EC-Lab® Software: Techniques and Applications

Version 10.38 – August 2014

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 shall not be used for any 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 is connected to a protective ground through the AC supply cable. The continuity of the ground connection should be checked periodically.

ATMOSPHERE

The equipment shall not be operated in corrosive atmosphere. 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 performed 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 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 unauthorized 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.

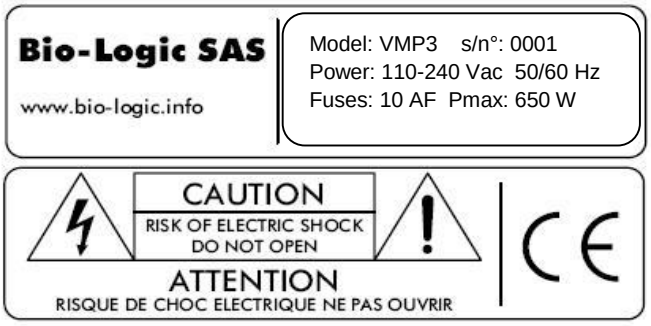
- Improper use of the device,
- Improper installation, operation or maintenance of the device,
- Operating the device when the safety and protective devices are defective and/or inoperable,
- Non-observance of the instructions in the manual with regard to transport, storage, installation,
- Unauthorized 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. 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,
- Improper installation, operation or maintenance of the device,
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- 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.

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 our potentiostats (single or multi-channels: SP-50 SP-150, SP-200, SP-240 and SP-300, MPG2xx series, VMP2(Z), VMP3, VSP, VSP-300, VMP300, HCP-803, HCP-1005, CLB-500 and CLB-2000). 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 interrupting the experiment. The channels can be interconnected and run synchronously, for example to perform multi-pitting experiments using a shared counter-electrode in a single bath (N-Stat mode).

One computer (or several for multichannel instruments) connected to the instrument controls and monitors the system. The computer is connected to the instrument through an Ethernet or USB connection. With the Ethernet connection, each one of the users is able to control his/her own channel from his/her 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 shutdown of the controlling 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 **Electrochemical Techniques** contain general voltamperometric (Cyclic Voltammetry, Chronopotentiometry) techniques, differential techniques, impedance techniques, and a technique builder including modular potentio and galvano, triggers, wait, and loop options. The **Electrochemical 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 the working electrode potential or 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 each technique and application available in the EC-Lab® software. The first part is an introduction. The second part describes the electrochemical techniques. The third part explains the electrochemical applications. The fourth chapter 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. Please note that another manual is available detailing the various graphic and analysis toolsoffered by EC-Lab®.

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

Note that for all these techniques (except OCV), in addition to the time, the potential and the current, the charge $Q\text{-}Q_0$ is calculated and saved in the data file.

2.1.1 OCV: Open Circuit Voltage

The Open Circuit Voltage (OCV) consists in a period during which no current can flow and no potential can be 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 the system to reach a thermodynamic equilibrium.

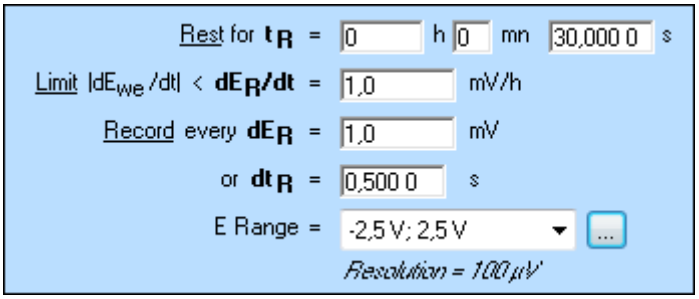


Fig. 1: Open Circuit Voltage Technique.

Rest for t_R = ... h ... mn ... s
sets a defined duration t_R for the recording of 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 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.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment).

2.1.2 SOCV: Special Open Circuit Voltage

As the OCV period, the Special Open Circuit Voltage (OCV) consists in 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. An additional limit condition on Analog In1 or Analog In2 is added, which makes it special.

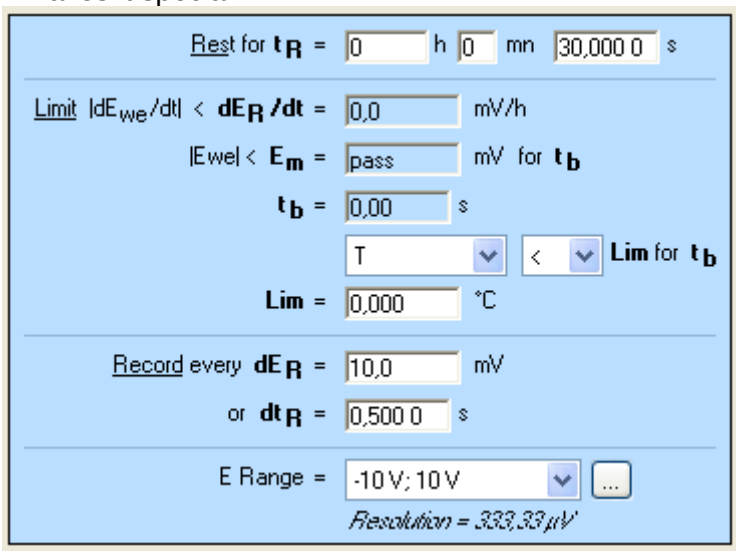


Fig. 2: Special Open Circuit Voltage Technique.

Rest for t_R = ... h ... mn ... s
sets a defined time duration t_R for recording the rest potential.
Limit $|dE_{we}/dt| < |dE_R/dt|$ = ... 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 $|E_{we}| < |E_m|$ = ... 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 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.

2.1.3 CV: Cyclic Voltammetry

Cyclic Voltammetry (CV) is the most widely used technique to acquire quantitative information about electrochemical reactions. CV provides information on redox processes, heterogeneous electron transfer reactions and adsorption processes. It offers a rapid location of redox potentials of the electroactive species.
The CV technique consists in scanning the potential of a stationary working electrode using a triangular potential waveform. During the potential sweep, the potentiostat measures the cur-

rent resulting from electrochemical reactions occurring at the electrode interface and consecutive to the applied potential. The cyclic voltammogram is a current response plotted as a function of the applied potential.
Traditionally, this technique is performed using an analog ramp. Due to the digital nature of the potentiostat, the actual applied ramp consists in a series of small potential steps that approximate the targeted linear ramp (see the control potential resolution part in the EC-Lab® Software User's Manual).

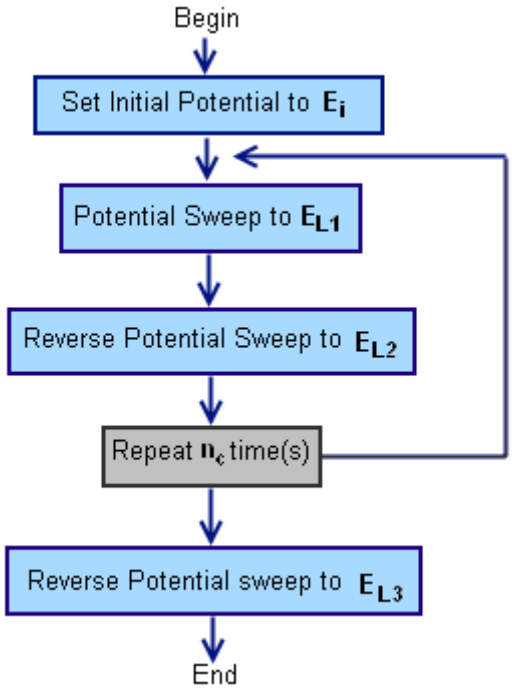


Fig. 3: General diagram for Cyclic Voltammetry.

The "Cyclic Voltammetry" technique has been briefly detailed in the EC-Lab® Software User's Manual. This technique corresponds to normal cyclic voltammetry, using a digital potential staircase *i.e*. it runs defined potential increments at regular time intervals. The software adjusts the potential steps (composing the increment) to be as small as possible.

The technique is composed of (Fig. 2, Fig. 3 and Fig. 4):
- 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 (in the Fig. below) is made of five blocks (it is also possible to display the column diagram Fig. 5):

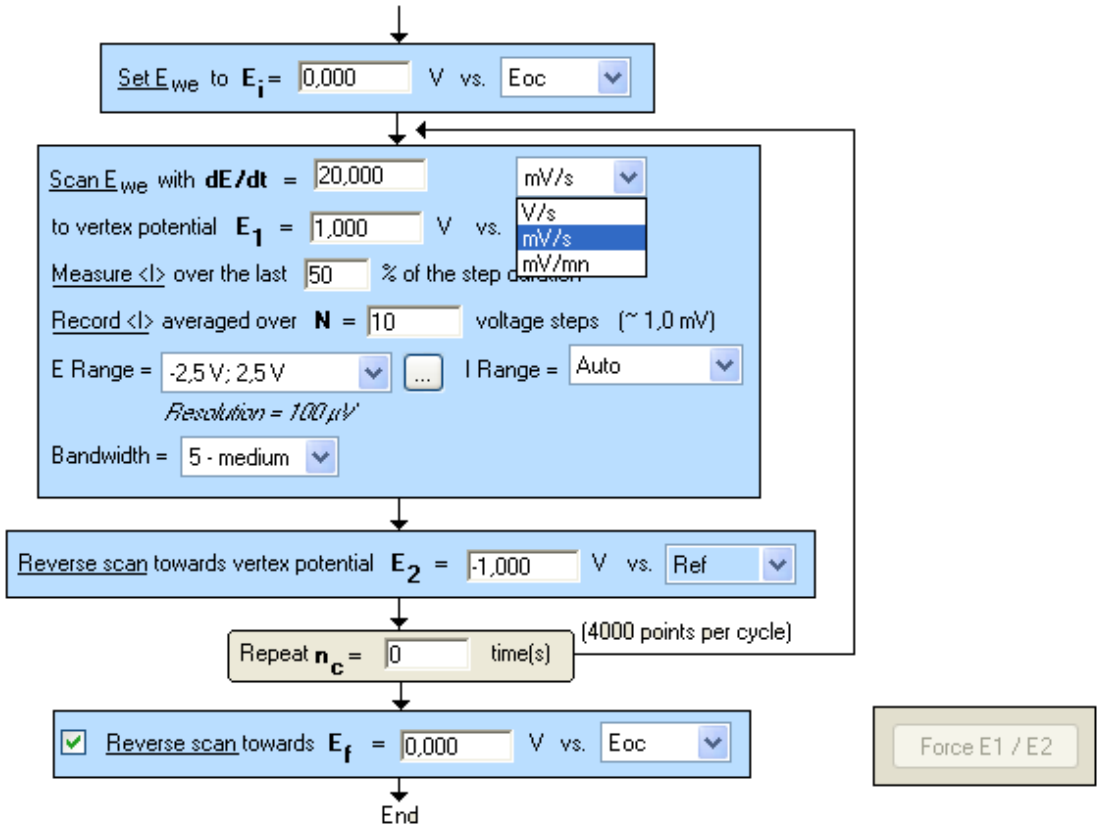


Fig. 4: Cyclic Voltammetry detailed flow diagram.

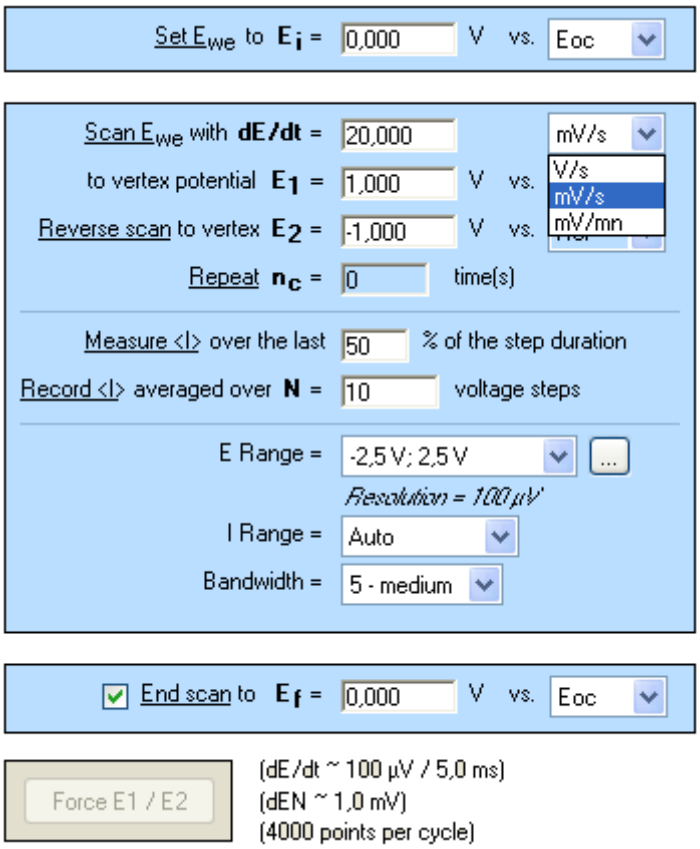


Fig. 5: Cyclic Voltammetry detailed column diagram.

- **Starting potential**

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

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

Scan E_{we} with dE/dt = ... V/s / mV/s / mV/mn
allows the user to set the scan rate in V/s, mV/s or mV/mn. 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 User's Manual).

to vertex potential E_1 = ... V *vs.* Ref/Eoc/Ei.
sets the first vertex potential value *vs.* reference electrode potential or *vs.* the open circuit potential (E_{oc}) or *vs.* the potential of the previous experiment (E_i).

- **Reverse scan**

Reverse scan to 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 *vs.* reference electrode potential 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**

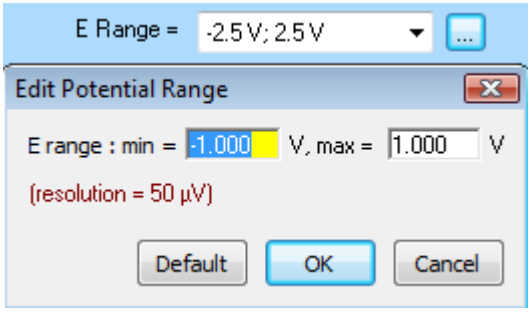
Repeat n_c = ... times
repeats the scan from E_i to E_1 and to E_2, n_c time(s). Note that the number of repetition does not include the first sequence: if n_c = 0 then the sequence will be done once; if n_c = 1 the sequence will be done twice, if n_c = 2, the sequence will be done 3 times, etc…

- **Data recording conditions**

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. It may be necessary to exclude the first points of the current response, which may only be due to the capacitive rather than faradic behavior of the system.

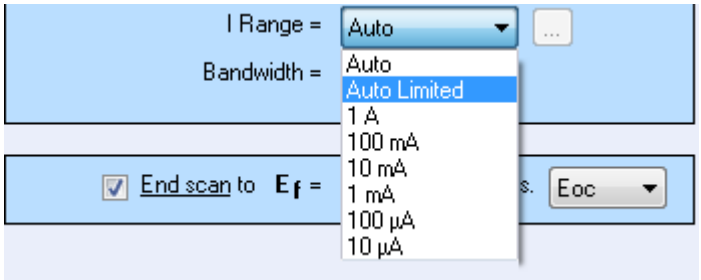
Record <I> averaged over N = ... voltage step(s)
averages N current values on N potential steps, in order to reduce the data file size and smooth the trace. The potential step between two recording points is indicated between brackets. Once selected, an estimation of the number of points per cycle is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

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment. (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment)

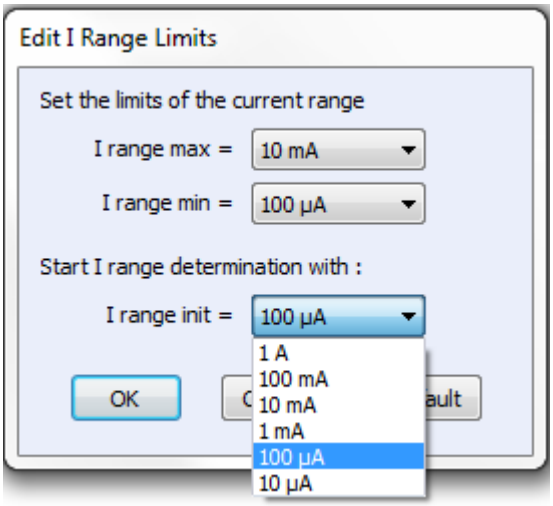


Some potential ranges are defined by default, but the user can customize the E Range in agreement to the system by clicking on ... .
Information on the resolution is given simultaneously to the change of minimum and maximum potentials.

I Range = …
enables the user to select the current range. For controlled voltage techniques three kinds of current range are availables on EC-Lab software: Auto, Auto Limited and fixed current ranges.



The automatic current range is selected when the user has no idea about the amplitude of the measured current. A fixed current range is selected when the amplitude of the measured current is known. Auto limited current range is selected when the measured current varies in wide values ganges (between numerous current ranges). In this last case the user has to set the maximum current range and the minimum current range and also the Inintial current range in the Edit I range Limits window.



In galvano mode only the fixed current range are availables in EC-Lab software.

Bandwidth = …
enables the user to select the bandwidth (damping factor) of the potentiostat regulation.

- **Final potential**

<u>End scan</u> to 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: <u>Force E_1/E_2</u>
During the experiment, 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 to 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 clicking on the "Modify" button, setting the running potential as E_1 or E_2 and validating the modified parameters with the Accept button. The **Force E_1/E_2** button allows the user to perform the operation in a faster way in the case where the potential limits have not been properly estimated and to continue the scan without damaging the cell.

<u>Note:</u> it is highly recommended to adjust the potential resolution from 300 µV (for 20 V of amplitude) to 5 µV (for 0.2 V of amplitude, with a SP-150, VSP or VMP3) according to the experiment potential limits. This will considerably reduce the noise level and increase the plot quality.

<u>Graph tool: Process data to Generate cycles</u>

It is not necessary to process the data file to generate the cycle numbers. The software can generate the cycle numbers by itself. For data recorded with older versions, the user must process the file to generate the cycle numbers.

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

If a data file with several cycles is produced with an older software version, the procedure to generate cycles is:

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

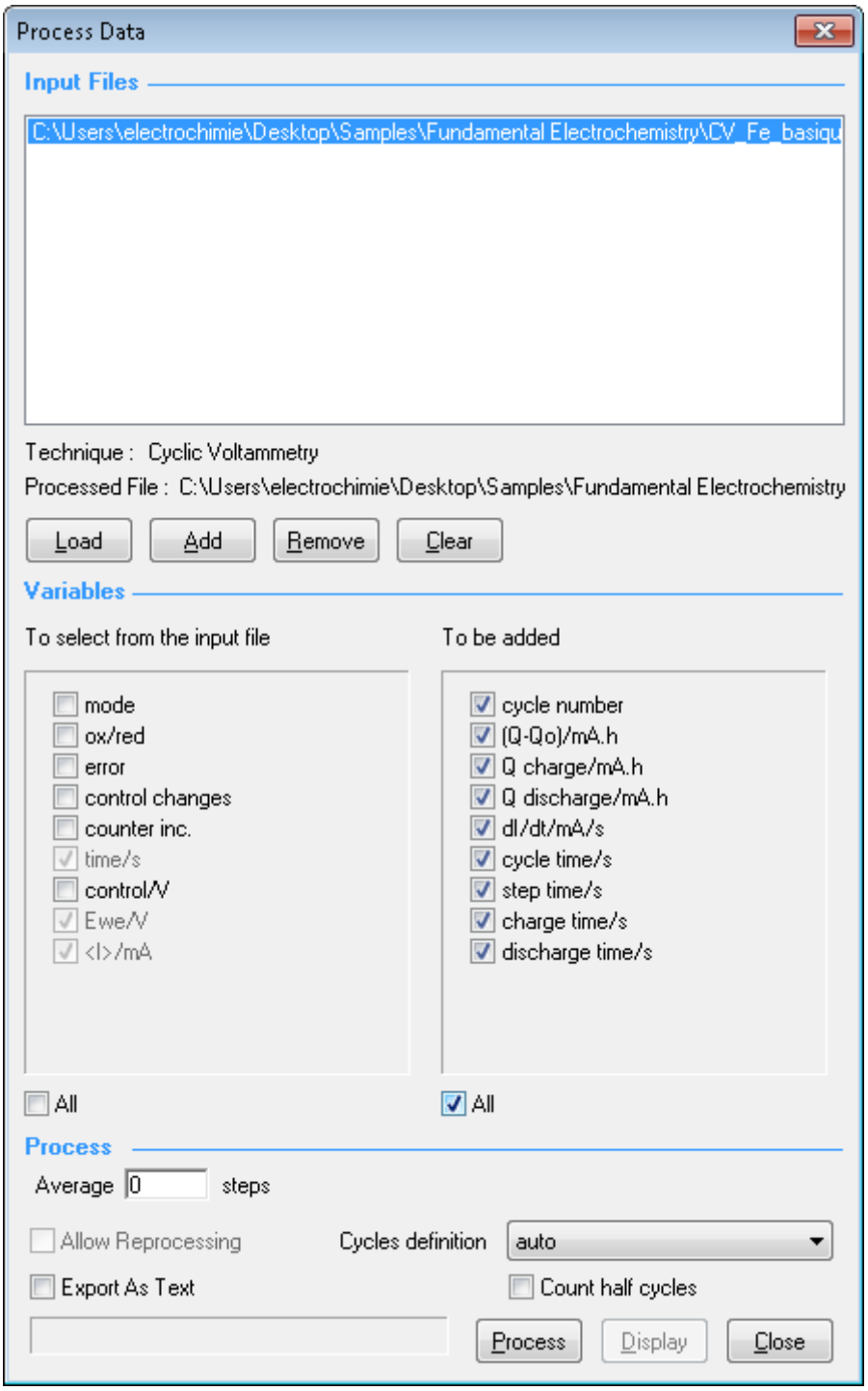


Fig. 6: Cyclic Voltammetry process window.

2) Select the variables to process.
3) Click on the Process box.
4) The process is finished when DONE appears.
5) 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:

- Q charge, the charge passed during the oxidation step where the current is positive
- Q discharge the charge passed during the reduction step where the current is negative
- ($Q-Q_0$), the total charge exchanged from the beginning of the experiment
- dI/dt, the time derivative of the current
- time cycle is the time elapsed during one cycle. The definition of a cycle is chosen in the process window (cf. Fig. 5). One cycle being considered as one potential scan forward and one potential scan backward (i.e. from OCP to E1 to E2, and then from E2 to E1 to E2). The time cycle is reset each time the number of cycles is incremented.
- time charge and time discharge are the total duration of the charge (positive current) or discharge (negative current)
- time step is the time elapsed during one sequence, which can be different from the time elapsed during one cycle.

2.1.4 CVL: Cyclic Voltammetry Linear

The Cyclic Voltammetry Linear is available only for the SP300-based (see Voltamperometric Technique menu, Fig. 6) instruments when the LSG option is installed (see section **8.1 Linear Scan Generator (LSG)** in the installation and configuration Manual). This technique allows the user to apply a true analog voltage scan (not a staircase scan) between two vertexes of potential.

This option can be coupled with fast scan rate and the hardware ohmic drop compensation could be made.

This technique could be used to detect *e.g.* electroactive species with a short lifetime in a resistive medium.

The data sampling could be made every µs. When the recording timebase (dt) is below 15 µs the instruments switches to a fast acquisition mode. In this mode auto-ranging are disabled.

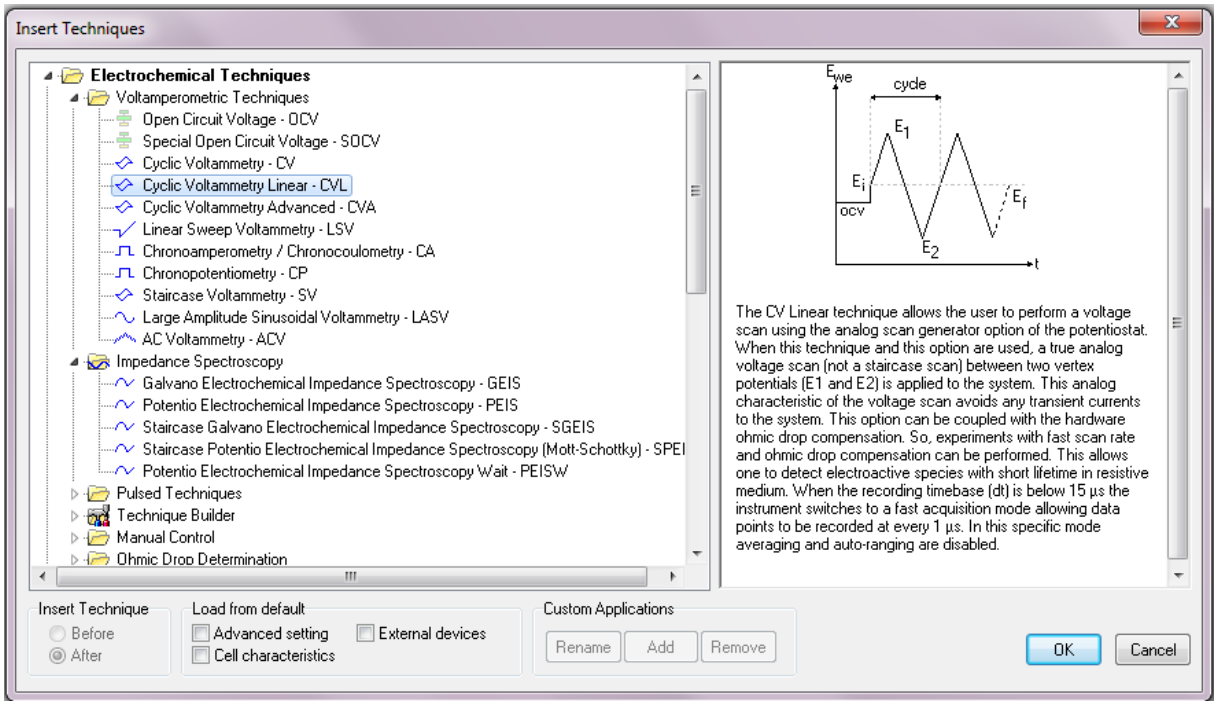


Fig. 7: Technique windows when the LSG option is available.

The technique is composed of (Fig. 7 and Fig. 8):

- 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 initial potential, E_i.

The detailed flow diagram (in the Fig. 8 below) is made of five blocks (it is also possible display the column diagram Fig. 8)

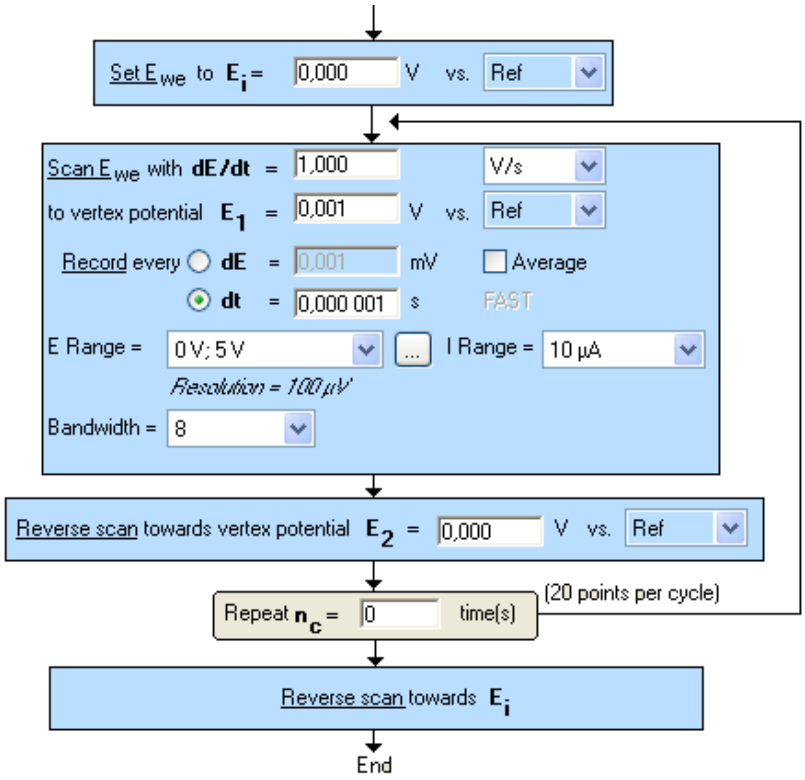


Fig. 8: Cyclic Voltammetry Linear detailed flow diagram.

- **Starting potential**

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

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

Scan E_{we} with dE/dt = ... kV/s / V/s / mV/s / mV/mn
allows the user to set the scan rate in kV/s, V/s, mV/s or mV/mn. As mentioned above a real analog voltage scan.

to vertex potential E_1 = ... V *vs.* Ref/Eoc/Ei.
sets the first vertex potential value *vs.* reference electrode potential or *vs.* the open circuit potential (E_{oc}) or *vs.* the potential of the previous experiment (E_i).

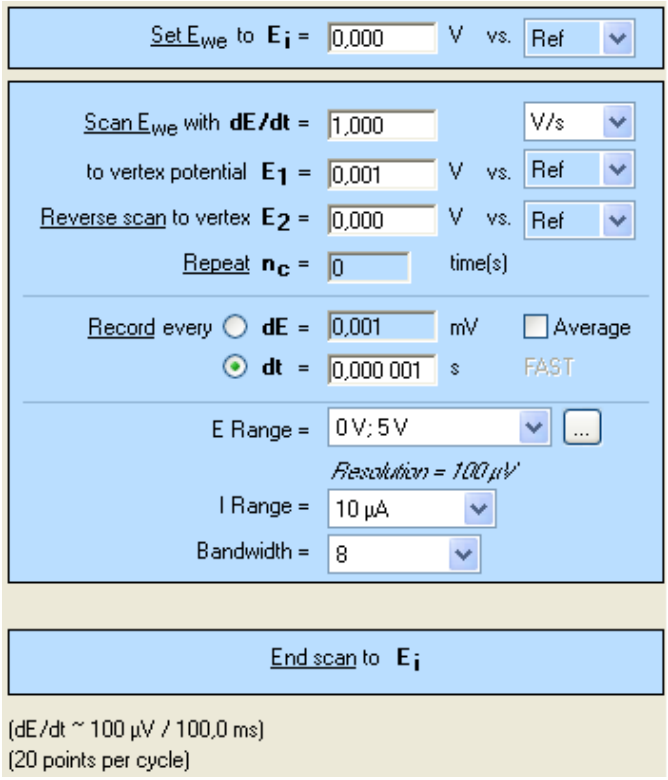


Fig. 9: Cyclic Voltammetry Linear detailed column diagram.

- **Reverse scan**

Reverse scan to 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 *vs.* reference electrode potential 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 scan from E_i to E_1 and to E_2, n_c time(s). Note that the number of repetition does not include the first sequence: if n_c = 0 then the sequence will be done once; if n_c = 1 the sequence will be done twice, if n_c = 2, the sequence will be done 3 times, etc…

- **Data recording conditions**

Record every dE = ... mV
dt = ... s

defines the recording conditions during the potential scan. Only one condition can be selected.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment. (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**

End scan to E_i
the measurement is finished at the starting potential.

Note: CVL technique is not available with CE to ground or WE to ground connections.

2.1.5 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 was implemented to offer the user all the extended capabilities that can be required during a potential sweep. In particular, a table was 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 at 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 choose which cycle to record. 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:
- a starting potential setting block,
- a 1st potential sweep with a vertex limit E_1,
- a 2nd potential sweep in the opposite direction with a vertex limit E_2,
- a possibility to repeat n_c times the 1st and the 2nd potential sweeps,
- a 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 using different rates for each sequence.

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

- **Starting potential:**

Set E_{we} to E_i = ... V *vs.* Ref/Eoc/Ectrl/Emeas
sets the starting potential *vs.* reference electrode potential or *vs.* the open circuit potential (E_{oc}) or the previous 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 = ... V/s / mV/s / mV/mn
allows the user to set the scan rate in V/s, mV/s or mV/mn. 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 User's Manual).

to vertex potential E_1 = ... V *vs.* Ref/Eoc/Ei.
sets the first vertex potential value *vs.* reference electrode potential or *vs.* the open circuit potential (E_{oc}) or *vs.* the potential of the previous experiment (E_i).

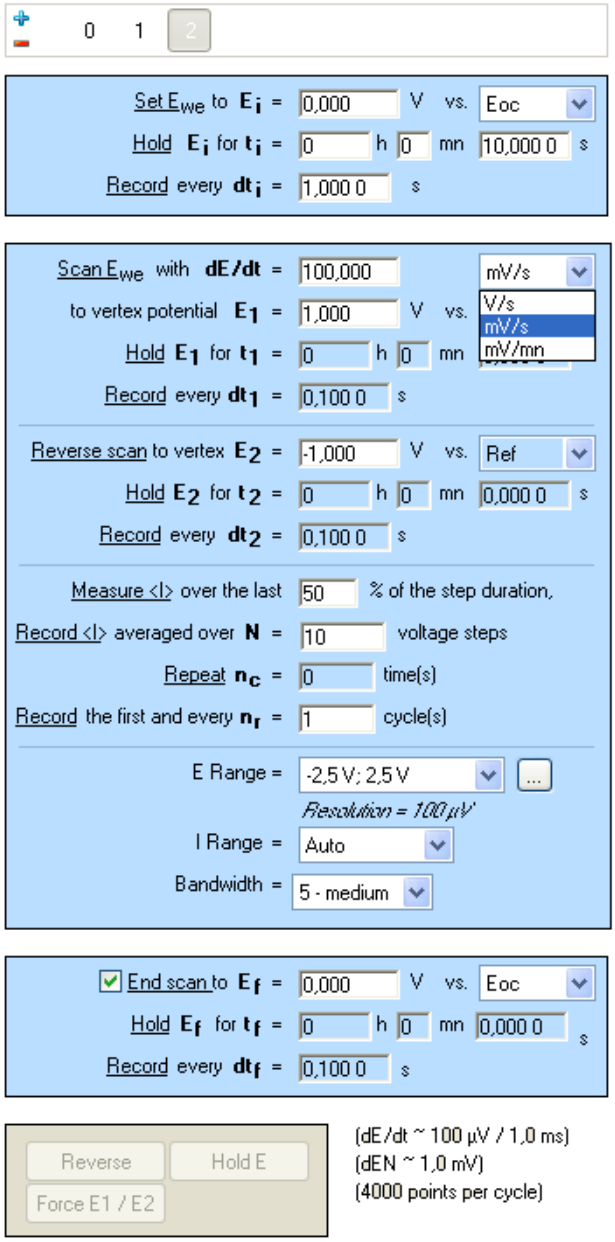


Fig. 10: Cyclic Voltammetry Advanced detailed diagram.

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 to record data points during this holding period.

- **Reverse scan:**

Reverse scan to 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 *vs.* reference electrode potential 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.

- **Data recording conditions**

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. It may be necessary to exclude the first points of the current response, which may only be due to the capacitive rather than faradic behavior of the system.

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.

- **Repeat option for cycling:**

Repeat n_c = ... times
repeats the scan E_i to E_1 to E_2 n_c time(s). Note that the number of repetition does not include the first sequence: if $n_c = 0$ then the sequence will be done once; if $n_c = 1$ the sequence will be done twice, if $n_c = 2$, the sequence will be done 3 times, etc…

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.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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:**

End scan to 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

During the experiment, 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 to 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 clicking on the "Modify" button, setting the running potential as E_{L1} or E_{L2} and validating the modified parameters with the Accept button. The **Force E_1/E_2** button allows the user to perform the operation in a faster way in the case where the

potential limits have not been properly estimated and to 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-50 SP-150, VSP, MPG-2 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 ($Q-Q_0$).

2.1.6 LSV: Linear Sweep Voltammetry

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

- **Rest period**

Rest for t_R = ... h ... mn ... s
sets a defined duration t_R for the recording of the rest potential.

Limit $|dE_{we}/dt| < |dE_R/dt|$ = ... 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.

- **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 E_i = ... V *vs.* Ref/Eoc/Ectrl/Emeas.
sets the intial potential value *vs.* reference electrode potential 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.
sets the limit potential value *vs.* reference electrode potential or according to the previous open circuit potential (E_{oc}), or according to the potential of the previous experiment (E_i).

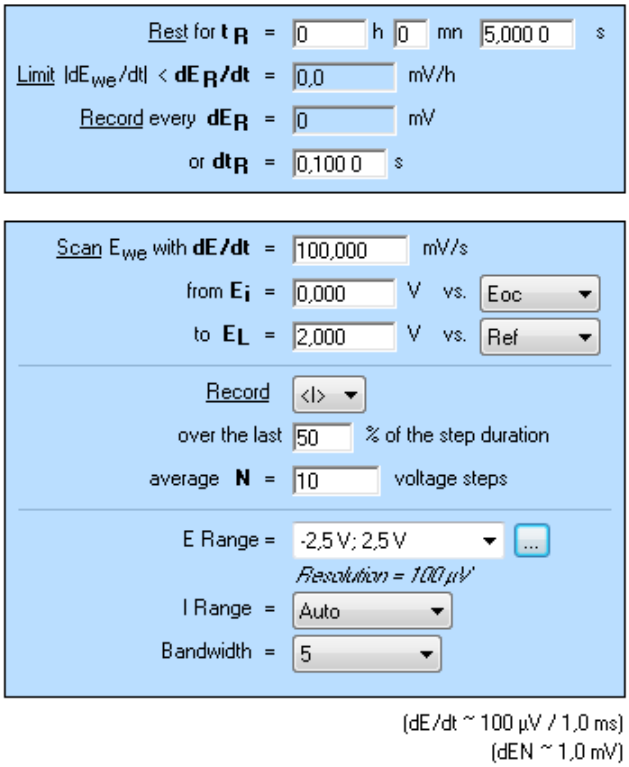


Fig. 11: Linear Sweep Voltammetry detailed diagram.

<u>Record</u> <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.

average N = ... voltage step(s)
averages N current values over 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 and to adjust the potential resolution according **to the experiment** (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.

2.1.7 CA: Chronoamperometry / Chronocoulometry

The basis of the controlled-potential techniques is the measurement of the current response to an applied potential step.
In the Chronoamperometry technique a constant potential E_i is applied for a duration t_i and the current is measured. The current-time response reflects the change of the concentration gradient in the vicinity of the surface. Chronoamperometry is often used to measure 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 way of recording the electrochemical response is to integrate the current, so that one obtains the charge passed as a function of time. This is the chrono-coulometric mode that is particularly used for measuring the quantity of adsorbed reactants.

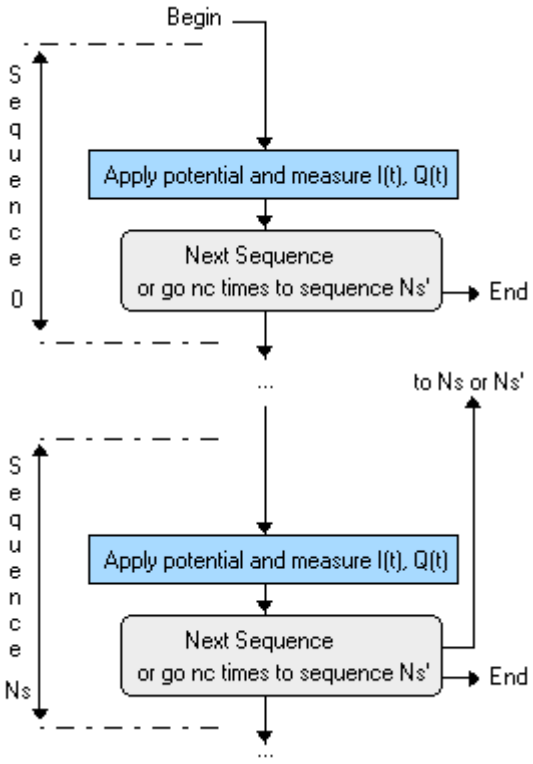


Fig. 12: Chronoamperometry / Chronocoulometry general diagram.

The detailed diagram is composed of two blocks:

- potential step
- loop.

- **Potential step**

<u>Apply</u> E_i = ... V *vs.* Ref/Eoc/Ectrl/Emeas.
the potential step is defined *vs.* 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
sets the potential step duration.

<u>Limits</u> I_{Max} = ... pA/ … /A
I_{min} = … pA/ … /A
$|\Delta Q| > \Delta Q_M$ = ... fA.h/ … /A.h/pC/ … /kC.
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.

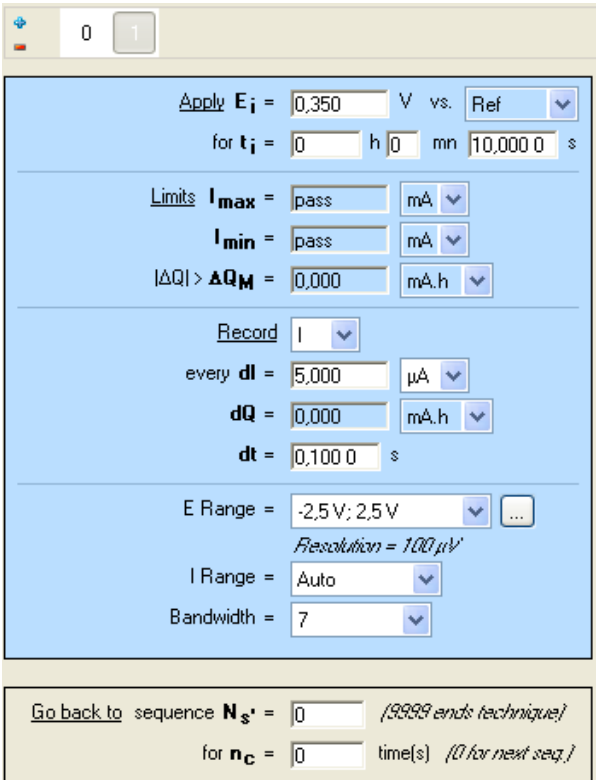


Fig. 13: Chronoamperometry / Chronocoulometry detailed diagram and table.

- **Data recording conditions**

Record I every dI_p = … pA/ … /A, dQ_p = ... fA.h/ … /A.h/pC/ … /kC and dt_p = … s
<I> every dt_a = … s

Either an instantaneous current value I or an averaged current value <I> can be recorded. The recording conditions during the potential step depend on the chosen current variable. For the instantaneous current the recording values can be entered simultaneously. It is the first reached condition that determines the recording. A zero value disables the recording for each condition. For the averaged current, the user defines the time for the calculation of the average. In this, case the data points are recorded in the channel board memory every 200 µs for all instruments.
Set dQ=0 for Chronoamperometry experiments, and dI=0 for Chronocoulometry experiments.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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**

Go back to Ns' = ... for nc = ... time(s)
allows the experiment to go back to a previous sequence $N_{s'}$ (<= N_s) for n_c times. For example, on N_s = 3, if one enters "go back to $N_{s'}$ = 2 for n_c = 1 time", the sequence N_s = 2, N_s = 3 will be executed twice.
n_c = 0 disables the loop and the execution continues to the next sequence ($N_{s'}$ = N_s + 1). If there is no next sequence, the execution stops.

In the current technique, it is possible to loop to the first sequence (N_s = 0) and the current sequence ($N_{s'} = N_s$). This is different from battery experiments (GCPL and PCGA).
Report to the battery techniques section (3.1, page 107) for more details on loop conditions.

Example: Setting $E_i = E_{i1}$ on the first sequence (N_s = 0) and $E_i = E_{i2}$ on the next sequence (N_s = 1), with a loop on the first sequence (goto $N_{s'}$ = 0), will perform the next recording:

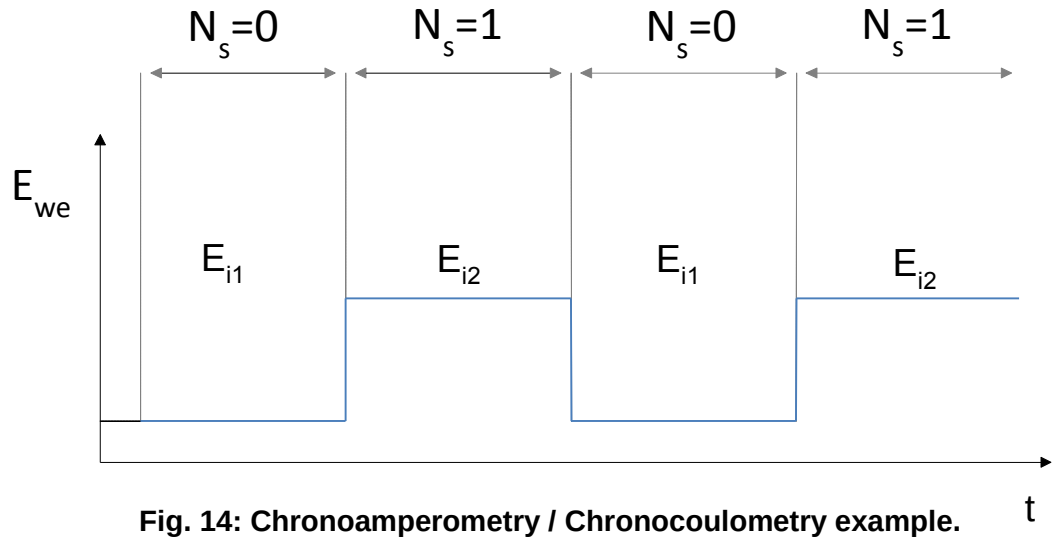


Fig. 14: Chronoamperometry / Chronocoulometry example.

In addition to the usual variables (time, control voltage, measured working potential E_{we}, measured current I and power P), EC-Lab calculates directly another variable dQ, which is the total charge passed during a potential step.

Process: chronocoulometry

A process is associated with chronoamperometry / chronocoulometry technique (see Fig. 14).

The variable that can be processed are:
- Q charge, the charge passed during the oxidation step where the current is positive,
- Q discharge the charge passed during the reduction step where the current is negative,
- $(Q-Q_0)$, the total charge exchanged from the beginning of the experiment,
- dI/dt, the time derivative of the current,
- time cycle, the time elapsed during one cycle, one cycle being considered as one potential scan forward and one potential scan backward (i.e. from OCP to E1 to E2, and then from E2 to E1 to E2, see Fig. 6). The cycle time is reset each time the number of cycles is incremented (see Fig. 6). The step time is the time elapsed during one step (sequence or cycles).

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

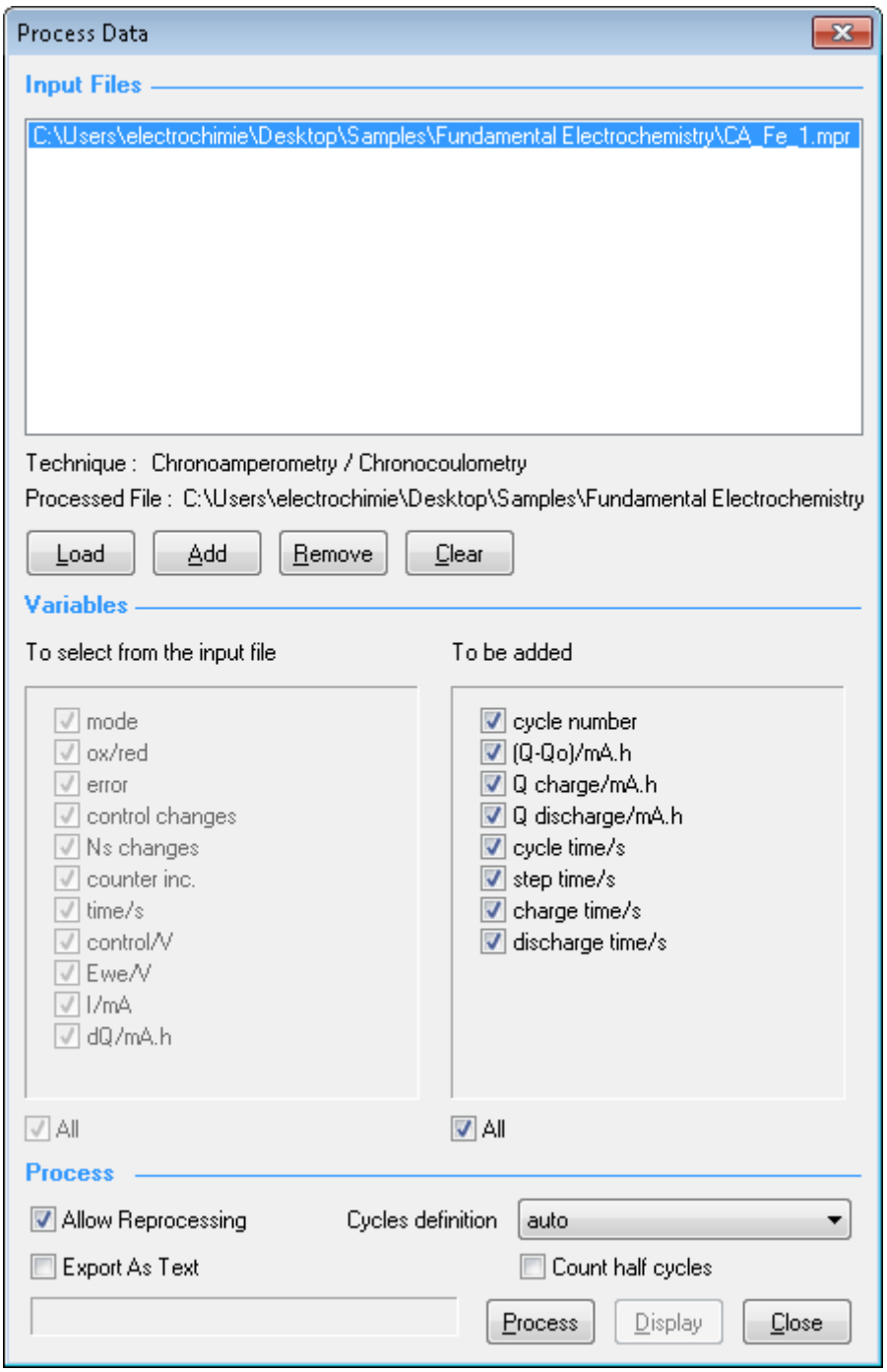


Fig. 15: Chronoamperometry/chronocoulometry processing window.

2.1.8 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 step being replaced by current steps. The constant current is applied between the working and the counter electrode.

This technique can be used to investigate electrode kinetics but 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.

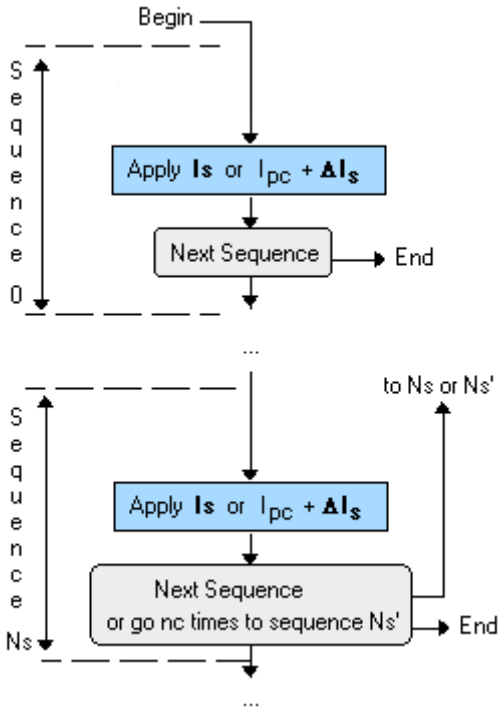


Fig. 16: Chronopotentiometry general diagram.

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.

- **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
sets the current step duration.

Limits $|E_{we}| > E_M$ = ... V
$|\Delta Q| > \Delta Q_M$ = ... 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.

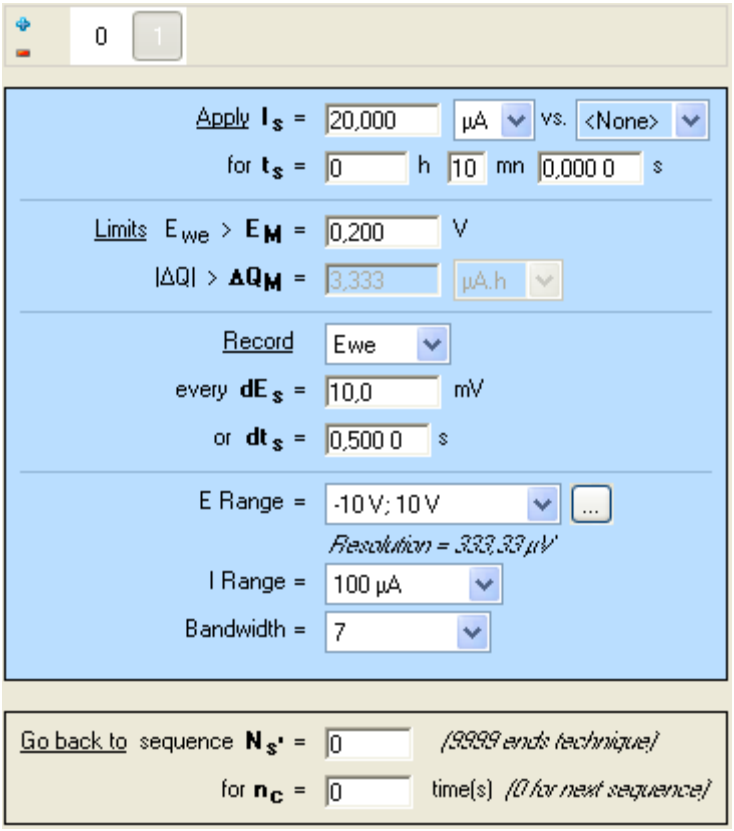


Fig. 17: Chronopotentiometry detailed diagram.

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 remains blue. These values can be entered simultaneously, and this is the first condition that is reached that determines the recording. When <Ewe> is selected, the number of averaged data points is displayed.

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

- **Loop**

Go back to sequence Ns' = ... for nc = ... time(s)
allows the experiment to go back to a previous sequence $N_{s'}$ (<= N_s) for n_c times. For example, on N_s = 3, if one enters “go back to $N_{s'}$ = 2 for n_c = 1 time”, the sequence N_s = 2, N_s = 3 will be executed twice.
n_c = 0 disables the loop and the execution continues to the next sequence ($N_{s'}$ = N_s + 1). If there is no next sequence, the execution stops.
In the current technique, it is possible to loop to the first sequence (N_s = 0) and the current sequence ($N_{s'}$ = N_s). This is different from battery experiments (GCPL and PCGA).
Report to the battery techniques section (3.1, page 107) for more details on loop conditions.

- **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.

2.1.9 SV: Staircase Voltammetry

Staircase Voltammetry (SV) is one of the most widely used techniques for acquiring qualitative information about electrochemical reactions. SV, similarly to 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 in linearly scanning the potential of a 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 the electrochemical reactions consecutive to the applied potential. The cyclic voltammogram is displayed as a current response *vs.* the applied potential. Unlike the CV technique, the potential steps are not minimized by the software but adjusted exactly to the user's convenience.

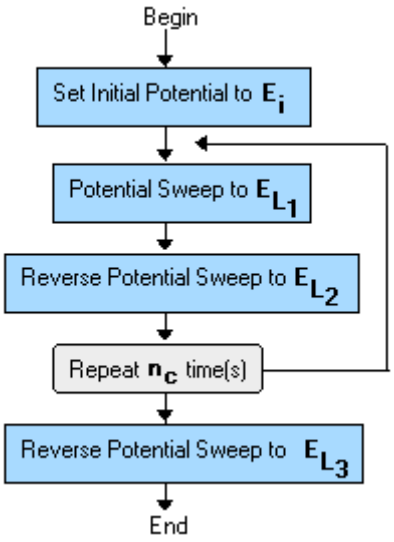


Fig. 18: General diagram for Staircase Voltammetry.

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:

- **Starting potential**

Set E_{we} to E_i = ... V *vs.* Ref/Eoc/Ectrl/Emeas
sets the starting potential *vs.* reference electrode potential or *vs.* the open circuit potential (E_{oc}) or the previous 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
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 User's Manual).

to vertex potential E_1 = ... V *vs.* Ref/Eoc/Ei.
sets the first vertex potential value *vs.* reference electrode potential or *vs.* the open circuit potential (E_{oc}) or *vs.* the potential of the previous experiment (E_i).

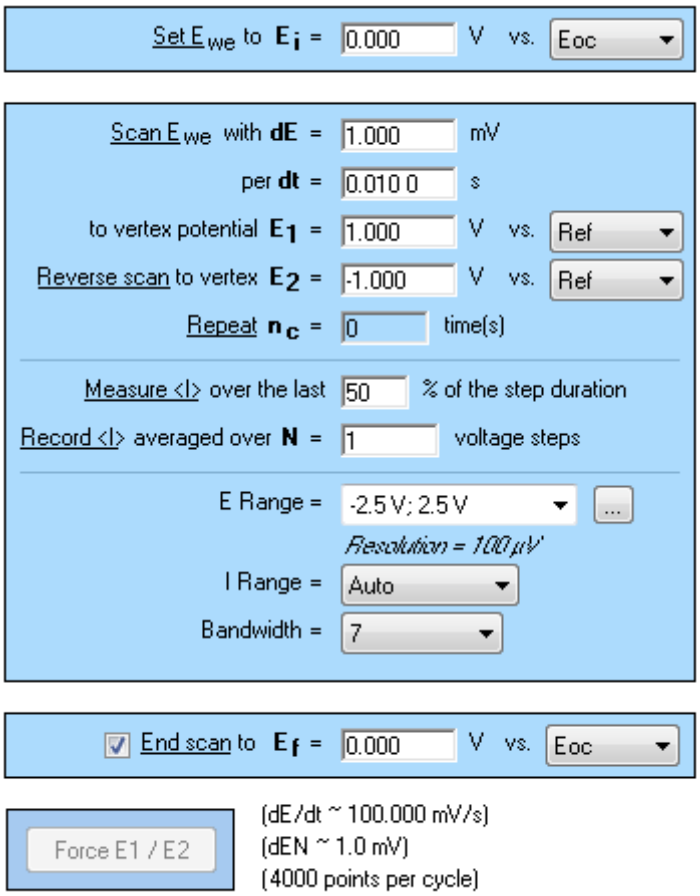


Fig. 19: Staircase Voltammetry detailed diagram.

- **Reverse scan**

Reverse scan to 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 *vs.* reference electrode 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 scan E_i to E_1 to E_2 n_c time(s). Note that the number of repetition does not include the first sequence: if n_c = 0 then the sequence will be done once; if n_c = 1 the sequence will be done twice, if n_c = 2, the sequence will be done 3 times, etc…

- **Data recording conditions**

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. It may be necessary to exclude the first points of the current response, which may only be due to the capacitive rather than faradic behavior of the system.

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 and to adjust the potential resolution according to the experiment. (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**

End scan to 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
During the experiment, 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 to 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 clicking on the "Modify" button, setting the running potential as E_1 or E_2 and validating the modified parameters with the Accept button. The **Force E_1/E_2** button allows the user to perform the operation in a faster way in the case where the potential limits have not been properly estimated and to continue the scan without damaging the cell.

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

Graph tool: Generate cycles

See the CV technique for more details.

2.1.10 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 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 transitions at 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.

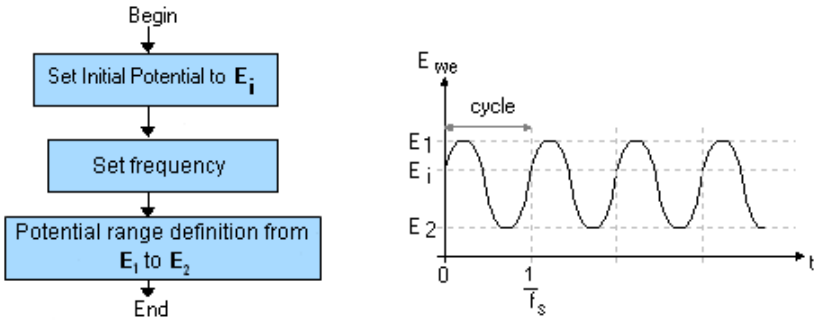


Fig. 20: General diagram for Large Amplitude Sinusoidal Voltammetry.

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 (see Fig. 17) is made of two blocks:

- **Starting potential:**

Set E_{we} to E_i = ... V *vs.* Ref/Eoc/Ectrl/Emeas
sets the starting potential *vs.* 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 f_s = ... kHz/Hz/mHz/µHz
allows the user to set the value of frequency to define the scan rate.

between vertex potential E_1 = … V *vs.* Ref/Eoc/Ei
Sets the first vertex potential value *vs.* reference electrode potential or according to the previous open circuit potential (E_{oc}) or previous potential (E_i).

and vertex E_2 = … V *vs.* Ref/Eoc/Ei
Sets the second vertex potential value *vs.* reference electrode potential, or according to the previous open circuit potential (E_{oc}) or previous potential (E_i).

