

EC-Lab[®] Software User's Manual

Version 10.32 – March 2013



Equipment installation

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

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

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

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

General description

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

Intended use of the equipment

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

Instructions for use

To avoid injury to an operator the safety precautions given below, and throughout the manual, must be strictly adhered to, whenever the equipment is operated. Only advanced user can use the instrument.

Bio-Logic SAS accepts no responsibility for accidents or damage resulting from any failure to comply with these precautions.

GROUNDING

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

ATMOSPHERE

You must never operate the equipment in corrosive atmosphere. Moreover if the equipment is exposed to a highly corrosive atmosphere, the components and the metallic parts can be corroded and can involve malfunction of the instrument.

The user must also be careful that the ventilation grids are not obstructed. An external cleaning can be made with a vacuum cleaner if necessary.

Please consult our specialists to discuss the best location in your lab for the instrument (avoid glove box, hood, chemical products, ...).

AVOID UNSAFE EQUIPMENT

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

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

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

LIVE CONDUCTORS

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

EQUIPMENT MODIFICATION

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

GUARANTEE

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

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

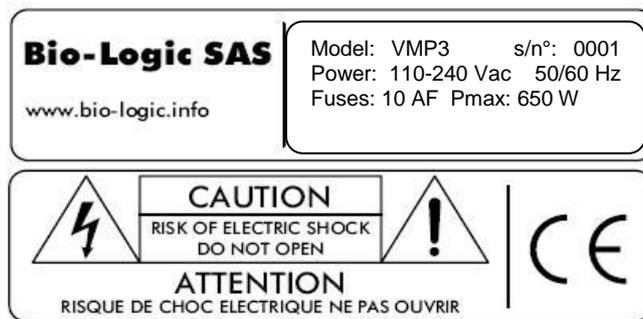
IN CASE OF PROBLEM

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

If you have any questions or if any problem occurs that is not mentioned in this document, please contact your local retailer (list available following the link: <http://www.bio-logic.info/potentiostat/distributors.html>). 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,
 - 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,
 - Unauthorised structural alterations to the device,
 - Unauthorised modifications to the system settings,
 - Inadequate monitoring of device components subject to wear,
 - Improperly executed and unauthorised repairs,
 - Unauthorised opening of the device or its components,
 - Catastrophic events due to the effect of foreign bodies.
-



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

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1. Introduction

EC-Lab[®] software has been designed and built to control all our potentiostats (single channel: SP-50, SP-150, HCP-803, HCP-1005, CLB-500, CLB-2000, SP-300, SP-200, SP-240 or multichannels: MPG, VMP, VMP2(Z), BiStat, VMP3, MPG-2XX series, VSP, VSP-300 and VMP-300). 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 protocols. 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 common counter-electrode in a single bath.

One computer (or eventually several for multichannel instruments) connected to the instrument can monitor the system. The computer can be connected to the instrument through an Ethernet connection or with a USB connection. With the Ethernet connection, each one of the users is able to monitor his own channel from his computer. More than multipotentiostats, our instruments are modular, versatile and flexible multi-user instruments. Additionally, thanks to the multiconnexion, several instruments can be controlled by one computer with only one EC-Lab session open.

Once the protocols have been loaded and started from the PC, the experiments are entirely controlled by the on-board firmware of the instrument. 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 very safe operations since a shutdown of the monitoring PC does not affect the experiments in progress.

The application software package provides useful protocols for general electrochemistry, corrosion, batteries, super-capacitors, fuel cells and custom applications. Usual electrochemical techniques, such as Cyclic Voltammetry, Chronopotentiometry, etc..., are obtained by associations of elementary sequences.

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

Standard graphic functions such as re-scaling, zoom, linear and log scales are available. The user can also overlay curves to make data analyses (peak and wave analysis, Tafel, R_p , linear fits, EIS simulation and modeling, ...).

Post-processing is possible using built-in options to create variables at the user's convenience, such as derivative or integral values, etc... Raw data and processed data can be exported as standard ASCII text files.

The aim of this manual is to guide the user in EC-Lab[®] software discovery. This manual is composed of several chapters. The first is an introduction. The second and third parts describe the software and give an explanation of the different techniques and protocols offered by EC-Lab[®]. Finally, some advanced features and troubleshooting are described in the two last parts.

The other supplied manual “EC-Lab[®] Software Techniques and Applications” is aimed at describing in detail all the available techniques.

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

WHEN AN 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 BEFORE STARTING AN EXPERIMENT.

2. EC-Lab[®] software: settings

At this point, the installation manual of your instrument has been carefully read and the user knows how to connect his/her instrument to the potentiostat. The several steps of the connection will not be described in this manual but in the installation manual of the instrument.

2.1 Starting EC-Lab[®]

Double click on the EC-Lab[®] icon on the desktop, EC-Lab[®] opens and connects to an instrument. See the Instrument's Manuals for more details about the instruments connection. Once an instrument is connected to EC-Lab[®] the main window will be displayed:

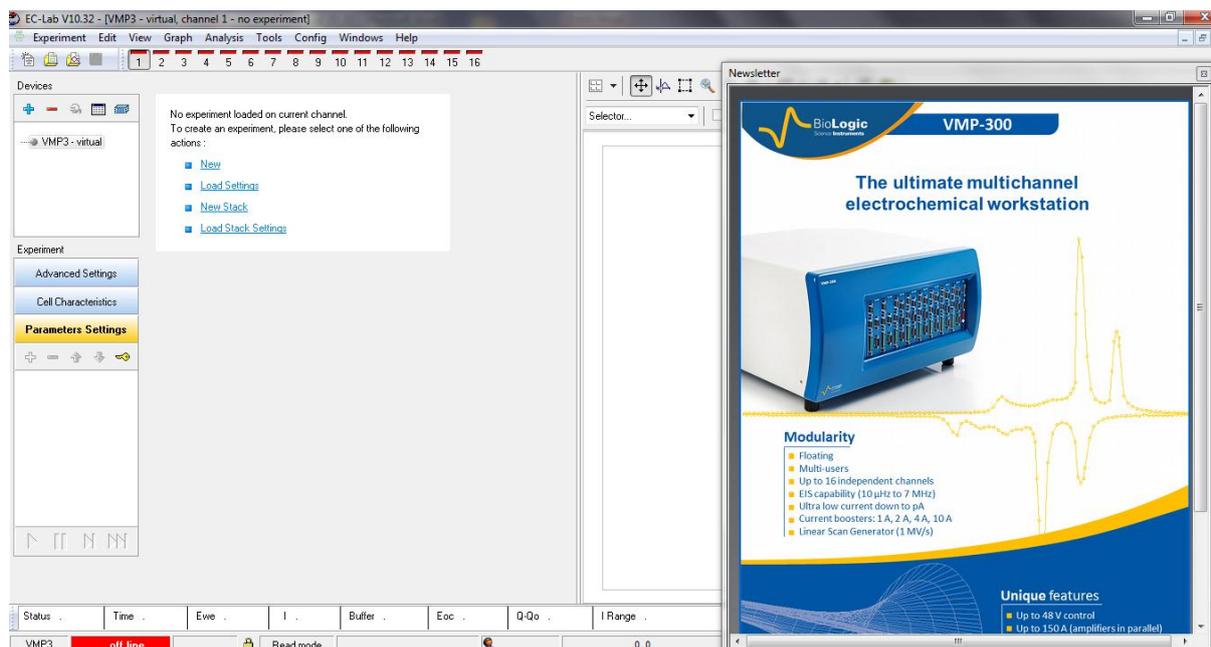


Fig. 1: Starting main EC-Lab[®] window.

If the computer is connected to the Internet, the Newsletter with information on the latest Bio-Logic product appears.

Furthermore, on the left column, two boxes can be seen:

- **Devices** that lists the instruments to which the computer can be connected. For more information on this box, please see the Instrument's Manual.
- **Experiments** that list the series of techniques that are used to perform the desired experiment on the selected channel of the selected instrument.

The following Username window also can be seen:

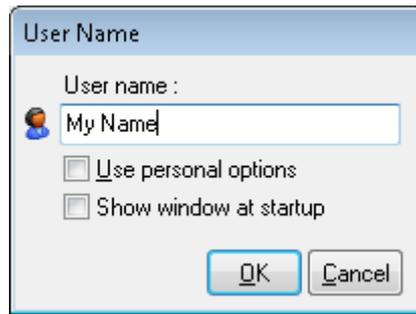


Fig. 2: User name window.

Type your username (*example: My Name*), and click **OK** or press < ENTER >.

This User Name is used as a safety password when the instrument is shared between several users. When you run an experiment on a channel, this code will be automatically transferred to the section "user" on the bottom of EC-Lab® software window. This allows the user to become the owner of the channel for the duration of the experiment. All users are authorized to view the channels owned by the other users. However, change of parameters on a channel is authorized only if the present User Name corresponds to the owner of that channel (even from another computer). If another user wants to modify parameters on a channel that belongs to "My Name", the following message appears:

"Warning, channel X belongs to "My Name". By accepting modification you will replace current owner. Do you want to continue?"

The command **U**ser... in the **C**onfig. menu allows you to change the User Name at any time. You can also double click on the "User" section in the bottom of the EC-Lab® software window to change the User Name.

The user can specify a personal configuration (color display, tool bar buttons and position, default settings), which is linked to the User Name. If it is not selected, the default configuration is used. For the user's convenience it is also possible to hide this window when EC-Lab® software is starting.

Once your instruments are connected, you can have all the details about the experiments that are run and on which channels of which instruments they are run by accessing the **Global View**.

There are several ways to access the **Global View** window:

1. It automatically appears once the User Name is set the first time EC-Lab® is opened.
2. In the **Devices** box, click on 
3. Press **Ctrl+W**
4. Go to **View\Global View**

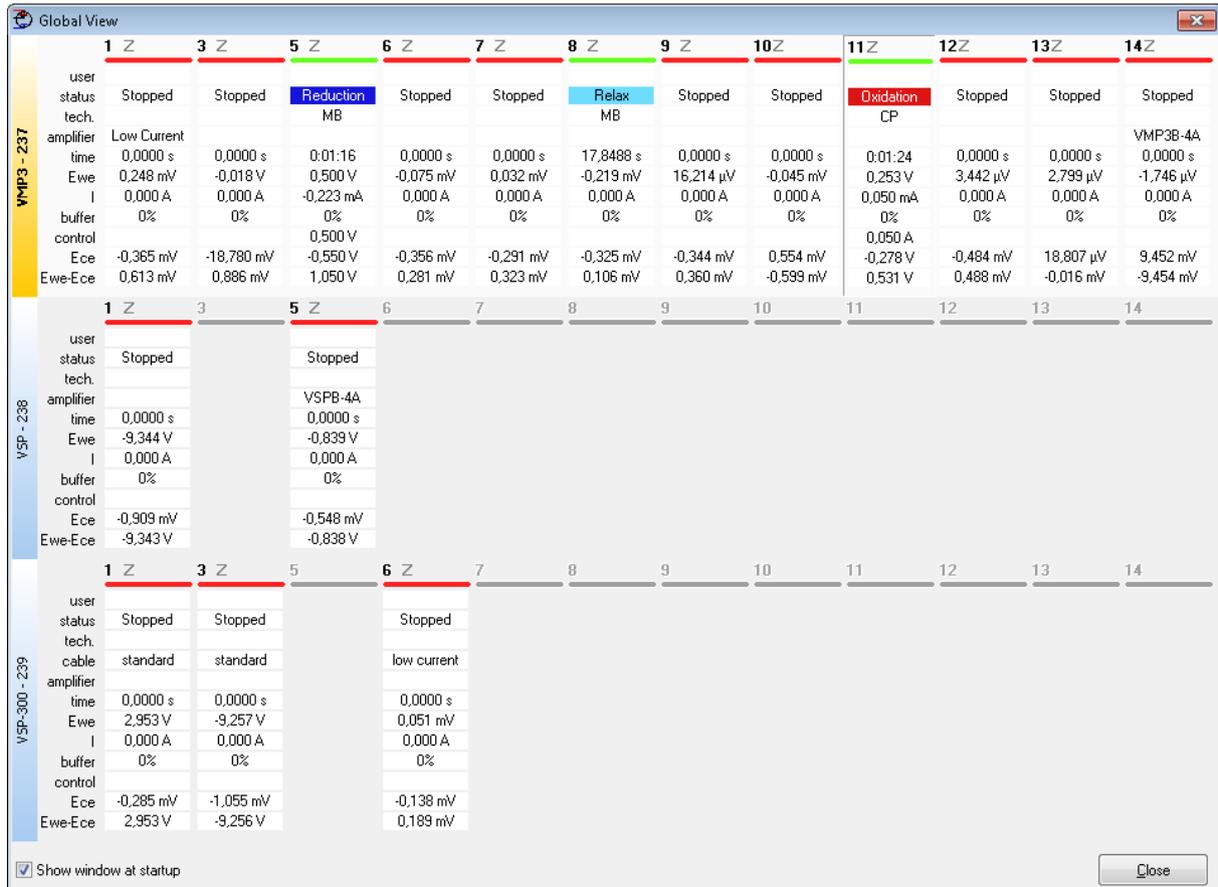


Fig. 3: “Global View” window.

The global view of the channels shows the following information:

- On the left the instruments to which the computer is connected. The active or selected instrument will appear in a different color
- **channel** number with **Z** if impedance option is available on the channel. If the channels are synchronized, grouped, stacked or execute a bipotentiostat technique, they will appear in a different color.
- an indicative ‘**BAR**’ in - **red** if there is no experiment running, **green** if the channel is running. and **grey** if there is no pstat board in the corresponding slot.
- **user** - the channel is available (no username) or is (was) used by another user. Several users can be connected to the instrument, each of the users having one or several channels.
- **status** - the running sequence if an experiment is in progress: **Oxidation**, **Reduction**, **Relax** (open circuit potential) **Stopped**
- **tech.** - the experiment type once loaded (e.g. **CV** for Cyclic Voltammetry, **GCPL** for Galvanostatic Cycling with Potential Limitation, **PEIS** for potentiometric impedance, etc...).
- **cable** - *only for SP-300, SP-200, SP-240 VSP-300 and VMP-300* - the type of cable connected to the board, **standard**, **low current** if the Ultra Low Current option is connected or **straight** if no cable is connected
- **amplifier** - the booster type if connected: 1 A, 2 A, 4 A, 5 A, 8 A 10 A, 20 A, 80 A, 100 A, a 500 W, a 2 kW load or none (VMP2, VMP3 technology), 1 A/48 V, 2A/30V, 4A/14V and 10A/5V (for SP-300 technology).
 - the "p" low current board if connected (for VMP3 technology)

The user has the ability to add several current variables on the global view such as “**time**, **E_{we}**, **I**, **buffer**, **control E_{ce}**, **E_{we}-E_{ce}**”. These variables can be chosen by right-clicking any-

where on the Global View. Note that the displayed variables are the same for all the channels and all the instruments. Double-clicking on any of the channel window will replace the global view by the specific view of the selected channel.

Double click on a channel of the global view to select it. You will get the following window:

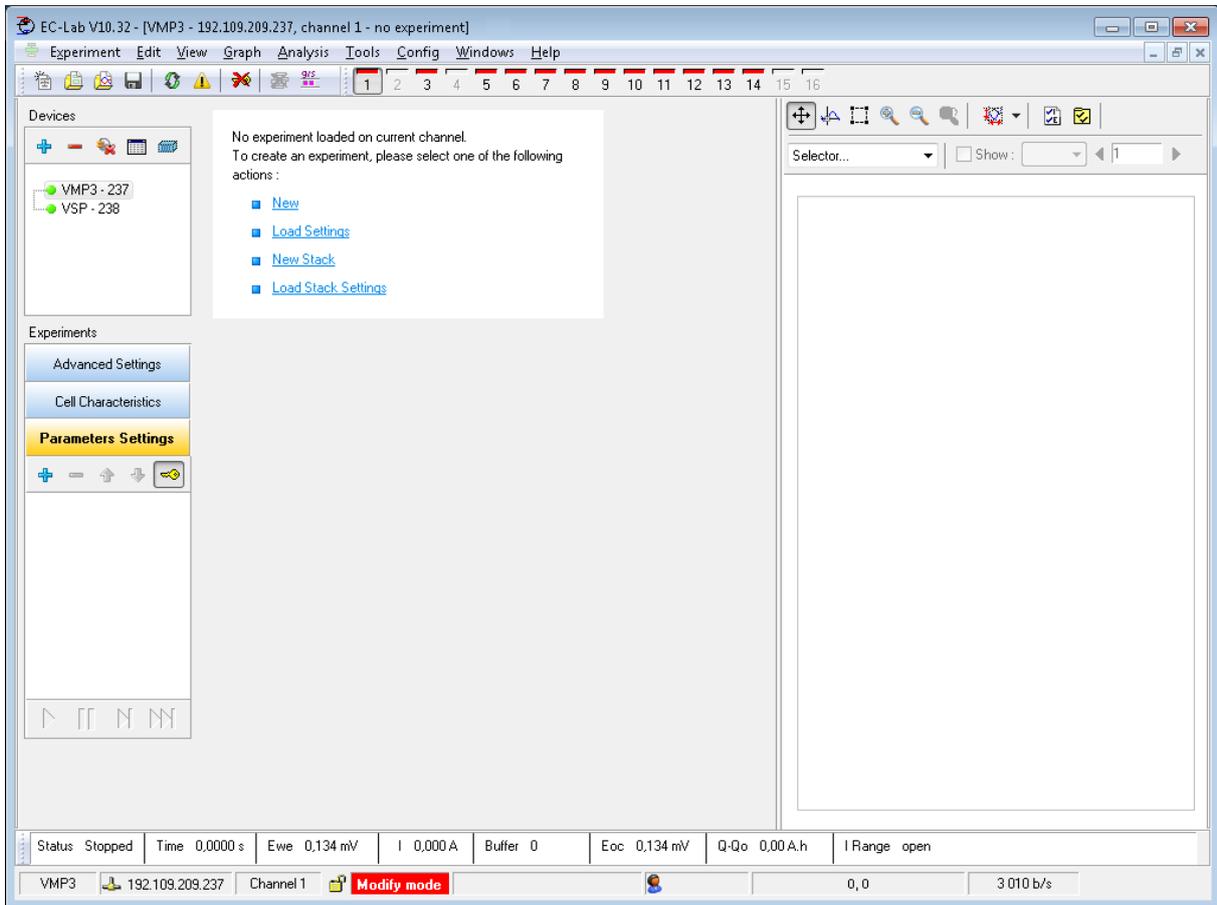


Fig. 4: Main window for experiment setting.

This window shows at the very top, in the blue title bar: the software version, the connected instrument, the IP address (if connected through a LAN), the active channel, the name of the experiment (i.e. name of the data file) and the selected technique (if any). Several tool bars are available.

Top of the main window

2.2 The EC-Lab[®] Main Menu

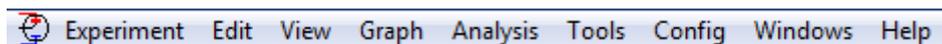


Fig. 5: The bar menu of EC-Lab[®] software main window.

The Main Menu bar has been designed in such a way that it follows a progression from the experiment definition to the curves analysis. Each menu is described below.

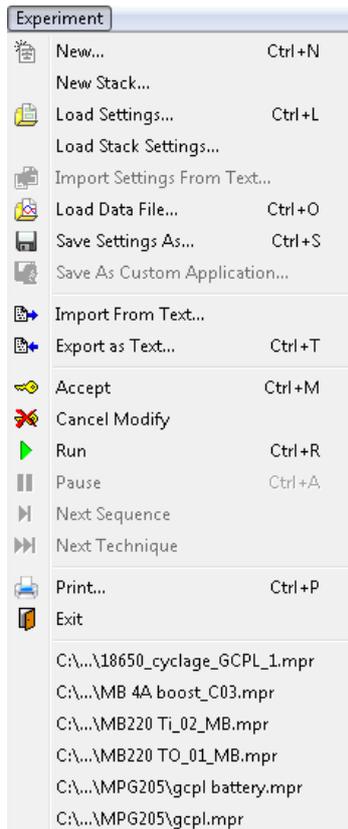


Fig. 6: Experiment Menu.

This menu allows the user to build a new experiment and load an existing setting file or an existing data file made with our potentiostat or another one. Our software is able to read other manufacturer files formats. Saving options are also available.

The second frame offers the user the possibility to **Export as** or **Import from Text**.

Experiment commands (**Accept**, **Cancel Modify**, **Run**, **Pause**, **Next Sequence** and **Next Technique**) are in the third frame.

Print and **Exit** commands can be found in the fourth frame.

The last opened files are listed in the fourth frame.

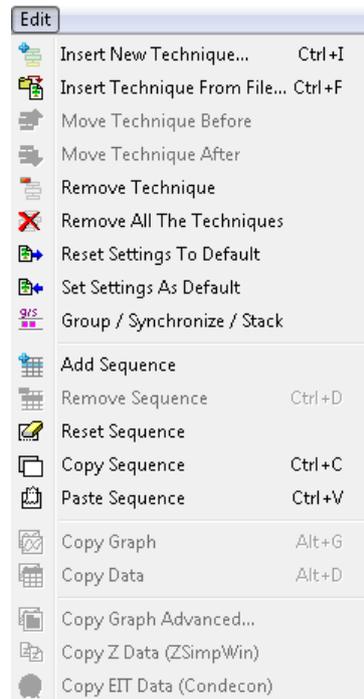


Fig. 7: Edit Menu.

The **“Edit”** menu can be used to build an experiment, insert (**Move up** or **Move down**), or **Remove a Technique** from an experiment. The **Group/Synchronize/Stack/Bipot** window is also available in this menu.

The second frame is for sequence addition or removal from a technique (when this is possible), and the two last ones offer **Copy** options (**Graph**, **Data**, **ZSimpWin** format) on the graphic window.

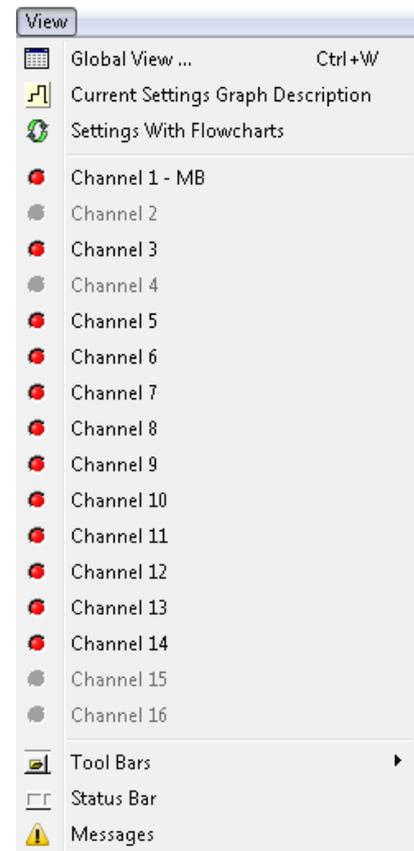


Fig. 8: View Menu.

This menu is very useful as it allows the user to show the **Global View**, a **Graph Description** of the technique, to switch between the **Column/Flowchart** view of the settings.

The second frame shows the active channel and its status. The third frame allows the user to choose which **Tool Bars** to have displayed or to show the **Status Bar** or warning **Messages**.

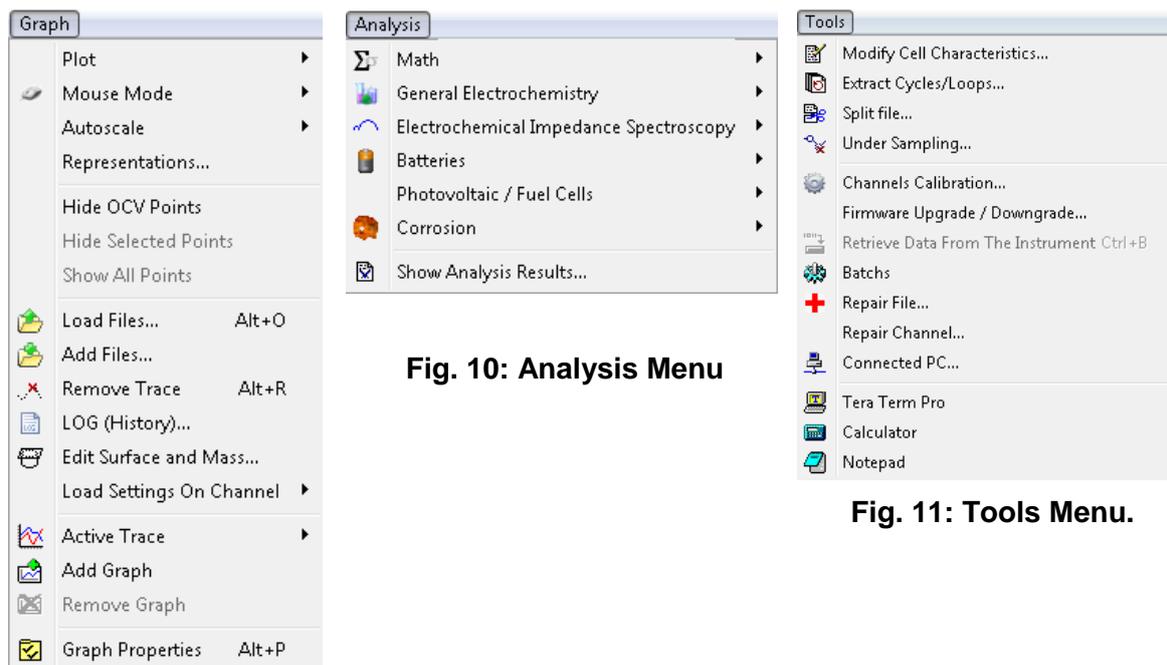


Fig. 10: Analysis Menu

Fig. 11: Tools Menu.

Fig. 9: Graph Menu.

This menu includes all the **Graph** tools (zoom in and out, points selection, auto scale, and **Graph Properties**) and the graph representation menu. This menu also allows the user to load or add new files to the graph. This menu is equivalent to the Right-Click menu on the Graph window.

The **Analysis** menu contains various Analysis tools, sorted by themes: **Math**, **General Electrochemistry**, **EIS**, **Batteries**, **Photovoltaic/Fuel Cells** and **Corrosion**. More details will be given in Part 4.

The **Tools** menu is composed of three frames. The first one is for the data file modification (**Modify Cell Characteristics**, **Split File**, **Under Sampling**).

The second frame is related to operations performed on the firmware (**Channel Calibration**, **Repair Channel**, **Downgrade** or **Upgrade the Firmware**) or the file (**Repair File**, **Batches**).

The last frame gives access to various tools such as **Tera Term Pro** (used to change the instrument configuration), **Calculator** and **Notepad**.

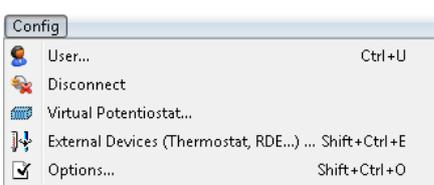


Fig. 12: Config Menu.

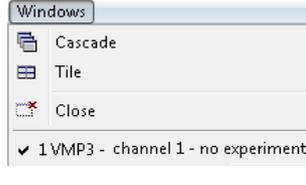


Fig. 13: Windows Menu.

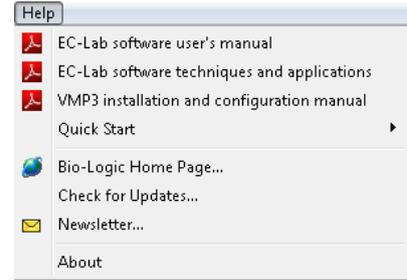


Fig. 14: Help Menu.

The config menu is dedicated to the configuration of the instrument and the software configuration. All the functions here (except the **Options**) are available from the **Devices** or **Experiments** boxes.

This menu is used to choose how to display the windows and close them.

The **Help** menu contains pdf files of the **Software**, the **Instrument** installation and configuration **Manuals** and several quickstarts. This menu provides also a direct link to the **Bio-Logic website** and a way to check for software **Updates**. It is also possible to access to the **Newsletter** (automatically displayed when the software is installed for the first time on the computer and for each upgrade).

2.3 The Tool Bars

2.3.1 The Main Tool Bar



Fig. 15: Main Tool Bar.

The user can change the buttons displayed in the tool bar. To do that, the user can either click on **Config\Options\Tool bars/menus/Main Tool Bar** and select or deselect the desired buttons (see part 2.14.6, page 62 for more details) or right-click with the mouse on the Main Tool Bar and choose **Options**.

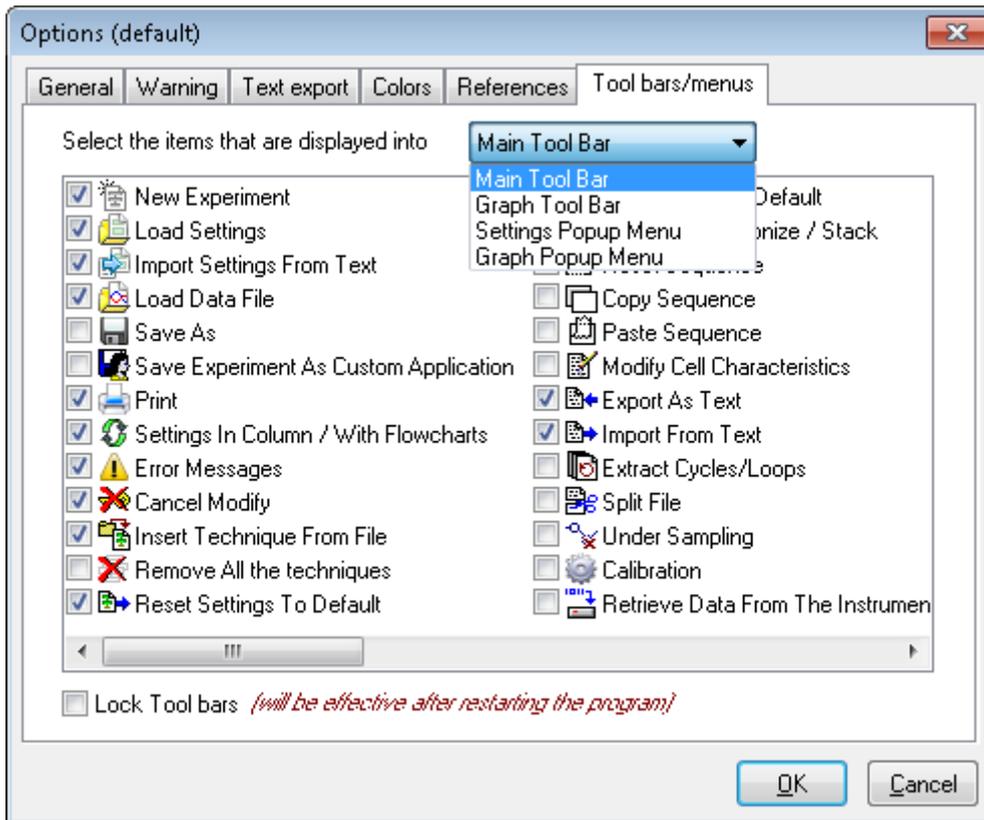


Fig. 16: Main Tool Bar menu to choose the icons to be displayed.

2.3.2 Channel tool bar

You can see below 16 buttons (depending on the instrument and on the number of channels that can be inserted into the chassis). These buttons correspond to the actual slots. They are greyed and inactive if the slot is unused or if there is a booster board or low current board inserted in it. The channel number is always the slot number.

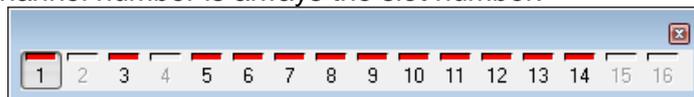


Fig. 17: Channel Selection Tool Bar.

By clicking on the button, the user can select the current channel(s). Clicking on one of the buttons enables the user to see the channel status. The corresponding bars give the on/off status of the channels: **red** if there is no experiment running or **green** if the channel is running.

Top right of the main window

2.3.3 The Graph Tool Bar

The Graph Tool Bar with shortcut buttons (including zoom, rescale, analyses, and graph properties) is attached to the graph. Report to the graphics tools part for more details



Fig. 18: Graph Tool Bar.

Also attached to the Graph window is the Fast Graph Selection Tool Bar that can be used to rapidly plot certain variables and choose the cycles to be displayed:



Fig. 19: Fast Graph Selection Tool Bar.

Bottom of the main window

2.3.4 Status Tool Bar

At the bottom of the main window, the Status Tool Bar can be seen

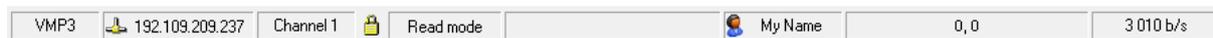


Fig. 20: Status Tool Bar.

The following informations are displayed:

- the connected device
- the instrument's IP (internet protocol) address if the instrument is connected to the computer through an Ethernet connection or USB for an USB connection,
- the selected channel,
- a lock showing the Modify/Accept mode in relation with the box near: "Read mode" or "Modify mode",
- the remote status (received or disconnected),
- the user name,
- the mouse coordinates on the graphic display,
- the data transfer rate in bit/s.

2.3.5 Current Values Tool Bar

On the left side or at the bottom, the Tool Bar with the Current Values can be seen.

Channel 1 values	
Status	Stopped
Time	0,0000 s
E _{we}	-0,550 mV
I	0,000 A
Buffer	0
E _{oc}	-0,550 mV
Q-Q ₀	0,00 A.h
I Range	open

Fig. 21: Current Values Tool Bar in a column format.

- **Status** gives the nature of the running sequence: **oxidation**, **reduction**, **relax** (open circuit, measuring the potential), **paused** or **stopped**. Buffer full will be displayed in the case where the instrument's intermediate buffer is full (saturated network...),
- **Time**, **E_{we}** and **Current** are the time, the working electrode potential and the current from the beginning of the experiment,
- **Buffer** indicates the buffer filling level
- **E_{oc}** is the potential value reached at the end of the previous open circuit period,
- **Q - Q₀** is the total charge since the beginning of the experiment,
- I range **The current range**,
- **I₀** (or **E₀**). **I₀** is the initial current value obtained just after a potential step in potentiodynamic mode,
- **N_s** is the number of the current sequence,
- **n_c** is the number of the current cycle or loop.

Note: Two protocols (Batteries: GCPL and PCGA) propose two additional variables $X - X_0$, which is the insertion rate and the power P in W.

This Tool Bar can be unlocked with the mouse and set as a linear bar locked to the status bar at bottom of EC-Lab® window or to the graphic bar at the top of the window.

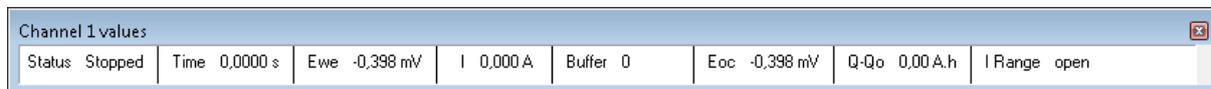


Fig. 22: Current Values Tool Bar in a linear format.

Note: In the default configuration, all the tool bars are locked in their position. At the user's convenience, tool bars can be dragged to other places in the window. To do so, click on **Config\Option\Tool bars/menus** and deactivate the "Lock Tool bars" box. This will be effective after restarting the software. Once the user has defined a new configuration of the tool bars, the tool bar can be relocked the same way it was unlocked.

Note also that some of the current values can be displayed in bold using the **Config\Option\Colors** tab.

Middle of the main window

2.4 The Devices box

As mentioned earlier, it is now possible with only one EC-Lab® open session to be connected to and control several instruments. In earlier versions of EC-Lab®, it was necessary to open as many EC-Lab® sessions as the number of instruments.

The Multi-Connection is performed using the Devices box on the main window (See Fig. 4 and 23). The  and  buttons allow the user to add or remove instruments linked to the computer either through USB or Ethernet. The  and  buttons are used to connect and disconnect, respectively, an instrument to the computer. The  button is used to show the global view, as described in the beginning of part 2.1. Finally, the  button is used to connect to a virtual potentiostat (see part 2.13).



Fig. 23: Multi-device connection box

If more details are needed about the connection of the instrument, please refer to the corresponding "Installation and configuration manual".

2.5 The Experiments box

By default, the highlighted tab in the Experiments box is the "Parameters Settings" tab. Three tabs allow the user to switch between three settings associated to the protocol: the "Advanced Settings", the "Cell Characteristics" and the "Parameters Settings".

2.5.1 The Parameters Settings Tab

When no technique or application is loaded in the Experiments box, a small text is displayed indicating how to proceed:

"No experiment loaded on current channel.

To create an experiment please selects one of the following actions:

- **New**
 - **Load Settings**
 - **New Stack** (if connected to a multichannel)
 - **Load Stack Settings** (if connected to a multichannel)
- The column will contain the techniques of a linked experiment. The settings of each technique will be available by clicking on the icon of the technique.
 - The "Turn to OCV between techniques" option offers the possibility to add an OCV period between linked techniques.



Fig. 24: Top row in the Parameters Settings window.

The button  is available to show the graph describing the technique and its variables.

2.5.1.1 Right-click on the "Parameters Settings" tab

EC-Lab[®] software contains a context menu. Right-click on the main EC-Lab[®] window to display all the commands available on the mouse right-click. Commands on the mouse right-click depend on the displayed window. Other commands are available with the mouse right-click on the graphic display.

