in several techniques as conditional limits of an experiment.

Note: - The parameters set in Analog In1 and Analog In2 to define the linear slope can be inverted to have an opposite variation of the recorded value with the plotted value.

3.5.1 SOCV: Special Open Circuit Voltage

As the OCV period, the Special Open Circuit Voltage (OCV) consists of a period during which no potential or current is applied to the working electrode. The cell is disconnected from the power amplifier. On the cell, the potential measurement is available. So the evolution of the rest potential can be recorded. This period is commonly used as preconditioning time or for equilibration of the electrochemical cell. As for OCV, different limits can be applied and especially a limitation with the Analog Input 1 value.

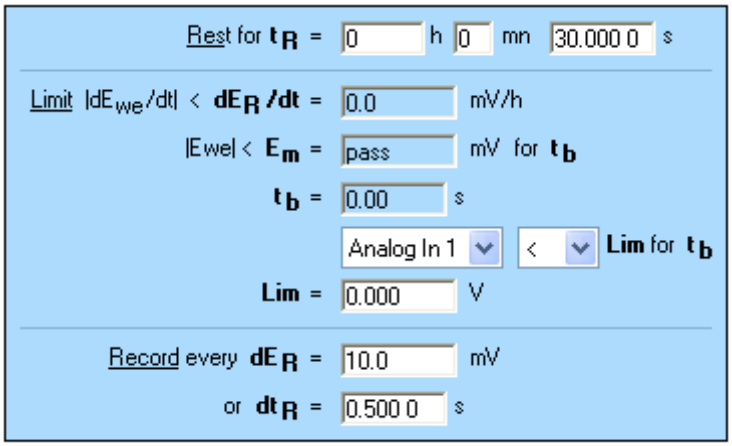


Fig. 164: Special Open Circuit Voltage Technique.

Rest for t_R = h mn s
fixes a defined time duration t_R for recording the rest potential.
or until $|dE_{we}/dt| < |dE_R/dt|$ = mV/h
stops the rest sequence when the slope of the open circuit potential with time, $|dE_R/dt|$ becomes lower than the set value (value 0 invalidates the condition).
or until $|E_{we}| < |E_m|$ = mV for t_b = s
stops the rest sequence when the potential of the working electrode reached E_m during t_b
or until Analog In 1/Anolog In 2/ </> Lim = V for t_b
stops the rest sequence when the limit defines in the Lim box is reached during t_b.

Record E_{we} every dE_R = mV resolution and at least every dt_R = s
allows the user to record the working electrode potential whenever the change in the potential is $\geq dE_R$ with a minimum recording period in time dt_R.

Data recording with dE_R resolution can reduce the number of experimental points without loosing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded but if there is a sharp peak in potential, the rate of recording increases.

3.5.2 SMP: Special Modular Potentio

As the Modular Potentio technique, the SMP allows performing OCV, potentiostatic and potentiodynamic periods. It is possible to chain these periods in any orders and to perform loops that give a lot of flexibility. Moreover, an additional limit condition is added.

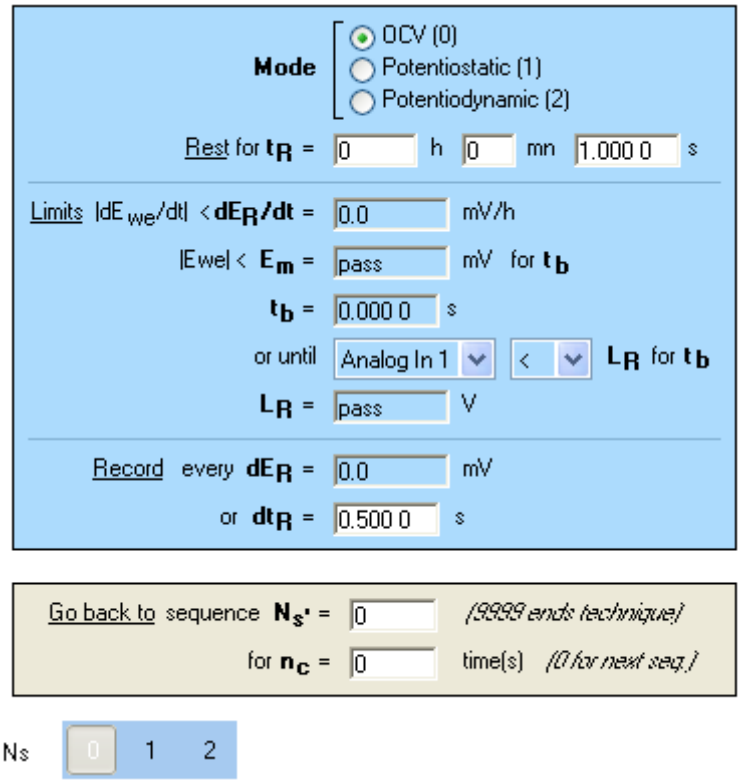


Fig. 165: Special Modular Potentio, OCV detailed diagram.

- **Mode selection:**

clicks on **Mode** = OCV(0), Potentiostatic(1) or Potentiodynamic(2) to select the corresponding mode.

- **Open Circuit Voltage (Mode = 0)**

The open circuit voltage is the same block as those reported for the SOCV technique section for more information.

- **Loop:**

goto N_s' = …… for n_c = …… time(s)
each one of the OCV, potentiostatic and potentiodynamic periods is represented by a single sequence. If n_c is set to 0, the sequence lines are executed one after one. Then an OCV, potentiodynamic and OCV sequence for example will be programmed by 3 lines into the parameters table. Setting $n_c > 0$ will loop to a previous line $N_{s'}$ ($< N_s$) for n_c times.
Report to the battery techniques section (3.1, page 83) for more details on loops conditions.
It is possible to loop to $N_{s'} = 0$, but $N_{s'}$ must be $< N_s$ (current sequence line number).

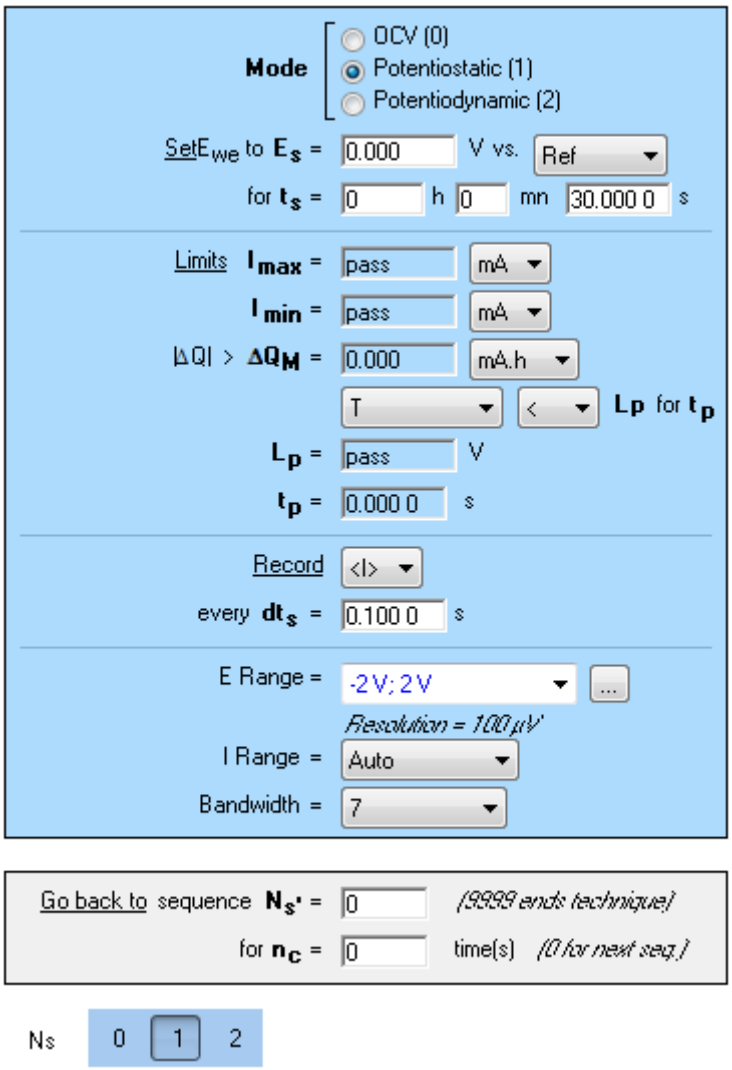


Fig. 166: Special Modular Potentio, potentiostatic detailed diagram.

- **Potentiostatic (Mode = 1)**

Set E_{we} to Es = …….. V vs.Ref/Eoc/Ectrl/Emeas
sets the potential to a FIXED value (vs. Ref the reference electrode potential) or RELATIVELY to the previous open circuit potential (E_{oc}) or to the previous controlled (E_{ctrl}) or measured (E_{meas}) potential (in linked experiments or linked sequences).

for t_s = ……. h ……. mn ……. s
defines the potential step duration (if not stopped on limits)

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = …… and Bandwidth = ……..
fixes the current range and the bandwidth for this experiment.

Record I every dI_p = …. pA/…/A, dQ_p = …… fA.h/…/A.h/pC/…/kC and dt_p = …. S

<I> every dts = …….. s

You can record either an instantaneous current value I or an averaged current value <I>. The recording conditions during the potential step depend on the chosen current variable. For the instantaneous current the recording values can be entered simultaneously, then the first condition is reached and determines the recording. A zero values disable the recording for each criterion. For the averaged current the user defines the time for the average calculation. In that case the data points are recorded in the channel board memory every 200 µs for the VMP3, VMP2, VSP, SP-150 and the BiStat and 20 ms for the VMP and the MPG.