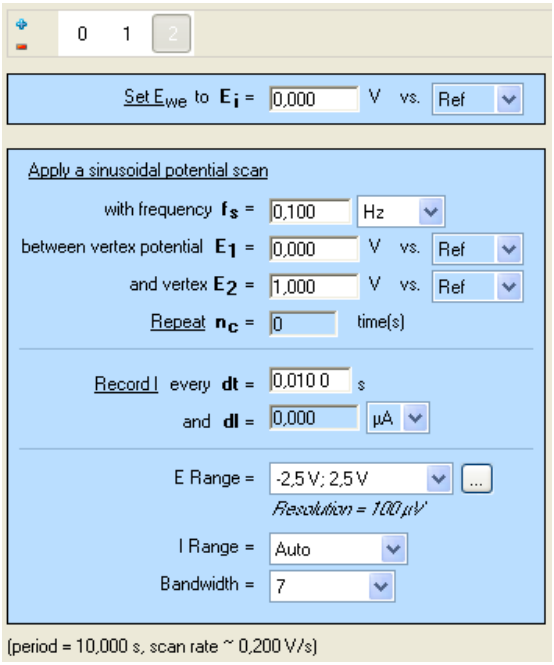


Fig. 21: Large Amplitude Sinusoidal Voltammetry detailed diagram.

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 I every dt = … s and dI = … pA/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 and to adjust the potential resolution according to the experiment. (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.

2.1.11 ACV: Alternating Current Voltammetry

Alternating Current Voltammetry (ACV) is assimilated to a faradaic impedance technique. With 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 mechanisms for instance the fact that a forward and a backward scans are identical characterizes a reversible redox system.

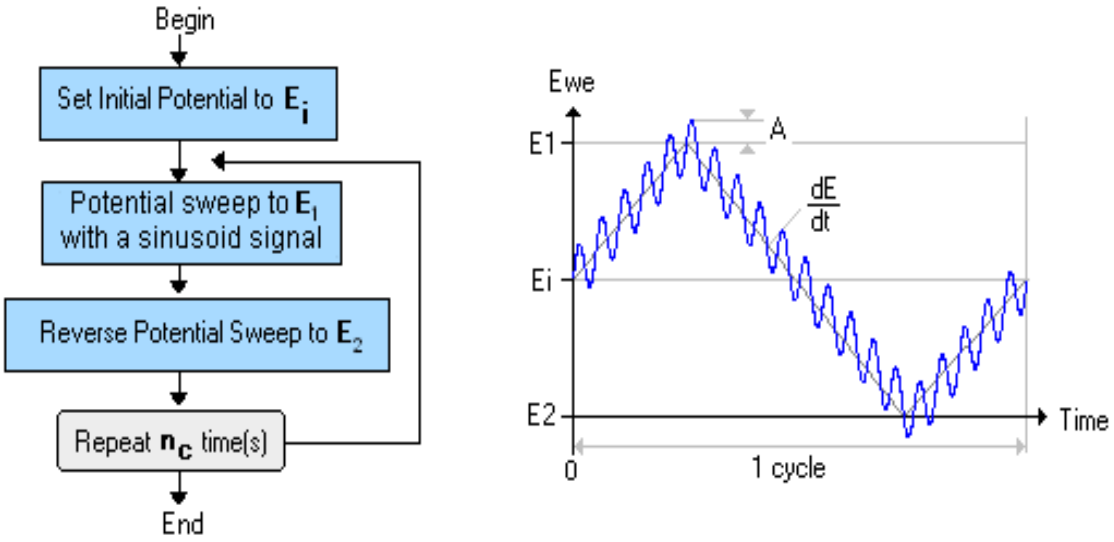


Fig. 22: General diagram for Alternating Current Voltammetry.

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. 19):

- **Starting potential**

Set E_{we} to E_i = … V *vs.* Ref/Eoc/Ectrl/Emeas
sets the starting potential *vs.* reference electrode potential 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
sets the first vertex potential value *vs.* reference electrode potential or according to the previous open circuit potential (E_{oc}) or previous potential (E_i).

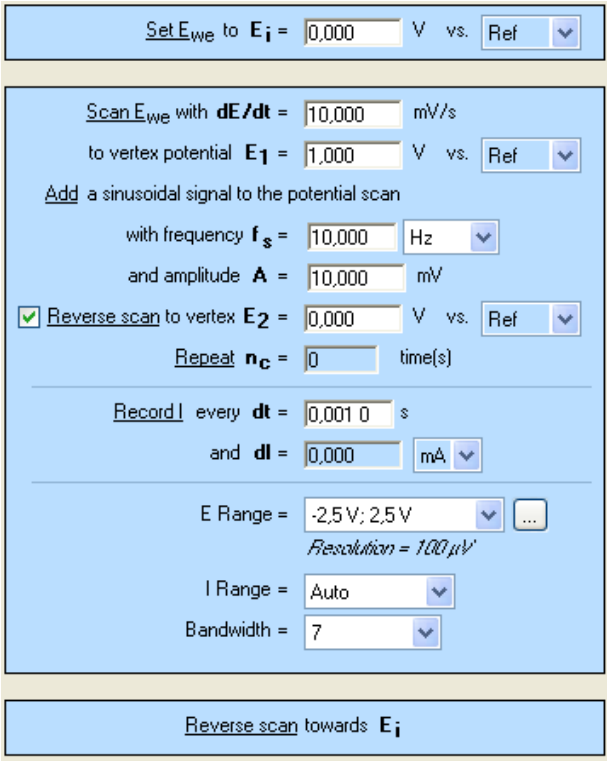


Fig. 23: Alternating Current Voltammetry detailed diagram.

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 fix the value of the vertex potential value *vs.* 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 I 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 and to adjust the potential resolution according to the experiment. (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

The methods based on the 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. The principle of Electrochemical Impedance Spectroscopy (EIS) is to perturb the cell with an alternative signal, and to observe how the systems follows the perturbation at the steady state (the amplitude of perturbation should be small in order to assume the linear behaviour of the system). A high precision is obtained with this method and it is frequently employed to evaluate the heterogeneous charge-transfer parameters and to study the double-layer structure. 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, SP-200, SP-240, VSP-300 and VMP-300, the maximum frequency is 7 MHz. Refer to the application notes for more information on Impedance measurements using EC-Lab®.
Multisine measurements are also available and will be described at the end of this chapter.

2.2.1 PEIS: Potentiostatic Electrochemical Impedance Spectroscopy

2.2.1.1 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.

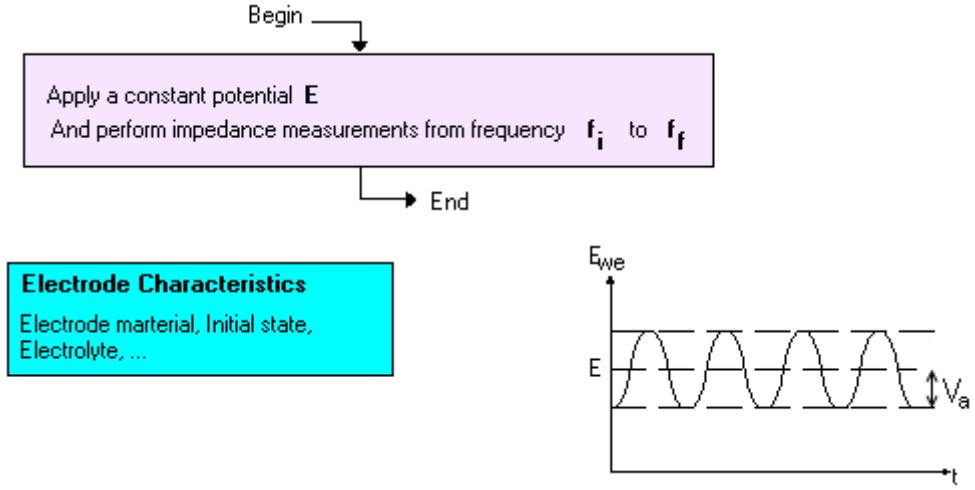


Fig. 24: PEIS general diagram.

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.

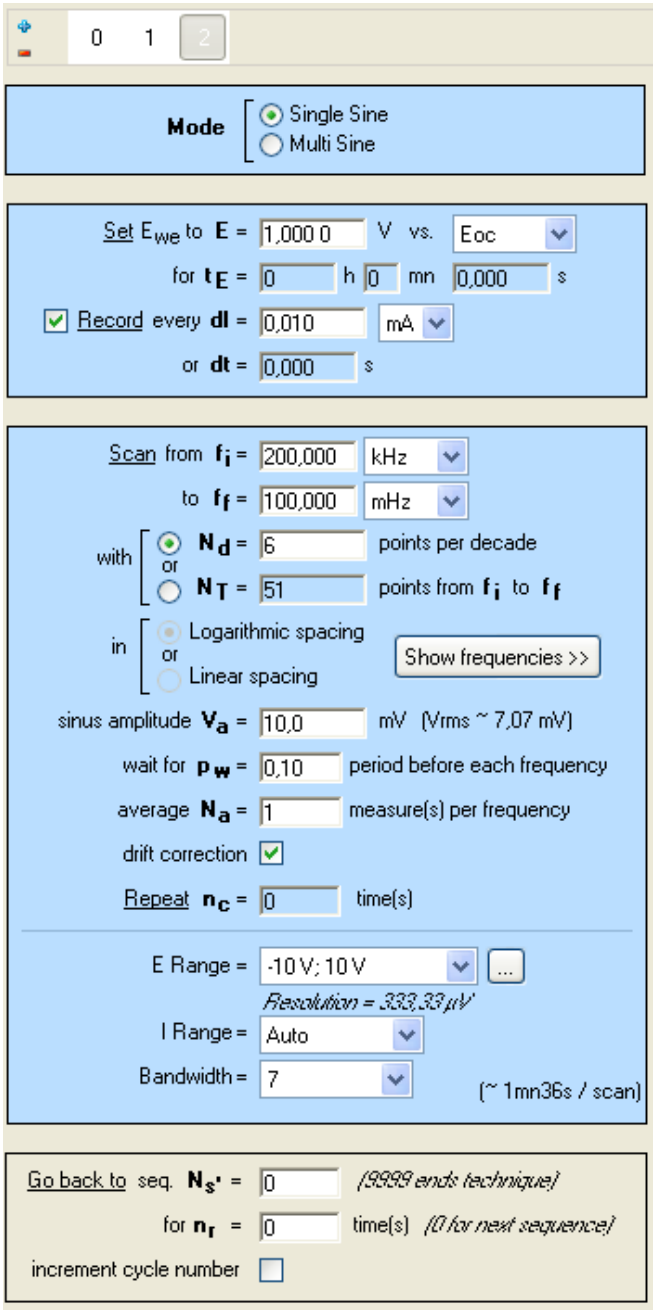


Fig. 25: PEIS detailed diagram.

- **Initial potential**

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

sets the fixed potential *vs.* reference electrode potential or relatively to the previous:
- OCV potential (E_{oc}),
- controlled potential (E_{ctrl}),
- measured potential (E_{meas}),

for a t_E = …

sets t_E large enough to wait for the cell current stabilization, in the case where 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 = … pA/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 dt.

- **Impedance scan**

Scan from f_i = … MHz/ ... /µHz to f_f = … 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
N_t = … points from f_i to f_f

in Logarithm spacing
Linear spacing

defines the frequencies distribution between the scan boundaries 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
Clicking 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.

sinus 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.

□ Drift correction
corrects the drift of the system. It needs to be used when the system has not reached its steady-state regime. This feature is more specifically dedicated to low frequencies at which the impedance measurement can be pretty lengthy and for which the effect of the drift can be seen.
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. For more information about the drift correction, please refer to the Application Note #17.

- **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 and to adjust the potential resolution according to the experiment. (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**

Go back to sequence Ns' = ... for nc = ... time(s)
allows the experiment to go back to a previous sequence $N_{s'}$ (<= N_s) for n_c times. For example, on N_s = 3, if one enters "go back to $N_{s'}$ = 2 for n_c = 1 time", the sequence N_s = 2, N_s = 3 will be executed twice.
n_c = 0 disables the loop and the execution continues to the next sequence ($N_{s'} = N_s + 1$). If there is no next sequence, the execution stops.
In the current technique, it is possible to loop to the first sequence (N_s = 0) and the current sequence ($N_{s'} = N_s$). This is different from battery experiments (GCPL and PCGA).
Report to the battery techniques section (3.1, page 107) for more details on loop conditions.

- **Sequence repetition**

The last part of this technique is dedicated to repeat sequences when many sequences are done. It is possible to add sequence in impedance measurements. This tool is convenient to save time, indeed during the same experiment it is possible to work in single sine mode at high frequencies and in multisine 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.

2.2.1.2 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 save 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}).

2.2.2 GEIS: Galvanostatic Electrochemical Impedance Spectroscopy

This technique is very close to the Potentiostatic Impedance technique (PEIS), except that the current is controlled instead of the potential. Please refer to the PEIS experiment section 2.2.1 for more details.

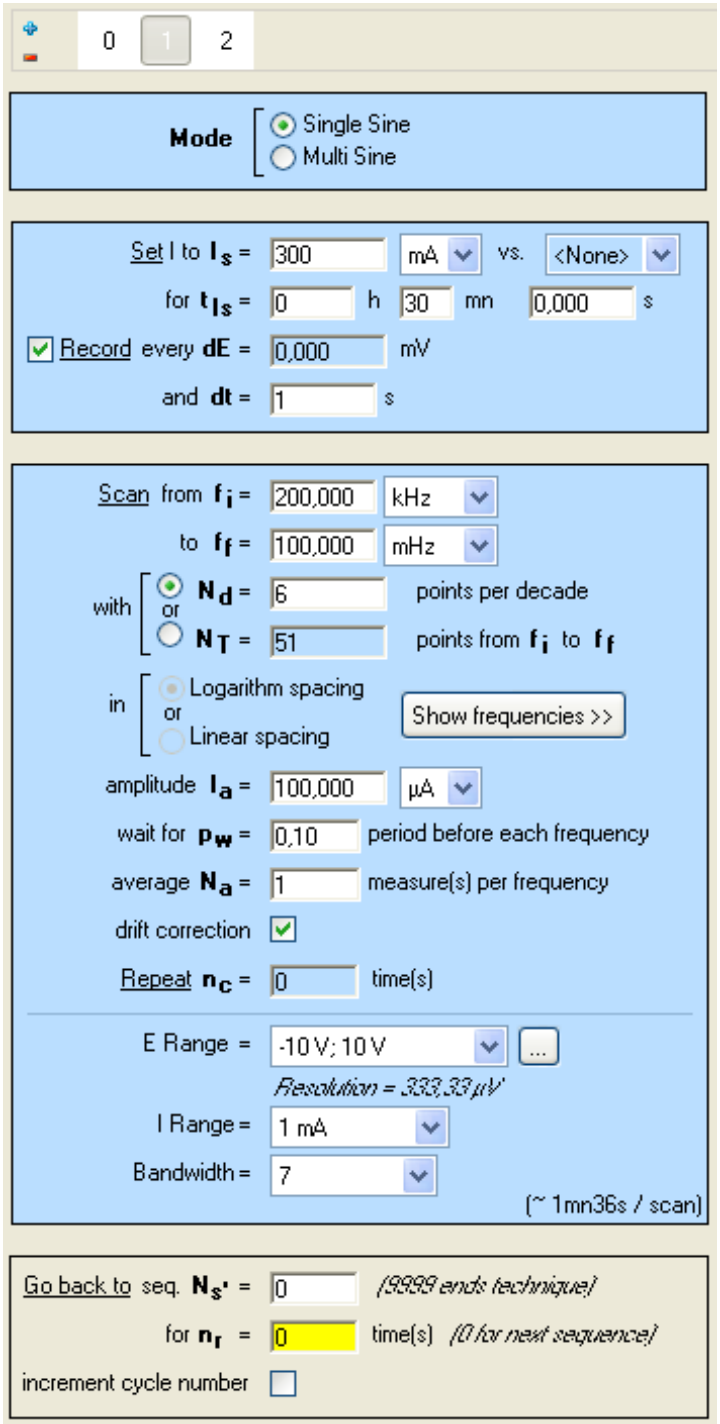


Fig. 26: GEIS detailed diagram.

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 $I_{RMS} = I_a/\sqrt{2}$.

2.2.3 SPEIS: Staircase Potentio Electrochemical Impedance Spectroscopy

The SPEIS and SGEIS powerful techniques are designed to perform successive impedance measurements (on a whole frequency range) during a potential scan (SPEIS) or during a current scan (SGEIS). The main application of these techniques is to study electrochemical reaction kinetics along voltamperometric (*I(E)*) curves in analytical electrochemistry. 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 the study of semi-conductor materials. 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.

2.2.3.1 Description

The SPEIS technique consists in 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.

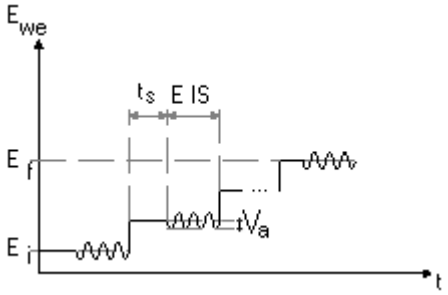


Fig. 27: SPEIS description diagram.

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:

- 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.

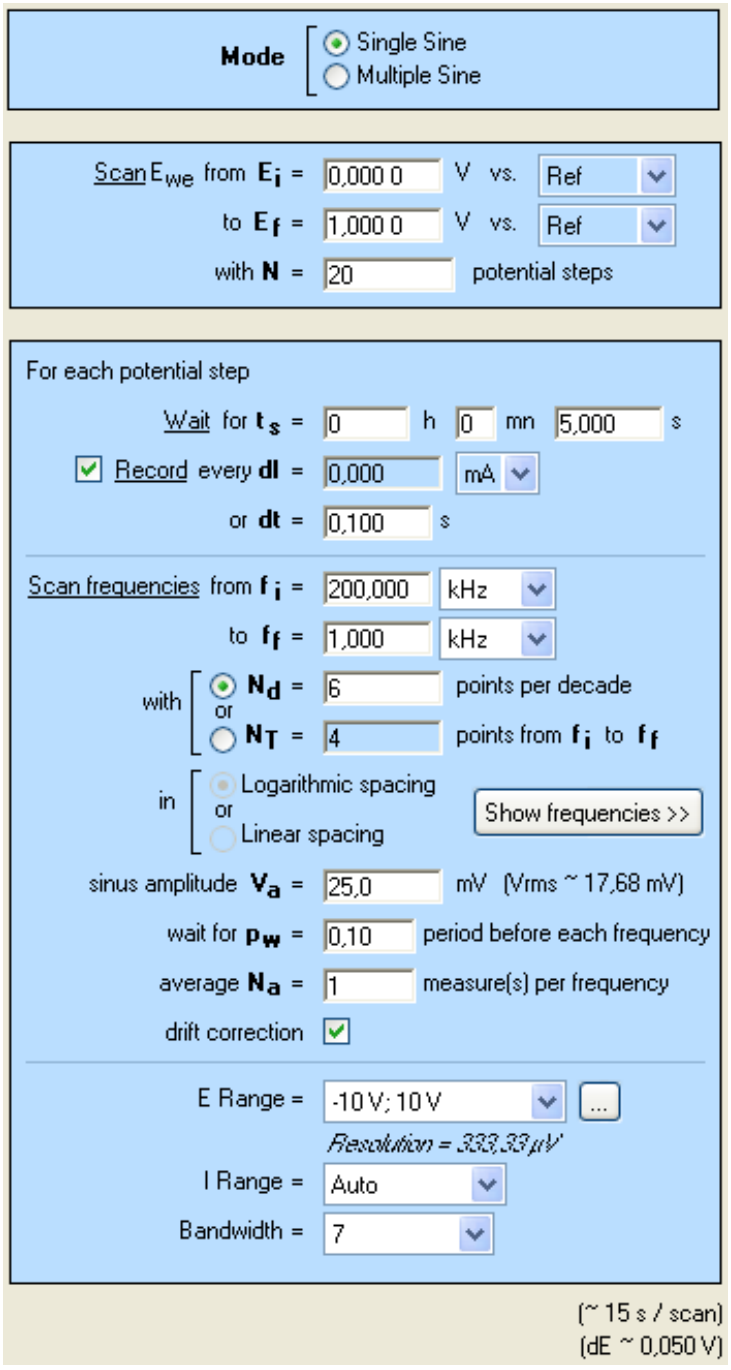


Fig. 28: SPEIS detailed diagram.

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

<u>Scan</u> E_{we} from E_i = … V *vs.*Ref/Eoc/Ectrl/Emeas to E_f = … V *vs.* previous Ref/Eoc/Ei With N = ... potential steps

sets the initial potential to a fixed value *vs.* 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 *vs.* 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**

For each current step
Wait for t_s = … h … mn … s

□ **Record every dI = … pA/nA/../A 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 frequencies from f_i = … MHz/ ... /µHz to f_f = … 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
N_t = … points from f_i to f_f

in Logarithm spacing
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.
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

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 $V_{RMS} = V_{pp}/(2\sqrt{2})$.

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.

□ **Drift correction**
corrects the drift of the system. It needs to be used when the sytem has not reached its styeady-state regime. This feature is more specifically dedicated to low frequencies at which the impedance measurement can be pretty lengthy and for which the effect of the drift can be seen.
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. For more information about the drift correction, please refer to the Application Note #17.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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.

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. As capacitance values are automatically calculated during the experiment this representation is available during the run. 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 User's 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 while it is running.

2.2.3.2 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).

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

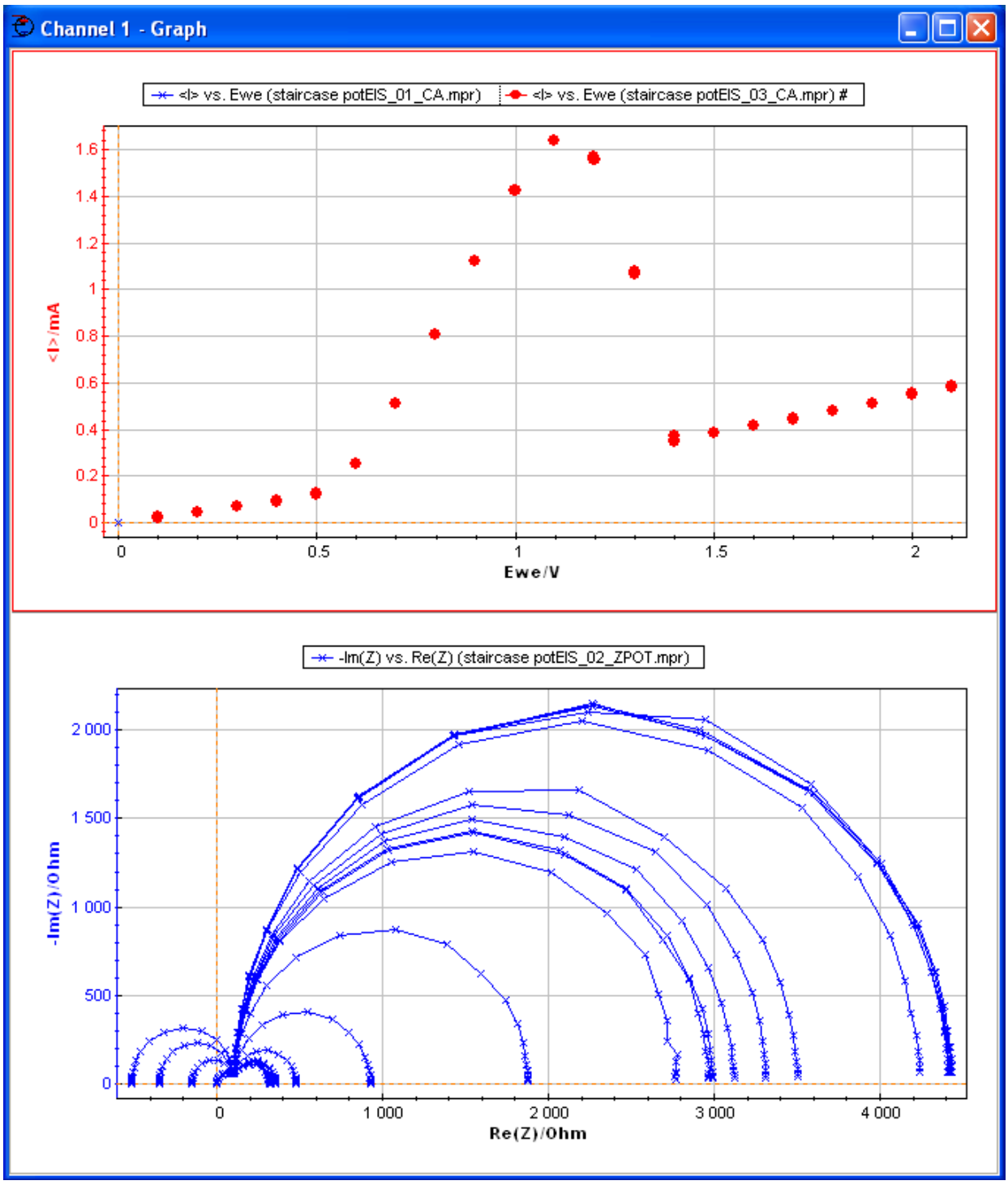


Fig. 29: Application of the SPEIS technique.

2.2.4 SGEIS: Staircase Galvano Electrochemical Impedance Spectroscopy

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

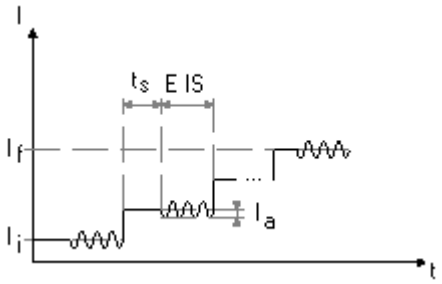


Fig. 30: SGEIS description diagram.

The detailed diagram is made of three blocks (see Fig. 31):

- 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.

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

<u>Scan</u> I from I_i = … pA/ /A *vs.* <None>/Ictrl/Imeas to I_f = … pA/ /A *vs.* <None>/I_i
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**

For each current step
<u>Wait</u> for t_s = … h … mn … s
□ <u>Record</u> every dE = … mV and dt = … s
before the EIS measurement, the sample can rest for a duration t_s. The current can be recorded and no impedance measurement is done.

- **Impedance scan**

<u>Scan frequencies</u> from f_i = … MHz/... /µHz to f_f = … 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
N_t = … points from f_i to f_f

in Logarithm spacing
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.

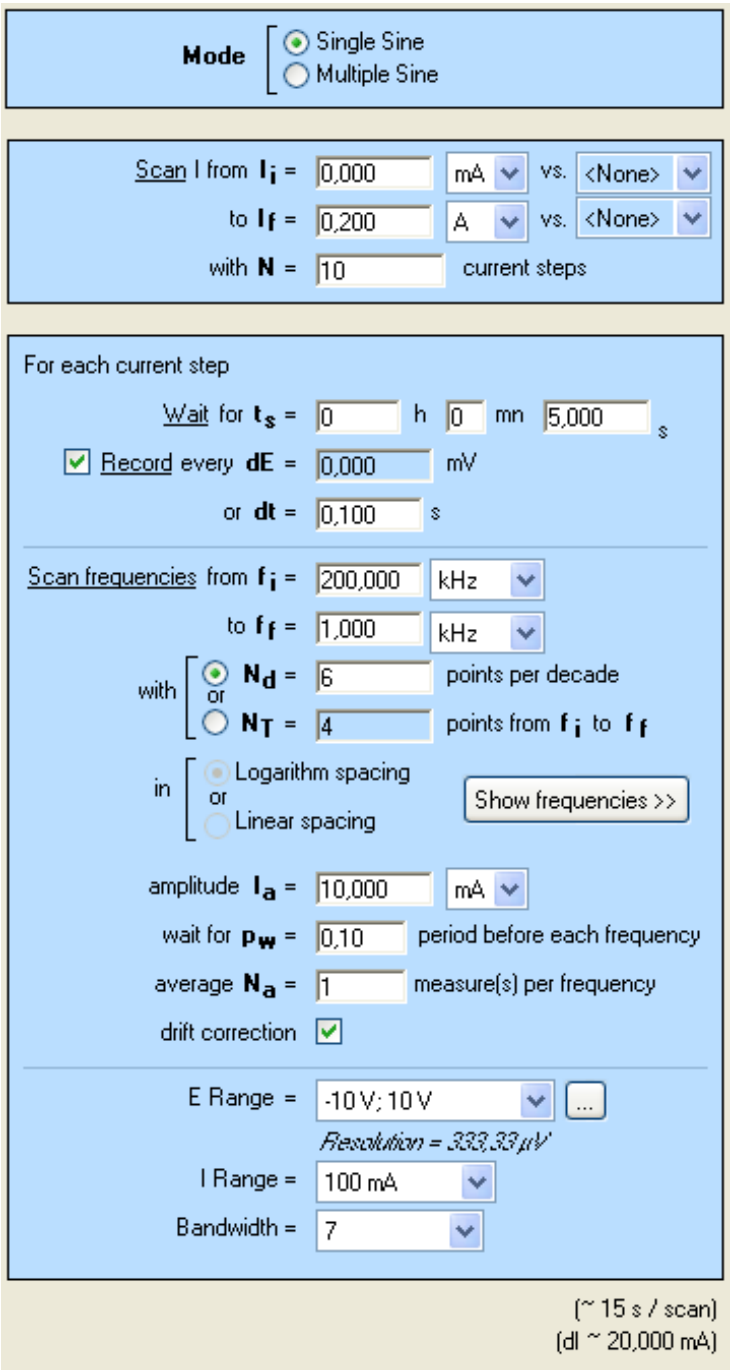


Fig. 31: SGEIS detailed diagram.

with a sinus amplitude I_a = … pA/…/A
sets the sinus amplitude to I_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 = … mesure(s) per frequency
repeats N_a measure(s) and average values for each frequency.

□ **Drift correction**
corrects the drift of the system. It needs to be used when the sytem has not reached its styeady-state regime. This feature is more specifically dedicated to low frequencies at which the impedance measurement can be pretty lengthy and for which the effect of the drift can be seen.
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. For more information about the drift correction, please refer to the Application Note #17.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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 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 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 reaches a defined value or after a certain time.

- **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.

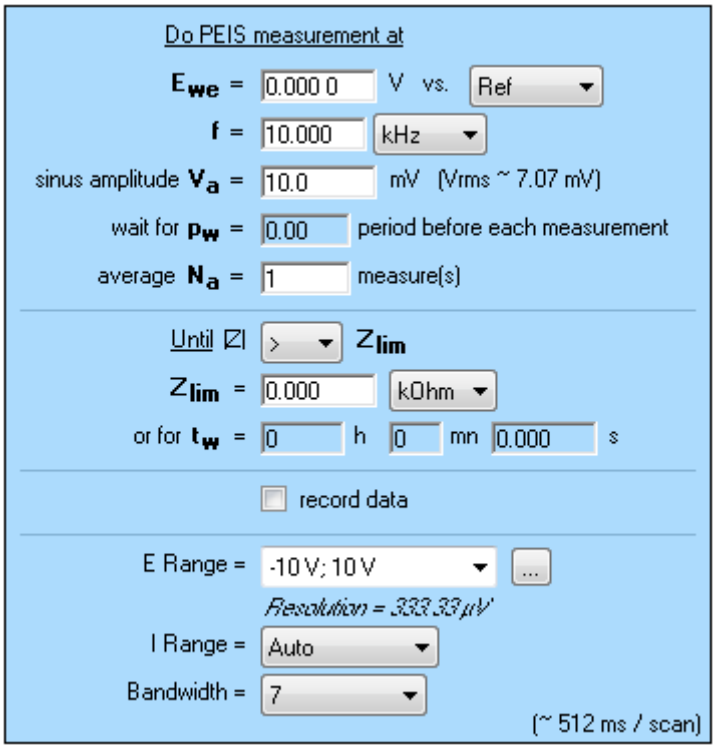


Fig. 32: PEISW detailed diagram.

- **Wait period**

Until IZI >/< Z_{lim}
defines the duration of the wait as a function of a IZI value

Z_{lim} = ... MΩ/kΩ/Ω/mΩ/µΩ
sets the value of |Z|.

Or for tw = ... h ... mn ... s
or as a function of the time.

□ **record data**
offers the user the possibility to record the data before reaching the limit condition.

E Range = …
enables the user to select the potential range for adjusting the potential resolution with his/her 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.

2.2.6 Visualization of impedance data files

2.2.6.1 Standard visualization modes

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

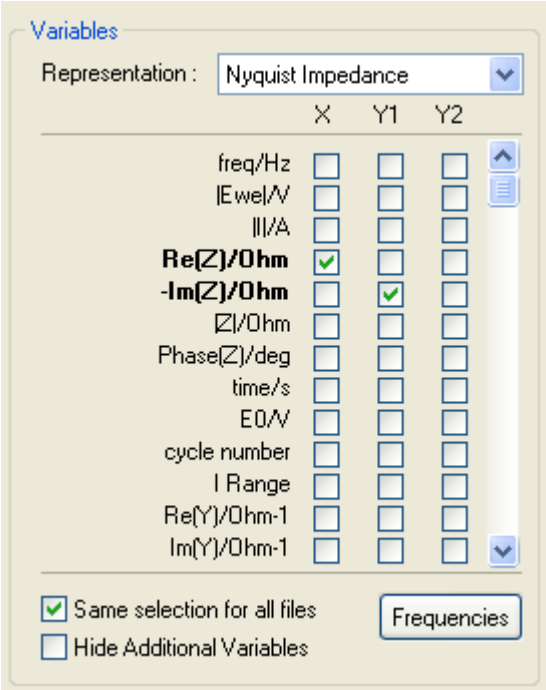


Fig. 33: Impedance data file selector.

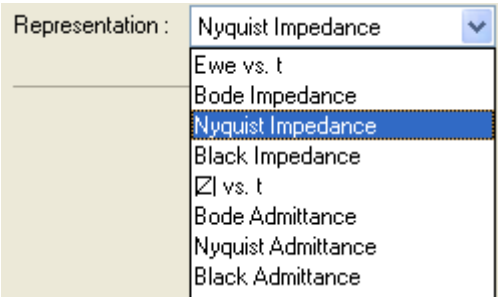


Fig. 34: Impedance graph plot selector.

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| *vs.* log(f) and Z-phase *vs.* log(f) for the impedance
- log|Y| *vs.* log(f) and Y-phase *vs.* 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.

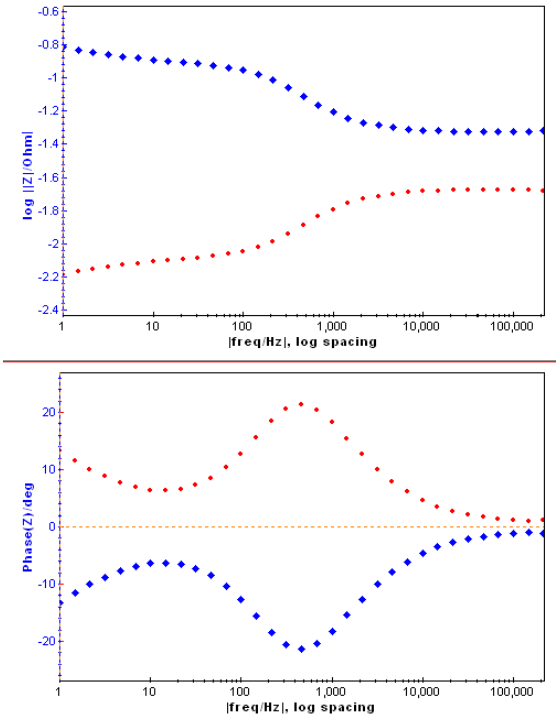


Fig. 35: BODE diagrams for both impedance (blue) and admittance (red).

- Nyquist diagram

The Nyquist diagram is the plot of:

- –Im(Z) *vs.* Re(Z) for impedance
- Im(Y) *vs.* 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 displayed orthonormally.

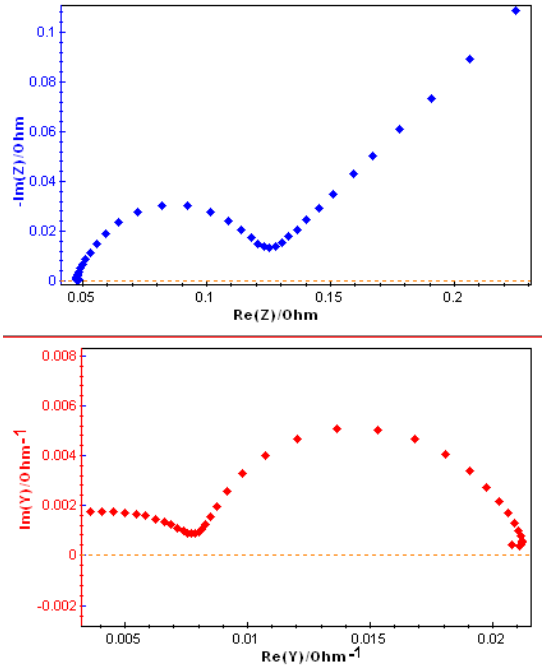


Fig. 36: NYQUIST diagrams for both impedance (blue) and admittance (red).

- Black Diagram

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

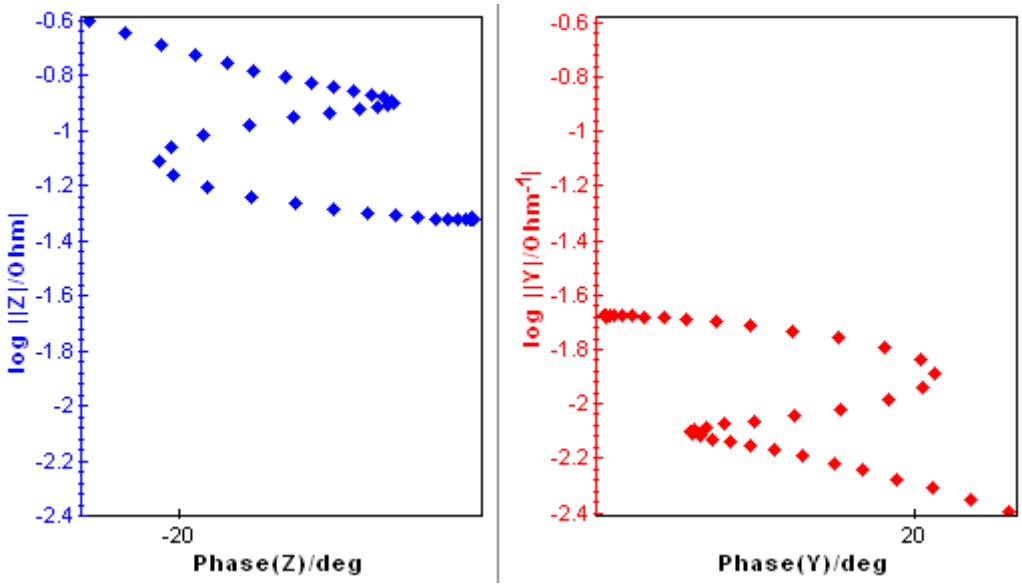


Fig. 37: BLACK diagrams for both impedance (blue) and admittance (red).

2.2.6.2 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.

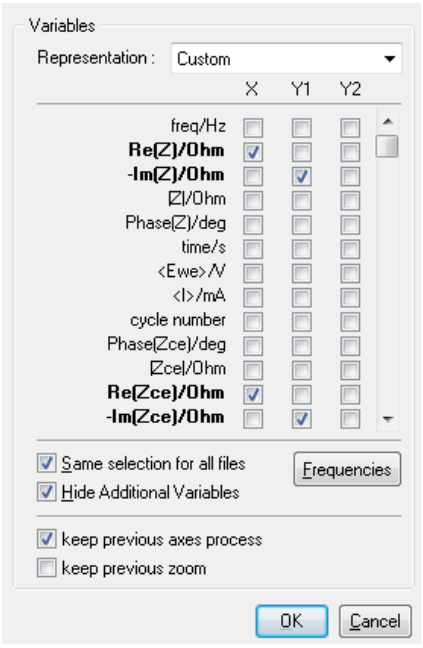


Fig. 38: EIS variable selection window with WE and CE.

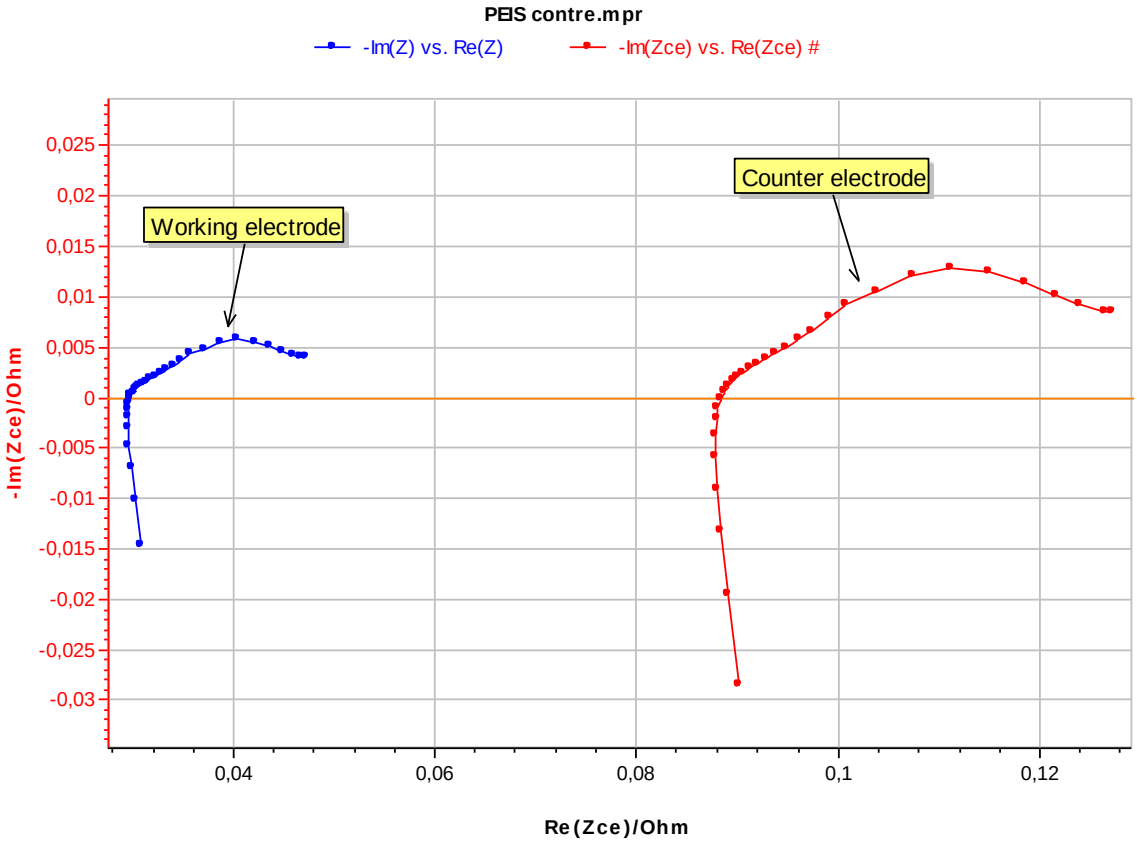


Fig. 39: PEIS data curves with WE and CE recording.

2.2.6.3 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)) *vs.* time for each frequency value.
The user can repeat a PEIS experiment for which the potential E_{we} 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).

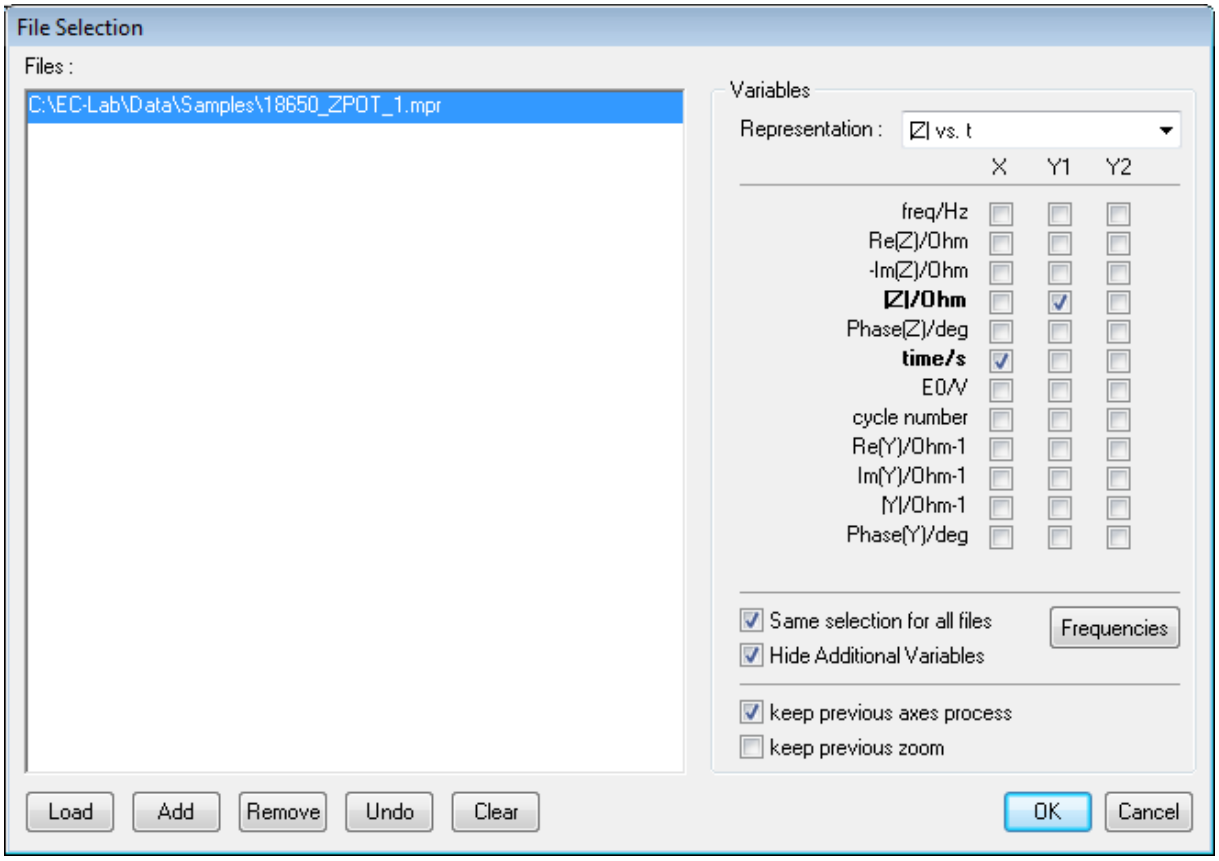


Fig. 40: File selection display.

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

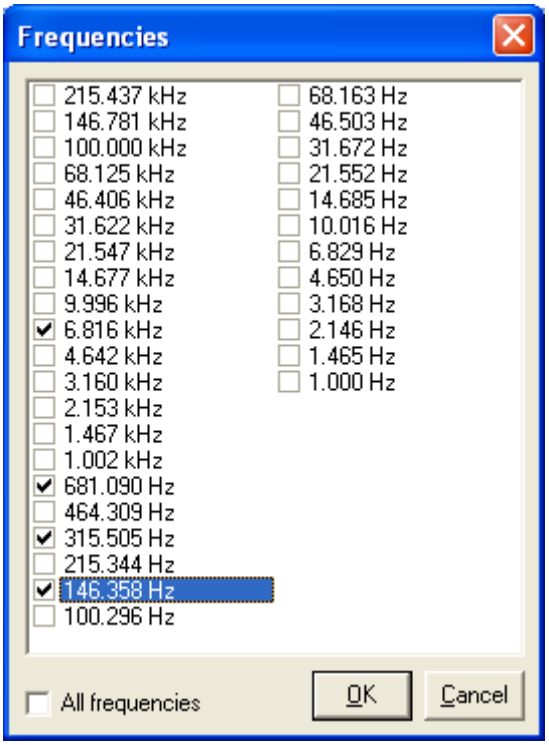


Fig. 41: Z *vs.* time display used to select frequencies.

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 displayed for the four different frequencies selected before.

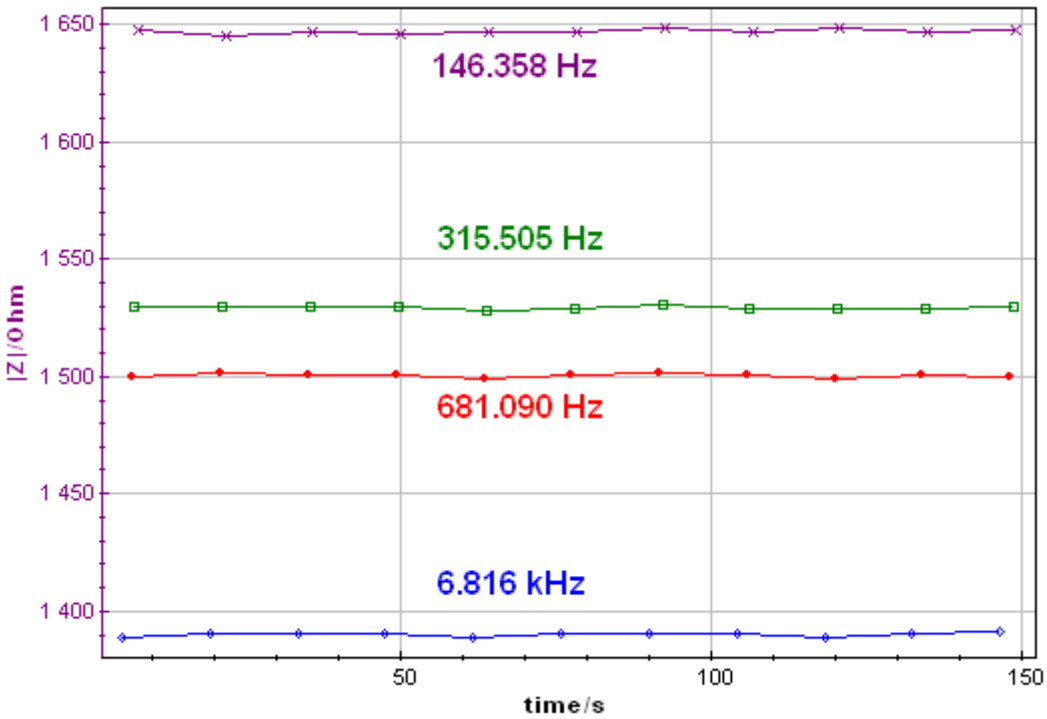


Fig. 42: Graphic display for four different frequencies.

2.2.7 Multisine option

The main advantage of using a multisine excitation signal is that it is faster than single frequencies excitation. Significant amounts of time can be saved especially if the measurement requires low frequencies and measurement drifts can be avoided if the system changes quickly with time.
With single frequencies excitation, the system is excited by one frequency at a time, resulting in a very long experiment. The total time taken for the complete analysis is the sum of the individual measurement times.
In multisine measurement, the system is excited by all the frequencies at the same time, using a Schroeder multisine.
The multisine signal is 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 equation [1]:

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

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

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

The crest factor values are between 2 and 3.

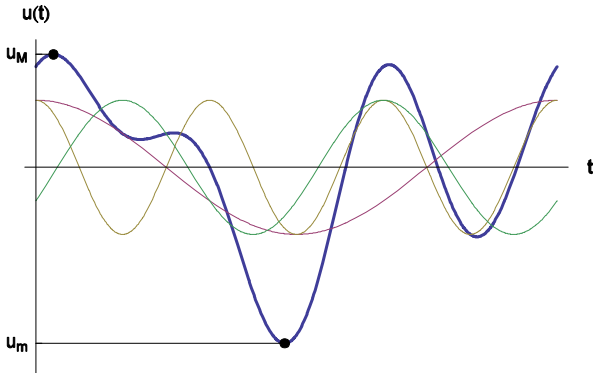


Fig. 43: Scheme of multisine signal.

To avoid a large excitation at the sine origin that could damage the electrochemical cell, all the sine waves are out of phase. 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 not to exceed 50 mV of sinus amplitude.
If the excitation amplitude – which is the sum of the maximum amplitude of all the applied frequencies – is too large, the system response can begin to be non-linear. This is why the sine amplitude values need to be minimized.
However, since a lot of frequencies are stimulated at the same time, there is less signal level at each frequency and impedance measurement results tend to be noisier.
These two effects have to be taken into account when choosing the frequency.

The number of frequencies depends on user needs and is defined in the settings of the electrochemical impedance spectroscopy technique. In EC-Lab® software, the multisine measurement is done simultaneously on a maximum of two decades. If more than two decades of twenty sine waves are chosen, the software automatically divides the frequencies by sets of twenty.

The maximum amplitude of the signal is 0.5 V or IRange/2, 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 one single sine measurement is available. Note that if the frequency range defined by the user is included in the two kinds of techniques (single sine and multisine), the measurement will be done in continuity with first a single sine measurement and afterwards a multisine measurement.

In EC-Lab® software, multisine measurements are faster than single sine ones (by an order of 3), which is very interesting for fast systems. Nevertheless, the definition of the measurement conditions, especially the value of the excitation of the electrochemical cell, has to be done in agreement with the preservation of a linear response of the system.
Please refer to the Application Note #19 for more information.

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.

2.3 Pulsed Techniques

2.3.1 DPV: Differential Pulse Voltammetry

DPV is considering as an electroanalytical method. It is very useful for analytical determination (for example, metal ion quantification in a sample). The differential measurements discriminate a faradaic 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.

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 *vs.* reference electrode potential or according to the previous open circuit potential (E_{oc}), reference potential (E_{ref}) or initial potential (E_i).
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 *vs.* reference electrode potential or *vs.* 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 of pulse height P_H amplitude and pulse width P_W duration. These steps are superimposed on a staircase of step height amplitude S_H and step time S_T duration.
As mentioned above, 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.

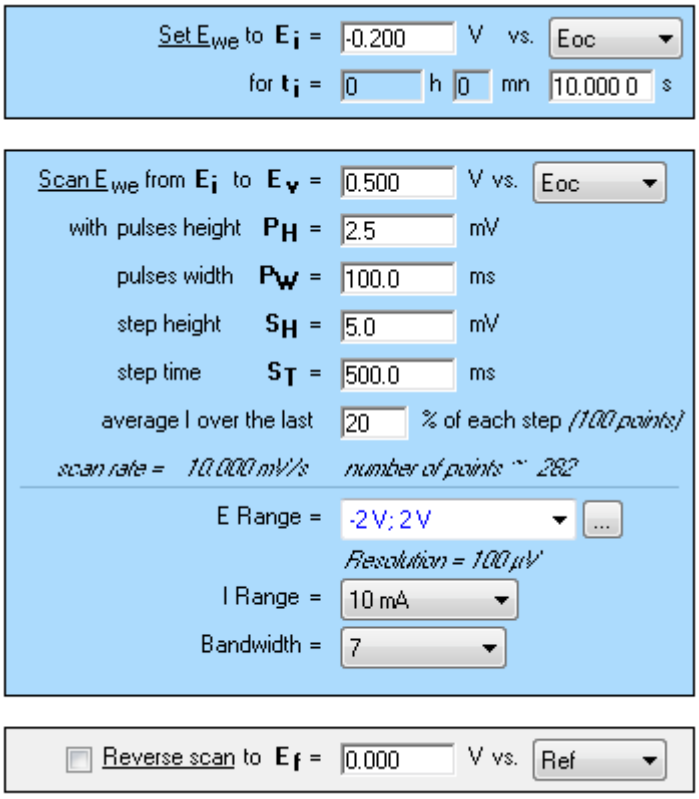


Fig. 44: DPV detailed diagram.

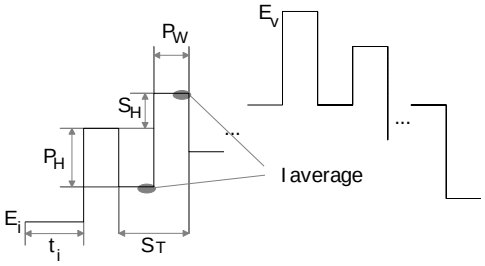


Fig. 45: DPV waveform.

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.

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.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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 avoid using 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 *vs.* reference electrode potential or *vs.* E_{oc} or E_i.

Running the settings defined into **Fig. 44** will result in the following output:

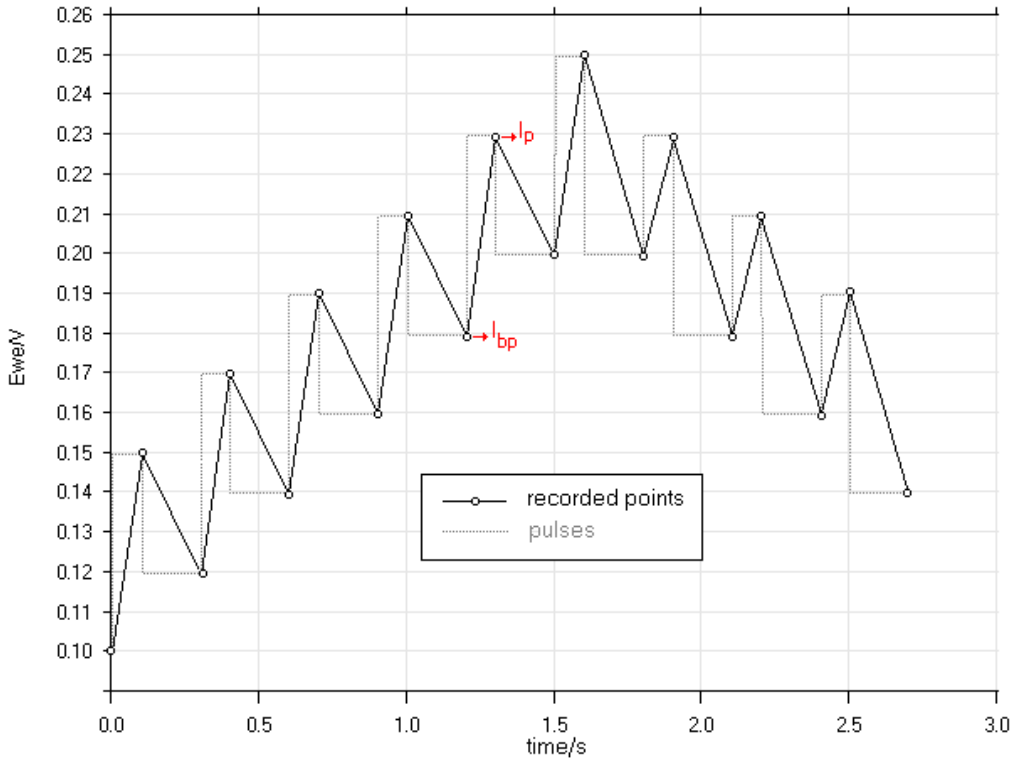


Fig. 46: DPV output (E_{we} *vs.* time).

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 space on disk):
- I forward/mA: <I> values at the end of the pulses (I_p, on **Fig. 46**),
- 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}).

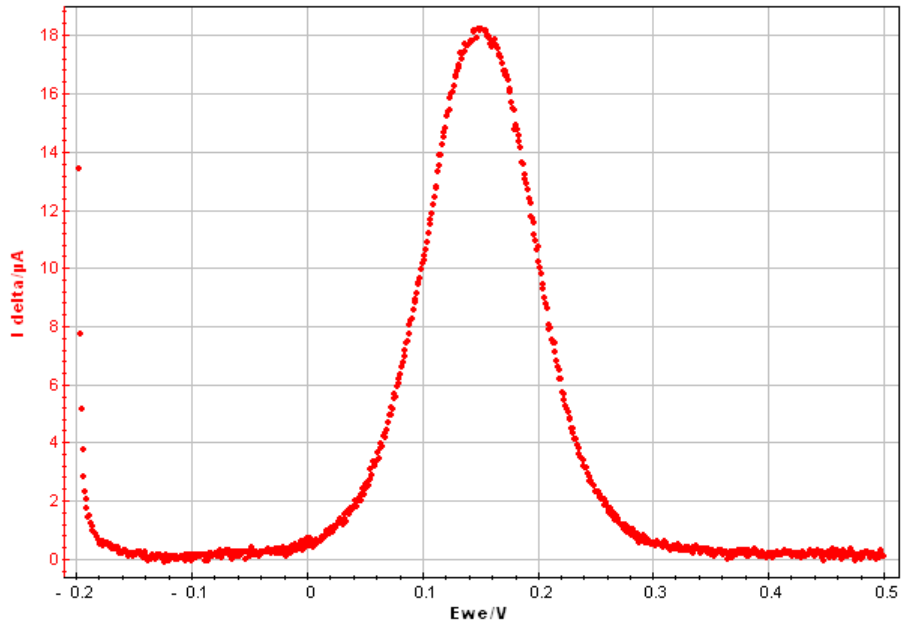


Fig. 47: DPV measurement in a Fe(II) solution.

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 the **Normal Pulse Voltammetry** (**NPV**, *c.f.* 2.3.3). The SWV is a large amplitude differential technique in which a symmetrical square wave (with one pulse in the forward direction and one in the reverse direction) is superimposed on a base staircase potential and 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 the square wave frequency f = $1/(2P_W)$. The scan rate v is $P_H/(2P_W)$. 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 the reverse components (since the net current is the difference between the forward and the reverse currents).