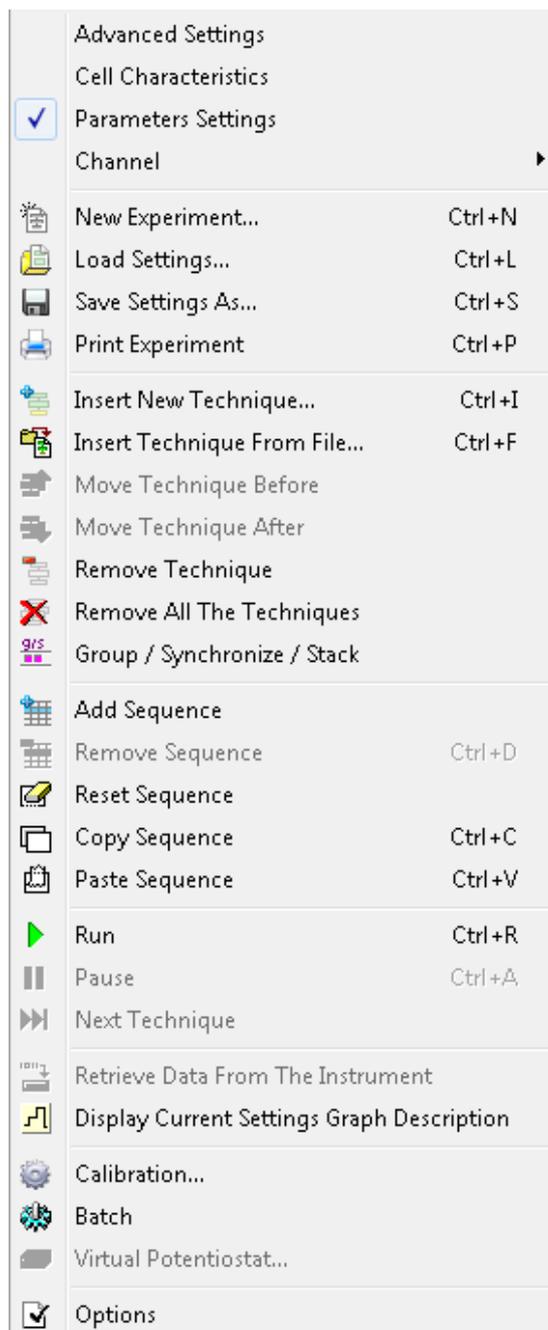


Fig. 25: Mouse right-click on the main window of EC-Lab® software.

Most of the commands are available with the right-click. They are separated into 6 frames. The first frame concerns the available setting tabs, the second one is for the experiment from building to printing. The third frame is for the modification of an experiment (actions on techniques) and the creation of linked experiments. The fourth one is dedicated to sequences (addition, removal) and the fifth one to the controls during the run. The sixth and seventh frames are additional functions described above and the last frame is a direct access to the **Options** tab.

2.5.1.2 Selecting a technique

First select a channel on the channel bar. There are three different ways to load a new experiment.

- 1-Click on the “New Experiment” button .

2-Click on the blue **“New”** link on the parameter settings window.

3-The user can also click on the right button of the mouse and select **“New Experiment”** in the menu.

Note:

- It is not always necessary to click on the **“Modify”** button before selecting a command. The software is able to switch to the **“Modify”** mode when the user wants to change the settings parameters. In that case the following message is displayed:

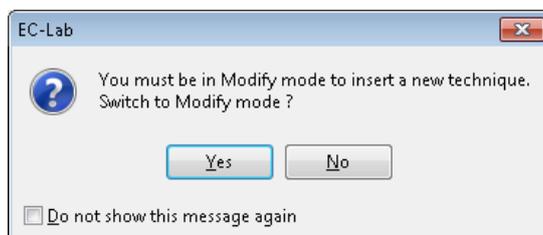


Fig. 26: Message displayed before switching to Modify mode.

Click on **Yes** and the **“Insert Techniques”** window will appear with the different techniques available with EC-Lab® software.

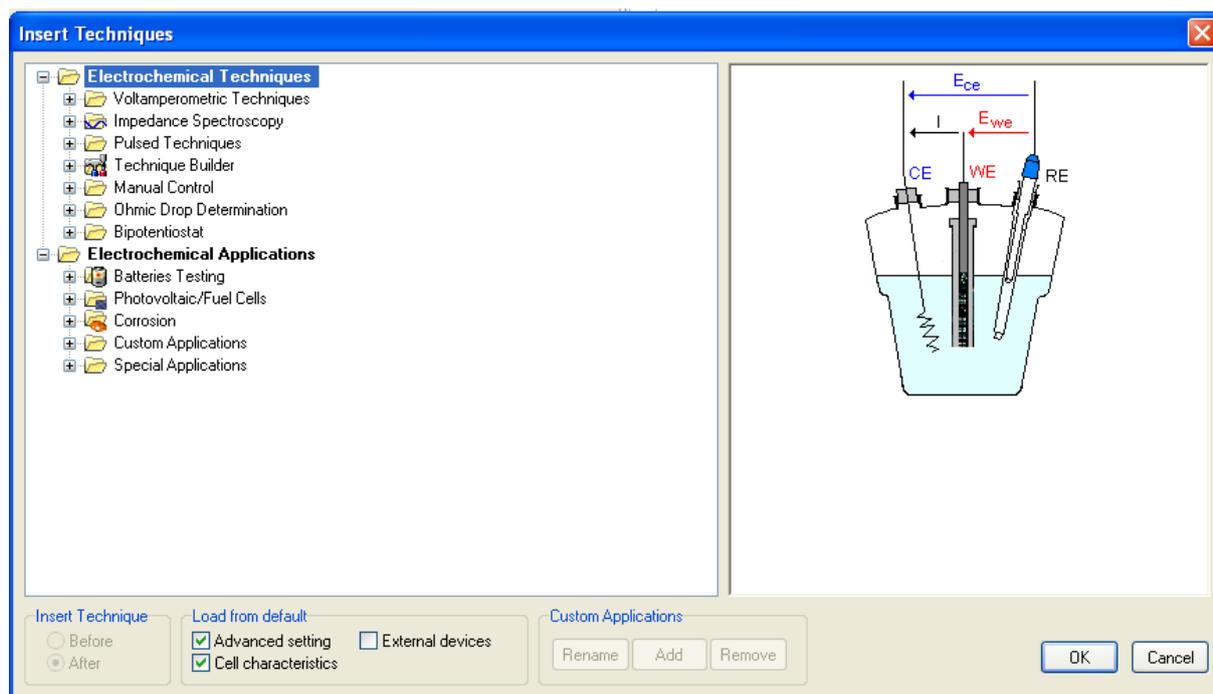


Fig. 27: Techniques selection window.

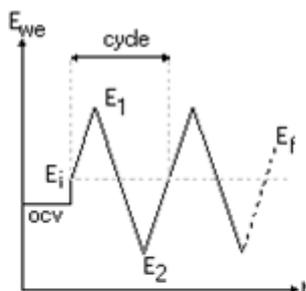
The techniques available with EC-Lab® software are divided in two different sections: *Electrochemical Techniques* and *Electrochemical Applications*.

Electrochemical Techniques include voltamperometric techniques, electrochemical impedance spectroscopy, pulsed techniques, a tool to build complex experiments, manual control and also ohmic drop determination techniques. *Electrochemical Applications* include battery testing, photovoltaic/fuel cell testing, corrosion measurements, custom applications and special applications.

At the bottom of this window different options can be selected when a protocol is loaded. In the case of linked techniques, the user can insert the technique either before or after the technique already loaded in the Experiments Box. This option will be described in detail in

the Linked Techniques section (part 2.7). The technique can be loaded with or without the “Cell Characteristics” and the “Advanced Settings” of the default setting file. The experiment can be saved as a custom application (see **Custom Applications** section (in the **Techniques and Applications** manual).

For example, choose the cyclic voltammetry technique and click **OK** or double click. On the right frame, a picture and description is available for each protocol.



Cyclic voltammetry (CV) is the most widely used technique for acquiring qualitative informations about electrochemical reactions. CV provides informations on redox processes, heterogeneous electron-transfer reactions and adsorption processes. It offers a rapid location of redox potential of the electroactive species. CV consists of scanning linearly the potential of a stationary working electrode using a triangular potential waveform. During the potential sweep, the potentiostat measures the current resulting from electrochemical reactions (consecutive to the applied potential). The cyclic voltammogram is a current response as a function of the applied potential.

Fig. 28: CV technique picture and description on the experiment window.

2.5.1.3 Changing the parameters of a technique

When a technique is selected the default open window is the "Parameters Settings" window. The user must type the experiment parameters into the boxes of the blocks. Two ways are available to display a technique: either the detailed *flow* diagram (Fig. 29) and its table, or the detailed *column* diagram (Fig. 30).

It is possible to switch between the two modes of display using the  button. Setting parameters can also be done using selected settings files from user's previous experiment files.

Click on the **Load Settings** icon  then select an .mps setting file or a previous .mpr raw file corresponding to the selected technique and click **OK**. You can right-click on the mouse and select "Load settings..."

Note: Most of the techniques allow the user to add sequences of the same techniques using mouse right-click or using the Edit menu. On the "**Parameters Settings**" tab, the CV detailed flow diagram or the column diagram is displayed:

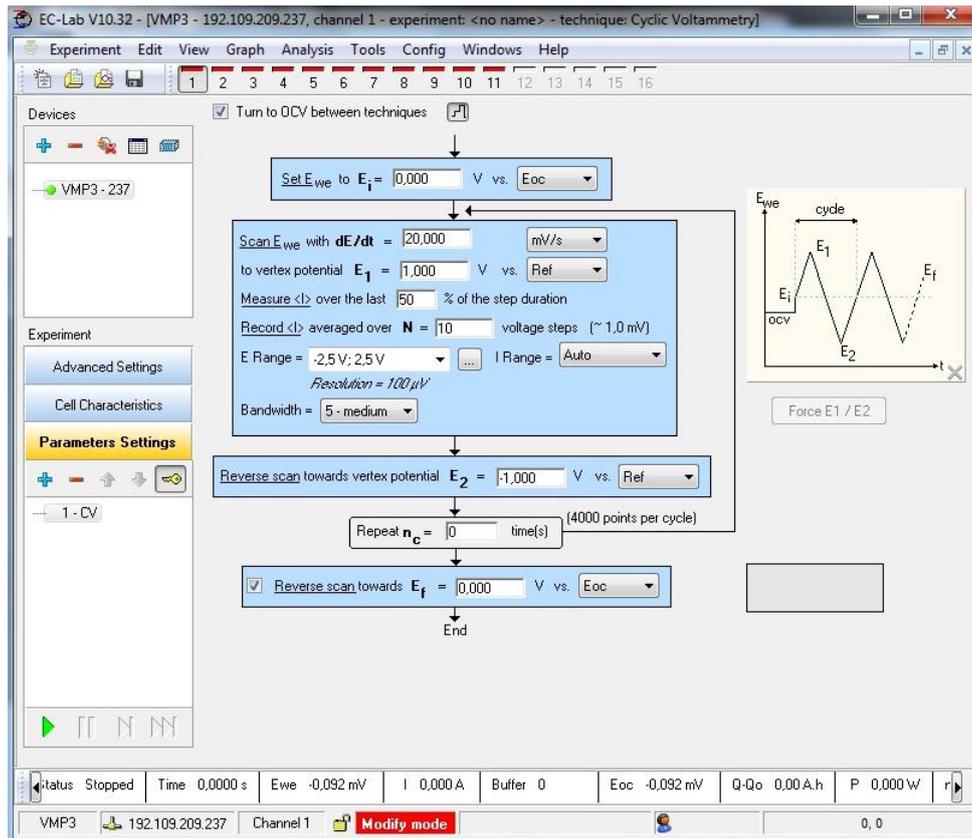


Fig. 29: Cyclic Voltammetry detailed flow diagram.

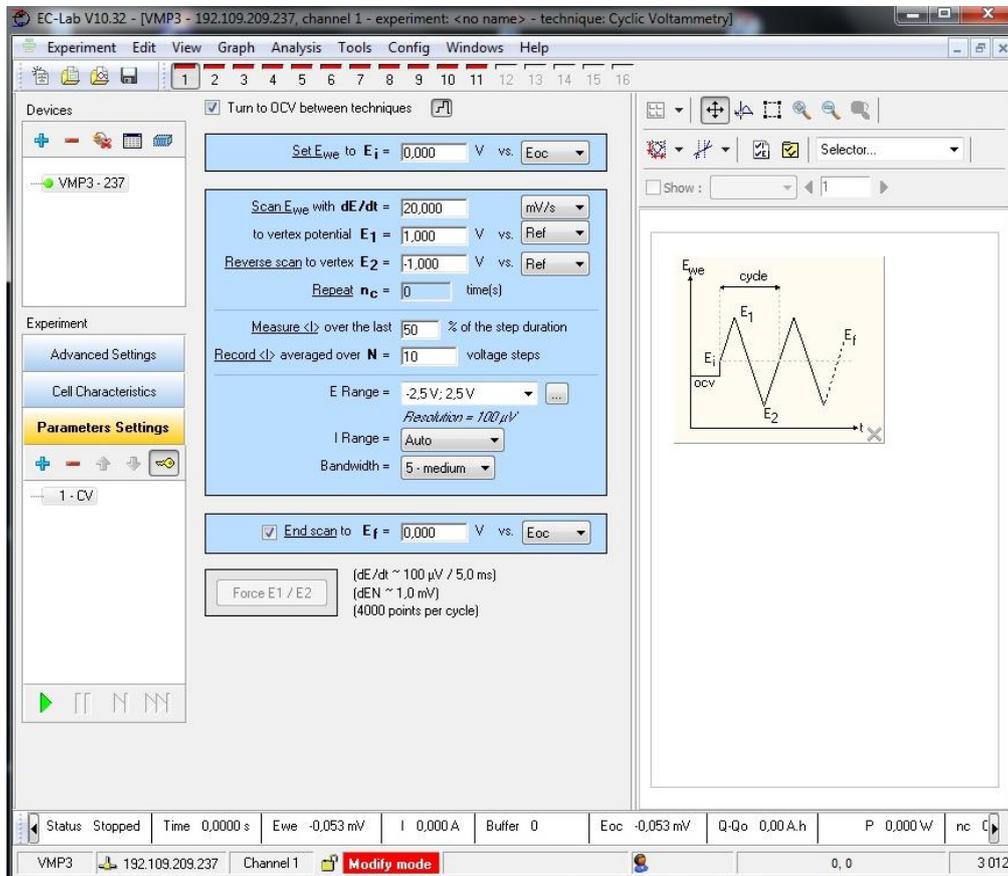


Fig. 30: Cyclic Voltammetry detailed column diagram.

When a technique is loaded on a channel, the detailed column diagram is displayed. On top of the diagram, the Turn to OCV option can be seen as well as the button , available to show the graph describing the technique and its variables (cf. Fig.31).

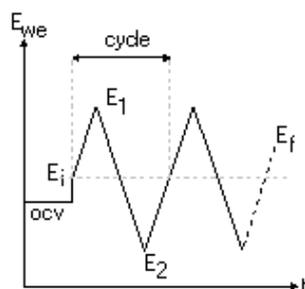


Fig. 31: CV graphic description.

The EC-Lab® software protocols are made of blocks. Each block is dedicated to a particular function. A block in grey color means it is not active. The user has to set parameters in the boxes to activate a block, which becomes colored.

When available, the recording function "**Record**" can be used with either dE_R or dt_R resolution or with both. Data recording with dE_R resolution reduces the number of experimental points without losing any relevant changes in potential. If there is no potential change, only points according to the dt_R value are recorded. If there is a steep change in potential, the recording rate increases according to dE_R .

In every technique with potential control and current measurement, the user can choose the current recording conditions between an averaged value (per potential step for a sweep) and an instantaneous value every dt (see the **Techniques and Applications** manual).

When a technique is loaded in the parameters settings window, a small icon is displayed on the left of the flow diagram with the name of the technique and its number (rank) in the experiment (in case of linked techniques). During a run, the technique that is being performed is indicated by a black arrow.

Notes:

- E Range adjustment

On the technique the user can define the potential range (min and max values) to improve the potential resolution from 305 μV (333 μV for VMP-300, VSP-300, SP-240, SP-300 and SP-200) down to 5 μV .

- Scan rate setting

When entering the potential scan rate in mV/s the default choice of the system proposes a scan rate, as close as possible to the requested one and obtained with the smallest possible step amplitude. The scan rate is defined by dE/dt .

- I Range

The current range has to be fixed by the user. When the current is a measured value, I measured can be greater than the chosen I Range without "current overflow" error message. In this case the potential range is reduced to ± 9 V instead of ± 10 V. The maximum measurable current is $2.4 \cdot I$ Range. For example with I Range = 10 mA, the current measured can be 24 mA with a potential range ± 9 V. The same thing is possible when the current is controlled (For more details about that, please see section 6.3).

With booster ranges and 1 A range of VMP-300, VSP-300, SP-240, SP-300 and SP-200, this relationship is not valid.

- Bandwidth

The VMP2/Z, VMP3, VSP, MPG2-XXX series, SP-50, SP-150, HCP-803, HCP-1005 and BiStat devices propose a choice of 7 bandwidths ("damping factors"), 8 for the VMP and MPG devices and 9 for SP-300, SP-200, SP-240 VSP-300 and VMP-300 devices in the regulation loop of the potentiostat. The frequency bandwidth depends on the cell impedance and the user should test filtering effect on his experiment before choosing the damping factor.

The following table gives typical frequency bandwidths of the control amplifiers poles for the VMP3, VSP, MPG2, SP-50, SP-150, HCP-803, VMP2, and BiStat:

Bandwidth	7	6	5	4	3	2	1
Frequency	680 kHz	217 kHz	62 kHz	21 kHz	3.2 kHz	318 Hz	32 Hz

The following table gives typical frequency bandwidths obtained with a 2 kΩ resistor connected between the working electrode and the reference electrode coupled with the counter electrode (2 points connection) for the VMP and MPG.

Bandwidth	8	7	6	5	4	3	2	1
Frequency	2 MHz	600 kHz	200 kHz	60 kHz	20 kHz	6 kHz	2 kHz	600 Hz

Note: For more details about bandwidth definition for the SP-300, SP-200/SP-240, VSP-300, VMP-300 instruments, refer to the installation and configuration manual for SP-300 based instruments.

When the mouse pointer stays for several seconds on a box a hint appears. The hint is a visual control text that gives the user information about the box. It shows the min and the max values of the variable as well as the value that cancels the box i.e. the value for which the box will be skipped.



Fig. 32: Hint.

- Sequences within a technique.

If the user wants to perform an experiment composed of the same technique but with different parameters, the sequences can be used. These sequences are accessible in two different ways depending on the type of diagram used.

Column Mode

Below the "Turn to OCV" line, "+" and "-" buttons can be seen (Fig. 33).

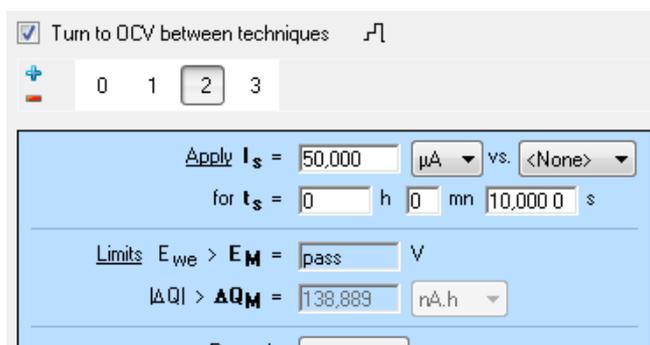


Fig. 33 : The "+" and "-" buttons to add sequences.

Clicking on the "+" button will add a sequence with the same parameters as the previous sequence. Clicking on the "-" sequence will remove the sequence. Up to 99 sequences can

be added. Note that only one data file will be created and that you can only add sequences of the same technique.

Flow Chart Mode

In the flow diagram mode, a table appears automatically. One row of the table is a sequence of the experiment. The experiment parameters can be reached and modified in the table cells as well as in the flow diagram of the parameter settings window

Ns	tR (h:m:s)	dER/dt (mV/h)	dER (mV)	dtR (s)	Ei (V)	vs.	ti (h:m:s)	IM	unit IM
0	0:00:2.0000	0.0	0.00	1.0000	0.350	<None>	0:00:10.0000	0.000	mA
1	0:01:0.0000	0.0	0.00	0.1000	0.300	<None>	0:01:0.0000	0.000	mA
2	0:00:1.0000	0.0	0.00	0.1000	-0.300	<None>	0:01:0.0000	0.000	mA
3									

Fig. 34: EC-Lab® table (shown in Flow Chart mode).

During the run, the active row of the table (running sequence) is highlighted. The default number of rows is 30. The user can insert, delete, append, copy, and paste up to 99 rows by clicking the right button of the mouse. It can be a very interesting tool when the user wants to repeat an experiment with one different parameter in a sequence. It is also possible to cut, copy and paste only one cell of the table.

Note:

- The user can define different current ranges for each sequence if an OCV period separates the sequences (at the beginning of each sequence for example).
- It is possible to repeat a block in a sequence (go to sequence N_s').

2.5.2 The Cell Characteristics Tab

Clicking on the "**Cell Characteristics**" tab will display the cell characteristics window. This window is composed of three blocks: **Cell Description**, **Reference Electrode** and **Record**. Please see below:

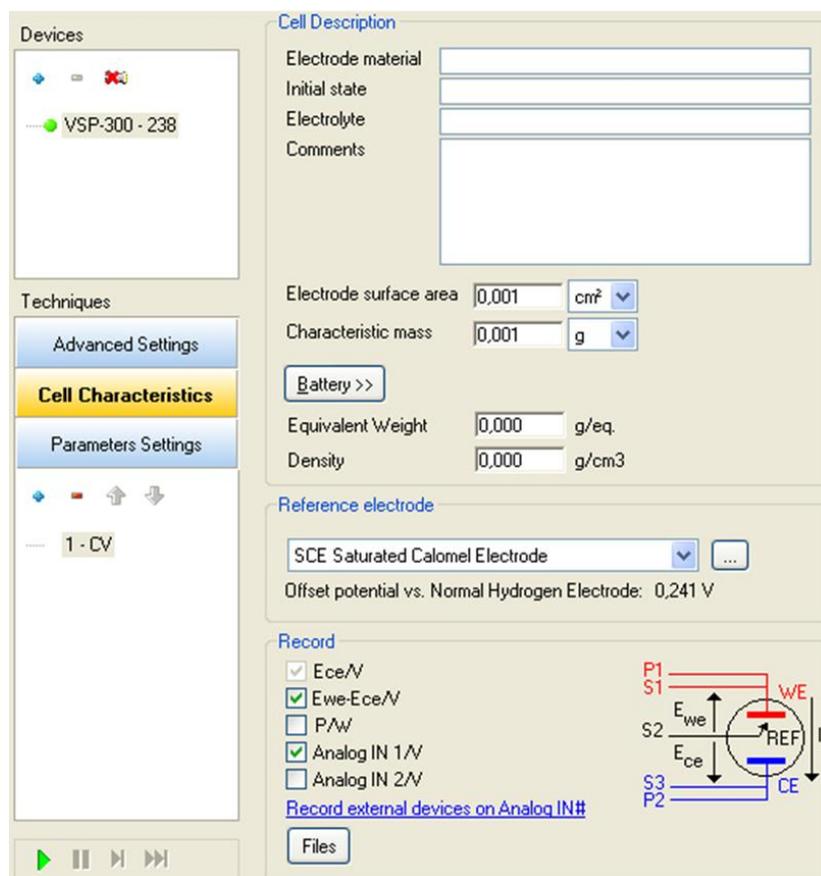


Fig. 35: Cell Characteristics tab (standard connection with SP-300 technology).

2.5.2.1 Cell Description

This window has a standard configuration and the “battery” configuration can be activated by clicking on the “Battery” button.

2.5.2.1.1 Standard “Cell Description” frame

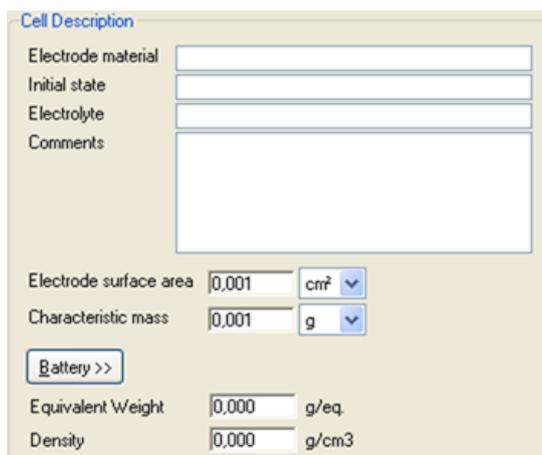


Fig. 36: Standard Cell Description frame.

You can either fill the blank boxes manually, entering comments and values, or load them from a **.mps** setting file or a **.mpr** raw file using **Load Settings...** on the right-click menu. This window allows the user to:

- add information about the electrochemical cell (material, initial state, electrolyte and comments)

- set the electrode surface area, the characteristic mass, the equivalent weight and the density of the studied material.
 - The surface area is the area of the sample used as a working electrode and exposed to the electrolyte. :
 - The characteristic mass is needed if the user needs to express any variable per unit of mass. It can be the mass of a whole battery or the mass of a sample.
 - The equivalent weight is the characteristic mass divided by the number of electrons exchanged during the electrochemical reaction, in most cases the dissolution of the metal.

Once defined, these parameters are automatically used to calculate, for example, the corrosion rate after a Tafel Fit or display the current as a current density. It is also possible to modify the electrode surface area or characteristic mass after the experiment by selecting “**Edit surface and mass**” in the Graph Tool Bar. The window below appears

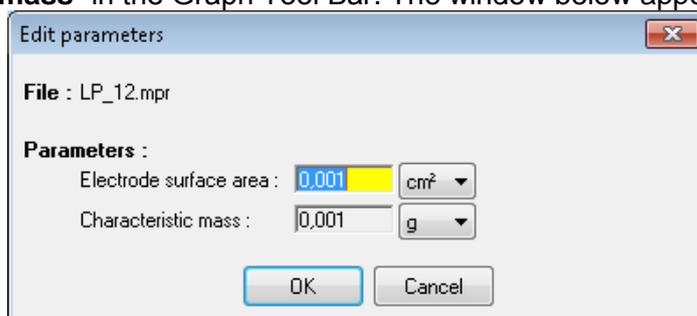


Fig. 37: Edit surface and mass window.

Another way is to use the Modify Cell Characteristics in the Tools tab of the main tool bar. (see 2.2.2.1)

2.5.2.1.2 Battery “Cell Description” frame

When the “Battery” button is pressed, additional parameters related to batteries show up. Note that these parameters are automatically displayed when a battery testing setting file is loaded. The corresponding window is as follows:

Fig. 38: Cell description window for a battery experiment or when the battery button is pressed.

In addition to the parameters described above, this window allows the user to enter the physical characteristics corresponding of the intercalation material. This makes on-line monitoring of the redox processes possible in terms of normalized units.

Let us review all the parameters:

- The *mass* of active material in the cell has to be set with a given insertion coefficient *xmass* in the compound of interest (for example *xmass* = 1 for LiCoO₂). These two parameters *mass* and *xmass* are actually related to the battery itself. This *mass* is different from the *characteristic mass*. It is only used to calculate the insertion rate *x* and not the massic variables: (I, Q, P, C, Energy)/unit of mass
- The *molecular weight* of the active material is the *molecular weight* of the active material subtracted by the *atomic weight* of the intercalated ion. The *atomic weight* of the intercalated ion is set in a separate box. For example, for LiCoO₂, the molecular weight of CoO₂ is 90.93 g.mol⁻¹ and the atomic weight of the intercalated ion Li is 6.94 g.mol⁻¹.
- The initial insertion rate *x₀*.
- *ne* is the number of electrons transferred per mole of intercalated ion.

An intermediate variable *X_f* is calculated using the following formula:

$$X_f = - \frac{(\text{molecular weight} + xmass \times \text{atomic weight})}{(ne \times mass \times 0.001 \times F)}$$

Mass is in mg,

Molecular weight and the atomic weight are in g/mol, this is why mass needs to be multiplied by 0.001,

F is equal to 26801 mA.h/mol.

X_f quantifies the change of insertion coefficient of the considered ion when a charge of 1 mA.h is passed through the cell (or disintercalated when a discharge of -1 mA.h is passed).

The charge needed to increase X_f of 1 is given in the window:

“for $\Delta x=1$, $\Delta Q= 26802$ mA.h”.

The variable x , which is the insertion coefficient of the inserted ion (or stoichiometry of the inserted ion in the concerned compound) resulting from the charge, is calculated using the following formula:

$$x = x_o + X_f (Q - Q_o)$$

x is the sum of x_o the initial insertion coefficient and X_f the change of insertion coefficient during the charge (or disintercalated during the discharge) $Q - Q_o$.

Q_o is the initial state of charge of the battery and is calculated using x_o .

Finally, it is possible to enter the capacity C of the battery in A.h or mA.h. The capacity of the battery is the total charge that can be passed in the battery. A capacity of 3.2 A.h means that the fully charged battery will be totally discharged if a current of -3.2 A is applied during 1 hour.

In the techniques dedicated to batteries and especially the GCPL techniques and Modulo Bat technique (MB), it is possible to define the charge or discharge current as a function of the capacity. For instance, using a battery of 3.2 A.h, if the charge is set at $C/2$, it means that the battery will be charged with a current of 1.6 A. The time of the charge is defined elsewhere in the technique (see “EC-Lab Software Techniques and Applications”).

2.5.2.2 Reference electrode

It is possible to set the reference electrode used in the experiment (either chosen in the list or added while clicking on the corresponding tab). The common reference electrodes are available. If “unspecified” is entered, then the potential will be given in absolute value. Note that it is possible to add a custom reference electrode and that the Reference electrode menu is also available in **Config\Options\Reference**.

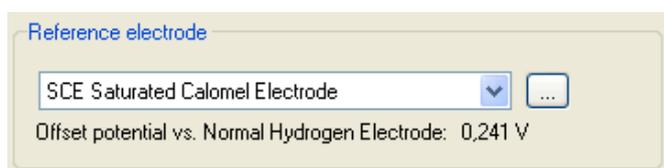


Fig. 39: The Reference electrode block

2.5.2.3 Record



Fig. 40: The Record block (with standard connection in SP-300 technology)

In addition to the variables recorded by default (mainly E_{we} (= Ref1-Ref2 or S1-S2) and I and other variables depending on the chosen techniques), the user can choose to record:

- the counter electrode potential ($E_{ce} = \text{Ref3-Ref2}$ or S3-S2)
- the compliance $E_{we}-E_{ce} = \text{Ref1-Ref3}$ or S1-S3)
- the power $P = E_{we} * I$
- analog external signals (pH, T, P,...) using auxiliary inputs 1 (Analog In1) and 2 (Analog In2). These signals must be configured using the window opened by clicking on the link in blue.

It must be noted that E_{we} , E_{ce} and the power P are hardware variables and are directly coming from the potentiostat board. If the user does not choose to record P , it will nonetheless appear as a default variable but will be calculated not by the potentiostat but by the software using the I and E_{we} values stored in the data file by the software.

The hardware P is generally more accurate. The variable $E_{we} - E_{ce}$ is calculated by the software.

The Record block gives also the possibility to see the properties of the data file in which the variables will be stored. All boxes (Acquisition started on, host, directory and file) are filled automatically when the experiment is started.

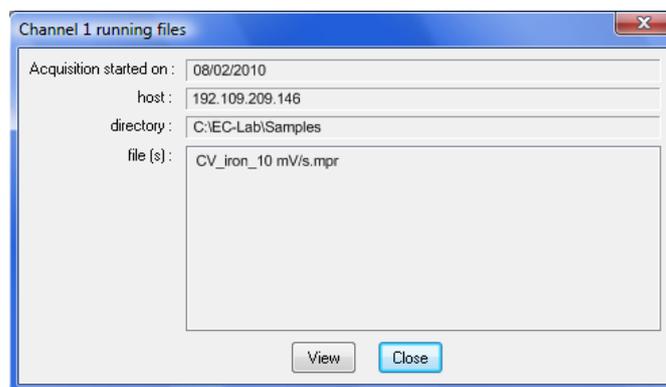


Fig. 41: Cell characteristics Files window.

2.5.3 Advanced Settings tab

The advanced settings window includes different hardware and software parameters that depend on the type of instrument. To change the values, click on the **Modify** button, enter the new settings, and click on the **Accept** button to send the new settings to the instrument.

Note: the "Advanced Settings" window is available for all the protocols.

2.5.3.1 Advanced Settings with VMP3, VSP, SP-50, SP-150, EPP-4000, Bi-Stat

The advanced settings window includes several hardware parameters and software parameters divided in four blocks: **Compliance**, **Safety Limits**, **Electrodes Connection**, and **Miscellaneous** (Cf Fig. 42). *Note that for SP-50 the compliance is not adjustable [-10V,+10V].*

Compliance
Modify on disconnected cells only !

Ewe from -10 V 10 V

Ece from -10 V 10 V

<< Less information

Ex: if Ewe = V
then Ece must be between
-10,000 V and 10,000 V.

Safety Limits

E_{We} max = V

E_{We} min = V

I_l = mA

I_{Q-Qol} = mA.h

Analog IN 1 = V

Analog IN 2 = V

E stack slave max = V

E stack slave min = V

for t > ms

Do not start on E overload

Electrodes Connection
Modify on disconnected cells only !

WE/CA2
ref1

RE/ref2

ref3
CE/CA1

Miscellaneous

Text export

Filter [Edit](#)

Smooth on points

Create one data file per loop (linked techniques only)

Fig. 42: Advanced Settings window for VMP3, VSP, SP-50, SP-150, EPP-4000, Bi-Stat instruments.

2.5.3.1.1 Compliance

The compliance corresponds to the potential range of the Counter Electrode versus the Working Electrode potential ($|E_{we}-E_{ce}|$). This option has to be modified only for electrochemical cells with more than 10 V potential difference between the counter and the working electrode. One can change the instrument compliance voltage between the CE and the WE electrodes from $-20\text{ V} \rightarrow 0\text{ V}$ to $0\text{ V} \rightarrow 20\text{ V}$, by steps of 1 V. In all the ranges the control and

measurement of the variables are available. **Note that for SP-50 the adjustable compliance is not available.**

The default compliance of CE vs. WE is ± 10 V. For example, while working with a 12 V battery, with the CE electrode connected to the minus and the WE connected to the plus, the potential of CE vs. WE will be -12 V. That is not in the default compliance. In order to have the CE potential in the right compliance, set the CE vs. WE compliance from -15 V to $+5$ V.

When the working electrode is connected to the minus and the counter electrode to the plus, the potential of CE versus WE will be $+12$ V. Then the compliance must be shifted between -5 and $+15$ V.

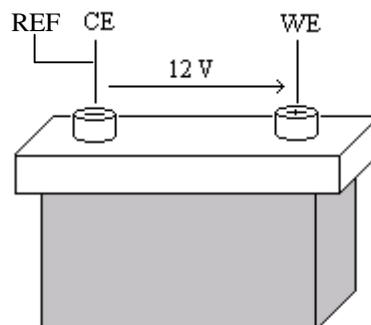


Fig. 43: 12 V battery, WE on +.

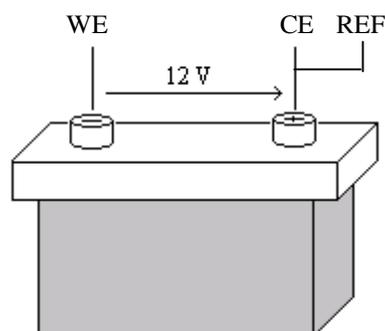


Fig. 44: 12 V battery, WE on -.

Warning: the compliance must be properly set before connecting the cells to avoid cell disturbance.

2.5.3.1.2 Safety Limits

Most of protocols already have potential, current or charge limits (for example Galvanostatic Cycling with Potential Limitation (GCPL): limit E_{we} to E_M and $|\Delta Q|$ to ΔQ_M , ...) that are used to make decision (in general, the next step) during the experiment run.

The experiment limits have been designed to enter higher limits than the limits set into the protocols to prevent cells from being damaged. Once an experiment limit is reached, the experiment is paused. Then the user can correct the settings and continue the run with the Resume button or stop the experiment.

To select an experiment limit, check the limit and enter a value and a time, for example: $E_{we} \text{ max} = 5$ V, for $t > 100$ ms. Then the limit will be reached if E_{we} is greater than 5 V during a time longer than 100 ms. Once selected, an experiment limit is active during the whole experiment run.

It is also possible to set an upper or higher limit on the external analog signals Analog IN1 or Analog IN2.

“E stack slave min” allows the user to set a lower limit that will be applied on each individual element (“slave”) of a stack of batteries. This ensures that no battery is damaged during the experiment.

“E stack slave max” allows the user to set an upper limit that will be applied on each individual element (“slave”) of a stack of batteries. This ensures that no battery is damaged during the experiment.

“Do not start on E overload” allows the user to not start an experiment in case of an overload of the potential E. It allows also the stop of an experiment in case of a potential overload.

Warning: the safety limits cannot be modified during the experiment run and must be set before.