Limit |ΔQ| to ΔQ_M = ….. fA.h/…/A.h/pC/…/kC and I to I_{max} = ….. pA/…A and to I_{min} = ….. pA/…/A.
sets limits for the potential step. If one limit is reached ($|\Delta Q| > \Delta Q_M$, $I > I_{max}$ or $I < I_{min}$) before the end of the step duration (t_s), then the program goes to the next sequence. A zero value disables the ΔQ_M limit and type "p" to enter "pass" to disable I_{max} and I_{min} limits.
Note: the ΔQ value tested here versus ΔQ_M is the current sequence (N_s) integral charge.

And Analog In 1/Analog In2 </> L_p = … V for t_p = s
sets limits of the sequence considering the value recorded with the analog input. If the value reached L_p during t, then the sequence is stopped and the next sequence is applied.

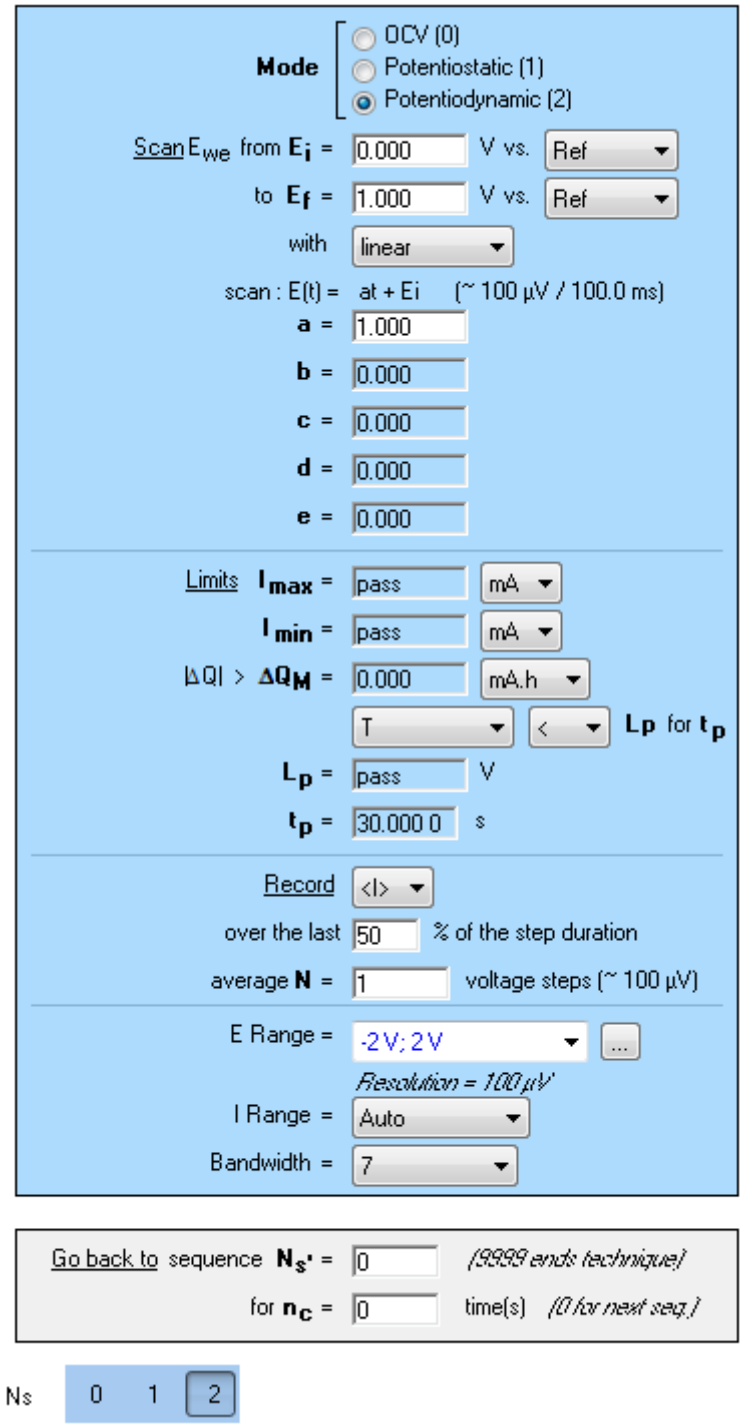


Fig. 167: Special Modular Potentio, potentiodynamic detailed diagram.

- **Potentiodynamic (Mode = 2)**

Scan E_{we} from E_i = V vs Ref/Eoc/Ectrl/Emeas to E_f = … V vs Ref/Eoc/Ectrl/Emeas

defines the initial potential E_i to a FIXED value (vs. Ref the reference electrode potential) or RELATIVELY to the previous sequence final open circuit potential (E_{oc}) or controlled potential (E_{ctrl}) or measured potential (E_{meas}) and defines the final potential E_f in absolute (vs. Ref the reference electrode potential) or relatively to the open circuit potential (E_{oc}) or to the initial potential E_i.

With Linear/Logarithm/Exponential/Polynomial scan

defines the potential scan speed and its mathematical expression .

And a = b = c = d = e =
defines the parameters of the mathematical expression.

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

I Range = and Bandwidth = …
fixes the current range and the bandwidth for this experiment.

Record I/<I> every dI_p = pA/…/µA/…/A dQp = fA.h/…/A.h/pC/…/kC and dt_p = s

two different recording conditions on current are available with the potentiodynamic mode: either recording an averaged current <I> on each potential step or recording an instantaneous current I with an instantaneous current variation (dI) and/or charge variation (dQ) and/or a time variation.

Limit IΔQI to ΔQ_M = fA.h/…/A.h/pC/…/kC and I to I_{max} = pA/…/µA/…/A and I_{min} = pA/…/µA/…/A
sets limits for the potential step. If one limit is reached ($|\Delta Q| > \Delta Q_M$, $I > I_{max}$ or $I < I_{min}$) before the end of the step duration (t_s), then the program goes to the next sequence. A zero value disables the ΔQ_M limit and type "p" to enter "pass" to disable I_{max} and I_{min} limits.

Note: the ΔQ value tested here versus ΔQ_M is the current sequence (N_s) integral charge.

And Analog In 1/Analog In2 </> L_p = … V for t_p = s
sets limits of the sequence considering the value recorded with the analog input. If the value reached L_p during t, then the sequence is stopped and the next sequence is applied.

3.5.3 Special Modular Galvano

The Special Modular Galvano technique is very close to the Modular Galvano technique. This technique allows the user to perform combination of OCV, galvanostatic and galvanodynamic periods. It is possible to chain these periods in any orders and to perform loops. It gives a lot of flexibility to create galvano techniques. The galvanodymamic mode can be used to study stepwise electron-transfer reactions and multicomponent systems. In the Special technique a limit condition on analog input is set.

- **Mode selection:**

Click on **Mode** = OCV(0), Potentiostatic(1) or Potentiodynamic(2) to select the corresponding mode. Then the detailed diagram is automatically displayed.

- **Open Circuit Voltage (Mode = 0)**

the open circuit voltage is the standard block. So report to the OCV technique section 2.1.1, page 5 for more details.

- **Loop:**

goto Ns' = …….. for nc = ……. time(s)
each one of the OCV, potentiostatic and potentiodynamic periods is represented by a single line into the grid parameters. If n_c is set to 0, the sequence lines are executed one after one. Then an OCV, potentiodynamic and OCV sequence for example will be programmed by 3

lines into the parameters table. Setting $n_c > 0$ will loop to a previous line $N_{s'}$ ($< N_s$) for n_c times.
Go to the battery protocols section (3.1, page 83) for more details on loops conditions. It is possible to loop to $N_{s'} = 0$, but $N_{s'}$ must be $< N_s$ (current sequence line number).

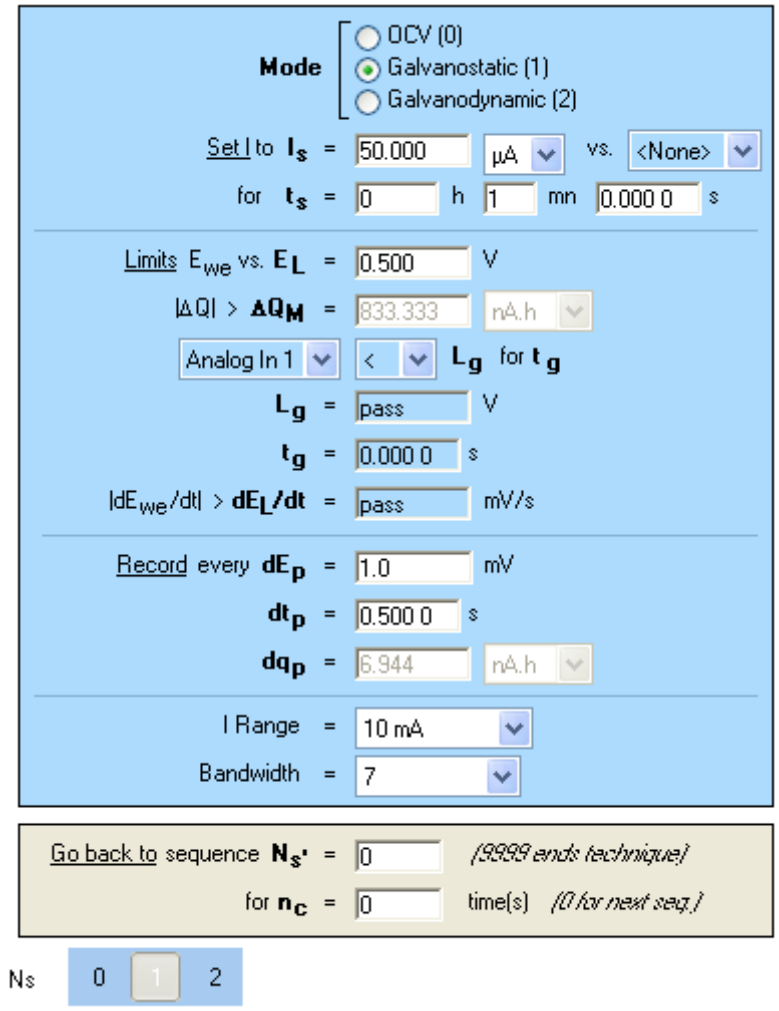


Fig. 168: Special Modular Galvano, Galvanostatic detailed diagram.