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 *vs.* 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 *vs.* reference electrode potential or *vs.* 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 of pulse height P_H amplitude and pulse width P_W duration. These steps are superimposed on a staircase of step height amplitude S_H and step duration $2*P_W$.
Note 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 below (**Fig. 48**) 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.

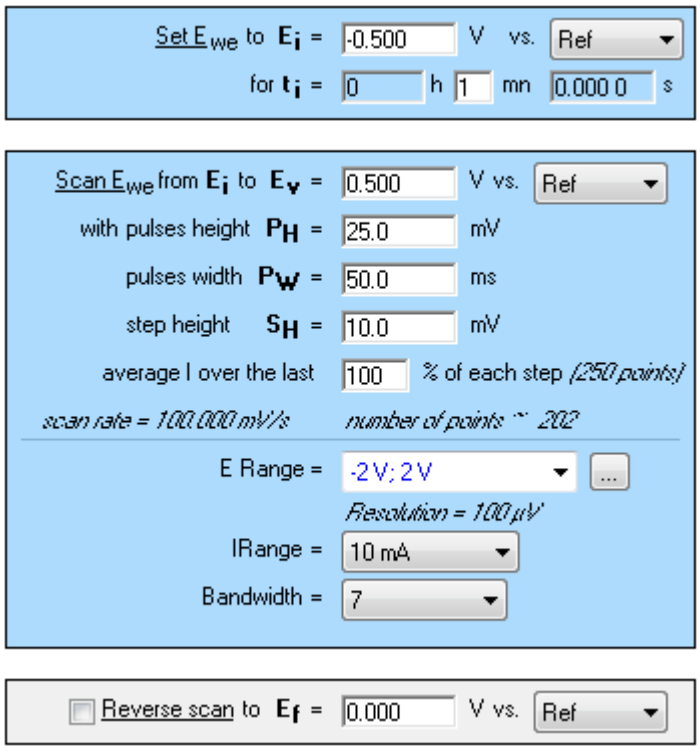


Fig. 48: SWV detailed diagram.

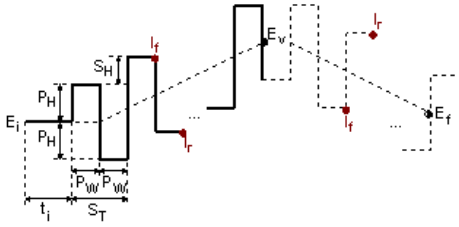


Fig. 49: SWV waveform.

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.

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.
E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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.

- **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 (*vs.* Ref. or versus E_{oc} or E_i).

Note: It is highly recommended to avoid using 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 space 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 NPV: Normal Pulse Voltammetry

Pulsed techniques have been introduced to increase the ratio between the faradaic and non-faradaic currents in order to permit a quantification of a species at very low concentration levels. The **Normal Pulse Voltammetry** (**NPV**) 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 Dropping mercury Electrode (DME), this is achieved by the stirring that follows the fall of the mercury drop. But at other electrodes, renewal may not be so easily accomplished.
NPV consists in 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 to 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).

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 *vs.* 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 *vs.* reference electrode potential or *vs.* 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 pulse height P_H (amplitude that is added to the pulse height of the previous pulse) and pulse width P_W duration. After each pulse the potential always

returns to the initial potential. The scan increment is defined by a pseudo staircase composed of steps with amplitude P_H and duration S_T.
As mentioned above 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. 50**) 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.

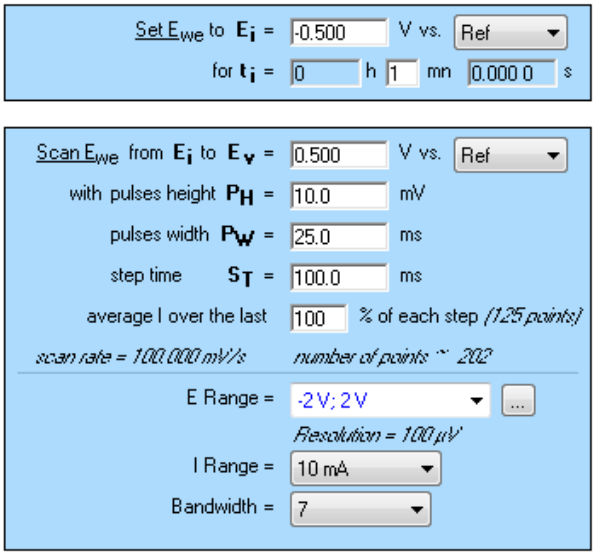


Fig. 50: NPV detailed diagram.

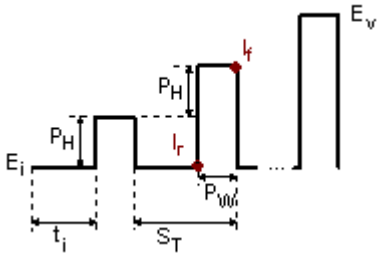


Fig. 51: NPV waveform.

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.

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.
E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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 avoid using 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.

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 space 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 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 RNPV experiment involves a significant faradic current. This method is a reversal experiment because of the detection of the product from a prior electrolysis.

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 *vs.* 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 *vs.* reference electrode potential or *vs.* 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 height of P_H (amplitude that is added to the pulse height of the previous one) and a width of 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.
As mentioned above 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. 52**) 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.

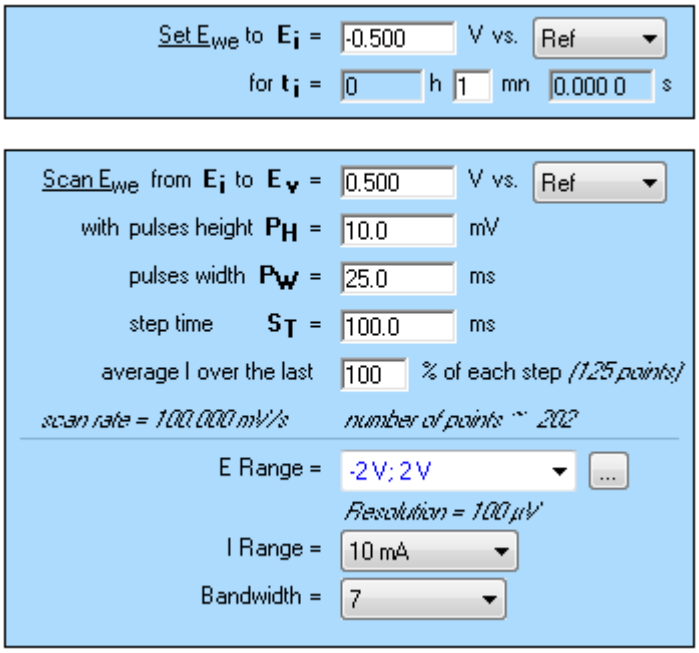


Fig. 52: RNPV detailed diagram.

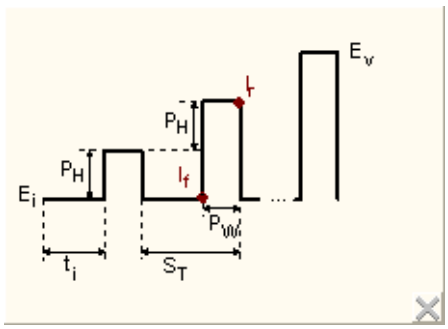


Fig. 53: RNPV waveform.

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.

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.
E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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 avoid using 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.

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.

2.3.5 DNPV: Differential Normal Pulse Voltammetry

Originally introduced as a polarographic technique (performed at a Dropping Mercury Electrode (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.

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 *vs.* 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 *vs.* Ref (reference electrode potential in the cell) 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**

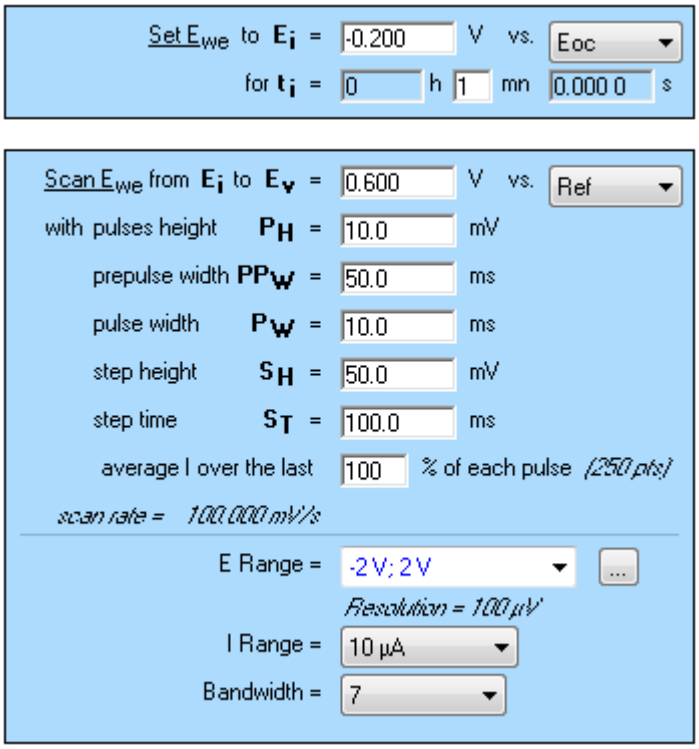


Fig. 54: DNPV detailed diagram.

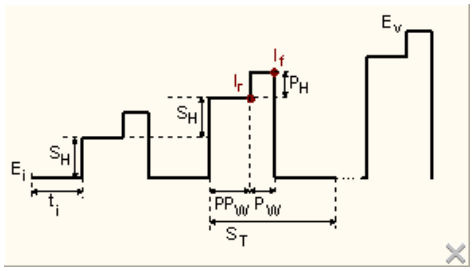


Fig. 55: DNPV waveform.

The scan increment is defined by a pseudo staircase made of steps of amplitude P_H and duration S_T.
As mentioned above 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. 54**) 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.

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.

Scan rate = … mV/s … number of points ~
These values are given as an indication and are calculated by the computer. 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.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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 avoid using 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 space 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.

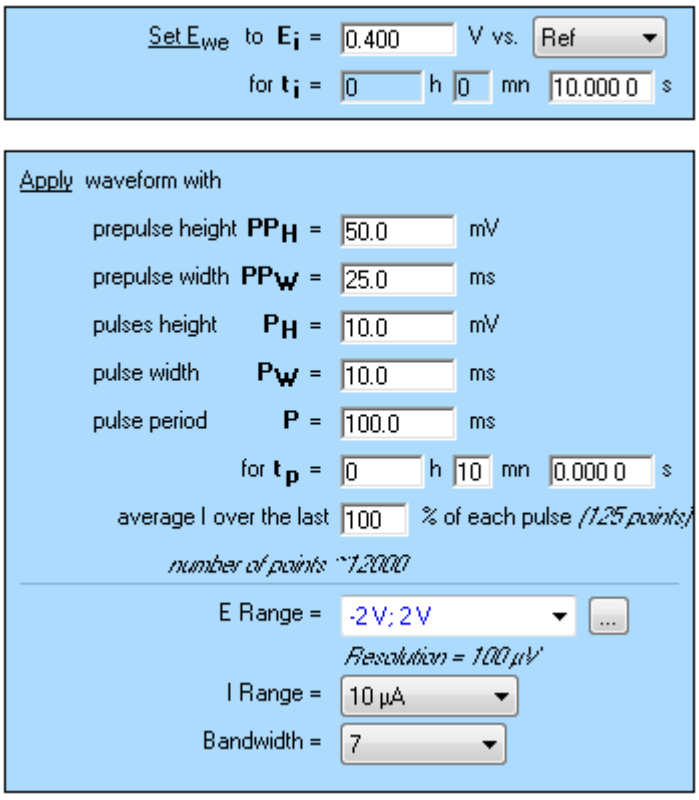


Fig. 56: DPA detailed diagram.

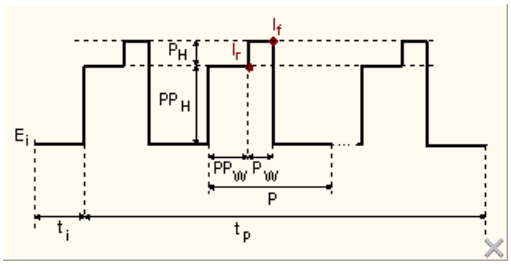


Fig. 57: DPA waveform.

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 *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

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

Note 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.

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.

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.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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 avoid using 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.

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 space 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

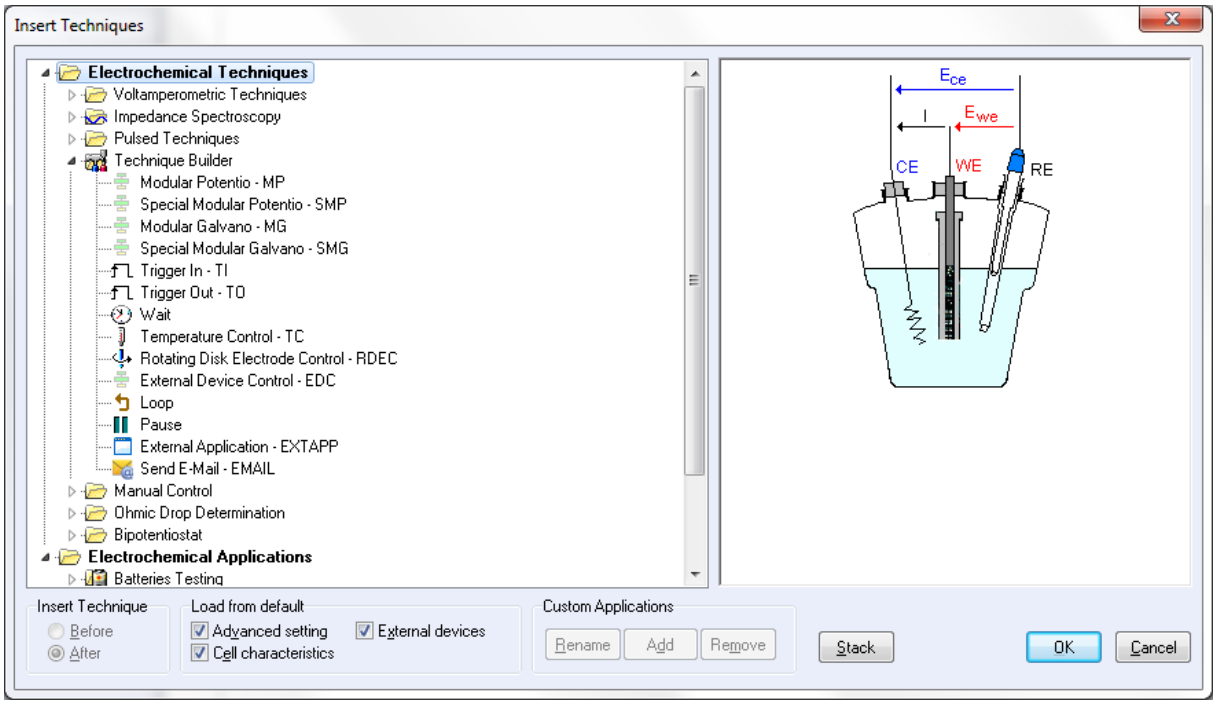


Fig. 58: Technique builder selection window.

This section is dedicated to experiment building. With the techniques and tools described in this section the user has the ability to easily create their own applications 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 to a modular approach. Linked with **Triggers**, **Wait** periods, external device control methods, **Loops,** External application and Email application, these techniques become powerful enough to build complex settings.

2.4.1 MP: Modular Potentio

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

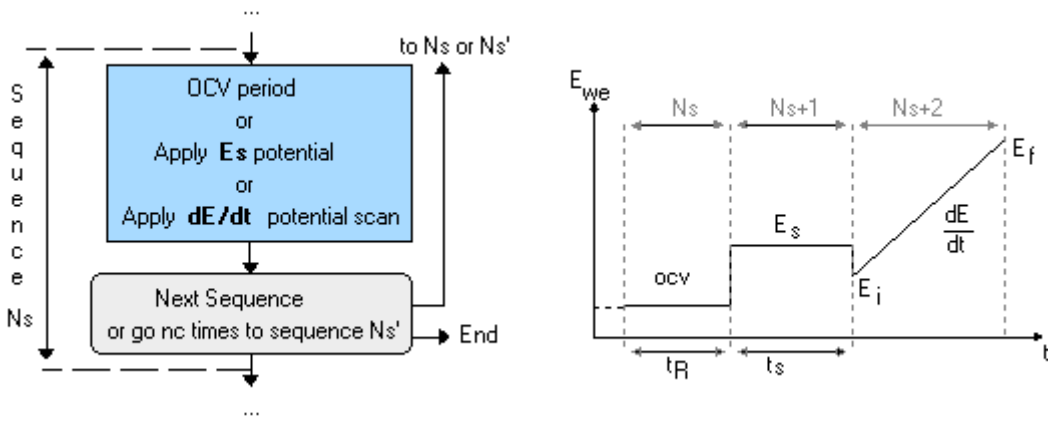


Fig. 59: Modular Potentio general diagram.

- **Mode selection:**

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

2.4.1.1 Open Circuit Voltage (Mode = 0)

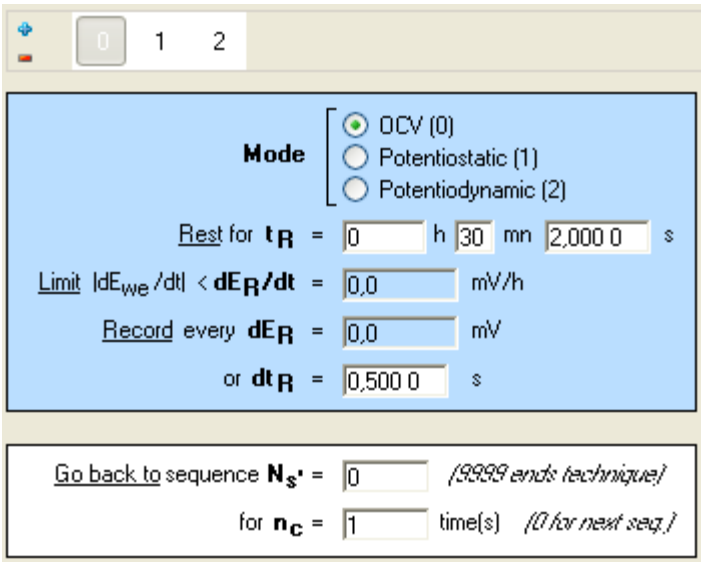


Fig. 60: Modular Potentio, OCV detailed diagram.

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

Go back to 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 107) 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).

2.4.1.2 Potentiostatic (Mode = 1)

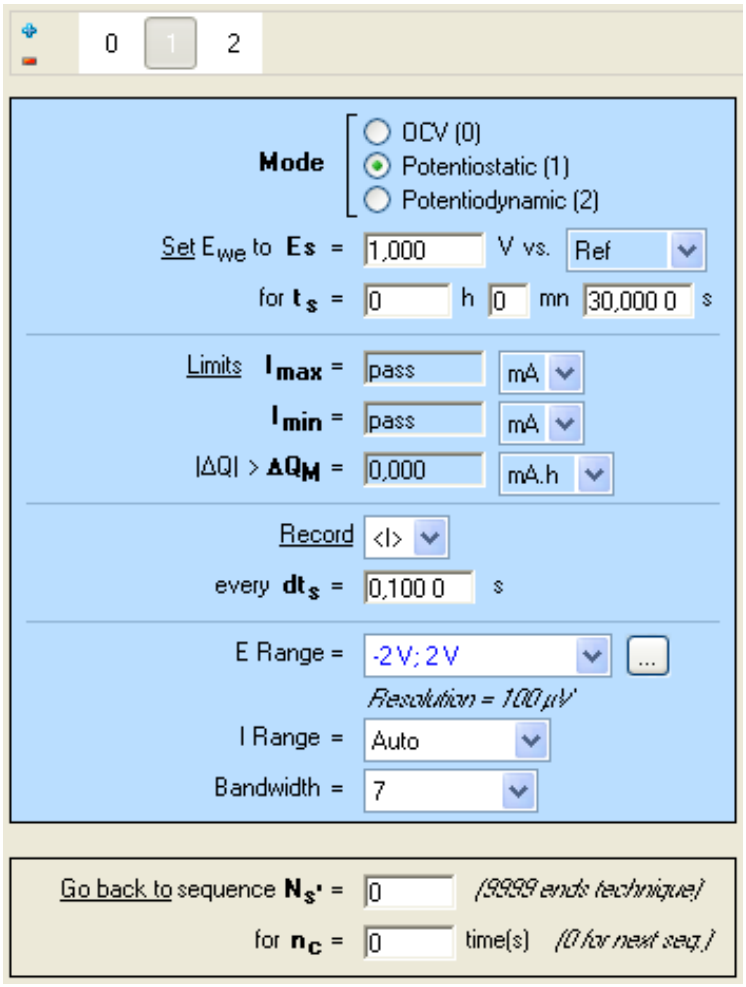


Fig. 61: Modular Potentio, potentiostatic detailed diagram.

Set E_{we} to Es = … V *vs.* Ref/Eoc/Ectrl/Emeas
sets the potential *vs.* reference electrode potential or 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).

Limits 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 VMP3 based instrument and for VMP300 based instruments.
E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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.

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.

2.4.1.3 Potentiodynamic (Mode = 2)

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 and to adjust the potential resolution according to the experiment (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.

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.

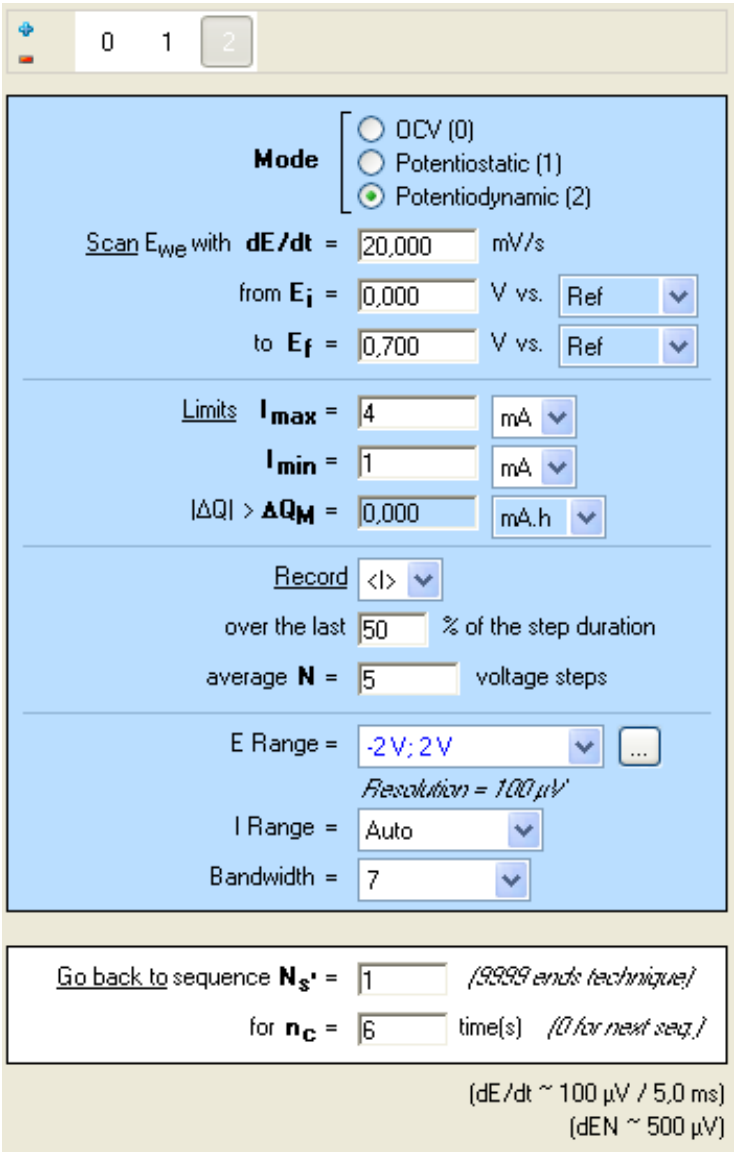


Fig. 62: Modular Potentio, potentiodynamic detailed diagram.

The three modes of the Modular Potentio technique can be linked 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 $N_s = 0$. The table view can be accessed with the following path: **View -> Settings With Flowcharts.**

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.

2.4.2 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. An additional limit condition on Analog In1 or Analog In2 is added, which makes it special.

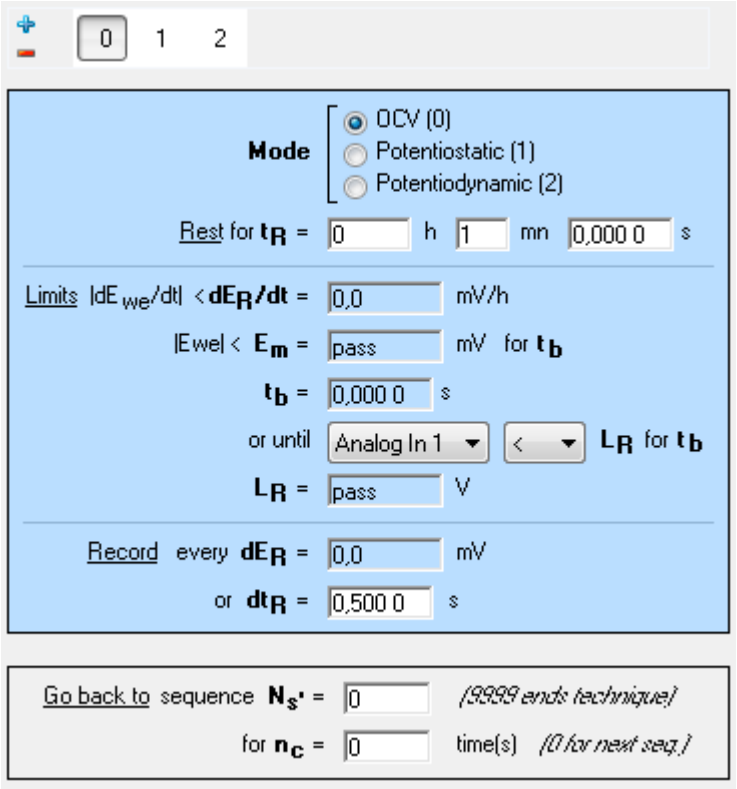


Fig. 64: Special Modular Potentio, Potentiostatic detailed diagram.

Mode selection

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

- **Open Circuit Voltage (Mode = 0)**

See SOCV.

Loop

<u>Go back to</u> 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 107) 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).

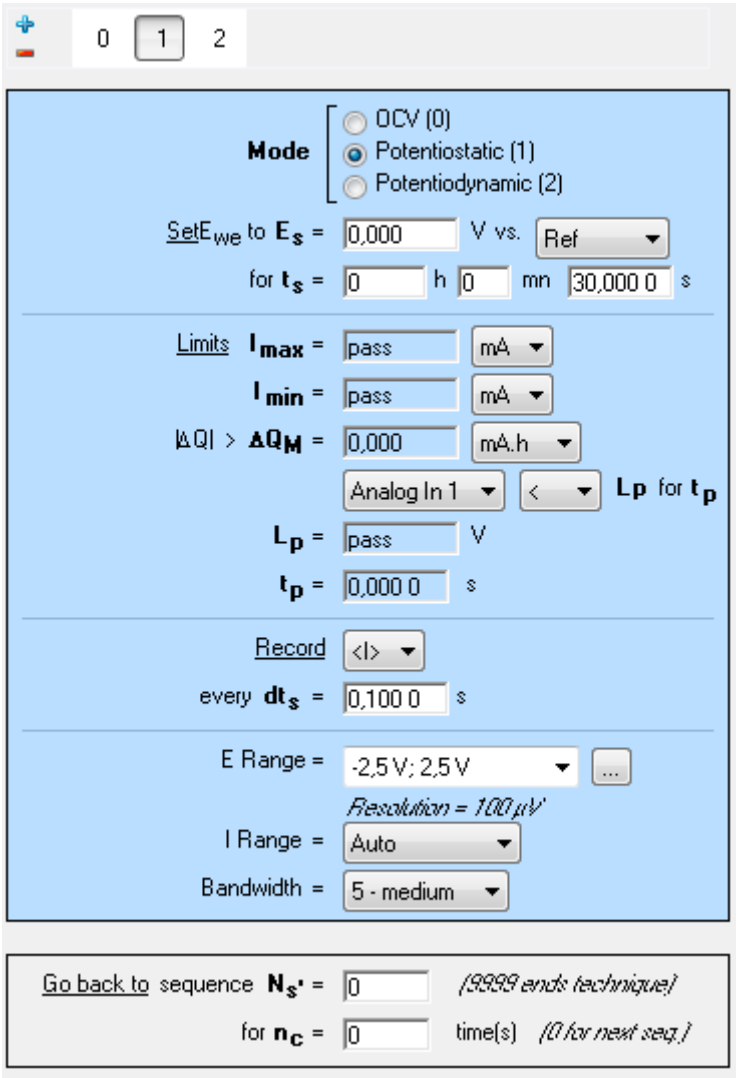


Fig. 65: Special Modular Potentio, potentiostatic detailed diagram.

- **Potentiostatic (Mode = 1)**

Set E_{we} to Es = … V *vs.* Ref/Eoc/Ectrl/Emeas
sets the potential to a fixed value *vs.* Ref or versusto 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 |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.

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 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 VMP3 based instruments and for VMP300 based instruments.

E Range = …
enables the user to select the potential range for adjusting the potential resolution with his/her system. (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment)

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

- **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 or 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 *vs.* Ref 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 and to adjust the potential resolution with his/her system. (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment)

I Range = ... and Bandwidth = …
sets 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.

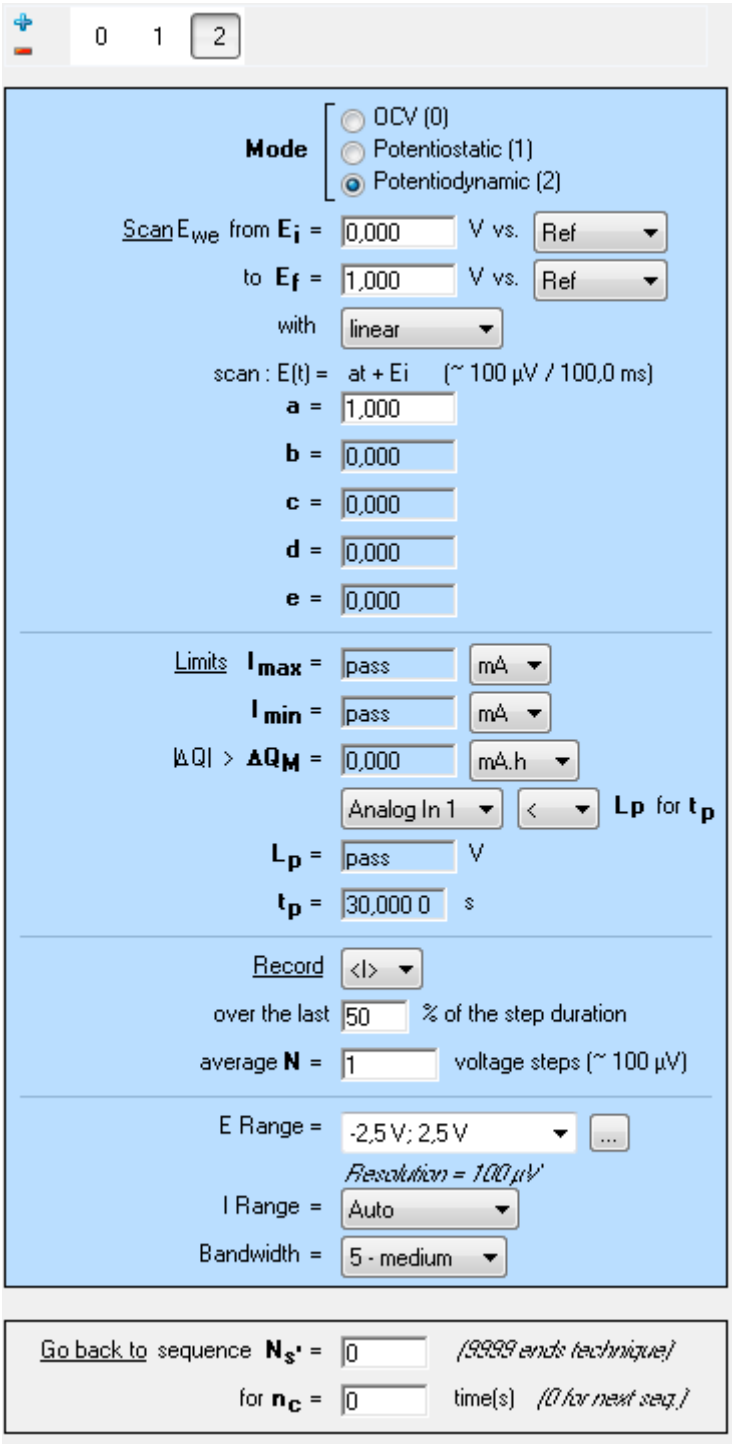


Fig. 66: Special Modular Potentio, potentiodynamic detailed diagram.

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.

2.4.3 MG: Modular Galvano

The Modular Galvano technique enables the user to perform combinations of OCV, galvanostatic, and galvanodynamic periods. It is possible to link 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.

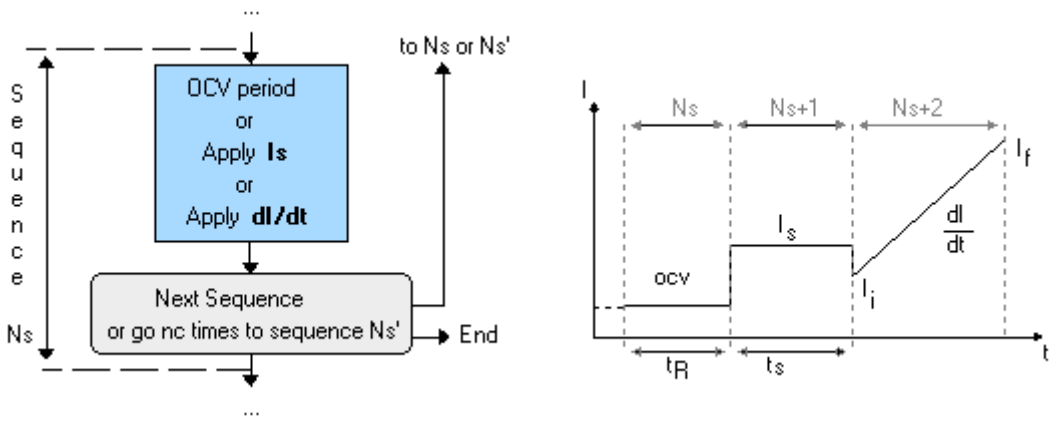


Fig. 67: Modular Galvano general diagram.

- **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).
By default, the technique contains 3 sequences : OCV, Galvanostatic and Galvanodynamic.

2.4.3.1 Open Circuit Voltage (Mode = 0)

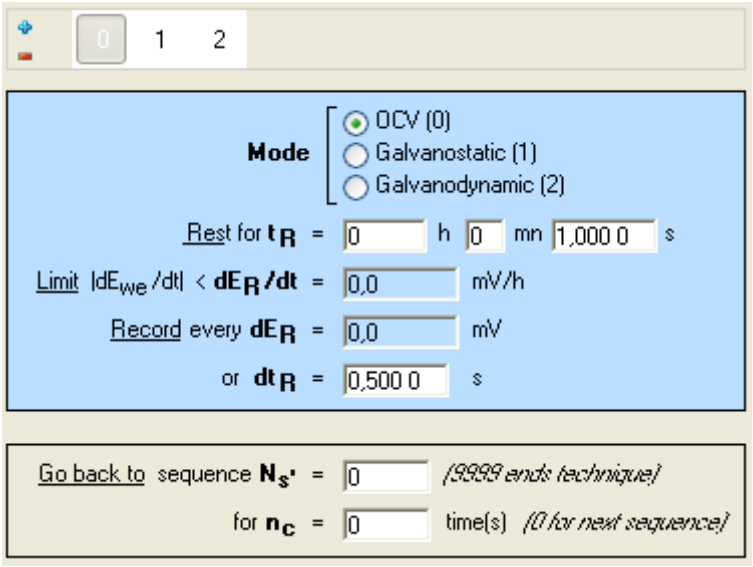


Fig. 68: MG OCV detailed diagram.

The open circuit voltage is the standard block. So report to the OCV technique section 2.1.1, page 6 for more details.

<u>Go back to</u> 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 107) 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).

2.4.3.2 Galvanostatic (Mode = 1)

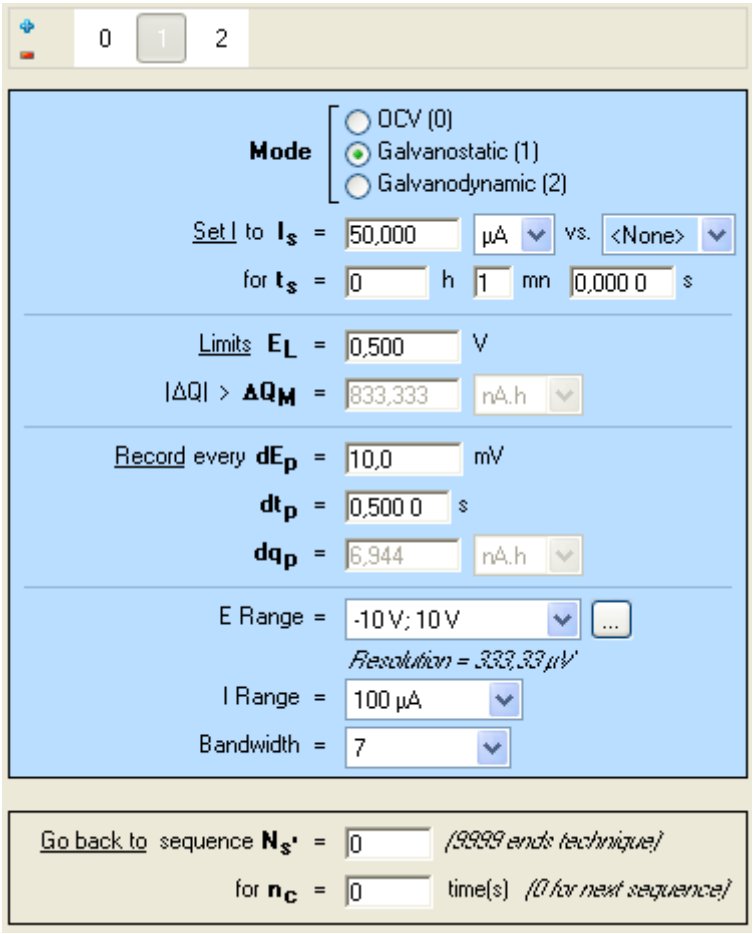


Fig. 69: Modular Galvano, Galvanostatic detailed diagram.

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.

Limits 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 $I_s > 0$
$E_{we} < E_L$ otherwise

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 and to adjust the potential resolution according to the experiment (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.

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.

2.4.3.3 Galvanodynamic (Mode = 2)

Scan I with dI/dt = … mA/s, with … pA/… /A per… 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.

Limits E_L = … V and $|\Delta Q|$ 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 and to adjust the potential resolution according to the experiment (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.

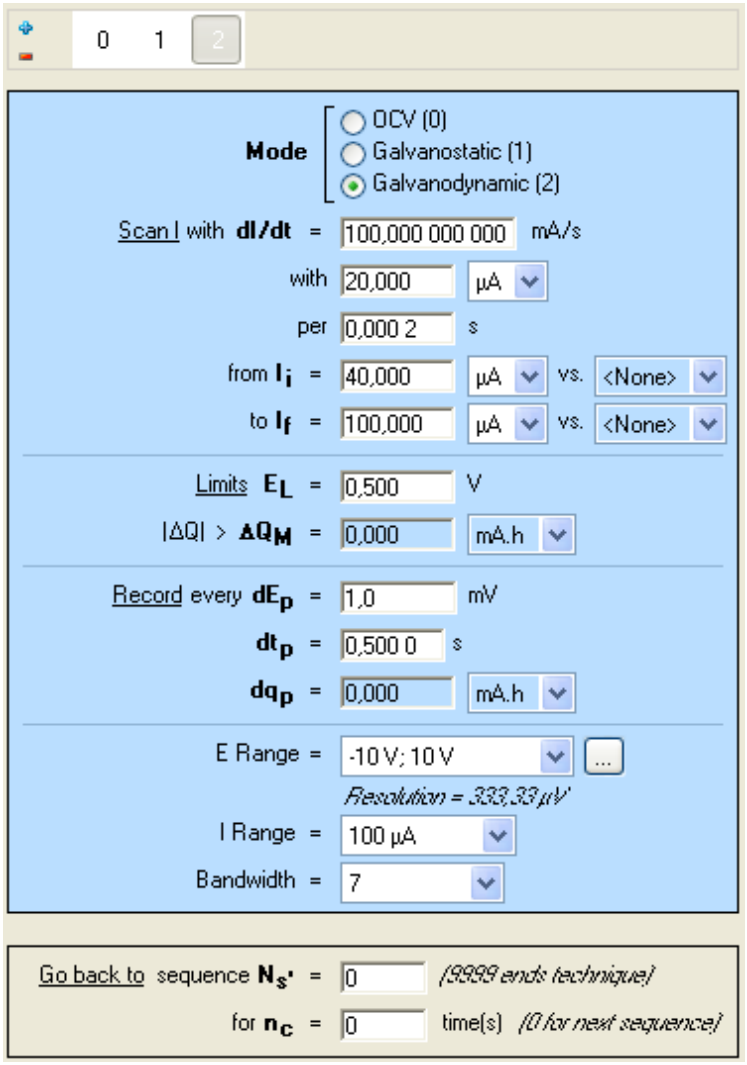


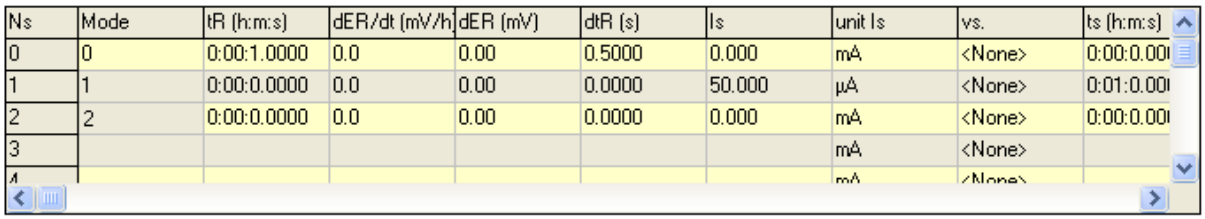
Fig. 70: Modular Galvano, Galvanodynamic detailed diagram.

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.

2.4.3.4 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. The table view can be accessed with the following path: **View -> Settings With Flowcharts.**

Management of the various steps can be done thanks to sequence or table (**Fig. 71**).



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. 71: Modular Galvano table.

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

2.4.4 SMG: 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. An additional limit condition on Analog In1 or Analog In2 is added, which makes it special.

- **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 6 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 107) 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).

- **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 = …
sets 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.

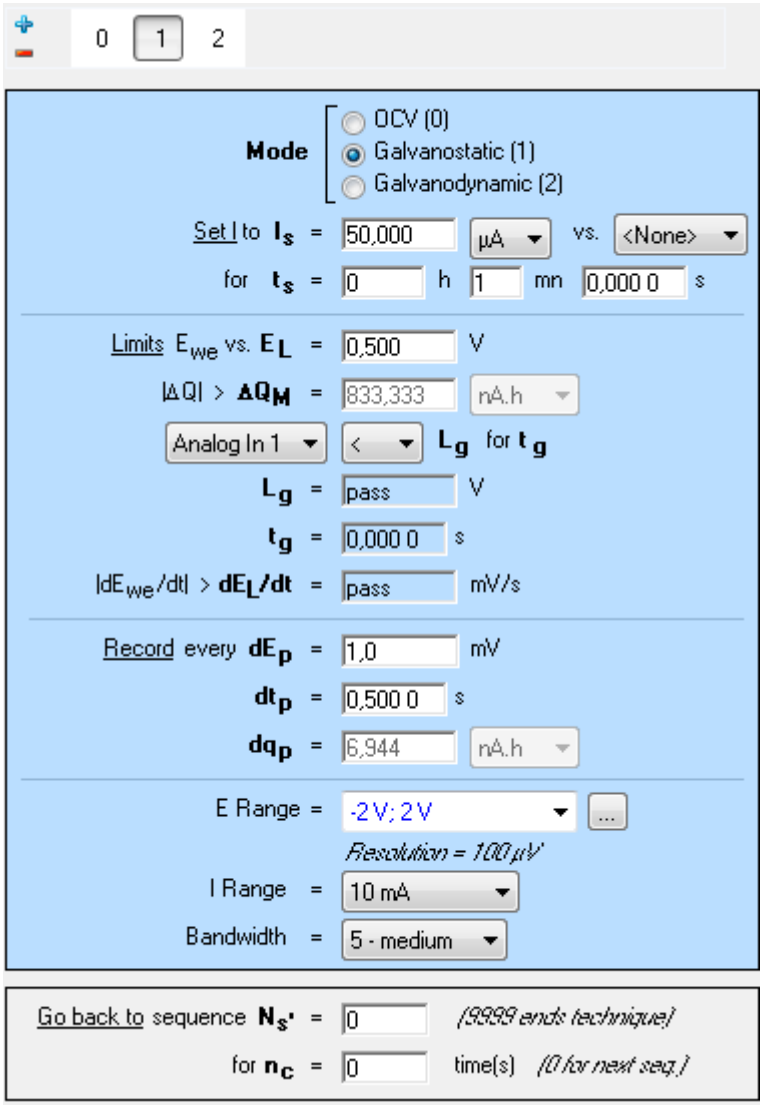


Fig. 72: Special Modular Galvano, Galvanostatic detailed diagram.

- **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>/I_i.

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.

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

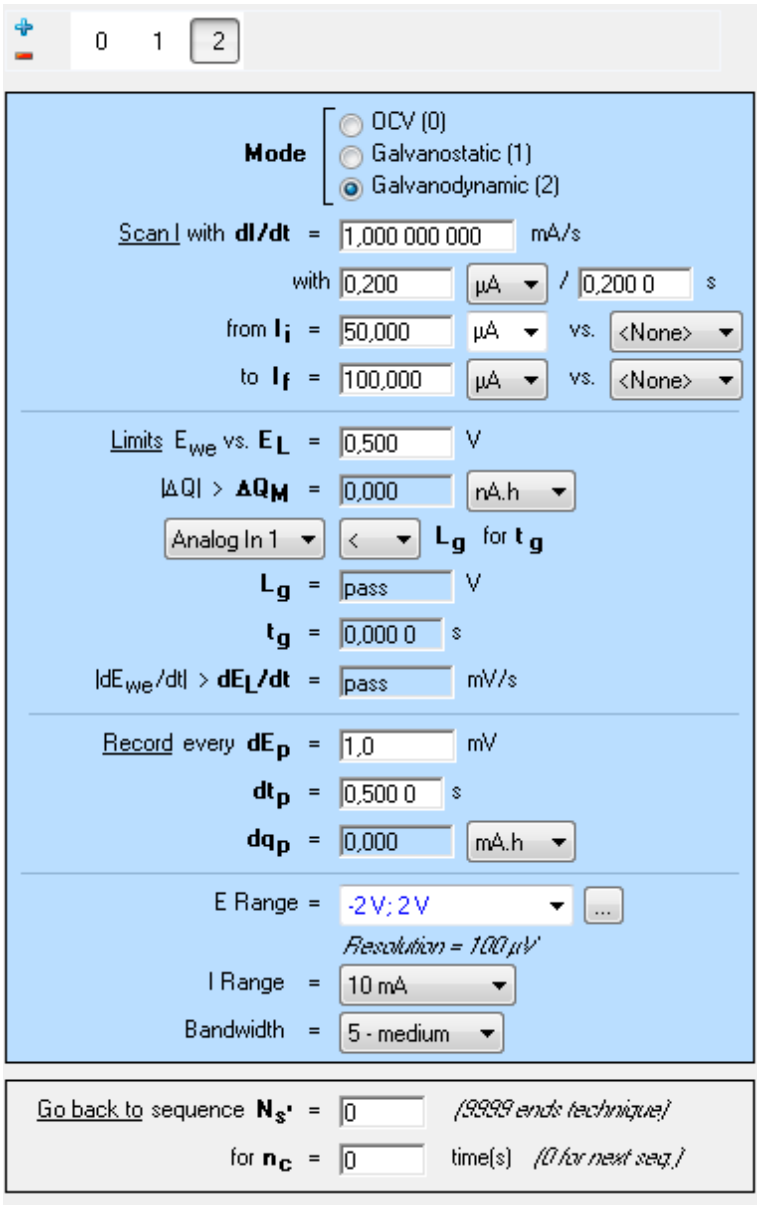


Fig. 73: Special Modular Galvano, Galvanodynamic detailed diagram.

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.

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

2.4.5 TI and TO: Trigger In and Trigger Out

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.

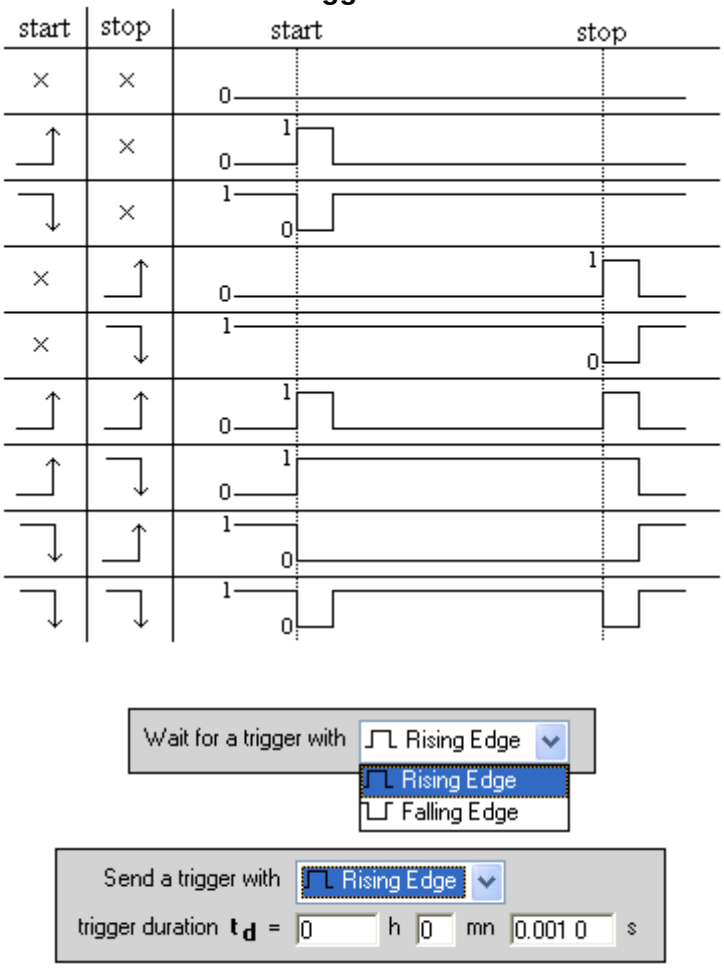


Fig. 74: Trigger In and Out.

The Trigger In option puts the instrument in a waiting configuration until it receives a trigger with a rising edge or a 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 a 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:

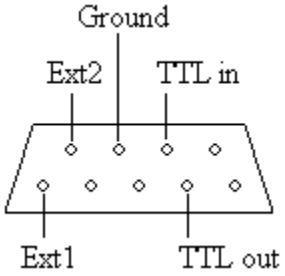


Fig. 75: DB9 Pin assignment (when facing the instrument).

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.

2.4.6 Wait

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

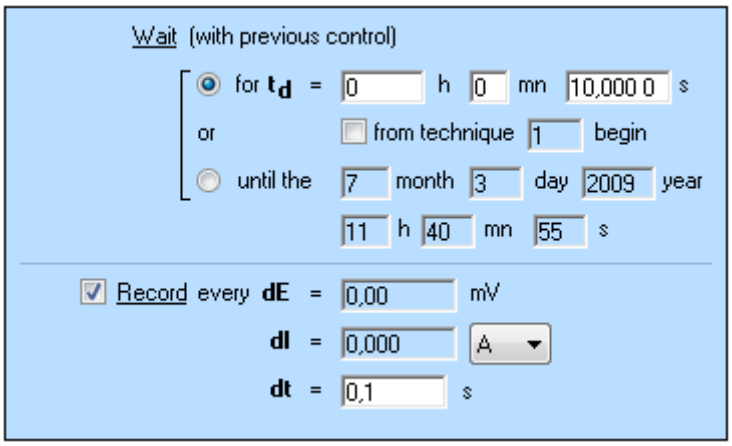


Fig. 76: Wait diagram.

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.

2.4.7 TC: Temperature Control

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 Control technique is done by clicking on External Thermostat.

The user can choose to apply different temperature successively for different durations and perform a certain experiment at this temperature. To do so, several sequences, each one with the desired temperature and duration, must be created.Then, the desired techniques need to be linked after the TC technique. Finally, the series of techniques must be ended with a Loop technique (see 2.4.10). The sequences in the TC technique will be incremented only at each time the Loop technique is reached.

See below for additional info.

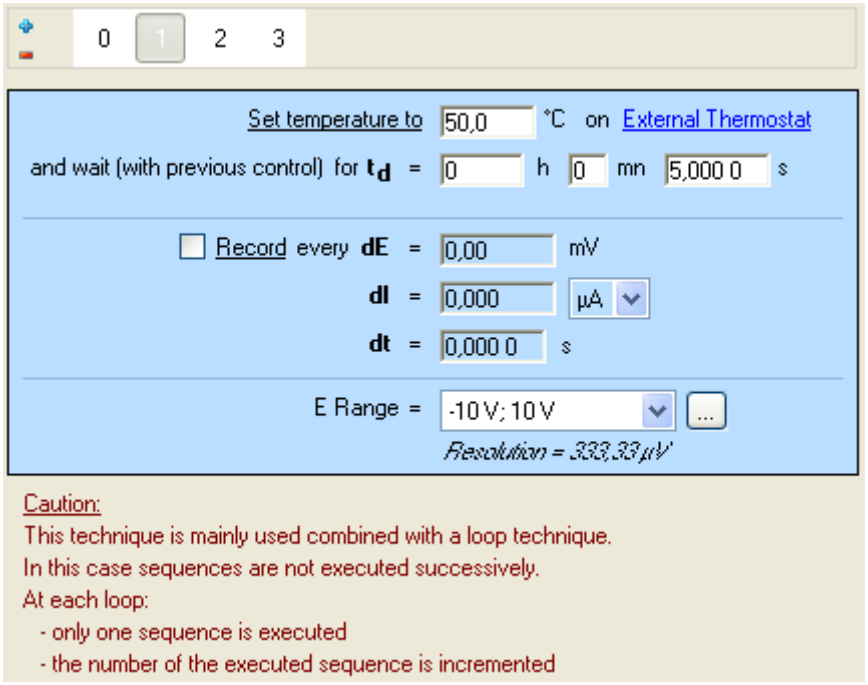


Fig. 77: Temparature control.

Set temperature to … °C on External Thermostat
one can set a temperature and configure the temperature recording using the External thermostat link.

☐ **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 and to adjust the potential resolution according to the experiment (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment).

The sequences in the TC, RDEC and EDC technique: The user can add several TC sequences (N_s = 0 to n). These sequences are linked differently from the other techniques. In other standard techniques, one sequence is executed directly after the other. For the TC (RDEC and EDC) technique each sequence corresponds to a loop of a linked technique. 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 the Loop number of increments is larger than the number of sequences in the TC technique, then the TC technique starts all over again as long as the total number of Loop increments is not reached.

2.4.8 RDEC: Rotating Disk Electrode Control

The Rotating Disk Electrode Control (RDEC) 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 External RDE.
The user can choose to apply different rotation speeds successively for different durations and perform a certain experiment at this rotation speed. To do so, several sequences, each one with the desired rotation speed and duration, must be created.Then, the desired techniques need to be linked after the RDEC technique. Finally, the series of techniques must be ended with a Loop technique. The sequences in the RDEC technique will be incremented only at each time the Loop technique is reached. See below for additional info.

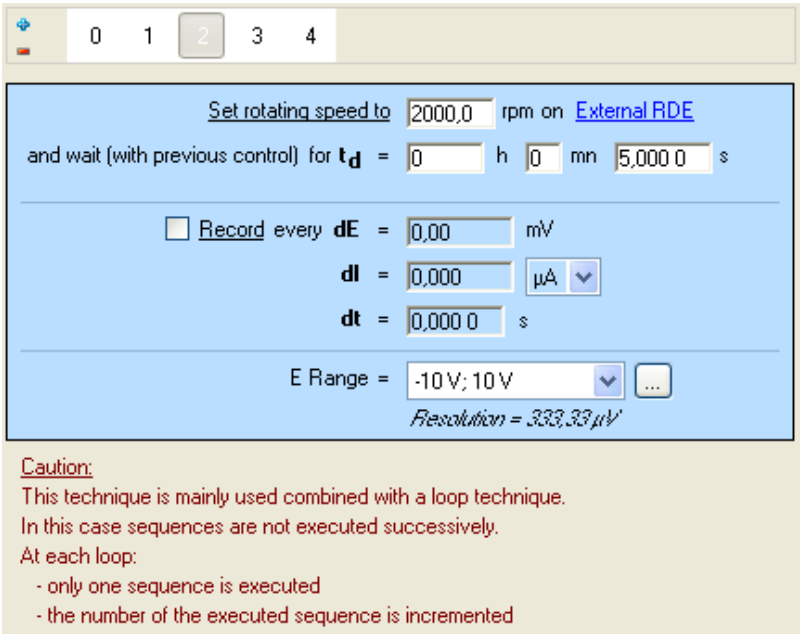


Fig. 78: Rotating Disk Electrode Control.

Set rotating speed to … rpm
one can set a temperature or the rotating electrodes speed if configured (**External devices** windows,...). 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 and to adjust the potential resolution according to the experiment (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. The table view can be accessed with the following path: **View -> Settings With Flowcharts.**

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. 79: RDEC, TC, EDC table.

The sequences in the TC, RDEC and EDC technique: The user can add several RDEC sequences (N_s = 0 to n). These sequences are linked differently from the other techniques. In other standard techniques, one sequence is executed directly after the other. For the RDEC (EDC and TC) technique each sequence corresponds to a loop of a linked technique. 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 the Loop number of increments is larger than the number of sequences in the RDEC technique, then the RDEC technique starts all over again as long as the total number of Loop increments is not reached.

2.4.9 EDC: External Device Control

The External Device Control (EDC) 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 External Device.
The user can choose to apply different values of the chosen parameter successively for different durations and perform a certain experiment at this value. To do so, several sequences, each one with the desired value and duration, must be created.Then, the desired techniques need to be linked after the EDC technique. Finally, the series of techniques must be ended with a Loop technique (see 2.4.10). The sequences in the EDC technique will be incremented only at each time the Loop technique is reached. See below for additional info.

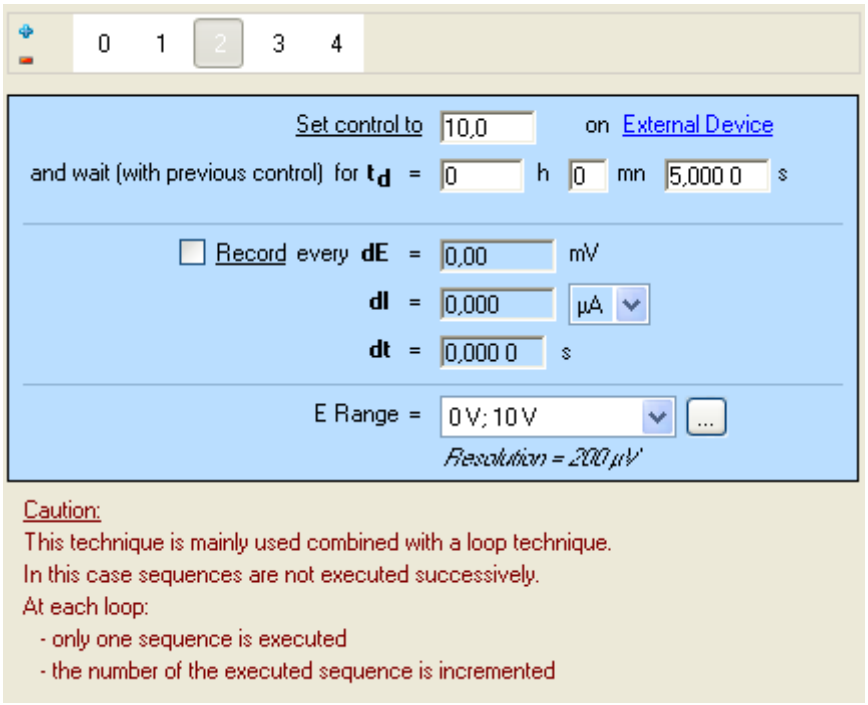


Fig. 80: External Device Control parameters.