2.5.3.1.3 Electrodes Connection

Standard connection mode

See Fig. 42: The working electrode is connected to CA2/Ref1, the reference electrode to Ref2 and the counter electrode to CA1/Ref3. Ref1, Ref2, Ref3 (Ref for reference) are used to measure the voltage and CA2 and CA1 (CA for Current Amplifier) to apply the current.

CE to Ground connection mode

It is possible to work with several WE (several RE) and one CE in the same bath. Then, counter electrodes must be connected together to the Ref1 lead and ground.

Disconnect the cables from the cell, select Electrodes connection = CE to ground and reconnect the cell as follows:

- CA1 and Ref3 leads to the working electrode
- Ref2 lead to the reference electrode
- GROUND and Ref1 leads to the counter electrode

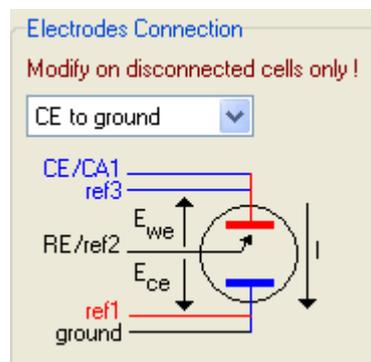


Fig. 45: Configuration CE to ground (N'Stat) for VMP3 technology.

2.5.3.1.4 Miscellaneous

Text export

This option allows the user to export data automatically in text format during the experiment (on-line exportation). A new file is created with the same name as the raw data file but with an .mpt extension.

Filter

This option allows the user to filter by the mean of the software the data just after the run by ticking this box before running the experiment. A new file is created with the same name as the raw data file but with an .mpp extension. This Filter tool is described in the paragraph dedicated to Analysis tools.

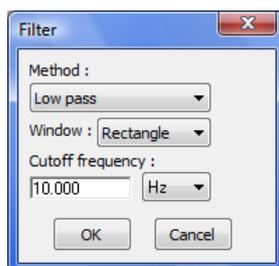


Fig. 46: Filter window.

Smooth (with sliding average)

For all the protocols, the user can smooth all values (I , E_{we} , E_{ce} , Aux1...) with a sliding average. To proceed, check smooth and enter the smooth window size (between 2 and 100 points).

Create one data file per loop

This option offers the possibility to create one data file per loop for each technique of a linked experiment. Then the data files will have a prefix number to define the order in the experiment.

For example, an experiment is composed of : OCV, CA and then a Loop on the OCV for 9 times.

If the “Create one data file per loop” box is not ticked, the data from the experiment will be stored in two .mpr files: one for the OCV and one for the CA.

If the “Create one data file per loop” is ticked, then the data from the experiment will be stored in twenty .mpr files: one for each OCV and CA of each loop.

2.5.3.2 Advanced Settings with HCP-803, HCP-1005, CLB-500 and CLB-2000

For HCP-1005, HCP-803 and CLB-500, the compliance value and the electrodes connection are fixed. The other limits and functions are the same as in 2.5.3.1.

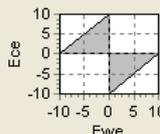
Compliance Modify on disconnected cells only !

Ewe from -10 V 10 V

Ece from -10 V 10 V

<< Less information

Ex : if Ewe = 0,00 V
then Ece must be between
-10,000 V and 10,000 V.



Safety Limits

$E_{we\ max} = 0,00$ V

$E_{we\ min} = 0,00$ V

$I = 0,000$ mA

$|Q-Qo| = 0,00$ mA.h

Analog IN 1 max = 0,00 V

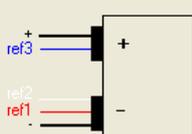
Analog IN 2 max = 0,00 V

for $t > 10$ ms

Do not start on E overload

Electrodes Connection Modify on disconnected cells only !

CE to ground v



Miscellaneous

Text export 

Filter v [Edit](#)

Smooth on 0 points

Create one data file per loop (linked techniques only)

Default

Fig. 47: Advanced settings window for HCP-803, HCP-1005, CLB-500 and CLB-2000 instrument.

2.5.3.3 Advanced Settings with MPG-2XX

It is the same window as Fig. 47 except that the electrodes connection is not displayed as only one connection is available with MPG-2XX.

Safety Limits

E_{we} max = 0,00 V

E_{we} min = 0,00 V

I_i = 0,000 mA

IQ-Qol = 0,00 mA.h

Analog IN 1 max = 0,00 V

Analog IN 2 max = 0,00 V

for t > 10 ms

Do not start on E overload

Miscellaneous

Text export

Filter [Edit](#)

Smooth on 0 points

Create one data file per loop (linked techniques only)

Default

Fig. 48: Advanced settings window for MPG-2XX instruments.

2.5.3.4 Advanced Settings for SP-200, SP-240, SP-300, VSP-300, VMP-300

The main differences with the VMP3 technology is that analog filters are available, the compliance cannot be adjusted and it is possible for the channel to be floating.

Filtering

Ewe, I 50 kHz

Safety Limits

E_{We}max = 0,00 V

E_{We}min = 0,00 V

I = 0,000 mA

|Q-Q_o| = 0,00 mA.h

Analog IN 1 max = 0,00 V

Analog IN 2 max = 0,00 V

for t > 10 ms

Do not start on E overload

Channel

Floating

Grounded

Electrodes Connection

Modify on disconnected cells only !

standard

P1
S1
S2
S3
P2

WE
REF
CE

E_{We}
E_{Ce}

Ultra Low Current Option

High speed scan

Definition of high speed value depends on the current range used.

Miscellaneous

Text export

Filter Edit

Smooth on 0 points

Create one data file per loop (linked techniques only)

Default

Fig. 49: Advanced settings window for SP-300 technology.

For SP-200, SP-240, SP-300, VSP-300 and VMP-300 instruments, the compliance is not adjustable and is equal to +/- 12 V. However for the booster SP-300 technology, the compliance depends on the booster type. For these boosters the compliance is as follows: +/- 49 V for the 1A/48V, +/-30V for the 2A/30V, [-3, +14V] for the 4A/14V and [0,5V] for the 10A/5V booster.

2.5.3.4.1 Filtering

This option is only available for the SP-300 technology. It is possible to filter potential (E) and current (I) by hardware. Three analog filters exist: 5 Hz, 1 kHz and 50 kHz. It is also possible to obtain the raw data by selecting No filter (None).

2.5.3.4.2 Channel

This menu is only available for the SP-300 technology. The Channel menu allows the user to select between Grounded and Floating mode for the used channel. The Floating mode must be used when the potentiostat is connected to a grounded cell (e.g. autoclave, pipeline etc...). The potentiostat needs to be floating to prevent current from looping in the cell.

2.5.3.4.3 Ultra Low Current Option

This option is only available with the SP-300 technology when the Ultra Low Current option is connected to the channel. This option is necessary when low current ability at relatively high speed is required. What is considered a high speed depends on the magnitude of the measured current. Lower is the current lower is the high speed. Ticking "High Speed Scan" helps compensate the bias current (typically 300 fA), which can become not negligible anymore at

low currents (typically <1 nA). In these extreme conditions, measurements can appear distorted. For instance, a loop can show up at the vertex (Fig. 50) as a result of an asynchronicity of the measured potential and measured current.

The value of current scan for which the correction must be applied also depends on the intrinsic characteristics of the cell (type of electrode, distance between electrodes, ...). The correction offered in the “Advanced Settings” window is automatically selected when Ultra Low Current Option is connected.

Note that if the High Speed Scan box is ticked, the data may be noisier especially for ranges below 1 nA (Fig. 51). It is possible to reduce the noise by numerically filtering the data after their acquisition (the numerical filtering is available in the “Math” menu of the “Analysis” tab).

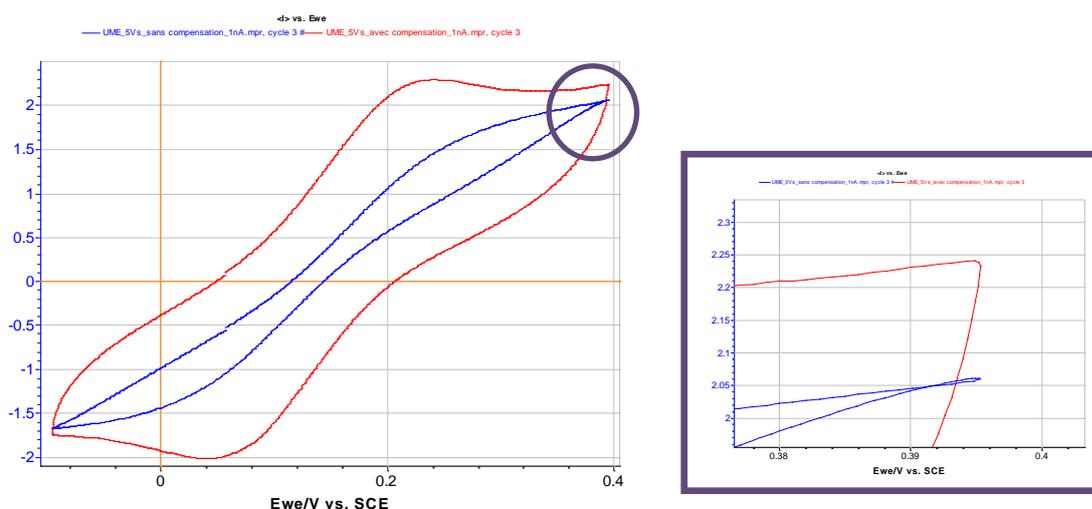


Fig. 50: CV carried out with an Ultra Microelectrode of 10 μm in a solution of ferrocene in EtOH with TBAP as a supporting salt. The range of current is 1 nA and scan rate is $5 \text{ V}\cdot\text{s}^{-1}$. Zoom at the vertex. **Blue line:** no compensation, **Red line:** High Speed Scan compensation.

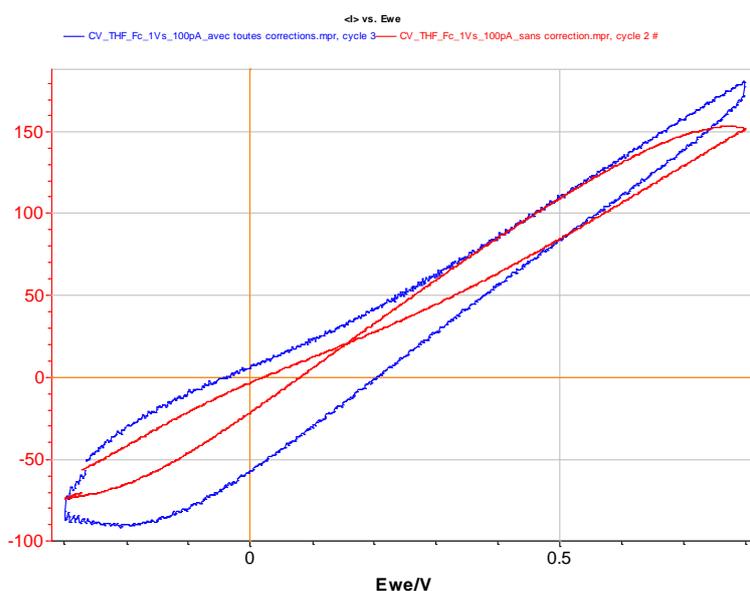


Fig. 51: CV carried out with Ultra Microelectrode of 10 μm in a solution of ferrocene in THF without any supporting salt. The range of current is 100 pA and scan rate is 1 $\text{V}\cdot\text{s}^{-1}$. Blue line: no compensation, Red line: High Speed Scan compensation.

2.5.3.4.4 Electrodes Connection

Standard connection

See Fig. 49: The working electrode is connected to P1/S1, the reference electrode to S2 and the counter electrode to P2/S3. S1, S2, S3 (S for Sense) are used to measure the voltage and P1 and P2 (P for Power) to apply and measure the current. To set the standard connection, proceed in the same way: **disconnect first S1, S2 and S3 from the cell, and only after disconnect P1 and P2**, select Electrodes connection = standard and set the next connections:

- P1 and S1 leads to the working electrode,
- S2 lead to the reference electrode,
- S3 and P2 leads to the counter electrode.

Then click on Apply configuration button.

CE to ground

See Fig. 52: Disconnect the cables from the cell, select Electrodes connection = CE to ground and reconnect the cell as follows:

- P1 and S1 leads to the working electrode
- S2 lead to the reference electrode
- GROUND and S3 lead to the counter electrode

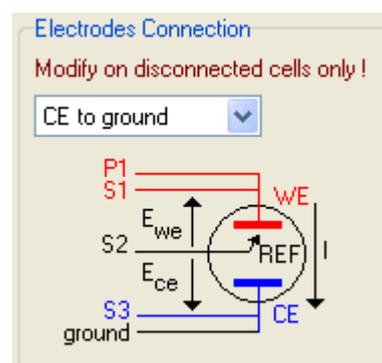


Fig. 52: Configuration CE to ground (N'Stat) for SP-300 technology.

Refer to the “**Installation and configuration manual**” of the corresponding instruments for more details on the CE to ground connection.

Warning: it is important to disconnect the electrodes from the cell, before changing the electrode connection, because of the difference between the leads assignment, the OCV may not be properly applied.

Note: with CE to ground connection, CE vs. WE compliance is set to ± 12 V.

The CE to ground option is not available with the ZRA protocol (Zero Resistance Ammeter).

+/- 48 V control mode

This connexion mode is available with the SP-300/VSP-300/VMP-300 when a 1 A/48 V booster connected to the standard channel board.

Disconnect the cables from the cell, select Electrodes connection = +/- 48 V control and reconnect the cell as follows:

- P2 and S3 lead to the working electrode
- S2 leads to the reference electrode
- P1 and S1 lead to the counter electrode

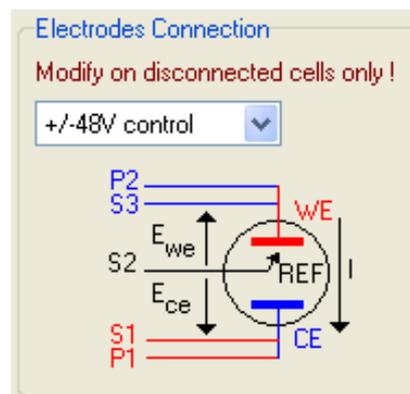


Fig. 53: +/- 48 V control mode for SP-300 technology.

Refer to the “Installation and configuration manual” of your instrument for more details on the +/- 48 V control connection mode.

+/- 30 V control mode

This connexion mode is available with the SP-300/VSP-300/VMP-300 when a 2A/30 V booster connected to the standard channel board.

Disconnect the cables from the cell, select Electrodes connection = +/- 30 V control and reconnect the cell as follows:

- P2 and S3 lead to the working electrode
- S2 leads to the reference electrode
- P1 and S1 lead to the counter electrode

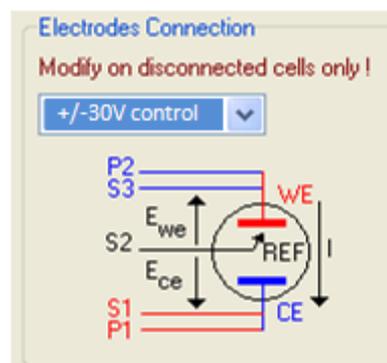


Fig. 54: +/- 30 V control mode for SP-300 technology.

Refer to the “Installation and configuration manual” of your instrument for more details on the +/- 30 V control connection mode.

-3V;+14V control mode

The +14V;-3V is two-electrodes connexion mode available with the SP-240 and with SP-300/VSP-300/VMP-300 when a 4A/14 V booster connected to the standard channel board.

Disconnect the cables from the cell, select Electrodes connection = -3V,+14 V control and reconnect the cell as follows:

- P1, S1 and S2 leads to the working electrode
- S3 and P2 leads to the counter electrode

P.S: The impedance techniques are not available with -3V;+14V control mode.

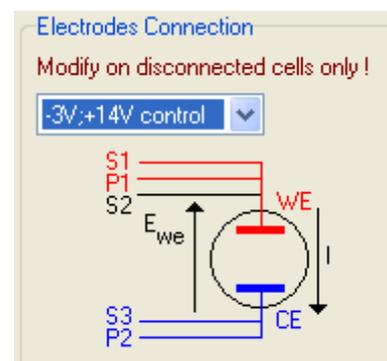


Fig. 55:-3V;+14V control mode for SP-300 technology.

WE to ground connection mode

In addition to the CE to ground mode, a “WE to ground” connection mode is available with the SP-200, SP-300, VSP-300 and VMP-300.

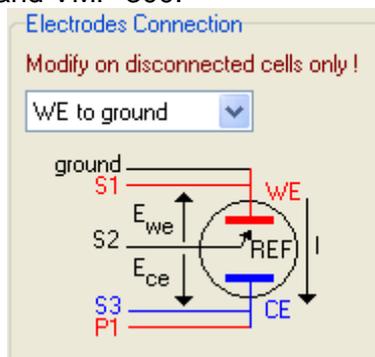


Fig. 56: WE to ground connection for SP-300 technology.

This configuration is very useful for hydrogen permeation measurements where one working electrode is grounded and connected to two different couples of counter electrode and reference electrode.

2.6 Accepting and saving settings and running a technique

2.6.1 Accepting and saving settings

Once you have set the parameters of your experiment, click on the **Accept** icon . It validates the **Parameters Settings**, the **Cell Characteristics** and the **Advanced Settings** and sends them to the instrument. If the option is activated in the **Config\option\Warning menu**, the following window will appear before accepting the settings:



Fig. 57: Summary window before accepting settings (VMP3 technology).

This window summarizes several parameters of the experiment. Click on **Yes** to accept the settings and start the experiment. The settings can be set as default settings for the current technique. Right-click on the mouse and select “**Set settings as Default**”. The parameter settings can be saved as an *.mps file in Experiment\save as\ or right-click on **Save Experiment...**, or click on .

2.6.2 Running an experiment

Click on the **Run** button . A filename selection window will appear:

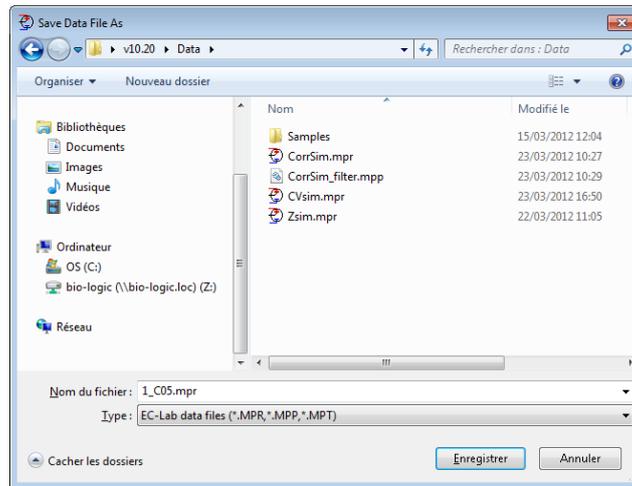


Fig. 58: Filename selection window.

The default folder to save the data is called “Data”. The user can choose and create another folder to save his data files. Type the filename.

Note: the filenames can be forced to end with the channel number using the **Config\Option\General**. This option is always fixed for grouped channels.

Clicking **Save** or pressing <ENTER> will start the experiment, and the **Run** button turns into the **Stop** button.

One file is created when running the experiment: a binary raw data file, with an **.mpr** extension automatically added that contains all the information for the experiment usually contained in the Log file (the selected protocol, initial settings, instrument IP and channel N°, files director.). The user can choose to separately save the Log file using the **Config\Options\General** menu.

2.7 Linking techniques

2.7.1 Description and settings

It is possible to link different protocols within the same run. This allows the user to create and build complex experiments composed of up to 20 techniques. When created, the linked experiment settings can be saved either as an **.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 and can be reloaded whenever necessary.

Linked experiments can be made using the “**Technique Builder**” in the technique window. The **WAIT** and **LOOP** options have been designed especially for linked experiments. Building linked experiments is very easy with settings on the right-click menu. When the user right-clicks on the parameter settings window, the following menu pops up:

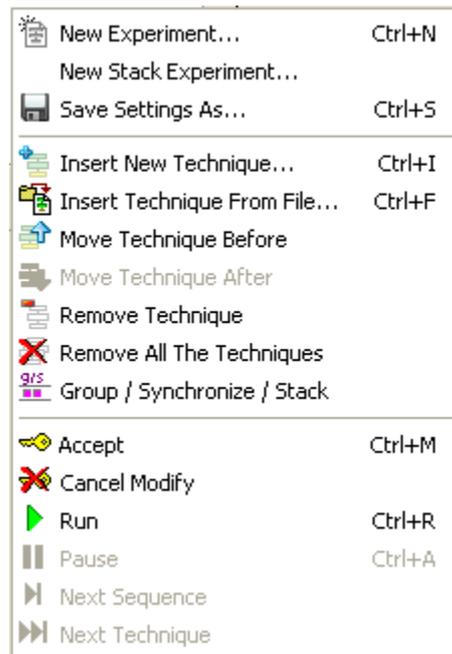


Fig. 59: Mouse right-click with the insert and remove options.

The second frame is especially dedicated to linked experiments. The “**Insert New Technique**” function opens the technique selection window and can insert a new technique into the experiment. The additional technique can be added before or after the activated/selected technique using the **Insert Technique** frame at the bottom left corner of the technique selection window:



Fig. 60: Insert before/after option of the technique selection window.

If the technique is not in the correct position in the series of experiments, the user can easily move it up or down using the “**Move Technique Before**” and “**Move Technique After**” options respectively.

Note: it is possible with the protocol linker to apply 50 ms OCV period between two protocols (reduced to 0.6 ms if the previous protocol is an OCV). The user has just to activate “**Turn to OCV between techniques**” in the **Advanced Settings** window. If this option is not selected the user will not have the ability to select different current ranges for each linked technique.

When inserting a technique, other options are available:

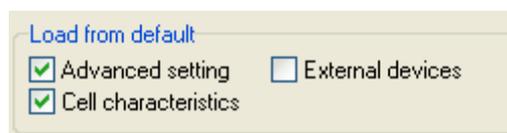


Fig. 61: Loading options of the technique selection window.

If the boxes are checked it means that the default advanced settings, cell characteristics and external devices settings will be associated with the inserted technique, regardless of any change that was made.

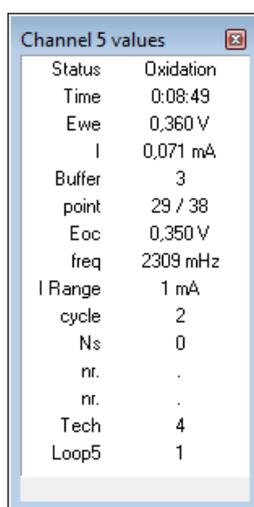
Note that the Advanced Settings, Cell Characteristics and External devices are the same for all the linked techniques.

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.

Once the file name typed the acquisition starts, and the program shows the graphic display with the data files.

During the run the technique in progress can easily be identified by an arrow next to the corresponding button. Its number is displayed in the **Channel Values** box (see next figure) as **“Tech”**. The number of loops executed is displayed as **“Loop”**.

As for a single experiment run, it is possible to **Pause**  / **Resume**  and **Stop**  the experiment. 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 Technique** button  in the tool bar. One can also move on to the next sequence using the **Next Sequence** button .



Channel 5 values	
Status	Oxidation
Time	0:08:49
Ewe	0,360 V
I	0,071 mA
Buffer	3
point	29 / 38
Eoc	0,350 V
freq	2309 mHz
I Range	1 mA
cycle	2
Ns	0
nr.	.
nr.	.
Tech	4
Loop5	1

Fig. 63: Linked experiment current values.

Notes:

- The bipotentiostat techniques and the manual controls cannot be linked to any other technique.
- The Polarization Resistance process calculation can be performed on the protocol 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 menu **Load settings...**

Linked experiments settings files are text files with the *.mps extension like the standard settings files.

Please be aware that the recording of auxiliary signals from Analog In1 or Analog In2, Ewe-Ece and power is disabled with an impedance technique. No external data points will be recorded during the EIS measurement period. If the user accepts such settings, the following warning message appears:

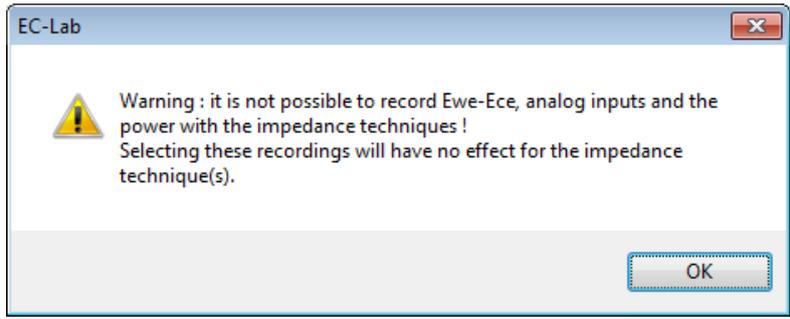


Fig. 64: Warning message on external signals recorded with EIS techniques

2.7.2.2 Application of linked experiments with ohmic drop compensation

The following experiment is given as an example of linked techniques but also to show how to use the Ohmic drop compensation techniques. This experiment is composed of CA, CV, PEIS and Loop techniques. This series of linked techniques illustrates the effect of the ohmic drop compensation. Indeed, to compensate the ohmic drop during an experiment, the ZIR technique has to be set before the techniques for which the compensation is done. To illustrate this the Fig. 65 is given as an example. In the left side of the figure, the series PEIS + CV + ZIR + CV is defined. On the right side of the figure, the second graph shows the superimposition of two CV graphs: one compensated and one uncompensated.

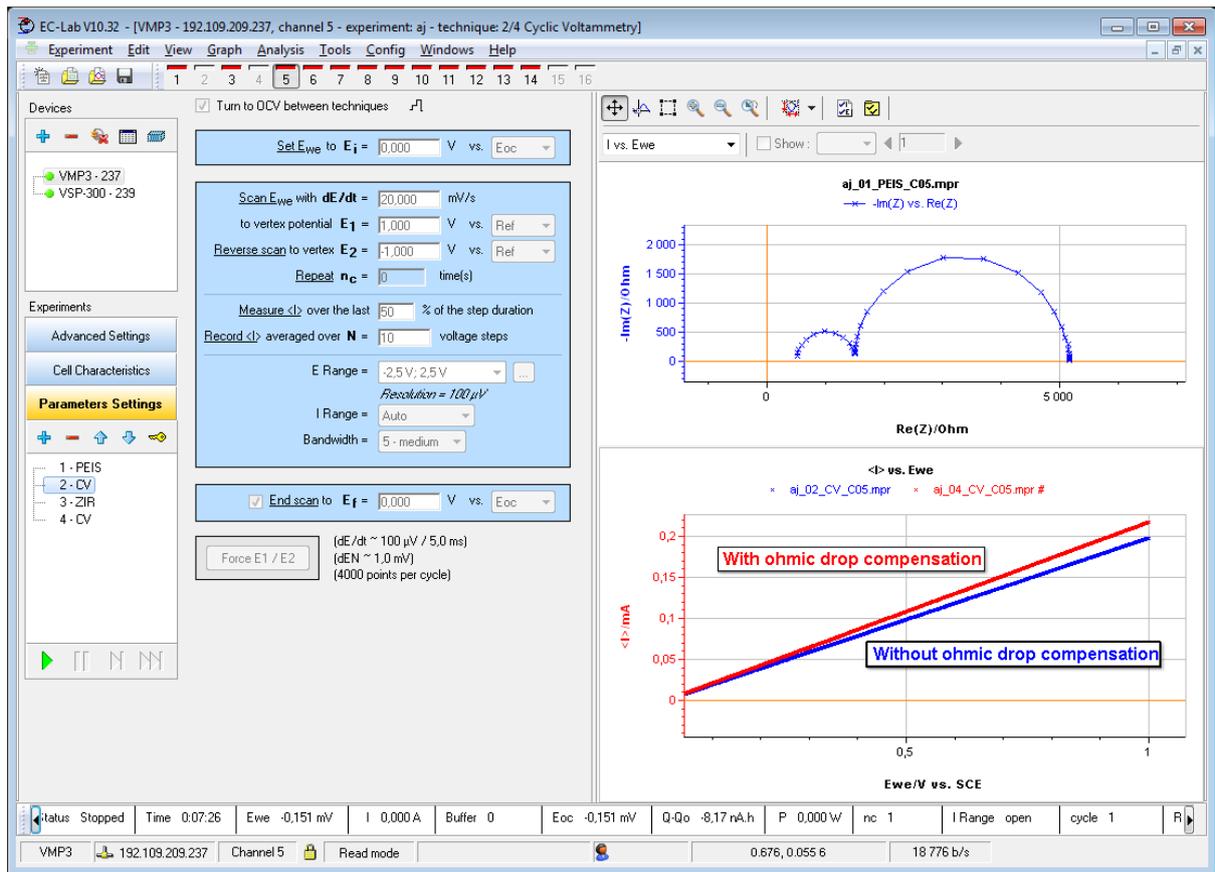


Fig. 65: Linked experiments example with ohmic drop compensation technique.

2.8 Available commands during the run

During the experiment several commands remain active. Most of the settings can be changed while the experiment is running. These changes appear in the log file.

2.8.1 Stop and Pause

Clicking on the **Stop** button  will display a message asking for confirmation. Clicking OK stops the measurement. At that time a binary version of the **.mpl** file is appended to the **.mpr** file. A raw data file **.mpr** is then obtained, which contains all the information on the experiment, while the **.mpl** file is erased. The Log file can be kept as a separate file by checking the corresponding in **Config\Options**.

Clicking on the **Pause** button  will lead to a pause in the progress of the protocol and in the measurement recordings. The cell will be disconnected from the current generator (but not from the potential measurements). Then the **Pause** button switches to the **Resume** button  and clicking on this button continues the experiment (with a gap corresponding to the pause time).

2.8.2 Next Technique/Next Sequence

It is possible during an experiment to move on to the **Next Technique** using the  button or to the **Next Sequence** using the  button.

2.8.3 Modifying an experiment in progress

The **Modify** button  enables the user to modify most of the parameter settings while the experiment is running.

The new set of parameters is sent to the instrument when clicking on the **Accept** button . It is taken into account within 200 μ s for instruments of the VMP3 family and SP-300 and SP-200 and 20 ms for the VMP and the MPG. All information on the change, the time it was done, the new settings etc., is appended to the Log file (see section 3.2.6, page 78). Note that a warning message could appear before accepting the modification if this option is selected in **Config\Option\Warning**. Among all the parameters, some of them cannot be modified on the fly such as Irange, Erange and Bandwidth.

2.8.4 Repair channel

This tool allows a user to repair a channel board.

To have repair channel window, click on Tools menu and then repair channel windows.

The window below will be open.

The window contains four blocks:

- 1-Channel
- 2-Data buffer
- 3-Change saved file name
- 4-Reset

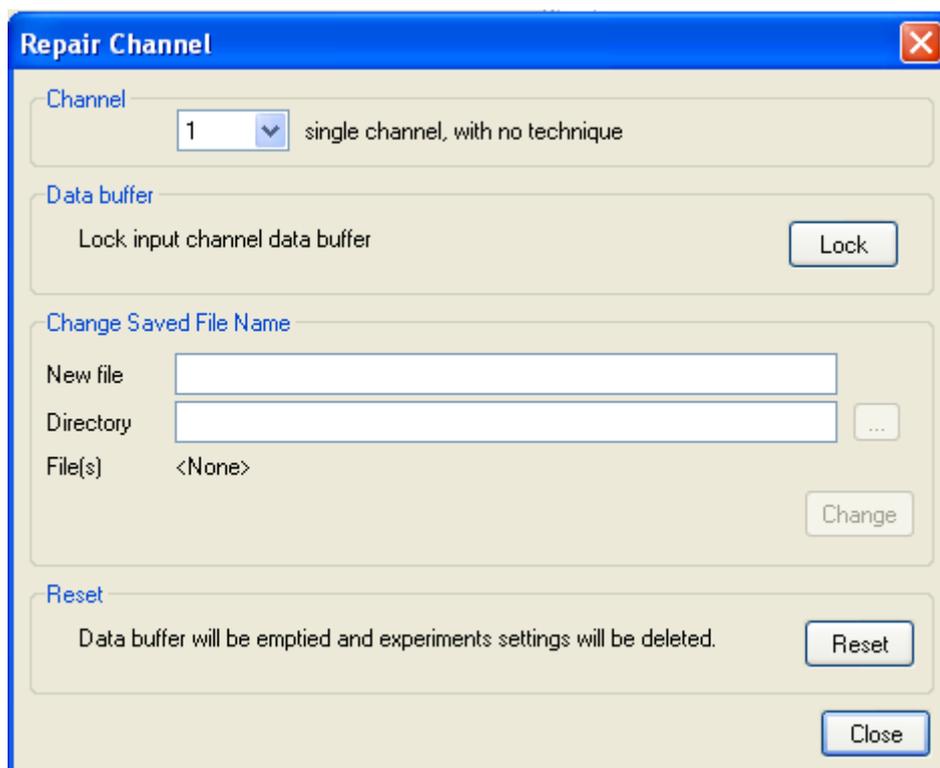


Fig. 66: Repair channel window

First block:

Selection of the channel the user wants to repair.

Second block:

This block allows user to lock the data transfer of the selected channel.

In the case of a multichannel, because of a wrong recording parameter (most of time dE or dI) on one channel, many data points may be recorded and fill the buffer of the com board. The data transfer procedure is stuck to this specific channel and is much slower for the other channel of the instrument. This tool allows user to block the data transfer of this channel, the data point of the other channel will be retrieved.

Third block:

Allow the user to create a new file to store the coming data point.

It is useful for example when the user moves an experiment file during the experiment. In that case, the user will have one file for the first part of the experiment and another one for data point which are not yet transferred to the PC (after the creation of the new file).

Fourth block:

This will reset all the data point stored in the buffer of the communication board related to the selected channel. This tool has to be used if the tool of the second and the third block doesn't work.

2.9 Multi-channel selection: Grouped, Synchronized Stacked or bipotentiostat experiments

2.9.1 Grouped or synchronized experiments

The button corresponding to the Group/Synchronize/Stack window is .

Grouping: It is possible to run the same experiment on several channels this is what we call to group channels. It is possible to group channels from two different instruments if :

- the instruments are from the VMP3 family (SP-50, SP-150, VMP3, VSP, Bi-Stat, EPP-4000, MPG-2)
- the channels share the same current ranges

It is possible to group one channel with impedance and the other without but then impedance measurements will not be available on any of the two channels. It is also possible to choose to begin the experiment with the average potentials value of all the selected channels (by ticking the box “Start grouped channels at averaged potential”) or to begin the experiment on each channel with its own potential.

Synchronizing: It is also possible to run different techniques on several channels and make them start together at the same time. This is what is called to synchronize channels. Any channels from any instruments can be synchronized. The user can choose whether or not to stop the channels at the same time.

To enter the **Group/Synchronize/Stack** window , click on the **Modify** button then, in the **Edit** menu select “**Group/Synchronize channel X**” (where X is the number of the selected channel) or the button can be available in the **Main Tool Bar** or by right-clicking on the main window (Settings Pop Up Menu) (if it has been previously configured using Config\Options). The following window appears:

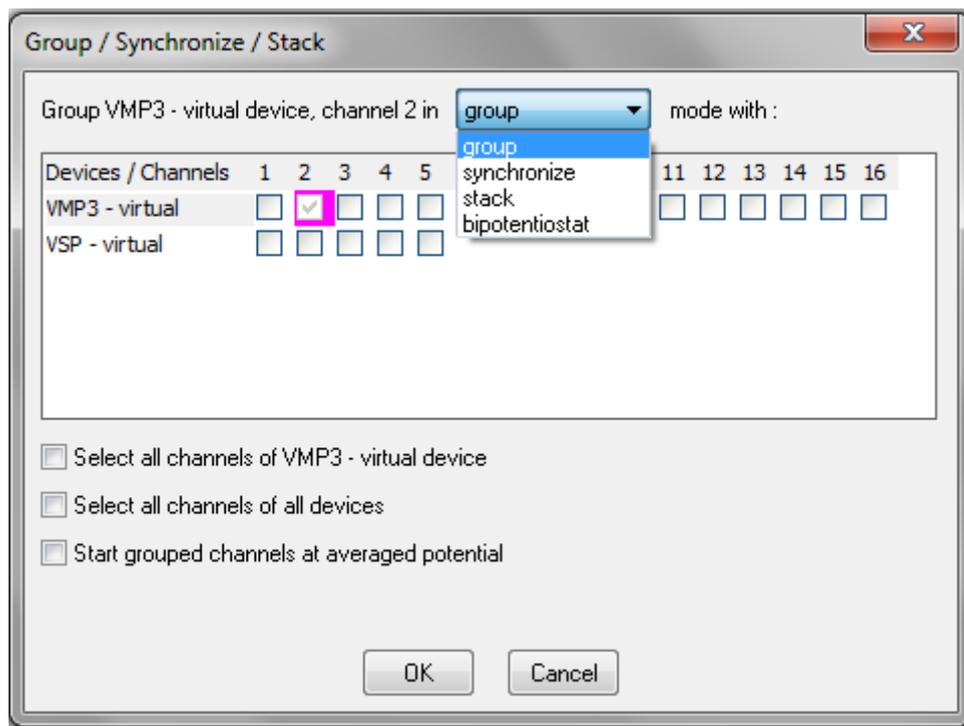


Fig. 67: Group/Synchronize/Stack/Bipotentiostat window.