- **Galvanostatic (Mode = 1)**

Set I to I_s = …….. pA/…/A vs.<None>/Ictrl/Imeas for t_s = …… h ….. mn ….. s
sets the current to a fixed value I_s for t_s time. The current value can be defined in absolute or versus a previous controlled current or measured current.

With I Range = …… and Bandwidth = ……..
fixes the current range and the bandwidth for this experiment.

Record every dE_p = …… mV, dt_p = ….. s and dQ_p = …… fA.h/…/A.h/pC/…/kC
defines the recording conditions. A zero value cancels the corresponding recording criterion. These values can be entered simultaneously, then this is the first condition that is reached that determines the recording. For the galvanostatic mode dQ_p is not accessible and is calculated from I_s and dt_p ($dQ_p = I_s \,.\, dt_p$).

Limit E_{we} to E_L = ……. V and |ΔQ| to ΔQ_M = ……. fA.h/…/A.h/pC/…/kC
defines the potential and sequence charge limits. The E_L limit is depending on the charge sign, the limit is:

$E_{we} > E_L$ if $I_s > 0$

$E_{we} < E_L$ else
To cancel the limits type "p" for "pass" into the E_L edition box and zero for ΔQ_M.
For the galvanostatic mode ΔQ_M is not accessible and is calculated from I_s and t_s ($\Delta Q_M = I_s . t_s$).

And Analog In 1/Analog In2 </> L_g = … V for t_g = s
sets limits of the sequence considering the value recorded with the analog input. If the value reached L_p during t, then the sequence is stopped and the next sequence is applied.

- **Galvanodynamic (Mode = 2)**

Scan I with dI/dt = ……. mA/s, with …….. pA/…/A / …… s
defines the scan rate. By the same way than for the Modular Potentio technique, entering the dI/dt value will automatically calculate the dI and dt values in order to minimize the current steps dI. Nevertheless, one can enter dI and dt directly.

from I_i = …… pA/…/A vs. <None>/Ictrl/Imeas to I_f = pA/…/A vs. <None>/Ii.
defines the initial I_i and final I_f current of the scan.

Recording and limits are the same than for the galvanostatic period, except that dQ_p and ΔQ_M that can be accessible for the galvanodynamic mode.

With I Range = …… and Bandwidth = ……..
fixes the current range and the bandwidth for this experiment.

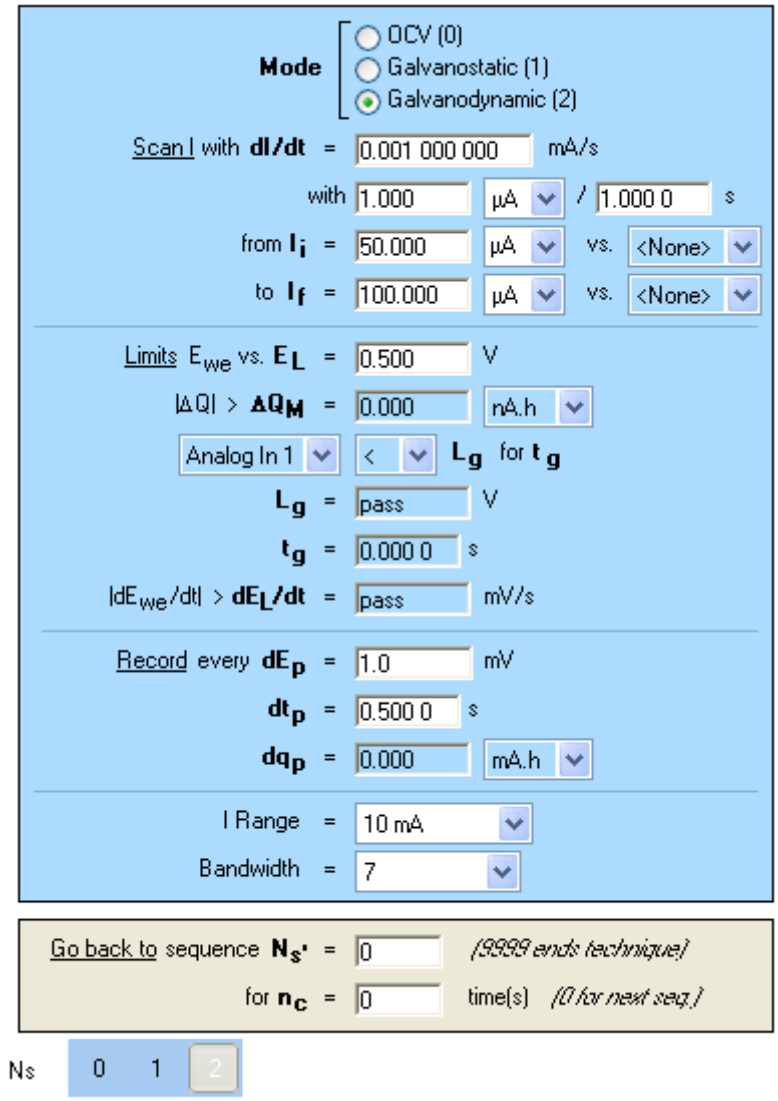


Fig. 169: Special Modular Galvano, Galvanodynamic detailed diagram.

The three modes of the Special Modular Galvano technique can be chained as sequences in the table in the order that the user wants. Each of the parameters can be modified in its box. But parameters like I Range or Bandwidth must keep the same value for all the sequences.
Note that the first sequence has got the number $N_s = 0$. To switch from a sequence to another one, click on the desired row in the table.
For more details about the Table frame see the chronoamperometry technique p.19.

Note: in this technique the first and the last data points of each current steps are not recorded automatically.

3.5.4 SGCPL: Special Galvanostatic Cycling with Potential Limitation

This technique, such as the GCPL technique, corresponds to battery cycling under galvanostatic mode (essentially), i.e. with an imposed current, but with possible potential limitations under current for both charge and discharge, and test on potential values during open circuit period. Additionally to the GCPL technique it is possible to limit the under current period by considering the value recorded with the analog input.
The main characteristics of this technique are the same than those of the GCPL one.

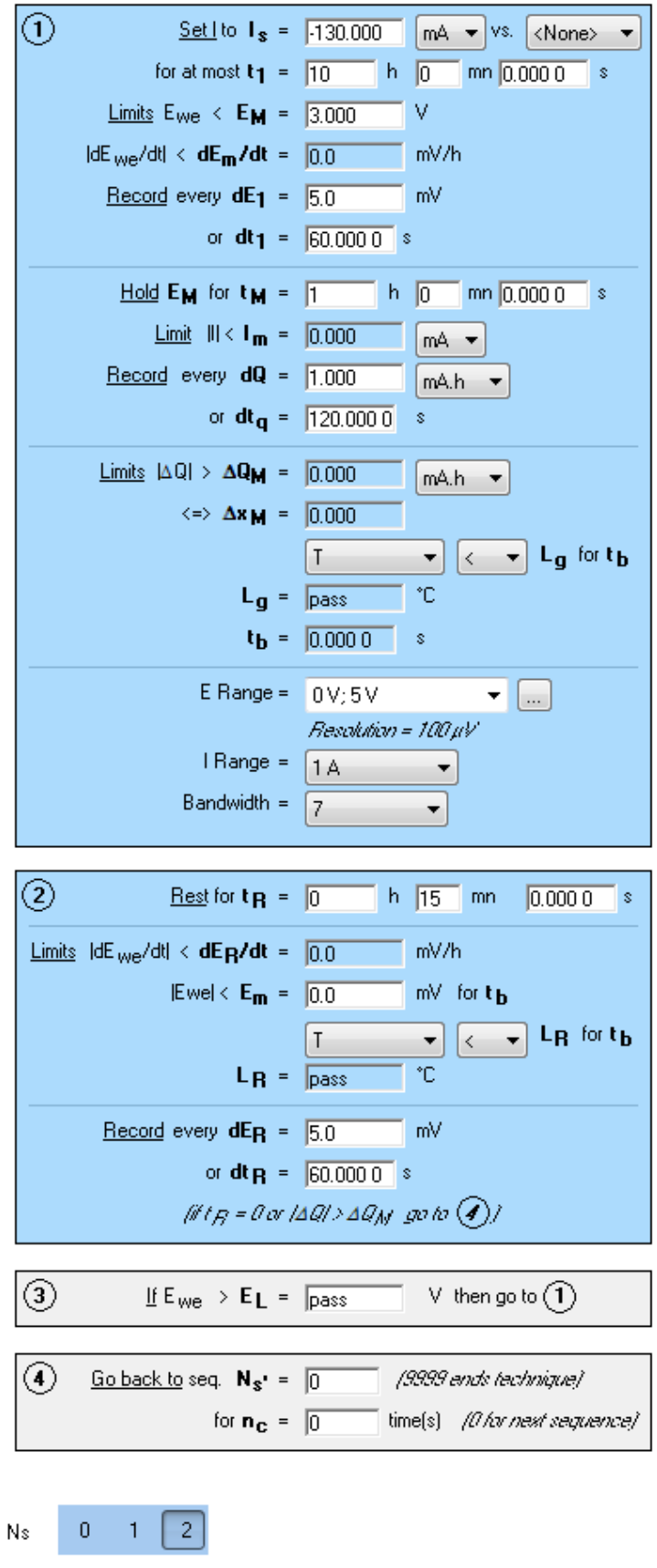


Fig. 170: Detailed diagram of one SGCPL sequence.