Set control to …
one can configure the "**External Device"** using the link External Device (**External Devices** windows). 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 and to adjust the potential resolution according to the experiment (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.

The sequences in the TC, RDEC and EDC technique: The user can add several EDC sequences (N_s = 0 to n). These sequences are linked differently from the other techniques. In

other standard techniques, one sequence is executed directly after the other. For the EDC (RDEC and TC) technique each sequence corresponds to a loop of a linked technique. 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 the Loop number of increments is larger than the number of sequences in the EDC technique, then the EDC technique starts all over again as long as the total number of Loop increments is not reached.

2.4.10 Loop

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

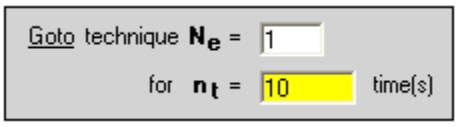


Fig. 81: Loop technique.

The techniques loaded before the Loop and after the technique N_e option are repeated n_t 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.

Note: **"Turn to OCV between techniques"** option forces the system to go to OCV but no OCV measurement is performed. If after this forced OCV period, a technique uses the OCV value as reference, the value used will be the last value measured during the previous techniques.

2.4.11 Pause

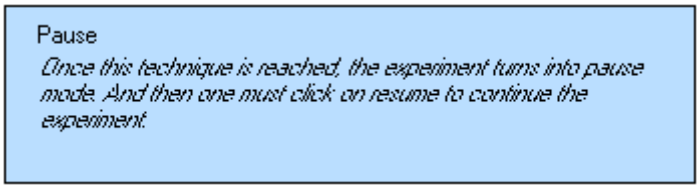


Fig. 82: Pause technique.

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

2.4.12 EXTAPP: External application

Fig. 83: External application technique.

This technique is included in an experiment with linked techniques. It allows one to execute an independent program from EC-Lab software. This can be used to start an external device controlled by another application.

Programe Name:
allows the user to select the external application
Parameters:
This option allows the user set the commands/parameters that will be sent to the external application.
In addition, selecting **"Wait until the application closes"**, it is possible to wait until this program is closed. Untils this time, the experiment turns into **Pause** mode until the external application is closed. If this box is not ticked the experiment will continue in parallel.

2.4.13 EMAIL: Send an E-Mail

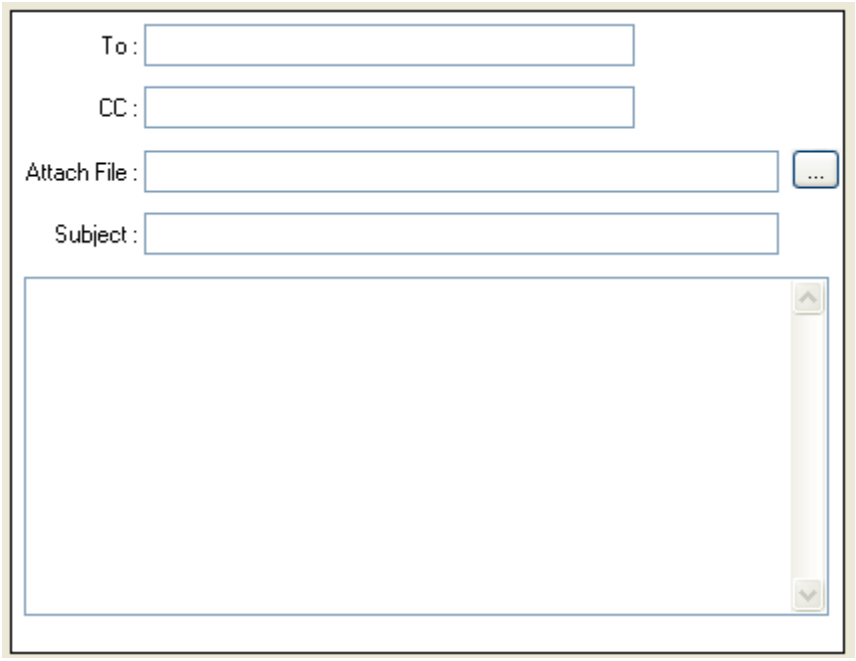


Fig. 84: Pause technique.

This technique can be added in an experiment including linked techniques. When this technique is reached allows one to send an email to one or several addresses. A file can be enclosed (Max. size: 8 Mb).

The exact file name must be indicated. Remember that the EC-Lab default file structure is the following: “name”_# technique position in the protocol _technique name _C # channel number.mpr.
In the example of Fig.79, if one can send the result of the PEIS technique, the file name is: “**test_02_PEIS_C04.mpr**” (supposing that this experiment is running in the channel 04)

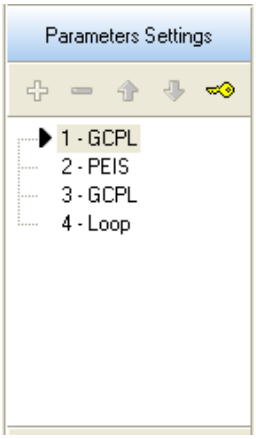


Fig. 85: Experiment windows.

Note: the exact location of the enclosed file has to be also indicated. This can be used to inform the user of the progress of the experiment.

Note: The email settings of the sender have to be configured in the **E-Mail** tab of the **Options** window (**Config** menu).

2.4.13.1 E-Mail Configuration

Before use the E-Mail technique, the email setting of the sender have to be configured. One can set the e-mail parameters in the **E-Mail** tab of **Option** windows in menu **Config**.

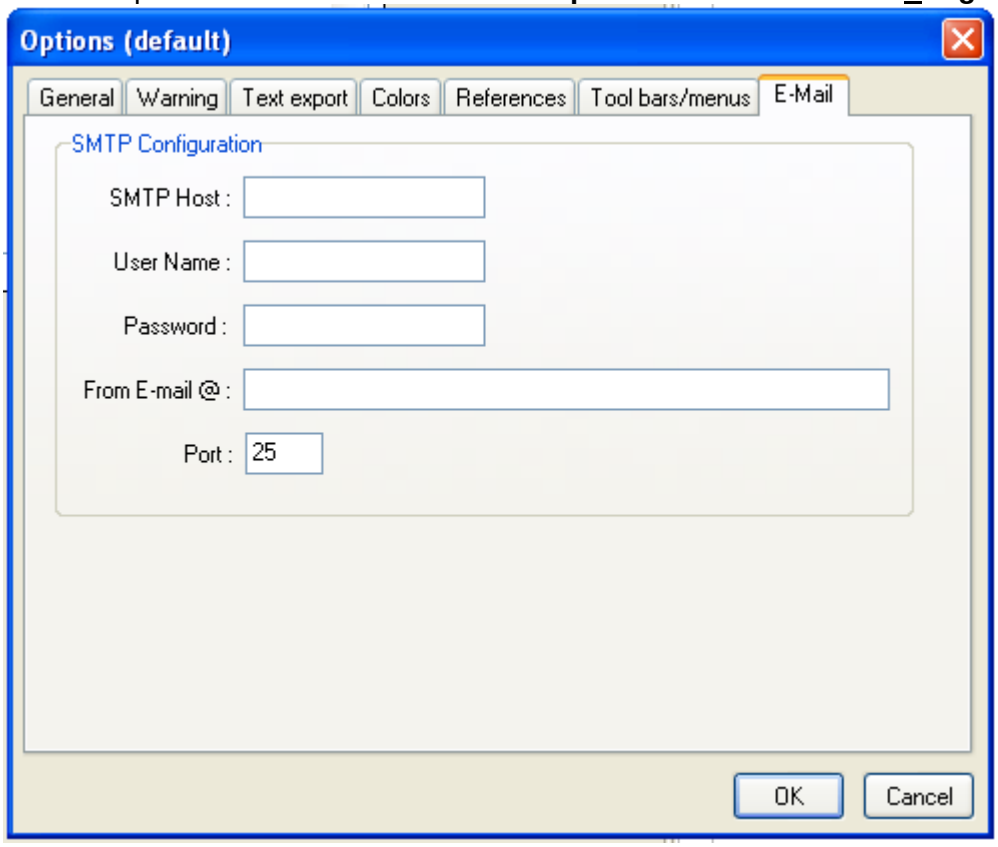


Fig. 86: E-Mail configuration tab.

2.5 Manual Control

2.5.1 PC: Potential Control

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

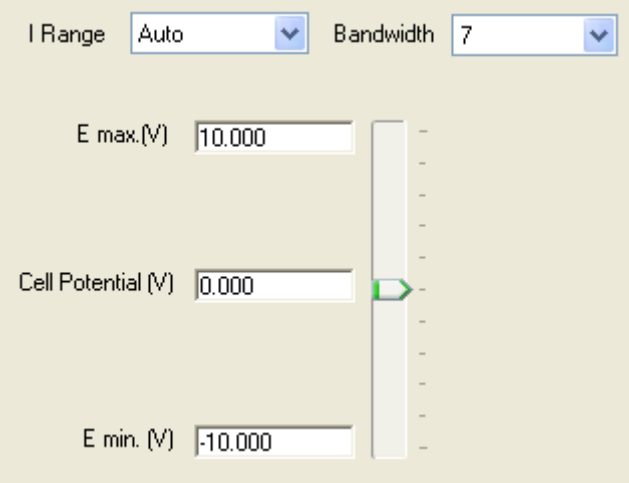


Fig. 87: Manual Potential Control.

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 set the potential limits and the controlled potential. Then you need to 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 IC: Current Manual Control

This menu proposes the same features as the Potential Manual Control by replacing the potential control by the current control. Therefore refer 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 non-aqueous media. It may lead to severe distortion of the voltammetric response as the applied potential and the potential “seen” by the electrodes can be significantly different. The best way to determine this ohmic drop, named in EC-Lab® the uncompensated resistance (R_u) is to perform an impedance measurement at high frequencies before running other experiments (ZIR). EC-Lab also proposes to calculate the ohmic drop using the Current Interrupt method (CI).
After determining Ru, it will be compensated on the techniques linked thereafter. Only techniques for which the potential is controlled are concerned by the ohmic drop compensation.
Note that, for the VMP3- based instruments, the compensation made in the linked techniques is software compensation. The consequences are that there is not limit on the value of R_u and Auto-Range can be used in the linked techniques for which the compensation is made. A drawback is that it can only be used with relatively low potential scan rates.

For the SP300-based instrument the compensation could be made by software as well as by hardware.
For more information, please refer to the Application Notes #27, #28, #29.

2.6.1 MIR: Manual IR compensation

If the user already knows the value of R_u, it can be entered in the box and the compensation percentage can be defined. This value can be used for IR compensation in linked techniques. For the SP300-based instruments, hardware ohmic drop compensation can be performed.

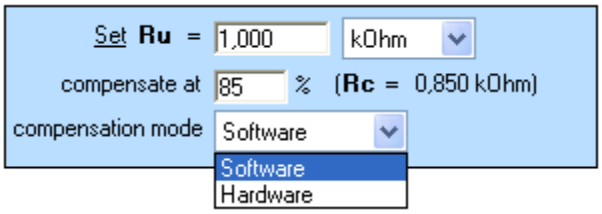


Fig. 88: MIR diagram.

Note: The hardware compensation is not available with the WE to Ground and CE to Ground connections.

2.6.2 ZIR: IR determination 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 not to 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 series of linked experiments. R_u value will be automatically accounted for in the following experiments of the series.
This technique is similar to the Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) technique, except that it is performed at a single frequency. Refer to the PEIS experiment section for more details. Please note that the ZIR technique is available on the SP-300 technology even if the board is not equipped with impedance ability. This technique is not available with WE to Ground and CE to Ground connections.

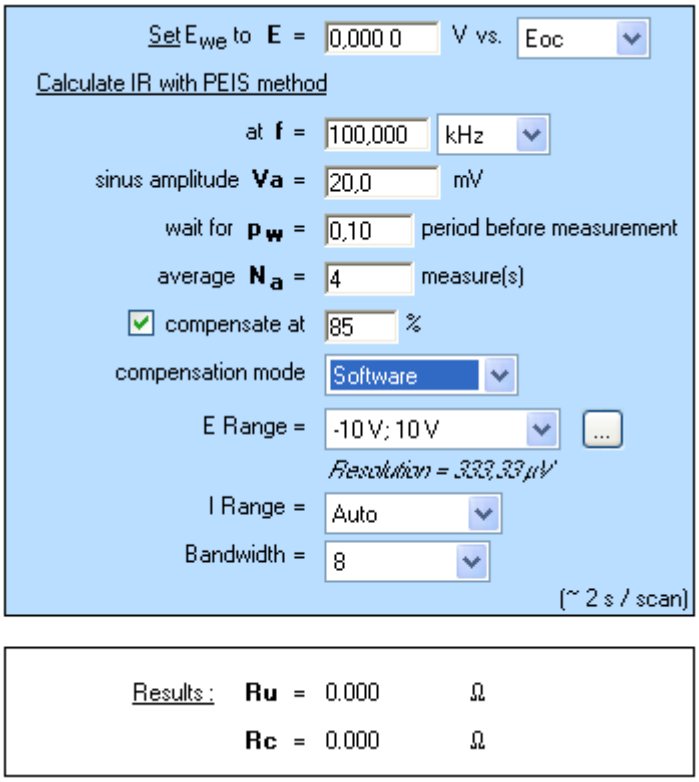


Fig. 89: ZIR diagram.

- **Impedance scan**

Set Ewe to E = … V *vs*. Ref/Eoc/Ectrl/Emeas
sets the potential to a fixed value *vs.* 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.

Compensation mode
in the SP300-based instruments the compensation could be made by software or by hardware. Note that the hardware compensation is not available with the CE to ground and WE to ground connections.

E Range = …

enables the user to select the potential range and to adjust the potential resolution according to the experiment (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.

Results: **Ru ... Ohm**

Rc ... Ohm

shows the uncompensated and compensate resistance obtained with this technique.

2.6.3 CI: IR determination by Current Interrupt

Some set-up induces ohmic drop, iR_u. In that case, ohmic drop can be significant and affect the measurement. A method to estimate the resulting uncompensated resistance (R_u) is to perform the Current Interrupt (CI) method. A current step is applied and the R_u 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 (Rising Edge, $(E_2 - E_1) / (I_2 - I_1)$) and/or interrupted (Falling Edge, $(E_4 - E_3)/(I_4 - I_3)$). Then an averaged correcting R_u value is calculated. Averaged values can be determined on several cycles. The user can select the percentage of compensation. It is highly recommended not to exceed 85% of the R_u measured value in order to avoid oscillations of the instrument.

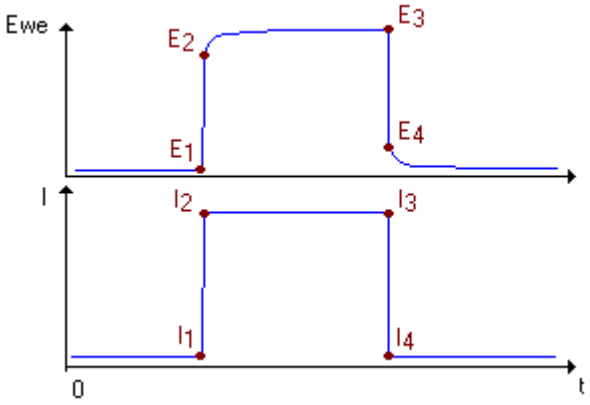


Fig. 90: Current Interrupt principle.

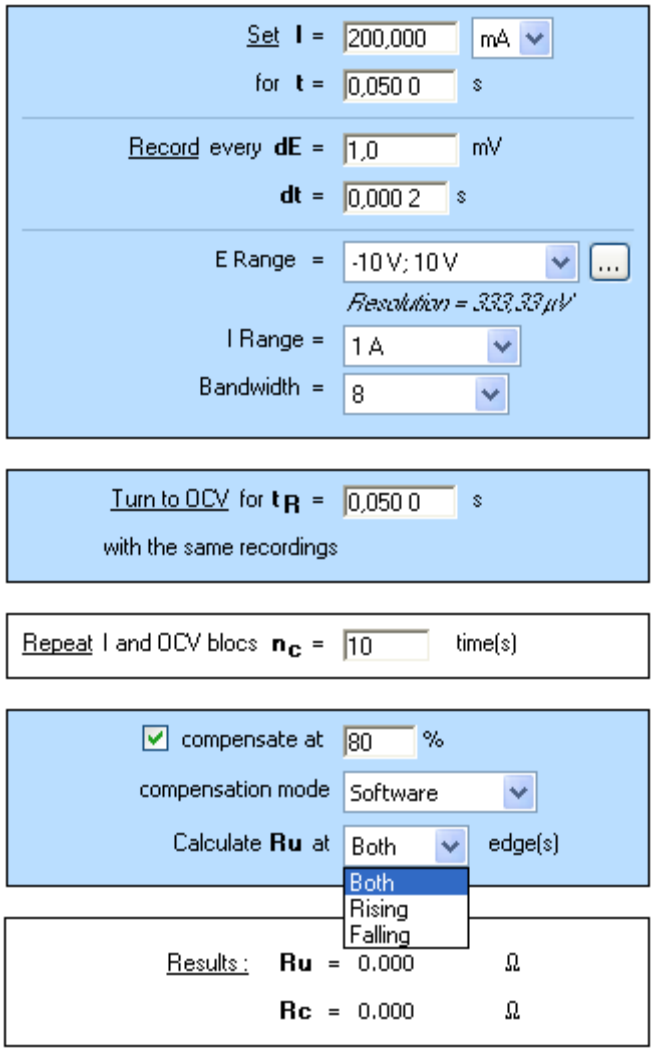


Fig. 91: Current Interrupt detailed diagram.

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 and to adjust the potential resolution according to the experiment (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
repeats 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.

Compensation mode
in the SP300-based instruments the compensation could be made by software or by hardware. Note that the hardware compensation is not available in WE to Ground and CE to ground connections.

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

Results: **Ru ... Ohm**

Rc ... Ohm
shows the uncompensated and compensate resistance obtained with this technique.

2.7 Bipotentiostat techniques

The bipotentiostat techniques were added to EC-Lab® software since the version 10.30. These techniques are available on multichannel potentiostat (VSP, VMP2, VMP3, SP-300, VSP-300 and VMP-300). This kind of experiment consists in applying two synchronized techniques on two electrodes (one technique on each electrode). This is the case of the Rotating Ring-Disk Electrode (RRDE) or hydrogen permeation investigations. Three couple of techniques are proposed in EC-Lab®: CV/RCA, CP/RCA and CA/RCA.

Note:

Both channels are totally independent, but the first technique controls the sampling rate and the total duration of the experiment. The first channel board is called disk channel and the second channel is the ring channel. The two channels have to be selected and defined in the “Select the bipotentiostat ring and disc channels” window (Fig. 81).

The bipotentiostat techniques are not linkable with other technique in EC-Lab software.

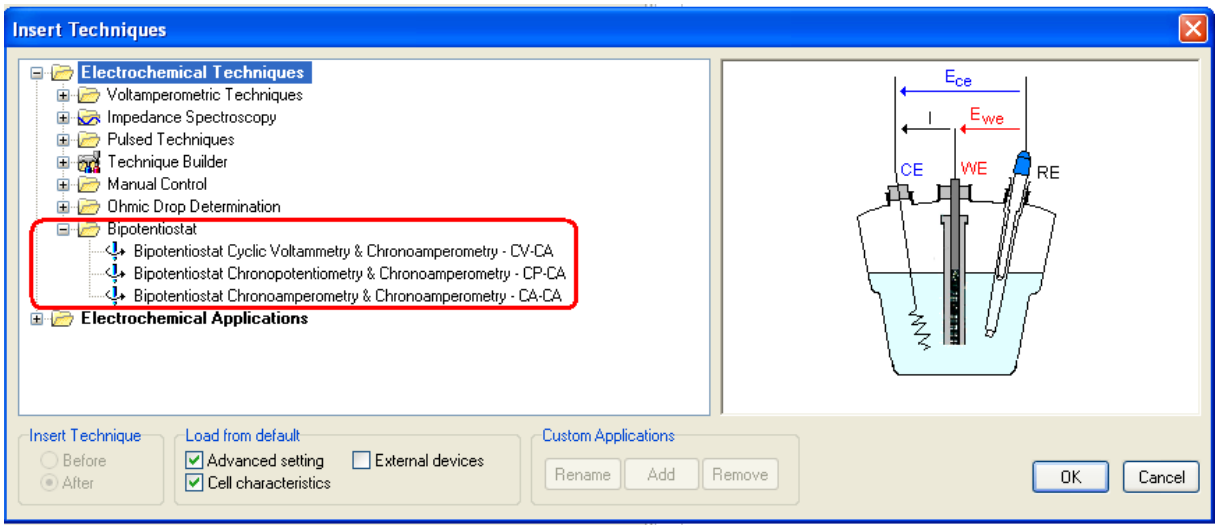


Fig. 92: Bipotentiostat techniques

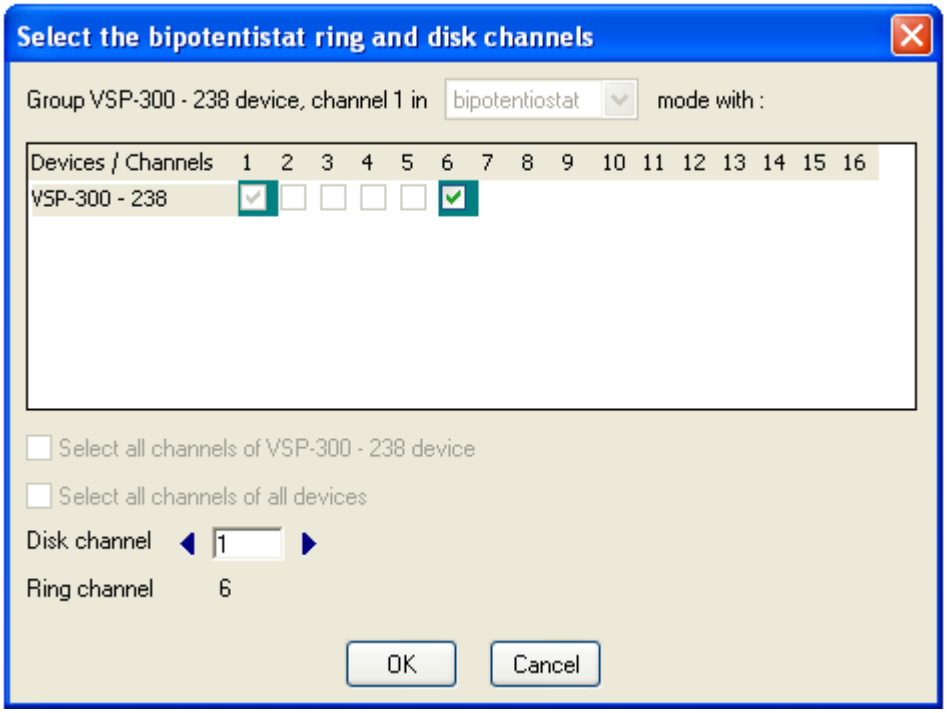


Fig. 93: Select the bipotentiostat ring and disk channels window

2.7.1 CV_RCA : CV synchronized with CA

The technique is composed of two blocks: CV on the disk channel and a RCA on the Ring channel.

CV block:

- a starting potential E_i,
- two vertex potentials E1 and E2,
- a final potential Ef,
- scan rate definition,
- recording conditions,
- repeat option,
- instrument parameters configuration.

RCA block:

- potential step,
- recording conditions,
- instrument parameters configuration.

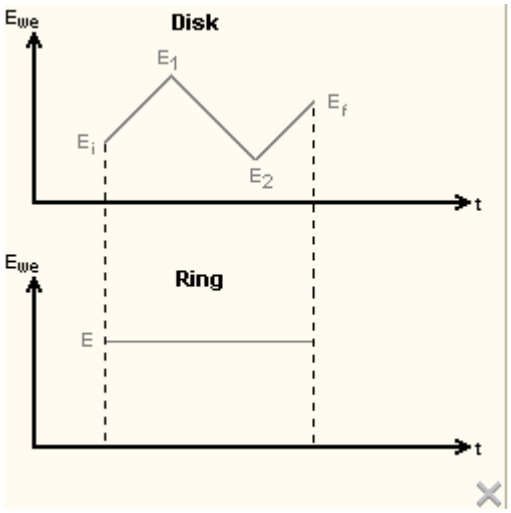


Fig. 94: CV_RCA description.

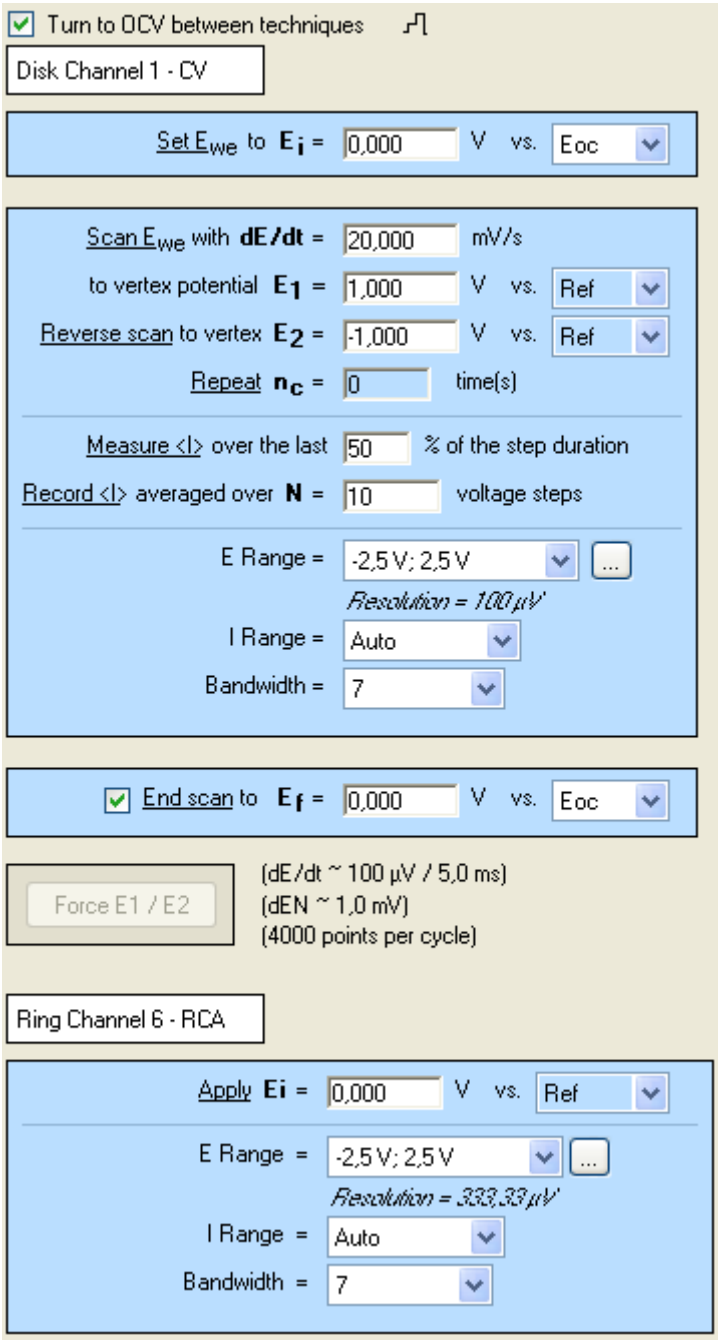


Fig. 95: CV_RCA detailed setup.

- **CV block:**

  - **Starting potential**

Set E_{we} to E_i = … V *vs.* Ref/Eoc/Ectrl/Emeas
sets the starting potential *vs.* reference electrode potential or *vs.* the open circuit potential (E_{oc}) or the previous 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
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 User's Manual).

to vertex potential E_1 = … V *vs*. Ref/Eoc/Ei.
sets the first vertex potential value *vs.* reference electrode potential or *vs.* the open circuit potential (E_{oc}) or *vs.* the potential of the previous experiment (E_i).

- **Reverse scan**

Reverse scan to 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 scan E_i to E_1 to E_2 n_c time(s). Note that the number of repetition does not include the first sequence: if n_c = 0 then the sequence will be done once; if n_c = 1 the sequence will be done twice, if n_c = 2, the sequence will be done 3 times, etc…

- **Data recording conditions**

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. It may be necessary to exclude the first points of the current response, which may only be due to the capacitive rather than faradic behavior of the system.

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 and to adjust the potential resolution according to the experiment (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.

- **Final potential**

End scan to 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
During the experiment, 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 to 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 clicking on the "Modify" button, setting the running potential as E_1 or E_2 and validating the modified parameters with the Accept button. The **Force E_1/E_2** button allows the user to perform the operation in a faster way in the case where the potential limits have not been properly estimated and to continue the scan without damaging the cell.

- **RCA block:**
  - **Potential step**

Apply E_i = … V *vs.* Ref/Eoc/Ectrl/Emeas.
the potential step is defined *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}).

the potential step duration depend on the duration set on the disc channel.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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.

2.7.2 CP_RCA : CP synchronized with CA

The CP_RCA technique is composed of a CP on the disc channel and a CA on the ring channel. Both protocols are displayed in the same technique.

CP block:

- current step,
- current sequences,
- recording conditions,
- repeat option,
- instrument parameters configuration.

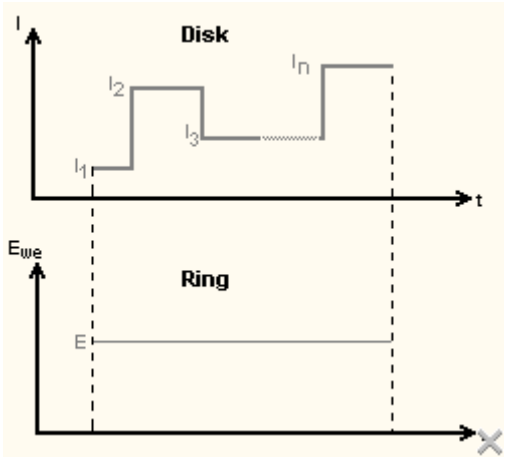


Fig. 96: CP_RCA description.

RCA block:

- potential step,
- recording conditions,
- instrument parameters configuration.

The detailed parameter setup is displayed on the following Fig. (97)

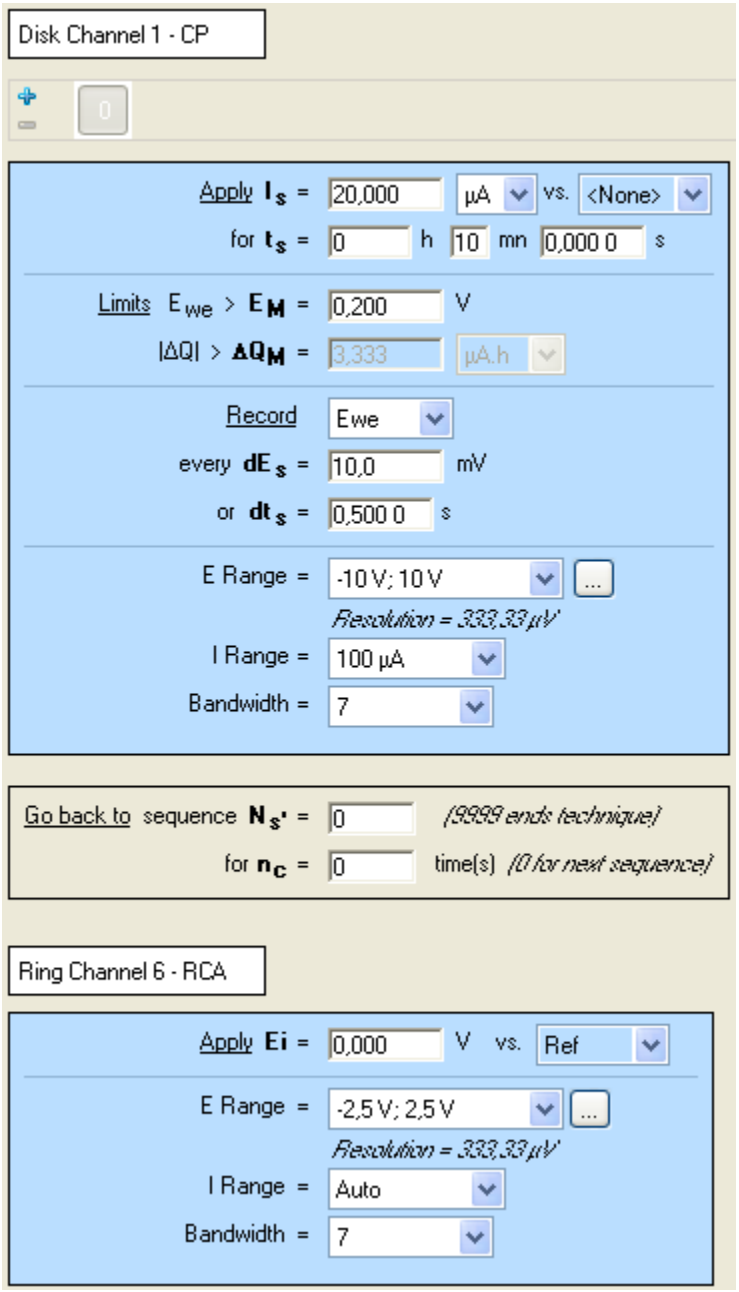


Fig. 97: CP_RCA detailed setup.

CP block:

- **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
sets the current step duration.

Limits E_{we} >/< E_M = … V

curtails the step duration if the potential 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 |ΔQ| 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 remains blue. These values can be entered simultaneously, and this is the first condition that is reached that determines the recording. When <Ewe> is selected, the number of averaged data points is displayed.

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

- **RCA block:**
  - **Potential step**

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

the potential step duration depend on the duration set on the disc channel.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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.

2.7.3 CA_RCA : CA synchonized with CA

The technique is composed of two CA one on the disc channel and another one on the ring channel. Both protocols are displayed in the same technique.

The detailed flow diagram is made as follows:

First CA block:

- potential step,
- potential sequences,
- recording conditions,
- repeat option,
- instrument parameters configuration.

Second RCA block:

- potential step,
- potential sequences,
- recording conditions,
- instrument parameters configuration.

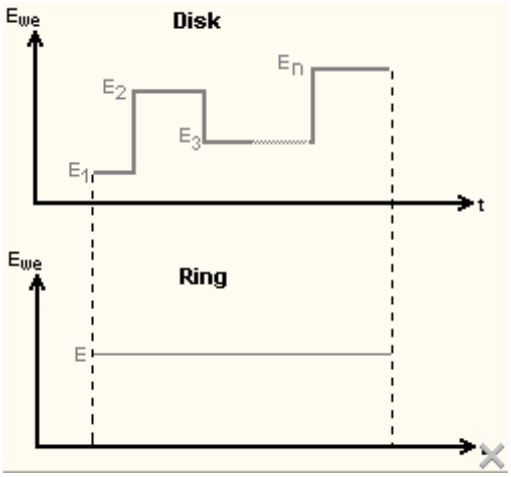


Fig. 98: CA_RCA description.

The detailed parameter setup is displayed on the Fig. 93:

First CA block:

- **Potential step**

Apply E_i = … V *vs.* Ref/Eoc/Ectrl/Emeas.
the potential step is defined *vs.* 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
sets the potential step duration.

Limits I_{Max} = … pA/…/A
I_{min} = … pA/…/A
$|\Delta Q| > \Delta Q_M$ = … fA.h/…/A.h/pC/…/kC.
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.

- **Data 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
Either an instantaneous current value I or an averaged current value <I> can be recorded. The recording conditions during the potential step depend on the chosen current variable. For the instantaneous current the recording values can be entered simultaneously. It is the first reached condition that determines the recording. A zero value disables the recording for each condition. For the averaged current, the user defines the time for the calculation of the average. In this, case the data points are recorded in the channel board memory every 200 µs for VMP3 based instruments and for VMP300 based instruments.
Set dQ=0 for Chronoamperometry experiments, and dI=0 for Chronocoulometry experiments.

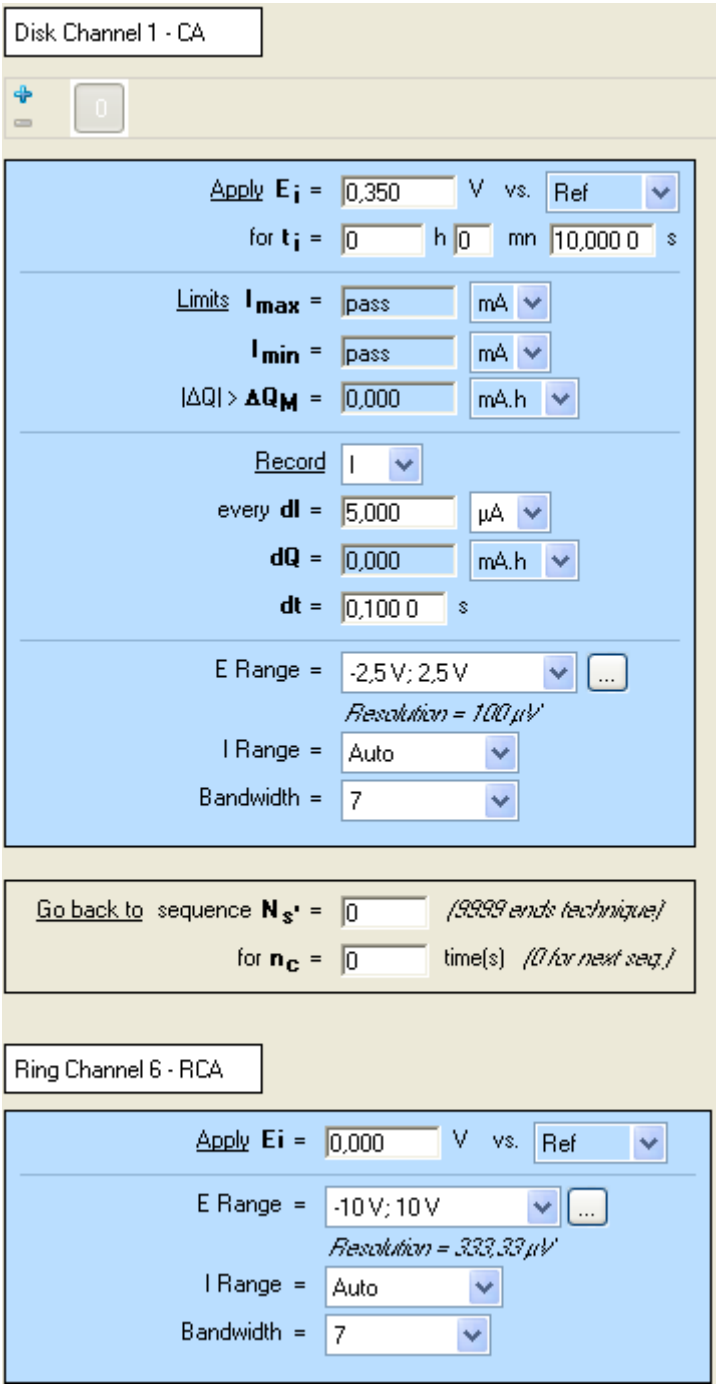


Fig. 99: CA_RCA detailed setup.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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**

Go back to Ns' = ... for nc = ... time(s)
allows the experiment to go back to a previous sequence $N_{s'}$ (<= N_s) for n_c times. For example, on N_s = 3, if one enters “go back to $N_{s'}$ = 2 for n_c = 1 time”, the sequence N_s = 2, N_s = 3 will be executed twice.
n_c = 0 disables the loop and the execution continues to the next sequence ($N_{s'} = N_s + 1$).

Second CA block:

- **Potential step**

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

the potential step duration depend on the duration set on the disc channel.

E Range = …
enables the user to select the potential range and to adjust the potential resolution according to the experiment (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.

3. Electrochemical applications

3.1 Batteries Testing

In this application domain, it is common to run successive 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 (accessible using the following path **View -> Settings With Flowcharts.** 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 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 $n_c + 1$). Moving on to the next sequence/sweep (or line) is obtained by setting n_c to 0.

An usual technique consists in 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 move on 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 BCD: Battery Capacity Determination

This technique is used to determine the capacity of a battery and permits to utilize this value in the following techniques of the experiment (adjust to the charge/discharge rate, C/N or CxN, in GCPL and Modulo Bat techniques).

This determination is made under galvanostatic mode, i.e. the same current value is fixed in the charge and discharge regime. The batteries are cycled between the potential limits E_{M1} and E_{M2}. The experiment can switch from galvanostatic mode to potentiostatic mode, holding the potential of the working electrode at the limit potential (while the limit in current, or time, is reached). The capacity value is displayed and it could be used in the next techniques. After this capacity determination, the battery can be charged / discharged to go back to the initial potential

3.1.1.1 Description of a galvanostatic sequence

The detailed diagram of the BCD technique is shown in Fig. 134.

<u>Set</u> I to I_s = … pA/… /A *vs.* <None>/Ictrl/Imeas, for at most t_1 = … h ... mn ... s
sets the current as an absolute value or versus the previous controlled or measured current (previous sequence, and the maximum duration of this 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).

Set I to C/N or CxN with N = … and I>0 or <0, for at most t_1 = … h ... mn ... s
Sets the rate C/N or CxN at wich the battery will be charged (I>0) or discharged (I<0). The estimated capacity of battery must be entered in the cell characteristics (see 3.1.10.2). Set C/3 mean that the battery will be charged (discharged) in 3 h.

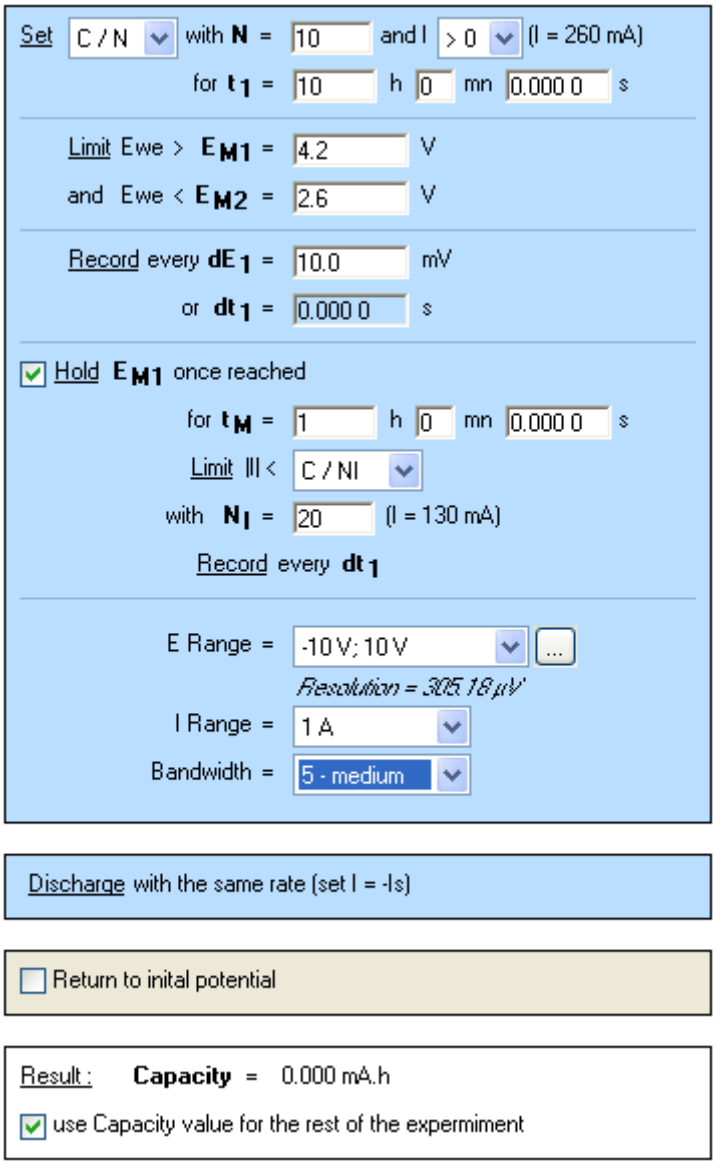


Fig. 100: BCD detailed diagram.

Limit E_{we} > E_{M1} = … V

E_{we} < E_{M2} = … V
sets the limits of the working electrode potential under charge and discharge regime (see warning 1 in Description of a galvanostatic sequence).

Record E_{we} every dE_1 = … mV or 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 every dt_1 time interval.

Hold E_{M1} for t_M = … h … mn … s
once E_{M1} is reached it is held for a given time t_M.

Limit |I|<I_m= ... pA/… /A
offers the possibility to stop the potentiostatic period when the limit current I_m is reached.

Record every dt_1
The potentiostatic period is recorded every dt_1 time interval (set in the galvanostatic period).

E Range = …
enables the user to select the potential range and to adjust the potential resolution with his/her 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 for this experiment.

Discharge with the same rate (set I=-I_s)
The discharge/charge period is preformed with the I=-I_S.

Return to initial potential
If this case is checked, the system will be charged/discharged (I=±I_s) to reach the initial potential.

Result: Capacity = ... mA.h
shows the obtained value.

□ **use Capacity value for the rest of experiment**
Selecting this option, the obtained value can be used in the rest of experiment, *e.g.* to set the rate C/N or CxN in the GCPL's protocols.

3.1.2 GCPL: Galvanostatic Cycling with Potential Limitation

This technique essentially corresponds to battery cycling under galvanostatic mode, 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. It can be used to perform GITT (galvanostatic Intermittent Titration Technique) experiment. Similarly to PCGA, GCPL can be used to have the chemical diffusion coefficient of the mobile species in the electrode. Since it is the current that is controlled, the effect of the ohmic drop in the cell can be overcome.

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.

The technique is by default composed of three sequences: resting period (i.e. OCV), charge and discharge.

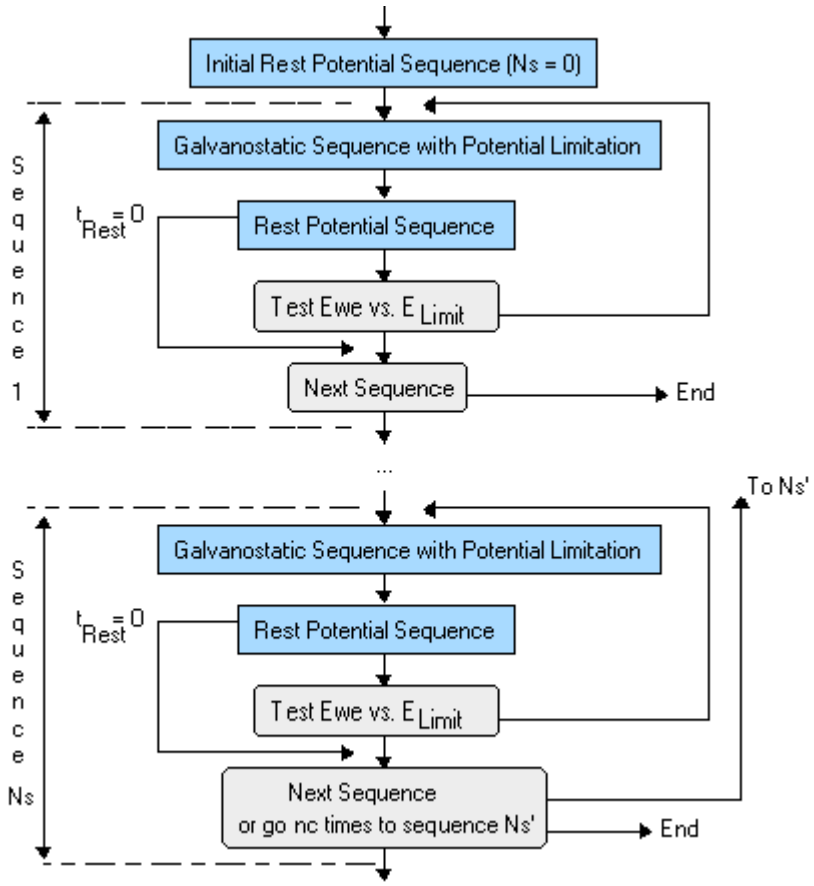


Fig. 101: General diagram of the GCPL application.

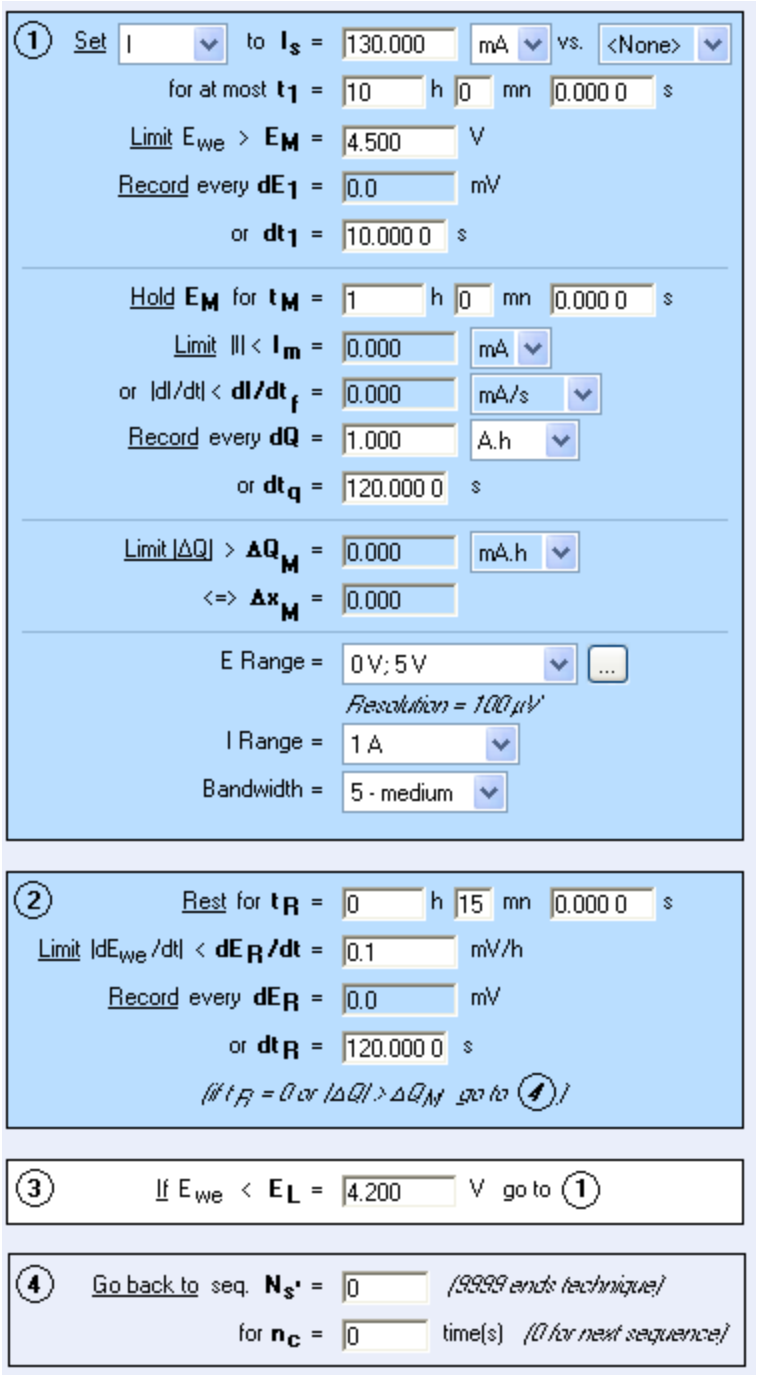


Fig. 102: Detailed diagram of one GCPL sequence.

In the battery applications, the current values panel displays additional information:
Q - Q_0 and x – x_0 are respectively the total charge and the normalized charge from the beginning of the experiment.
N_s is the current sequence number in the 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.

Reference

- Weppner W., Huggins R. A., J. Electrochem. Soc. 126 (1977) 1569-1578

3.1.2.1 Description of a galvanostatic sequence

See Fig. 102.

- **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
sets 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).
It is also possible to set the current relatively to the capacity of the battery entered in the cell characteristics (see 3.1.10.2).

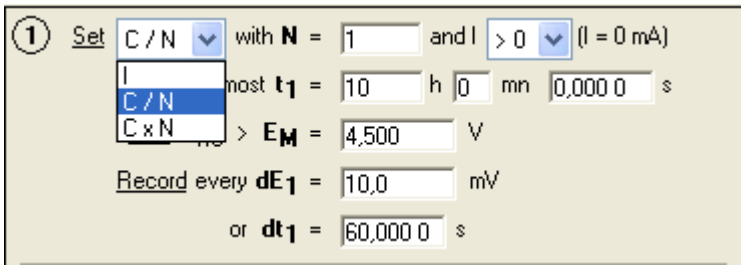


Fig. 103 : setting the charge/discharge using the capacity of the battery

Set C/N or CxN with N = … and I >0 or <0, for at most t_1 = … h ... mn ... s
sets the rate C/N or CxN at which the battery will be charged (I>0) or discharged (I<0). The C value could be a noninteger value.
For instance, if the capacity of a battery is 1800 mA.h, setting C/N with N=3, and I>0 means that a current of 600 mA will be passed during 3h. The total capacity of the battery will be reached in 3h.
Setting CxN with N=2 and I<0 means that a current of -3600 mA will be passed during 30 min. The total capacity of the battery will be reached in half an hour. There is still the possibility to set a time limit.

Limit E_{we} >/< E_M = … V
sets the limit of the working electrode potential under charge/discharge (see warning 1).
for t_M = ... h … mn … s or until $|I| < I_m$ = … pA/…/A or $|dI/dt| < dI/dt_f$ … A/s/ … /µA/mn
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 or when the variation of the current is lower than given value dI/dt_f.
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 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

Hold E_M for t_1 = … h … mn … s
once E_M is reached it is held for a given time t_1. If E_M is not reached this step is skiped.

Limit $|I| < I_m$
offers the possibility to stop the potentiostatic period when the limit current I_m is reached.

Record ΔQ every dQ = … A.h/…/fA.h/kC/…/pC 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 = … A.h/…/fA.h/kC/…/pC <=> Δx_M = ...
sets 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 and to adjust the potential resolution with his/her 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 for this experiment.

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

turn to Rest for t_R = … h … mn … s
sets a maximum time t_R to stay in open circuit mode.
Limit $|dE_{we}/dt| < |dE_R/dt|$ = … 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 ≥ 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.**

If 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 $N_{S'}$ ($N_{S'} < N_S$).**

Go back to seq. $N_{S'}$…for n_c…
If n_c is set to 0, then the technique executes the next sequence.
If the user wants to loop to a previous sequence, the 2 last columns of the table have to be filled
"**Go back to $N_{S'}$**" and " **n_c cycles**".
This table is visible using the following path: **View -> Settings with Flowcharts**

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

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 conditions (see Warning 2).

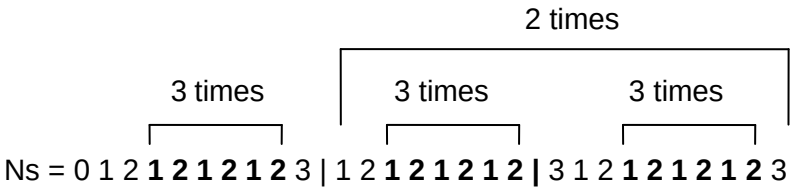
Note that it is always possible to force the end of a technique while it is running, at any sequence, using the **Modify** button and setting **Go back to** sequence $N_{S'}$ = 9999 at the sequence one wants to stop.

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. 104: 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 instead of blank. Otherwise the program will detect a blank 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).

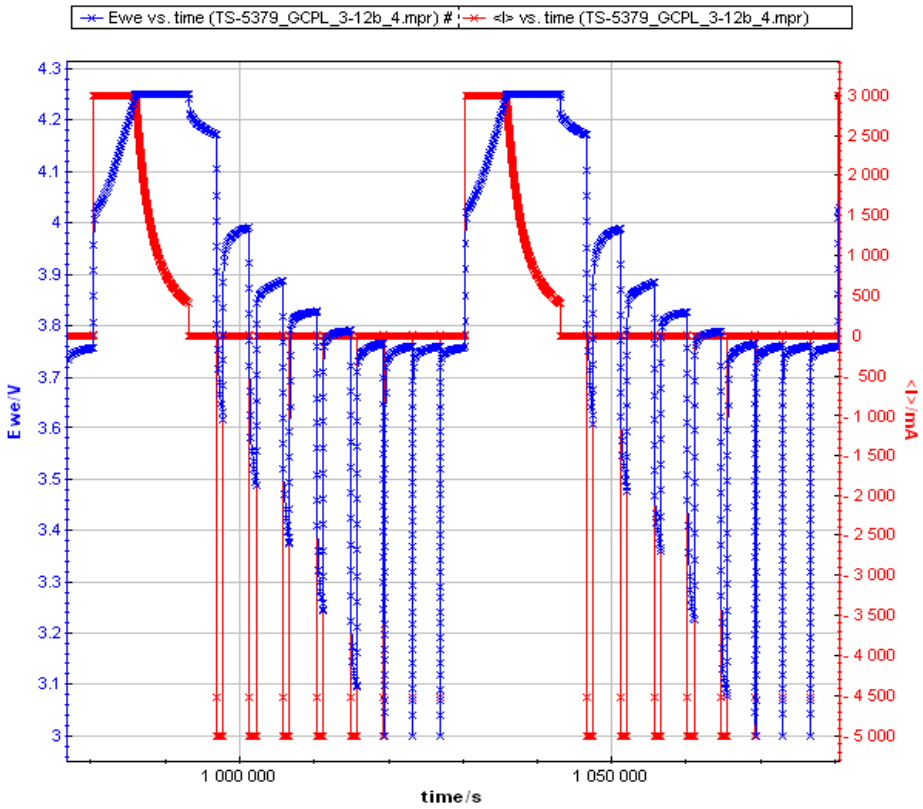


Fig. 105: Example of GCPL experiment obtained with a Li-ion battery (10 A.h).

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, the software 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.

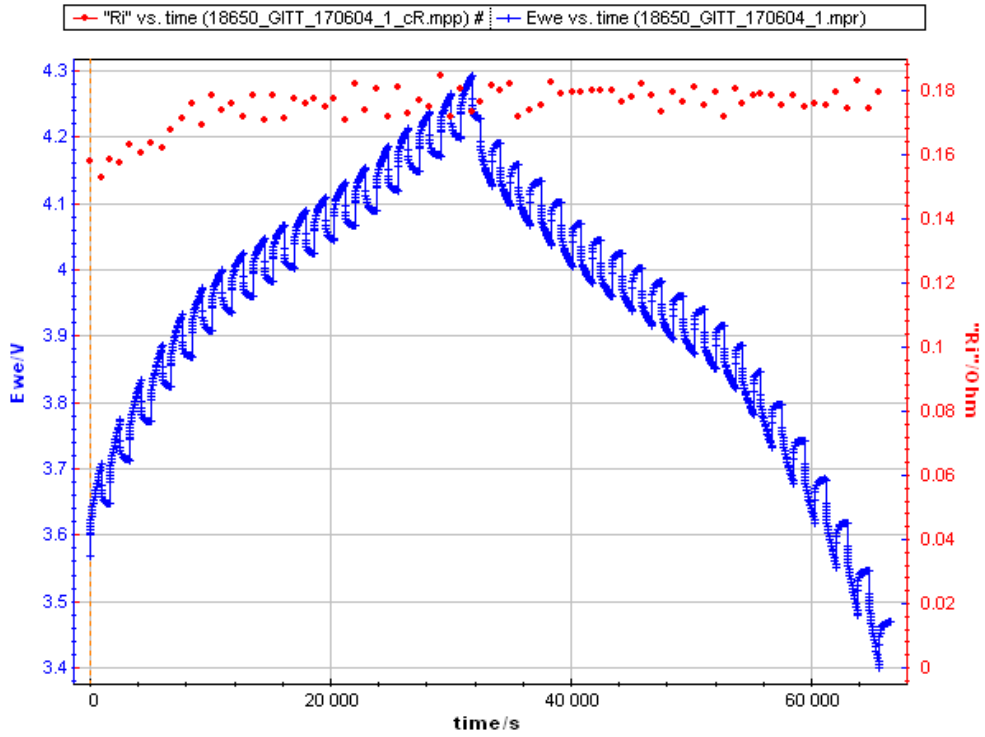


Fig. 106: Ri determination (red circles) after a GITT experiment (blue crosses) obtained with an 18650 Li-ion battery.

3.1.3 GCPL2: Galvanostatic Cycling with Potential Limitation 2

The GCPL2 application is similar to the GCPL one, but was designed to limit both the working electrode (WE) and the counter electrode (CE) potential. Additionally, the cell potential after the current charge/discharge is not held at a constant value.

The technique is by default composed of three sequences: resting period (i.e. OCV), charge and discharge.