Channels belonging to the same group or being synchronized appear with the same colour. To know if the channels are grouped or synchronized, the user can show the global view:

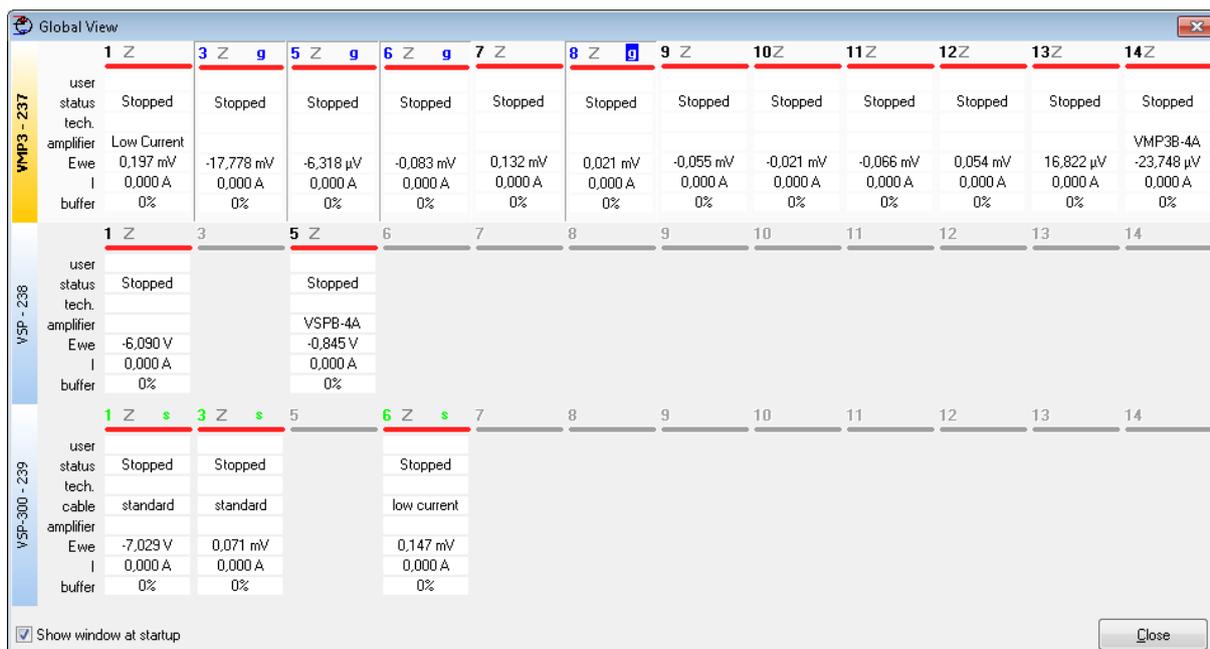


Fig. 68: Global view to show the grouped and synchronized channels.

Grouped channels are marked with a "g" in the channels global view window and synchronized channels are marked with an "s". The active channel has an highlighted "g" or "s". In the global view above, one can see that channels 3, 5, 6, 8 from the VMP3 are grouped and channels 1, 3, 6 from the VSP-300 are synchronized.

Note: one can group or synchronize channels by using keyboard shortcuts:

1- To group channels, first click on the **Modify** button and then select the channels while pressing the **SHIFT** key.



To deselect a channel from a group, click on the **Modify** button and deselect the channel while pressing the **SHIFT** key.

2- To synchronize channels, proceed in the same way as for grouping, but with the **CTRL** key instead of the **SHIFT** key.



3- Channel with linked experiments can either be grouped or synchronized.

Tip: Loading the same technique with different parameters on many channels

Let us say a user wants to perform the same technique on several channels but with slightly different parameters. Instead of setting up the techniques individually for each channel, the group function can be used to have the same technique on all channels. Then if the user "ungroups" the channels, the technique will still appear on each channel. The desired parameters can then be set and the channels synchronized.

2.9.2 Stack experiments

Stack experiments are available with our multichannel potentiostat with VMP3 technology i.e. VMP3, VSP and even Bi-Stat. In EC-Lab®, a stack is composed of several cells (batteries,

fuel cells, photovoltaic cells) connected in series. The current of the full stack and the current flowing through each element of the stack are the same. The voltage of the whole stack is the sum of the voltage of each element. The master channel controls the current flowing through the whole stack and the slave channels are used to measure the voltage of each element. Depending of the potential difference between the beginning and the end of the stack and the current needed, it might be necessary to couple a current booster or a load box to the master channel. Using our accessory SAM-50, which is a voltage sense adapter from 10 V to 50 V in addition with a 50 V load box (CLB-2000), the user can easily study stacks of fuel cells up to 50 V. (Please refer to the Technical Note [#27](#) for more details about SAM-50).

There are two ways to access the stack mode:

1. When launching the EC-Lab® software, if a multichannel system is detected the opening window will propose to create a **“New Stack”** experiment or to **“Load Stack Settings”**.

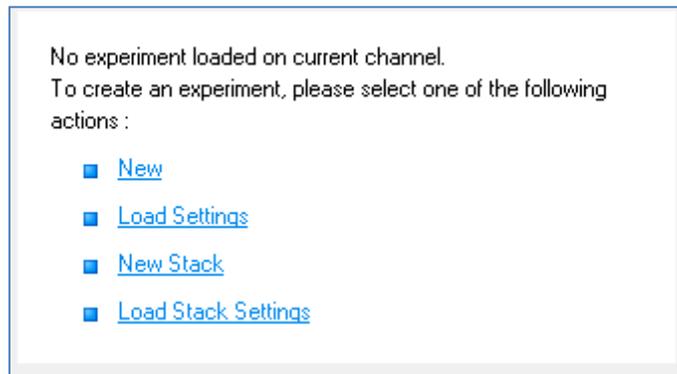


Fig. 69: Experiment selection.

2. If EC-Lab® is connected to a suitable multichannel, the **Group/Synchronize/Stack** window accessed using this button will show the **“Stack”** option in the drop box (cf Fig. 68).

When clicking on one of these choices, the following window appears for channels selection.

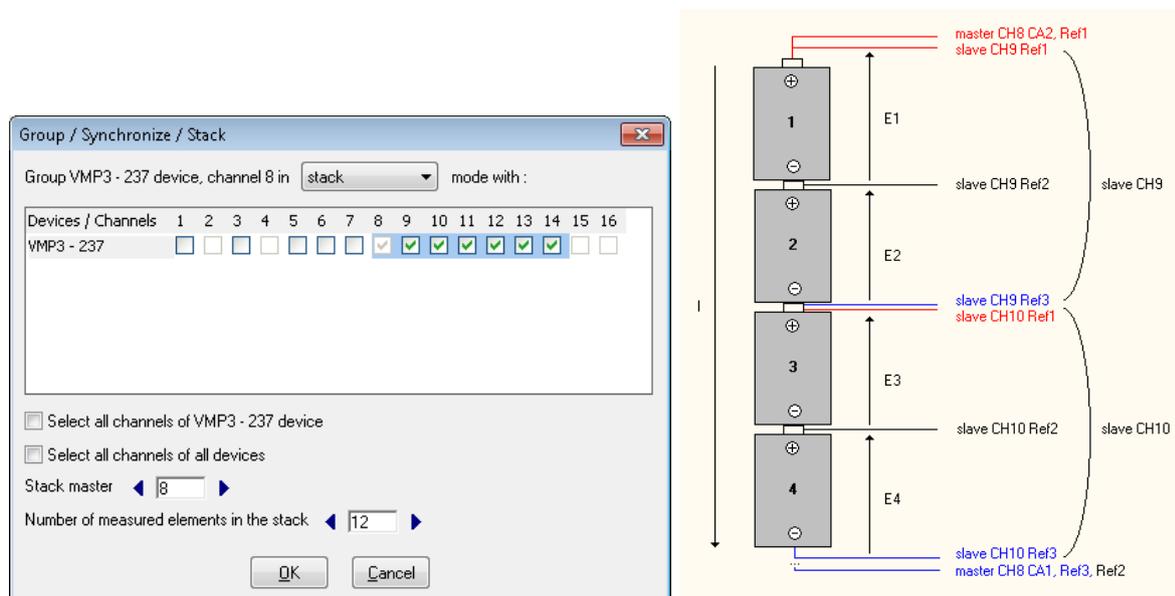


Fig. 70: Channel selection window for Stack measurements.

Using the graphic on the right, the user can select the master channel and the slaves. The master channel is the channel that is active when the Stack window is open.

Each slave channel will be able to measure the potentials on two elements using Ref1, Ref2 and Ref3. The potential of the first element is **Ref1-Ref2** and the potential of the second element is **Ref2-Ref3**.

As an example, with the picture above, the master channel is ch8 and the unit has 6 channels to follow the slaves so the total amount of measured elements in the stack is 12. On the slave channels the current wires (CA1 and CA2) are not used. Most of the techniques and applications can be used and linked in “Stack” mode. When the user clicks on the “OK” button, the “Techniques selection” window is automatically displayed. The user can create the experiment with one or more techniques.

Fig. 69 shows an example of an impedance measurement performed on a stack of batteries. The technique used was PEIS (for more information please refer to the “Techniques and Applications” Manual). In this example the master channel controls the potential of a stack of 10 elements and measures the current flowing through the whole stack. The impedance of the whole stack is shown in the bottom part of the graph and the impedance graphs of each element in the top part of the graph. Only 6 channels are necessary: one for the master channel and 5 for the slave channels.

Fig. 70 shows an example of a GCPL measurement (for more information please refer to the “Techniques and Applications” Manual) performed on a stack of four elements.

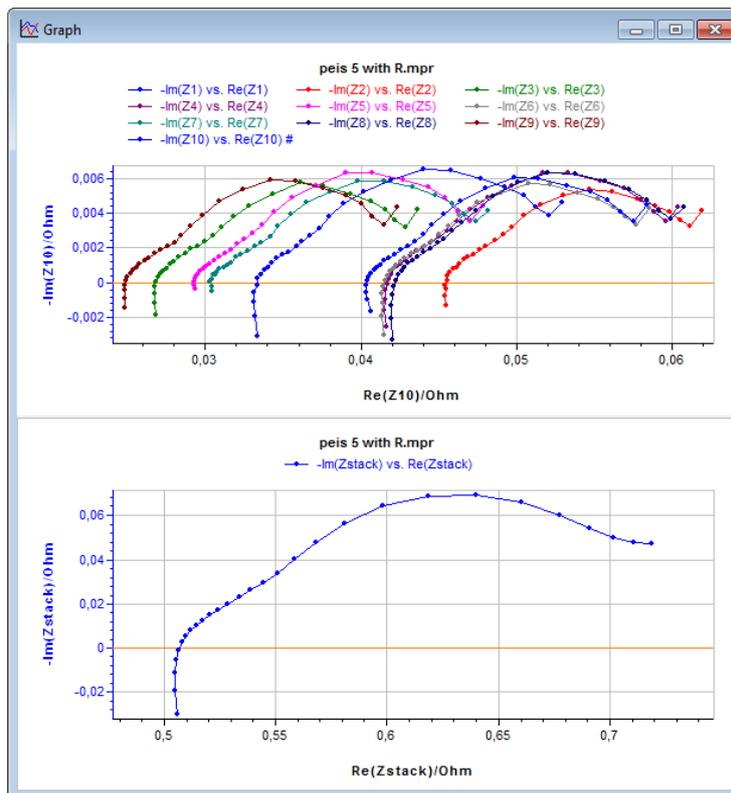


Fig. 71 : Stack PEIS measurement with the impedance graph of the whole stack (bottom) and of each slave channel (top).

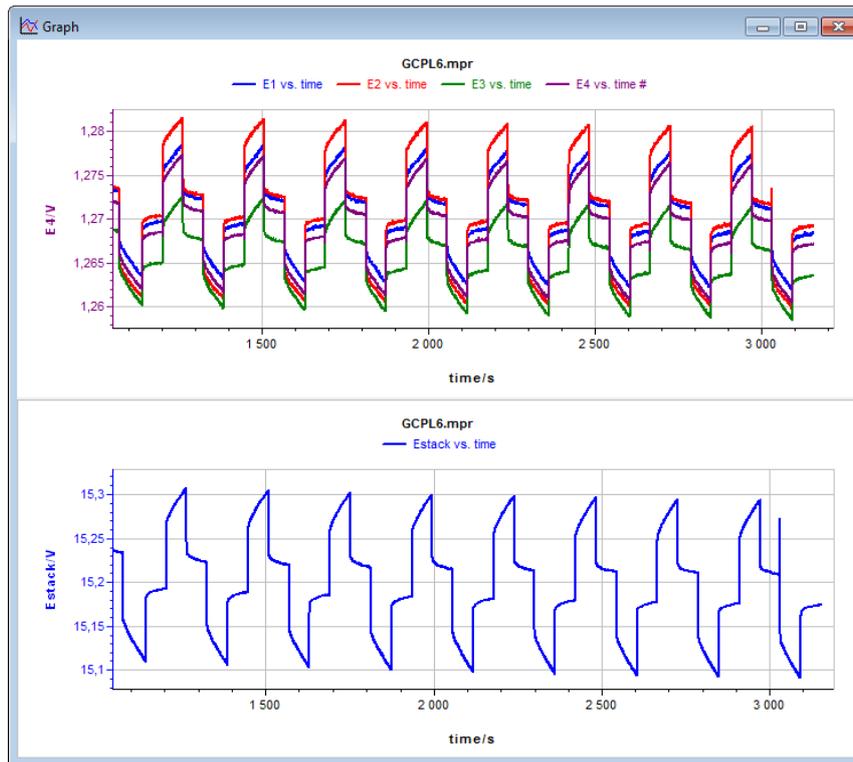


Fig. 72 : GCPL experiment on a stack of four elements (top) and on the whole stack (bottom).

On Fig. 71, one can see that for stack experiment a "Slave" selection is available to display all the slave data points in the same graphic window. For EIS experiments, Nyquist and Bode plots are available both for the whole stack and for the elements.

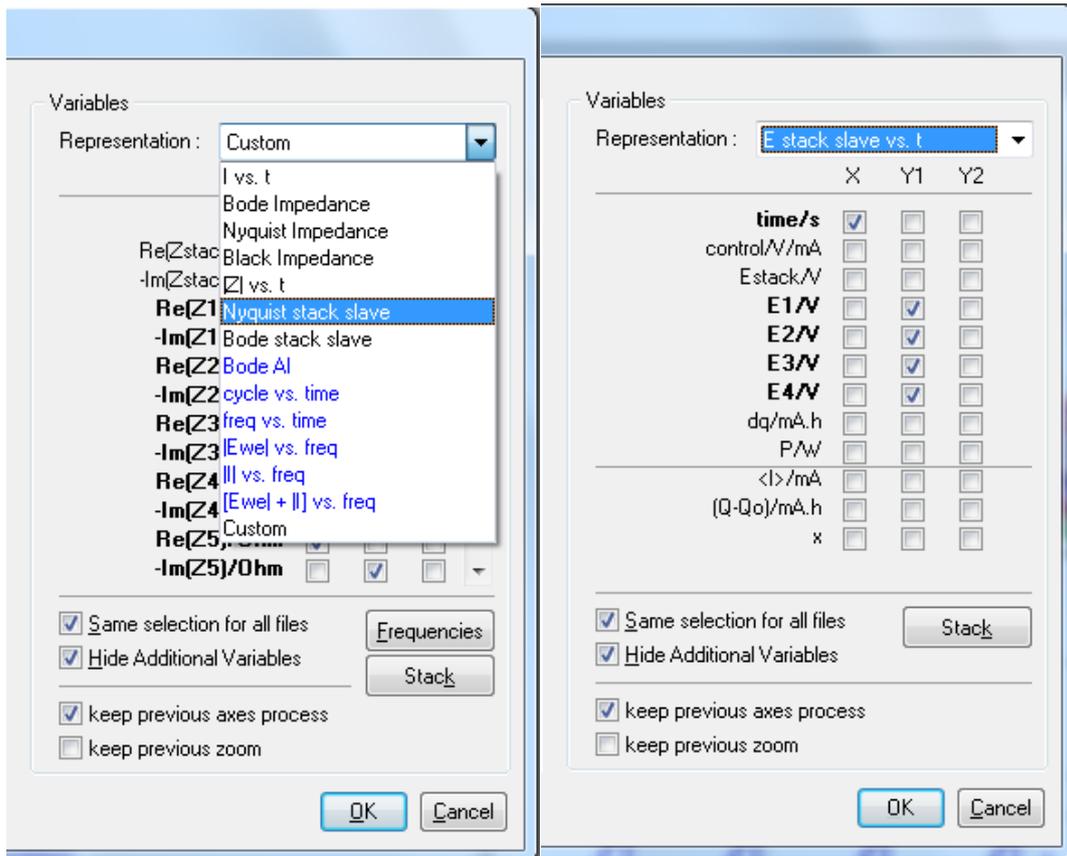


Fig. 73: PEIS (left) and GCPL (right) selection window for a stack experiment

Tips: if the user wants to perform impedance measurements on stacks, impedance ability is only needed on the master channel. With a VMP3 with 16 channels and only 1 with impedance ability, impedance measurements can be performed on up to 30 elements (assuming that the control voltage of the stack is lower than 20 V).

2.10 Batch mode

The batch offers the possibility to link a lot of experiments as a series of settings files (i.e. .mps files). In this configuration, the computer is the master of the experiment and sends one .mps file after the other (when the previous experiment is finished). The instrument is not autonomous in this case and a Network communications failure will stop the experiment. To display the batch selection window, click on **Batch** in the **Tools** menu:

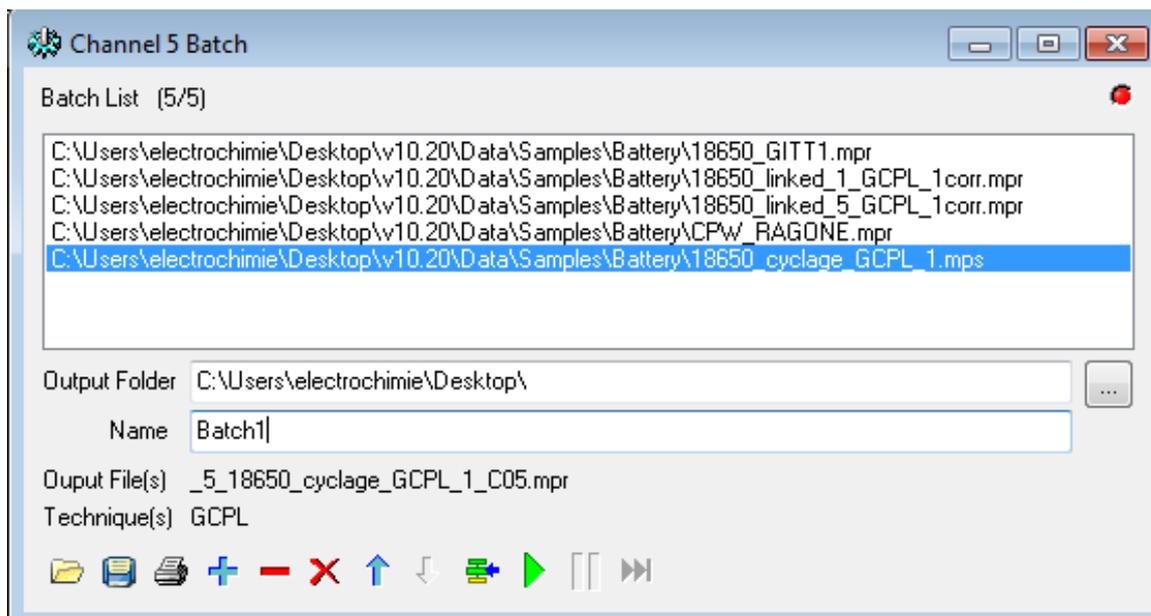


Fig. 74: Batch selection window.

When the batch window is open, it is empty. To add settings (*.mps) or data files (*.mpr) which also include the experiment settings, click on the “+” button then select the correct folder to find the files. Files from different folders can be loaded in the same batch.

The user must:

- a. define an output folder where the created batch experiment files will be stored,
- b. give a file name for the batch.

With the batch name the software will automatically generate a data file with the name for each source file:

“Batch name” + “_” + “number in the batch list” + “_” + “source file name” + “channel number”
+ “.mpr”

For the user’s convenience, the technique used in the selected file is displayed. Several functions are available with buttons at the bottom of the window to open, save, or print a batch, to add, remove move up and down, and insert setting files into the batch. During the Run, the user can pause the experiment and go to the next settings file.

Notes:

- if the number of techniques is lower than 20, it is often more convenient to use linked techniques.
- it is not possible to loop a batch i.e. to set the repetition of a batch a certain number of times.

2.11 Data properties

2.11.1 Type of data files

Several files using your filename with different extensions (.mp*) are created:

File extension	Description
Automatically created file	
.mpr	Raw data binary file, which contains the current parameter settings (refreshed at each modification) of the detailed diagram and cell characteristic windows. <i>This file includes all the information of the .mps file.</i>
Files created by the user	
.mps	Settings file, which contains all the parameters of the experiment. The settings can be saved as default for a given technique. It corresponds to the header of the raw data file. <i>This file can also be generated for linked techniques.</i>
.mpt	The .mpt file is a text format file generated when the user exports the raw .mpr file in text format.
.fit	This file is generated when the user makes one or several fits on an .mpr or a .mpp. The results of the fits are saved one after the other when the user clicks on the "Save" button. This file is a text file that can be opened. Each fit result can be printed alone or with other fits.
.mpp	Temporary binary file, available for particular protocols, derived from the .mpr file. This file is used for real time display of parameters obtained by raw data processing e.g. the integrated charge since the start of the experiment, the average current between two recordings (chronocoulometry).
Temporary files	
.mpl	Temporary text file, which contains the experiment conditions: the instrument IP number, the channel number, the username, the filename and its location, the parameters settings and the cell characteristics at the beginning of the experiment. <i>The user can choose to keep this file using Config\Options menu.</i>
Hidden files	
.mgr	Hidden file including the graphic properties of the corresponding raw .mpr file.
.mgp	As with the mgr file, the .mgp file is hidden and includes the graphic properties of the processed file (.mpp).

During the experiment:

- Data from measurement results are appended to the .mpr file,
- Possible modifications of the parameter settings are updated in the .mpl file and replaced in the header of the .mpr file. The .mpl file is then the "Log" of the experiment. During the experiment, this file can be read with a text editor, but users should not try to write in this file or to save it because any modification will make it unusable by the EC-Lab[®] software.

2.11.2 Variables description

Several variables are standard and common to any technique of the software. Every data file contains state bytes that can be hidden in the selector. Several additional variables are dependent of the technique used (cf Additional variables). Depending on the techniques, some

processed variables can be created (either automatically or by the user). For EIS techniques, the variables are related to Z and admittance variables can be obtained by processing.

Variables description	Variable name and unit
Common variables	
Time	time/s
I: current	I/mA
E_{we} : WE potential versus REF	E_{we}/V
dq : charge increment between two recorded values	dq/mA.h
E_{ctrl} : potential control	control/V
I_{ctrl} : current control	control/mA
E_{ctrl}/I_{ctrl} : potential or current control	control/V/mA
E_{ce} : CE potential versus REF	E_{ce}/V
$E_{we}-E_{ce}$: WE versus CE potential	$E_{we}-E_{ce}/V$
$\langle I \rangle$, average current over the potential step (calculated from $I = dQ/dt$)	$\langle I \rangle/mA$
State byte	
Mode = Intention/Potential/Relax, State byte (bits n°1 and 2)	mode
Oxidation/Reduction, State byte (bit n°3)	ox/red
Error bit, State byte (bit n°4)	error
Control changes, State byte (bit n°5)	control changes
Changes of N_s , State byte (bit n°6)	N_s changes
Experiment counter value has changed (bit n°8)	counter inc.
External devices: Temperature / rotating electrodes	
Temperature control	control/°C
Temperature measure	T/°C
Rotating electrode speed control value	speed/rpm
User defined recorded variable with its unit set as additional analog inputs	User/Unit
Additional variables	
Additional analog input 1	Analog In1/V
Additional analog input 2	Analog In2/V
Additional analog input 3 (for VMP only)	Analog In3/V
dQ: charge on a potential step	dQ/mA.h
ΔQ : charge on a cycle	$\Delta Q/mA.h$
I forward: in pulsed techniques current measured at the end of the pulse	I forward/A
I reverse: in pulsed techniques, current measured on the reverse part	I reverse/A
I delta: difference between I forward and I reverse	I delta/A
E step: potential step increment (sweep pulsed techniques)	E step/V

Variables description	Variable name and unit
Processed variables	
Q-Q ₀ : charge from the beginning of the experiment	(Q-Q ₀)/mA.h
Q charge: Q for a charge cycle reinitialized every cycle	Qcharge/mA.h
Q discharge: Q for a discharge cycle reinitialized every cycle	Qdischarge/mA.h
x: normalized charge	x
Apparent resistance	"R _i "/Ω
Cycle number	cycle number
Power: in CPW, calculated by E*I	P/W
Differential current over time (for potentiometric technique only)	dI/dt/mA/s
Energy: in CPW calculated by E*I*t	Energy/W.h
Energy charge: E*I*t for I>0	E charge/W.h
Energy discharge: E*I*t for I<0	E discharge/W.h
Cycle time: time elapsed during each cycle	cycle time/s
Step time: time elapsed	step time/s
Discharge time : time elapsed during each discharge (I<0) reset to 0 at the end of each charge	discharge time/s
Charge time: time elapsed during each charge (I>0) reset to 0 at the end of each discharge	charge time/s
Incremental (or differential) capacity over the potential dE during charge or discharge	d(Q-Q ₀)/dE/mAh/V
R _p : polarization resistance in corrosimetry	R _p /Ω
I _{corr} : corrosion current resulting from R _p calculation	I _{corr} /A
E _{corr} : corrosion potential resulting from R _p calculation	E _{corr} /V
C ⁻² : Inverse of square capacitance for Mott-Schottky plot	C ⁻² /F ⁻²
C: Capacitance for Mott-Schottky plot	C/F
Impedance	
Frequency	freq/Hz
E _{we} : module of E _w	E _{we} /V
I : module of I	I /A
Phase of Z	Phase(Z)/deg
Z : module of Z	Z /Ω
Re(Z): real part of Z	Re(Z)/Ω
-Im(Z):-imaginary part of Z	-Im(Z)/Ω
<E _{we} >: averaged E _w value for each frequency	<E >/V
<I>: averaged I value for each frequency	<I>/A
I Range: current range	I Range
Calculated Impedance variables	
Capacitance calculated using an R+C (series) equivalent circuit	Cs/F
Capacitance calculated using an R/C (parallel) equivalent circuit	Cp/F
Y : Admittance magnitude (in Ω ⁻¹)	Y /Ω ⁻¹
Admittance phase (in degrees)	Phase(Y)/deg
Re(Y): real part of Y (in Ω ⁻¹)	Re(Y)/Ω ⁻¹
-Im(Y):-imaginary part of Y (in Ω ⁻¹)	-Im(Y)/Ω ⁻¹

2.11.3 Data recording

In all the technique sequences, the user is able to define different modes for data recording. The main mode is to fix the recording resolution of the measured variable (potential **dE**, current **dI**, charge **dQ**) with at least a recording every predetermined time interval **dt** (from 0.1 to 9999 s). The time interval condition helps in having a minimum amount of recorded points in case the variation of the observed variable is less than the chosen resolution for a long period of time (potential close to equilibrium, process leading to a potential plateau, etc...).

On the contrary, if the system is very unstable or noisy and the chosen variable interval condition is too small, the amount of recorded points can be very high, which can lead to a saturation of the buffer.

For open circuit period (OCV) nothing is controlled and only the potential is recorded. The recording conditions for OCV periods are in time variation (dt) and/or in potential variation (dE).

For techniques with potential control, two different recording conditions are now available:

- 1- on a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ),
- 2- on an averaged current value either on a potential step (potentiodynamic mode) or a time variation (potentiostatic mode).

For techniques with current control, the recording conditions are on a time variation (dt), potential variation (dE) and/or charge variation (dQ). Recording conditions are described in the application section for each technique

If the user wants to force a periodic recording in time, a large value or more simply 0 must be set in the recording resolution of the variable. The box for which the resolution is 0 has the same color as the background. This color code means that this box is not activated and also not taken into account for recording.

2.11.4 Data saving

Each channel has its own memory buffer to store data points. This buffer is rather small (around 700 kB).

The data buffer on the communication board is much larger. The memory or number of bytes allocated to each channel depends on the number of used channels. The buffer size decreases when the number of channels in the instrument increases. The size represented by each datapoint depends on the technique used. Fig. 72 gives the minimal amount of stored data points for each buffer board.

	ARM (from 11/2005)	VM62	VM42
1 channel	640 000	480 000	48 000
16 channels	40 000	30 000	3 000

Fig. 75: Minimal memory size in data points of the buffer boards

Data transfer between the instrument and the PC via the Ethernet line is automatically started when its buffer is 5 % full. Please note that the user can define the data saving frequency in the “**Option\General**” menu (see section 2.14.1, page 59). In the same menu the user can also define an automatic creation of the data file name.

2.12 Changing the channel owner

Click on **C**onfig, **U**ser and enter your username in the following window:

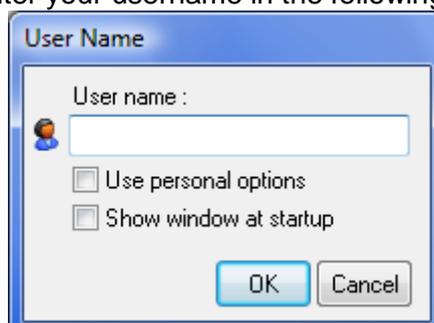


Fig. 76: User name window.

In the case where the new user replaces the current user of a channel (e.g. MyName), EC-Lab[®] software displays a warning message: **"WARNING: channel x belongs to "MyName". By accepting the modification you will replace the current owner. Do you want to continue?"**

It is not possible to change the user name of a channel when an experiment is running. Changing a channel owner is only possible when the channel is stopped.

2.13 Virtual potentiostat

If there is no instrument connected to the computer, it is nonetheless possible to setup an experiment in the virtual mode including boosters and options for the instrument. When the instrument is selected the corresponding number of available channels is displayed with additional choice for amplifiers and cables (for SP-300 technology if required). In this mode the user can create a setup and save it as an .mps file.

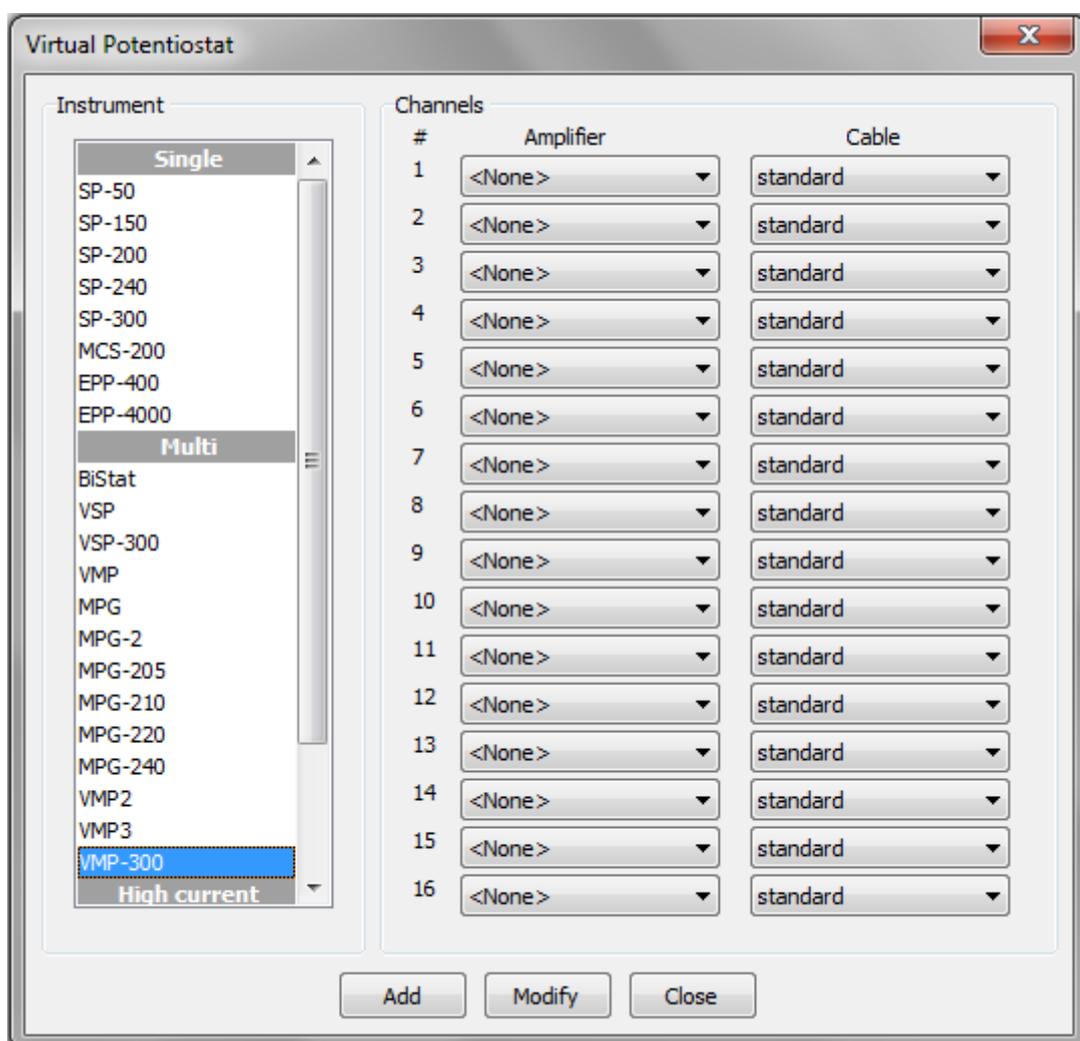


Fig. 77: VMP-300 Virtual mode.

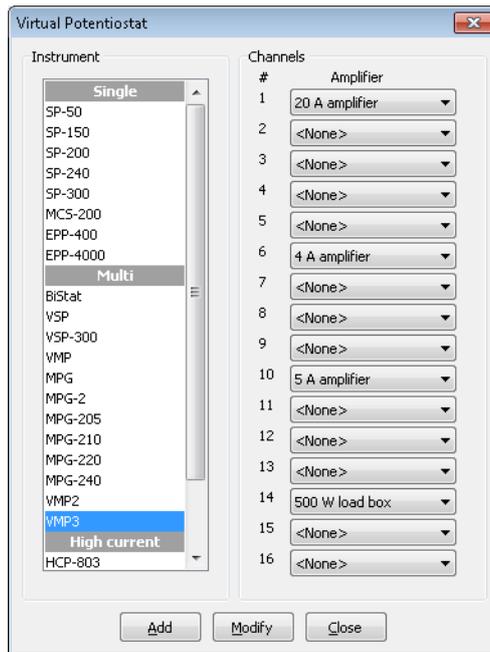


Fig. 78: VMP3 Virtual mode.

2.14 Configuration options

Choose the **Config\Options...** menu to load the Option window:

2.14.1 General Options

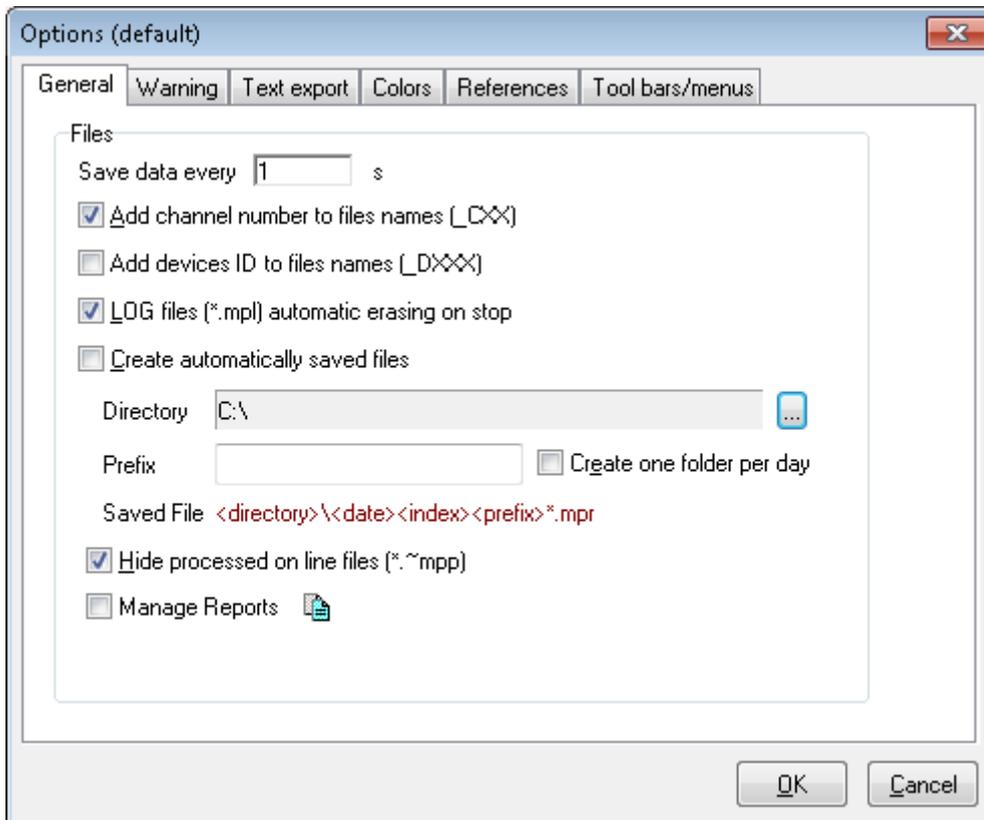


Fig. 79: Option window, General tab.