- **First step: galvanostatic period that can be followed by a potentiostatic period.**

1) Galvanostatic period

Set I to Is = …. pA/…/A vs. <None>/Ictrl/Imeas, for at most t_1 = ….. h …… mn …… s
fixes the current value in absolute, versus the previous controlled current (previous sequence) or versus the previous measured current and the maximum duration of the imposed current period. The sign of the current value is "-" for a discharge and "+" for a charge when the positive electrode of the cell is connected to the Working electrode cable (red).

E Range = …….

enables the user to select the potential range for adjusting the potential resolution with his system. (See EC-Lab software user's manual for more details on the potential resolution adjustment)

Or until $|dE_{we}/dt| < dE_m/dt$ = mV/h with I Range = …… and Bandwidth = ……..
gives to the user the possibility to shorten the period when the decay of the potential is lower than a given value and allow the user to fixe the current range and the bandwidth for this experiment.

Record E_{we} every dE_1 = ……. mV and at least every dt_1 = ……. s
allows the user to record the working electrode potential with a given potential resolution (whenever the change in the working electrode potential is $\geq dE_1$) or/and at least every dt_1 time interval .

2) Potentiostatic period

Limit $E_{we} < E_M$ = ……. V
fixes the limit of the working electrode potential under charge/discharge (see warning 1).
and stand for t_M = …… h ……. mn …… s or until $|I| < I_m$ = …… pA/…/A
allows the user to stand at the potential E_M for a given time or until the current reaches a low limit value I_M.
If the limit potential E_M is not reached within the time t_1, or if t_M is set to 0, the system skips to the next step.

Record ΔQ every dQ = ……. mA.h and at least every dt_q = ……. s
in the constant potential mode the system acts as a coulometer and a recording is performed every time the charge increment/decrement since the previous recording is $\geq$ dQ and/or every dt_q time interval.
Limit ΔQ to ΔQ_M = ……. mA.h <=> Δx_M = ……
fixes the maximum charge change from the beginning of this sequence during the sequence. This charge is equivalent to a Δx_M quantity, which corresponds to a normalized charge (related to intercalation electrodes).
And Analog In 1/Analog In2 </> L_p = … V for t_p = s
sets limits of the sequence considering the value recorded with the analog input. If the value reached L_p during t_p, then the sequence is stopped and the next sequence is applied.

- **Second step: open circuit period with monitoring of the electrode potentials.**

turn to Rest for t_R = ……. h ……. mn ……. s
fixes a maximum time t_R to stay in open circuit mode.
or until $|dE_{we}/dt| < |dE_R/dt|$ = ……. mV/h
gives to the user the possibility to shorten the open circuit period when the decay of the potential is lower than a given value.

Record E_{we} every dE_R = ……. mV and at least every dt_R = ……. s
allows the user to record the working electrode potential with a given potential resolution (whenever the change in the working electrode potential is $\geq dE_R$) or/and at least every dt_R time interval .

Note the conditional test, if $t_R = 0$ which bypasses the open circuit period.

- **Third step: test on the final open circuit potential.**

test E_{we} >(<) E_L = …….. V.

The test is performed with the conditional value > if the open circuit period (just before the test) occurs after a charge (I > 0) and with the conditional value < after a discharge (I < 0).

If the condition is not fulfilled, the above 3 steps will be repeated until the working electrode potential reaches the final open circuit condition $E_{we} \geq E_L$ after a charge, or $E_{we} \leq E_L$ after a discharge.

Note: the user is allowed to bypass this test by entering p (= pass) instead of a voltage value.

- **Fourth step: conditional test which proposes to go to the next sequence or to loop on a previous sequence $N_{S'}$ ($N_{S'} < N_S$).**

If n_c is set to 0, then the technique executes the next sequence.
If the user wants to loop to a previous sequence (line), he has to fill the 2 last columns of the table "**Go to $N_{S'}$**" and "**n_c cycles**".

The end of the technique is obtained by setting $N_{S'}$ and n_c to 0 in the last sequence, or setting **Goto** sequence $N_{S'} = 9999$ at any sequence, which then will be the last one executed even if the next sequence has its settings.

Such a complete sequence corresponds to one line of the table. This line is composed of the columns which represent the successive variables encountered when setting the diagram, the current range, and the loop conditions; all parameters which has to be set by the user.

Note that it is always possible to force the end of a technique while it is running, at any sequence/sweep, using the **Modify** button and setting **Goto** sequence $N_{S'} = 9999$ at the sequence one wants to stop.

4. Linked experiments

4.1 Description and settings

It is possible to link different techniques within the same run. This allows the user to create and build complex experiments with up to 20 techniques. When created the linked experiment settings can be saved either as a .mps file or a "**Custom application**". In the first case the settings can be loaded from the initial folder and in the second case they appear in the applications and can be reloaded when necessary.

Linked experiments can be made using the "**technique builder**" in the technique window. All the techniques of this section have been previously described (see section 2.4 page 64). The WAIT and LOOP options have been designed especially for linked experiments.
Building linked experiments is very easy with the right click menu. When the user right clicks on the parameter settings window, the following menu appears:

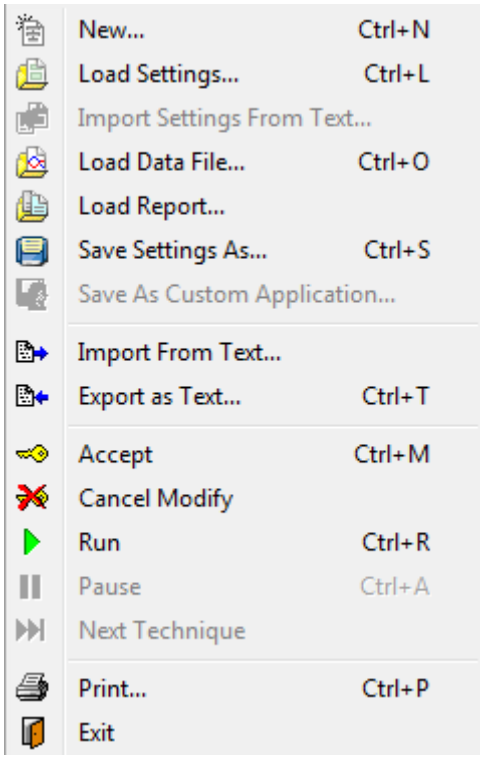


Fig. 171: Mouse right click with the insert and remove options.

The second frame is especially dedicated to linked experiments. The "**Insert New Technique**" function opens the technique selection window and offers the ability to insert a new technique into the experiment. The user can select where he wants to add the new technique into the settings according to the activated/selected technique (green frame around the technique name) in the parameter settings window at the bottom left corner frame of the technique selection window:

Fig. 172: Insert before/after option of the technique selection window.

If the technique is not in the correct position in the experiment the user can easily move it up or down using the "**Move Technique Before**" and "**Move Technique After**" options.

4.2 Example of linked experiment

Let us program the following experiment that could be used for a Levich plot:

1 – Trigger In
    wait for a trigger to start
2 – MP
    mode = 0: OCV period 5 s
    mode = 2 potential sweep from 0 V to 1 V with 10 mV/s.
3 – Wait 1 s with modification of the RRDE rotation speed, no recording
4 – Loop to MP technique five times.

To build the experiment click on **Modify** and select **New experiment** on the right click menu. In the technique selection window choose "TI Trigger In". The instrument will wait for a trigger to start. On the parameter settings window, right click with the mouse. Select insert new technique. Choose the Modular potentio technique and click Ok (check that the technique will be inserted after the trigger). Report to section 2.4.2 page 68 for more details about the Modular Potentio technique. For sequence N_s = 0 select mode = 0 (OCV) and for sequence N_s = 1 select mode = 2 (potential sweep) and set parameters for every sequence.
To add a wait and a loop technique, repeat the same operation (insert new technique) and set parameters. The wait technique with RRDE control is described in Fig. 66 of section 2.4.4 page 74. For the loop option choose "goto technique 2 (MP) for 5 times" and report to the section 2.4.8 page 77 for more details.
Then click on the **Accept** button. This will send the experiment list and the experiment parameters to the instrument.
Note that the current experiment number is now displayed for the 4 pages ("Advanced Settings", "Cell Characteristics", "Parameters Settings" and "Linked Experiments").
Note that one can accept all the experiment parameters at the end. Once in modify mode, one cannot change the current experiment number.