The GCPL2 technique is made of 4 blocks:

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

This is detailed Fig. 107.

- **Galvanostatic period**

Set I to Is = … pA/…/A *vs*. <None>/Ictrl/Imeas, for at most t_1 = … h … mn … s
sets 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).

Set C/N or CxN with N = … and I >0 or <0, for at most t_1 = … h ... mn … s
sets the rate C/N or CxN at which the battery will be charged (I>0) or discharged (I<0). The C value could be a noninteger value.

For instance, if the capacity of a battery is 1800 mA.h, setting C/N with N=3, and I>0 means that a current of 600 mA will be passed during 3h. The total capacity of the battery will be reached in 3h.
Setting CxN with N=2 and I<0 means that a current of -3600 mA will be passed during 30 min. The total capacity of the battery will be reached in half an hour. There is still the possibility to set a time limit.

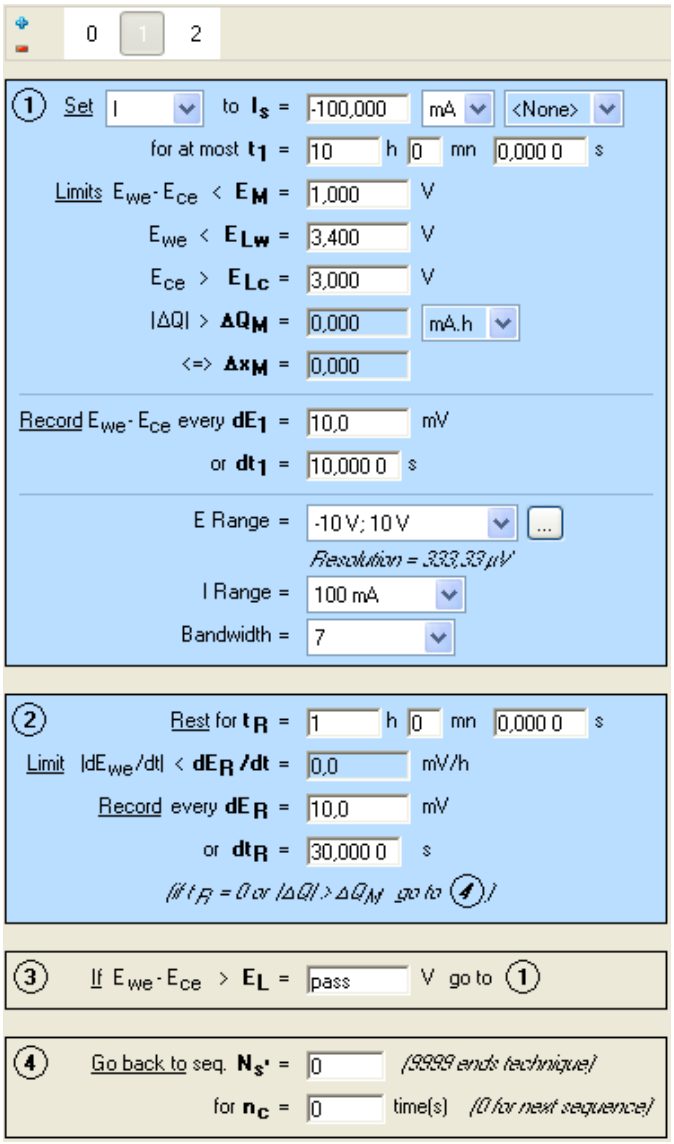


Fig. 107: GCPL2 detailed diagram.

<u>Limits</u> E_{we} - E_{ce} >/< E_M = … V
E_{we} >/< E_{Lw} = …V
E_{ce} >/< E_{Lc} = … V
Go to the next block if one of these conditions 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 = … A.h/… /fA.h/kC/…/pC <=> Δx_M = …
sets 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).

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 ≥ dE_1 and time ≥ 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.

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

- **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**

If E_{we} - E_{ce} >/< E_L … V
The third step is the test on the open circuit final potential. This test is skipped if there is no OCV period (t_R = 0).
The test performed takes the conditional value > or <, whether the open circuit sequence occurs after a charge (I > 0) or a discharge (I < 0).
The above 2 steps (Galvanostatic and resting period) 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 can bypass this test by entering p (= pass) instead of a voltage value.

- **Loop**

Go back to 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).
Note: 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 cell potential after the galvanostatic step.

The technique is by default composed of three sequences: resting period (i.e. OCV), charge and discharge.

- **Galvanostatic period**

Set I to Is = … pA/… /A *vs*. <None>/Ictrl/Imeas, for at most t_1 = … h ... mn … s
sets 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).

Set C/N or CxN with N = … and I >0 or <0, for at most t_1 = … h … mn … s
sets the rate C/N or CxN at which the battery will be charged (I>0) or discharged (I<0). The C value could be a noninteger value.

For instance, if the capacity of a battery is 1800 mA.h, setting C/N with N=3, and I>0 means that a current of 600 mA will be passed during 3h. The total capacity of the battery will be reached in 3h.
Setting CxN with N=2 and I<0 means that a current of -3600 mA will be passed during 30 min. The total capacity of the battery will be reached in half an hour. There is still the possibility to set a time limit.

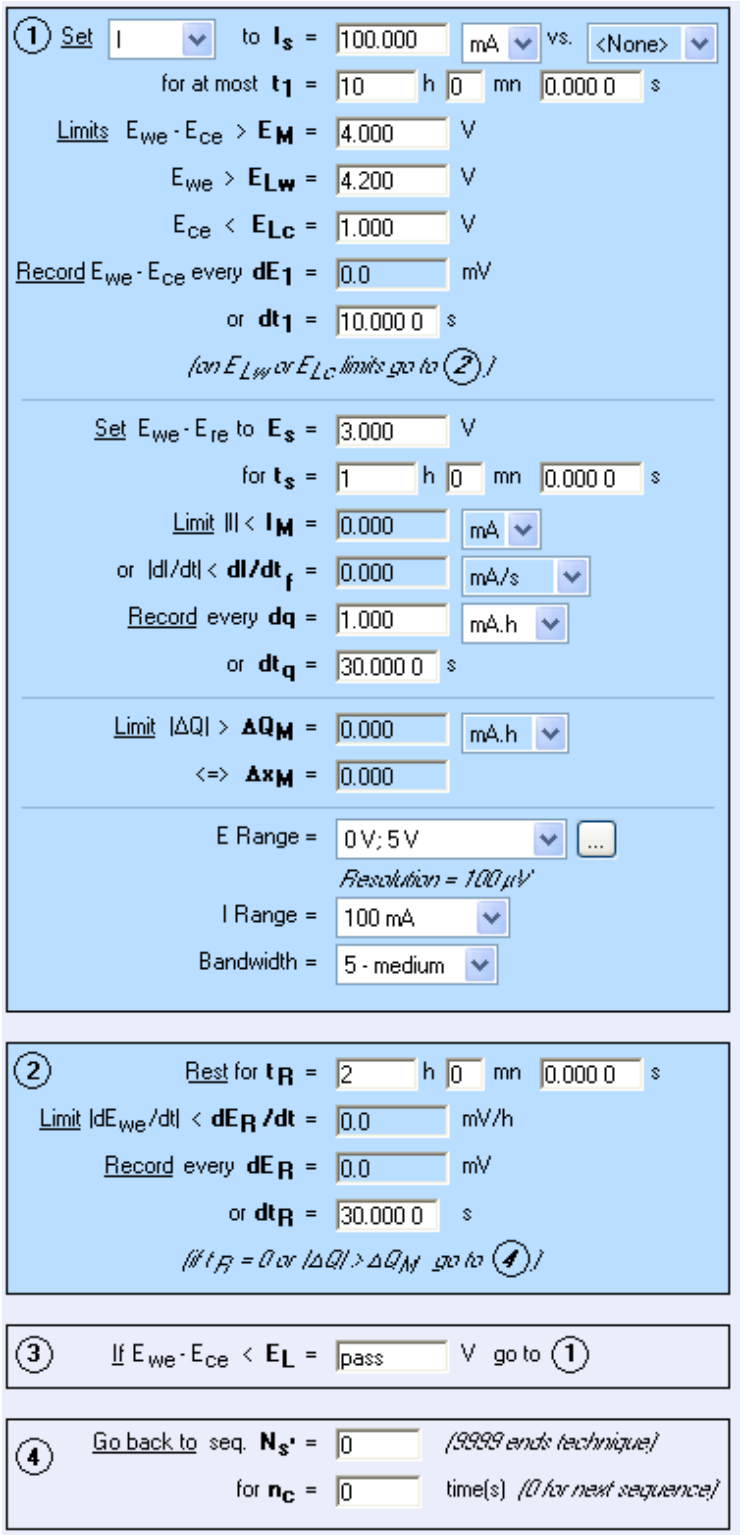


Fig. 108: GCPL3 detailed diagram.

Limits E_{we} - E_{ce} >/< E_M = … V
E_{we} >/< E_{Lw} = … V
E_{ce} >/< E_{Lc} = … V
Go to the next block if one of these conditions 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}.

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.

- **Potentiostatic period**

Set E_{we} - E_{re} to E_s = …V for t_s = … h … mn … s
after the galvanostatic period it is possible to maintain E_{we} - E_{re} (= E_{we} = Ref1 – Ref2) at a certain potential during a certain amount of time.
Limit |I| < I_m = … pA/…/A or |dI/dt|<dI/dt_f … A/s/ … /µA/mn
limits the absolute value of the current during the potentiostatic period at a value lower than I_m or when the variation of the current is lower than given value dI/dt_f..

Record every dq = … A.h/…/fA.h, kC/…/pC or dt_q = … s
records one point at each charge increment dq or at each time increment dt_q. In the case where both conditions are chosen, the faster of the two conditions will be taken into account. A zero value skips the recording condition.

Limit |ΔQ| to ΔQ_M = … A.h/…/fA.h/kC/…/pC <=> Δx_M = …
sets 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).

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

- **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**

If E_{we} - E_{ce} >/< E_L … V
The third step is the test on the open circuit final potential. This test is skipped if there is no OCV period (t_R = 0).
The test performed takes the conditional value > or <, whether the open circuit sequence occurs after a charge (I > 0) or a discharge (I < 0).
The above 2 steps (Galvanostatic and resting period) 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 can bypass this test by entering p (= pass) instead of a voltage value.

- **Loop**

Go back to 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).
Note: E_{ce} and E_{we}-E_{ce} recording are forced into the GCPL2 data files.

3.1.5 GCPL4: Galvanostatic Cycling with Potential Limitation 4

The GCPL4 application is similar to the GCPL application, but with a global time limitation for the charge/discharge period. The technique is by default composed of three sequences: resting period (i.e. OCV), charge and discharge.

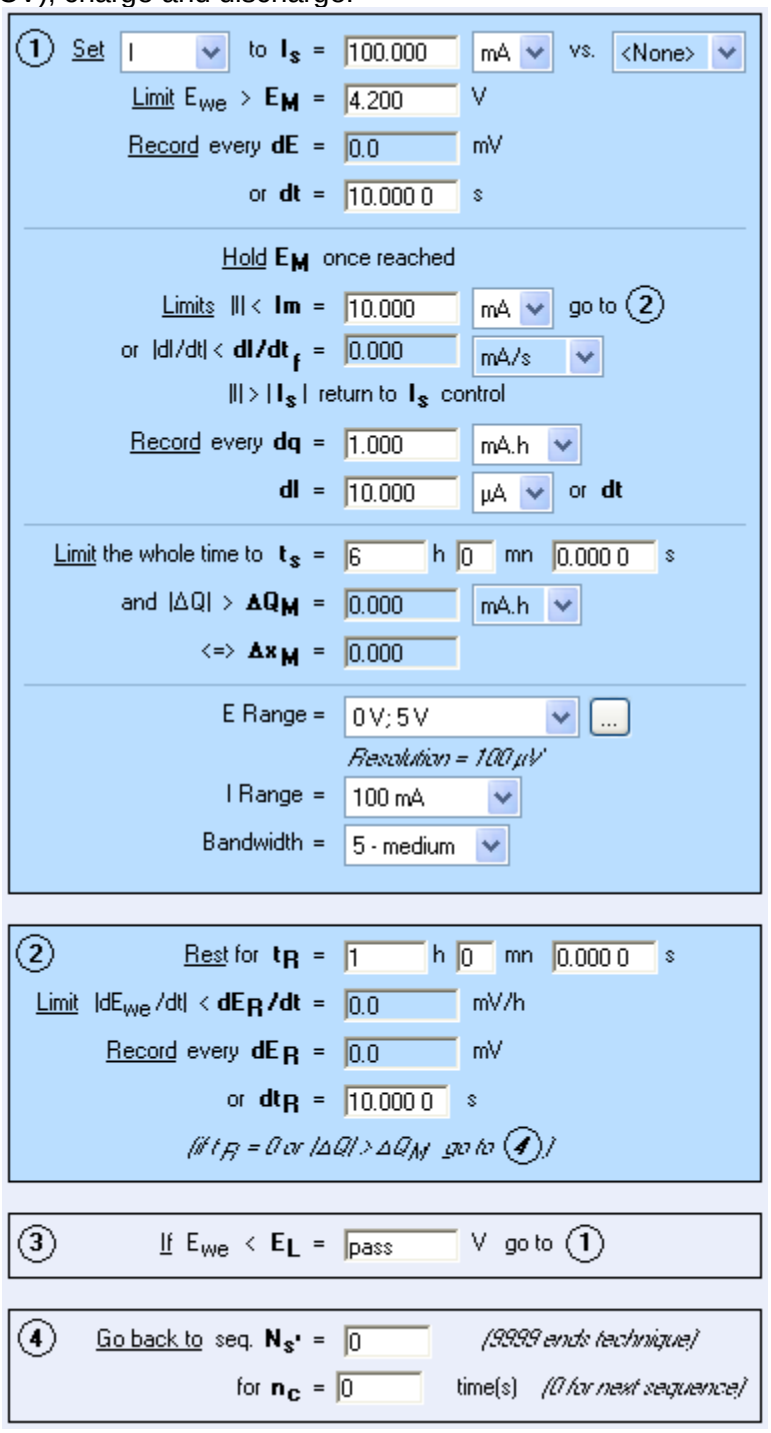


Fig. 109: GCPL4 detailed diagram.

- **Galvanostatic period**

Set I to Is = … pA/…/A *vs*. <None>/Ictrl/Imeas
sets 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).

Set C/N or CxN with N = … and I >0 or <0
sets the rate C/N or CxN at which the battery will be charged (I>0) or discharged (I<0). The C value could be a noninteger value.
For instance, if the capacity of a battery is 1800 mA.h, setting C/N with N=3, and I>0 means that a current of 600 mA will be passed during 3h. The total capacity of the battery will be reached in 3h. Setting CxN with N=2 and I<0 means that a current of -3600 mA will be passed during 30 min. The total capacity of the battery will be reached in half an hour. There is still the possibility to set a time limit.

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
sets 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.

- **Potentiostatic period**

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.

Limits |I| < Im = … pA/…/A
|dI/dt|<dI/dt$_f$ … A/s/ … /µA/mn
|I| > |Is| when holding E_M (return to Is on limit)
if the current |I| is over $|I_s|$ in constant potential mode, the system returns to constant current mode in order to protect the cell.

Record every dq = … A.h/…/fA.h, kC/…/pC, 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 the whole time to t_s = … h … mn … s
defines the total sequence duration (if not stopped on limits).

and $|\Delta Q|$ to ΔQ_M = … A.h/…/fA.h, kC/…/pC <=> 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 and to adjust the potential resolution with his/her 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 for this experiment.
Refer 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, written "R_i", ("i" stands for internal) is considered by manufacturers to be an internal characteristic of their cell. The R_i value is determined by the ratio = $(E_m – E_0)/(I_m – I_0)$, with E_m and I_m the data points on the current steps corresponding to a time $t_m = \Delta t2^{m-1}$ and m=1,2,3… E_0 and I_0 are the values corresponding to the last point of the OCV period. Such a geometric progression of time ensures a good distribution of points versus time. R_i determination is now available in EC-Lab® software using a GCPL application Refer to the process data section in EC-Lab® Software User's Manual, to the GCPL application section 3.1.2 page 109 or to the Application Note #38 for more details.

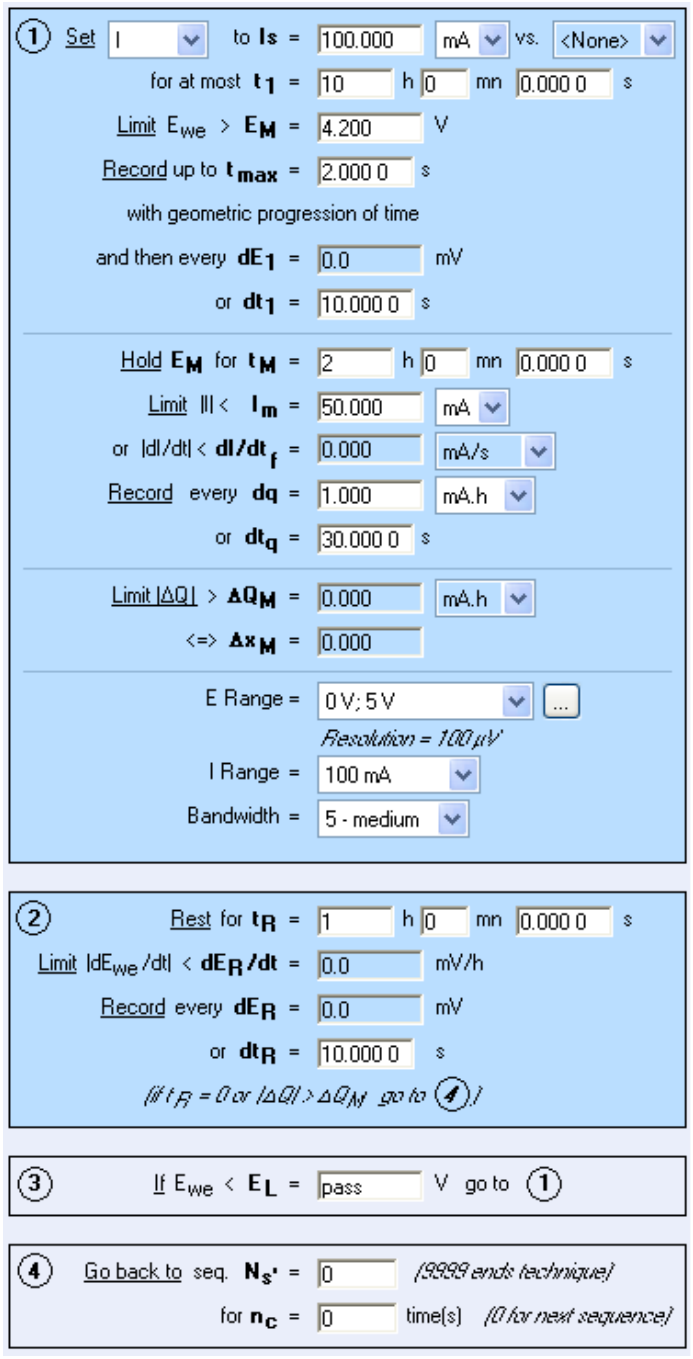


Fig. 110: GCPL5 detailed diagram.

- **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
sets 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.

Set C/N or CxN with N = … and I >0 or <0, for at most t_1 = … h ... mn ... s
sets the rate C/N or CxN at which the battery will be charged (I>0) or discharged (I<0). The C value could be a noninteger value.
For instance, if the capacity of a battery is 1800 mA.h, setting C/N with N=3, and I>0 means that a current of 600 mA will be passed during 3h. The total capacity of the battery will be reached in 3h.
Setting CxN with N=2 and I<0 means that a current of -3600 mA will be passed during 30 min. The total capacity of the battery will be reached in half an hour. There is still the possibility to set a time limit.

Limit E_{we} >/< E_M = ... V
sets the limit of the working electrode potential under charge/discharge (see warning 1).
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 E_{we} up to t_{max} = ... s with geometric progression of time and then every dE_1 = … mV or 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 ($t_{n+1}=a*t_n$) 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) Potentiostatic period

Hold E_M for t_1 = … h … mn … s
once E_M is reached it is held for a given time t_1.
Limit |I|<I_m…A/…/pA or |dI/dt|<dI/dt_f … A/s/ … /µA/mn
offers the possibility to stop the potentiostatic period when the limit current I_m is reached or when the variation of the current is lower than given value dI/dt_f.
Record ΔQ every dQ = … A.h/…/fA.h, kC/…/pC 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 = … A.h/…/fA.h, kC/…/pC <=> Δx_M = …
sets 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)..

3) Safety limit for the cell

If E_{we} - E_{ce} >/< E_L … V
The third step is the test on the open circuit final potential. This test is skipped if there is no OCV period (t_R = 0).
The test performed takes the conditional value > or <, whether the open circuit sequence occurs after a charge (I > 0) or a discharge (I < 0).

The above 2 steps (Galvanostatic and resting period) 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 can bypass this test by entering p (= pass) instead of a voltage value.

E Range = …
enables the user to select the potential range and to adjust the potential resolution with his/her 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 for this experiment.

- 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.

(See the data processing section in the EC-Lab® Software User's 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 or apparent resistance ("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 R_i is the only processed variable.

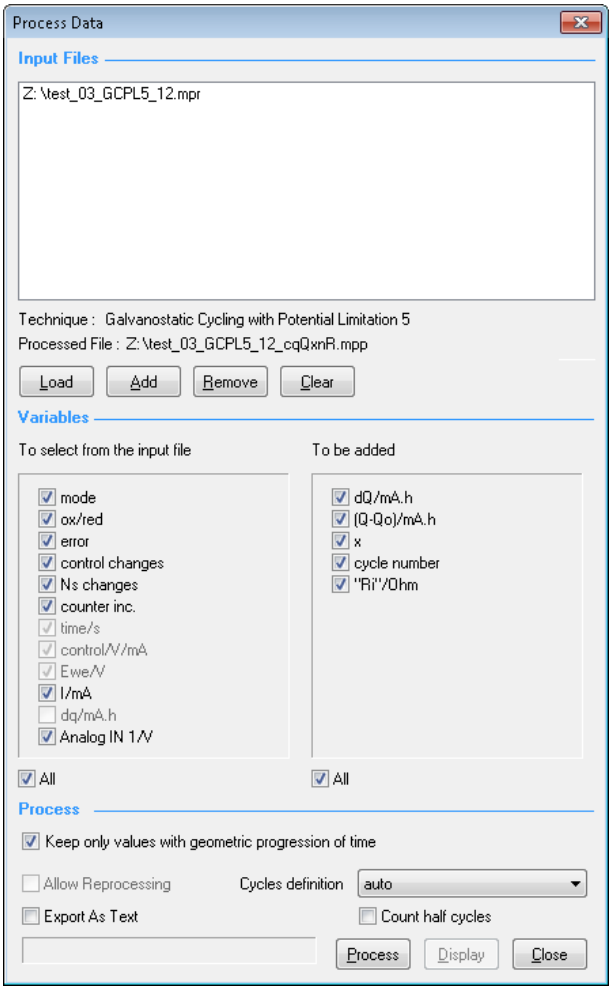


Fig. 111: GCPL 5 Process window.

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.

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

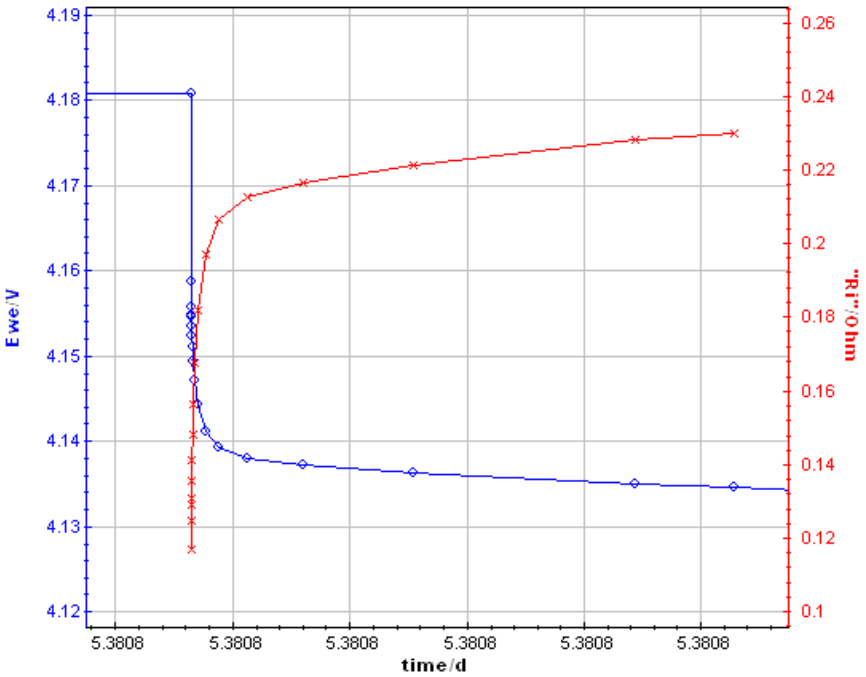


Fig. 112: GCPL 5 processed file display for Ri determination.

3.1.7 GCPL6: Galvanostatic Cycling with Potential Limitation 6

This technique is similar to the GCPL technique Contrary to the GCPL technique, the potential control during the potentiostatic period value is not done between Ref1 and Ref2 (Ewe) but between Ref1 and Ref3 (Ewe-Ece). This technique offers the user the possibility to follow the voltage of each electrode Ref1 and Ref3 *vs.* a reference electrode in the battery. This technique is only available with SP-50, SP-150, VSP, VMP3, HCP-803, HCP-1005, CLB-500 and CLB-2000 as it requires the measurement of the potential on Ref3.

1) <u>Galvanostatic period</u>

<u>Set I</u> to Is = … pA/…/A *vs.* <None>/Ictrl/Imeas, for at most t_1 = … h ... mn … s
sets 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).

<u>Set</u> C/N or CxN with N = … and I >0 or <0, for at most t_1 = … h ... mn … s
sets the rate C/N or CxN at which the battery will be charged (I>0) or discharged (I<0). The C value could be a noninteger value.
For instance, if the capacity of a battery is 1800 mA.h, setting C/N with N=3, and I>0 means that a current of 600 mA will be passed during 3h. The total capacity of the battery will be reached in 3h.

Setting CxN with N=2 and I<0 means that a current of -3600 mA will be passed during 30 min. The total capacity of the battery will be reached in half an hour. There is still the possibility to set a time limit.

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

Limit E_{cell} >/< E_M = … V
sets 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 .

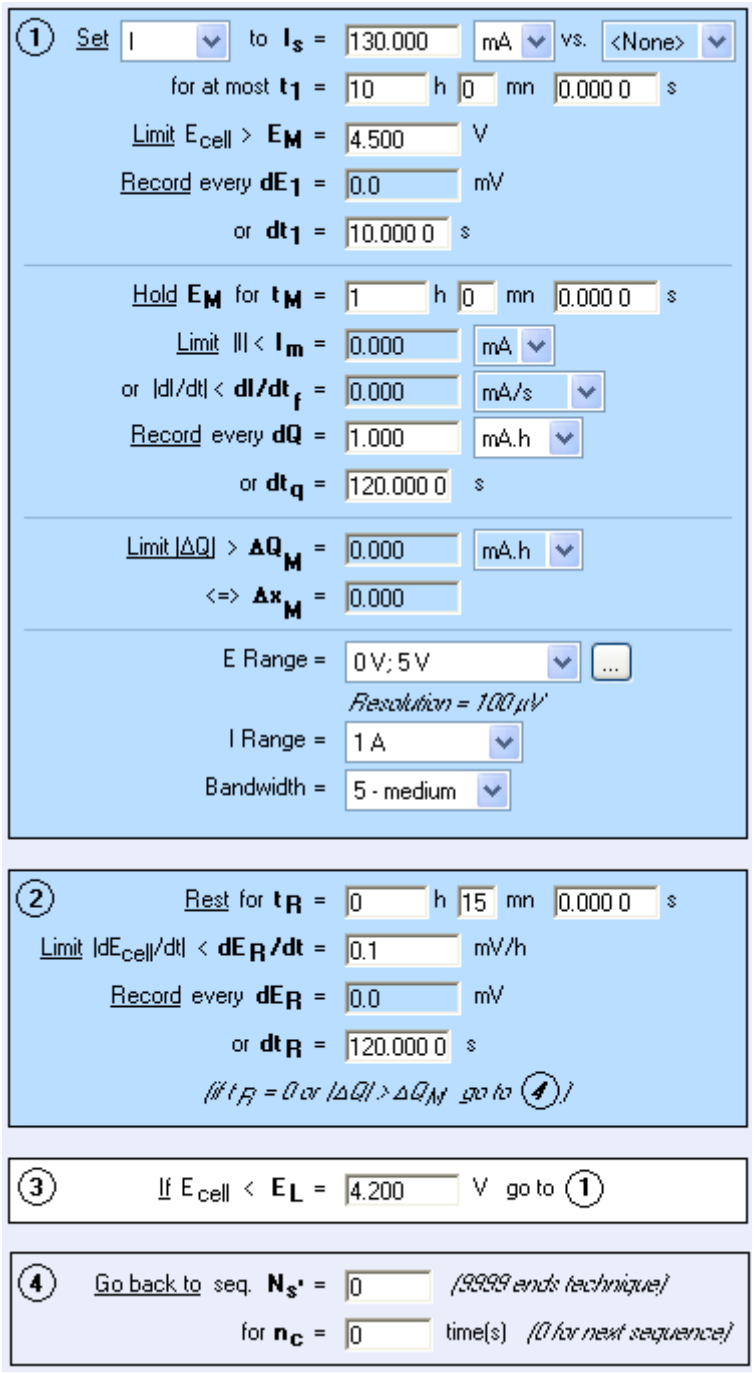


Fig. 113: GCPL6 detailed diagram.

2) Potentiostatic period

Hold E_M for t_M = … h … mn … s and Limit $|I| < I_m$ = … pA/…/A
or $|dI/dt| < dI/dt_f$ … A/s/ … /µA/mn
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 or when the variation of the current is lower than given value dI/dt_f.
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 every dQ = … A.h/…/fA.h, kC/…/pC 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 $\Delta Q > \Delta Q_M$ = … A.h/…/fA.h, kC/…/pC <=> Δx_M = …
sets 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 and to adjust the potential resolution with his/her 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 for this experiment

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

Rest for t_R = … h … mn … s
sets a maximum time t_R to stay in open circuit mode.
Limit $|dE_{cell}/dt| < |dE_R/dt|$ = … 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 or 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.**

If 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), the 2 last columns of the table needs to be filled "**Go back 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 **Go back to** 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 GCPL7: Galvanostatic Cycling with Potential Limitation 7

This technique is very similar to the GCPL technique (see 3.1.1). The main and only difference is that the potential EM is held constant not by controlling the potential but by controlling the current. By doing so, the whole experiment (charge/discharge and EM maintained constant) is performed under current control and not by current and then potential control as is done in GCPL. With GCPL7, the current glitch that occurs in GCPL and is associated to the switch from a potential to a current control, is avoided.

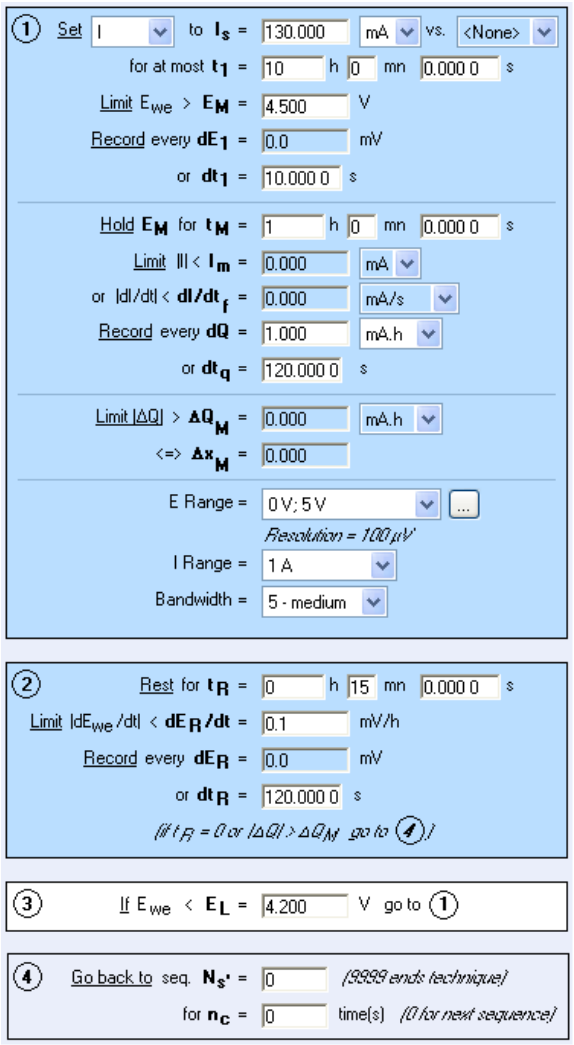


Fig. 114: GCPL7 detailed diagram

- **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
sets 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).

Set C/N or CxN with N = … and I >0 or <0, for at most t_1 = … h … mn … s
sets the rate C/N or CxN at which the battery will be charged (I>0) or discharged (I<0). The C value could be a noninteger value.
For instance, if the capacity of a battery is 1800 mA.h, setting C/N with N=3, and I>0 means that a current of 600 mA will be passed during 3h. The total capacity of the battery will be reached in 3h.
Setting CxN with N=2 and I<0 means that a current of -3600 mA will be passed during 30 min. The total capacity of the battery will be reached in half an hour. There is still the possibility to set a time limit.

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

Record E_{we} every dE_1 = … mV and or 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

Hold E_M for t_1 = … h … mn … s
once E_M is reached it is held for a given time t_1.
Limit |I|<I_m…A/…/pA or |dI/dt|<dI/dt_f … A/s/ … /µA/mn
offers the possibility to stop the potentiostatic period when the limit current I_m is reached or when the variation of the current is lower than given value dI/dt_f.

Record ΔQ every dQ = … A.h/…/fA.h, kC/…/pC 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 = … A.h/…/fA.h, kC/…/pC <=> Δx_M = …
sets 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 and to adjust the potential resolution with his/her 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 for this experiment.

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

turn to Rest for t_R = … h … mn … s
sets a maximum time t_R to stay in open circuit mode.
Limit |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 or 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.**

If 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), the 2 last columns of the table needs to be filled "**Go back 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 **Go back to** 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.

3.1.9 **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 as those of the GCPL one.

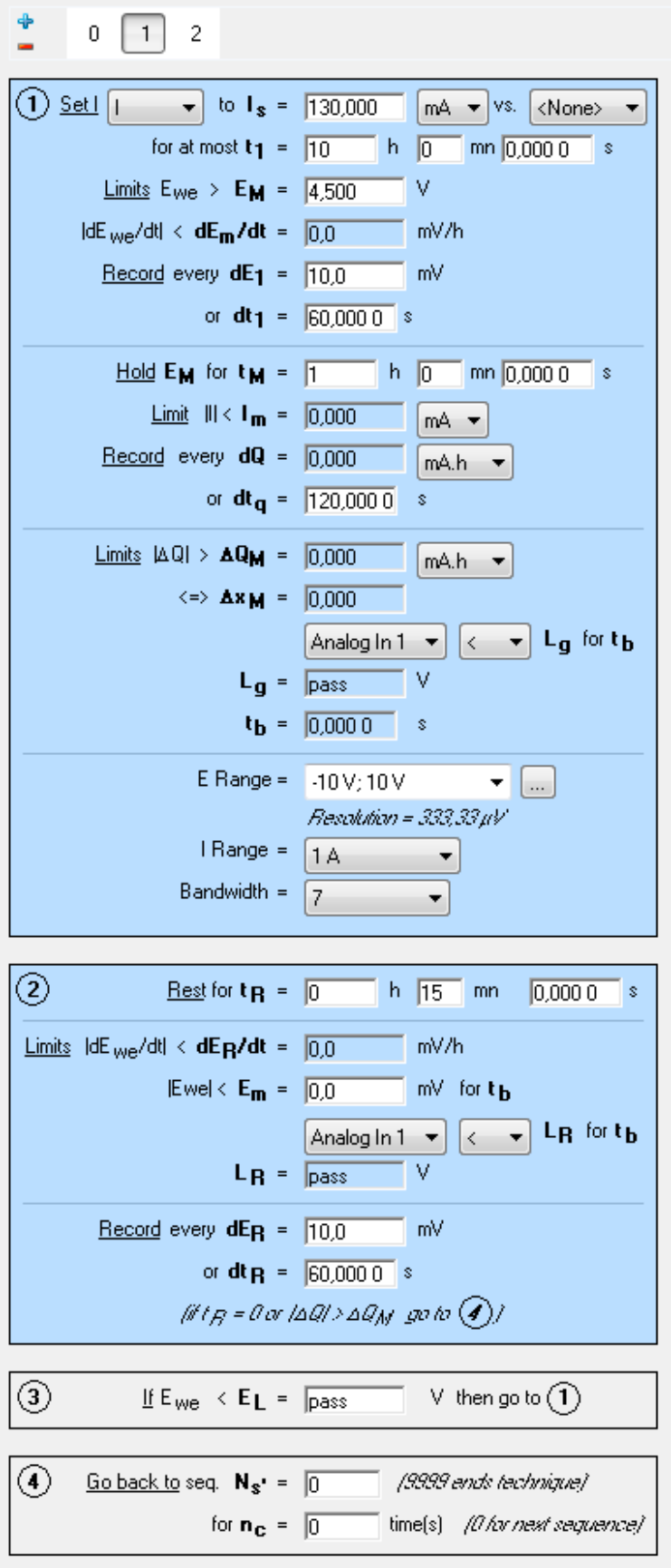


Fig. 115: Detailed diagram of one SGCPL sequence.

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

Galvanostatic period

Set I to Is = … pA/…/A *vs.* <None>/Ictrl/Imeas, for at most t_1 = … h … mn … s
sets 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 $|dE_{we}/dt| < dE_m/dt$ = ... 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 or 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 .

Potentiostatic period

Hold $E_{we} = E_M$ = … V
sets the limit of the working electrode potential under charge/discharge (see warning 1).
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 or 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 = … A.h/…/pC <=> Δx_M = ...
sets 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.

E Range = …
enables the user to select the potential range and adjust the potential resolution with his/her system. (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment)

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

Rest for t_R = … h … mn … s
sets 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 ≥ 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 If 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), the 2 last columns of the table "**Go to $N_{S'}$**" and "**n_c cycles**" need to be filled.

The end of the technique is obtained by setting $N_{S'}$ and n_c to 0 in the last sequence, or setting **Go back to** 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 **Go back to** sequence $N_{S'}$ = 9999 at the sequence one wants to stop.

3.1.10 PCGA: Potentiodynamic Cycling with Galvanostatic Acceleration

This application corresponds to electrode cycling under stepwise potentiodynamic mode. It is the technique to use to perform PITT (Potential Intermittent Titration Technique) experiment. 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 end of the potential steps if the charge or discharge currents are lower than a given value, while it is still cycling with a minimum galvanostatic rate.

This is a direct technique for the determination of the incremental capacities, - dx/dV - of insertion electrode materials. The magnitude of the current transient can be used to provide a measure of the chemical diffusion flux of the mobile species as a function of time t. The compacting function is used (See 3.1.10.3). The quality of the determination is usually better than what is obtained by derivation of a titration curve made with chronopotentiometry under galvanostatic mode (See 2.1.8). The main reason is the significant noise on the potential derivative with respect to the charge, i.e time.

References :
- Wen C. J., Boukamp C. A., Huggins R. A., J. Electrochem. Soc. 126 (1979) 2258-2266.

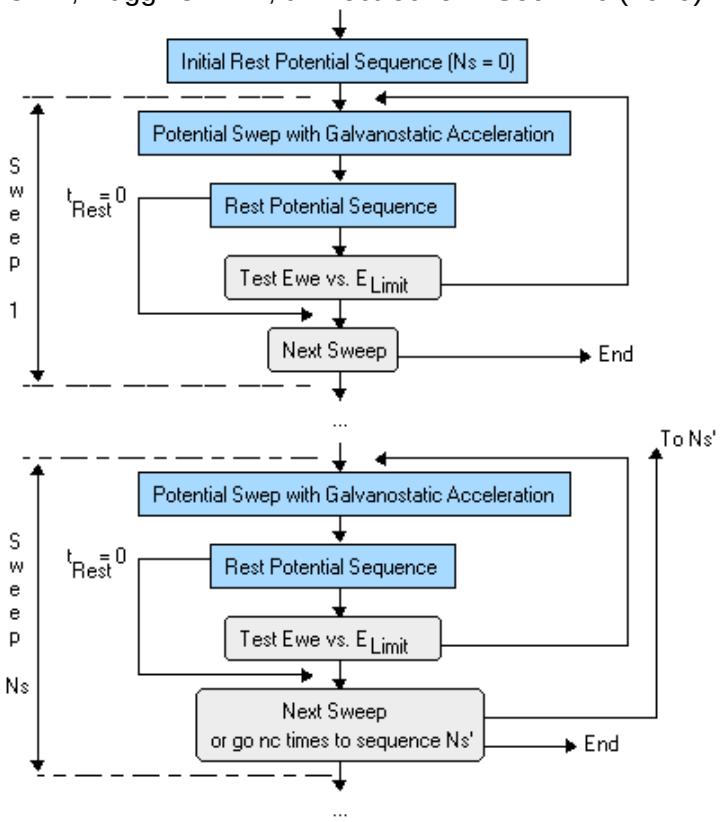


Fig. 116: General diagram of the PCGA application.

3.1.10.1 Description of a potentiodynamic sequence

See Fig. 118.

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

Scan E_{we} with dE_s= … mV per dt_s = … h … mn … s
sets 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 VMP3 based instrument and 333µV for VMP300 based instrument. For example this resolution cannot lead to exact 5 mV steps (because 5/0.3 = 16.67 is not an integer). In that case the user will receive the following warning message:

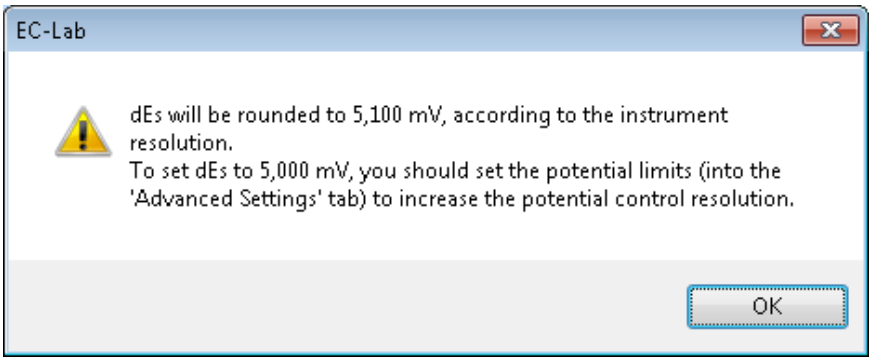


Fig. 117: PCGA warning message for the step amplitude.

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 User's Manual for more details).

From E_i = … V *vs*. Ref/Eoc/Ectrl/Emeas
sets the starting potential *vs.* 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.

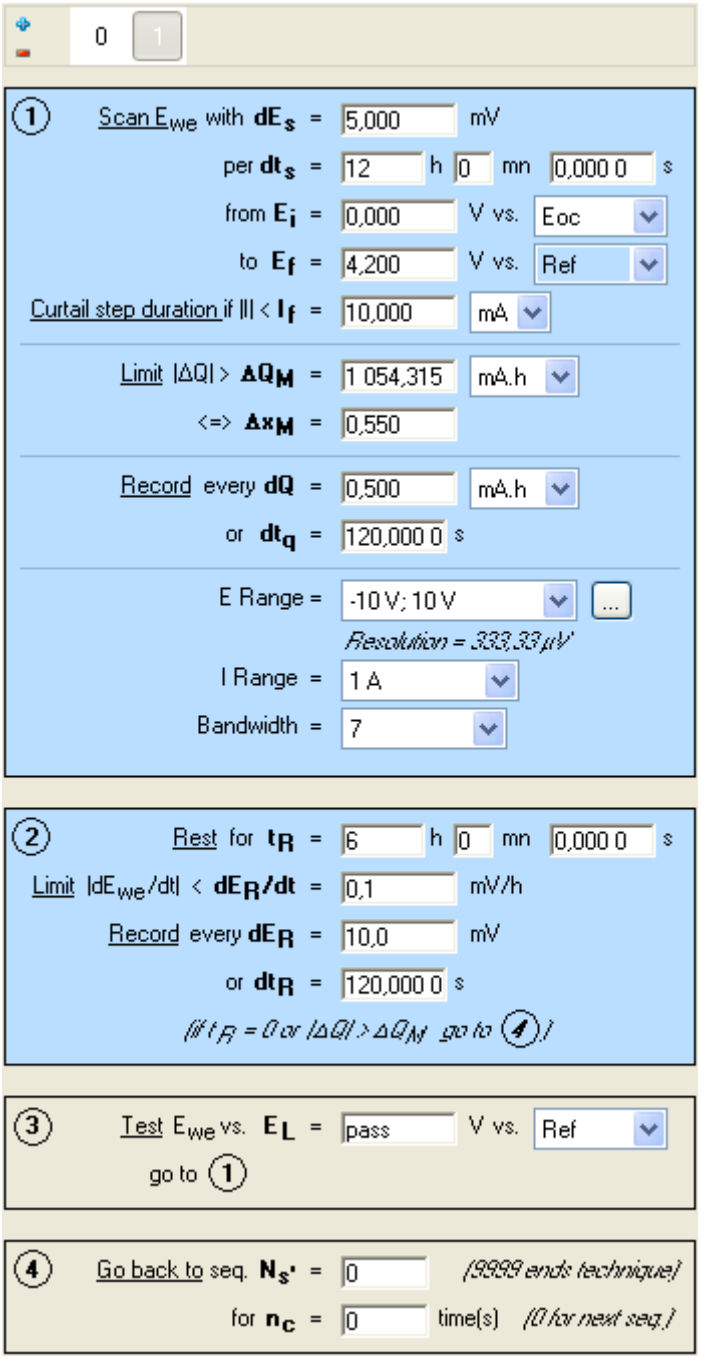


Fig. 118: Detailed diagram of a PCGA sweep.

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

Curtail step duration if |I| < I_f = … pA/…/A
sets 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 = … A.h/…/fA.h/kC/…/pC 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 = … A.h/…/fA.h/kC/…/pC <=> Δx_M = …
sets 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/her system. (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment)

I Range = … and Bandwidth = …
sets 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 6).

- **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 sets 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.

3.1.10.2 Description of the cell characteristics window for batteries

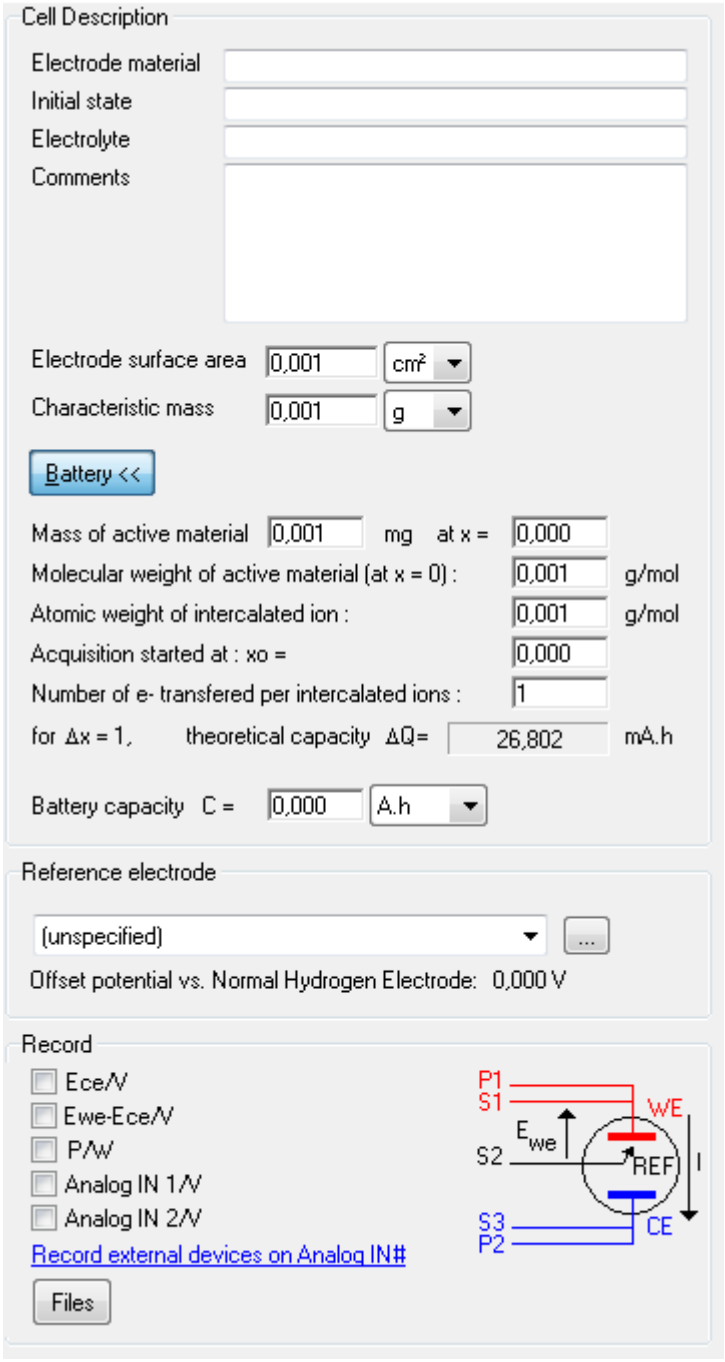


Fig. 119: Cell characteristics window for battery applications.

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 terms of normalized units (molar amounts of intercalation). You can also enter the capacity of the cell and use this capacity as a parameter or a limit in your experiment.
- Select the recording of the counter electrode potential.
- Select the recording of external signals (pH, T, P,...) using auxiliary inputs 1, 2.

Additional info on this window can be found in the User's Manual.

3.1.10.3 PCGA Data processing

3.1.10.3.1 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 for every potential step. See the EC-Lab® Software User's Manual.

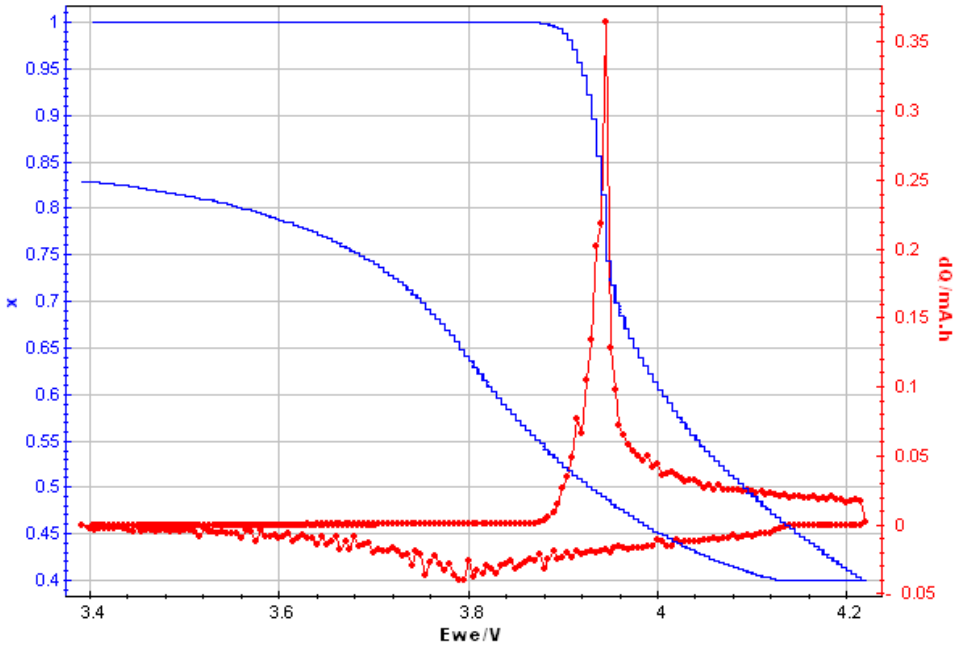


Fig. 120: Incremental capacity (dQ *vs.* Ewe) graph (red dots) and x the insertion rate *vs.* Ewe plot (blue lines) of a Li coin cell.

3.1.10.3.2 **Intercalation coefficient determination**

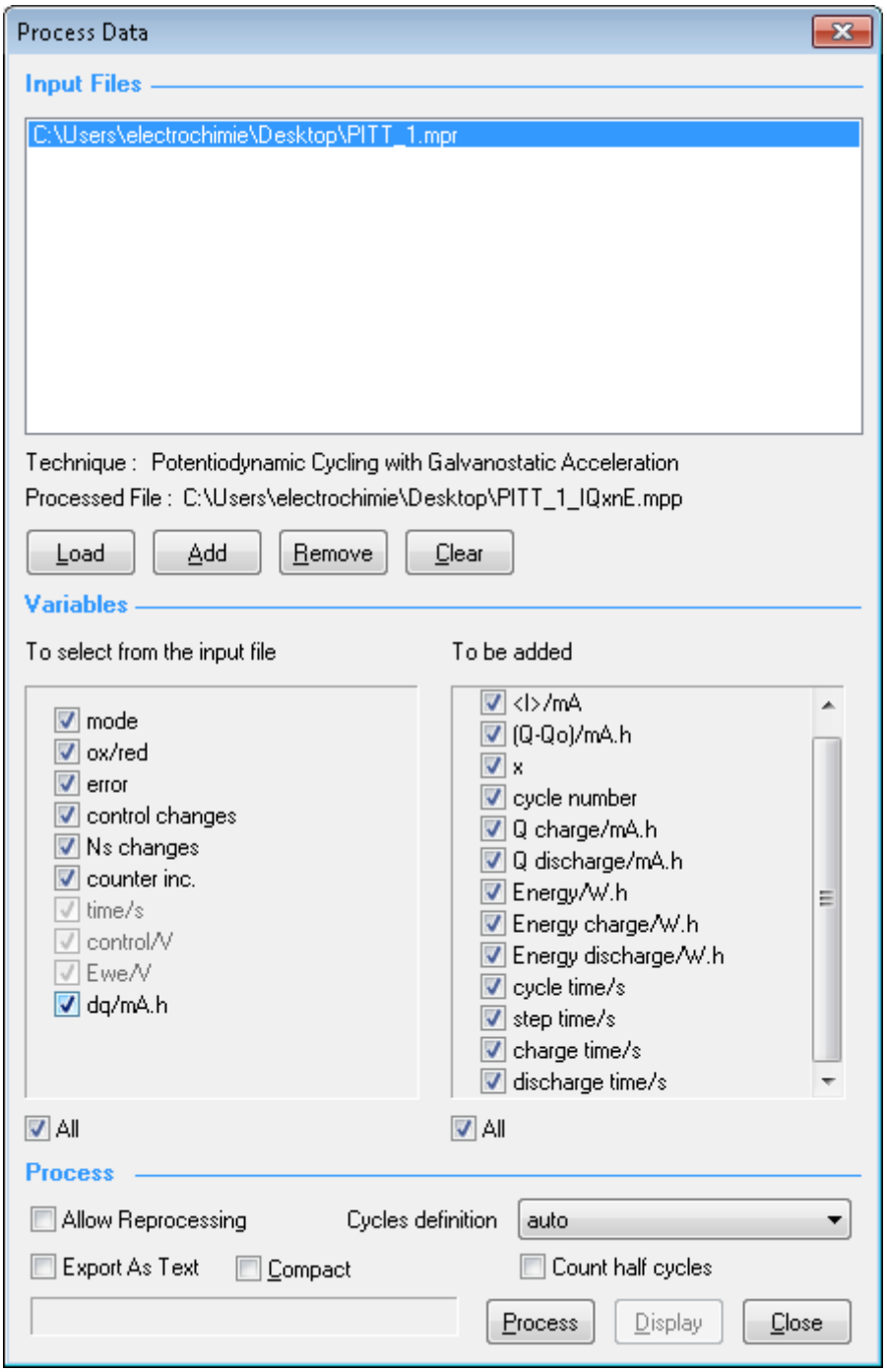


Fig. 121: Process window for PCGA technique.

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 forgot 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**.

3.1.11 MB: Modulo Bat

Modulo Bat (a modular technique designed for battery applications) is a protocol including in one technique all the control modes available in a potentiostat/galvanostat. These control modes are:

- CC (Constant Current)
- CV (Constant Voltage)
- CR (Constant Resistance)
- CP (Constant Power)
- CS (Current Scan)
- VS (Voltage Scan)
- CI (Current Interrupt)
- Rest
- Loop
- PEIS (Potentio Electrochemical Impedance Spectroscopy)
- GEIS (Galvano Electrochemical Impedance Spectroscopy)
- TI (Trigger In)
- TO (Trigger Out)

All the control modes can be sequenced to create a unique experiment. For each sequence, up to three limits and three recording conditions can be set. Different actions can be taken when a limit is reached. Only one data file is created per technique. To have several data files, several Modulo Bat techniques can be linked. A general description of the diagram is given and then each control type is described separately.

3.1.11.1 General Description of the Modulo Bat technique

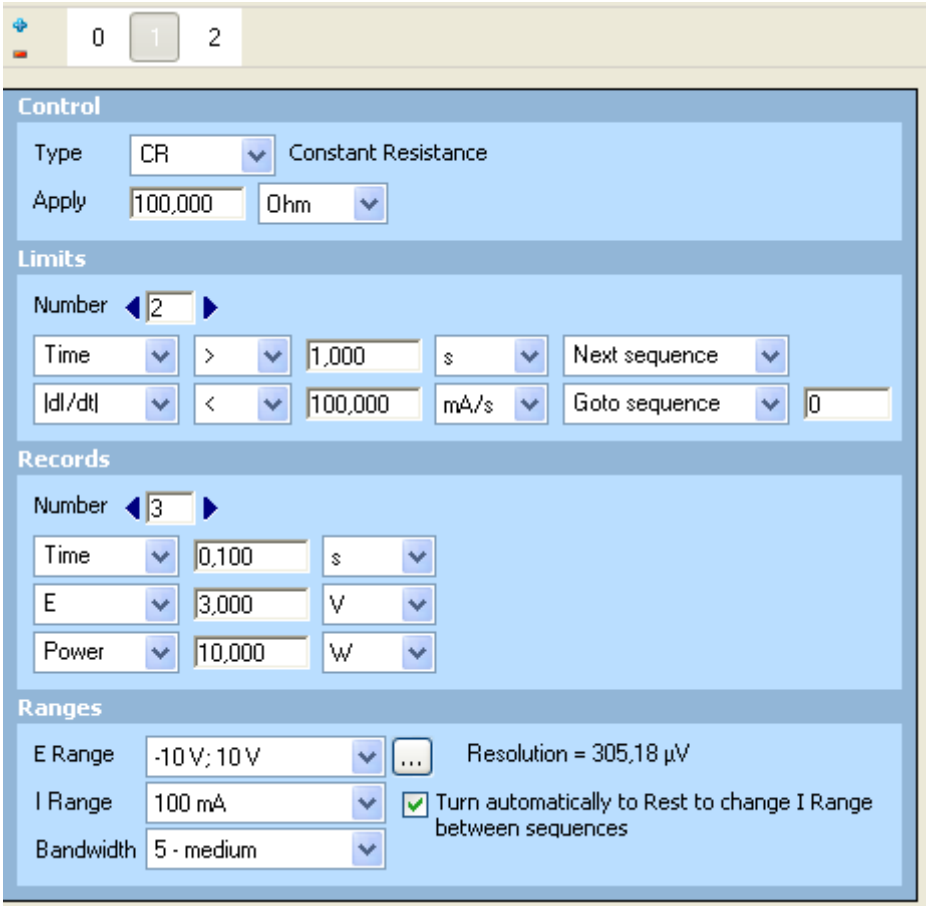


Fig. 122 : General Modulo Bat diagram

This technique is composed of four blocks:

Control: The first block is related to the control mode. Each control type is explicited below.

Limits: The second block is related to the limits of the experiment. The maximum number of limits is 3. They can be set on:

- the **Time** in **day**, **h**, **mn**, **s**, **ms**
- the working electrode potential **Ewe** in **V**, **mV**
- the counter electrode potential **Ece** in **V**, **mV**
- the potential difference **Ewe – Ece** in **V**, **mV**
- the current **I** in **A**, **mA**, **µA**, **nA**, **pA**
- the charge **Q** in **A.h**, **mA.h**
- the power **P** in **W**, **mW**, **µW**
- the **Energy** in **kW.h**, **W.h**, **mW.h**, **µW.h**
- the potential time variation **|dE/dt|** in **V/s**, **mV/s**, **mV/mn**, **mV/h**
- the current time variation **|dI/dt|** in **A/s**, **mA/s**, **µA/s**, **A/mn**, **mA/mn**, **µA/mn**
- the temperature **T** in **°C**
- the temperature time variation **|dT/dt|** in **°C/mn**, **°C/h**

For each parameter the limit can either a lower or an upper boundary. For example in Fig. 124, the first limit must be understood as "*if the time of the experiment is longer than 1 s then move to the next sequence*". The second limit must be understood as "*if the current variation with time is less than 100 mA/s then move to sequence 0*".
The other action that can be taken when a limit is reached is **Stop**.