The general options window is composed of the following options:

- “**Save data every...s**” defines the data transfer rate between the buffer board to the computer. Enter a non-zero time value into the edit box. The data will be then transferred at this defined time interval.
- Select the automatic adding of the channel number to the file name.
- Select the automatic adding of the device ID to the file name. Either the last three digits of the IP address if connected through Ethernet or USB if connected through USB. *Example : an experiment created with the channel 3 of a VSP connected through Ethernet with the IP address 192.109.209.207 will be named : experiment_D207_C03*
- Erase the LOG file automatically on stop. The LOG file will still be contained in the .mpr file.
- Create an automatic data saving. The user must choose the directory to save the data file. The prefix name must be defined and the software will automatically add the date and the index number.
- By default, the on-line automatically processed files are hidden to reduce the number of files in directories. The on-line processed variables are now automatically displayed on the graphic window.
- Ability to manage reports of the experiment (See section 5.3 for more info).

2.14.2 Warning Options

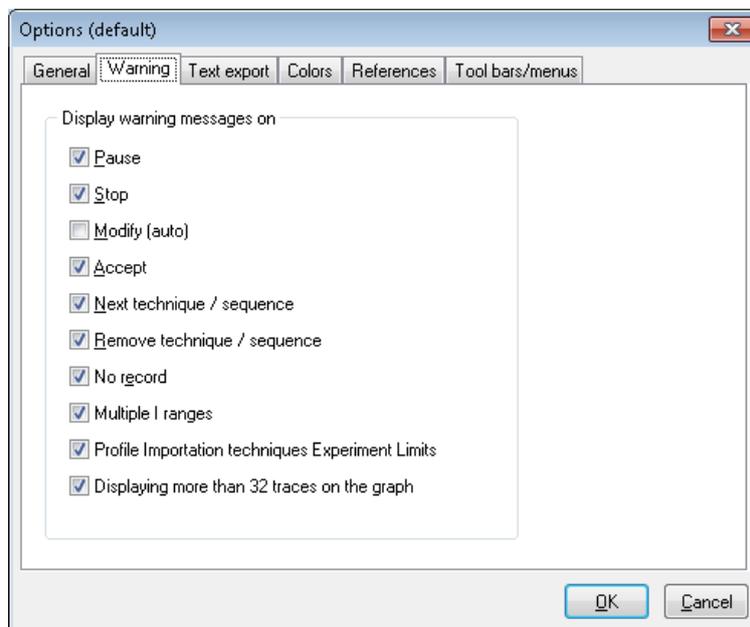


Fig. 80: Option window, Warning tab.

Display or hide warning messages when the following functions are used: Pause, Stop, Modify, Accept, Next technique, Remove technique, No data points recorded, Multiple I ranges (different current ranges are selected in the different sequences), when the Experiment Limits are reached using a Profile Importation technique and finally when 32 traces (curves) are plotted on one single graph.

2.14.3 Text Export Options

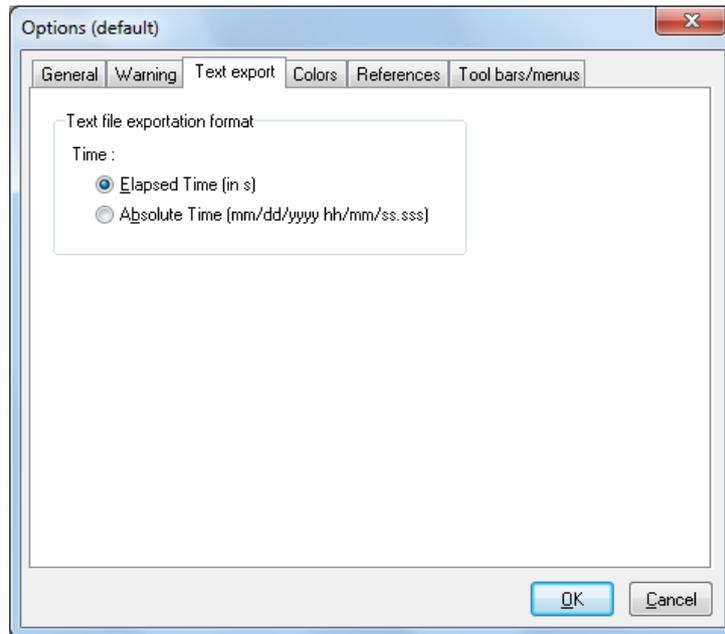


Fig. 81: Option window, Text export tab.

The time recording format for the exported files can be chosen.

2.14.4 Color Options

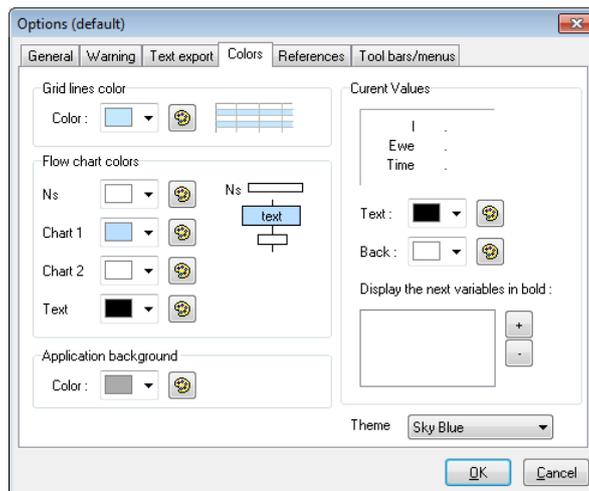


Fig. 82: Option window, Colors tab.

- The grid line color of the grid lines, for the multi-line parameters settings (see the GCPL protocol) can be chosen.
 - The background of the flow chart and text color can be chosen.
- The custom buttons allow the user to define additional colors that appear at the end of each drop box. The default color theme is Sky Blue.

2.14.5 References Options

- Displays all the reference electrodes registered in EC-Lab[®]. The default reference electrodes are in black.

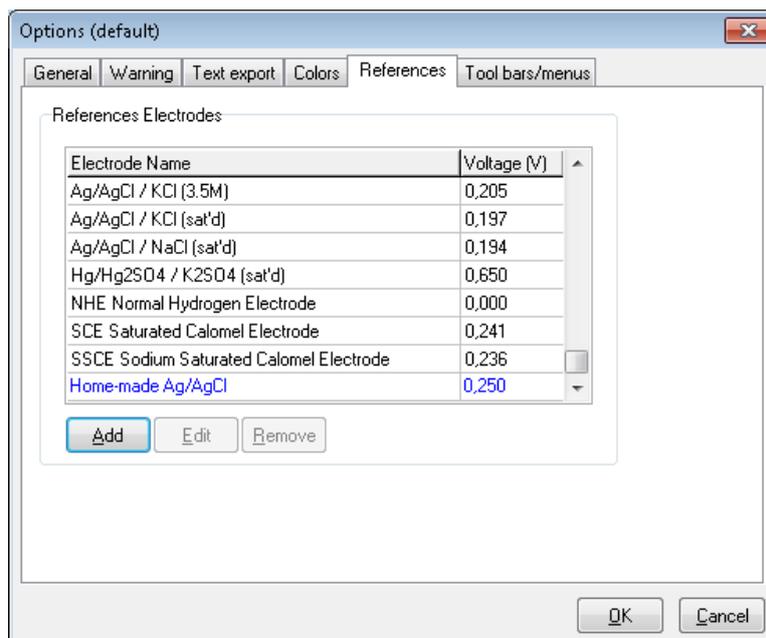
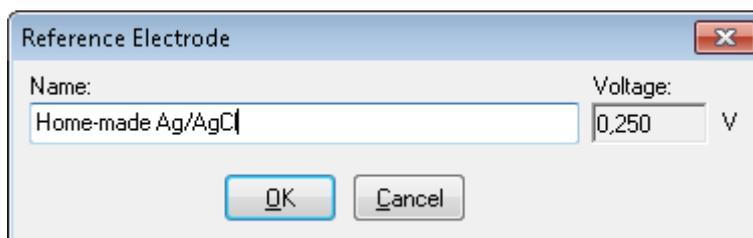


Fig. 83: Option window, references tab.

- Allows the user to add, edit, or remove his own reference electrode (and its potential vs. NHE). Then the following window appears:



The new reference electrode will now be displayed in blue characters in the table.

The standard potentials of reference electrodes have been extracted from the following references.

- Electrochemical Methods, A. J. Bard & L. R. Faulkner, Wiley, New York, 1980.
- Electrochemistry for Chemists, D. T. Sawyer, A. Sobkowiak, J. L. Roberts Jr, 2nd Ed, Wiley, New York, 1995.
- Handbook of Analytical Chemistry, L. Meites, Ed McGraw Hill, New York, 1963.

2.14.6 Tool bars/menus Options

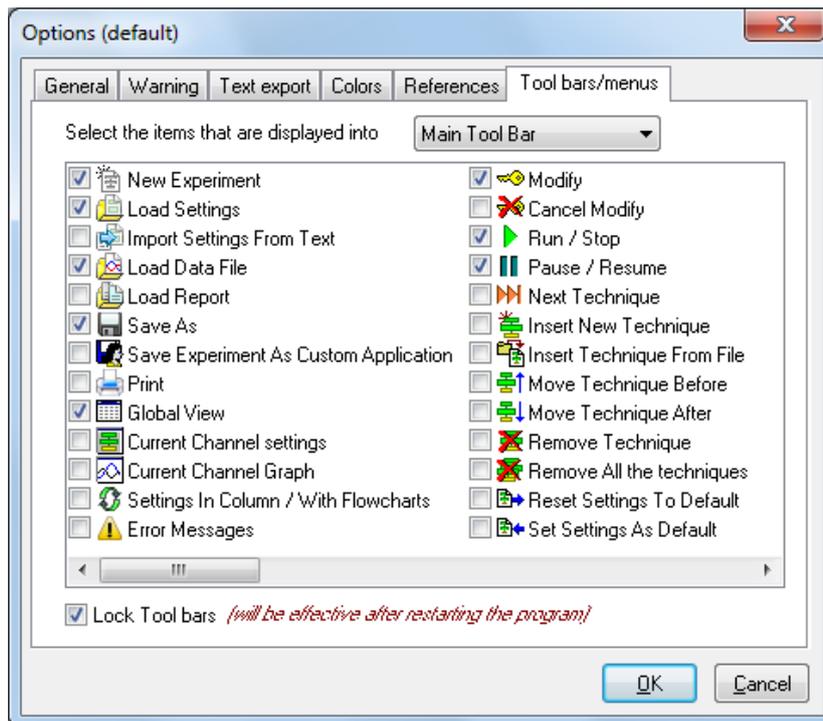


Fig. 84: Options window, Tool bars tab.

The tool bar option can be used to select the icons wanted in the main tool bar and the graph tool bar from all icons available in EC-Lab® software. Both tool bars can be locked or unlocked. This is effective only when the software is restarted. It is also possible to select the functions available on the graphic right-click menu (“Graphic Popup Menu”) and on the settings window right-click menu (“Settings Popup Menu”).

3. EC-Lab® software: Graphic Display

3.1 The Graphic window

The EC-Lab® application includes a graphic facility to display experiments on-line or/and off-line. Several independent graphic windows can be opened while an experiment is running. The user can perform an electrochemical experiment and follow the plot on the current graphic window and fit or analyze results from previous experiments on another graphic window. The user has also the possibility to add graphs to existing graphic window. In that case the window is divided in two graphs or more.

When an experiment is run, the graphic window is automatically opened. Default graphic parameters are chosen (for example plot I vs. E for the CV technique). The default graphic parameters can be replaced by other chosen parameters. To do so, right-click on the graph, select “**Graph properties...**” and activate the box “**Save as default**”.

In the case of linked techniques, two different graphic windows will be displayed, one for all voltamperometric techniques (as a function of time) and one for the impedance spectroscopy (Nyquist plot). For synchronous multi-channel protocol, all the corresponding files are displayed in the same way as linked techniques. The graphic window contains a right-click menu different from the Parameters Settings window right-click.

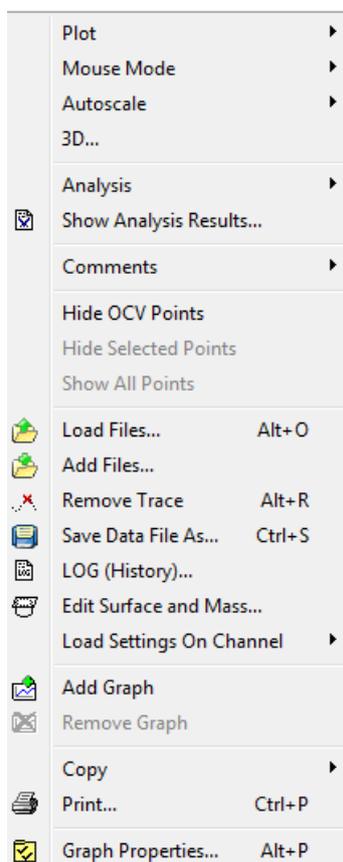


Fig. 85: Mouse right-click on the graphic window.

The right-click window is divided into several blocks.

- In the first block, four menus are available:

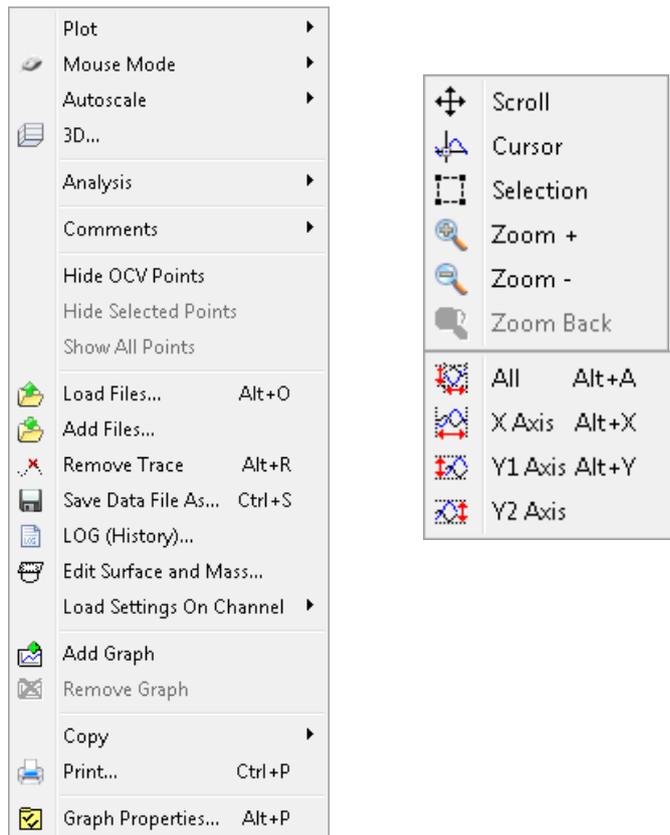


Fig. 86: Plot, Mouse mode selection and mouse auto scale options.

The **Plot** tab for the selection of variables displayed on the graph. More info on this are given in part 3.1.4. You can either display the predefined representations available in the Rapid Plot selection tool bar or a custom representation (see 3.1.3).

The **Mouse Mode** selection contains:

The **scroll** is used to move the curve on the graphic window.

The **cursor** allows the user to display the coordinates of all the points of the curve.

The **selection** allows the user to select zone of the curve (data points) either before a fit or an analysis or to hide bad data points.

Zoom + and **Zoom -** are used either with a zone selection (smoothing) or by a mouse left click on the part of the curve that you want to zoom.

Zoom Back is very useful when you have zoomed an undesired zone. It is not limited in the number of actions.

The **Autoscale** is made of different autoscaling functions according to each axis.

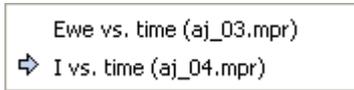
3D is used to displaying the graph in a 3D mode

- The second block contains the **Analysis** tools. More information on **Analysis** are given in part 4.

- The third block is dedicated to the addition of comments or notes on the graph with the possibility to Add and delete a comment zone and paste a comment from the clipboard. The graphic parameters of the comment (background, size font and color, etc...) can be edited by double-clicking on the comment.

- The fourth block is to show or hide OCV points and abnormal (artefact) data points that the user wants to remove before an analysis or a print.

- The fifth block is more dedicated to file selection with **Load files...**, **Add files...**, **Selector...**, **LOG (history)....** The selector will be described in a following section.
- The sixth block is about the graphic display with the **Active trace...**, **Add graph** and **Remove graph**.



This option shows the active trace that can switch to the one of the other trace with a click.

- The seventh block can be used to start, stop, pause or go to the next technique of the experiment
- The eighth block “**Copy** and **Print...**” includes interesting tools:

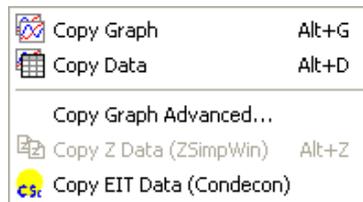


Fig. 87: Mouse copy mode.

The copy mode contains the graph copy, the data copy and the Z data copy.

Copy graph is a copy of the graph to the clipboard in a bitmap format.

Copy data makes a copy of the active data plot (X, Y1, Y2 displayed variables).

Copy Z data copy data in ZsimpWin compatible format in order to paste data directly in this software.

- The ninth block **Graph properties...** can be used to change all the graphic parameters of the trace.
- All these options are explained in more details in the following paragraphs.

3.1.1 Loading a data file

The EC-Lab® software is provided with sample data files. The user can load data file in **Experiment\Load Data File...** or in the graphic window with the mouse right-click select **Load Files....** The following window is displayed:

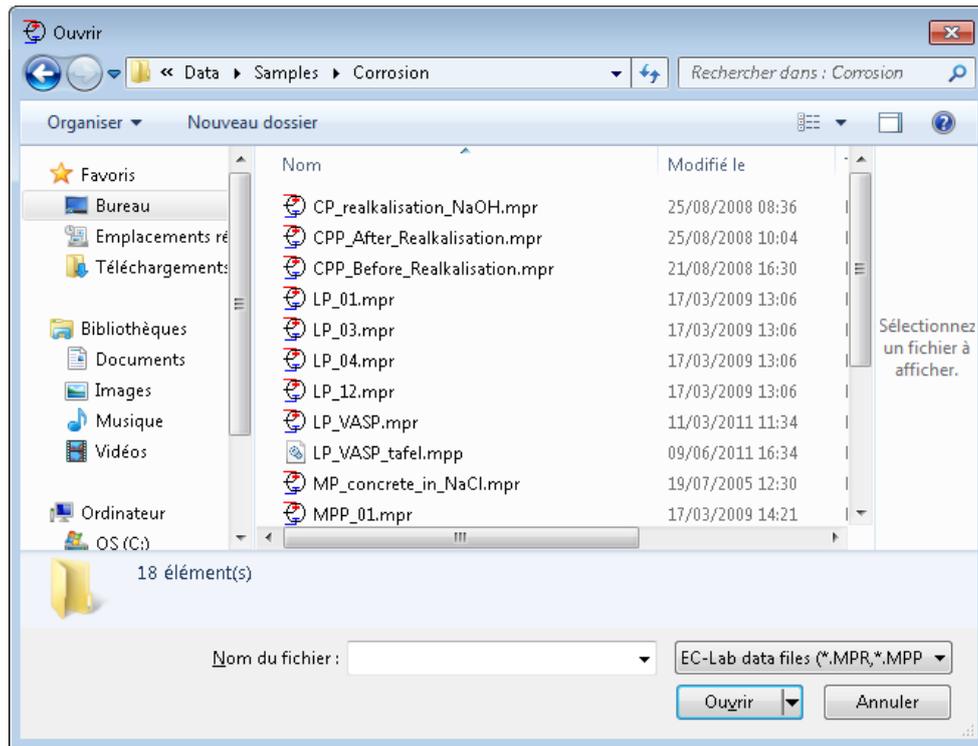


Fig. 88: Open file window.

Select the data file you want to open and click on **Open**. The user can also select and open data file from other manufacturers. In the file type box many file formats have been defined to help the user load data files for analysis. Most of them are text files that can be exported from software controlling other systems. The different available formats are displayed on the figure below:

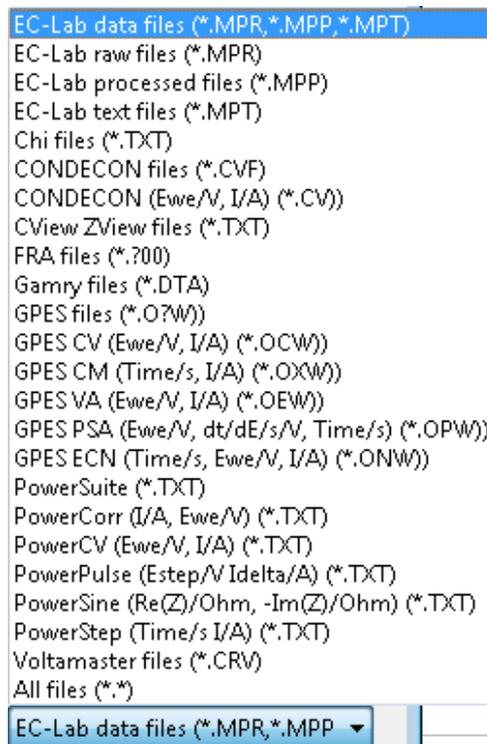


Fig. 89: File type selection.

If a file format is not listed above, the user can use the **Import From Text** option in the **Experiment** menu to manually load its data file. This option is described in section 5.2.3.

3.1.2 EC-Lab® graphic display

Running a Cyclic Voltammetry setting will display the graphic window shown in Fig. 90. The default plot mode for the Cyclic voltammetry technique is **<I> vs. Ewe**. During the run the current recorded data point is displayed in another color (a red circle) and moves along the curve.

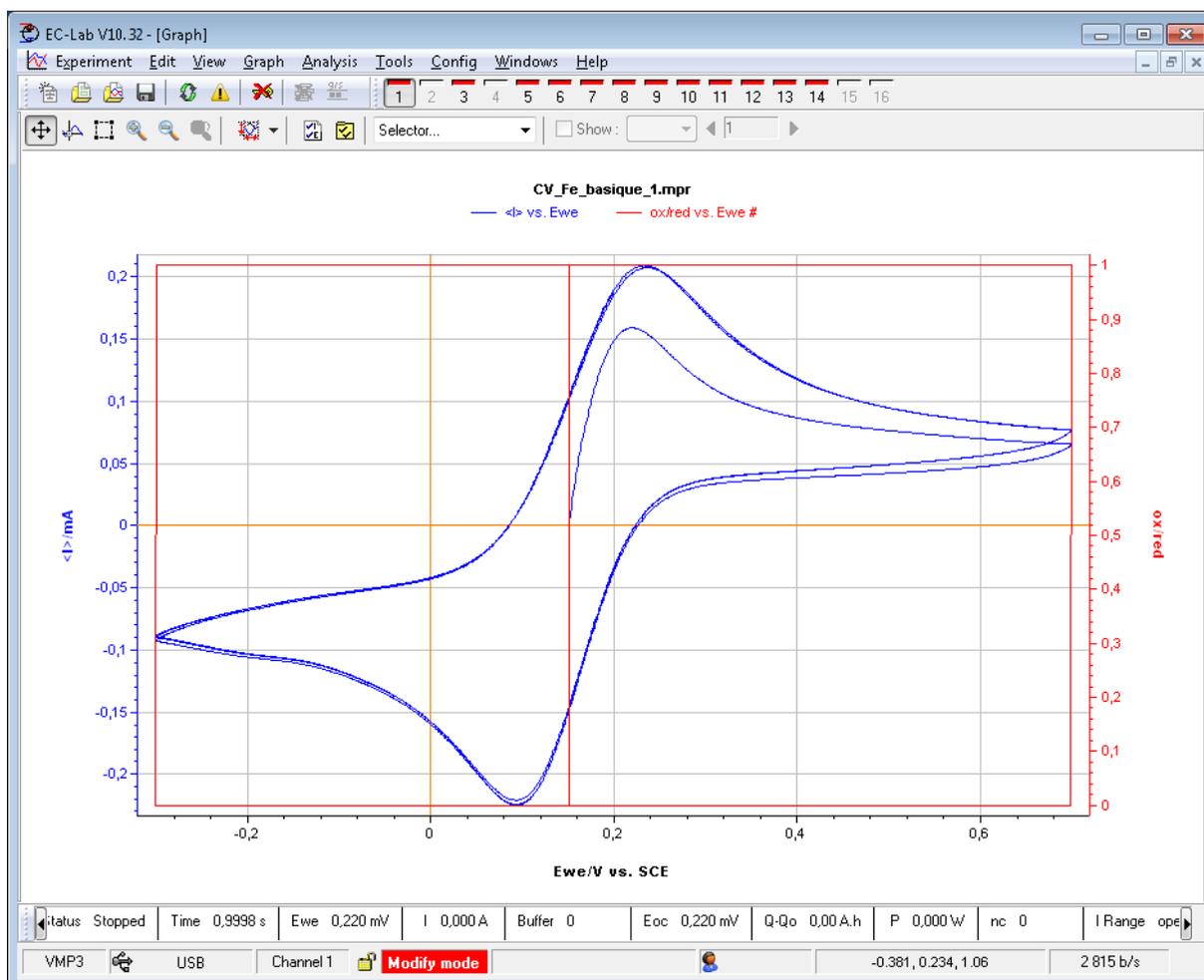


Fig. 90: Graphic window.

As can be seen, the above window (Fig. 90) displays a loaded Cyclic Voltammetry *.mpr file.

To select points, use the selection button . Select a zone by holding the left mouse button. The cursor will draw a rectangle zone around the selected points. Then release the mouse button. The selected points will be highlighted in bold red. The selected zone can be analyzed with fits or hidden from the graph before copying or fitting the graph.

The user can have every point coordinate with the mouse when holding the **SHIFT** key of the keyboard or clicking in the  box. This comment box contains the point number in the experiment and the point coordinates. Origin axes can be displayed with another color on the graphic window.

3.1.3 Graphic tool bar

When the graphic window is displayed the graphic tools bar automatically appears at the top. This bar is attached to the graphic window.

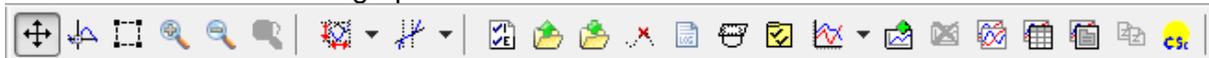
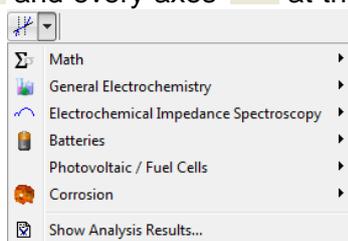


Fig. 91: Graphic tool bar.

This tool bar can contain all commands usable on the graphic window. The five first buttons are for the different mouse modes. The four buttons in the second frame concern rescaling. Data transfer from the instrument to the PC leads to immediate display in an automatic scaling mode. The graphic window is always rescaled. These buttons allow rescaling on X axis , Y1 axis , Y2 axis  and every axes  at the same time. All the **Analysis** tools



are available using a drop box:

The icon of the last used analysis is displayed in the graph tool bar. The analysis can be performed as many times as needed just by clicking on the icon.

Another tool bar is available with EC-Lab® graphic window. On the left, a scroll menu allows to choose among several predefined representations the desired one. The available plots are dynamic and depend on the file type (time evolution or frequency evolution).



Fig. 92: Fast selection plot tool bar.

At the end of this menu, the user can find a “Custom” option that opens the File selection window for further graphic visualization. On the right part of the tool bar a “Show” option makes possible to the user to show only one cycle or one loop.

The user can define his own fast graphic displaying mode. To do that, see the section below.

3.1.4 The data file and plot selection window

Right-click on the mouse and select “Plot”, select “Selector...” in EC-Lab® **Graph** menu or click on the “Selector” button  to open the selection window. The following window will be displayed:

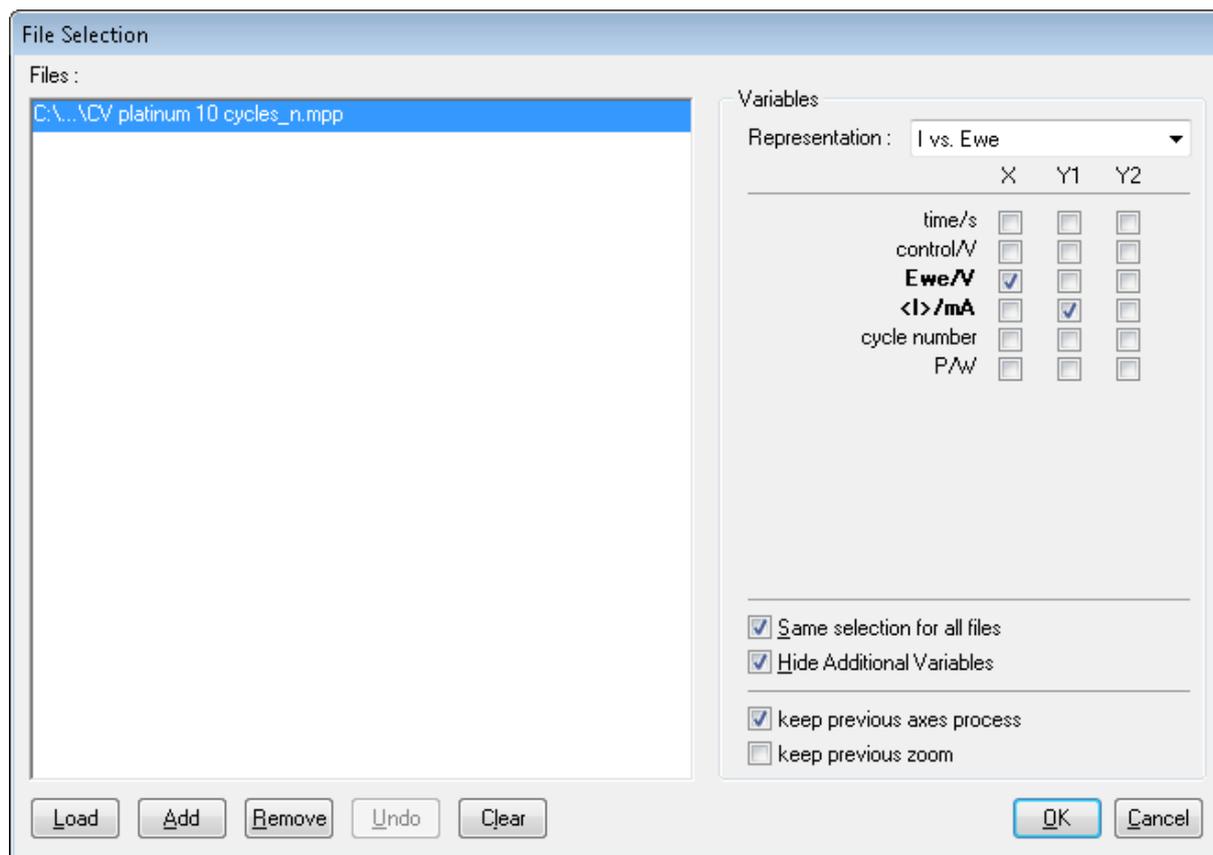


Fig. 93: File selection window.

The user can choose to plot other variables as the predefined ones. The loaded file contains the recording of the following variables: the time (time/s), the working electrode controlled potential (control/V), the working electrode measured potential (E_{we}/V), the average current (average values on every potential steps, $\langle I \rangle / mA$), and the state byte. Other variables (such as cycle number) may be displayed depending on the protocol of the experiment. The state byte includes the variables: mode, ox/red, error, control changes and counter inc. (cycle increment) that indicates different status of the experiment. Most of the time, the user may not be interested in showing the state byte (that is more dedicated to internal files processing). The option **Hide Additional Variables** is checked by default. Unchecking the option will add the state byte variables to the file selection window. It is also possible to keep some previous processes or zooms by ticking the boxes **Keep previous axes process** and **Keep previous zoom**.

Several commands are available to use files:

- **L**oad: replace all files by others.
- **A**dd: add file(s) to the list in order to overlay curves.
- **R**emove: remove the selected file from the list.
- **U**ndo: undo the last operation done.
- **C**lear: remove all files from the window.

X, Y1, and Y2 represent the X axis and two different Y axes (left and right). EC-Lab® users are able to plot data in X, Y1 coordinates or in X, Y1&Y2 coordinates. Select the variables to be displayed on a given axis by clicking the corresponding box (click again to deselect). Select **Same selection for all files** to get the same axis display for several files. A shortcut scroll menu allows a quick selection of the graph plot.

3.2 Graphic tools

3.2.1 Cycles/Loops visualization

The cycles in the **CV** (Cyclic Voltammetry), **CVA** (Cyclic Voltammetry Advanced) and **SV** (Staircase Voltammetry) techniques are automatically generated without any additional action from the user. For experiments made with an older version, the user will have to process the cycle number according to the procedure described below to display each cycle separately. If the selected file contains loops or several cycles then one can display specific loops or cycles.

To access the Cycle/Loop selection, the user needs to make sure the cycle number variable is contained in the data file (either recorded automatically or through processing. In EC-Lab® **Analysis** menu select **General Electrochemistry/Process data**. After loading the data file, select “**Cycle Number**” and “**Process**”. The following window appears:

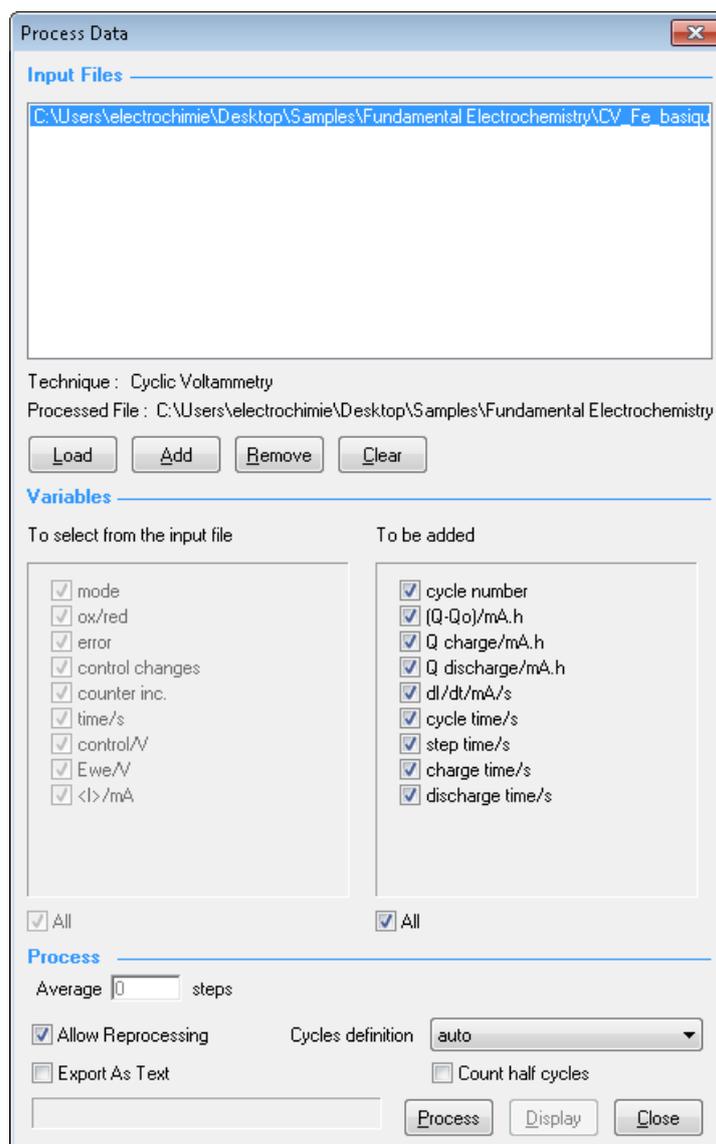


Fig. 94: Loops/cycles process.