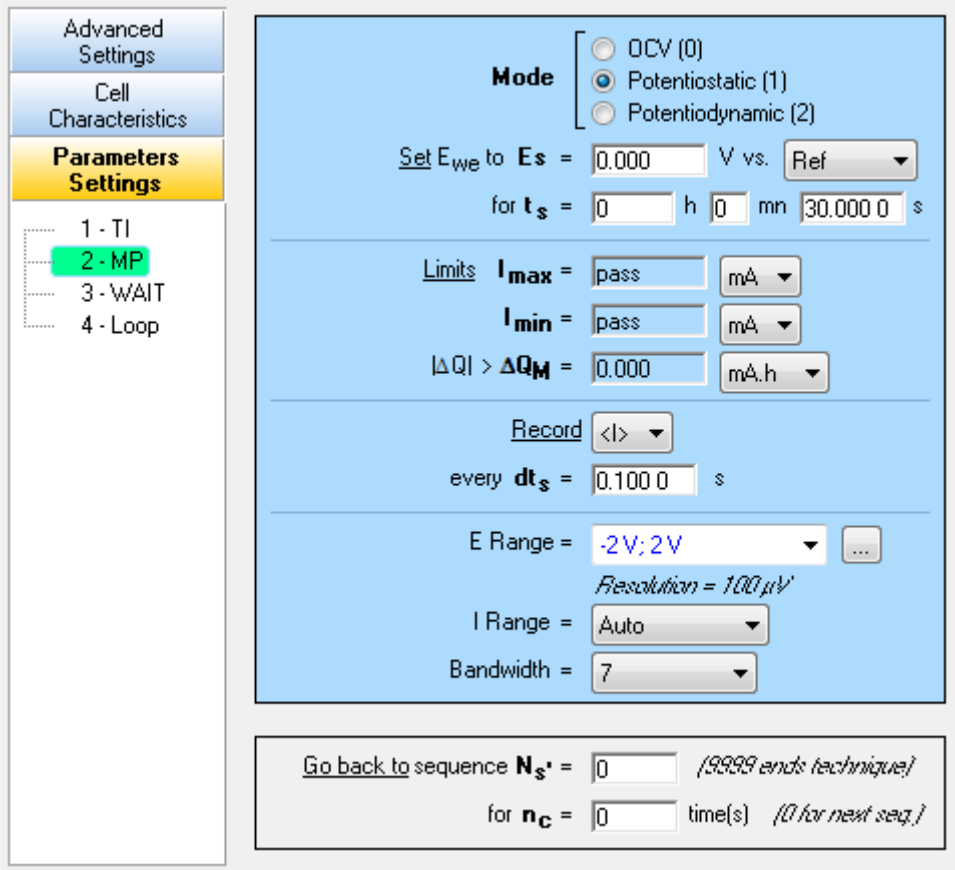


Fig. 173: Linked experiment parameter setting window.

The linked techniques are displayed on the left of the window with their number in the experiment. Click on the button corresponding to the technique you want to see to display the detailed diagram.

Note: it is possible with the technique linker to apply 50 ms OCV period between two techniques (reduced to 0.6 ms if the previous technique is an OCV). The user has just to activate **"Turn to OCV between techniques"** in the advanced settings window.

Click on the **Run** button  to run the acquisition. The program will then ask for a file name that will be used for all the linked experiments with the following rules:

experiment file name = user file name + "_" + experiment number + "_" + experiment (short) name + "_" + "channel number" + ".mpr"

For example: the user file name "MyFileName", will be used to generate the following files:

experiment 1: no file name for the Trigger In option
experiment 2: MyFileName_2_MP_01.mpr
experiment 3: MyFileName_3_WAIT_01.mpr
experiment 4: no file name for the technique linker loop

Each of these files will store the corresponding data points for all the loops.

Note: it is possible to synchronize linked experiments on several channels.

4.3 Application

Once the file name has been entered, the acquisition starts, and the program shows the graphic display with the data files.

During the run the running technique can easily be identified by the green color around the corresponding button. Its number is displayed in the **running experiment** box (see next figure) in "**Run Tec**". The number of loops executed is displayed in "**Tec Loop**".
As for a single experiment run, it is possible to **Pause** / **Resume** and **Stop** the acquisition. The **Stop** button will terminate the whole experiments acquisition. Nevertheless, one can stop the current experiment and continue to the next one with the **Next Exp** button in the tool bar.

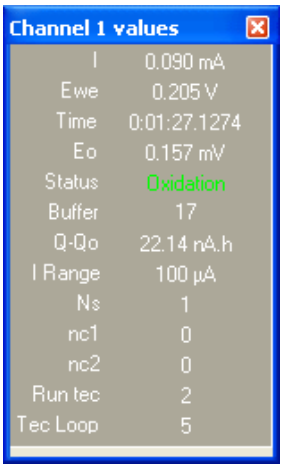


Fig. 174: Linked experiment current values.

In our example, the output files will be:

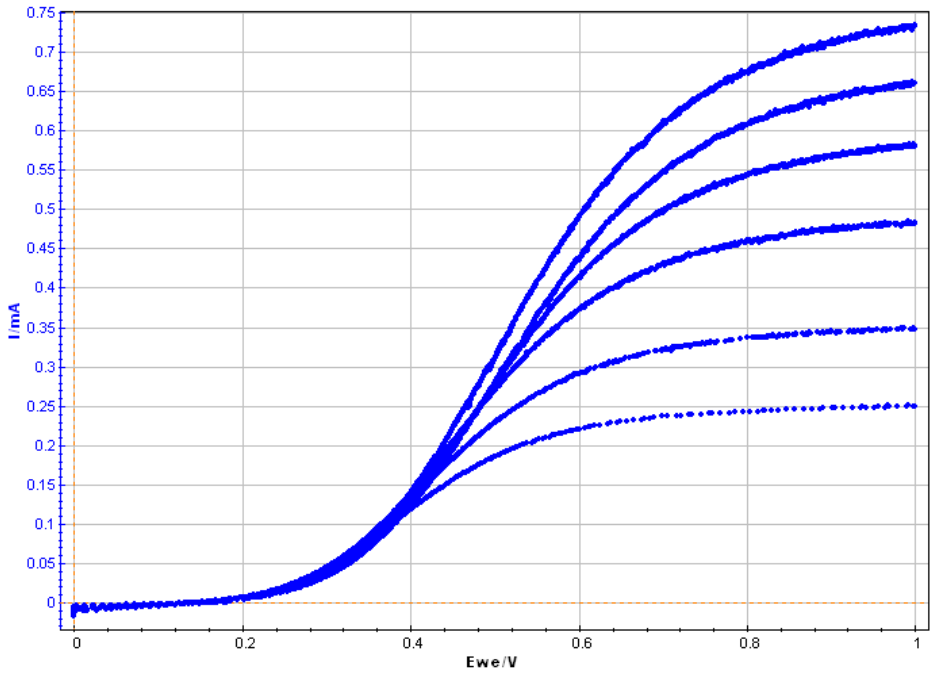


Fig. 175: Linked experiment results.

Notes:

- The ZRA, MUIC techniques and the manual controls cannot be linked.

- The Polarization Resistance process calculation can be performed on the technique linker loops separately.

Linked experiments settings can be saved with **Experiment, Save As,** or on the right click menu with **Save experiment…** and reloaded with **Experiment, Load settings...** or with the right click **Load settings...**.
Linked experiments files are text files with the *.mps extension like the standard settings files.

5. Stack experiments

EC-Lab software has the capability to perform measurements (DC or AC) on a stack of energy devices or other electrochemical system. In this kind of devices, we can mention Lithium battery stacks, solar cells, fuel cell stacks. Using our accessory SAM-50 which is a voltage sense adapter from 50 V to 10 V in addition with a 50 V load box, we can easily study stacks of fuel cells up to 50 V.
In this case, one channel is used as a master channel to control the whole stack and the other are managed by the master and used to do measurements on each element of the stack. In series, the current crossing each element is the same and it is the current of the full stack. But the voltage of the stack in series is the sum of the voltage of each element of the stack. The slave channels are used to measure the voltage of each element. The master channel controls the full stack. Of course to do that a current booster or a load box must be coupled to the master channel.

When launching the EC-lab software, if a multichannel system is detected the opening window will propose to create a "**New Stack**" experiment or to "**Load a Stack Setting**".

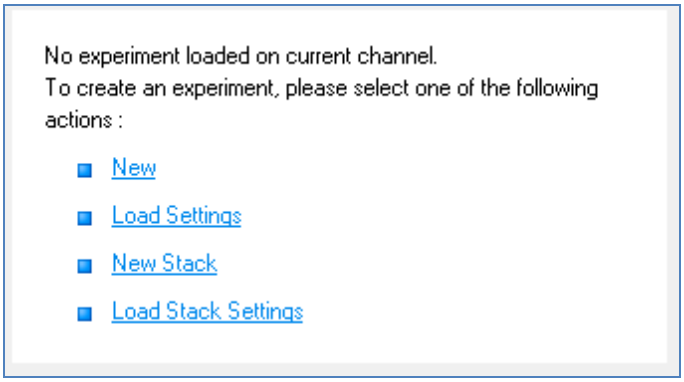


Fig. 176: Experiment selection.

When clicking on one of these choices, the following window appears for channels selection.