Records: it is possible to set three different recording conditions on:

- the **Time** in **day**, **h**, **mn**, **s**, **ms**
- the working electrode potential **Ewe** in **V**, **mV**
- the counter electrode potential **Ece** in **V**, **mV**
- the potential difference **Ewe – Ece** in **V**, **mV**
- the current **I** in **A**, **mA**, **µA**, **nA**, **pA**
- the charge **Q** in **A.h**, **mA.h**
- the power **P** in **W**, **mW**, **µW**
- the **Energy** in **kW.h**, **W.h**, **mW.h**, **µW.h**

If several conditions are used, the one taken into account is the one that is met the most quickly. For instance, on Fig. 115, one point will be recorded every 0,1 s unless the potential varies more than 3 V during this time in which case one point will be recorded when the potential variation reaches 3 V. The same applies for the current: if the current change of 10 pA occurs faster than 0,1 s then one point will be recorded when the current change of 10 pA is reached.

Ranges:

E Range = …
enables the user to select the potential range and to adjust the potential resolution with his/her 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 this experiment.

Turn automatically to Rest to change I Range between sequences: this button has for the sequences in Modulo Bat the same function as the **Turn to OCV** button for linked techniques

in an Experiment. If the current ranges are different between the different sequences then the potentiostat must have a short open period during which the change of current range will be performed. This period lasts 100 ms during which no points are recorded. Ticking the box will force a Rest period at the beginning of the sequence.
If there is current range change between sequence 0 and 1, then the "Turn to rest" box must be ticked on sequence 1.
If this box is not ticked on all the sequences and there is a current range change, the following warning message will show up:

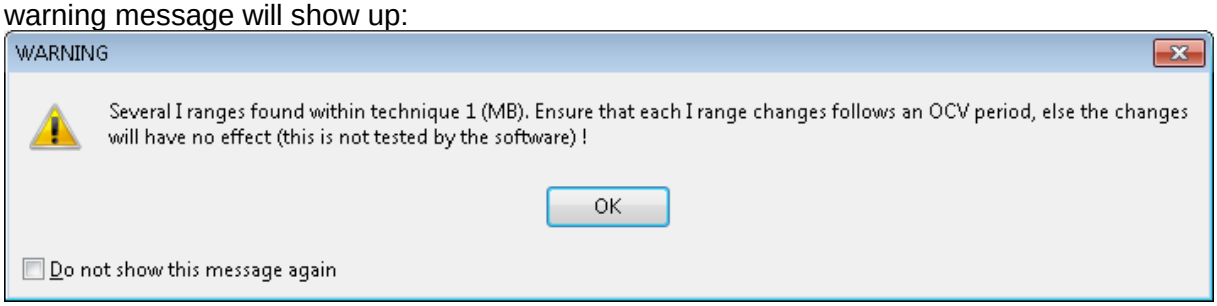


Fig. 123 : Warning message when several current ranges are chosen

If your experiment is set up properly, just ignore this message.

Note: **Turn to OCV** button forces the system to go to OCV but no OCV measurement is performed. If after this forced OCV period, a technique uses the OCV value as reference, the value used will be the last value measured during the previous techniques.

3.1.11.2 Control types

3.1.11.2.1 CC: Constant Current

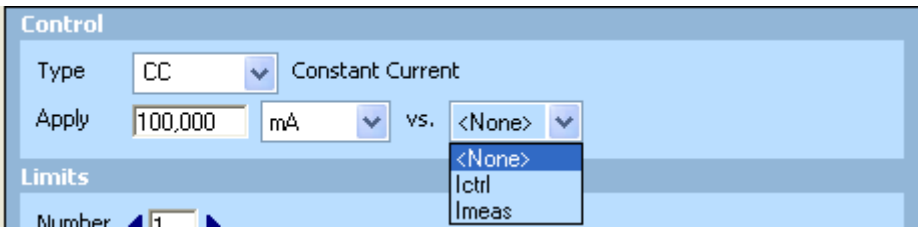


Fig. 124 : Constant Current control

Apply … pA/…/A *vs.* <None>, Ictrl, Imeas
sets the current value in absolute value, *vs.* **Ictrl** the previous controlled current (from the previous sequence or technique) or *vs.* **Imeas** the previous measured current. For a charge a positive value must be entered and for a discharge a negative value.

3.1.11.2.2 CV: Constant Voltage

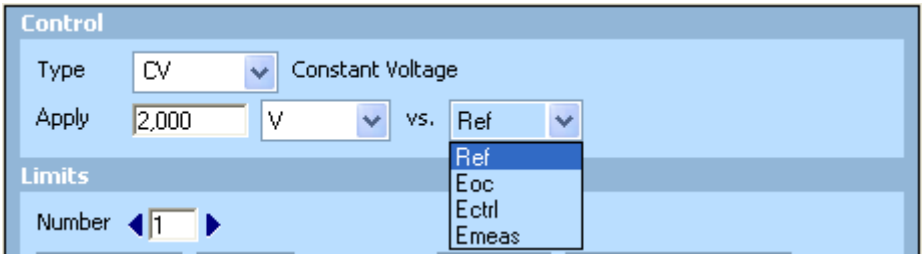


Fig. 125 : Constant Voltage control

Apply … V, mV *vs.* Ref, Eoc, Ectrl, Emeas
Applies a constant potential value defined *vs.* **Ref** the reference electrode potential, *vs.* **Eoc** the open circuit potential, *vs.* **Ectrl** the previous controlled potential (from the previous sequence or technique) or *vs.* **Emeas** the previous measured potential.

3.1.11.2.3 CR: Constant Resistance

Fig. 126 : Constant Resistance control

Apply… MOhm, kOhm, Ohm, mOhm, µOhm
Applies a constant load on the system. A constant load means that the battery is being discharged. The value of the load is maintained constant by controlling the current such that the ratio E/I is constant.

3.1.11.2.4 CP: Constant Power

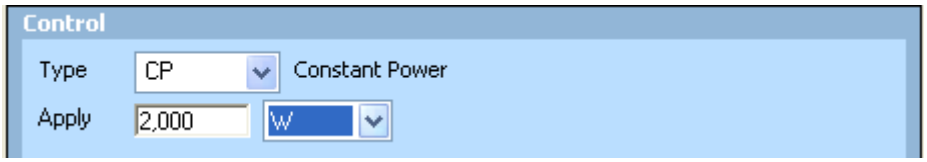


Fig. 127 : Constant Power control

Apply… W, mW, µW
A constant power is applied to the system. The current is controlled to maintain the product E*I constant so, if the potential decreases the current increases.

CAUTION!

Applying a constant power during a discharge experiment corresponds to an increase of the current (in absolute value) when the potential decreases. The user must be careful to note the final current of the first constant power step. For example, let us 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.

3.1.11.2.5 CS: Current Scan

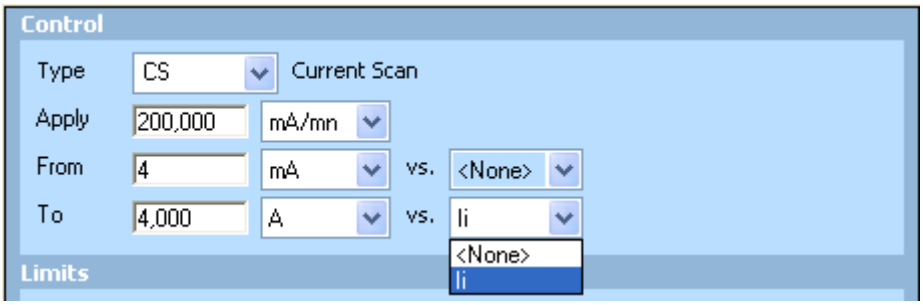


Fig. 128 : Current Scan control

Apply… A/s, mA/s, µA/s, A/mn, mA/mn, µA/mn
From… pA/…/A vs <None>, Ictrl, Imeas
To … pA/…/A vs <None>, Ii

applies a current scan from an initial current value **Ii** (defined in absolute value, *vs.* **Ictrl** the previous controlled current or *vs.* **Imeas** the previous measured current) to a final value If defined in absolute value or *vs.* **Ii** at a scan rate defined above. This technique is similar to the galvanodynamic mode available in the Modular Galvano technique (see 2.4.3.3).

3.1.11.2.6 VS: Voltage Scan

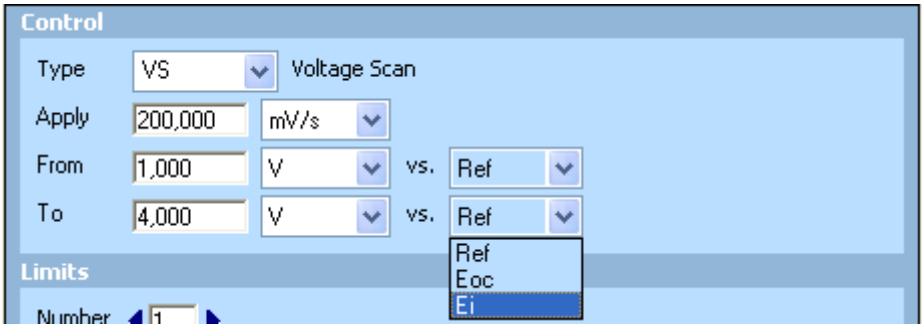


Fig. 129 : Voltage Scan control

Apply… V/s, mV/s, mV/mn
From… V, mV vs Ref, Eoc, Ectrl, Emeas
To … V, mV vs Ref, Eoc, Ei
applies a potential scan from an initial potential value **Ei** defined *vs.* **Ref** the reference electrode potential, *vs.* **Eoc** the open circuit potential, *vs.* **Ectrl** the previous controlled potential or *vs.* **Emeas** the previous measured potential) to a final value Ef defined *vs.* **Ref** the reference electrode potential, *vs.* **Eoc** the open circuit potential or *vs.* **Ei,** at a scan rate defined above.

3.1.11.2.7 CI: Current Interrupt

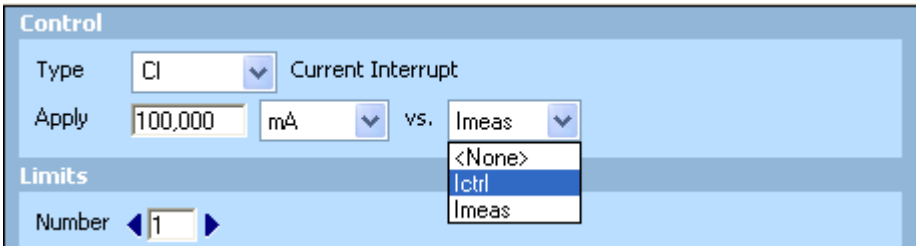


Fig. 130 : Current Interrupt control

See 2.6.3 for more information about the application of this technique.

3.1.11.2.8 Other types

- **Rest :** see 2.1.1
- **Loop :** see 2.4.10
- **PEIS:** it is a simplified version of the PEIS technique described in 0.

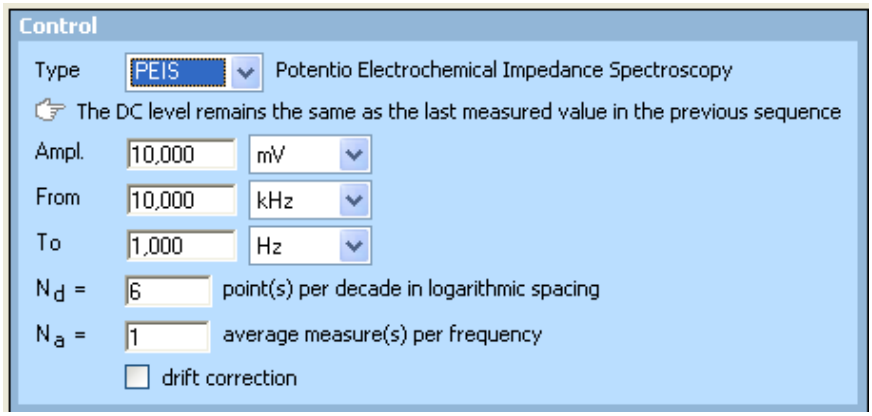


Fig. 131 : PEIS control

- **GEIS**: it is a simplified version of the GEIS technique described in 2.2.2

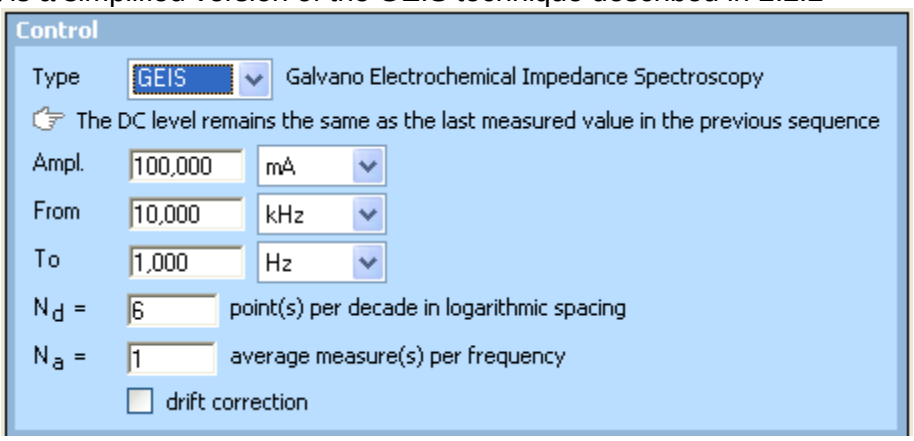


Fig. 132: GEIS control

- **TI (Trigger In) :** see 2.4.4
- **TO (Trigger Out):** see 2.4.4

3.1.12 CED: Coulombic Efficiency Determination

In the last years, several researches were focused on the Coulombic Efficiency (CE) as a tool to study the battery lifetime. Quantifying the influence on the battery lifetime by changes in the electrodes or electrolytes, under classical testing conditions (simply charge-discharge conditions), requires extremely longtimes. Contrarily to a simply cycle cells measurements (until the cells reach the end of life), CE measurements can be improved in short amount of time (3-4 weeks) and also provide a tool to evaluate and compare the stability of different cells.

This technique is used to determine and follow the evolution of the coulombic efficiency of a battery during a charge/discharge protocol.This determination is made under galvanostatic mode, i.e. the same current value is fixed in the charge and discharge regime. The batteries are cycled between the potential limits E_{M1} and E_{M2}.

3.1.12.1 Description of a galvanostatic sequence

The detailed diagram of the CED technique is shown in Fig. 133.

<u>Set</u> I to I_s = … pA/… /A, for t_1 = … h ... mn ... s

sets the current as absolute value. 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).

Set I to C/N or CxN with N = … and I>0 or <0, for t_1 = … h ... mn ... s
Sets the rate C/N or CxN at wich the battery will be charged (I>0) or discharged (I<0). The capacity of battery must be entered in the cell characteristics (see 3.1.10.2). Set C/3 mean that the battery will be charged (discharged) in 3 h.

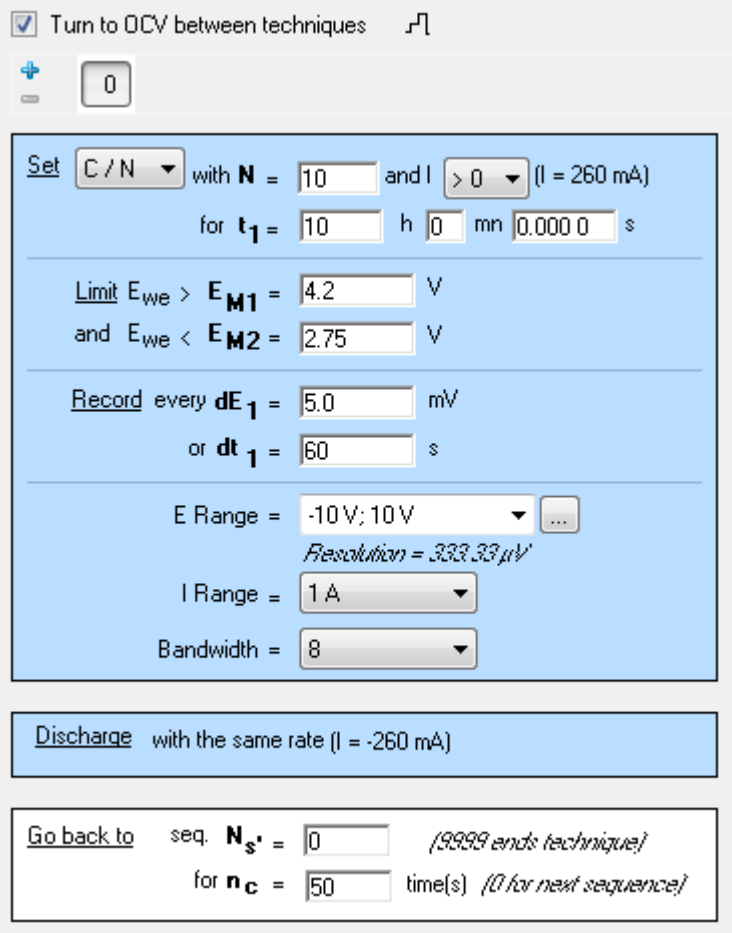


Fig. 133: CED detailed diagram.

Limit E_{we} > E_{M1} = … V

E_{we} < E_{M2} = … V
sets the limits of the working electrode potential under charge and discharge regime (see warning 1 in Description of a galvanostatic sequence).

Record E_{we} every dE_1 = … mV or 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 every dt_1 time interval.

E Range = …
enables the user to select the potential range and to adjust the potential resolution with his/her 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 for this experiment.

Discharge with the same rate (set I=-I_s)
The discharge/charge period is preformed with the I=-I_S.

- **Loop**

Go back to sequence $N_{s'}$ = … n_c = … time(s)
loops to a 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).

3.1.13 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.

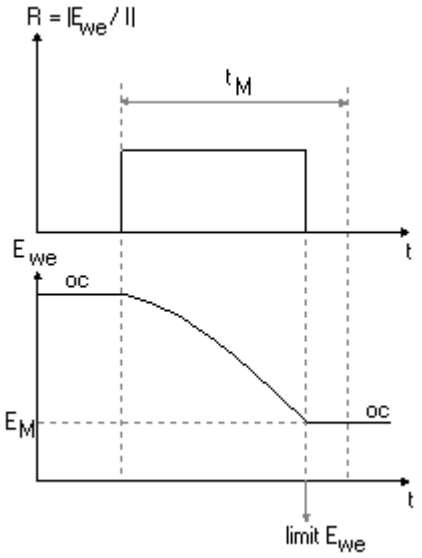


Fig. 133: CLD control (I) and measure (E_{we}) sample *vs.* time.

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

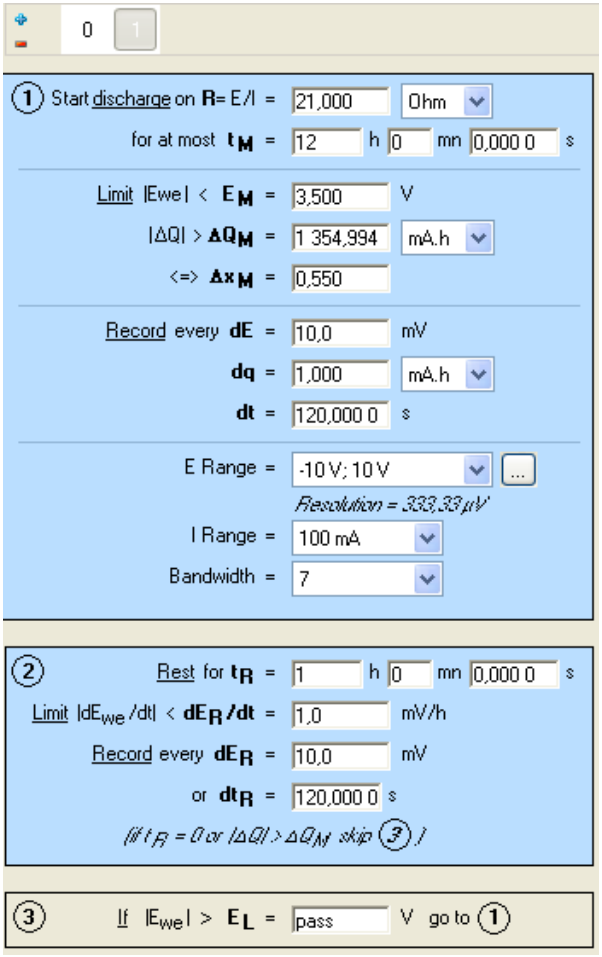


Fig. 134: CLD detailed diagram.

Start <u>discharge</u> on R=E/I= … µOhm/… /Mohm for at most t_M = … h … mn … s
sets the cell resistance to R = E/I for t_M duration.

<u>Limit</u> $|E_{we}|$ < E_M = … V, $|\Delta Q|$ > ΔQ_M = … A.h/…/fA.h, kC/…/pC <=> Δx_M = …
sets 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.

<u>Note:</u> 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.

<u>Record</u> every dE = … mV, dq = … A.h/…/fA.h, kC/…/pC 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.

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

The other blocks were already described above.

3.1.14 CPW: Constant Power

3.1.14.1 Description

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

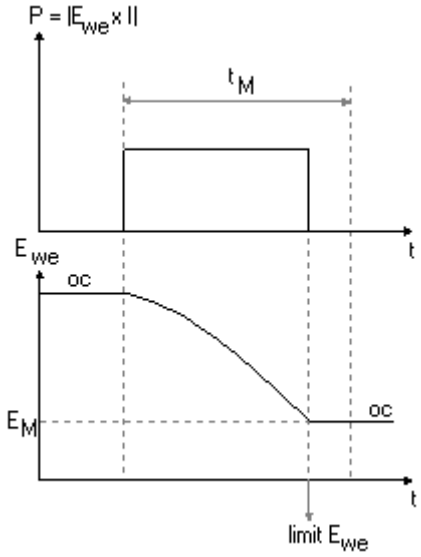


Fig. 135: CPW discharge control (P) and measure (E_{we}) sample *vs.* time

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

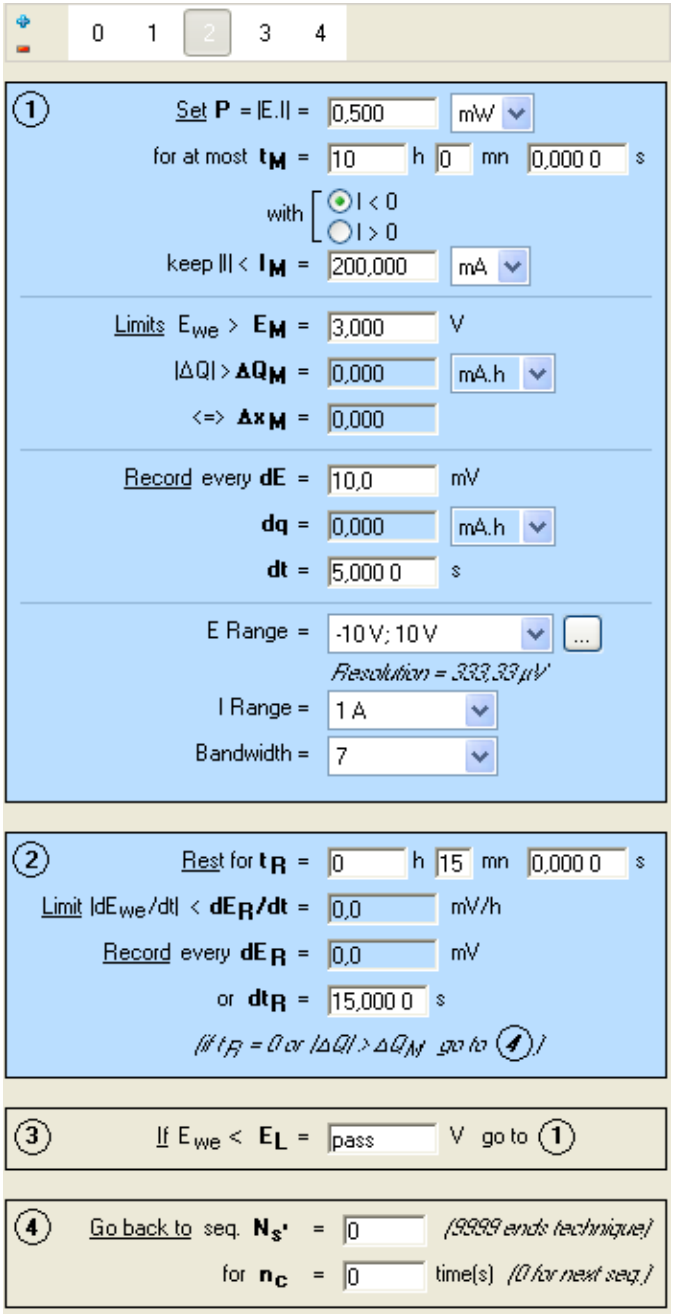


Fig. 136: CPW detailed diagram.

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.

Limit E_{we} >/< E_M = … V, $|\Delta Q|$ > ΔQ_M = … A.h/…/fA.h, kC/…/pC <=> Δx_M = …
sets 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 the 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 by-passed 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.

Record every dE = … mV, dq = … A.h/…/fA.h, kC/…/pC 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.

I Range = … Bandwidth = …
sets the current range and bandwidth for this experiment.
The other blocks were already described above.

Note:
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 us consider a 30 W 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.

3.1.14.2 Application of the CPW technique

The constant power technique is commonly used for a Ragone plot representation (power *vs.* energy). The usual technique consists in a succession of 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.

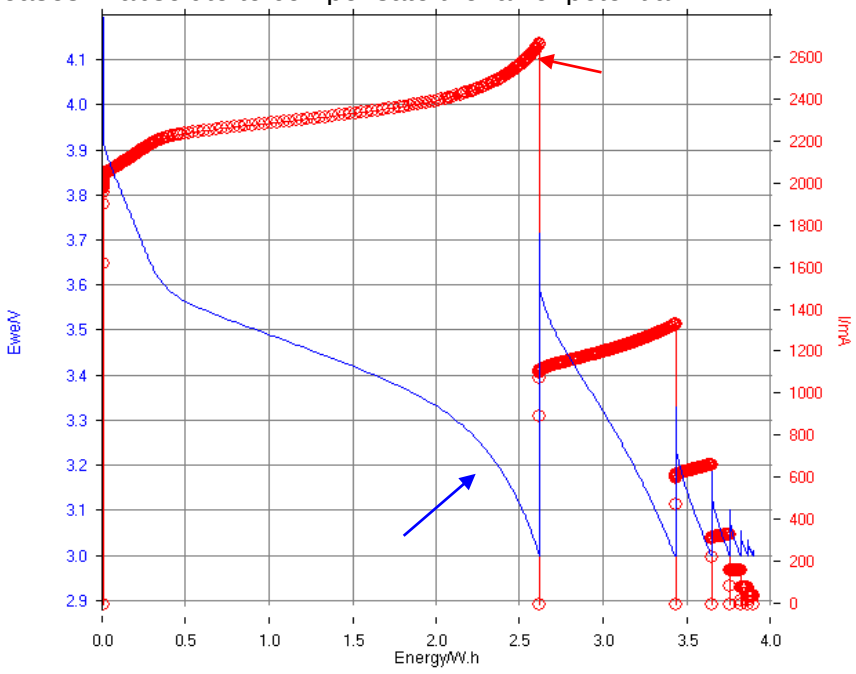


Fig. 137: E measured (blue line) and I adjusted (red circles) evolution *vs.* energy during a CPW experiment on a Li-ion battery (1.35 A.h) P = 8 W.

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.

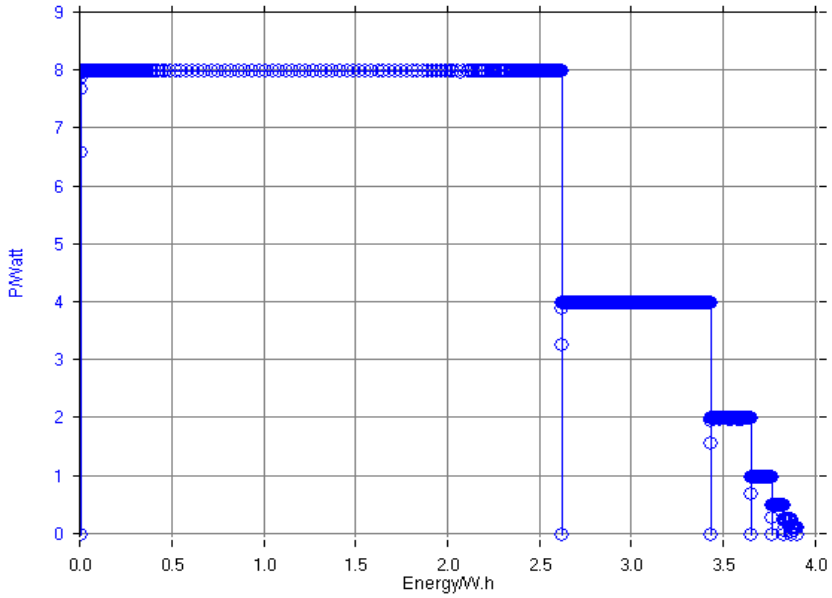


Fig. 138: Power *vs.* energy plot for a Li-ion cell (1.35 A.h). P = 8 W.

A process called "Constant Power protocol summary" has been specially 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 **Batteries Analysis** menu. Then the following processing window will be displayed:

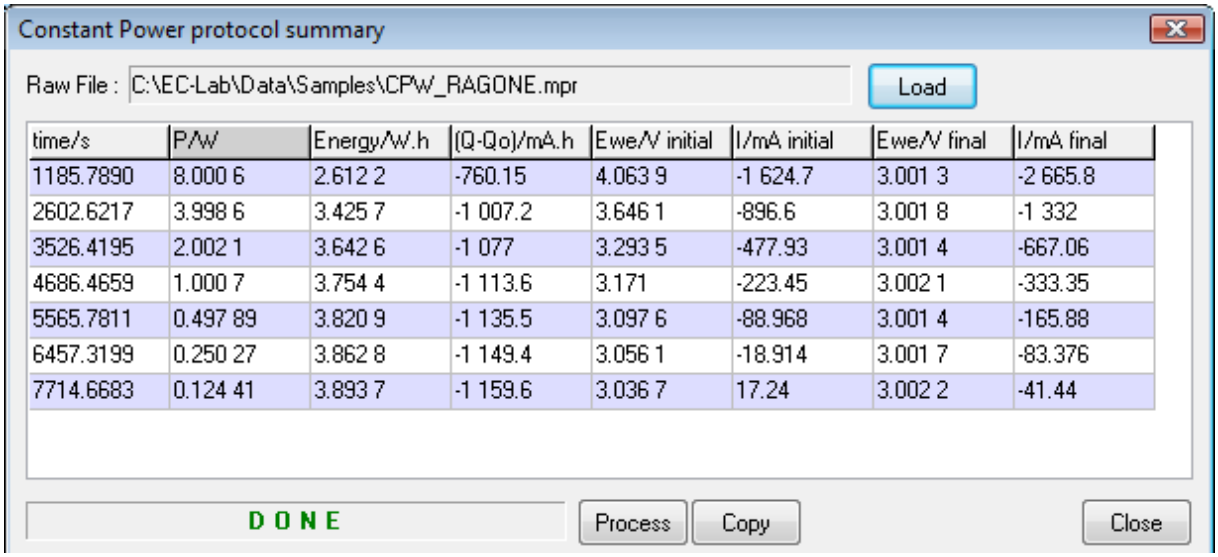


Fig. 139: CPW process window.

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).

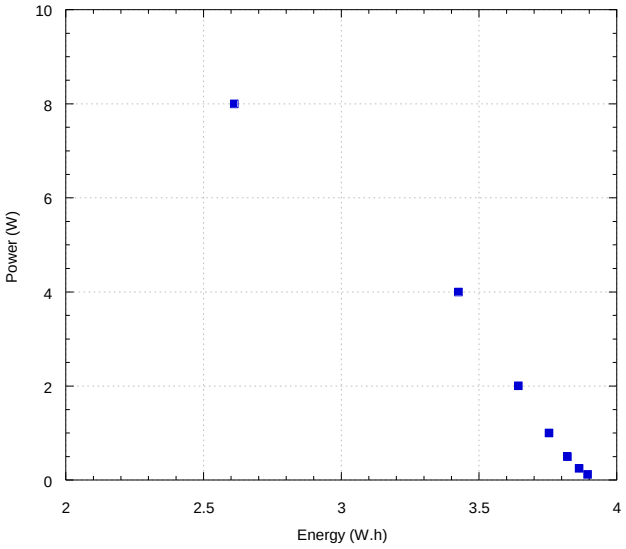


Fig. 140: Ragone plot for a Li-ion cell (1.35 A.h).

3.1.15 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.

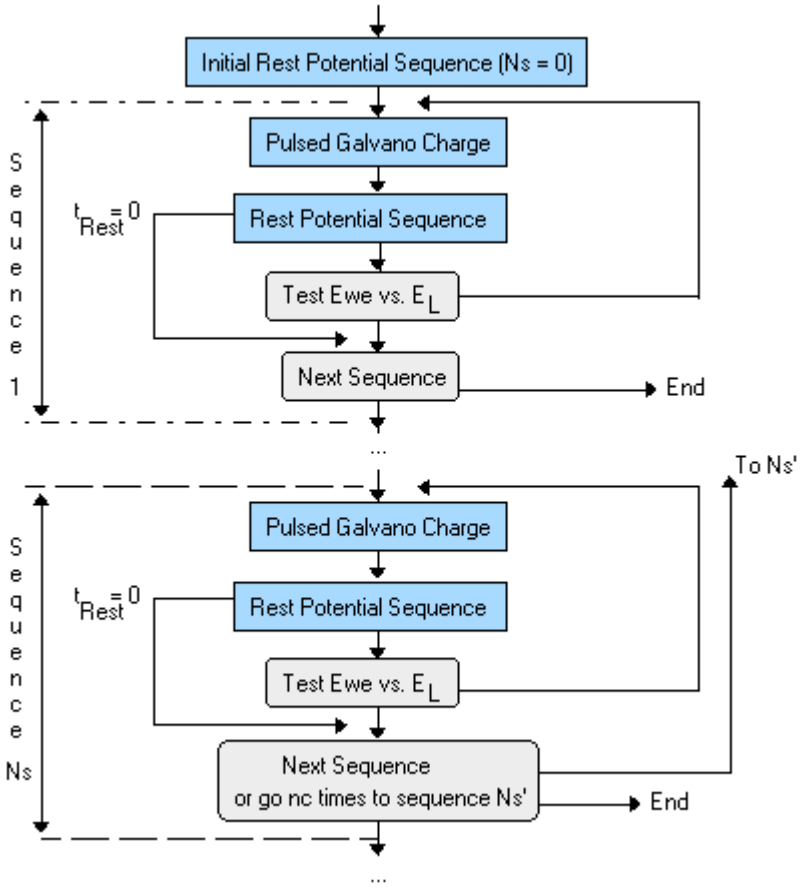


Fig. 141: APGC general diagram.

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

The detailed diagram is described in Fig. 123:

- **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.

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.

Limit on I_1 $|E_{we}|$ 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 = … A.h/…/fA.h, kC/…/pC
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.

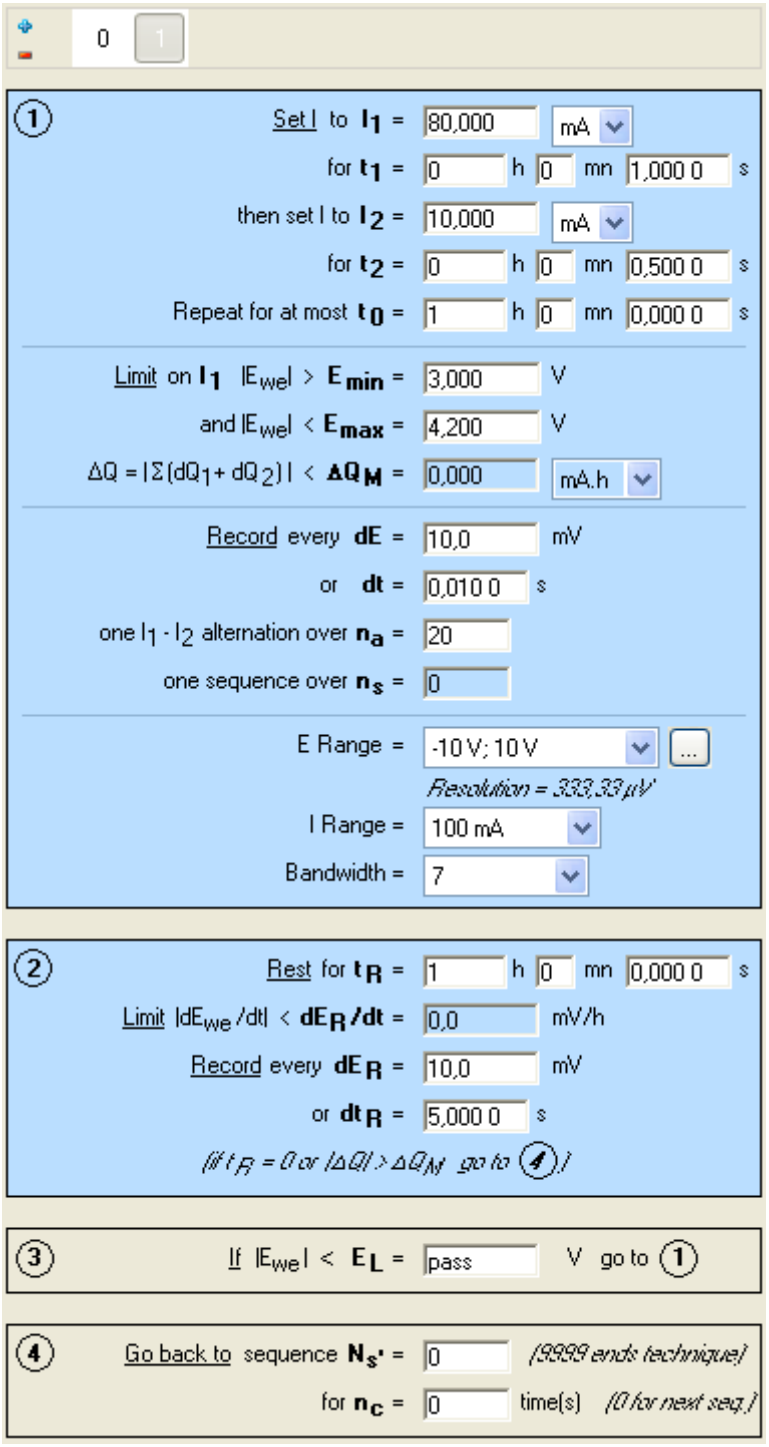


Fig. 142: APGC detailed diagram.

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 ≥ dt. These recording conditions can be set separately or together. The first condition reached determines the recording. A zero value cancels the recording condition.

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

- **Rest Potential Sequence**

The open circuit voltage is the standard block, so refer 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 Go back to 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.

3.1.16 PPI: Potentio Profile Importation

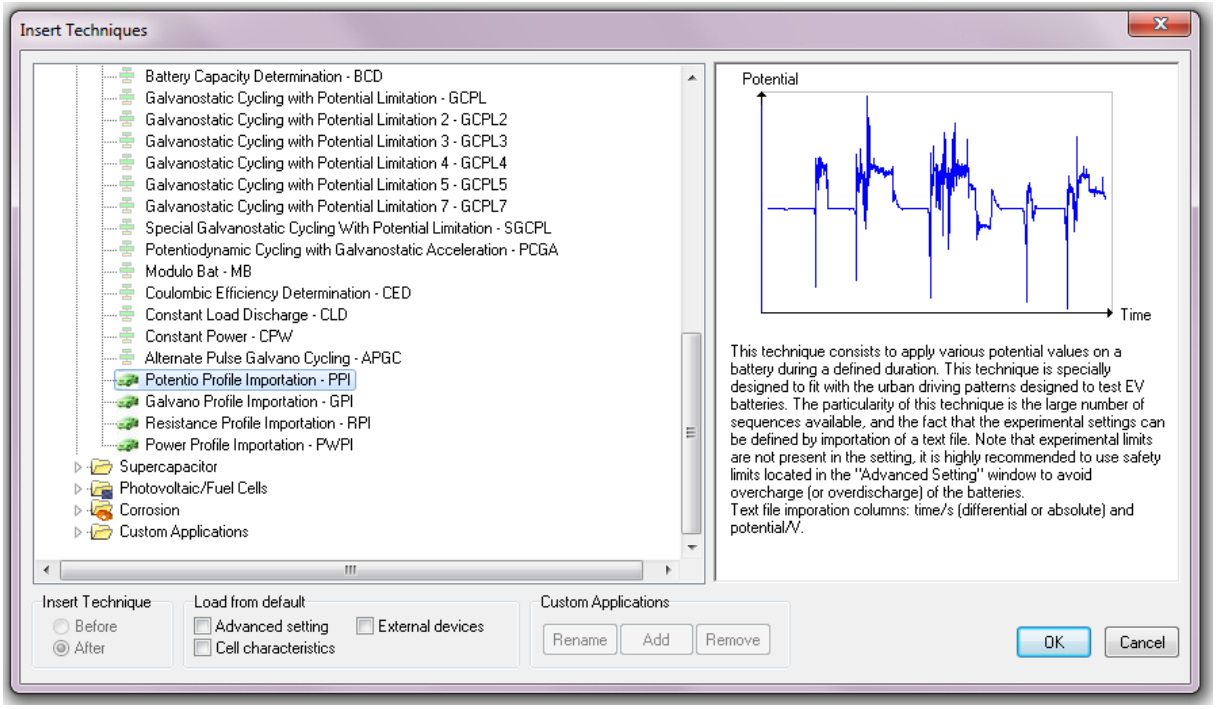


Fig. 143: Selection window for a profile importation.

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

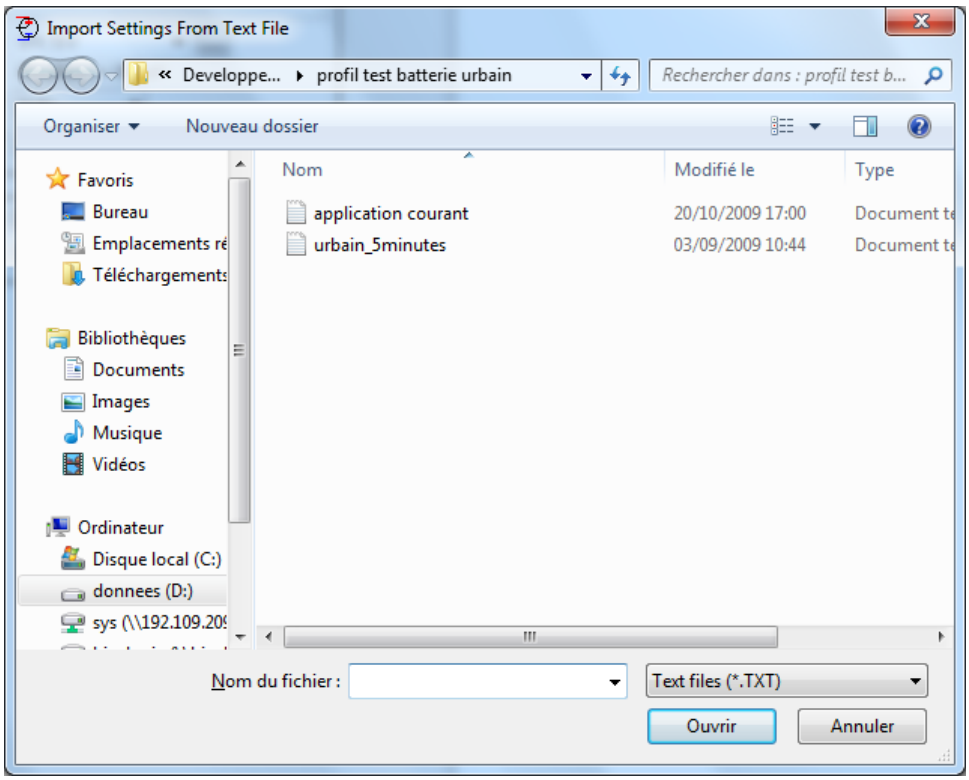


Fig. 144: Text Import window.

The user has to select the text file to import (with two columns: time and potential in this case).. This technique is specially designed to fit 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 importing a text file. Note that experimental limits are not present in the settings, it is consequently highly recommended to use safety limits located in the "Advanced Settings" tab to avoid overcharge (or overdischarge) of the batteries. The text file importation columns are time/s (differential or absolute) and current/A.

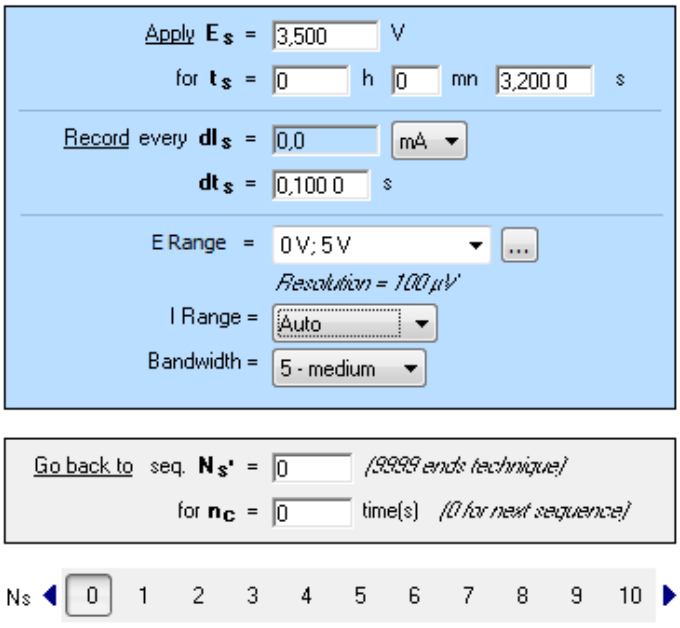


Fig. 145: PPI detailed diagram.

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 where the software finds two lines with the same parameters, they will be merged in only one line to save memory. In the table to be imported, the first column must be 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
defines 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 and to adjust the potential resolution with his/her 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 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), the 2 last columns of the table needs to be filled "**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 **Go back to** sequence $N_{S'}$ = 9999 at any sequence, which then will be the last one executed even if the next sequence has its settings.

3.1.17 GPI: Galvano Profile Importation

This technique consists in applying various current values on a battery during a defined time. This technique corresponds to battery cycling under galvanostatic mode. This technique can be used in charge and in discharge mode (depending on the sign of the current). 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 importing 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 Settings" tab to avoid overcharge (or overdischarge) of the batteries. The text file importation columns are time/s (differential or absolute) and current.

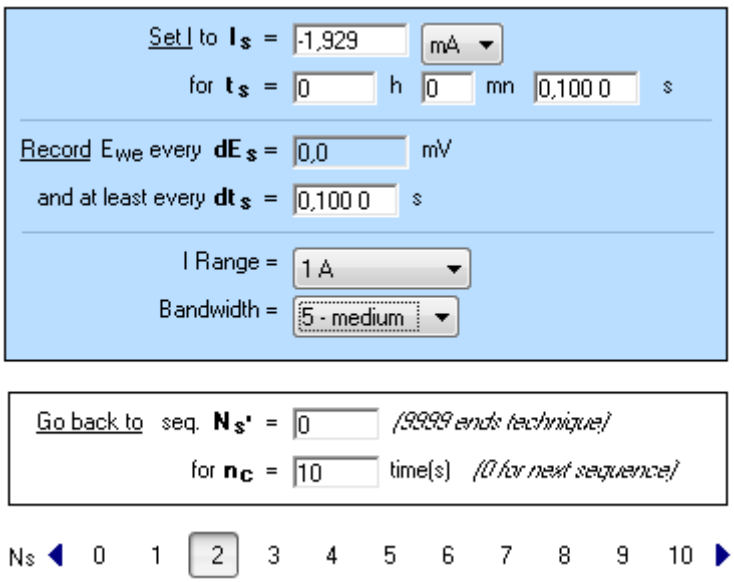


Fig. 146: GPI detailed diagram.

- **Pulsed galvano Charge**

Set I to I_s = … pA/…/A, 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 = ... Bandwidth = …
sets the current range and the bandwidth for this experiment.

- **Conditional test**

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

3.1.18 RPI: Resistance Profile Importation

This technique consists in applying various resistance values on a battery during a defined duration. This technique is specially designed to fit 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 importing a text file. Note that experimental limits are not present in the settings, it is highly recommended to use safety limits located in the "Advanced Settings" tab to avoid overcharge (or overdischarge) of the batteries. The text file importation columns are time/s (differential or absolute) and resistance/Ohm.

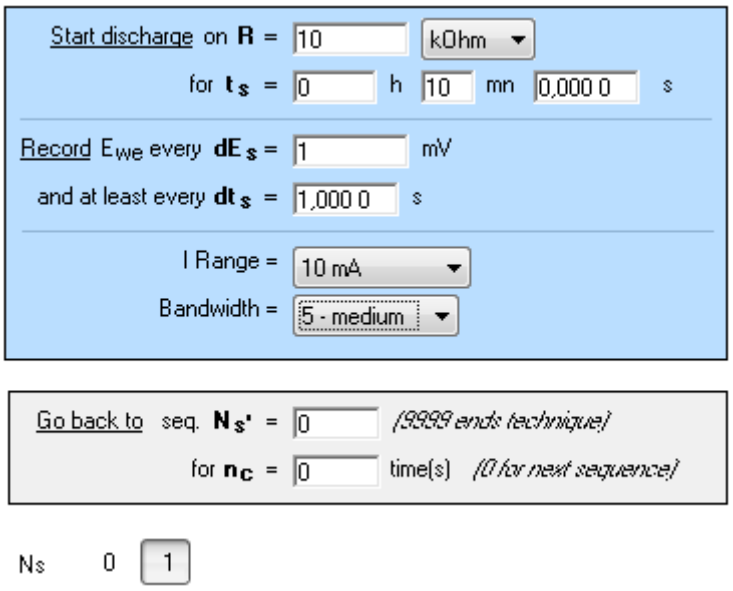


Fig. 147: RPI detailed diagram.

- **Pulsed Resistance discharge**

Start discharge on R = … µOhms/... /MOhms for t_s = … h … mn … s
defines the resistance 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 = ... Bandwidth = …
sets the current range and the bandwidth for this experiment.

- **Conditional test**

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

3.1.19 PWPI: Power Profile Importation

This technique consists in applying 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 Settings" tab to avoid overcharge (or overdischarge) of the batteries. The text file importation columns are time/s (differential or absolute) and power/Watt.

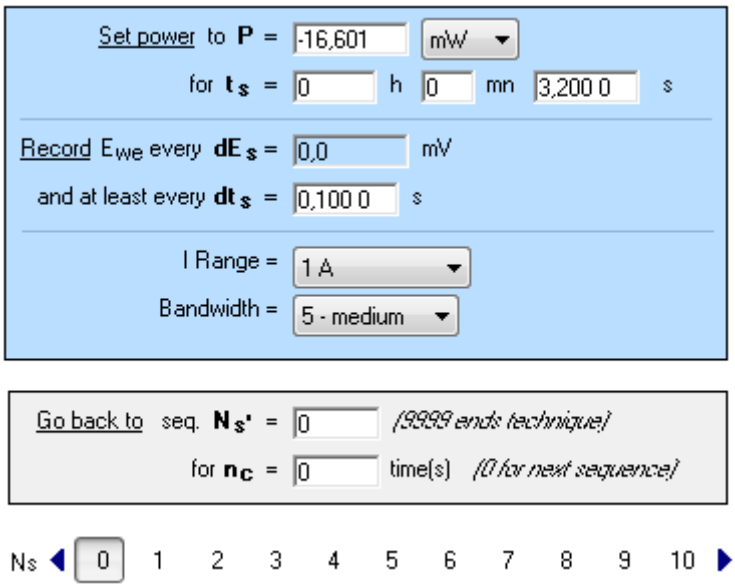


Fig. 148: PWPI detailed diagram.

- **Pulsed power discharge**

Set power to P = … mW/..../W 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 = …
sets 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 Super Capacitor

This section is especially dedicated to supercapacities. This section includes a cyclic voltametry, constant voltage, constant current and current scan techniques.

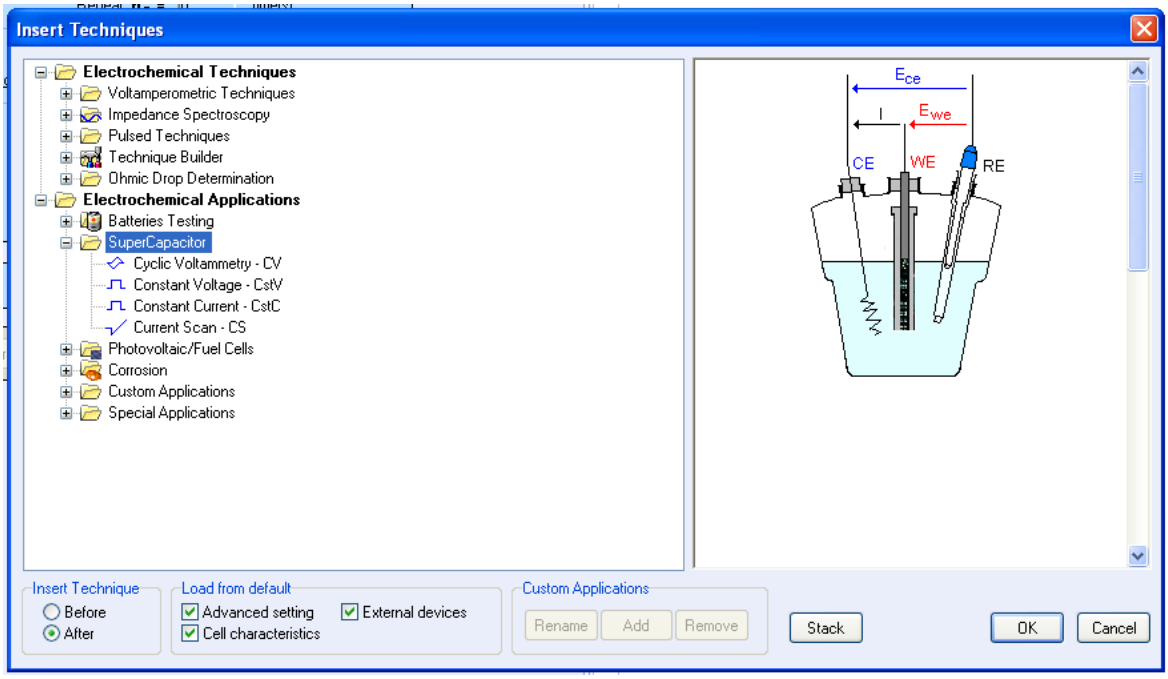


Fig. 149: Supercapacity applications.

3.2.1 Cyclic voltammetry

The CV technique consists in scanning the potential of a stationary working electrode using a triangular potential waveform. During the potential sweep, the potentiostat measures the current answer of the system. The cyclic voltammogram is a current response plotted as a function of the applied potential.
Traditionally, this technique is performed using an analog ramp. Due to the digital nature of the potentiostat, the actual applied ramp consists in a series of small potential steps that approximate the targeted linear ramp (see the control potential resolution part in the EC-Lab® Software User's Manual).

The technique is composed of (Fig. 150):

- 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).

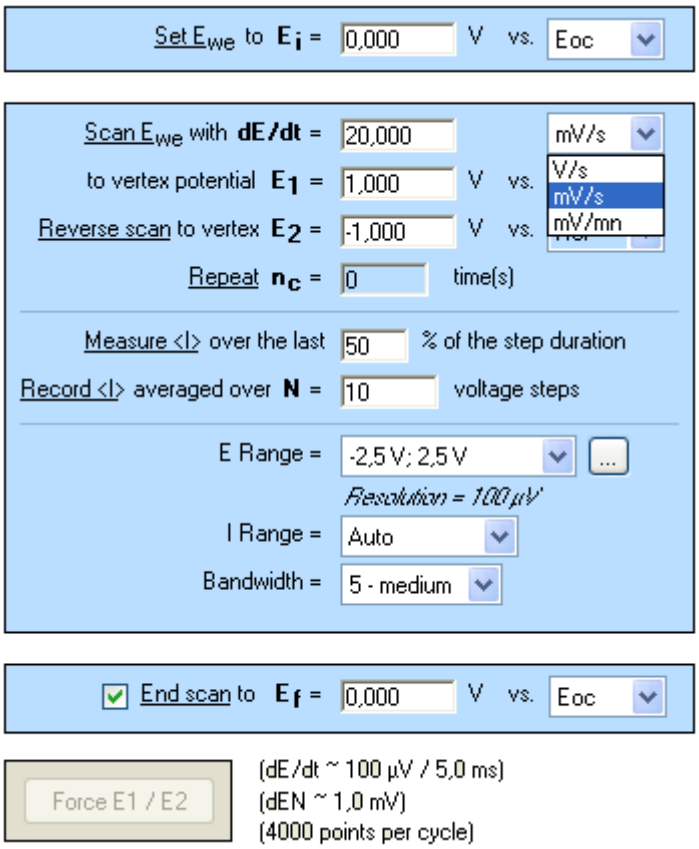


Fig. 150: Cyclic Voltammetry detailed column diagram.

- **Starting potential**

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

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

Scan E_{we} with dE/dt = ... V/s / mV/s / mV/mn
allows the user to set the scan rate in V/s, mV/s or mV/mn. 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 User's Manual).

to vertex potential E_1 = ... V *vs.* Ref/Eoc/Ei.
sets the first vertex potential value *vs.* reference electrode potential or *vs.* the open circuit potential (E_{oc}) or *vs.* the potential of the previous experiment (E_i).

- **Reverse scan**

Reverse scan to 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 *vs.* reference electrode potential 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**

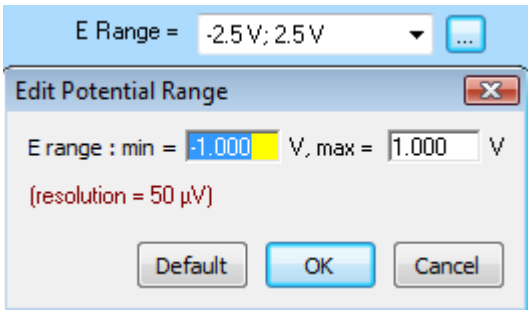
Repeat n_c = ... times
repeats the scan from E_i to E_1 and to E_2, n_c time(s). Note that the number of repetition does not include the first sequence: if n_c = 0 then the sequence will be done once; if n_c = 1 the sequence will be done twice, if n_c = 2, the sequence will be done 3 times, etc…

- **Data recording conditions**

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. It may be necessary to exclude the first points of the current response, which may only be due to the capacitive rather than faradic behavior of the system.

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 and to adjust the potential resolution according to the experiment. (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 to the 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.

- **Final potential**

End scan to 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
During the experiment, 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 to 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 clicking on the "Modify" button, setting the running potential as E_1 or E_2 and validating the modified parameters with the Accept button. The **Force E_1/E_2** button allows the user to perform the operation in a faster way in the case where the potential limits have not been properly estimated and to continue the scan without damaging the cell.

Note: it is highly recommended to adjust the potential resolution from 300 µV (for 20 V of amplitude) to 5 µV (for 0.2 V of amplitude, with a SP-150, VSP or VMP3) according to the

experiment potential limits. This will considerably reduce the noise level and increase the plot quality.

3.2.2 CstV: Constant Voltage

The constant voltage (CstV) technique is especially dedicated to supercapacity 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.

- **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**

<u>Apply</u> E_i = … V *vs.* Ref/Eoc/Ectrl/Emeas.
the potential step is defined *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
sets the potential step duration.

<u>Limits</u> |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.

<u>Record</u> I every dI_p = … pA/…/A, dQ_p = ... fA.h/…/A.h/pC/…/kC and dt_p = … s

<I> every dt = … 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 VMP3 based instruments and for VMP300 based instruments.
Leave dI alone for Chronoamperometry experiments, and dQ for Chronocoulometry experiments.