Check the variables you need to have. These will be more detailed in part 5. At the end of this operation, **DONE** is displayed and a processed file (*.mpp) is generated in the same folder as the raw data file (*.mpr). Click on the “**Display**” button to automatically display the

processed file. A cycle selection tool is now activated on the graphic tool bar to select the cycle to display:

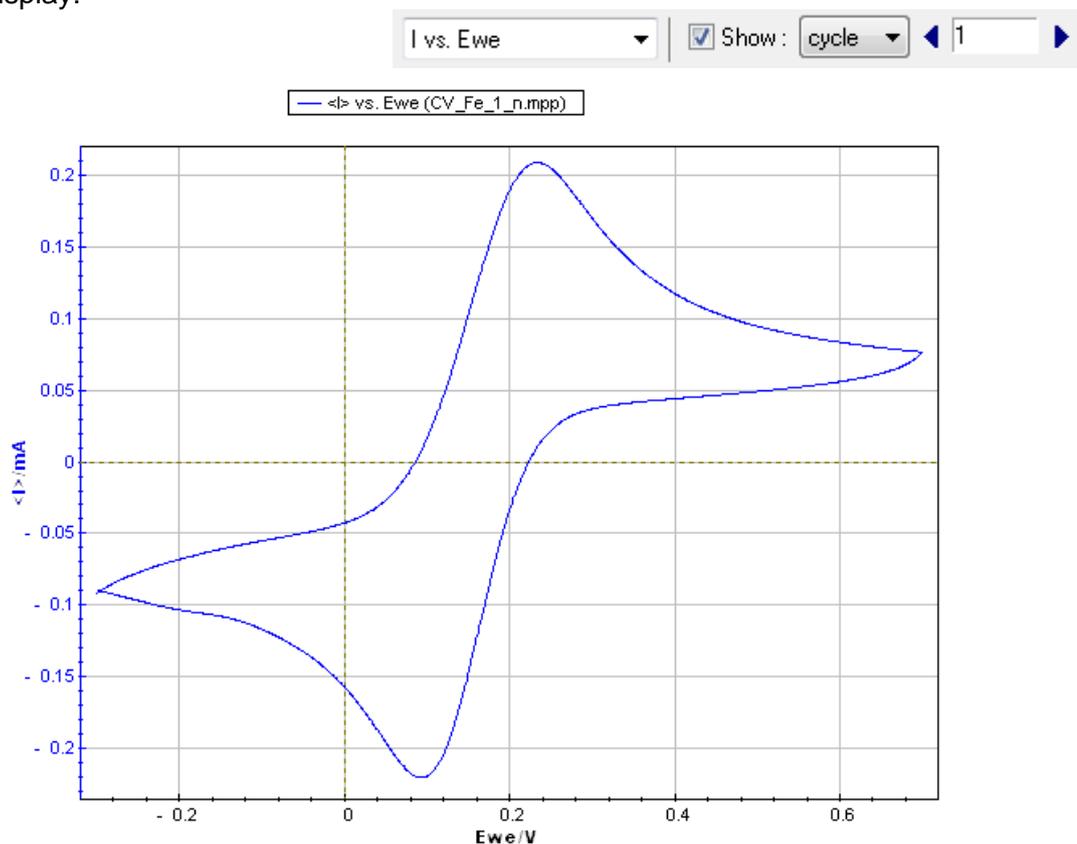


Fig. 95: Cycle selection on a processed file.

The user can see either all cycles or a selected cycle chosen with the scroll box. This option is very useful for peak analysis on a given cycle, especially in analytical electrochemistry.

Note: - If the user wants to copy data (mouse right-click) and paste in a spreadsheet software only data corresponding to the displayed cycle will be copied.

- A title can be added to the data file and appear at the top of the graphic window. Right-click, Select **Graph properties** and choose the **Title** tab.

3.2.2 Show/Hide points

The EC-Lab® software is equipped with a show/hide option on the right-click menu. Abnormal points can now be hidden on the graph in order to perform data fitting without any troubling points. The hidden data points are not removed from the data file. They are only graphically hidden for better fitting. The data points must be selected with the selection mouse mode



before being hidden. Then click on **Hide Selected Points** to reject points.

3.2.3 Add comments on the graph

The graphic package allows the user to add comment zones on the graph. The number of comments zones that can be added on the graph is unlimited.

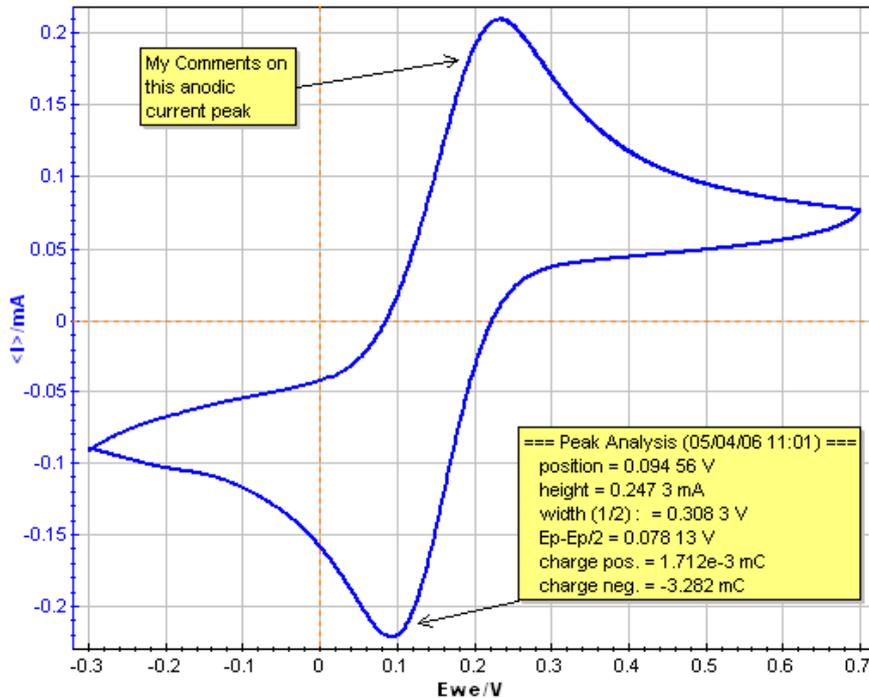


Fig. 96: Comment zones on the graph.

To add **Comment** zones on the graph the user must right-click and select “**Add comments...**”. Then an empty comment zone appears on the graph. To modify this zone, double click on it or right-click on the zone and select “**Edit comments...**”. The following window appears:

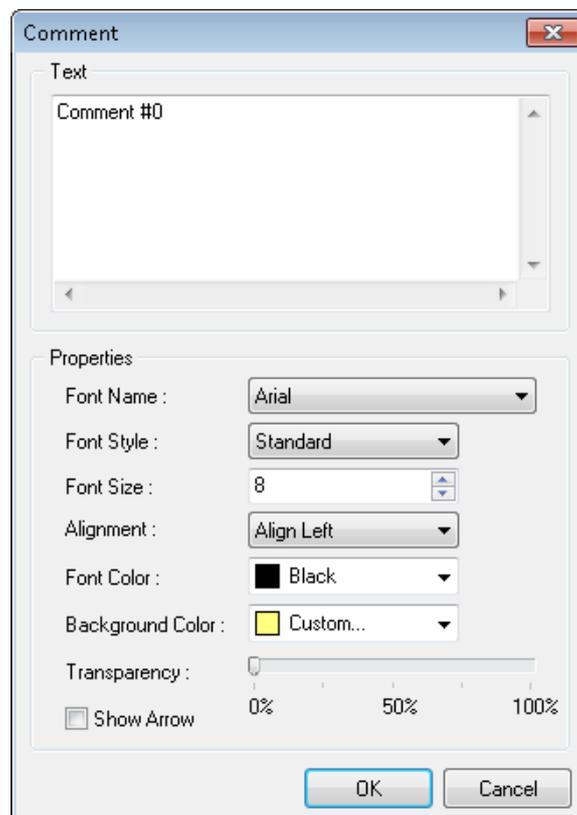


Fig. 97: Comment window.

The user can paste analysis results or other comments into the text frame. Several comment zone properties are available and the user can display an arrow and direct it through the desired part of the curve (by clicking on the end of the arrow).

To remove comments, right-click on the zone and select “Delete comment” or click on the Del. keyboard button.

Note:

- The comment zone is automatically printed on the graph.
- If the graph window is being resized, the size of the comment will remain the same. Make sure the graph window is at the convenient size before adding a comment zone.

3.2.4 Three-Dimensional graphic

A 3D representation is available by right-clicking on the graph menu. It is possible for files having less than 15000 points. After clicking on the 3D menu, the **Selector** menu is available and allows the user to choose the variables to display. An example of the Bode diagram obtained with the 3D representation tool is given Fig. 98.

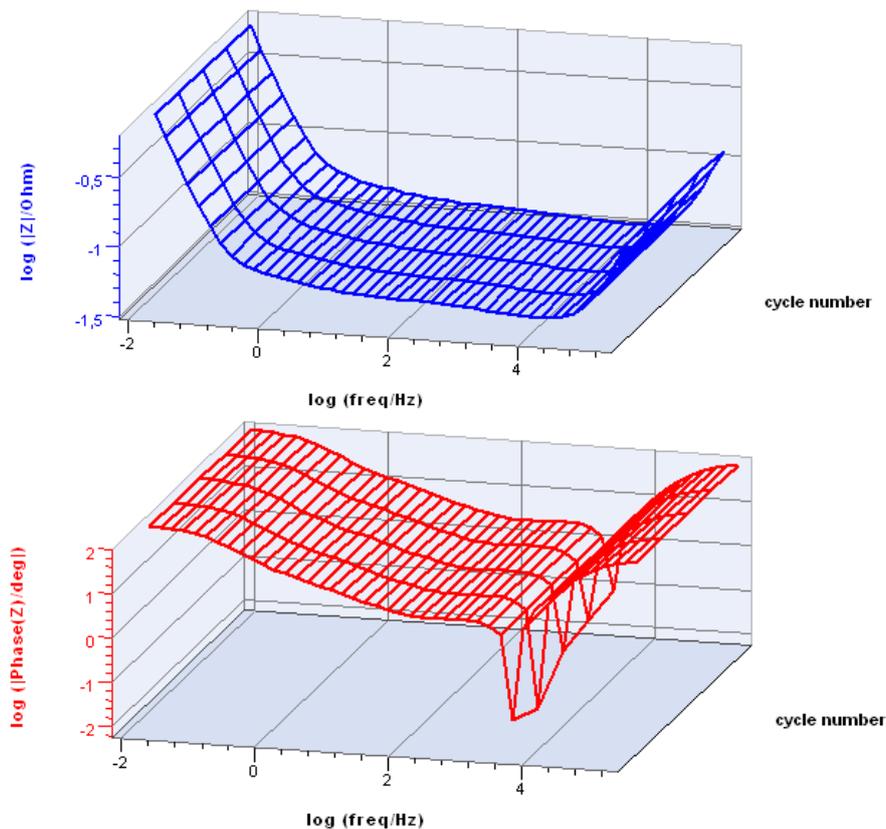


Fig. 98: Bode diagram obtained with the 3D representation.

Once on the 3D representation, it is possible to reach the 3D menu by right-clicking on the graph (Fig. 99). Thanks to this menu, it is possible to come back to the 2D representation or to display simultaneously 2D and 3D graphs. Similarly to the 2D representation, it is possible to Copy and Print the graph as explained in section 0 page 79. The Graph properties menu for the 3D representation is the same as the Graph properties menu for the 2D graph, detailed in the following paragraph.

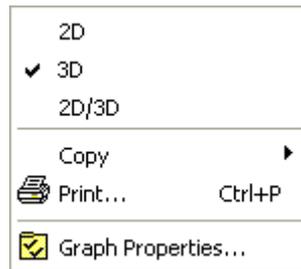


Fig. 99: 3D menu.

3.2.5 Graph properties

On the graphic window, right-click on the mouse and select “**Graph properties**”. This Graph properties window is divided into 5 themes: **Traces**, **Axes**, **Units**, **Graph** and **Options**. Each of them allows the user to define properties of the graphic display.

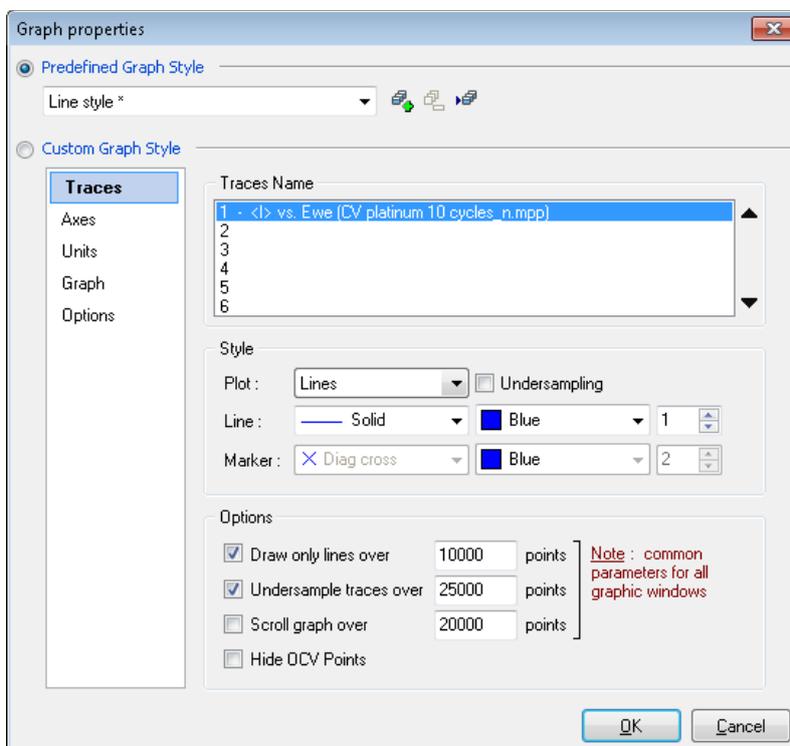


Fig. 100: Traces window.

In the **Options** frame, it is possible to choose to hide OCV points or to draw only lines over a number of points or to undersample traces over a number of points. Note that the two last possibilities should be the same for all the traces.

Note: When several traces are plotted on the same graph the user can change the active trace with a left click on the desired trace.

It is also possible to select between four predefined graph styles:

- Line style = only blue solid line,
- Line Markers style = blue line + circle markers,
- XY prop.style = blue line + circle markers and proportionality between X and Y axes,
- Monochromatic = black line. The other curves in this style will be in black with dash or dot lines. This style is specially dedicated to scientific articles.

The **Traces** window allows the user to define all the properties of the selected traces. Select the trace you wish to modify in the **Traces Name** frame.

The available trace properties are

- the plot style: Line, Line+Markers, Markers
- the line properties: solid, dash..., color and size,
- the marker properties: rectangle, circle, ..., color and size.

An undersampling option is available when the results are plotted as lines.

Nevertheless, the user can define his own style defined with all the functions of the Graph Properties window (Traces, Axes, Units, Graph, Options).

Creation of a new graph style is possible with the  button. This new graph style will be recorded automatically.

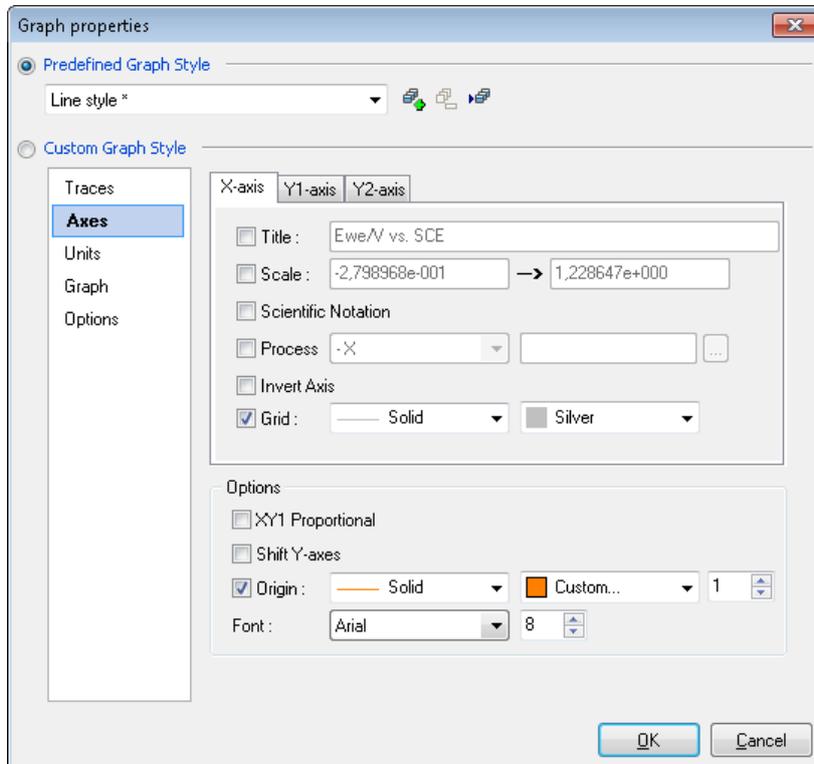


Fig. 101: Axes window.

In the Options part, the user can choose to display his data with the X and Y axes proportional (generally used for Nyquist representation) and to differentiate from the rest of the grid the axis origin (color, style or line size).

The font type and size is also available from this option menu.

Note: - On the graph the user can move one of the Y axes with the mouse (left click) in order

to adjust the origin of both Y axes. Put the mouse on the axis to see the  and move the axis.

All the Axes properties can be changed in this tab. Select the axis you want to modify in the index tabs.

It is possible to change the title of the axis, but also to adjust the axis range to the user's convenience. The user can also change the notation to scientific mode or invert the axis (positive values on the left and negative values on the right).

The grids can be hidden while deselecting the box. The user can choose the color and the style of the grid.

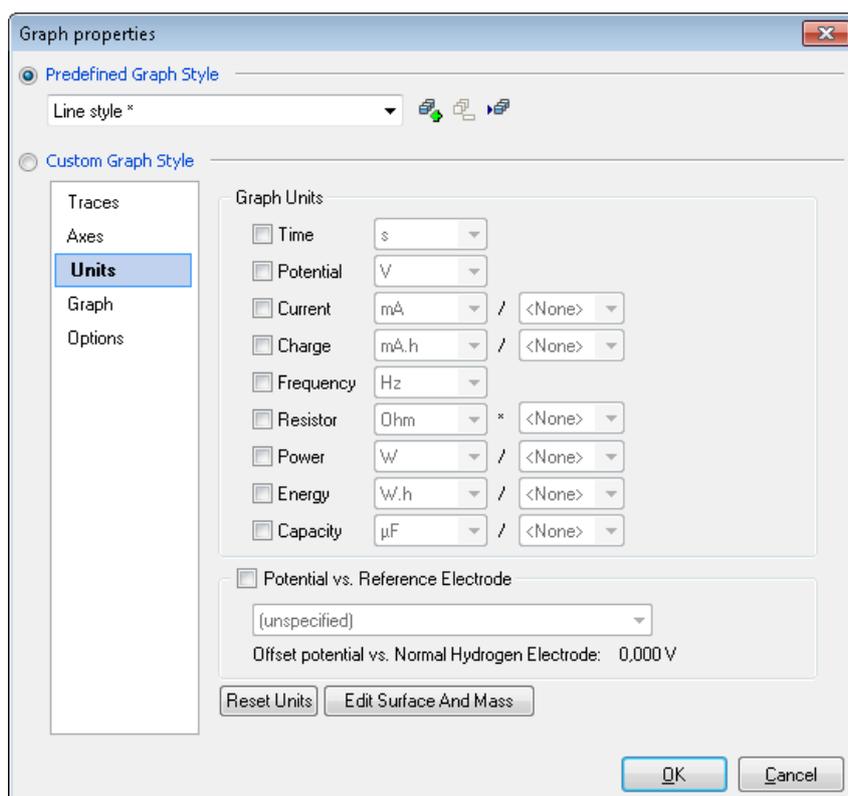


Fig. 102: Units window.

Graph Units window is used to choose the correct graph units for the different variables. The default units are in gray boxes. If the user chooses another unit, the box corresponding to the represented variable must be ticked for the choice to be activated. Specific units are available for current and charge on one hand and for power and energy on the other hand. For current and charge, the user can choose to display the current or the charge divided by the electrode area or by the electrode characteristic mass.

Power and energy can be plotted according to the electrode characteristic mass. In such a case the software will ask for the electrode surface area or for the characteristic mass. The following window will be displayed:

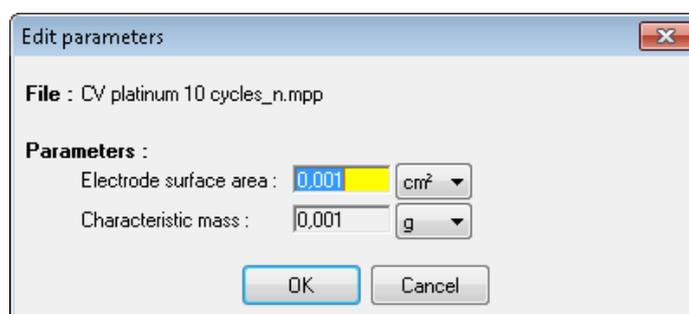


Fig. 103: Electrode Surface Area and Characteristic Mass window.

The Electrode Surface Area and Characteristic Mass window is used in the unit window for charge density or current density plot. The characteristic mass is also used for specific power or energy plot. The user has to set the working electrode surface area/characteristic mass and choose the unit. Clicking **OK** will modify the graph according to the new surface but this area is not saved in the raw file.

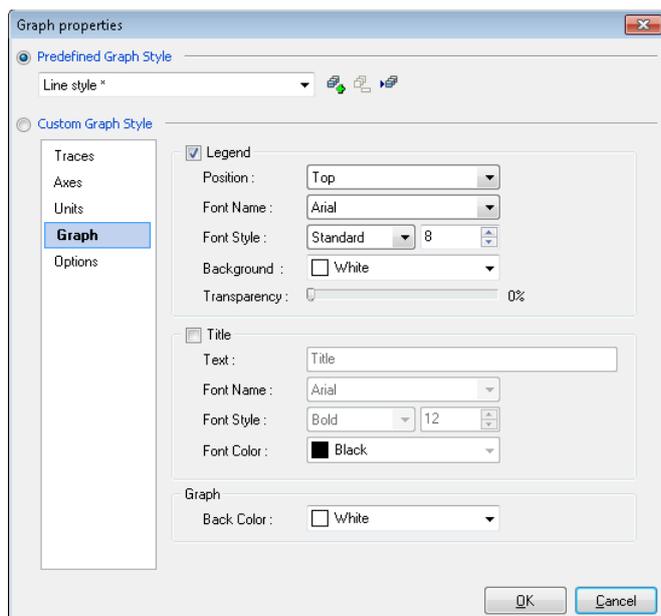


Fig. 104: Graph window.

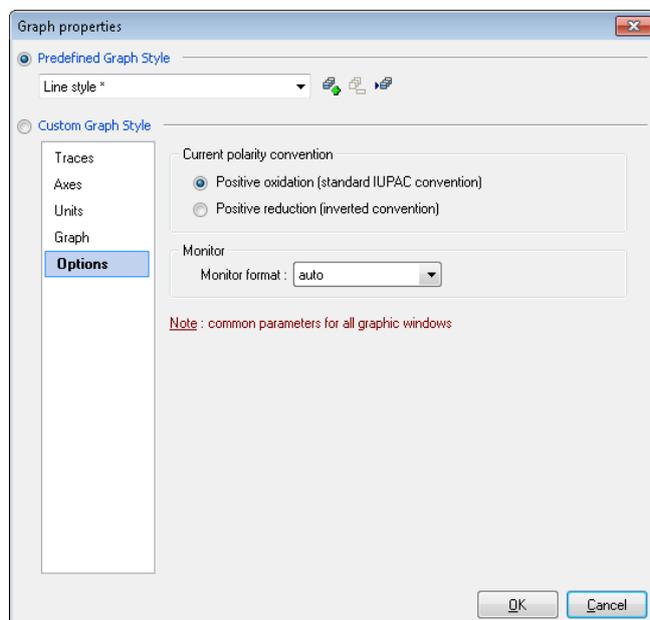


Fig. 105: Options window

3.2.6 The LOG (History) file

The log file summarizes all parameters used for an experiment (with the possible modifications on-line). Log  displays the history of the experiment from its beginning.

The user can show or hide the graph legend. The position, the font name, style and size, the background color and the transparency of this background can be defined. The legend includes the file name. **Note:** When several traces are plotted on a graph, the user can select the active trace by clicking on the corresponding legend. A title can be added to the graph to describe the experiment. The text must be typed in the box. The user can choose the title's format (font, font style, size and color). To improve contrast and legibility for a presentation for example, the user can change the color of the graph background.

This window allows the user to select the current polarity conventions to display data files. The standard current convention from IUPAC with a positive value for the oxidation current. The inverted current convention with a positive value for the reduction current. It is also possible to adjust the graph size to the monitor format.

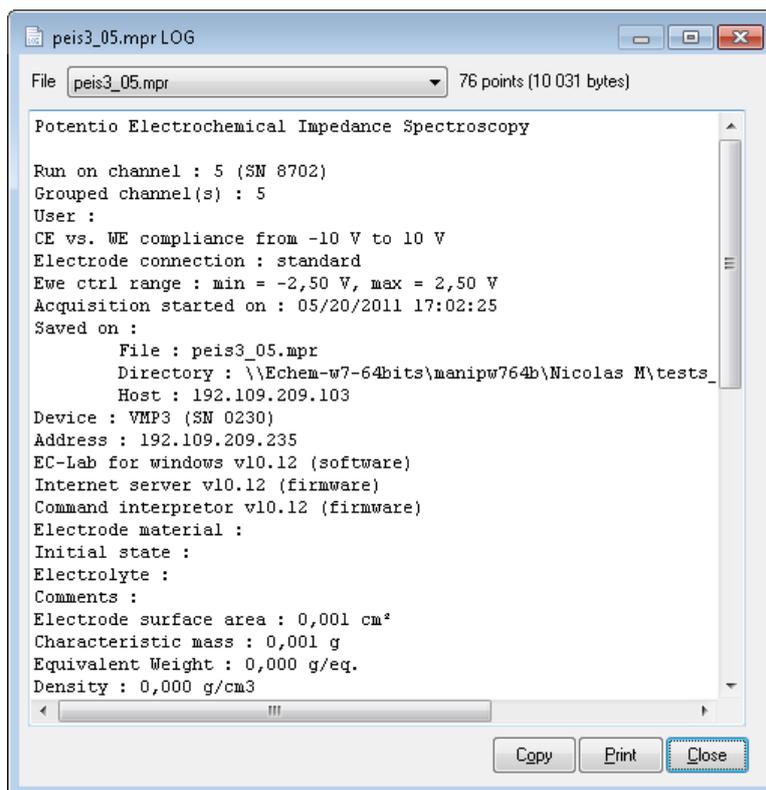


Fig. 106: Experiment history window.

The parameter modifications while the experiment is running are added to the end of the file. The number of points and the file size are displayed on the top of the window near the file name. This file is contained in the .mpr file but can be separately saved if needed using **Config\Options\General**.

For bipotentiostat technique the log file includes the parameters of setting and probable modifications for both disc technique and ring technique. The user can display and shift from the experiments detail of the technique performed on the channel disc channel to the experiment details of the technique performed on the ring disc by checking the appropriate box.

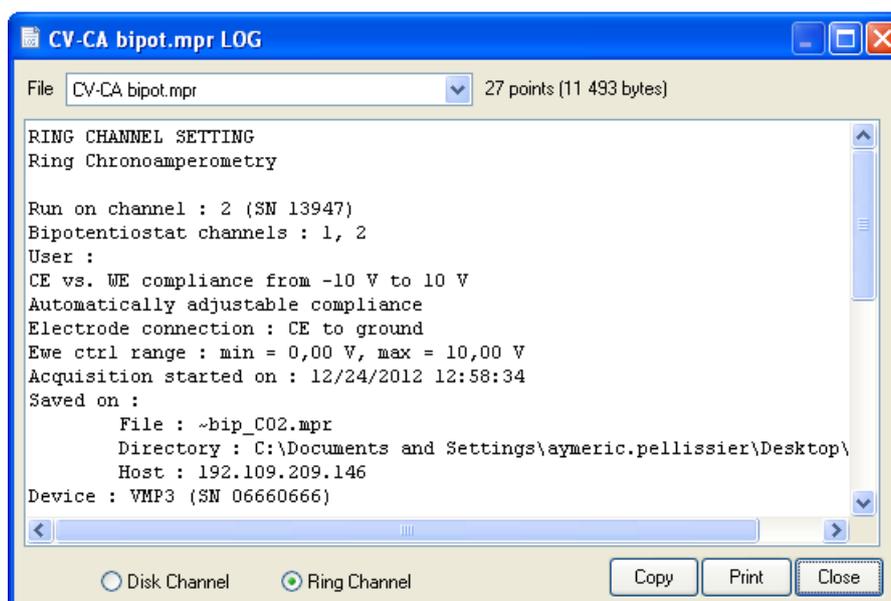


Fig. 107: Experiment history window for bipotentiostat technique.

3.2.7 Copy options

On the graphic display several copy options are available. When the user right-click on the mouse the following copy options can be found in the “**Copy**” menu:

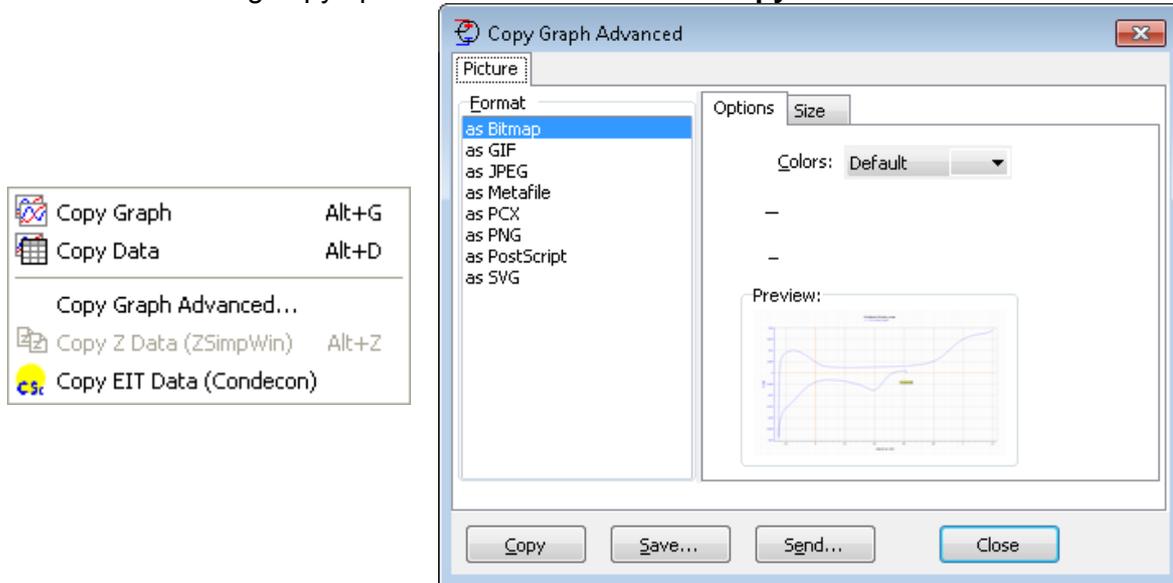


Fig. 108: Copy option and copy graph advanced menu.

3.2.7.1 Standard copy options

On the top of the copy options menu two standard options allow to copy either the graph or the data. The “**Copy Graph**” option will copy the graph to the clipboard as displayed on the computer screen in an enhanced metafile format (*.emf). The user can paste the file in . The “**Copy Data**” option will copy the data selected on the graph (if data points are selected) or data as they are displayed on the screen in a text format in two columns with X and Y only. Data can directly be pasted in spreadsheet software.

3.2.7.2 Advanced copy options

Three advanced copy options are also available.

- The “**Copy Graph Advanced...**” option offers eight different file formats for the graph copied: enhanced metafile, Bitmap, SVG, Post Script, PCX, GIF, PNG and JPG with a possibility to choose the size of the picture in pixels.
- The “**Copy Z Data (ZSimpWin)**” option is a gateway to ZSimpWin® software. This copy option is only available with impedance data files. Three data rows (frequency, Re(Z) and Im(Z)) are copied in the ZSimpWin format and can be pasted by the user in this software. If the impedance experiment is repeated several times, only the displayed cycle is copied.
- The “**Copy EIT Data (Condecon)**” option is a gateway to Condecon® software. This copy option is available only with data files including potential, current and time. Three data rows are copied to the clipboard in the following order E, I, and t. this option only copies the data points corresponding to the displayed points on the graph.

3.2.8 Print options

Print displays the print window. The user can print only the graph. The log file and some comments added by the user in the comments tab can also be printed on the same paper page. The printer setup is also available with the setup button. A print preview is available to see the different parts of the page.

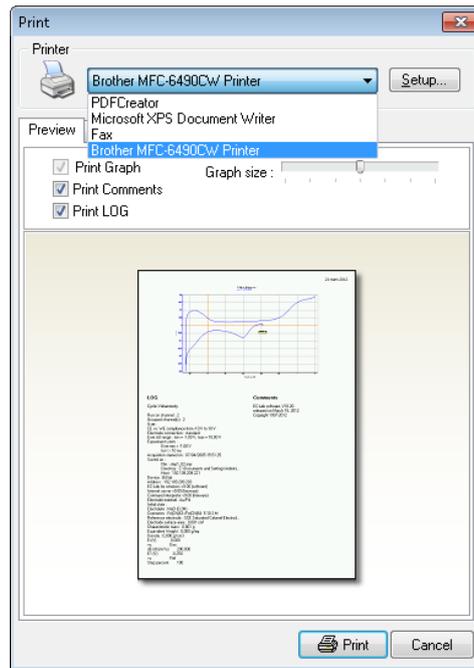


Fig. 109: Print window.

Note: the date is displayed and printed automatically in the top right corner.

3.2.9 Multi-graphs in a window

The EC-Lab® software graphic window is capable of displaying several different and independent graphs. The number of graphs is not limited.

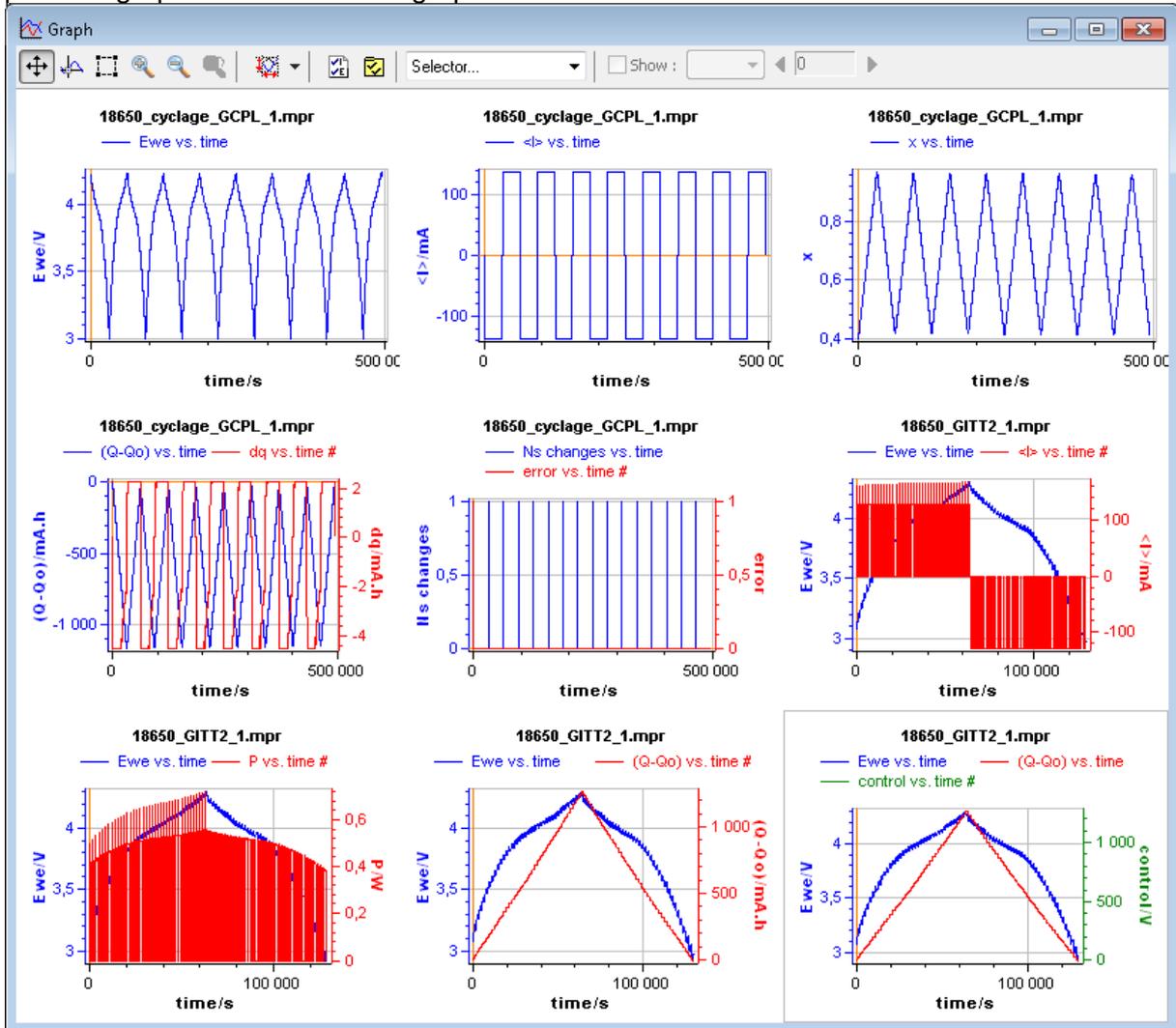


Fig. 110: Multigraph window.