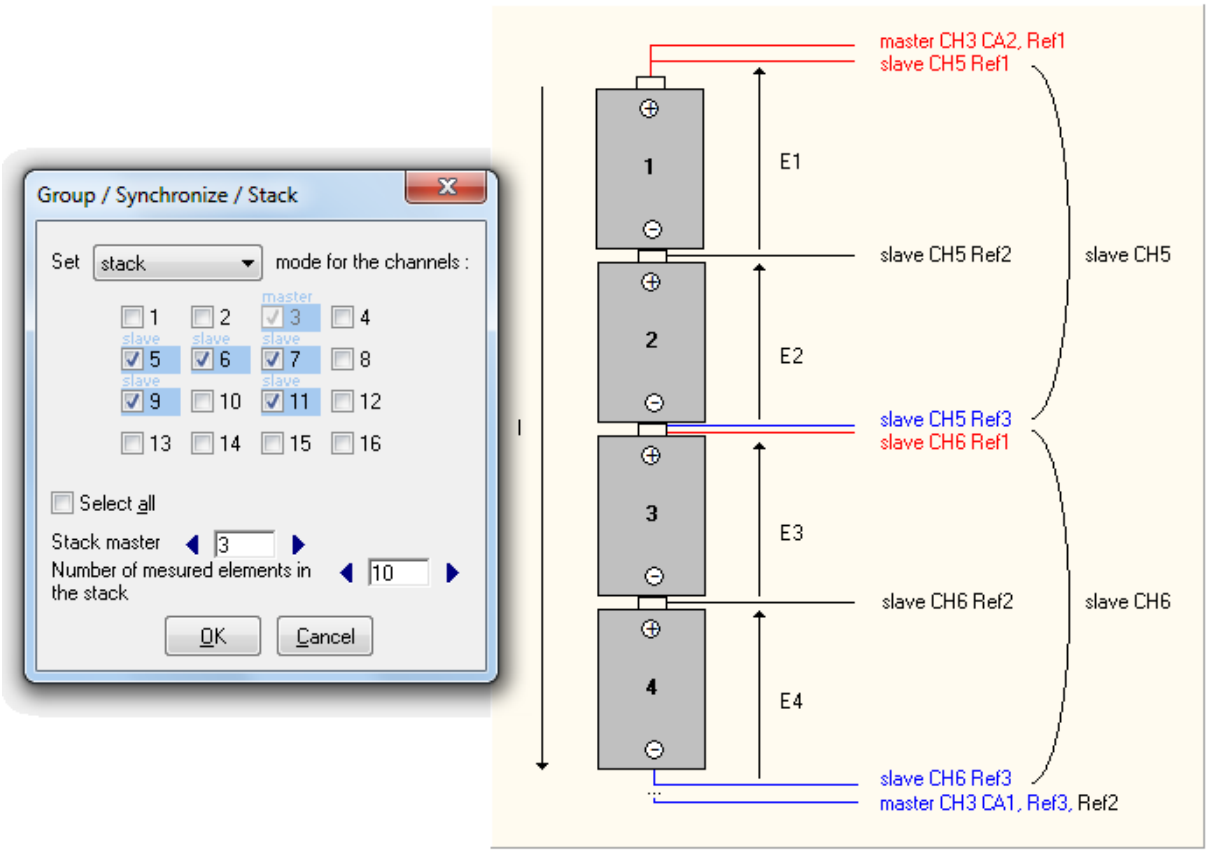


Fig. 177: Channel selection window for Stack measurements.

Thanks to the description on the right, the user will have to select the master channel and the slaves. The user must have in mind that each slave channel will measure the voltage of two elements as follow: E1= Ref1-Ref2, E2= Ref2-Ref3. As an example, with the picture above, the master channel is ch3 and the unit has 5 channels to follow the slaves so the total amount of measured elements in the stack is 10. But the stack can be constituted with more than 10 elements. Only 10 elements will be measured in this configuration. On the slave channels the current wires (CA1 and CA2) are not used. Note also that most of the techniques and applications can be used and linked in “Stack” mode. When the user clicks on the “Ok” button, the “Techniques selection” window is automatically displayed. At this step the user can create the experiment with one or more techniques.

When the connection is done and the channels (master and slave) selected, the user has to click on the ok button. The technique selection window is displayed. All the techniques in EC-Lab can be used and linked in the stack mode. When an experiment is run on a stack, the master channel measurement is displayed on one graph and the slave channels curves are displayed together on a separate graph.
Here after are several examples of stack measurements.

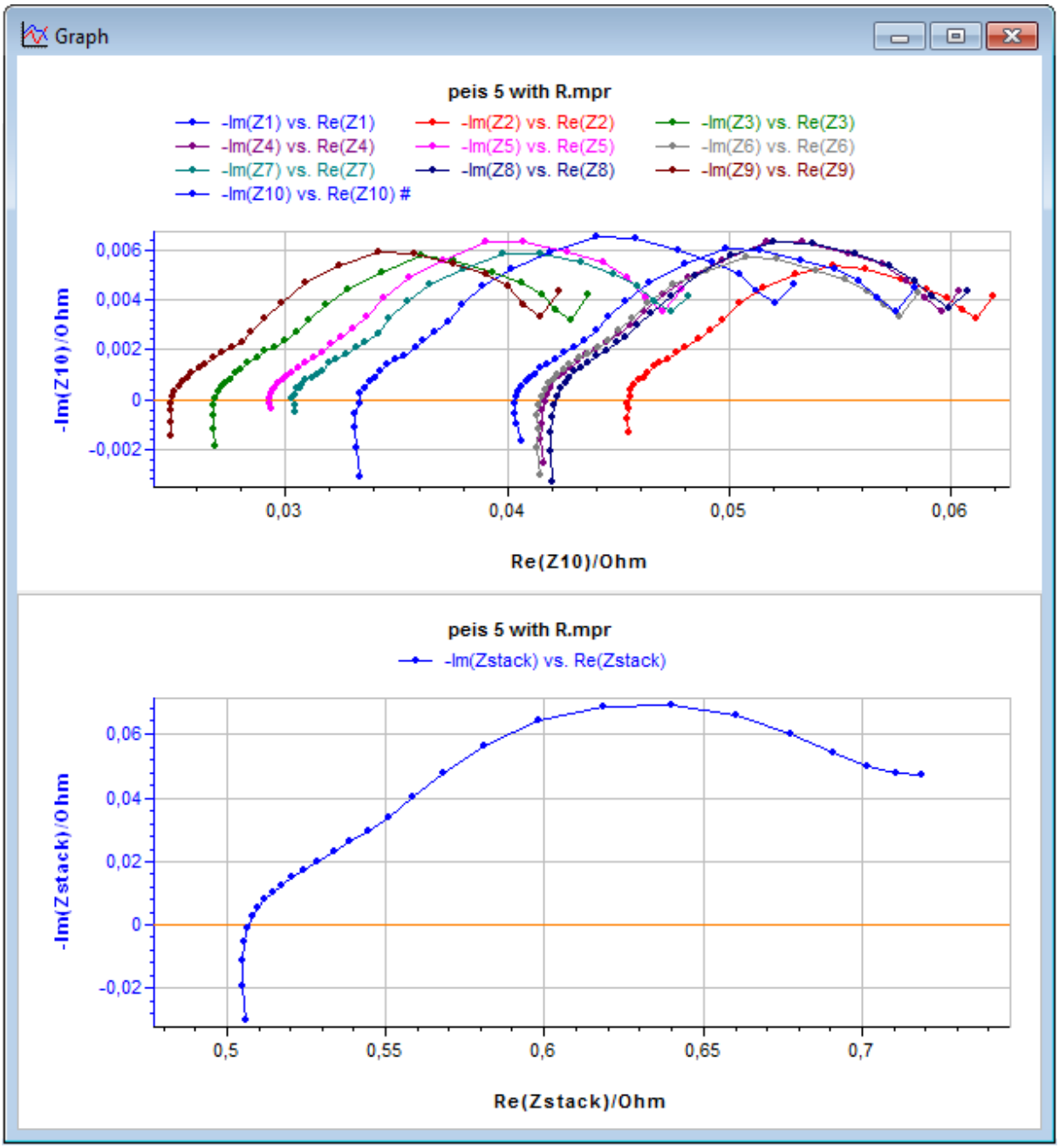


Fig. 178: Stack PEIS measurement with the master channel (bottom) and the slave channels (top).

In this experiment 10 elements are studied in the stack of 15 Ni-MH cells. For this measurement, one master channel and 5 slaves are necessary. So the configuration is a 6 channels system.