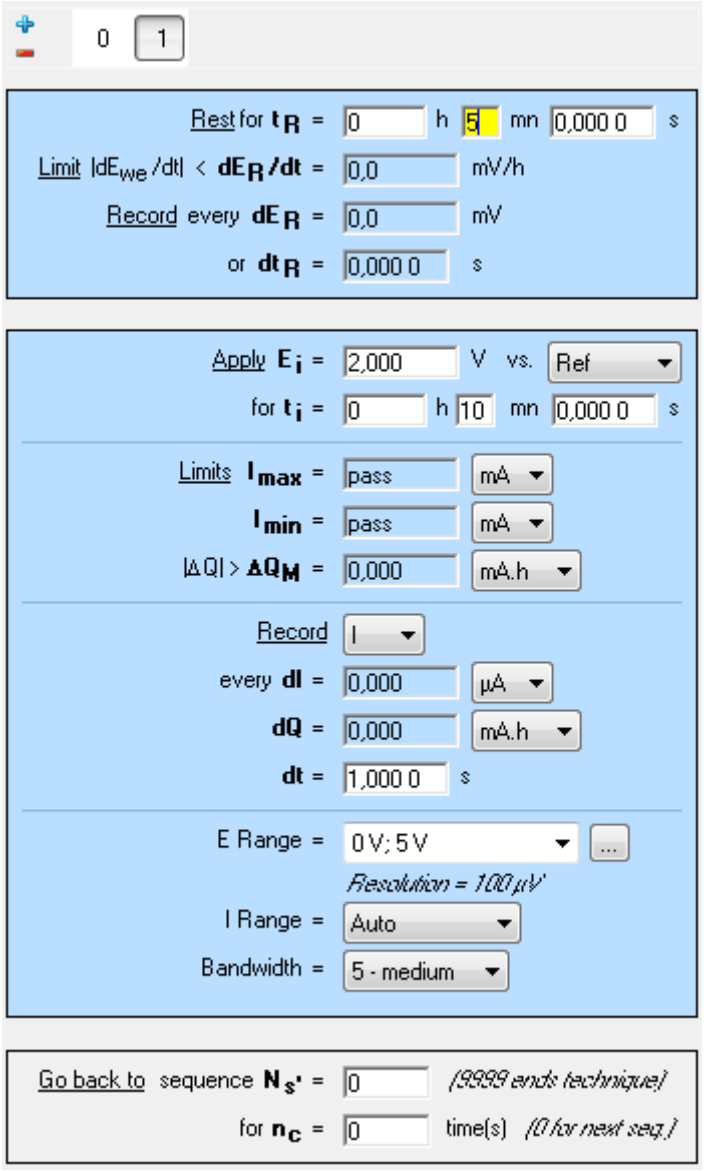


Fig. 151: Constant Voltage detailed diagram.

E Range = …
enables the user to select the potential range and adjust the potential resolution to his/her 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**

Go back to 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 ($N_{s'} = N_s$).

3.2.3 CstC: Constant Current

The constant current (CstC) technique is especially dedicated to supercapacity 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.

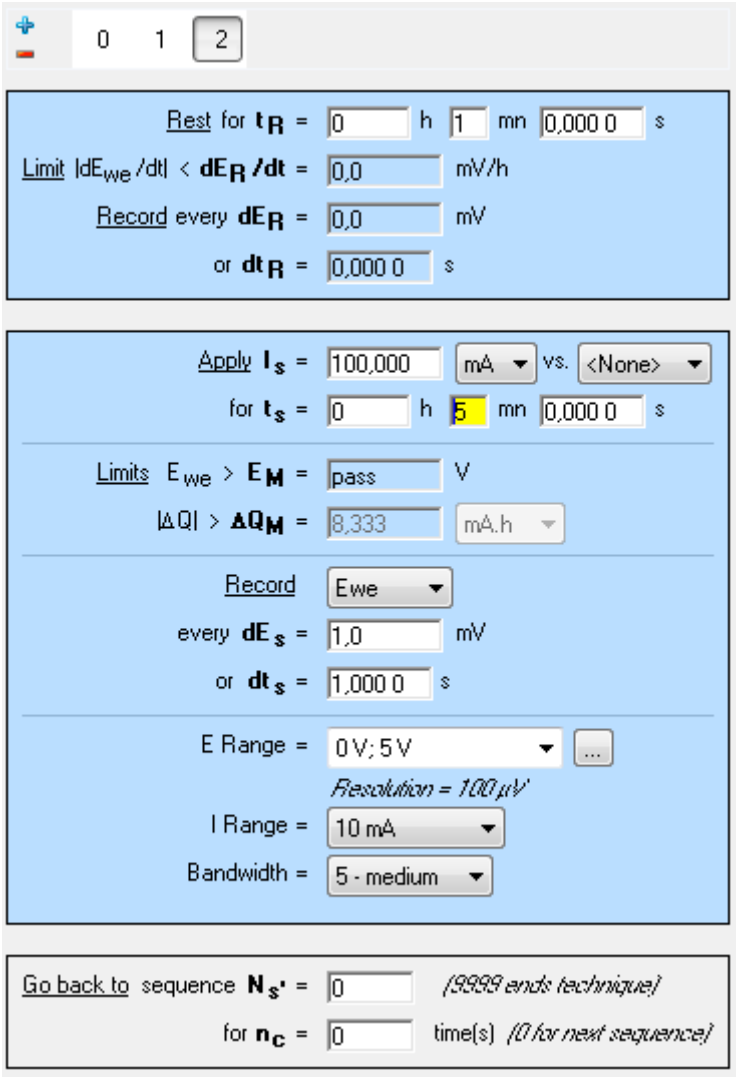


Fig. 152: Constant Current detailed diagram.

- **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
sets the current step duration.

Limits $|E_{we}|$ >/< E_M = … mV and $|\Delta Q|$ < ΔQ_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 turns blue. These values can be entered simultaneously, and this is the first condition that is reached that determines the recording.

E Range = …
enables the user to select the potential range and adjust the potential resolution to his/her 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**

Go back to 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.

3.2.4 CS: Current Scan

The CS technique consists of a current scan between two limits of current. The voltage is measured instantaneously. Different limits could be set, such as voltage (Ewe, Ece Ecell), or charge…

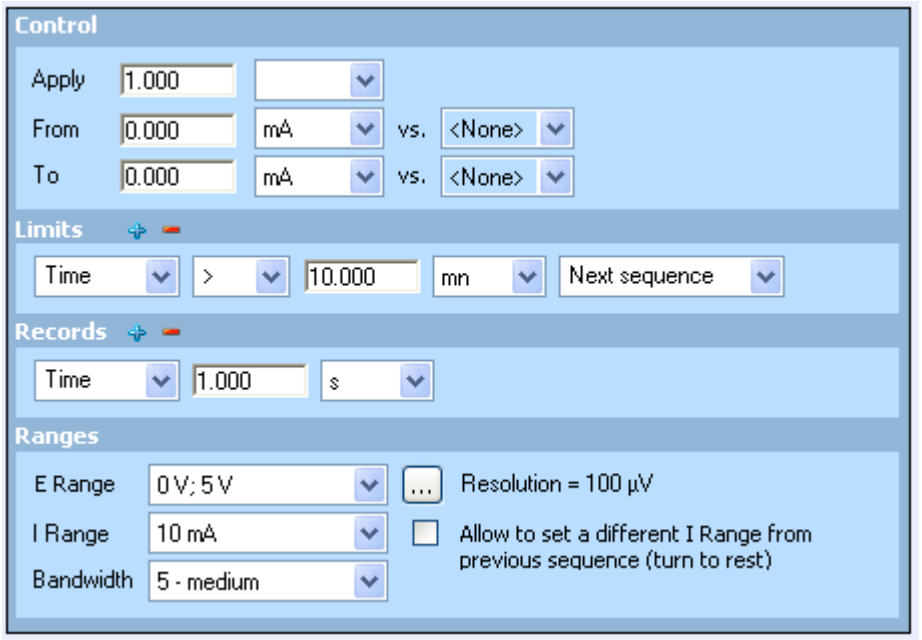


Fig. 153 : Current Scan detailed diagram

Apply… A/s, mA/s, µA/s, A/mn, mA/mn, µA/mn
From… pA/…/A vs <None>, Ictrl, Imeas
To … pA/…/A vs <None>, Ii
applies a current scan from an initial current value **Ii** (defined in absolute value, *vs.* **Ictrl** the previous controlled current or *vs.* **Imeas** the previous measured current) to a final value If defined in absolute value or *vs.* **Ii** at a scan rate defined above.

Limits: The second block is related to the limits of the experiment. The maximum number of limits is 3. They can be set on :

- the **Time** in **day**, **h**, **mn**, **s**, **ms**
- the working electrode potential **Ewe** in **V**, **mV**
- the counter electrode potential **Ece** in **V**, **mV**
- the potential difference **Ewe – Ece** in **V**, **mV**
- the current **I** in **A**, **mA**, **µA**, **nA**, **pA**
- the charge **Q** in **A.h**, **mA.h**
- the power **P** in **W**, **mW**, **µW**
- the **Energy** in **kW.h**, **W.h**, **mW.h**, **µW.h**
- the potential time variation **|dE/dt|** in **V/s**, **mV/s**, **mV/mn**, **mV/h**
- the current time variation **|dI/dt|** in **A/s**, **mA/s**, **µA/s**, **A/mn**, **mA/mn**, **µA/mn**
- the temperature **T** in **°C**
- the temperature time variation **|dT/dt|** in **°C/mn**, **°C/h**

Records: it is possible to set three different recording conditions on :

- the **Time** in **day**, **h**, **mn**, **s**, **ms**
- the working electrode potential **Ewe** in **V**, **mV**
- the counter electrode potential **Ece** in **V**, **mV**
- the potential difference **Ewe – Ece** in **V**, **mV**
- the current **I** in **A**, **mA**, **µA**, **nA**, **pA**
- the charge **Q** in **A.h**, **mA.h**
- the power **P** in **W**, **mW**, **µW**

- the **Energy** in **kW.h**, **W.h**, **mW.h**, **µW.h**

If several conditions are used, the one taken into account is the one that is met the most quickly.

3.3 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.

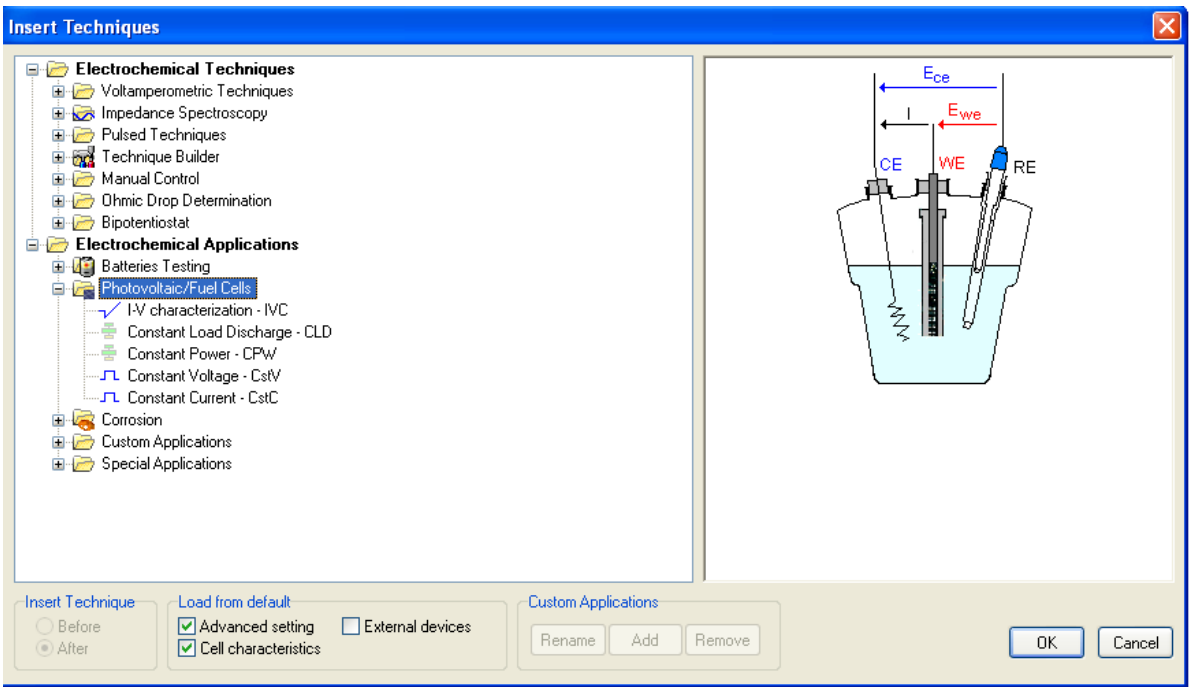


Fig. 154: Photovoltaic / fuel cell applications

3.3.1 IVC: I-V Characterization

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.

3.3.1.1 Description

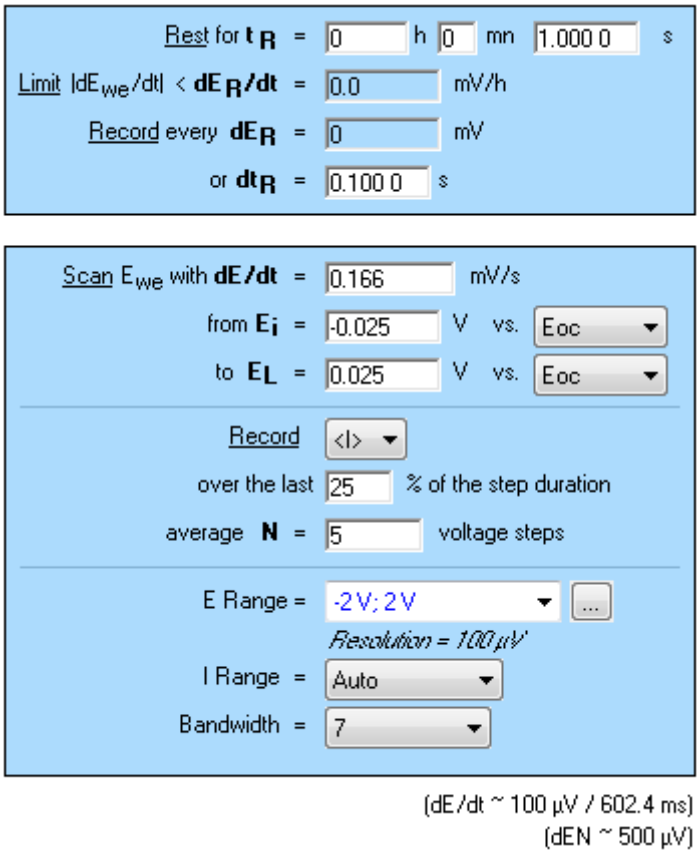


Fig. 155: Detailed diagram of the I-V Characterization.

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

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

Limit $|dE_{we}/dt| < dE_R/dt$ … 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 or 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 User’s Manual for more details).

From E_i = … V *vs.* Ref/Eoc/Ectrl/Emeas to E_L = … V *vs.* Ref/Eoc/Ei
from a potential E_i defined *vs.* Ref the reference electrode potential or *vs.* a previous open circuit potential (E_{oc}), previous controlled potential (E_{ctrl}) or previous measured potential (E_{meas}) to E_p value 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 and to adjust the potential resolution with his/her system (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment).

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

3.3.1.2 Process

Associated with the I-V characterization, an analysis is available for this section offering the determination 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 0 A
- 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.

3.3.2 CLD: 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 necessary to maintain the ratio E/I constant.

Start discharge on R=E/I= ... µOhm/…/MOhm for at most t_M = ... h … mn … s
sets the cell resistance to R = E/I for t_M duration.

Limit $|E_{we}| < E_M$ = ... V, $|\Delta Q| > \Delta Q_M$ = … A.h/…/fA.h, kC/…/pC <=> Δx_M = …
sets 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.

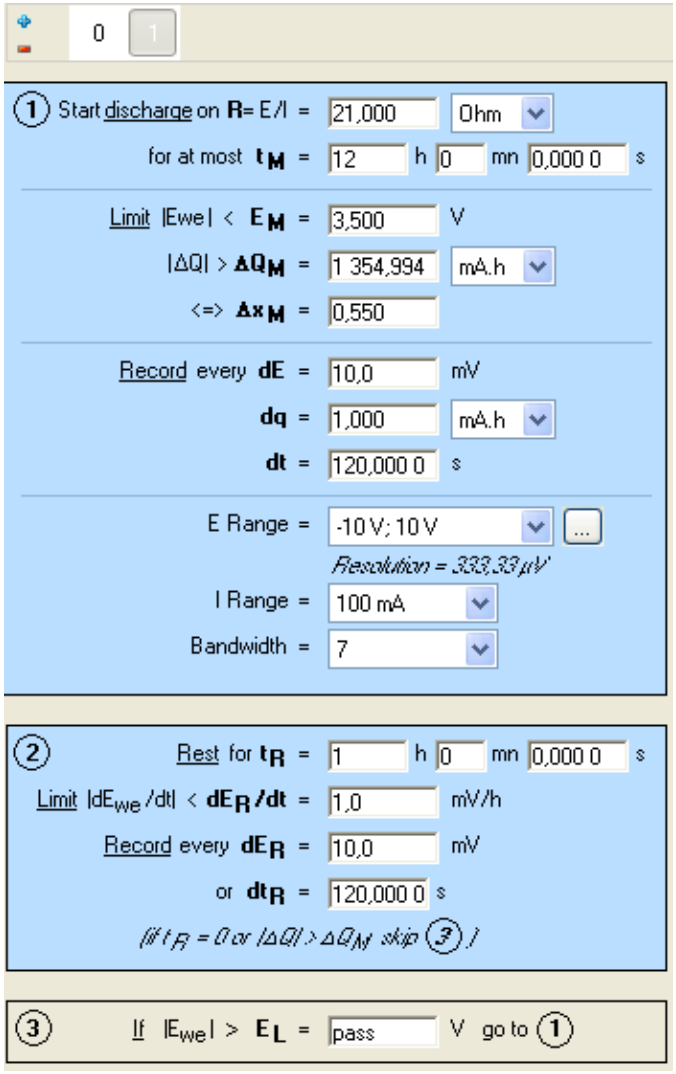


Fig. 156: CLD detailed diagram.

Record every dE = … mV, dq = … A.h/…/fA.h, kC/…/pC 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.

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

3.3.3 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.

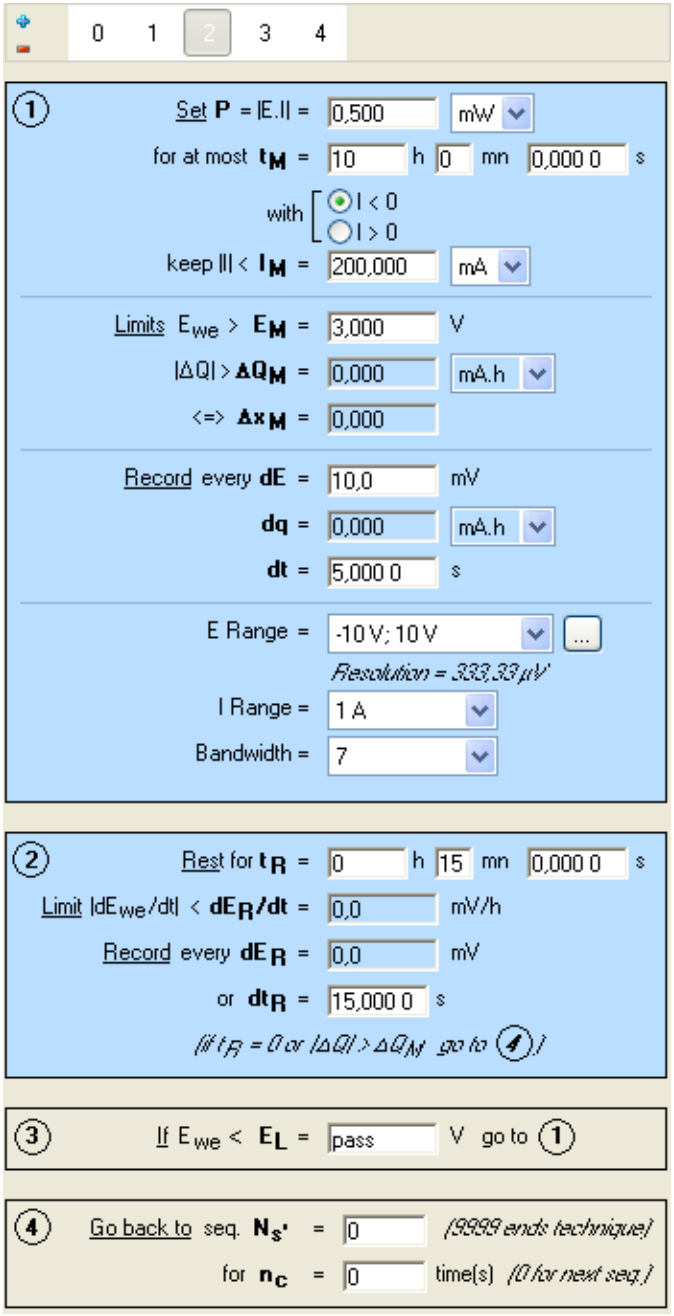


Fig. 157: CPW detailed diagram.

- **Choice of the power value**

<u>Set</u> 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.

<u>Limits</u> E_{we} < E_M = … V, |ΔQ| to ΔQ_M = … A.h/…/fA.h, kC/…/pC <=> Δx_M = …
sets 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 (|ΔQ|, |Δx|), 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.

Record every dE = ... mV, dq = … A.h/…/fA.h, kC/…/pC 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.

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

- **Rest period**

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

CAUTION!

Applying a constant power during a discharge experiment corresponds to an increase of the current (in absolute value) when the potential decreases. The user must be careful to note the final current of the first constant power step. For example, let us 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.

3.3.4 CstV: Constant Voltage

The constant voltage (CstV) technique is especially 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.

- **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**

Apply E_i = … V *vs.* Ref/Eoc/Ectrl/Emeas.
the potential step is defined *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
sets the potential step duration.

Limits |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.

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

<I> every dt = … 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 VMP3 based instruments and for VMP300 based instruments.
Leave dI alone for Chronoamperometry experiments, and dQ for Chronocoulometry experiments.

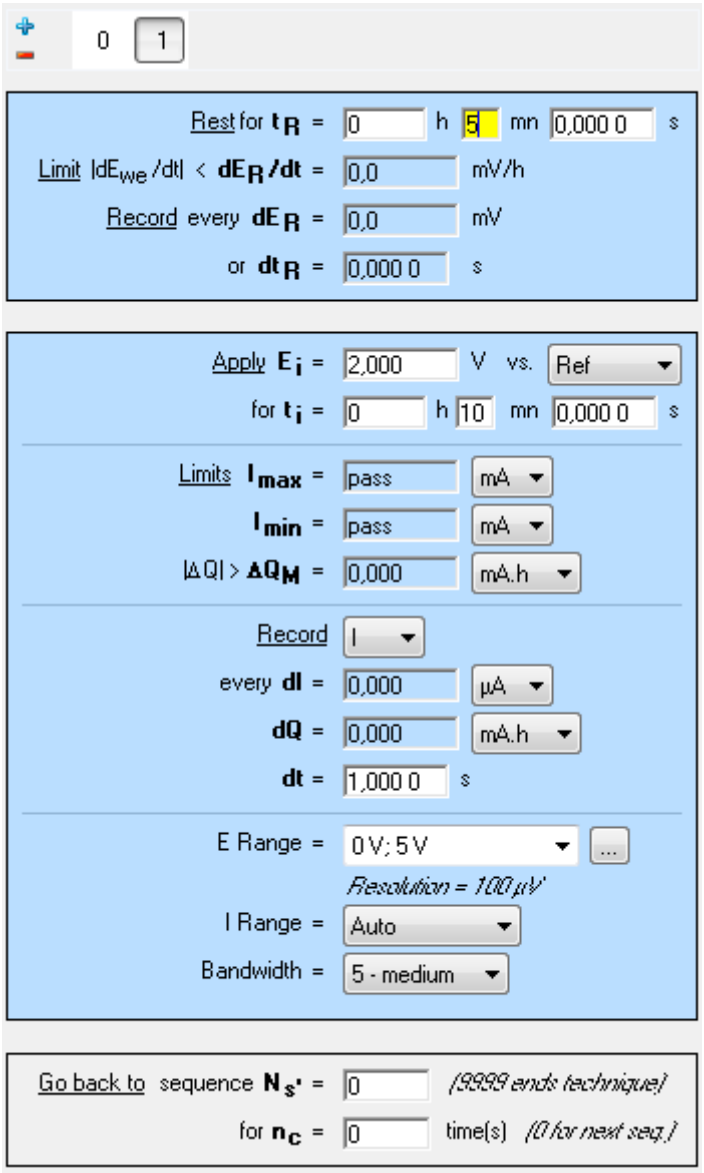


Fig. 158: Constant Voltage detailed diagram.

E Range = …
enables the user to select the potential range and adjust the potential resolution to his/her 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**

Go back to 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).

3.3.5 CstC: Constant Current

The constant current (CstC) technique is especially 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.

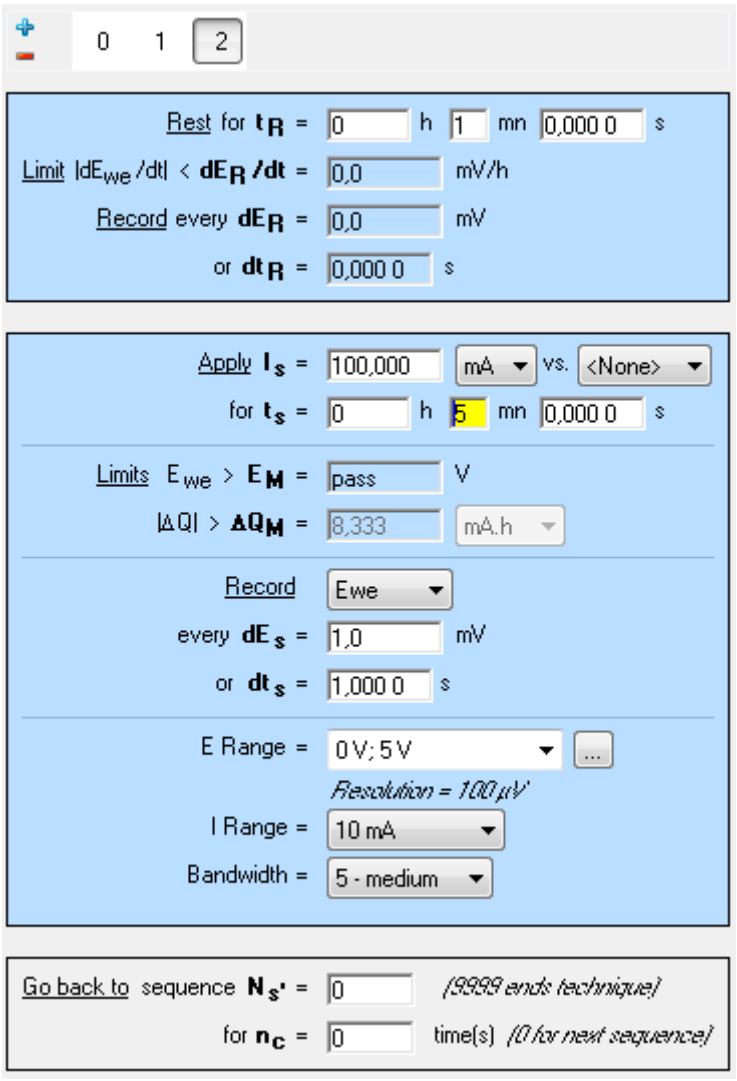


Fig. 159: Constant Current detailed diagram.

- **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
sets the current step duration.

Limits $|E_{we}|$ >/< 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 turns blue. These values can be entered simultaneously, and this is the first condition that is reached that determines the recording.

E Range = …
enables the user to select the potential range and adjust the potential resolution to his/her 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**

Go back to 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.

3.4 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.

3.4.1 EVT: E_{corr} versus Time

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

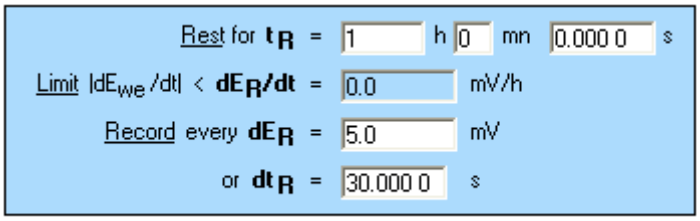


Fig. 160: E_{corr} *vs.* time diagram.

Rest for t_R = ... h ... mn ... s
sets 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.

3.4.2 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 inverse of the slope of the current density vs potential curve at the free corrosion potential (at which the overpotential *dE* → 0)

$$R_p = \frac{1}{\frac{dI}{dE}} \qquad dE \to 0$$

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 Tafel coefficients with the Tafel Fit tool.

3.4.2.1 Description

- **Rest potential (or open circuit) sequence.**

See EVT technique above

- **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 User’s 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 *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.

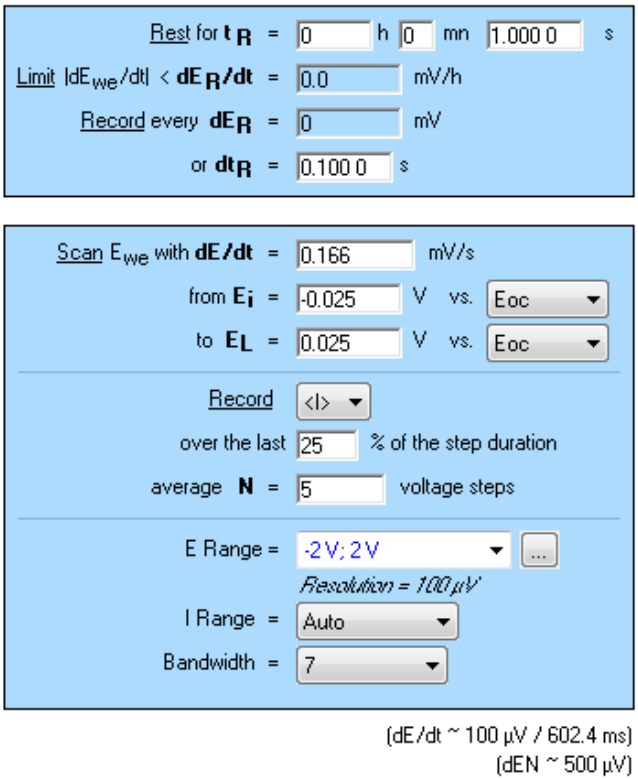


Fig. 161: Detailed diagram of the Linear Polarization application.

<u>Record</u> <I> over the last … % of the step duration averaged N = … voltage steps

I every dI_p = … pA/nA/µA/mA/A
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 and adjust the potential resolution to his/her 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.
Contrary to the MPP technique (see 3.4.8), no current limitation is available with the linear polarization application.

3.4.2.2 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 User's Manual for more details).

3.4.3 CM: Corrosimetry (R_p 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 a very long time: several months). It consists in applying 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.

3.4.3.1 Description

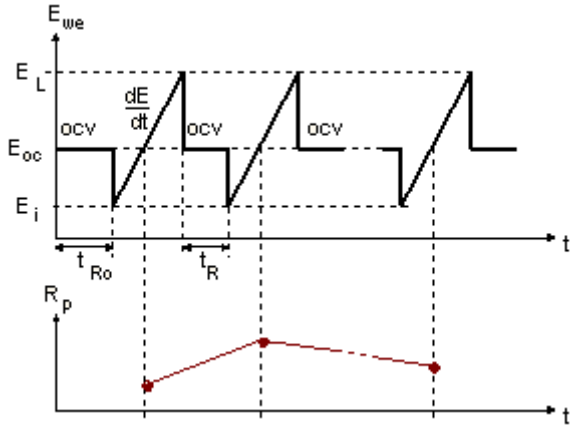


Fig. 162: Graphic description of the Corrosimetry application.

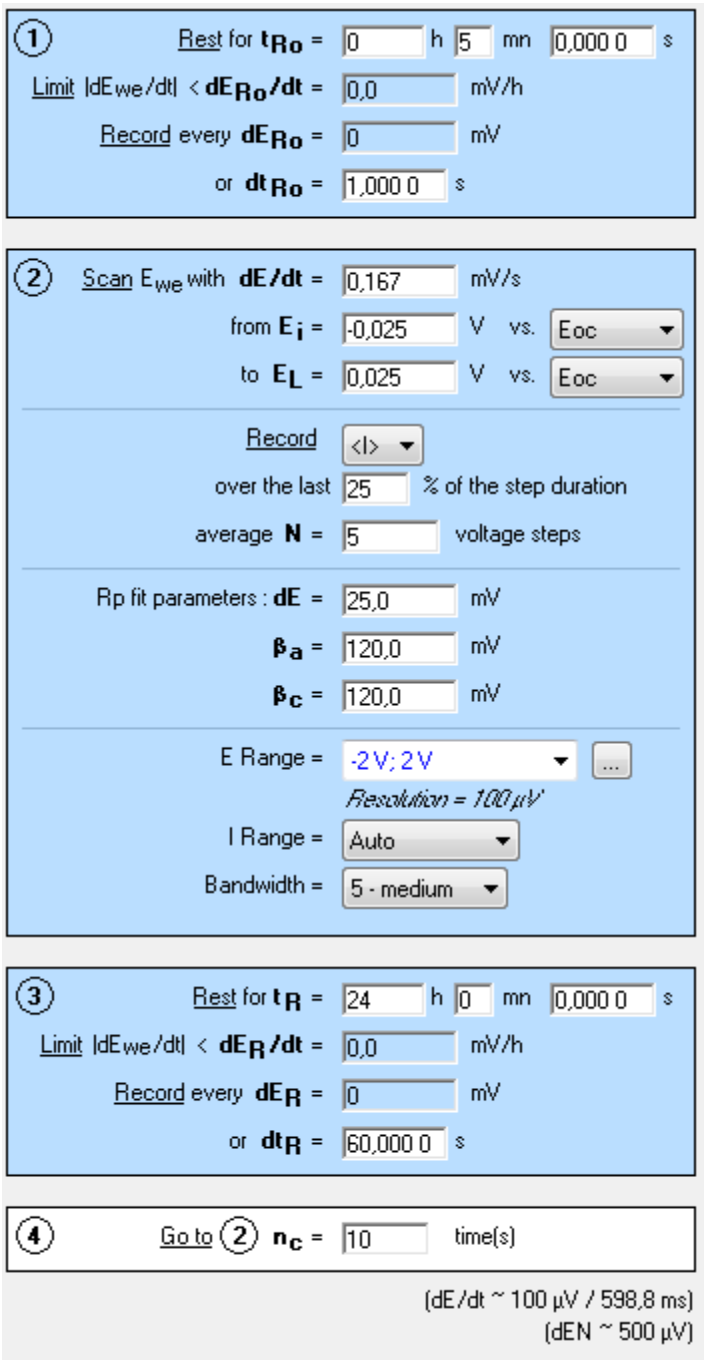


Fig. 163: Detailed diagram of the Corrosimetry application.

- **Rest potential (or open circuit) sequence.**

Equivalent to the EVT technique described above.

- **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 User’s 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 *vs.* Ref the reference electrode potential 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
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 and adjust the potential resolution to his/her 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.

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.

- **Rest potential (or open circuit) sequence**

Equivalent to the EVT technique described above.

- **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.

3.4.3.2 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.

3.4.4 GC: Generalized Corrosion

The generalized corrosion technique is applied for general corrosion (sometimes called uniform corrosion) study. In this type of 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-150/50, the SP-300/200/240/VSP-300 and VMP300, the potential step and its duration are defined according to the potential control

resolution (see the EC-Lab® Software User's Manual for more details). 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.

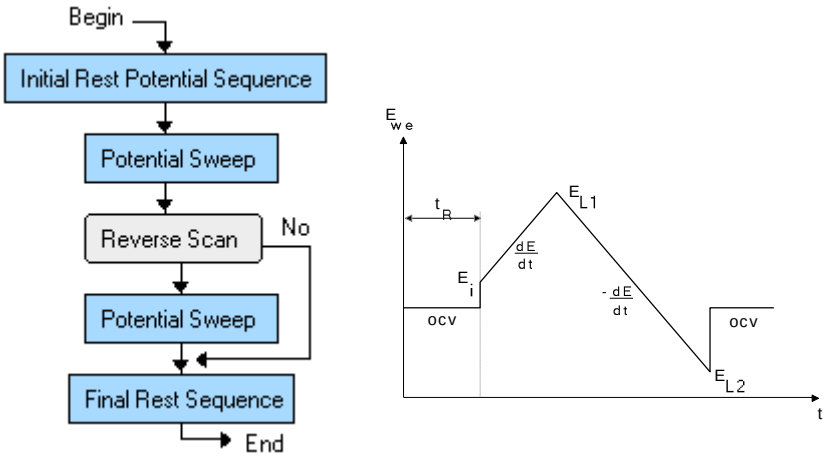


Fig. 164: General diagram of the Generalized Corrosion technique.

3.4.4.1 Description

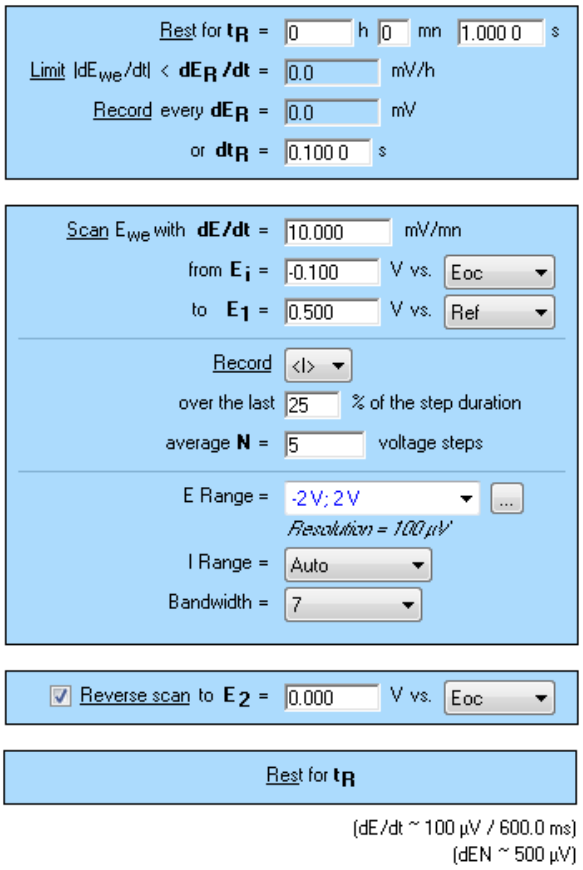


Fig. 165: Detailed diagram of the Generalized Corrosion technique.

- **Rest potential (or open circuit) sequence.**

See EVT technique above.

- **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 User’s 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 *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 and adjust the potential resolution to his/her 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 with same scan rate, towards final limit E_2 = … 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.

- **Rest**

Executes a rest potential period similar to the initial one. At the end, the working electrode is disconnected.

3.4.4.2 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 User’s Manual for more details). It can also be used to determine the corrosion rate with the Tafel Fit (see the EC-Lab® Software User’s Manual for more details).

3.4.5 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 over 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 which is done before the potentiostatic one, some phases are optional and there is an additional potentiodynamic phase:

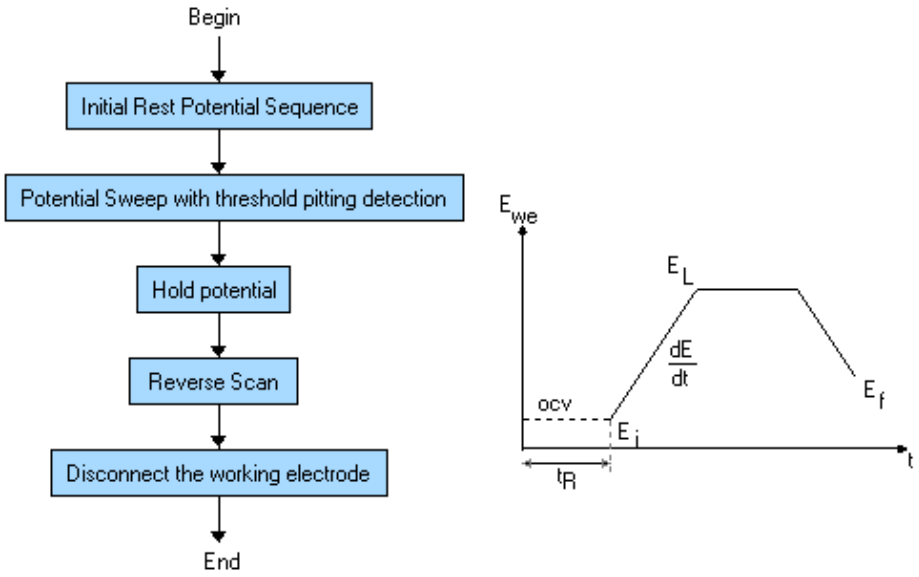


Fig. 166: CPP general diagram.

The detailed diagram is made of five blocks:

- Initial Rest Potential Sequence,
- Potential sweep with threshold pitting detection,
- Hold potential,
- Reverse scan.

- **Rest potential (or open circuit) sequence.**

See EVT technique above.

- **Potential scan.**

<u>Scan E_{we}</u> 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 User's 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 *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.

<u>Limit</u> |I| > I_P = ... pA/…/A, after t_b = ... s
sets 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 and adjust the potential resolution to his/her 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.

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).

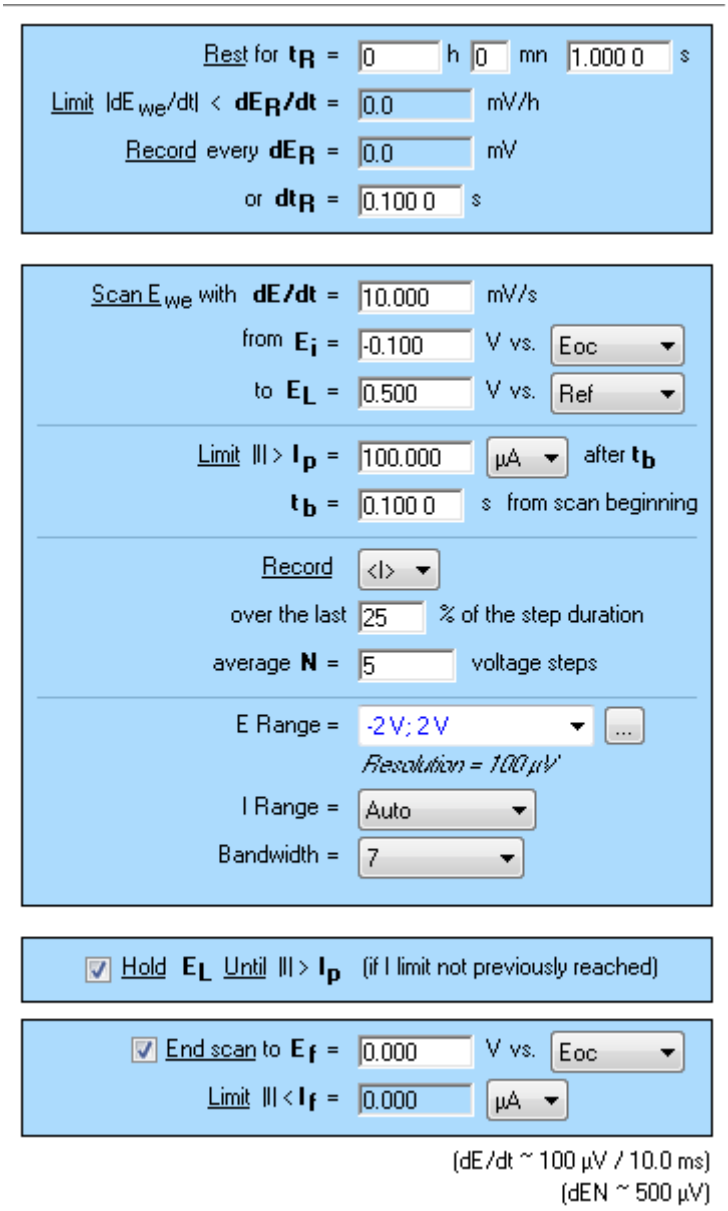


Fig. 167: CPP detailed diagram.

- **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.

- **Reverse scan**

End 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}.

Limit $|I| < I_f$ **= ... 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.

3.4.6 DP: Depassivation Potential

The Depassivation Potential technique 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 pitting corrosion.

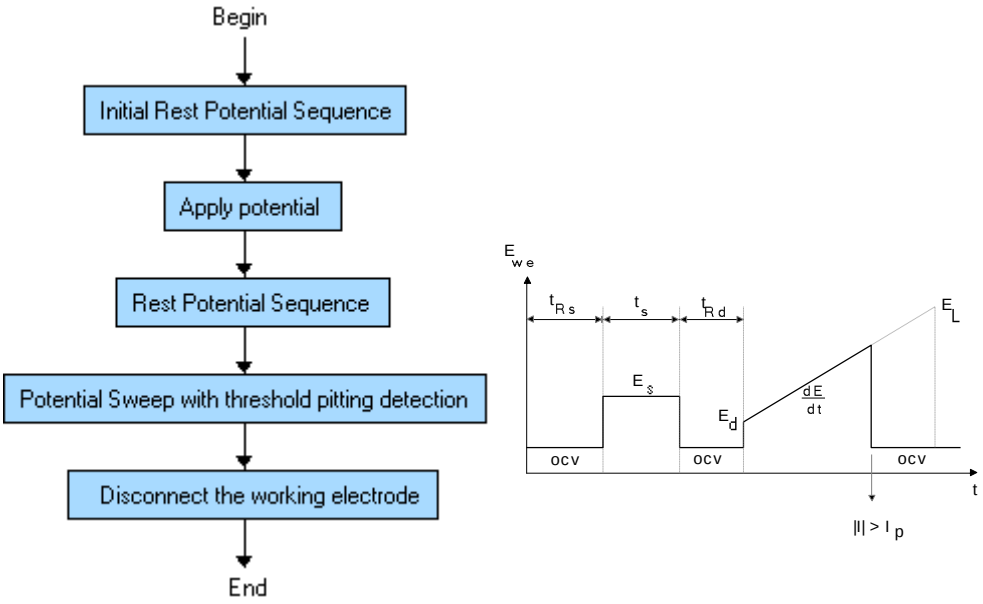


Fig. 168: General diagram of the Depassivation Potential application.

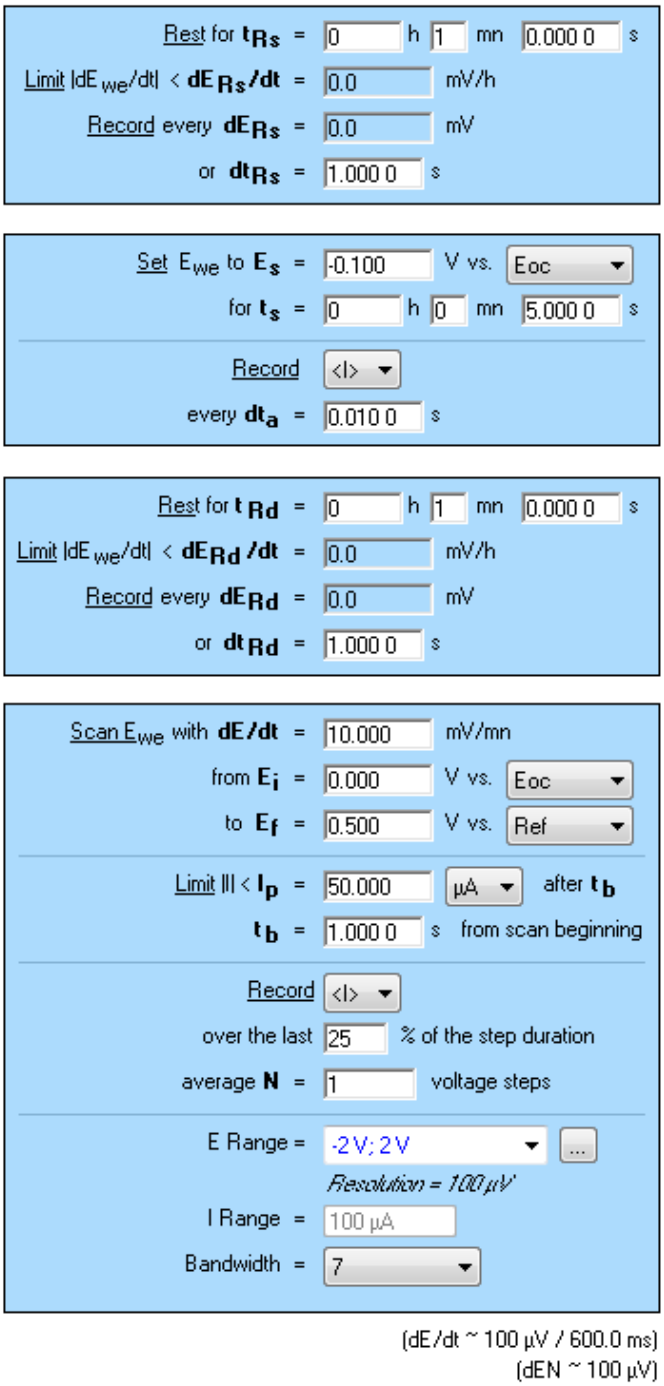


Fig. 169: Detailed diagram of the Depassivation Potential application.

- **Rest potential (or open circuit) sequence.**

See EVT technique above

- **Potentiostatic period.**

Set Ewe = Es = … V *vs.* Ref/Eoc/Ectrl/Emeas for t_s = … h … mn … s
sets the potential *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_s = … s.
I every dI_s = … pA/…/A or dt_s = … 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).

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 User's 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.

- **Rest potential (or open circuit) sequence.**

See the first step for more details about the open circuit period

- **Potential sweep with threshold pitting detection sequence.**

Scan E_{we} with dE/dt = ... mV/mn
Sets 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 *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.

Limit |I| < I_P = ... pA/…/A, after t_b = ... s
sets 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).

Record <I> over the last … % of the step duration averaged N = … voltage steps

I every dI_d = … pA/…/A
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).

E Range = …
enables the user to select the potential range and adjust the potential resolution to his/her system. (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment)

The cell is disconnected at the end of the experiment.

3.4.7 CPT: Critical Pitting Temperature

The CPT technique is based on the AST G150 standard for the determination of the lowest temperature on the test surface at which stable propagating pitting occurs under specified test conditions indicated by a rapid increase beyond a set limit of the measured anodic current density of the specimen.

Before running any CPT experiment, one must first calibrate the temperature controls. Select **"Thermostat"** (Device Type) "**Device Name**" in the list, in the **External Device** windows, as is shown in Fig. 170.

Either the standard supplied Ministat or an external thermostat can be selected. If external thermostats are used, the user needs to define the control calibration values (temperatures 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.
Once this is done, the T/°C box allows manual setting and activation of the temperature of the cell.

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.

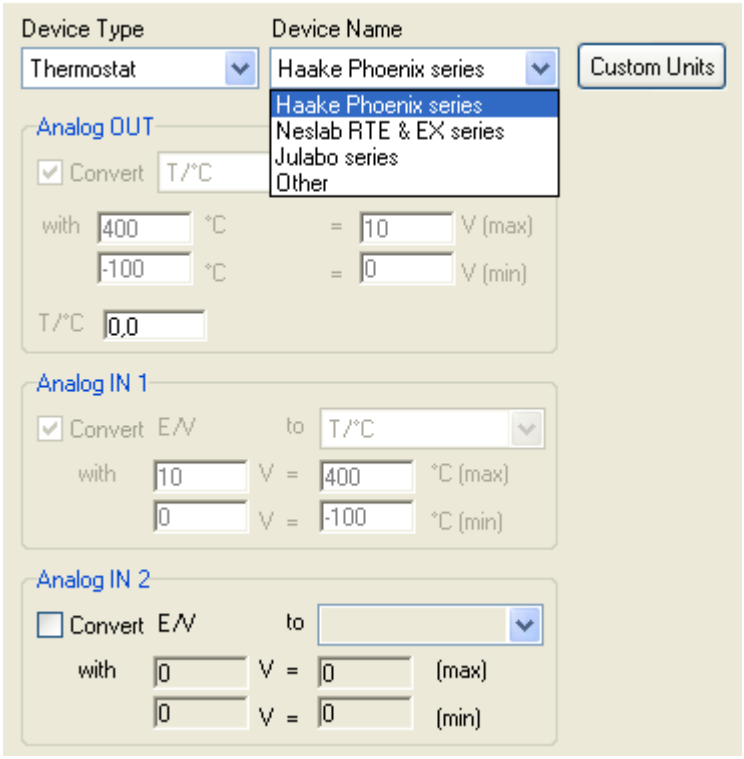


Fig. 170: Temperature configuration for the Haake Phoenix series

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:

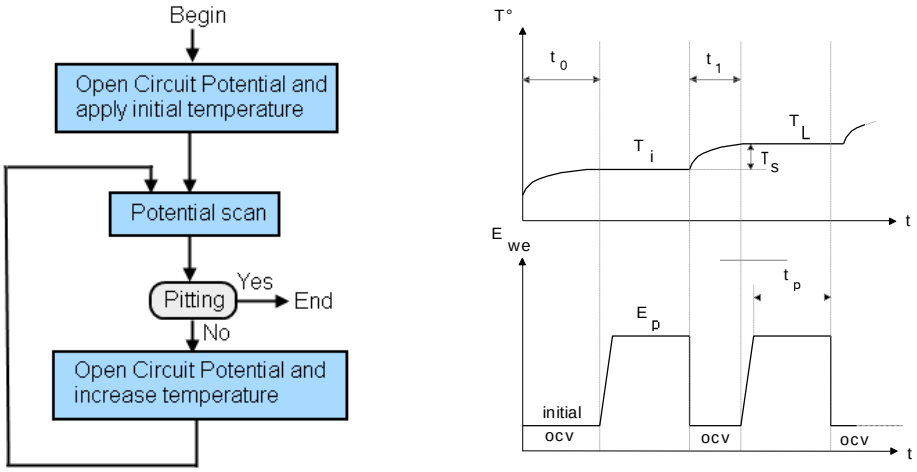


Fig. 171: General diagram of the CPT technique.

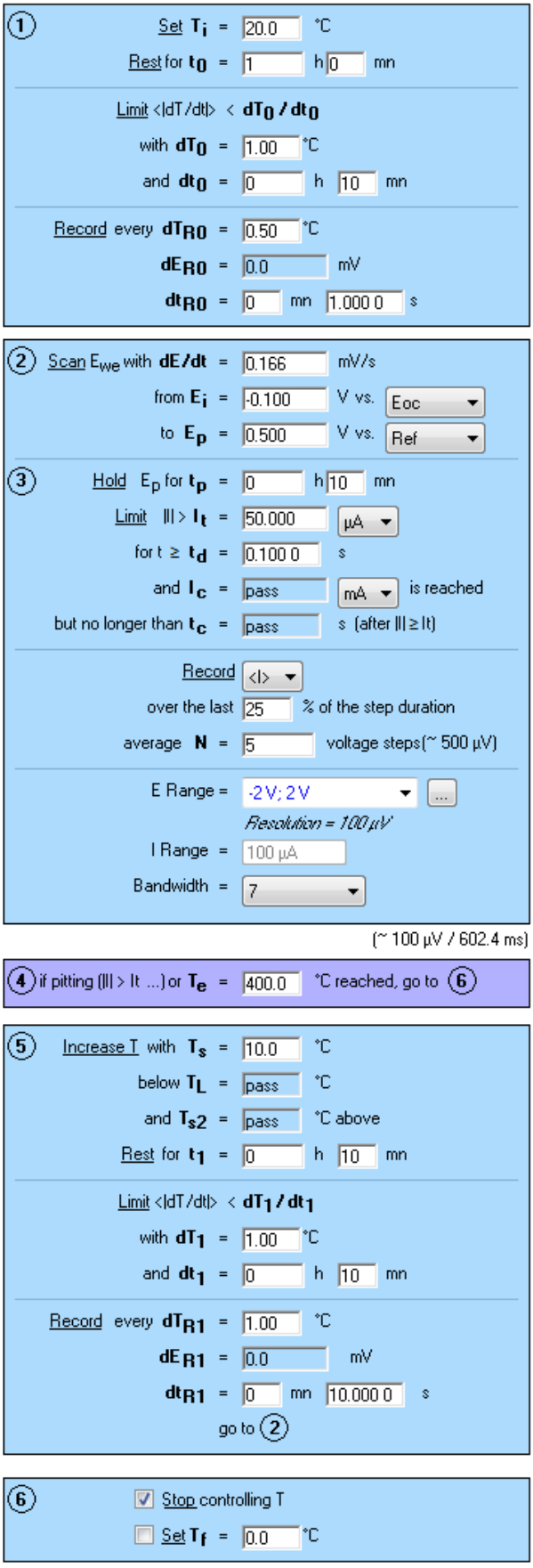


Fig. 172: Detailed diagram of the CPT technique.

The whole sequence can be described with the following figure:

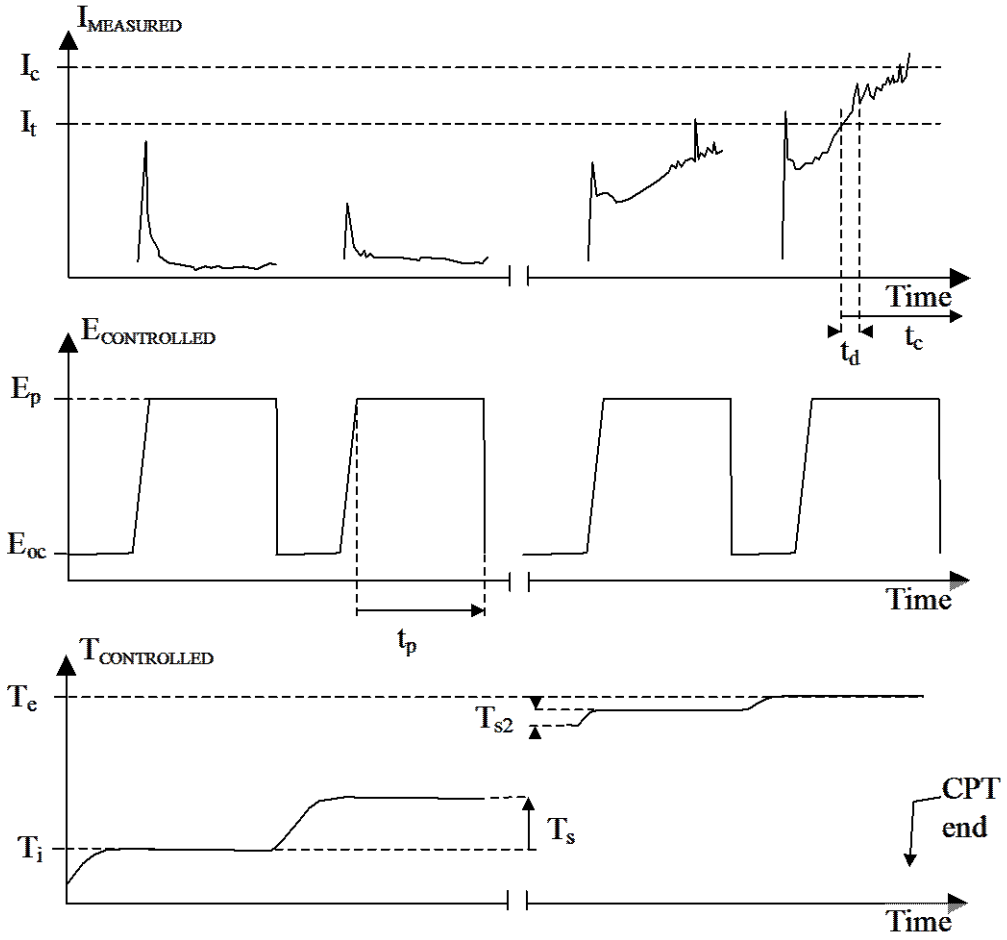


Fig. 173: I, E_{we} and T vs. time for the CPT experiment.

- **First step: set the initial temperature and turn to rest.**

<u>Set</u> T_i = … °C
sets the temperature T_i.

<u>Rest</u> 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).

<u>Record</u> 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 User's 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 *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 = … A/…/pA for t ≥ t_d = … s
And I_c = … A/…/pA 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. 173** illustrates these conditions.

Record <I> over the last … % of the step duration averaged N = … voltage steps

I every dI_p = … A/…/pA 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 and adjust the potential resolution to his/her 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.

If 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 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.

3.4.8 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.

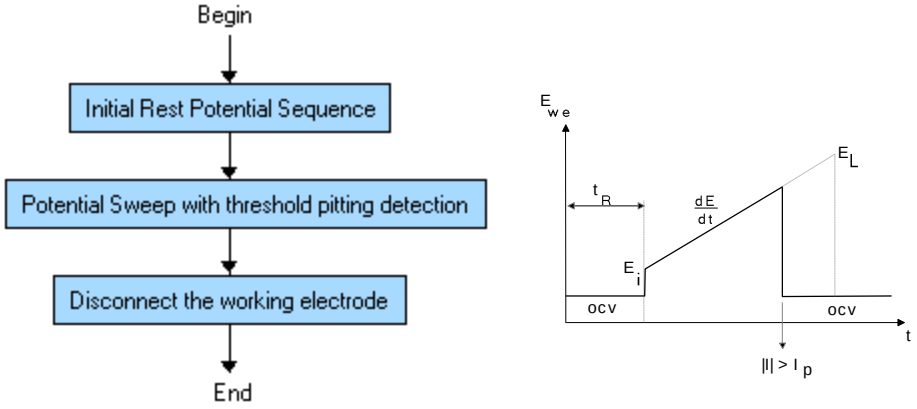


Fig. 174: General diagram of the Potentiodynamic Pitting technique.