To display several graphs on the same window, right-click on the graphic window, select **“Add Graph...”** and choose the data file to display. One graph is active on the window (with a red frame in the left bottom corner). The other graphs are not. In the multigraph mode fits and analysis remain possible on the active trace of the active graph. The graph properties can be modified for each graph independently.

3.2.9.1 Multi windows

When several windows are displayed in the EC-Lab® software the user can either show windows in cascade or tile the windows on the screen. Choose **Windows, Tile** to display several graphic windows at the same time.

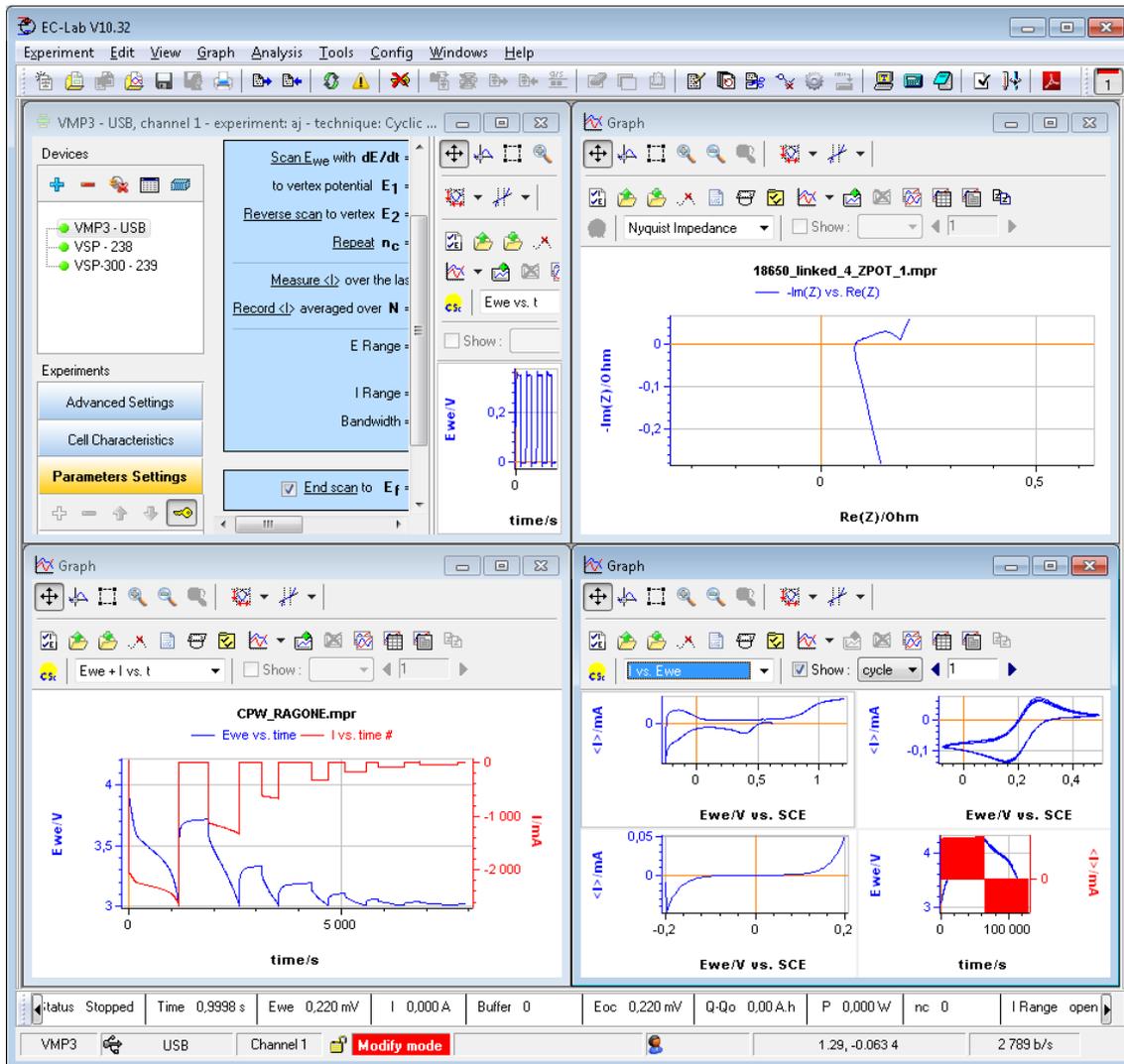


Fig. 111: Multi-windows.

This can lead to a very complex displaying mode that may be very useful for multichannel display.

3.2.10 Graph Representation menu

It is possible for the user to define fast graphic displaying modes with the Representation tool in the Graph menu.

The **Graph Representations** window already offers some standard representations. For each representation, a scheme of the axes is given. For example, in the Fig. 112, the Bode impedance representation is given. This representation is defined as:

- the frequency value on the X axis. This value is processed with the log spacing function,
- the $|Z|$ value on the Y1 axis. This value is processed with the log function,
- the Phase(Z) value on the Y2 axis.

It is possible to display the two Y axes on the same graph or to separate them selecting the "Separate traces" box.

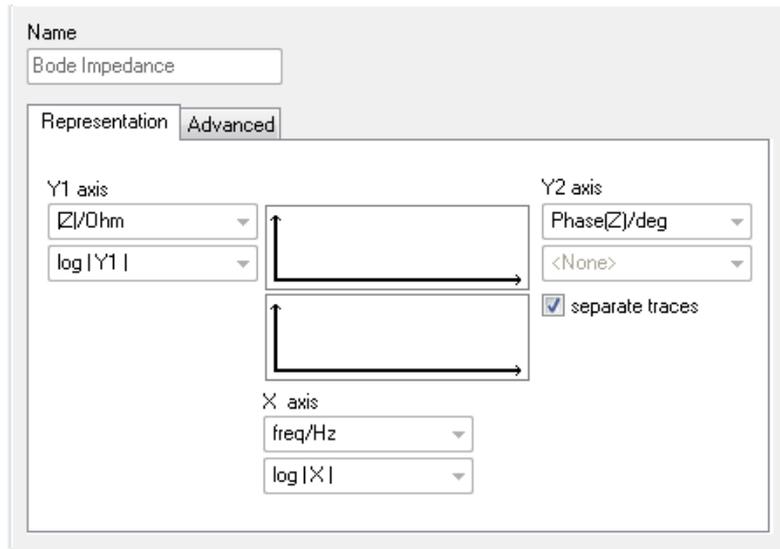
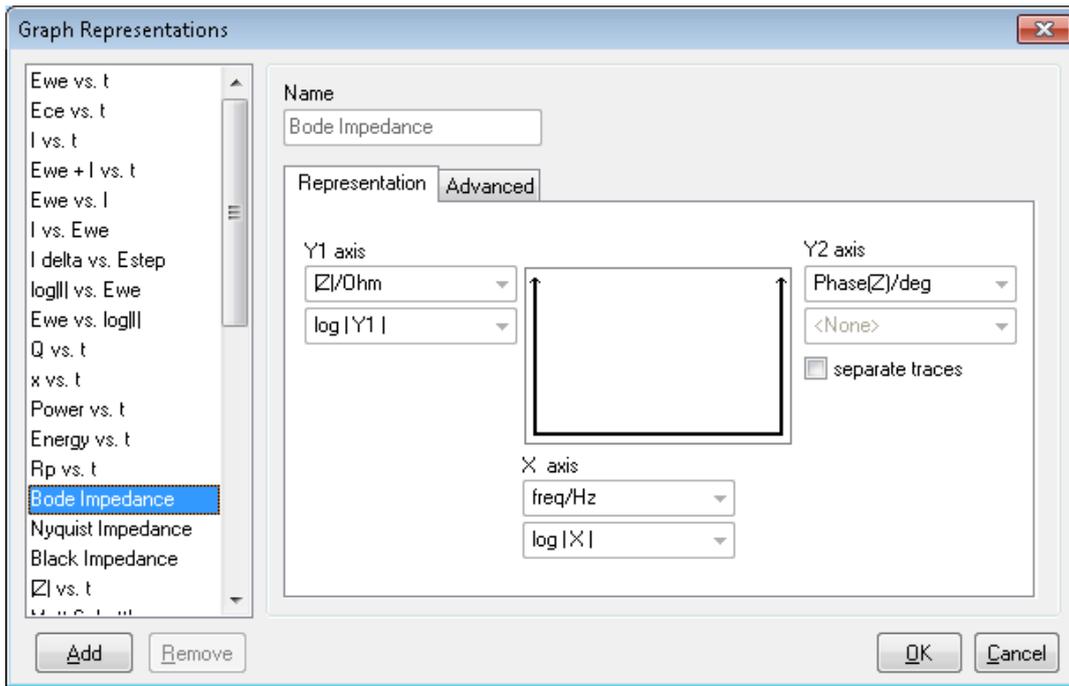


Fig. 112: Graph representations window.

3.2.10.1 Axis processing

As shown previously, it is possible to apply a mathematical function on each axis. By default standard functions such as $\log X$, $-X$, $|X|$, $1/X$ are proposed (Fig. 113). Nevertheless it is possible for the user to define his own processing function using the **Custom** menu.

Then in the window given Fig. 113, the user can define an operation in the Variable box (in this example it is the box). Mathematical functions are available ticking the box more.

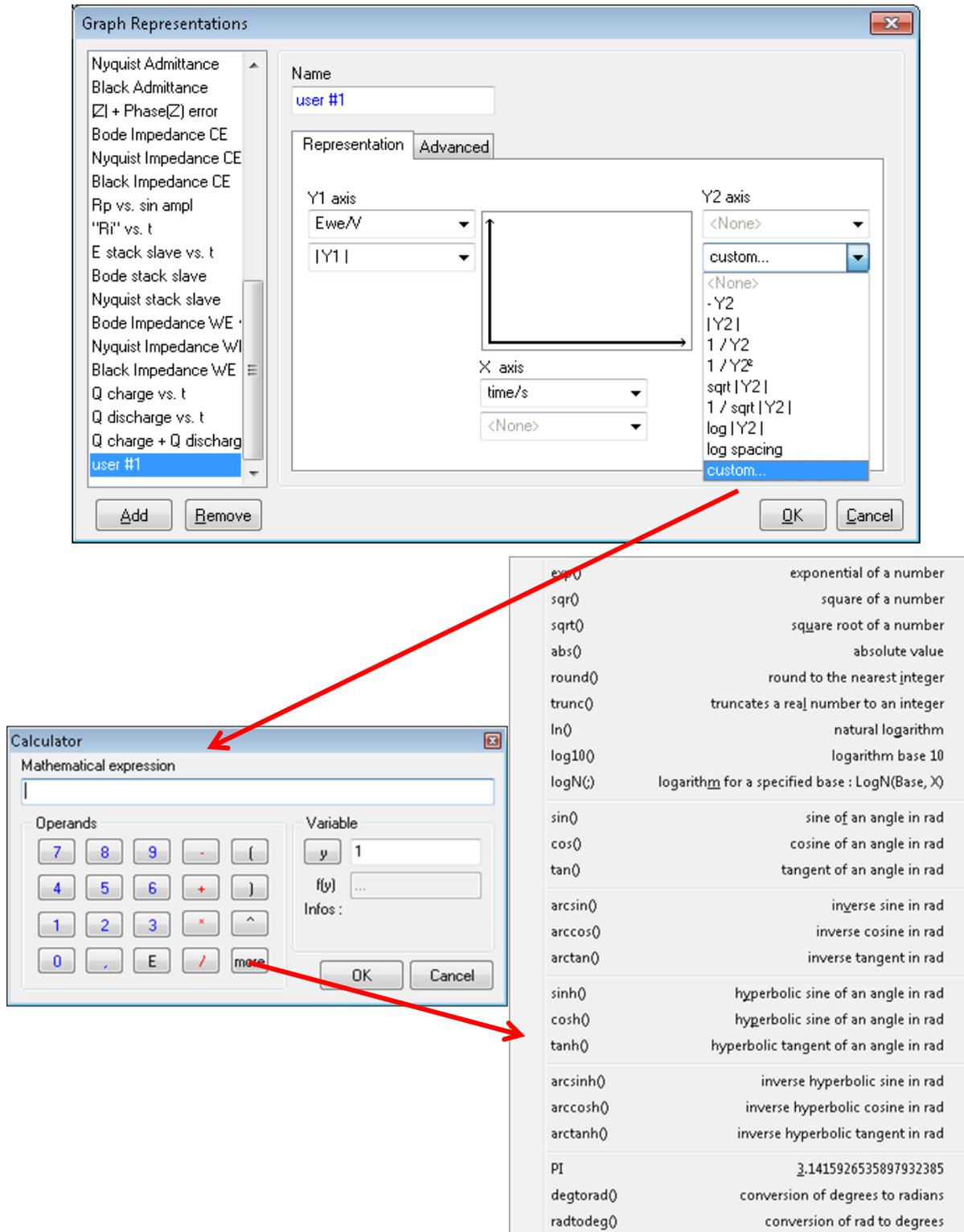


Fig. 113: Axis processing window and available mathematical functions.

3.2.10.2 How to create your own graph representation for a specific technique?

To facilitate data treatment, it is possible to create a specific representation for each technique. For this, the user has to click on “Add” in the bottom of the **Graph Representations** window; then a “User #x” variable is automatically created. The user can change the name of the display and select variables to be displayed on X-axis and on Y1 and Y2 axes in the

Representation window. A processed display for each axis in the **Advanced** window can also be defined.

Once definition of each axis done, it is possible for the user to define the Graph style but also the techniques to which apply this process. The selection of the Graph Style can be done on the **Advanced** menu as shown in Fig. 114. As mentioned in the Graph properties part the user can choose amongst four available **Graph Styles** or define himself a Graph Style that can be associated with defined techniques. This can be done selecting the **Edit** menu, see following paragraph for more details about the Graph Style creation.

Clicking on the second **Edit** button does the technique selection. Once the selection done, techniques are displayed in the selected techniques box as shown in the Fig. 114.

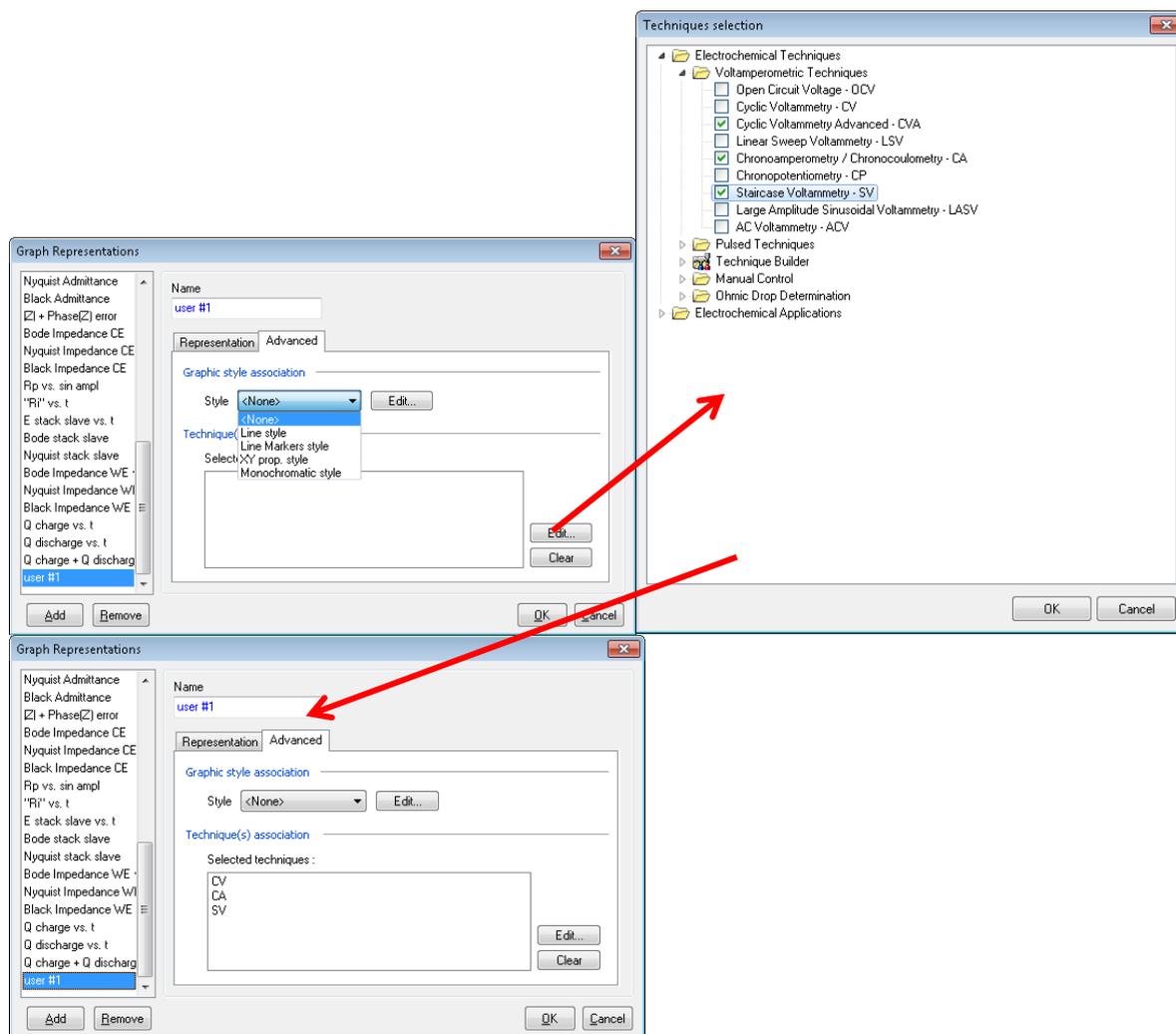


Fig. 114: Graph Style and technique selection.

Note: this graph representation will only be available if the variables to display are recorded in the current .mpr file for which the representation will be applied.

3.2.10.3 How to create a Graph Style?

It is often convenient to display the obtained data with the same way: same trace color, same markers, same units For this, it is possible with EC-Lab[®] to create a Graph Style. In the **Graph** tab, select the **Representations** menu. The **Graph Representations** window will be displayed, in this window select the **Advanced** tab and the four already predefined Graph

Styles will be displayed (Fig. 115). To define your own Graph Style, click on the  button, the window **Graph Properties** will be displayed as shown Fig. 116.

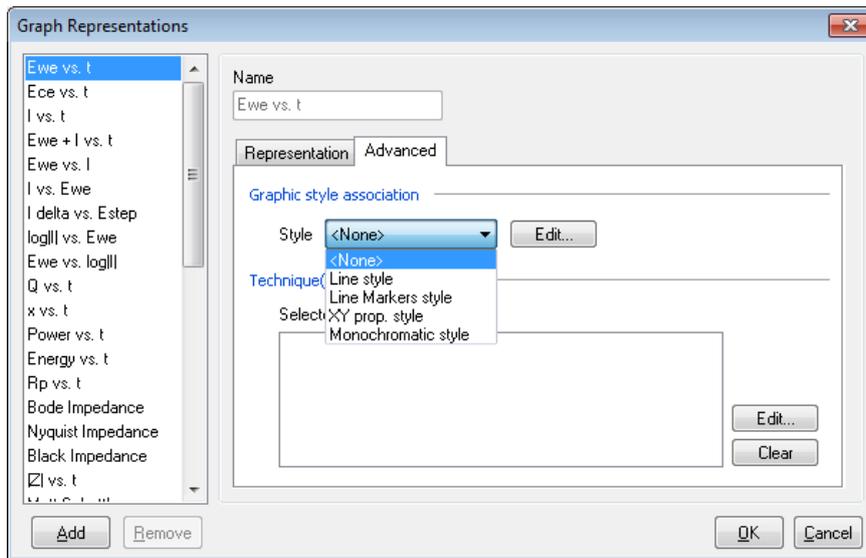


Fig. 115: Graph Style selection.

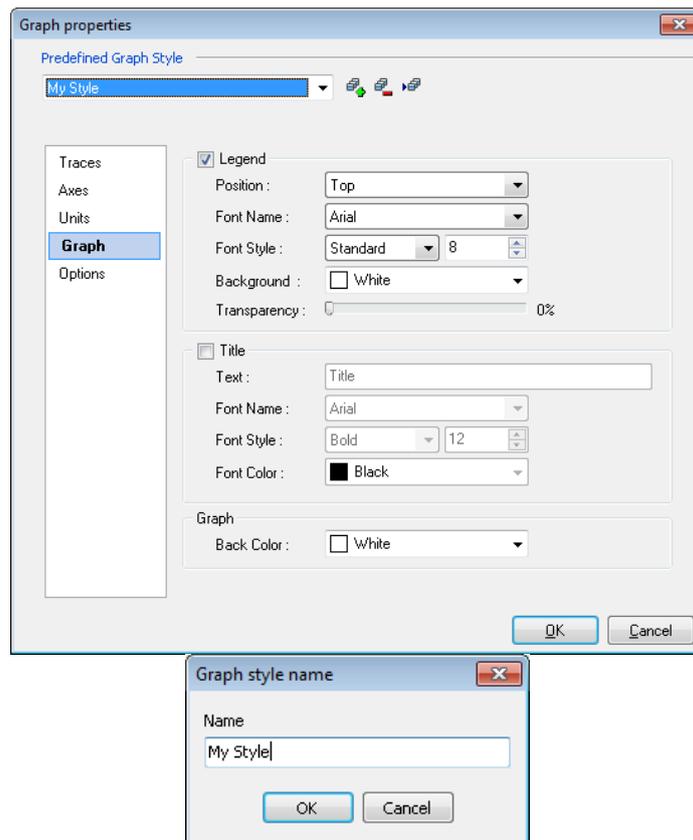


Fig. 116: Graph Properties window in the Graph Style creation.

When clicking on the  button, a Graph Style name window appears, then the user can choose the name of the new Graph Style. For this example, a Graph style named “Style example” is defined in such a way that the curve 1 is defined as red solid lines and red triangles markers (Fig. 117).

The Graph Style definition includes all the graph properties, these properties were previously defined in the section 3.2.5.

Once the definition of the Traces, Axes, Units, Graph and Option done, user has to click on **OK** and the new graph style is added to the Graph Style list.

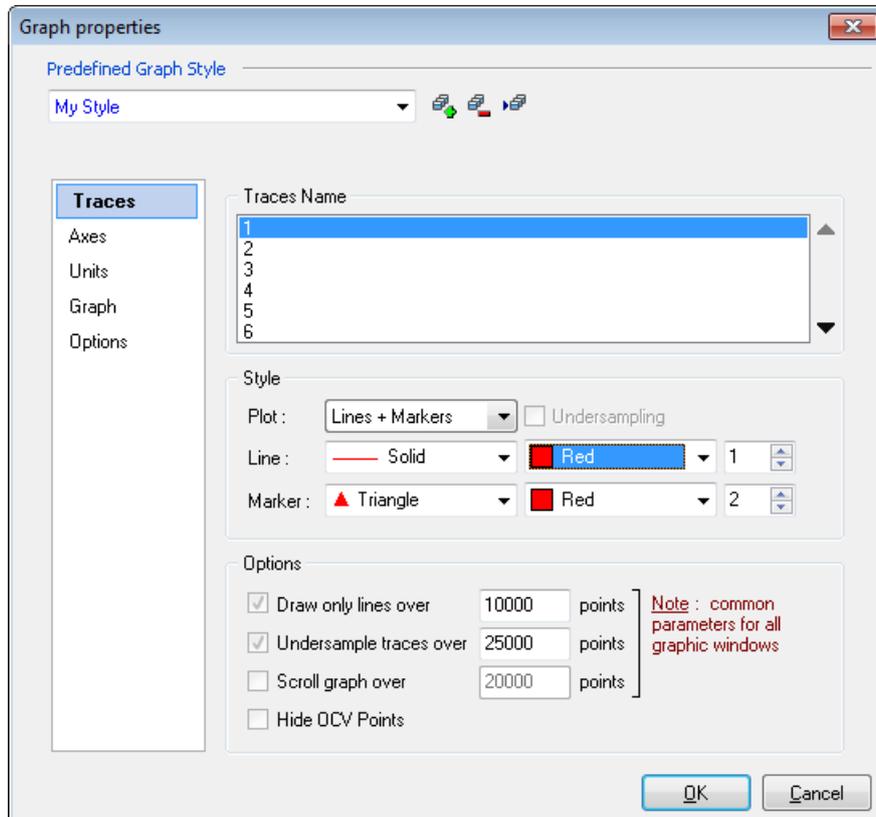


Fig. 117: Definition of traces properties in Graph style definition.

4. Analysis

The analysis menu is separated in six analysis sections depending on the application: **Math**, **General Electrochemistry**, **EIS**, **Batteries**, **Photovoltaic/Fuel Cells** and **Corrosion**. These sections contain both the analysis and the processes tools. The results of the analysis tools can be saved in a .txt file whereas the results of the processes tools are saved in an .mpp file, that was described in 2.11.2.

To use the analysis tools, the user needs to know how to select points. This is described in part 3.1.2.

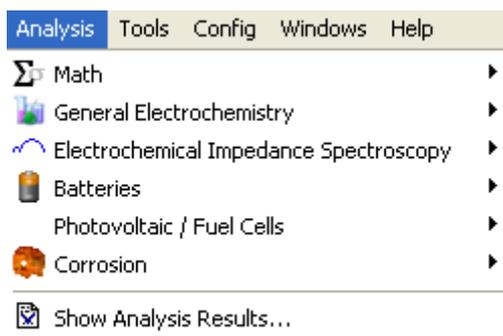


Fig. 118: Analysis menu

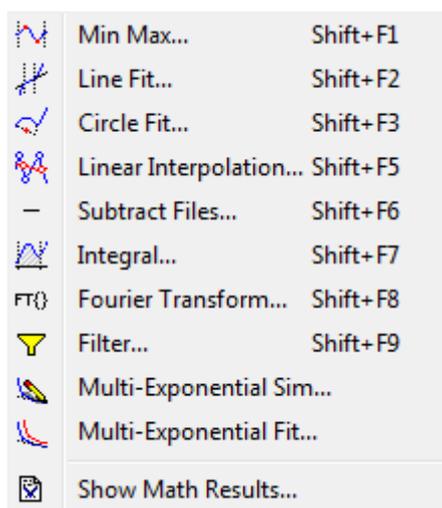


Fig. 119: Math Menu.

The Math menu contains the Linear and the Circle fits, but also the determination of the minimum and the maximum on a curve, a Multi Exponential Fit and Sim... This Math menu allows also the user to filter the obtained curve, to subtract curves, to do Integral on parts of the curve or to do a FFT transformation.

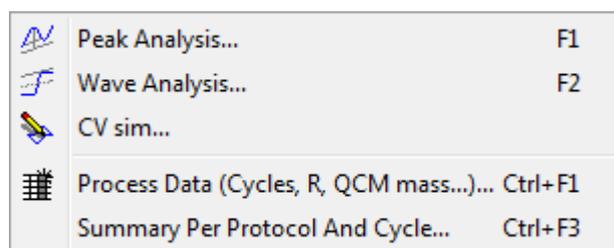


Fig. 120: General electrochemistry menu.

In this menu, the Peak and the Wave analysis are available but also two processes menu and CV Sim , a very powerful tool for the simulation of I-E curves obtained by voltammetry.

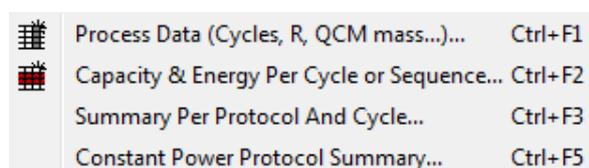


Fig. 121: Batteries menu

The Batteries menu is composed of processes allowing the user to add some variables, such as x, capacity during charge, energy, ... to his file or to calculate for each cycle the capacity and the energy values, to summarize all the significant parameters obtained during each cycle.



Fig. 122: EIS menu.

This menu is especially dedicated to the analysis of EIS data. It is possible to simulate various EIS diagrams with ZSim tool, or to fit with various electrical circuits an existing diagram with ZFit tool.

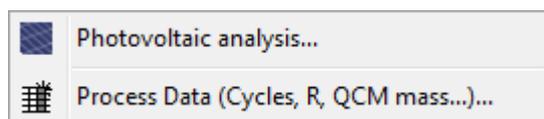


Fig. 123: Photovoltaic/fuel cell menu.

This menu provides analysis tools for experiments done on photovoltaic components and fuel cells.

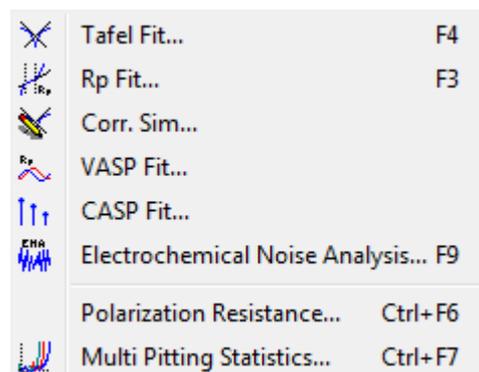


Fig. 124: Corrosion menu.

This menu contains the classical corrosion tools such as Rp Fit and Tafel Fit, but also a tool to simulate corrosion curves, an analysis of electrochemical noise and two tools to determine easily and quickly current and coefficients of corrosion. Moreover two dedicated processes are available for the VASP and CASp techniques.

4.1 Math Menu

4.1.1 Min and Max determination

On the graphic display, select **Min/Max** with the Min/Max button  or the mouse right-click. The Min/Max analysis window appears. Select the zone to fit on the trace and click on **Calculate**. The Min and Max values are automatically detected. The Min and Max coordinates are displayed in the fit window and highlighted in red on the trace (Fig. 122). The results can be copied to the clipboard and be pasted in the print window comment zone or in a text file. They can be saved in a text file.

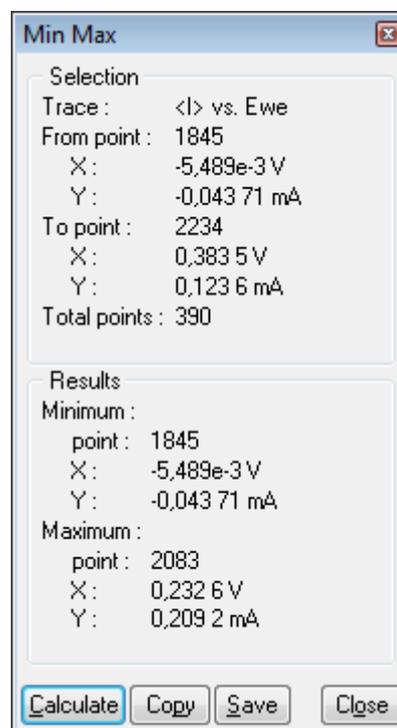


Fig. 125: Min/Max fit window.

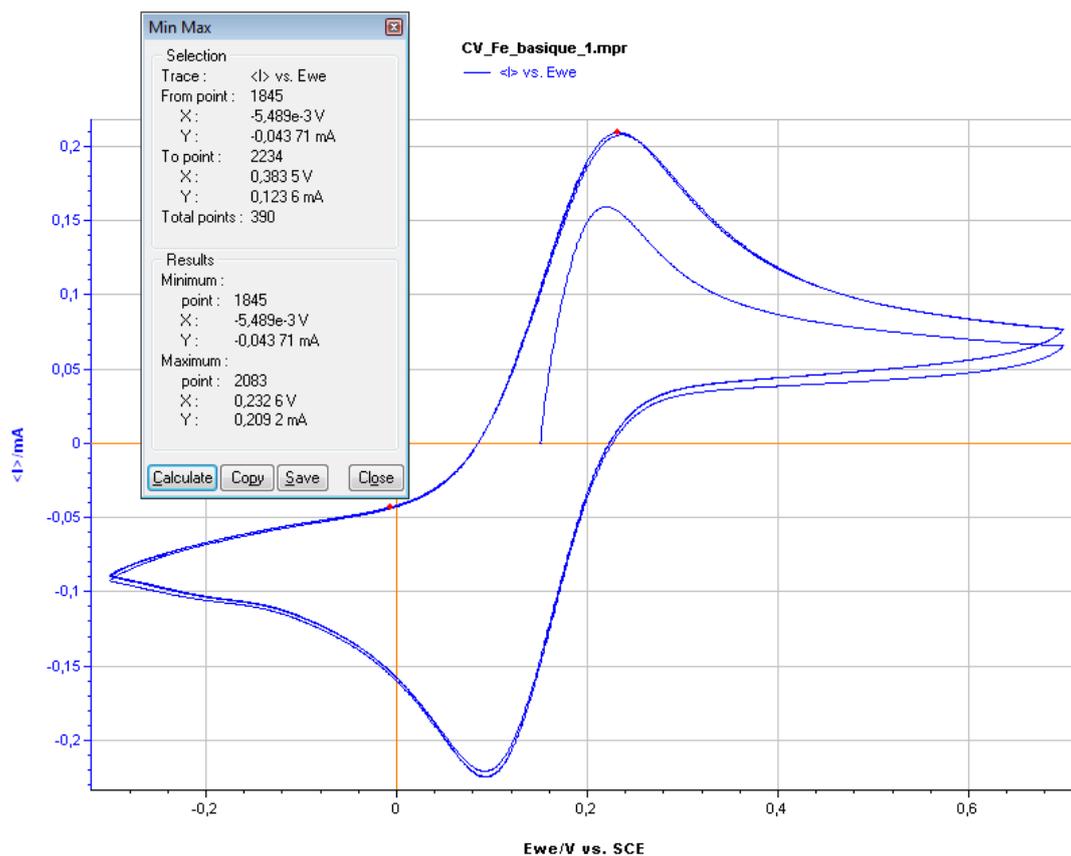


Fig. 126: Min/Max determination on the graph

4.1.2 Line Fit

When the zone to fit is selected, click on “**Calculate**” in the linear fit window (Fig. 127). A straight line is displayed as a result of the linear regression between two green circles with the Least Square Method fit (Fig. 128). Move the cursors with the mouse (by holding the mouse left button) to modify the range of data points selected for the fit. The new linear regression is automatically calculated when one of the cursors is moved.

The coordinates of the first and last data points used for the fit are displayed as well as the number of points used for the fit in the **Selection** frame.

The results can be copied to the clipboard and be pasted in the print window comment zone or in a text file. They can be saved in a text file

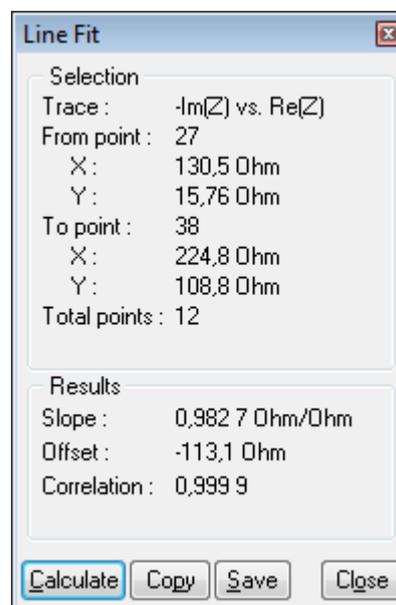


Fig. 127: Linear Fit window.

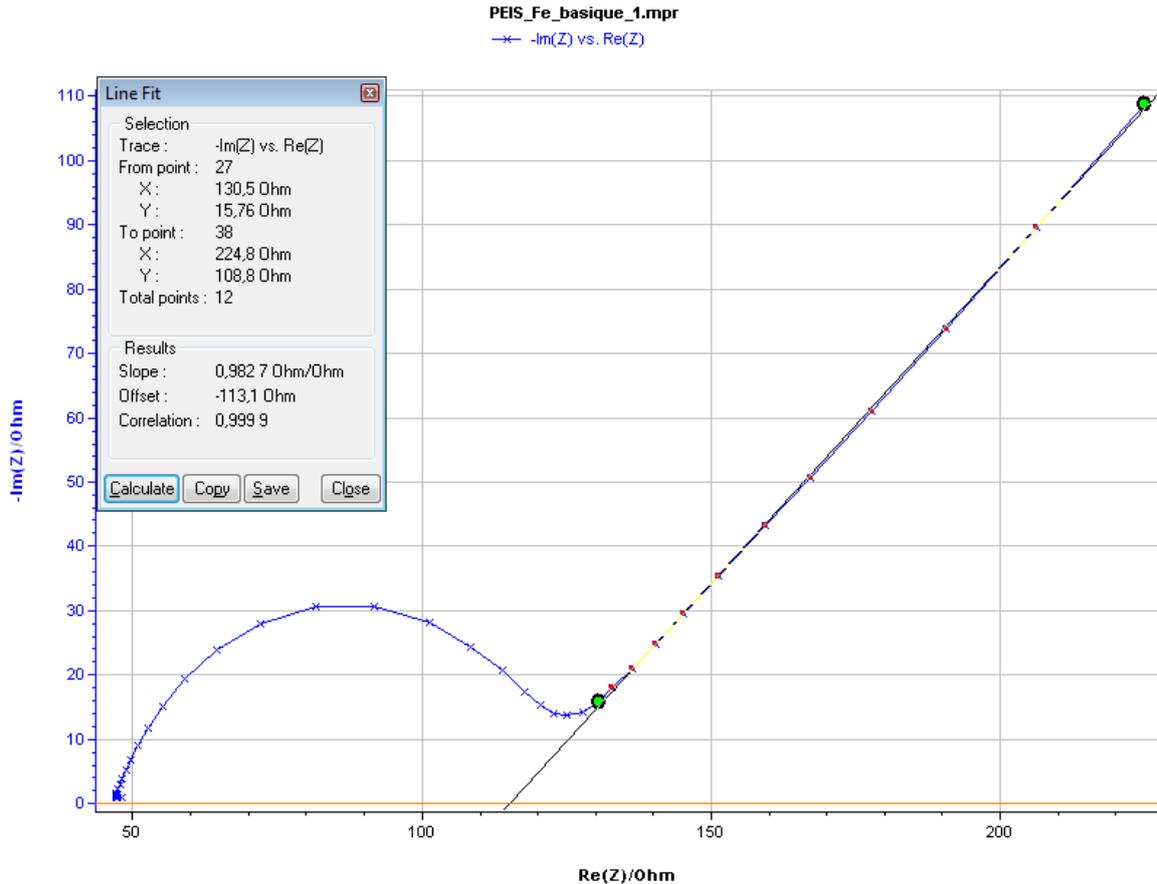


Fig. 128: Linear Fit on the graph.