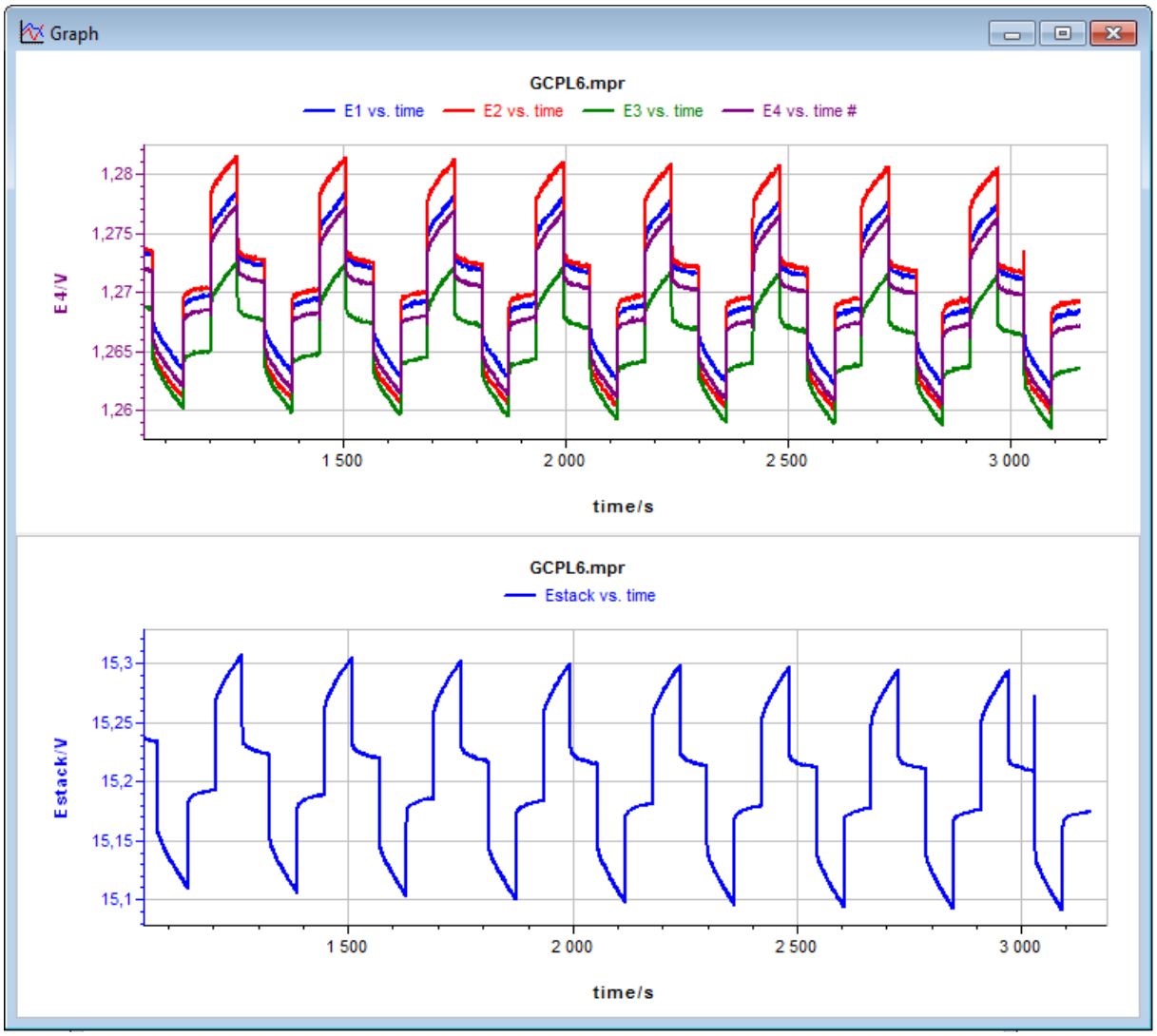


Fig. 179: GCPL experiment on a stack of 15 cells (bottom) with only four elements studied (top).

For stack experiments, all the data points (for the master and the slave channels) are stored in a unique data file.

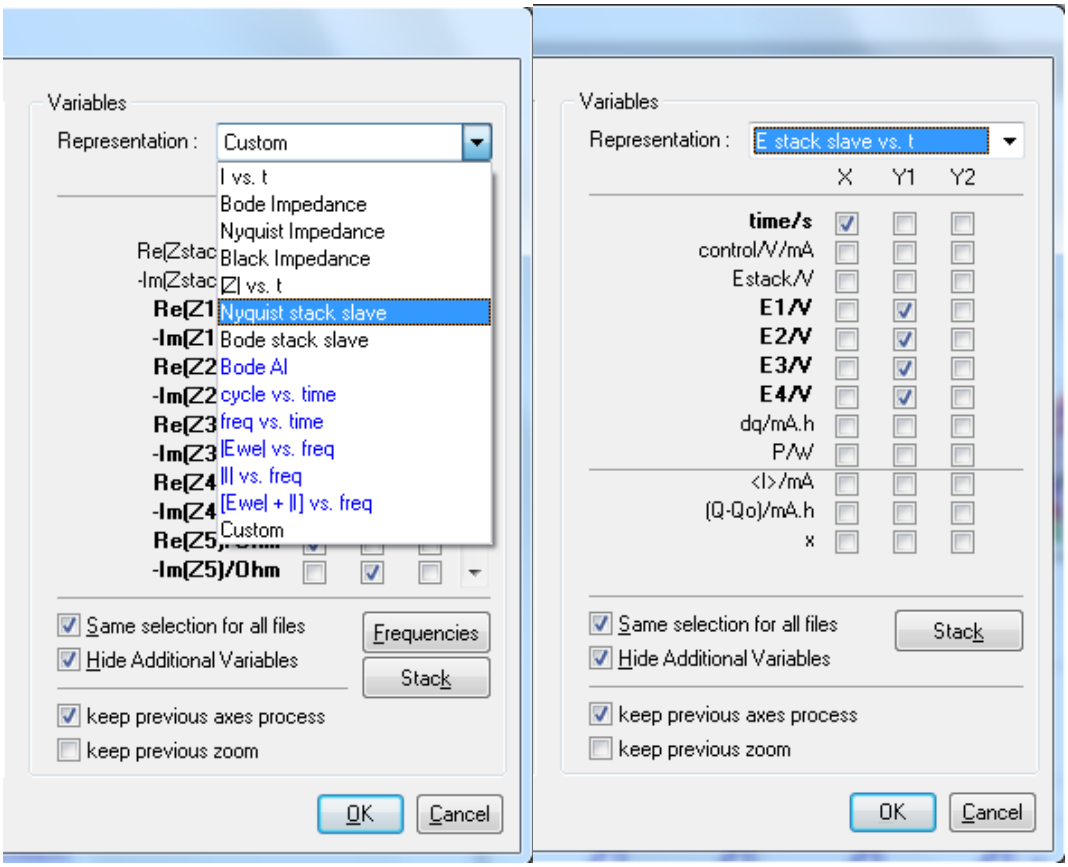


Fig. 180: PEIS (left) and GCPL (right) selection window for a stack experiment

One can see that for stack experiment a “Slave” selection is available to display all the slave data points in the same graphic window. For EIS experiments, Nyquist and Bode plots are available both for the whole stack and for the elements.

6. Summary of the available techniques and applications in EC-Lab®

TECHNIQUES	MPG	VMP	VMP2		BiStat	VMP3 VSP SP-150 HCP-803 HCP-1005	SP-300 SP-200	EPP series
			No Z	Z				
Voltamperometric techniques								
OCV	×	×	×	×	×	×	×	
CV	×	×	×	×	×	×	×	
CVA	×	×	×	×	×	×	×	
CA/CC	×	×	×	×	×	×	×	
CP	×	×	×	×	×	×	×	
SV	×	×	×	×	×	×	×	
LASV	×	×	×	×	×	×	×	
ACV	×	×	×	×	×	×	×	
Pulsed techniques								
DPV	×	×	×	×	×	×	×	
SWV	×	×	×	×	×	×	×	
DNPV	×	×	×	×	×	×	×	
NPV	×	×	×	×	×	×	×	
RNPV	×	×	×	×	×	×	×	
DPA	×	×	×	×	×	×	×	
EIS techniques								
GEIS				×		×	×	
PEIS				×		×	×	
SGEIS				×		×	×	
SPEIS				×		×	×	
Technique builder								
MG	×	×	×	×	×	×	×	×
MP	×	×	×	×	×	×	×	×
Trigger In	×	×	×	×	×	×	×	×
Trigger Out	×	×	×	×	×	×	×	×
Wait	×	×	×	×	×	×	×	×
Loop	×	×	×	×	×	×	×	×
Manual Control								
CMC	×	×	×	×	×	×	×	
PMC	×	×	×	×	×	×	×	
Ohmic Drop determination								
MIR	×	×	×	×	×	×	×	×
ZIR				×	×	×	×	×
Battery testing								
PCGA	×	×	×	×	×	×	×	
GCPL	×	×	×	×	×	×	×	
GCPL2	×	×	×	×	×	×	×	
GCPL3	×	×	×	×	×	×	×	
GCPL4	×	×	×	×	×	×	×	
GCPL5	×	×	×	×	×	×	×	
CLD	×	×	×	×	×	×	×	
CPW	×	×	×	×	×	×	×	

APGC			×	×	×	×	×	
Corrosion								
EVT		×	×	×	×	×	×	
LP		×	×	×	×	×	×	
CM		×	×	×	×	×	×	
GC		×	×	×	×	×	×	
CPP		×	×	×	×	×	×	
DP		×	×	×	×	×	×	
CPT		×	×	×	×	×	×	
CPT2		×						
MPP		×	×	×	×	×	×	
MPSP		×	×	×	×	×	×	
ZRA		×	×	×	×	×		
ZVC		×	×	×	×	×	×	
CASP				×	×	×	×	
VASP	×	×	×	×	×	×	×	
Custom applications								
PR	×	×	×	×	×	×	×	
SPFC			×	×	×	×	×	
MUIC		×						
PEISW				×		×	×	
Special applications								
SOCV	×	×	×	×	×	×	×	
SMP	×	×	×	×	×	×	×	
SMG	×	×	×	×	×	×	×	
SGCPL	×	×	×	×	×	×	×	

7. List of abbreviations used in EC-Lab® software

Abbreviations	Description
Technique: OCV	
t_R	Rest time
dE_R/dt	Limit condition on a variation of the WE potential
dE_R	Recording condition on a variation of the WE potential
dt_R	Recording condition on a variation of time
Voltamperometric Techniques	
E_i	Initial potential
Ref	Reference electrode potential versus which WE potential will be applied
E_{oc}	Open circuit potential versus which WE potential will be applied
E_{ctrl}	Last controlled potential versus which WE potential will be applied
E_{meas}	Last measured potential versus which WE potential will be applied
ti	Time duration to Hold Ei
dti	Recording condition on a variation of time
dE/dt	Potential scan rate
E_1	First vertex potential
t_1	Time duration to Hold E_1
dt_1	Recording condition on a variation of time
N	Number of averaged voltage steps between two data points
I Range	Current range
E_2	Second vertex potential
t_2	Time duration to Hold E_2
dt_2	Recording condition on a variation of time
n_c	Number of repeated cycles
n_r	cycle recording frequency
E_f	Final potential
t_f	Time duration to Hold E_f
dt_f	Recording condition on a variation of time
I_{min}	Minimum current Limit
I_{max}	Maximum current Limit
ΔQ_M	Maximum total Charge variation
dI	Recording condition on a variation of current
dQ	Recording condition on a variation of charge
N_S'	Previous sequence to go back to
I_s	Current step applied
t_s	Time duration to Hold I_s
I_{ctrl}	Last controlled current versus which the cell current will be applied
I_{meas}	Last measured current versus which the cell current will be applied
E_M	Maximum potential limit
dE_s	Recording condition on a variation of potential
dt_s	Recording condition on a variation of time
Impedance spectroscopy:	
f_i	Initial frequency
f_f	Final frequency
N_d	Number of points per decade
N_t	Total number of points
I_a	Sinus current amplitude
N_a	Number of averaged measures per frequency
V_{pp}	Peak to peak potential amplitude
I_f	Final current value
N	Number of current/potential steps

E_f	Final potential value
R_u	Uncompensated resistance
IR	Compensated ohmic drop
Pulsed techniques	
P_H	Pulse height
P_W	Pulse Width
S_H	Step height
S_T	Step time
PP_W	Pre Pulse Width
PP_H	Pre Pulse Height
P	Pulse period
t_P	Period duration
Technique Builder	
E_S	Step potential
t_S	Time duration of Es
t_d	Waiting duration
N_e	Sequence to go back to with a loop
n_t	Number of iterations of the experiment

8. Glossary

This glossary is made to help the user understand most of the terms of the EC-Lab® software and the terms mentioned in the manual. The terms are defined in alphabetical order.