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 pitting current limit value, 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.

3.4.8.1 Description

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

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

Limit $|dE_{we}/dt| < dE_R/dt$ ... 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.

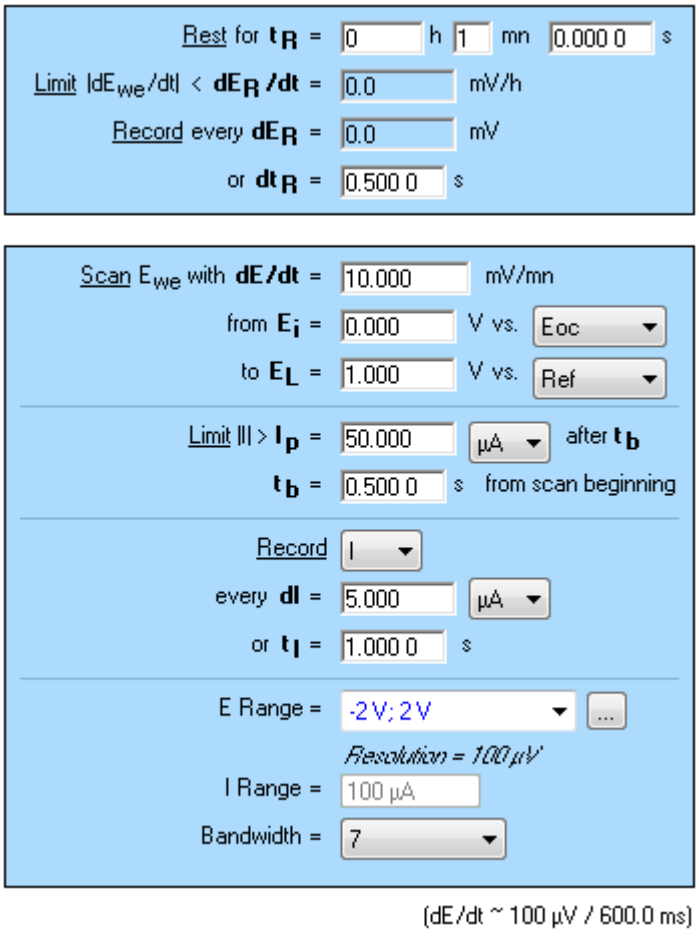


Fig. 175: Detailed diagram of the Potentiodynamic Pitting technique.

- **Second step: potential sweep with threshold pitting detection sequence.**

Scan E_{we} with dE/dt = ... mV/mn
sets 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 *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.

Limit $|I| > I_P$ = ... pA/…/A, after t_b = ... s
sets 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).

<u>Record</u> <I> over the last ... % of the step duration averaged N = … voltage steps

I every dI = … pA/…/A or dt_I = … 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).

E Range = …

enables the user to select the potential range and to adjust the potential resolution with his/her 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. 176**) shows the result of a potentiodynamic multi-pitting experiment performed on 8 passivated stainless steel electrodes.

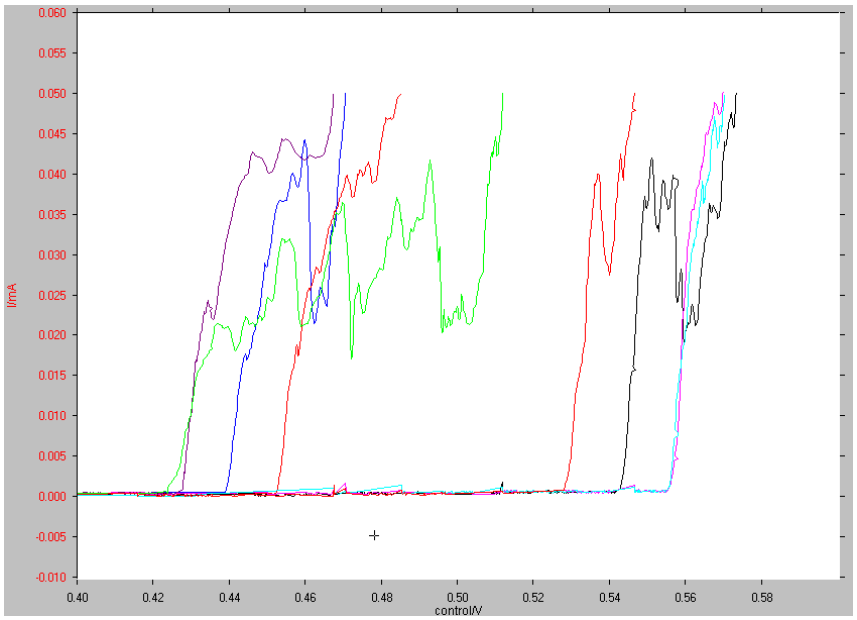


Fig. 176: 8 electrodes Potentiodynamic Pitting experiment. Electrode: Stainless steel in 0.02 M NaCl. Scan rate: 100 mV/mn. Recording resolution: 0.2 µA or 20 ms.

3.4.8.2 Data processing

Data processing using **<u>M</u>ulti-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 $I = I_p$.

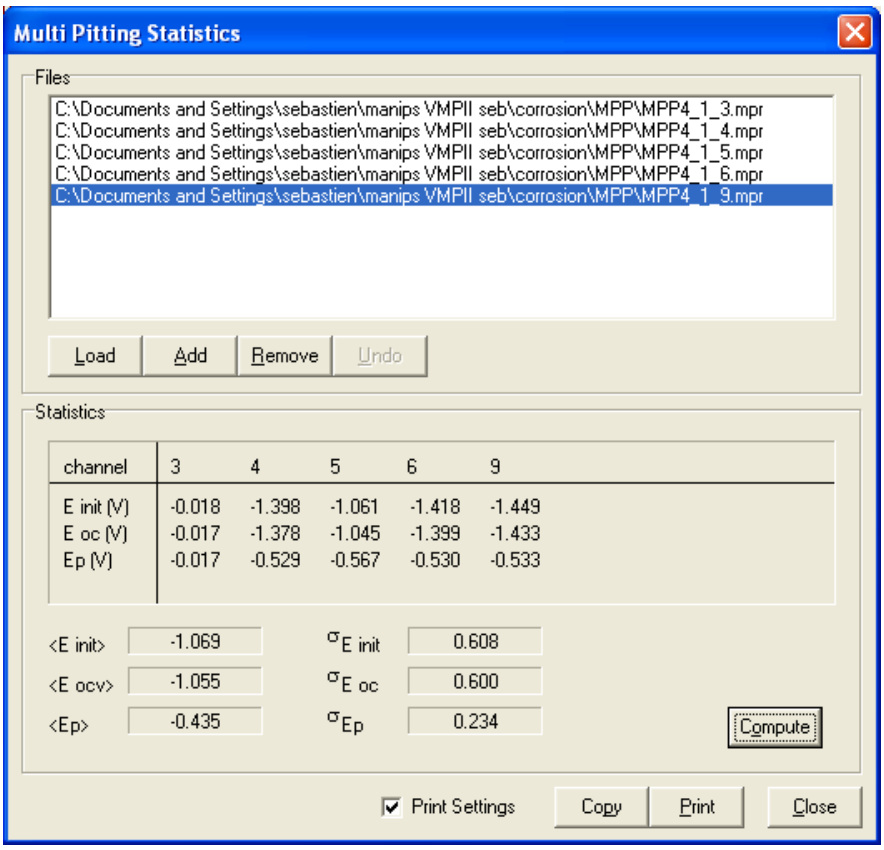


Fig. 177: Multi pitting statistics window.

Report to the multipitting statistics process for more details (in the EC-Lab® Software User's Manual).

3.4.9 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.

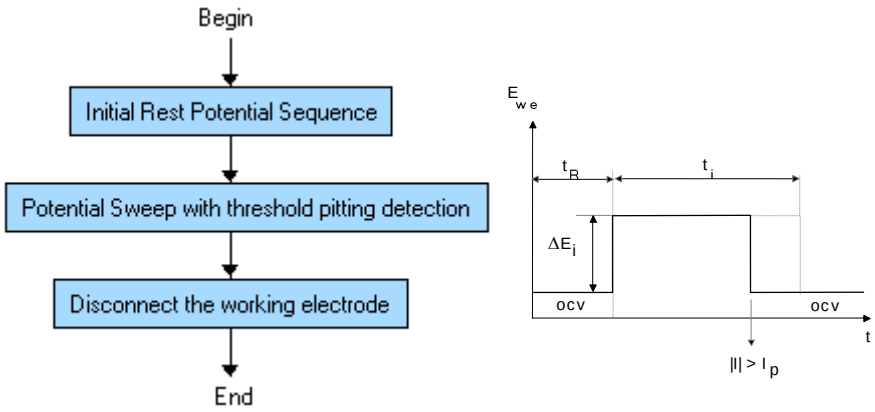


Fig. 178: General diagram of the Potentiostatic Pitting application.

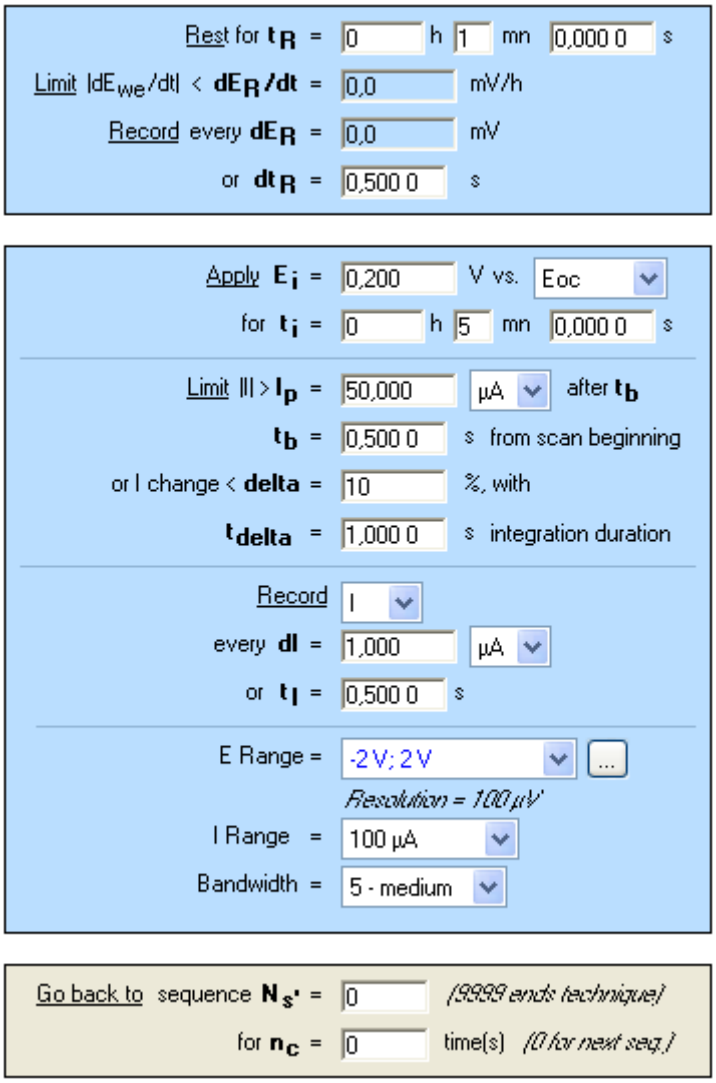


Fig. 179: Detailed diagram of the Potentiostatic Pitting application.

- **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 for t_i = … h … mn … s
sets the potential *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.

Limit |I| > I_P = ... pA/…/A, after t_b = … s

or I change <delta = ... %, with t_{delta}= ... s integration duration
Two different limits are available. Limit |I| > I_P sets 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).
I change <delta =... % stop the measurement if the current variation is lower than a percent of it (delta). The variation of the current is evaluated during an integration time of t_{delta}.

Record <I> every dt_a = … s.

I every dI_p = … A/…/pA or t_s = … 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).

E Range = …
enables the user to select the potential range for adjusting the potential resolution with his/her 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 set.
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.

3.4.10 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 electrochemical noise measurements. It consists in 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 cases, the coupling current is measured between two electrodes from the same material. The microstructure differences between these two electrodes result in the fact that one of them behaves anodically and the other one behaves cathodically.

The potential is controlled in this application between Ref1 (S1 for the SP300-based instruments) and Ref3 (S3 for the SP300-based instruments) in the standard connection mode. The first metal must be connected to Ref1+CA2 leads (S1 + P1 for the SP300-based instruments), and the other metal must be connected to Ref3+CA1 leads (S3 + P2 for the SP300-based

instruments). Ref2 (S2 in the SP300-based instruments) is connected to the reference electrode. Figs. 174 and 175 show the connections for the VPM3 and SP300-based instruments. It could be necessary to connect the ground lead if the signal is noisy.

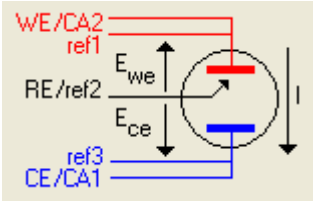


Fig. 180: VMP3-based instruments connection.

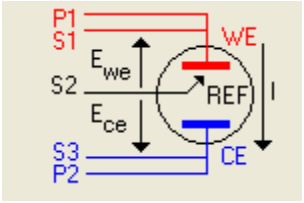


Fig. 181: SP300-based instruments connection.

The currents involved are generally very low (µA). The quality of the measurement will be greatly enhanced if the cell is placed in a Faraday cage, in order to remove environmental noise and other electrodynamics perturbations.

Note: 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.

They are detailed below:

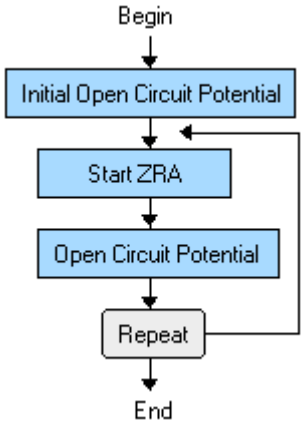


Fig. 182: ZRA general diagram.

- **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.

Limits |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.

Limit |ΔQ| to ΔQ_M = … A.h/…/pC
limits the charge per n_c loop to ΔQ_M. Setting ΔQ_M to 0 cancels the test.

Record E, I or <E>, <I> every dt_q = … s
defines the recording conditions current and potential, either instantaneous or average.

E Range = …
enables the user to select the potential range and to adjust the potential resolution with his/her system. (See EC-Lab® Software User's Manual for more details on the potential resolution adjustment)

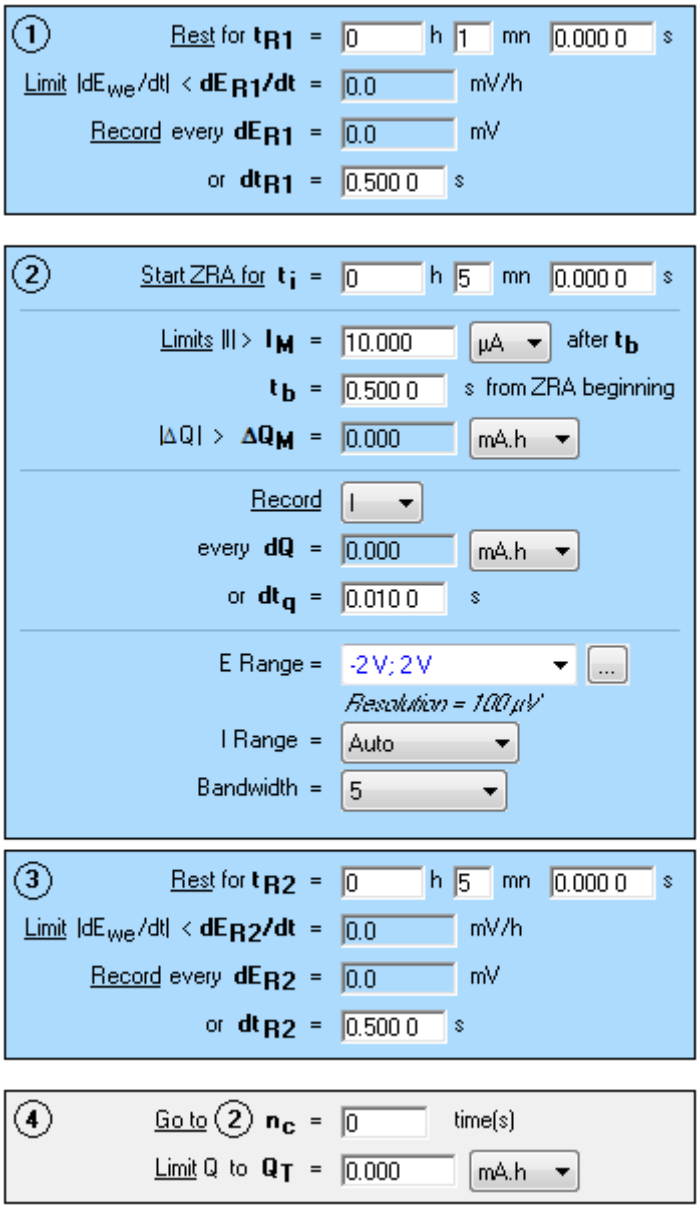


Fig. 183: ZRA detailed diagram.

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**

Go to 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.

3.4.11 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.

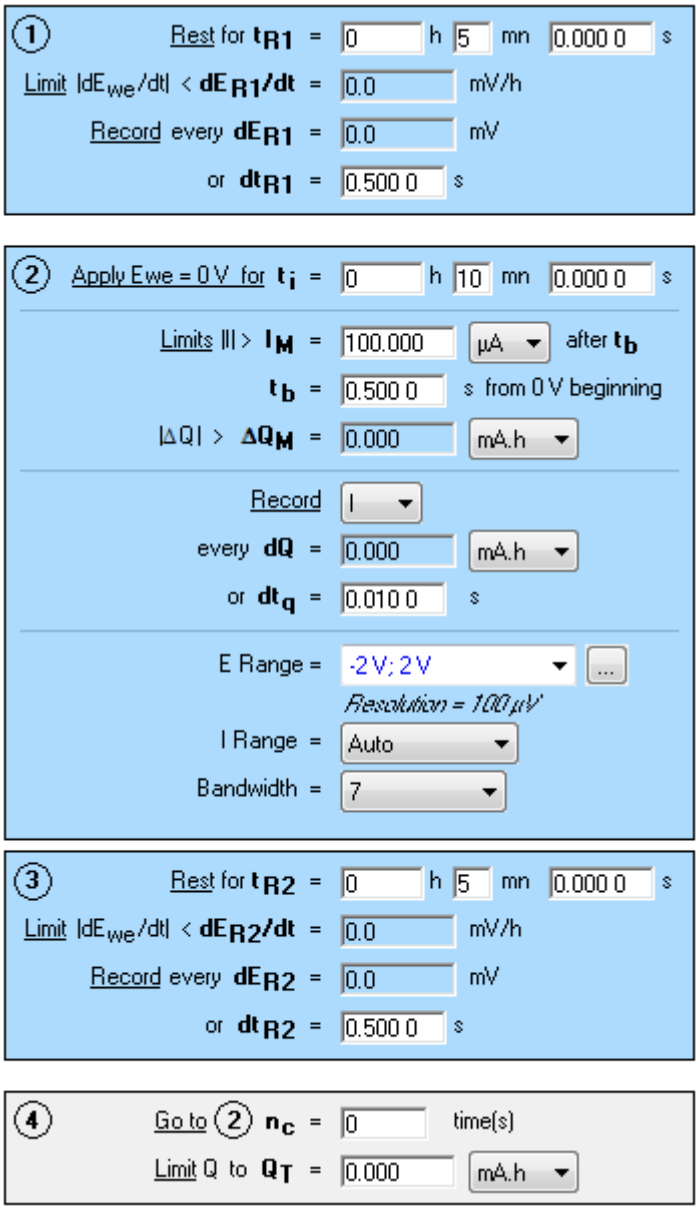


Fig. 184: ZVC detailed diagram.

3.4.12 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 (E_{corr}) with N amplitudes increasing from Va min and Va max. At each amplitude, the polarization resistance (R_p) 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.
This technique is essentially an intermediate that may be less destructive to a sample than Tafel polarization, but probes a more expanded voltage window than the Polarization Resistance technique. As a result, it is a balance of accuracy and sample damage that lies between the two techniques.

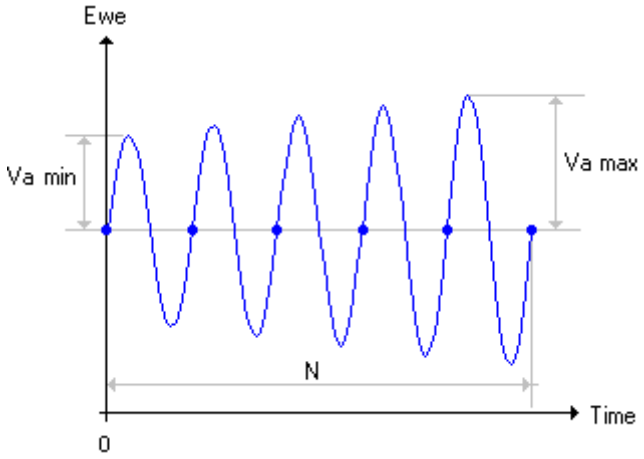


Fig. 185: Variable Amplitude Sinusoidal microPolarization technique.

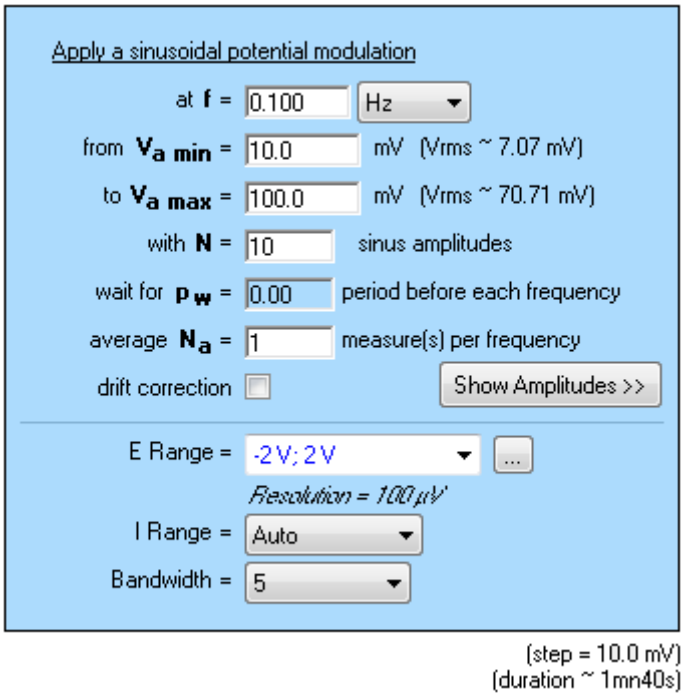


Fig. 186: Detailed diagram of the Variable Amplitude Sinusoidal microPolarization technique.

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. It needs to be used when the sytem has not reached its styeady-state regime. This feature is more specifically dedicated to low frequencies at which the impedance measurement can be pretty lengthy and for which the effect of the drift can be seen.
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. For more information about the drift correction, please refer to the Application Note #17.

E Range = …
enables the user to select the potential range and adjust the potential resolution to his/her 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.

3.4.13 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 (E_{corr}) with a small amplitude Va and a constant low frequency (fs). This technique is associated to a dedicated fit (CASP Fit), that uses a direct Fourier transform to determine the amplitude of the harmonics. They are then used to calculate the corrosion parameters. This technique is faster than the standard polarization technique and there is no need to know the corrosion coefficient values. This technique is available whether the channel board has EIS ability or not. This technique is essentially an intermediate that may be less destructive to a sample than Tafel polarization, but probes a more expanded voltage window than the Polarization Resistance technique. As a result, it is a balance of accuracy and sample damage that lies between the two techniques.

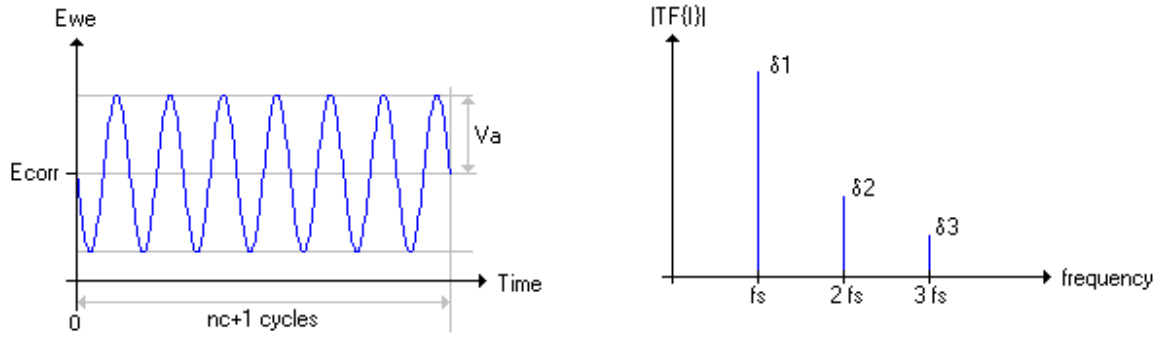


Fig. 187: Principle of the Constant Amplitude Sinusoidal microPolarization technique and its associated analysis.

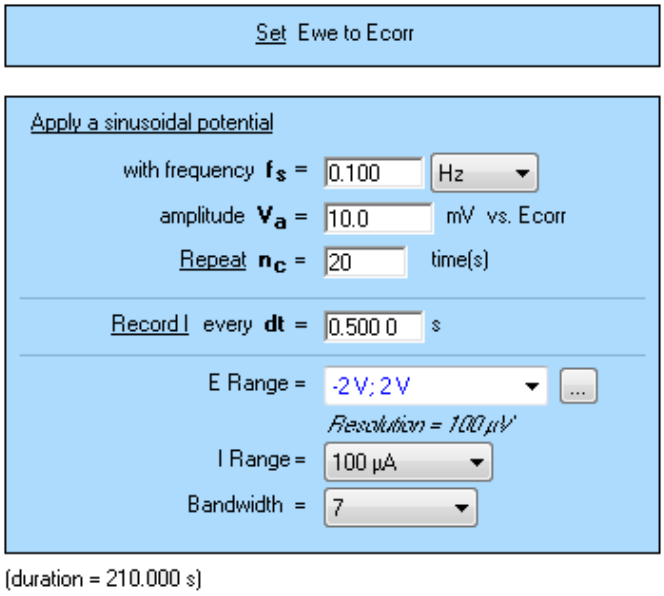


Fig. 188: Detailed diagram of the Constant Amplitude Sinusoidal microPolarization technique.

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 I every dt = ... s
sets the sampling rate of the measurement.

E Range = …
enables the user to select the potential range and adjust the potential resolution to his/her 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.
It is recommended to set a constant current range to have a constant sampling rate.

3.5 Custom Applications

3.5.1 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.

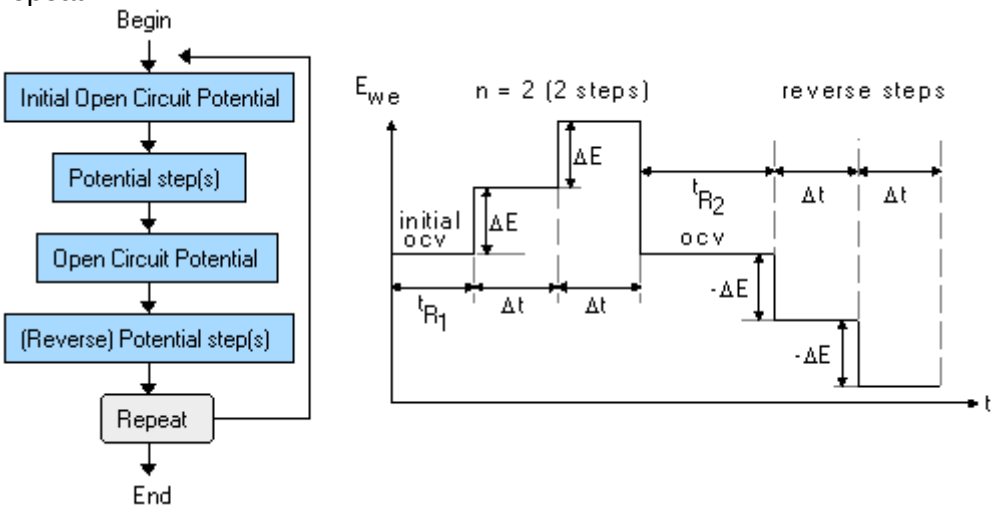


Fig. 189: Polarization Resistance general diagram.

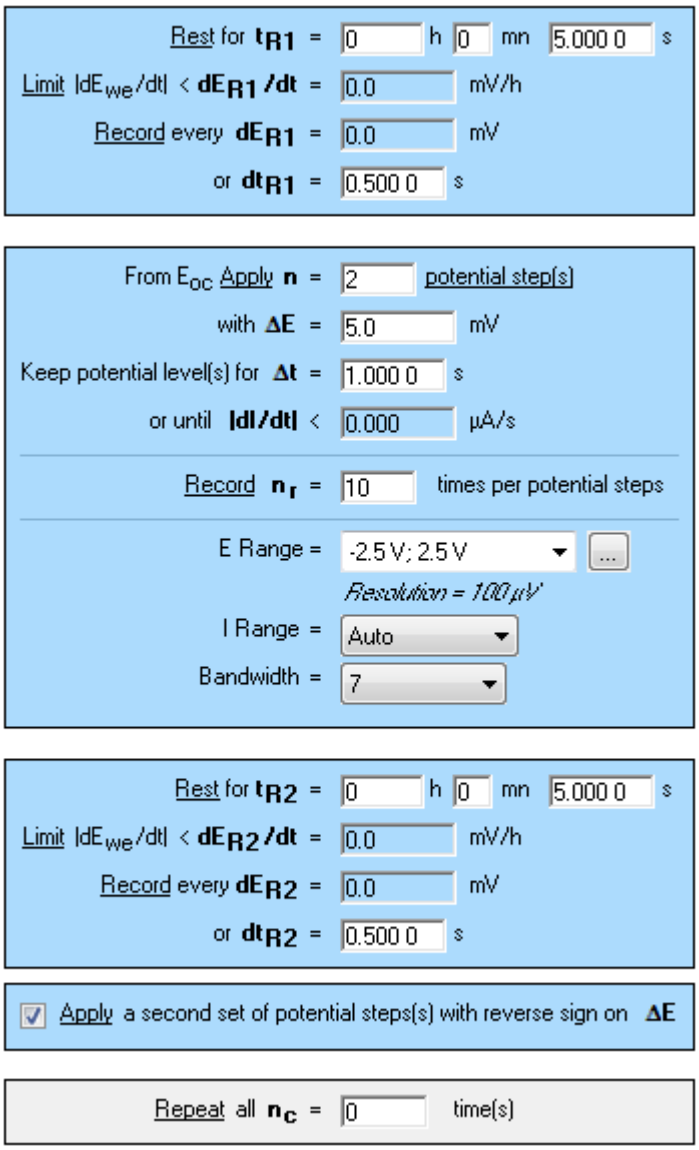


Fig. 190: Polarization Resistance detailed diagram.

- **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.

Record 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 and adjust the potential resolution with his/her 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, Corrosion, Polarization Resistance** to load the following window:

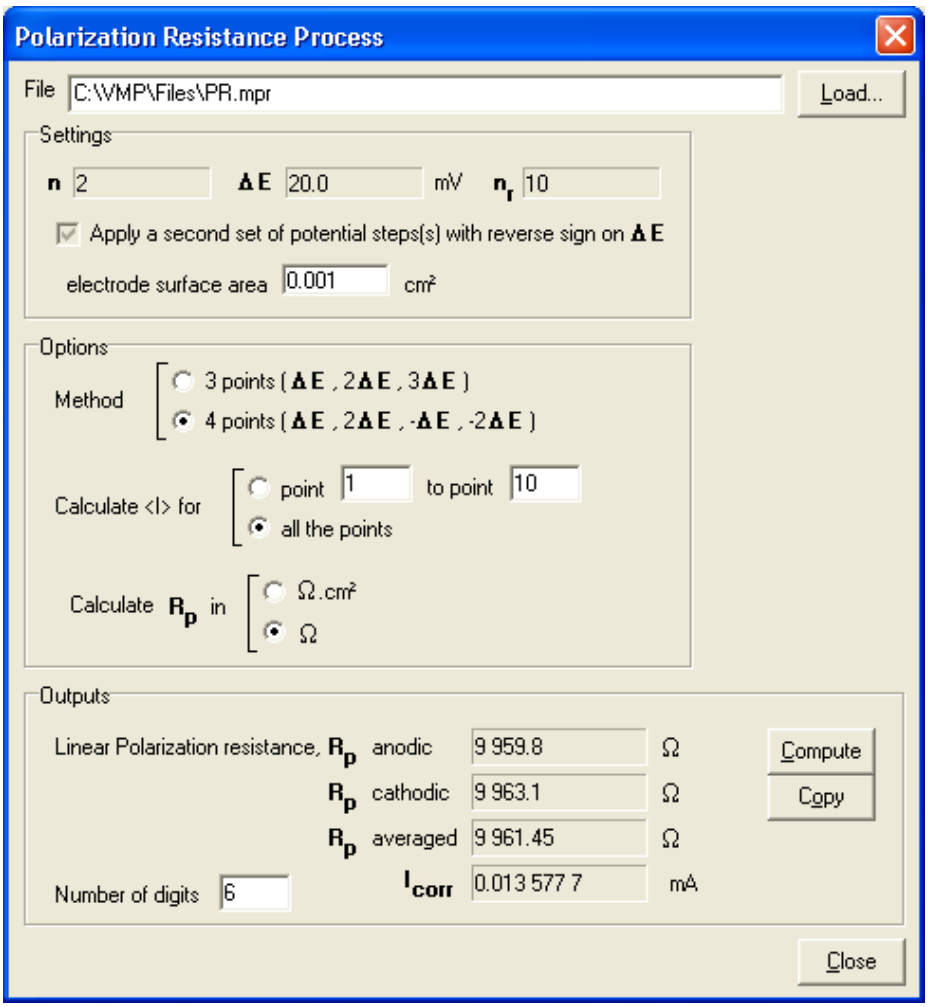


Fig. 191: Polarization Resistance process.

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:

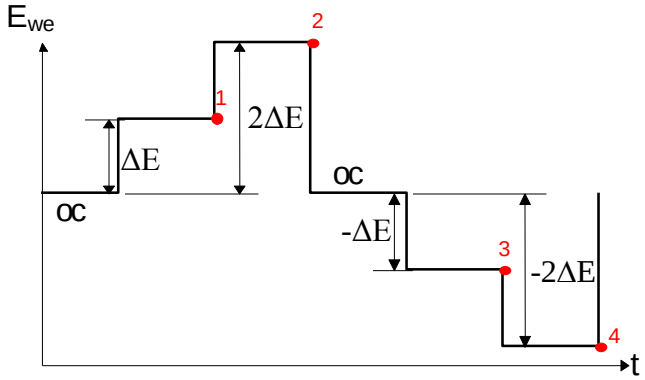


Fig. 192: 4 points method.

(n = 2, reverse steps)

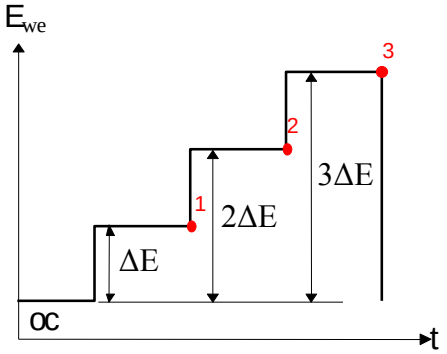


Fig. 193: 3 points method.

(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 choose the 3 points method.
Note: other methods can be performed with the Polarization Resistance technique, but the process here accepts only the 3 and 4 points method.

If several points have been recorded for each potential step (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 $2\Delta E$, (e_3,i_3) on $-\Delta E$ or $3\Delta E$ (according to the selected method) and (e_4,i_4) $-2\Delta E$
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.

3.5.2 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.

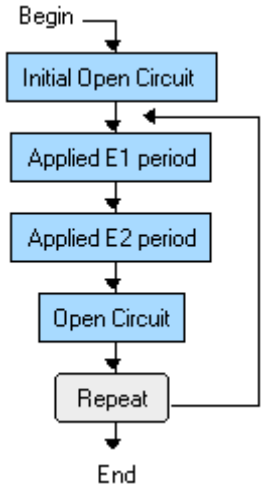


Fig. 194: SPFC general diagram.

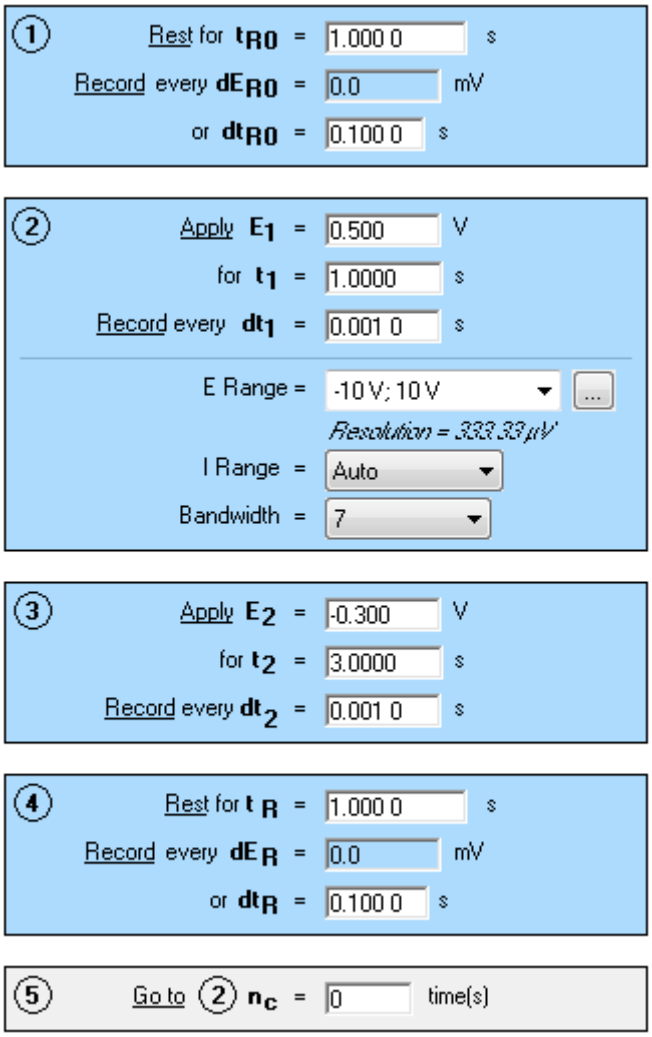


Fig. 195: SPFC detailed diagram.

- **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

Record <I> every dt_1 = … s
records points every dt_1 time.

E Range = …
enables the user to select the potential range for adjusting the potential resolution with his/her 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.

- **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**

refer to the OCV technique for more details.

- **Repeat**

Go to 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.

3.5.3 How to add a homemade experiment to the custom applications

EC-Lab® software offers the user the ability to create his/her 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.
Once 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 Applications" section of the technique window in blue. The blue color is used (like the user's reference electrode) to distinguish the standard EC-Lab® applications from the custom application. The custom applications are available only for a new experiment (not when one or several techniques are already loaded).

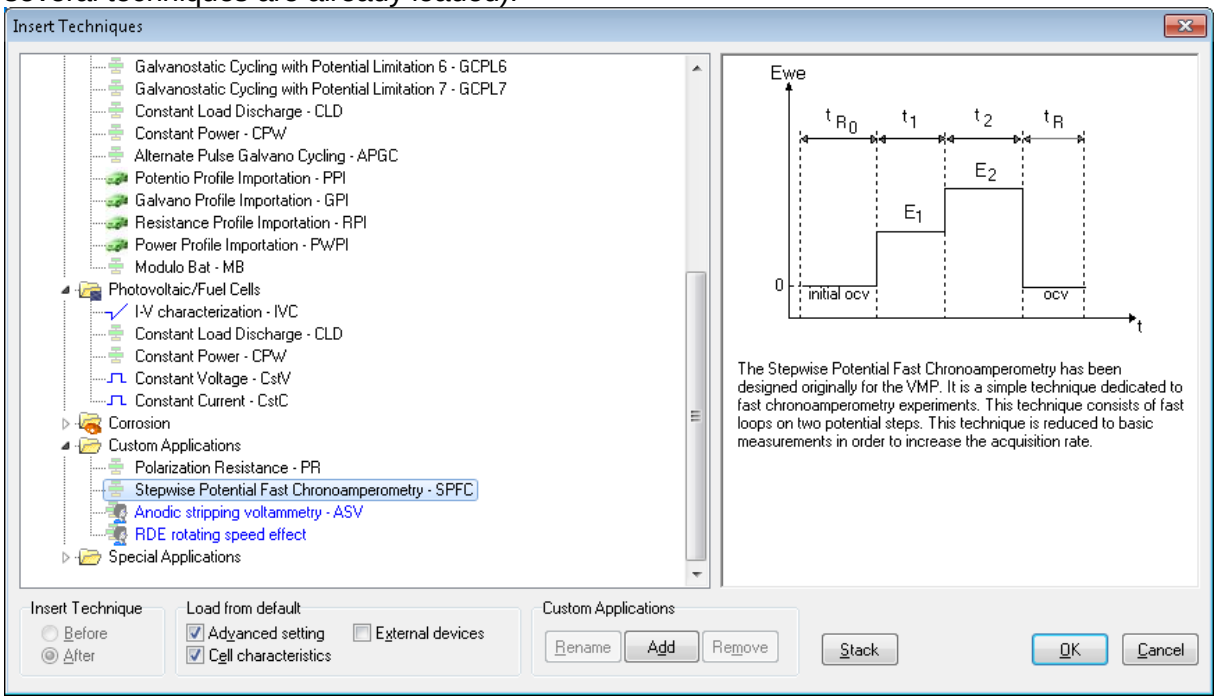


Fig. 196: Custom Applications section in the Techniques window.

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.

3.6 Special applications

For each special application, it is possible to stop the experiment with an external limit such as a temperature, a speed… Select **"Other"** (Device Type) in the "**External Device**" windows (Fig. 197). To record external analog signals through the auxiliary DB9 connector the user has to configure Analog In1 and/or Analog In2 inputs. Our instruments can control and record analog signals from – 10 to + 10 V. Most of the external devices work within a [0;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.

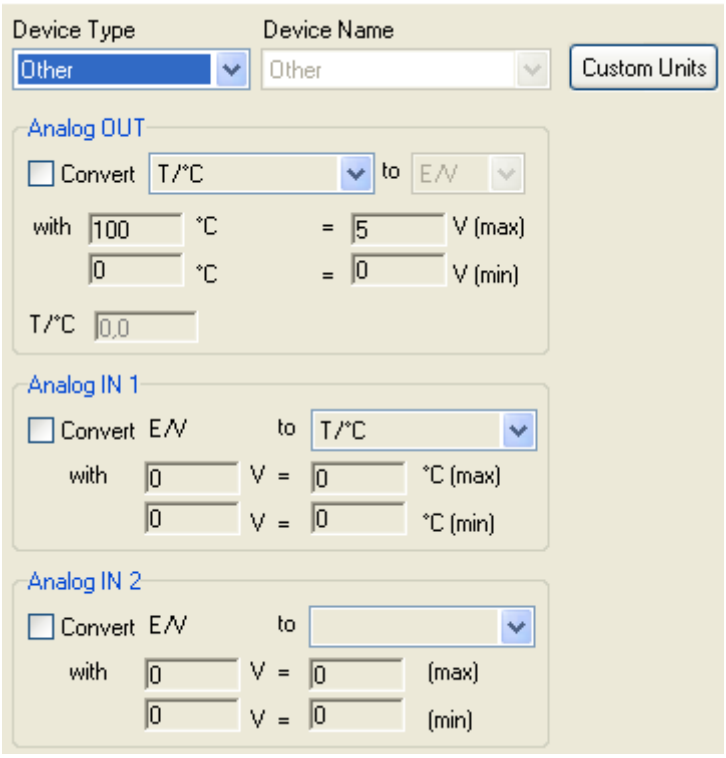


Fig. 197: External devices configuration window.

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. Each channel can record a separate 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 chosen variable. Click on "**Custom Units**". The figure below is displayed:

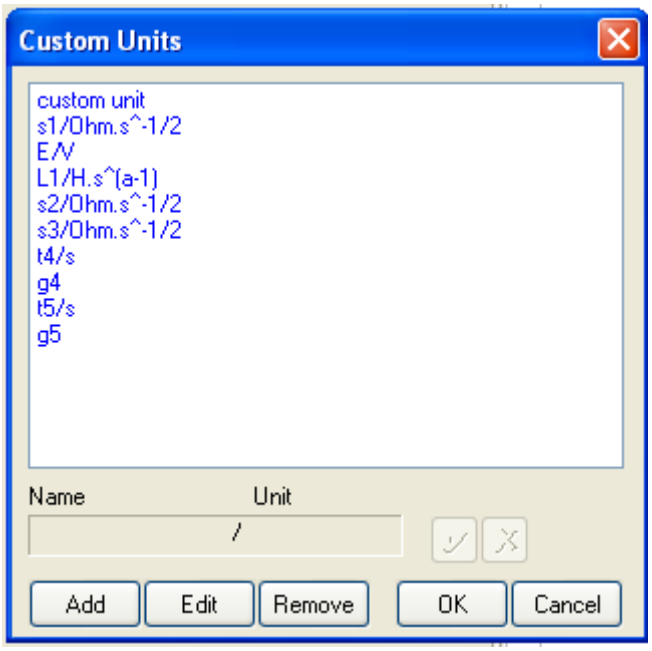


Fig. 198: Custom Units window to define new variables.

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.

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.

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. Once they are created the linked experiment settings can be saved either as a .mps file or as 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 forlder in the techniques menu and can be reloaded when necessary. Linked experiments can be created using the "**Technique Builder**" in the technique window. All the techniques of this section have been previously described (see section 2.4 page 68). 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:

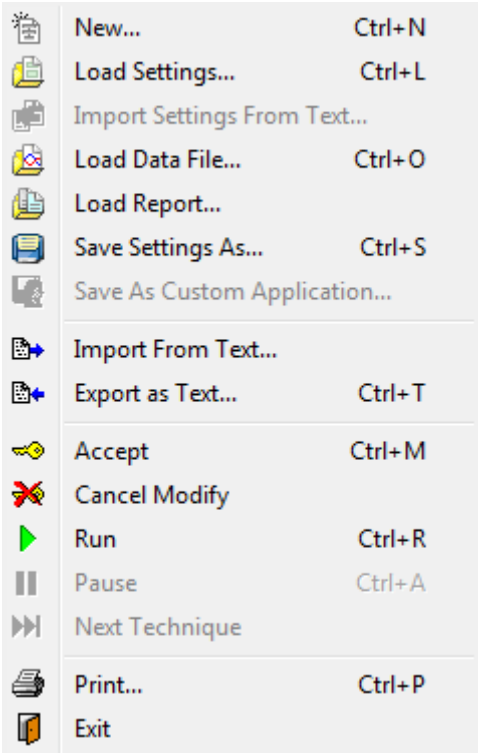


Fig. 199: Mouse right click with the insert and remove options.

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 to add the new technique into the settings according to the activated/selected technique (arrow on the left of the technique name) in the parameter settings window at the bottom left corner frame of the technique selection window:

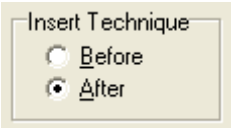


Fig. 200: Insert before/after option of the technique selection window.

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 2.4.1 page 69 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. 76** of section 2.4.6 page 85. For the **LOOP** option choose "**Goto** technique 2 (MP) for 5 times" and report to the section 2.4.10 page 89 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.

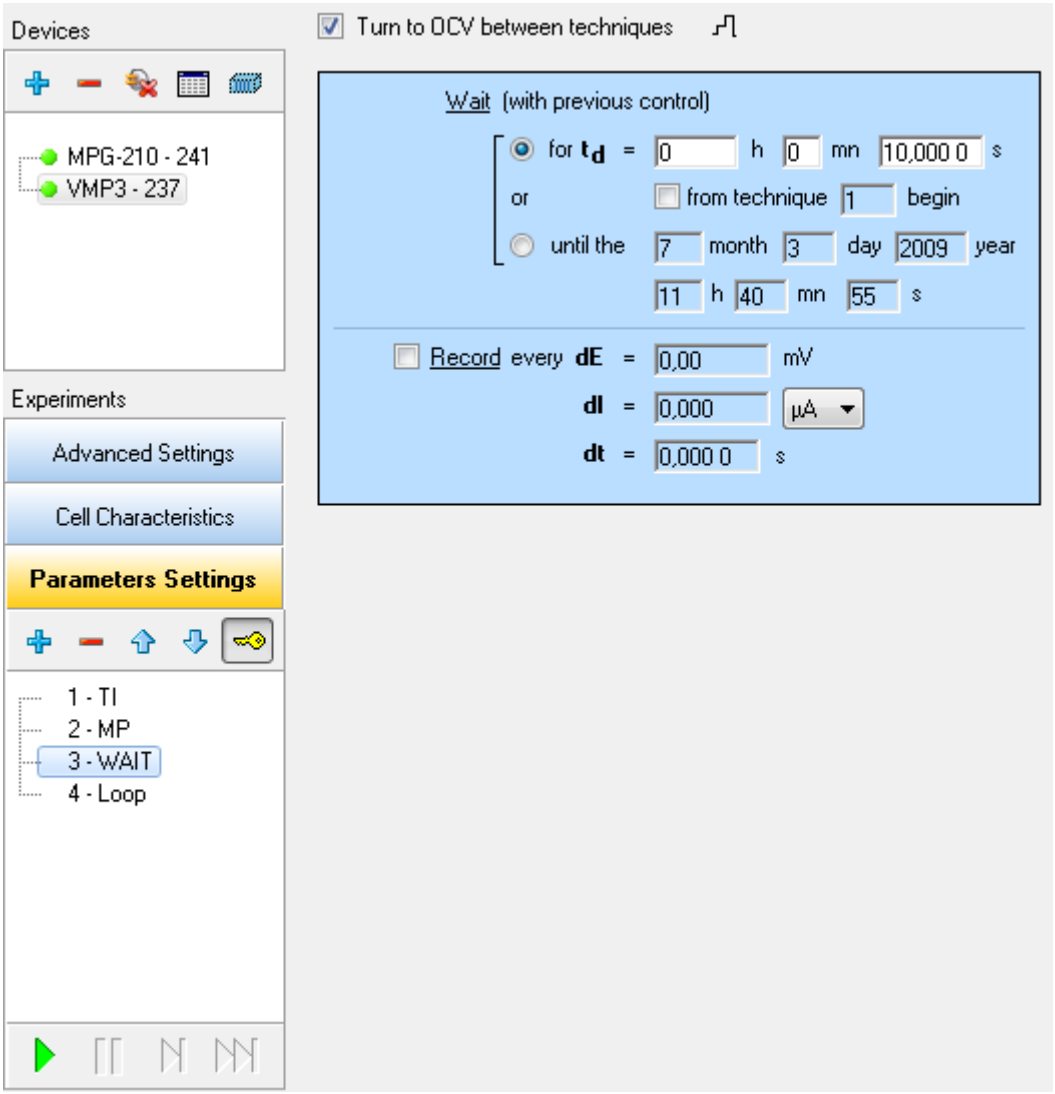


Fig. 201: Linked experiment parameters setting window.

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.

Note: **"Turn to OCV between techniques"** option forces the system to go to OCV but no OCV measurement is performed. If after this forced OCV period, a technique uses the OCV value as reference, the value used will be the last value measured during the previous techniques.

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 arrow on the left of it. 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.

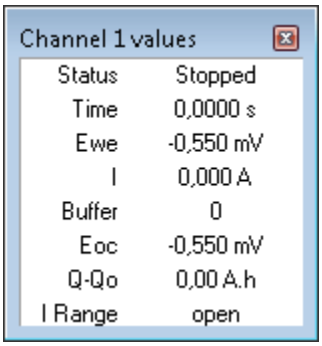


Fig. 202: Linked experiment current values.

In our example, the output files will be:

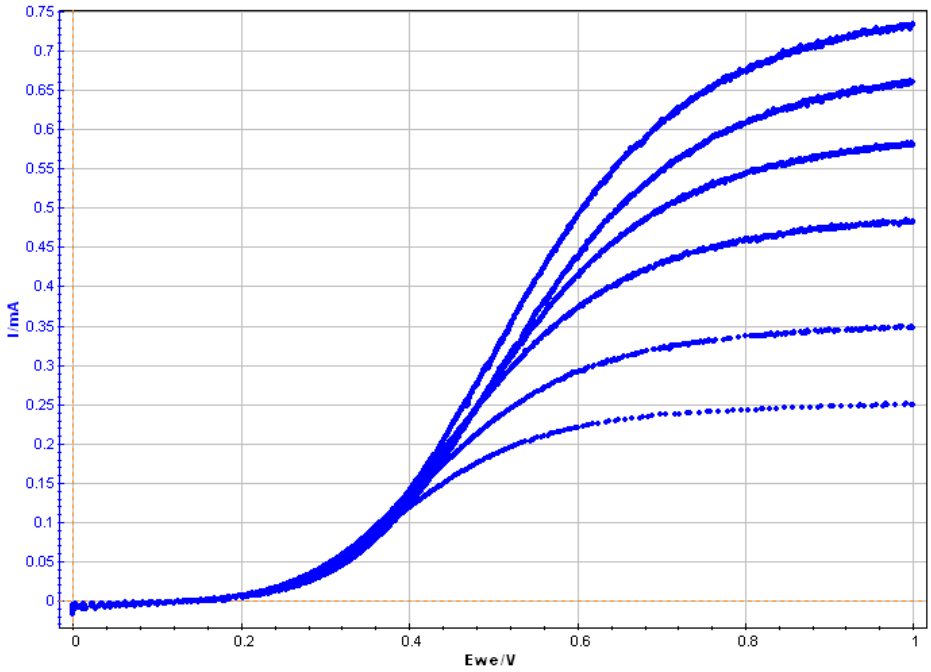


Fig. 203: Linked experiment results.

Notes:

- The ZRA technique 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. Summary of the available techniques in EC-Lab®

INSTRUMENTS	VMP2	SP-50	VMP3 VSP SP-150 HCP-803 HCP-1005 CLB-500	MPG-2XX Series	SP-240 SP-200 SP-300 VSP-300 VMP-300
Voltamperometric techniques					
OCV	×	×	×	×	×
SOCV	×	×	×	×	×
CV	×	×	×	×	×
CVA	×	×	×	×	×
CA/CC	×	×	×	×	×
CP	×	×	×	×	×
SV	×	×	×		×
LASV	×	×	×		×
ACV	×	×	×		×
Pulsed techniques					
DPV	×	×	×		×
SWV	×	×	×		×
DNPV	×	×	×		×
NPV	×	×	×		×
RNPV	×	×	×		×
DPA	×	×	×		×
EIS techniques					
GEIS	×		×	×	×
PEIS	×		×	×	×
SGEIS	×		×	×	×
SPEIS	×		×	×	×
PEISW	×		×	×	×
Technique builder					
MP	×	×	×	×	×
SMP	×	×	×	×	×
MG	×	×	×	×	×
SMG	×	×	×	×	×
Trigger In	×	×	×	×	×
Trigger Out	×	×	×	×	×
Wait	×	×	×	×	×
TC	×	×	×	×	×
RDEC	×	×	×	×	×
EDC	×	×	×	×	×
Loop	×	×	×	×	×
Pause	×	×	×	×	×

EXTAPP	×	×	×	×	×
Email	×	×	×	×	×
Manual Control					
CMC	×	×	×	×	×
PMC	×	×	×	×	×
Ohmic Drop determination					
MIR	×	×	×	×	×
ZIR	×	×	×	×	×
CI	×	×	×	×	×
Bipotentiostat techniques					
CV-CA	*		VMP3/VSP		SP/VSP/VMP300
CP-CA	*		VMP3/VSP		SP/VSP/VSP300
CA-CA	*		VMP3/VSP		SP/VSP/VSP300
INSTRUMENTS	**VMP2**	**SP-50**	**VMP3** **VSP** **SP-150** **HCP-803** **HCP-1005** **CLB-500** **CLB-2000**	**MPG-2XX series**	**SP-240** **SP-200** **SP-300** **VSP-300** **VMP-300**
Batteries testing					
BCD	×	×	×	×	×
GCPL	×	×	×	×	×
GCPL2	×	×	×	×	×
GCPL3	×	×	×	×	×
GCPL4	×	×	×	×	×
GCPL5	×	×	×	×	×
GCPL6	×	×	×	×	×
GCPL7	×	×	×	×	×
SGCPL	×	×	×	×	×
MB	×	×	×	×	×
CED	×	×	×	×	×
CLD		×	×	×	×
CPW	×	×	×	×	×
APGC	×	×	×	×	×
PPI	×	×	×	×	×
GPI	×	×	×	×	×
RPI	×	×	×	×	×
PWPI	×	×	×	×	×
MB	×	×	×	×	×
Photovoltaics/Fuel cells					
I-VC	×	×	×		×

CLD	×	×	×		×
CPW	×	×	×		×
CstC	×	×	×		×
CstV	×	×	×		×
Supercapacitors					
CV	×	×	×	×	×
CstV	×	×	×	×	×
CstC	×	×	×	×	×
CS	×	×	×	×	×
Custom Applications					
PR	×	×	×		×
SPFC	×	×	×		×

6. List of abbreviations used in EC-Lab® software

Abbreviations	Description
Technique: OCV	
dE_R	Recording condition on a variation of the WE potential
dE_R/dt	Limit condition on a time variation of the WE potential
dt_R	Recording condition on a variation of time
t_R	Rest 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 during ti
dE/dt	Potential scan rate
E_1	First vertex potential
t_1	Time duration to Hold E_1
dt_1	Recording condition during t1
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 during t2
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 during tf
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
R_u	Uncompensated resistance
IR	Compensated ohmic drop
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
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

7. 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 it. "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 vice versa.

Bandwidth: represents the frequency of the regulation loop of the potentiostat. Choosing the suitable one depends on the electrochemical cell impedance. A cell with a high impedance and slow response will require a low bandwidth. 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 (CA): controlled potential technique that consists in increasing step by step 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 (CP): 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 intervals.

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 in scanning the potential of the working electrode and measuring the current resulting from oxydo-reduction 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 in 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 in the repetition of a pulse sequences made with a prepulse and a superimposed pulse.

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 Cycling with Potential Limitation 5 (GCPL5): battery testing technique similar to the GCPL technique with a different recording conditions of the potential at the beginning of the galvanostatic period. The potential is recorded with a geometric time progression. The current/potential is used to calculate the apparent resistance of the cell.

Galvanostatic Cycling with Potential Limitation 6 (GCPL6): battery testing technique similar to the GCPL technique except that the Limit potential during the galvanostatic period is applied the potential difference between the working and the counter electrodes.

Galvanostatic Cycling with Potential Limitation 7 (GCPL7): battery testing technique similar to the GCPL technique except that the Limit potential is held by controlling the current needed to keep Ewe at E_M value. By doing so, the whole experiment is performed in galvano mode

Galvanostatic Electrochemical Impedance Spectroscopy (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 of Laplace Transform of E and the Laplace Transform of 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 in 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.

Modulo Bat (MB): A technique specially dedicated to batteries that combines all the available control modes, recording and limiting conditions. Almost all the DC techniques in EC-Lab can be recreated or customized by setting the adequate sequences.

Modular Galvano (MG): technique designed to perform a combination of OCV, galvanostatic and galvanodynamic periods. The user can link the MG sequences in any desired way.

Modular Potentio (MP): Technique designed to perform a combination of OCV, potentiostatic and potentiodynamic periods. The user is free to link the MP sequences the way in any desired way. This technique 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 same 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 return to the beginning potential.

Open Circuit Voltage (OCV): technique that consists in 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 pauses the progress of the technique and the measurement recording. During “Pause”, the cell is disconnected (OCV period). The "Pause" button turns to "Resume" when clicked.

Polarization Resistance (PR): technique similar to CV that is adapted to corrosion. This technique allows the determination of polarization resistance R_p and corrosion current I_{corr}.

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 Electrochemical Impedance Spectroscopy (PEIS): technique that performs impedance measurements in 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.

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 electrochemical noise measurements. A potential of 0 V is applied between the working and the counter electrode.

Zero Voltage Current (ZVC): technique similar to ZRA except that the control is done between the working and the reference electrode.

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