Absolute value: mathematical function that changes the negative values in positive ones.

Accept: button in EC-Lab® software that switches to "Modify" when the user clicks on. "Modify" must be displayed to run the experiment.

Apparent resistance (R_i): conventional term defining the electrolytic resistance in a solid electrochemical system such as a battery. R_i is defined as the ratio dE/dI when the potentiostat switches from an open circuit voltage mode to a galvanostatic mode or the vice versa.

Bandwidth: represents the frequency of the regulation loop of the potentiostat. It depends on the electrochemical cell impedance. The bandwidth values go from 1 to 7 with increasing frequency.

Calibration: operation that must be done for each channel in order to reduce the difference between a controlled value (for example E_{ctrl}) and the corresponding measured value (for example E_{we}).

Channels: each one of the boards corresponding to an independent Potentiostat/galvanostat.

Chronoamperometry/chronocoulometry: controlled potential technique that consists of stepping the potential of the working electrode from an open circuit potential to another potential E_i where electrochemical reactions occur. The resulting curve is a current-time response. Chronocoulometry is an alternative mode for recording the charged passed as a function of time with current integration.

Chronopotentiometry: controlled current technique where the potential is the variable determined as a function of time during a current step.

Compact: mathematical function allowing the user to compress data points from the raw data file. Compact functions are available with GCPL and PCGA techniques. All points of each potential step are replaced by their average taken at the end of the potential step. The number of points of the compacted data file decreases a lot according to the raw file.

Constant load discharge (CLD): technique especially designed for battery testing. This technique is used to discharge a battery at a constant resistance. The potentiostat is seen as a constant resistor by the battery.

Constant power (CPW): This technique is designed to study the discharge of a battery at constant power. The control is made by checking the current to maintain an E*I constant.

Corrosimetry: application used in corrosion for the determination of R_p versus time by a repetition of the polarization around the corrosion potential at fixed time interval.

Cycle: inside a technique, this term is used to describe a sequence repeated with time.

Cycle number: processing function that allows the user to display on the graphic one or several cycles chosen in the raw file. The selected cycles are lightened and the others are hidden.

Cyclic potentiodynamic pitting (CPP): corrosion technique used to evaluate pitting susceptibility and made with a potentiodynamic part and a conditional potentiostatic part which is taken into account if the pitting current is not reached during the potentiodynamic part.

Cyclic voltammetry (CV): this technique consists of linearly scanning the potential of the working electrode and measuring the current resulting from oxydoreduction reactions. Cyclic voltammetry provides information on redox processes, electron transfer reactions and adsorption processes.

Depassivation potential (DP): corrosion technique composed with a potentiostatic part used to depassivate the electrode metal and with a potentiodynamic part used to study the corrosion pitting.

Differential Pulse Voltammetry (DPV): technique used in analytical electrochemistry to discriminate faradic from capacitive current. This technique consists of pulses superimposed on a potential sweep.

Differential Normal Pulse Voltammetry (DNPV): technique used in analytical electrochemistry to discriminate faradic from capacitive current. This technique is made of increasing prepulses with time and pulses superimposed on the prepulses.

Differential pulse amperometry (DPA): technique used in analytical electrochemistry to discriminate faradic from capacitive current. This technique consists of the repetition of a pulse sequences made with a prepulse and a pulse superimposed.

EC-Lab®: software that drives the multichannel potentiostats/galvanostat

Galvanostatic cycling with potential limitation (GCPL): battery testing technique corresponding to battery cycling under galvanostatic mode with potential limitations and with the ability to hold a potentiostatic mode after the galvanostatic one.

Galvanostatic cycling with potential limitation 2 (GCPL2): battery testing technique similar to the GCPL but with two potential limitations on the working electrode and on the counter electrode potential. The potential is not held after the current charge/discharge.

Galvanostatic cycling with potential limitation 3 (GCPL3): battery testing technique similar to the GCPL2 with the ability to hold the working electrode potential after the galvanostatic phase.

Galvanostatic cycling with potential limitation 4 (GCPL4): battery testing technique similar to the GCPL with a global time limitation for the charge/discharge period.

Galvanostatic impedance (GEIS): technique for impedance measurement in galvanostatic mode.

Generalized corrosion (GC): technique used to study general corrosion. It consists of half a cycle or a cycle of usual cyclic voltammetry with a digital potential sweep.

I range: current range used in the experiment. It is related to the current resolution.

Impedance: defined by the ratio E/I

IR compensation: in the electrochemical cell, the resistance between the working and the reference electrode produces a potential drop that keeps the working electrode from being at the controlled potential. IR compensation allows the user to set a resistance value to compensate the solution resistance.

Linear polarization (LP): technique that consists of a potential ramp around the corrosion potential. It is often used to determine polarization resistance and corrosion current.

Linked experiments: EC-Lab® offers the ability to link up to ten different experiments with the technique linker.

Linked experiment settings: the user can save the settings of linked experiments as a .mpls file. This allows the user to easily load all the experiment settings.

Loop: technique available in the linked experiments and used to repeat one or more experiments. It is different from the cycle in an experiment.

Manual Potential control: application that enables the user to directly control the working electrode potential, using the mouse to move a sliding index.

Modify: button of EC-Lab® main window allowing the user to select a technique and change the experiment parameters (before or during the experiment). This button switches to "Accept" when the user clicks on.

Modular Galvano (MG): technique designed to perform a combination of OCV, galvanostatic and galvanodynamic periods. The user can link the MG sequences in the way he wants.

Modular potentio (MP): Technique designed to perform a combination of OCV, potentiostatic and potentiodynamic periods. The user can link the MP sequences how he wants. This technique is very useful because it can be used to couple potential sweep detections with preconditioning steps either in OCV or at a particular potential.

Multielectrode potentiodynamic pitting (MPP): corrosion technique designed to study pitting corrosion on one or several electrodes together in the electrochemical cell. This technique corresponds to the pitting potential determination of a material using a potential sweep.

Multielectrode potentiostatic pitting (MPSP): corrosion technique designed to study pitting corrosion on one or several electrodes together in the electrochemical cell using a potential step.

Normal pulse voltammetry (NPV): technique used in analytical electrochemistry to discriminate faradic from capacitive current. This technique is made of increasing pulses with time that always come back to the beginning potential.

Open Circuit Voltage (OCV): technique that consists of a period during which no potential or current is applied to the working electrode. The cell is disconnected and only the potential measurement is available.

Pause: Button of the EC-Lab® main window that leads to a suspension in the progress of the technique and in the measurement recording. The cell is disconnected (OCV period). The "Pause" button switches to "Resume" when clicked.

Polarization resistance (PR): technique of general electrochemistry that can also be used in corrosion monitoring. This technique allows measurement of polarization resistance R_p and corrosion current Icorr through potential steps around the corrosion potential.

Potentiodynamic cycling with galvanostatic acceleration (PCGA): Battery technique designed for battery cycling under stepwise potentiodynamic mode. The user can reduce the potential step duration if the charge or discharge is lower than a given value.

Potentiostatic impedance (PEIS): technique that performs impedance measurements into potentiostatic mode by applying a sinus around a potential E that can be set to fixed value or relatively to the cell equilibrium potential.

Technique linker: tool of EC-Lab® software used to link techniques in order to build a complete experiment with or without open circuit period between techniques.

Reverse Normal Pulse Voltammetry (RNPV): technique used in analytical electrochemistry to discriminate faradic from capacitive current. This technique is made of increasing pulses with time that always come back to the beginning potential. The current is sampled in the opposite way as for the NPV technique.

Run: button that starts the experiment.

Scan rate: speed of the potential sweep defined with the smallest possible step amplitude

Square Wave Voltammetry (SWV): technique used in analytical electrochemistry to discriminate faradic from capacitive current. This technique is made of successive positive and negative pulses according to the averaged potential sweep.

Stepwise Potential Fast Chronoamperometry (SPFC): Simple general electrochemistry technique used to loop quickly on two potential steps.

Triggers: option that allows the instrument to set a trigger out (TTL signal) at experiment start/stop or to wait for an external trigger in to start or stop the run.

Zero Resistance Ammeter (ZRA): technique used to perform measurements to examine the effects of coupling dissimilar metals or to perform some types of electrochemical noise measurements.

Zero Voltage Current (ZVC): technique similar to ZRA except that the control is done between the working and the reference electrode.

9. Index