4.1.3 Circle Fit

When the zone to fit is selected click on “**Calculate**” in the circle fit window (Fig. 129). A part of a circle curve is displayed as a result of the regression between two green cursors with the Least square method fit (Fig. 130).

Move the cursors with the mouse (by holding the mouse left button) to modify the range of data points selected for the fit. The new regression is automatically calculated when one of the cursors is moved.

The coordinates of the first and last data points used for the fit are displayed as well as the number of points used for the fit in the **Selection** frame.

In the **Parameters** frame, an iterative algorithm allows the adjustment of the results using a minimization with the simplex method.

The results displayed are the parameters of the circle. The depression is the angle between X-axis and the diameter defined from low x-intercept. R is the difference between high x-intercept and the low x-intercept. C is the capacitance determined for the experimental point in the selected zone where $-Im(Z)$ is max ($R\omega = 1$). The results can be copied to the clipboard and be pasted in the print window comment zone or in a text file. They can be saved in a text file.

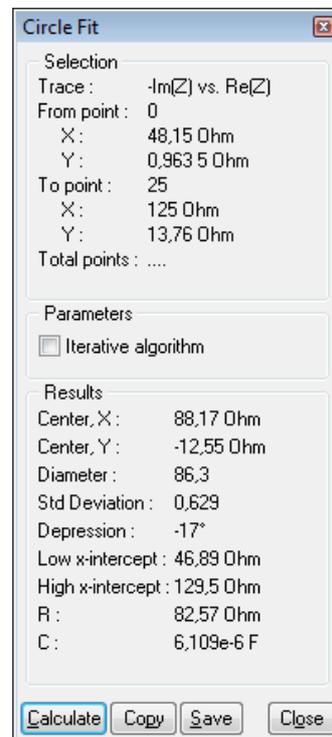


Fig. 129: Circle Fit window.

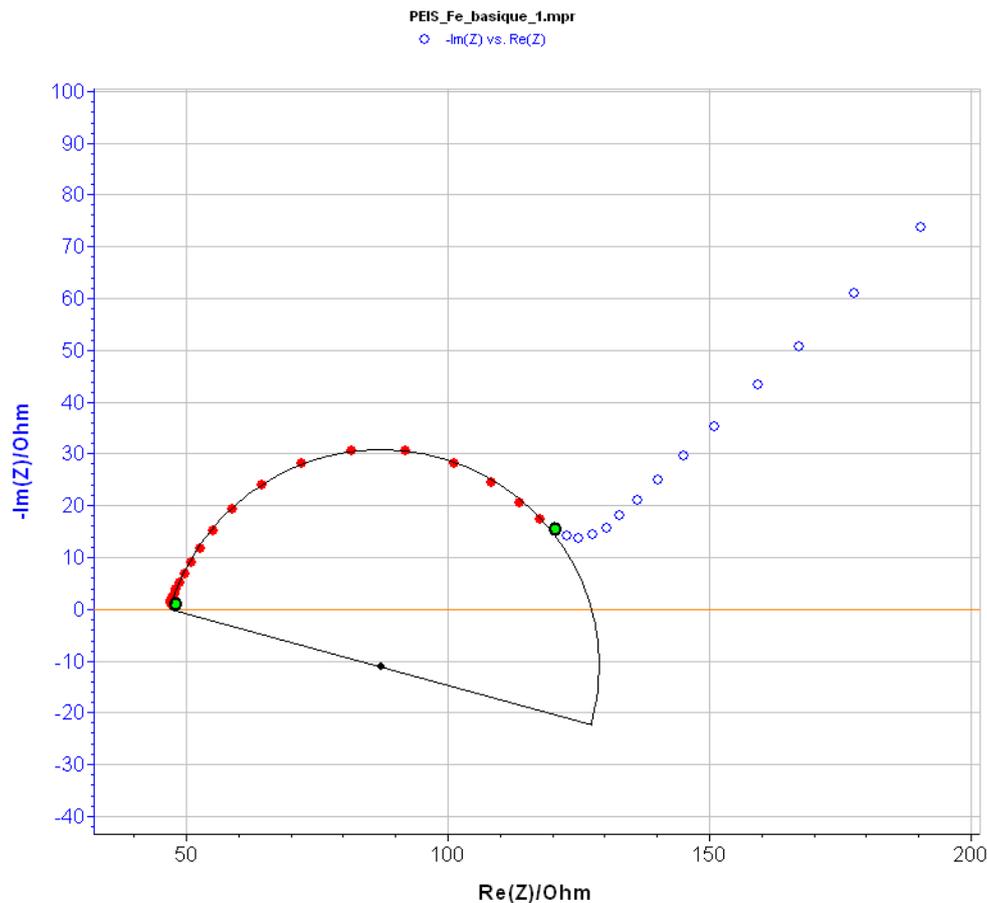


Fig. 130: Circular Fit on the graph.

4.1.4 Linear Interpolation

An interpolation tool  is available with EC-Lab®. The raw data file is not changed after this analysis. When a data point zone is selected click on “**Calculate**”. The linear interpolation allows the user to space out regularly in time each point of the data file. The user can choose to interpolate data using a defined number of points or a regular time between each point. Then a processed interpolated data file is created with the following name: filename_intpl.mpp.

This tool comes in handy if the user needs to subtract two data files as the subtraction between two files is only possible when the interval between each point is the same for both files.

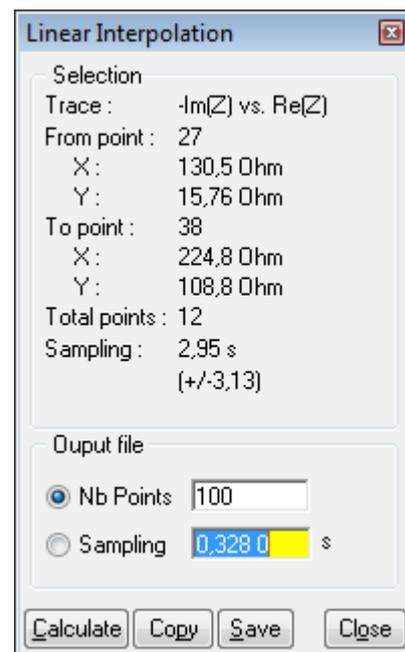


Fig. 131: Linear interpolation window.

4.1.5 Subtract Files

A tool  for subtracting curves is available with EC-Lab®. The raw data files are not changed after this analysis. The “**Subtract Files**” tool is available in the “**Math**” menu or via the right-click of the mouse.

The two files to subtract are selected as File 1 and File 2. Then, the resulting file (File 1 - File 2) is displayed. The sampling rate of the resulting file in *_filter.mpp format is defined by:

- the sampling rate of file 1 or/and file 2
- the total number of the points of the resulting curve (File 1 – File 2). The spacing can be defined in a linear or logarithmic spacing.
- a constant time step.

The results can be copied in the clipboard to be pasted in the print window comment zone or in a text file. They can be saved in a text file.

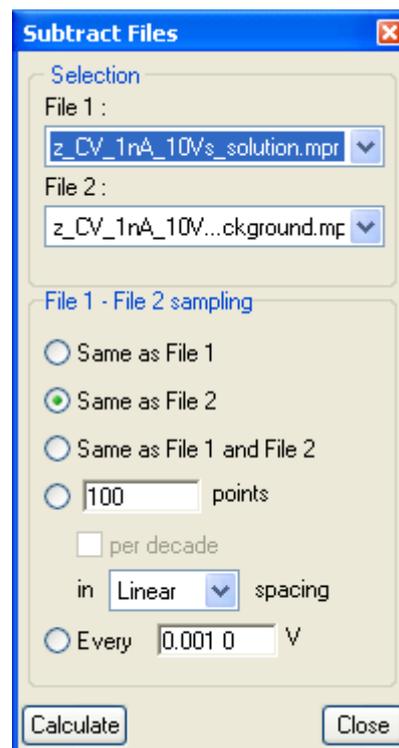


Fig. 132: Subtract files window.

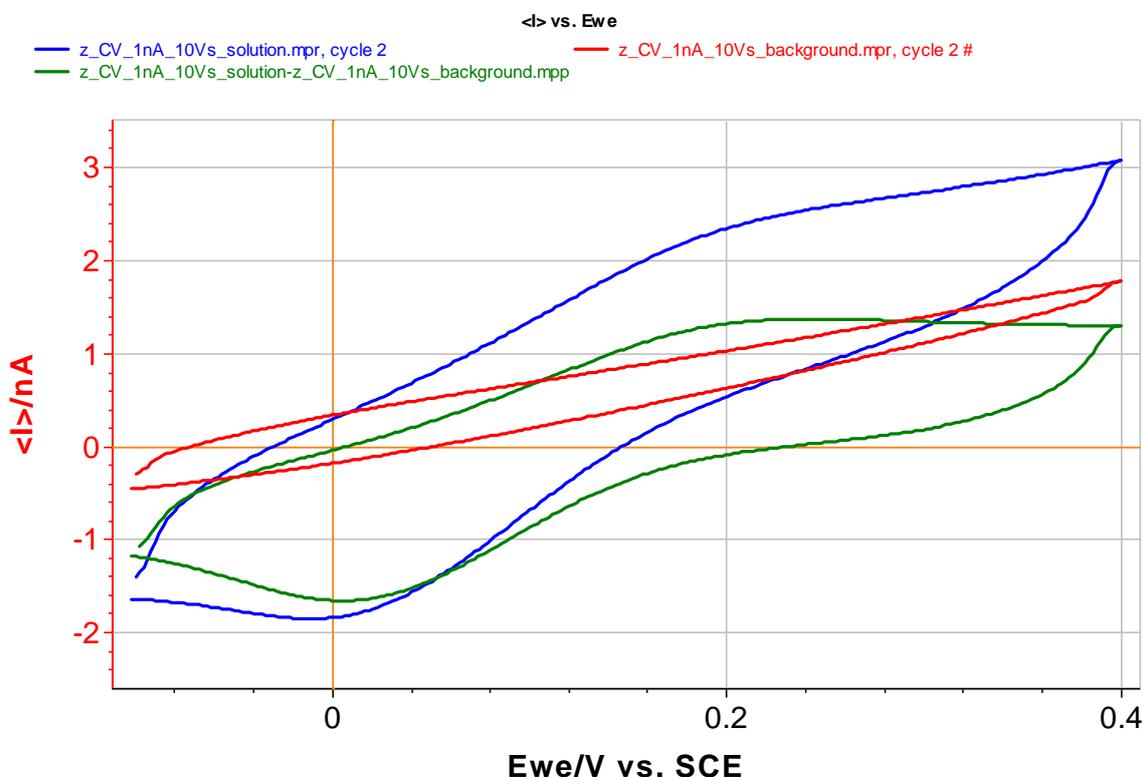


Fig. 133: Use of the Subtract Files tool on the blue and red curves. The obtained curve is shown in green.

4.1.6 Integral

One can calculate the integral value of a selected trace between two cursors.

On the graphic display, select the **Integral** with the

Integral button  in the analysis menu or the mouse-right-click and the data points where the fit will be performed. The Integral analysis window is displayed. Click on “**Calculate**”. Two cursors bound the integrated trace. The cursors can be moved to adjust the zone to be fitted. The fit is updated automatically. The integral is calculated according to X-axis. The integral is shown as a grey area. The units of the integral fit result depend on the plotted data points. For a cyclic voltammetry displayed as I vs E the units will be A V. If a current time trace is selected, the unit of the integral is A.s.

The results can be copied in the clipboard and pasted anywhere as text. They can also be saved in a text file.

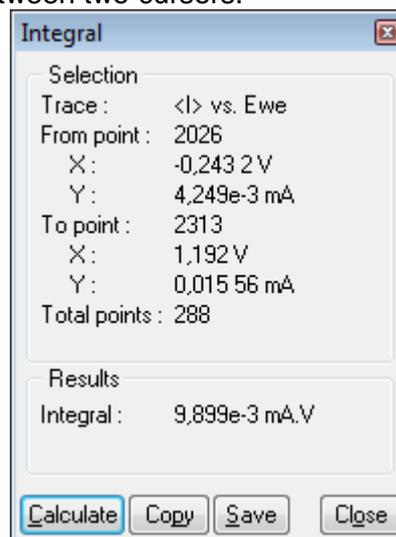


Fig. 134: Integral window.

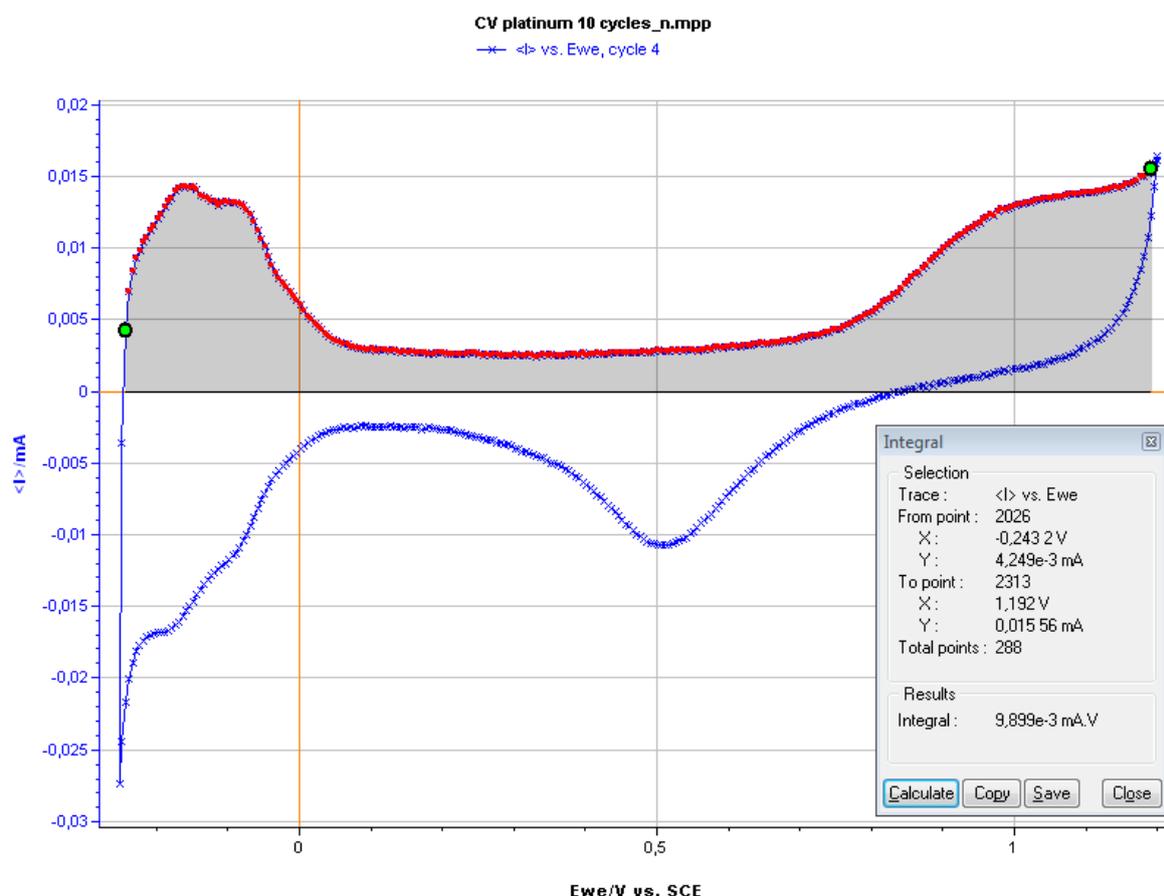


Fig. 135: Integral determination on a trace.

4.1.7 Fourier Transform

This mathematical tool $\mathcal{FT}()$ allows the user to calculate the Discrete Fourier Transform (DFT). The Fourier Transform of a time trace is a representation of this trace in the frequency domain. The DFT requires a discrete input.

The calculation is done following the formula:

$$X(f) = \frac{1}{N} \sum_{k=0}^{N-1} x_k \exp(-2i\pi f t_k) \text{ with}$$

$$(x_k)_{k=0 \dots N-1}, x_k = x(t_k) = x(kdt)$$

When a data point zone is selected, click on “**Calculate**”. Once the zone is selected, it is possible to choose the shape of the window.

In signal processing, a window function (also known as an apodization function or tapering function) is a function that is zero-valued outside of some chosen interval. When a time record is multiplied by a window function, the product is also zero-valued outside the interval. This removes the additional frequencies that appear if the time record is not periodic with the input, which is the case in Fig. 133.

The 6 windows possibilities are described below (the relationships are only valid within the interval [-1, 1] and 0 outside).

Rectangle: $w(t) = 1$

Barlett: $w(t) = 1 - t$

Hann: $w(t) = 0.5 + 0.5\cos(\pi t)$

Hamming: $w(t) = 0.54 + 0.46\cos(\pi t)$

Blackman: $w(t) = 0.42 + 0.5\cos(\pi t) + 0.08\cos(2\pi t)$

Welch: $w(t) = 1 - (t)^{1/2}$

The processed DFT data file is created with the following name: filename_dft.mpp.

This tool is very useful to determine if the measurement is affected by environmental noise, like 50 or 60 Hz.

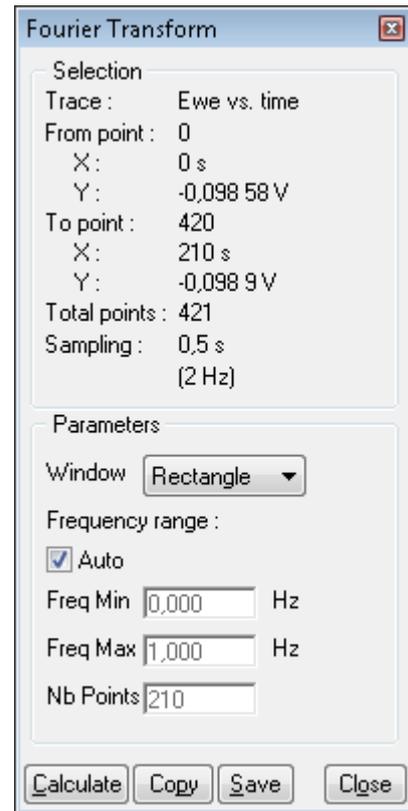


Fig. 136: Fourier Transform window.

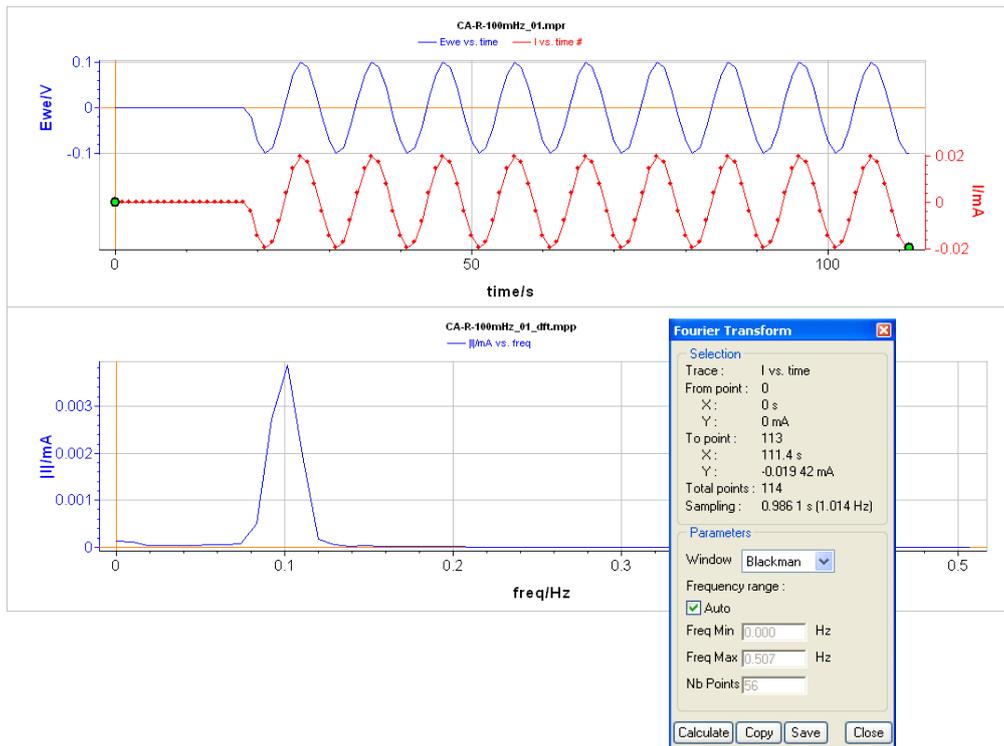


Fig. 137: Fourier transform analysis.

4.1.8 Filter

Data may be distorted by external perturbation, for instance in our example the 50 or 60 Hz frequency signal coming from the electrical grid. The “**Filter**” tool  available in EC-Lab® software allows the user to remove this additional undesirable signal.

Several filtering methods can be chosen:

- Moving average method: the window size must be defined.
- Savitzky-Golay method: it is based on a polynomial calculation in a defined window. The window size and the polynomial order must be defined.
- Low/high pass or band pass/reject methods. These methods are based on Fourier Transform. The window (Rectangle, Barlett, Hann, Hamming, Blackman, Welch) and the cutoff frequency(ies) must be defined (please refer to the Fourier transform part above for more details).

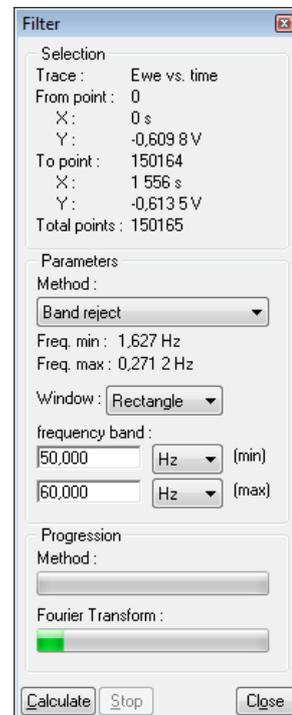


Fig. 138: Fourier Transform window.

The results can be copied in the clipboard and pasted anywhere as text. They can also be saved in a text file.

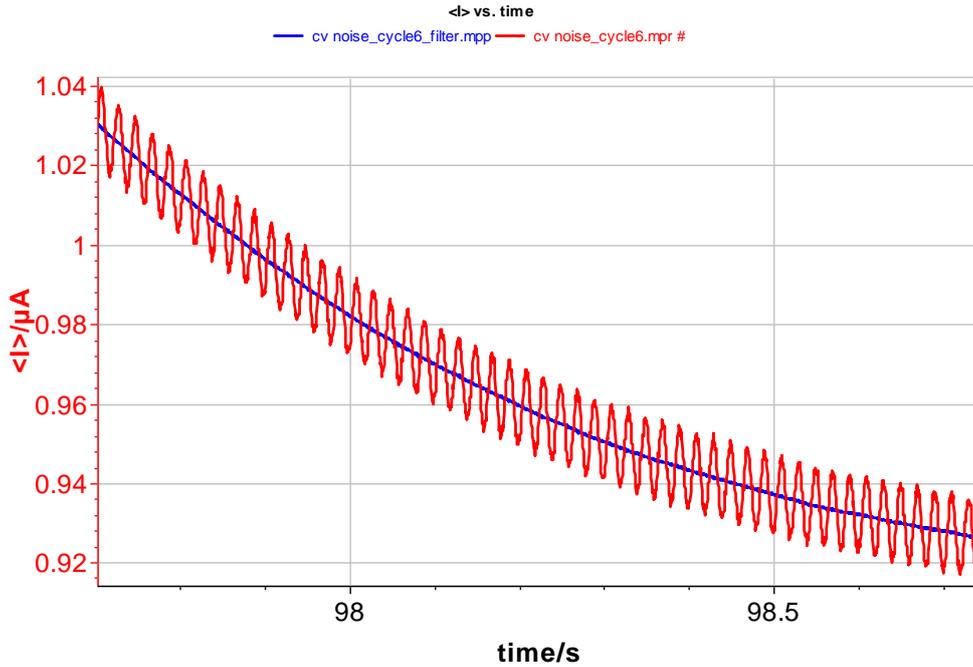


Fig. 139: Filter result. Red curve is the raw data file and blue curve is the filtered curve.

4.1.9 Multi-Exponential Sim/Fit

It is possible to model data with multiexponential behavior (up to order 6) with EC-Lab® software. This tool is particularly interesting for conductivity measurements. A simulation tool “Multi-Exponential Sim” and a fitting tool “Multi-Exponential Fit” are available in the “Math” menu.

Multi-Exponential Sim

This tool allows user to plot a curve from a multi exponential equation. First of all, the order of the multiexponential equation is selected (up to 6). Several units for X axis or Y axis can be chosen for the output graph. The window of the simulation is defined between X min and X max. In the third block of the window, it is possible to add noise if the box “Add noise” is ticked. Click on the “Calculate” button to obtain simulated curve.

Multi-Exponential Fit

The order of the exponential (up to 6) is selected. In the table, a line is created for each parameter. By clicking on “Calculate”, the calculation without randomization or fitting of the parameters will be done. If the result is not acceptable, it is possible to reach a better fit by clicking on “Minimize”. This minimization is only possible when the box associated to the value to minimize is ticked.

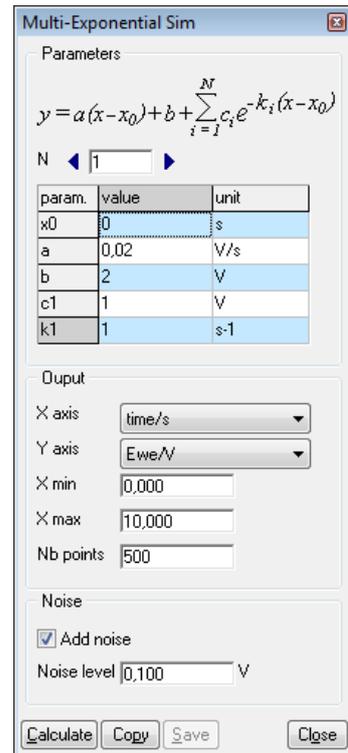


Fig. 140: Multiexponential Sim window.

The “**Multi-Exponential Fit**” is able to perform a fit on any data displayed in EC-Lab® software. The combo box in the “**Fit**” block offers two possibilities to initialize the fit from the “Auto estimate” values or from “Current parameters”. Note that the x_0 value cannot be fit and must be set manually by the user. The results can be copied in the clipboard and pasted anywhere as text. They can also be saved in a text file.

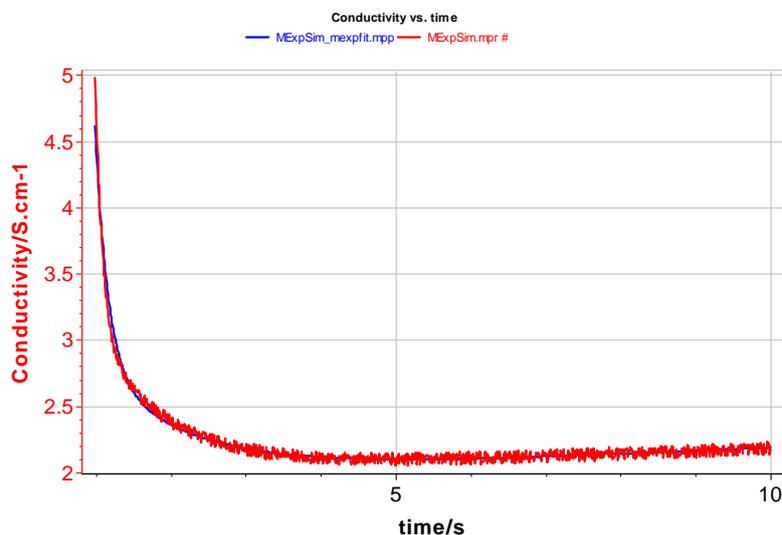


Fig. 141: MultiExponential fit result.

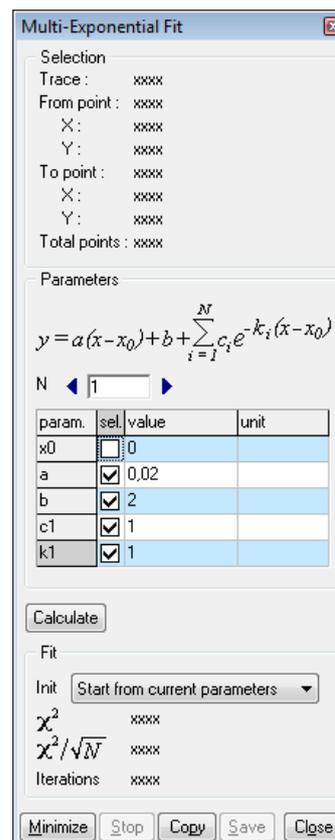


Fig. 142: Multiexponential Fit window.

4.2 General Electrochemistry Menu

4.2.1 Peak Analysis

A peak analysis, dedicated to Cyclic Voltammetry, is  available with the EC-Lab® software. Like other analyses with the EC-Lab® software, the user has to select the analysis and then select the data points to fit or select the data points before choosing the fit. To select the peak analysis, click on the  button in the graphic tool bar or select peak analysis in the right-click analysis menu. When this first part is done, the peak analysis consists of two steps. The user must choose the baseline and then click on calculate to have the results.

4.2.1.1 Baseline selection

When selected, the peak analysis window is displayed with two tabs **Baseline** and **Peak**. In the **Baseline** tab the user must select the baseline type. Three selections are available, **No Baseline**, **Linear Baseline** and **Polynomial Baseline**:

- If the user selects **No** the analysis will be performed according to the abscissa axis.

- If the user select **Linear** three different baselines can be set: **Manual** mode (with markers locked on the curve), **Regression** mode (with a linear regression made on the capacitive part of the curve before the peak) or in a **Free** mode (two cursors, unlocked to the curve, defining a straight line).

In the **Manual** mode the baseline is defined by two points represented by circles and set on the curve at the extremities of the zone of selected points.

In the **Regression** mode, the baseline is determined with the least square method. Data points used for the regression are automatically selected within the first quarter of the total number of points between the beginning of the selected zone and the point corresponding to the max current value.

- If the user selects **Polynomial**, a polynomial baseline is plotted between the two cursors using two data zones for the polynomial fit: twenty first points and twenty last points of the selected data zone.

The polynomial used to plot the baseline is the following: $y = ax^3 + bx^2 + cx + d$. The results of the fit are automatically updated when a cursor is moved.

The **Results** box displays the baseline equation and the data point zone used for the regression.

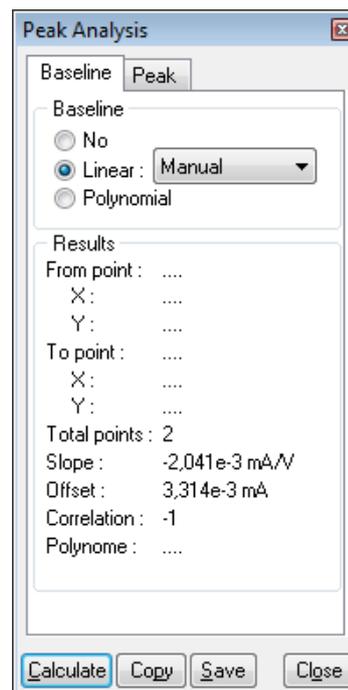


Fig. 143: Baseline selection tab.

4.2.1.2 Peak analysis results

When the baseline type is selected click on **Calculate**. The software will automatically find the max current value in the selected zone according to the baseline. Data points used for the peak analysis are within a zone starting at 35% (of an area defined by the first cursor and the max value) and ending at the location of a second cursor. The data point zone for the analysis is shown in the **Selection** frame by the *extrema*. The results of the analysis are displayed in the **Results** frame. Several values for the peak are displayed: the position (E_p), the height, the width (1/2), $E_p - E_{p/2}$, charge pos. and charge neg. These values are explained below.

The results can be copied in the clipboard and pasted anywhere as text. They can also be saved in a text file.

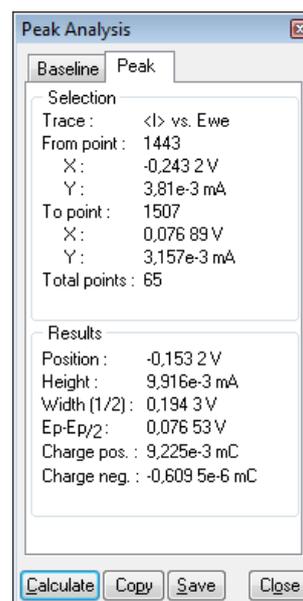


Fig. 144: Peak results tab.

4.2.1.3 Results of the peak analysis using a linear regression baseline

The following figure shows the result of the peak analysis performed on a cyclic voltammetry data file. The baseline used for the analysis is a linear regression baseline.

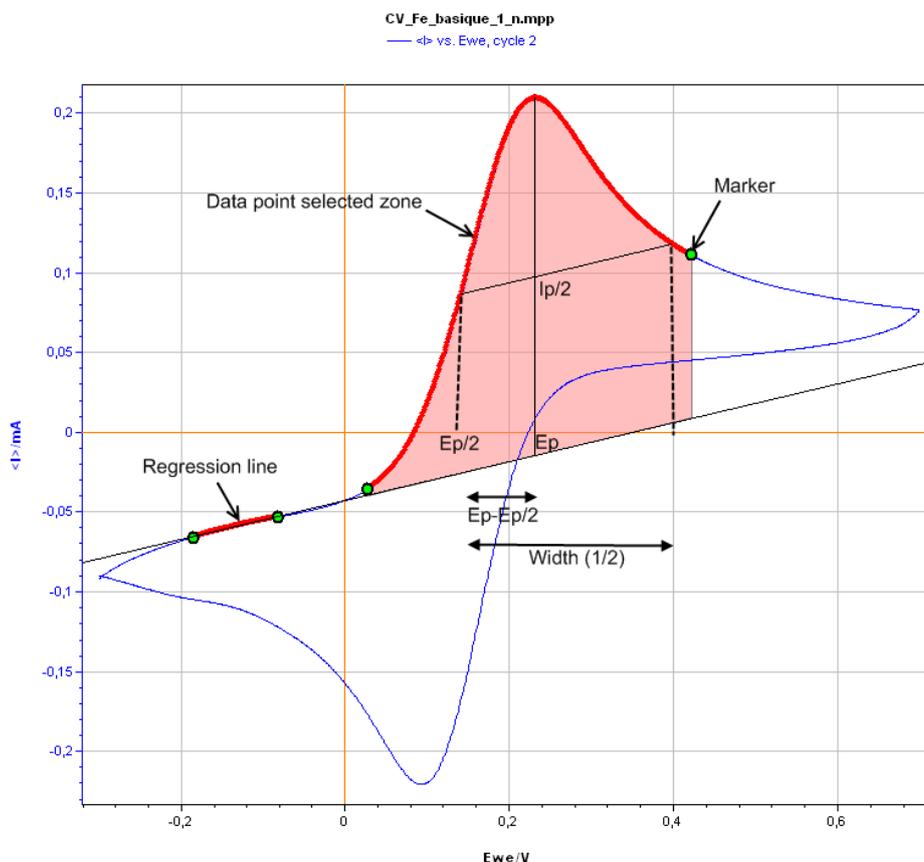


Fig. 145: Oxidation peak analysis on a cyclic voltammetry experiment using a linear regression baseline.

The different values in the **Results** frame of the peak analysis window are as follows:

- **Position** is the potential (E_p) corresponding to the max current value (determined according to the baseline).
- **Height** is the current value for the potential E_p (always according to the baseline).
- **Width (1/2)** is the peak potential width determined (when it is possible) at half the peak height, parallel to the baseline.
- $E_p - E_{p/2}$ is the semi-width for the first side of the peak.
- **Charge Pos.** is the charge related to the current above the baseline and **Charge Neg.** is the charge related to the current below the baseline. The area for the calculation of this charge is defined by the position of the green markers.

The results can be copied in the clipboard and pasted anywhere as text. They can also be saved in a text file.

4.2.1.4 Results of the peak analysis using a polynomial baseline

In fact, it is often difficult to apply a linear regression baseline to take into account the capacitive part of a curve or remove the beginning of a second current peak. A polynomial baseline could lead to a more significant fit. On Fig. 142, a polynomial baseline has been used to do a peak analysis. The oxidation peak of a polypyrrol film is analyzed using a polynomial baseline. With this baseline, we can avoid taking into account the beginning part of the pyrrol

monomer oxidation. The result variables are the same as for the analysis with a straight baseline.

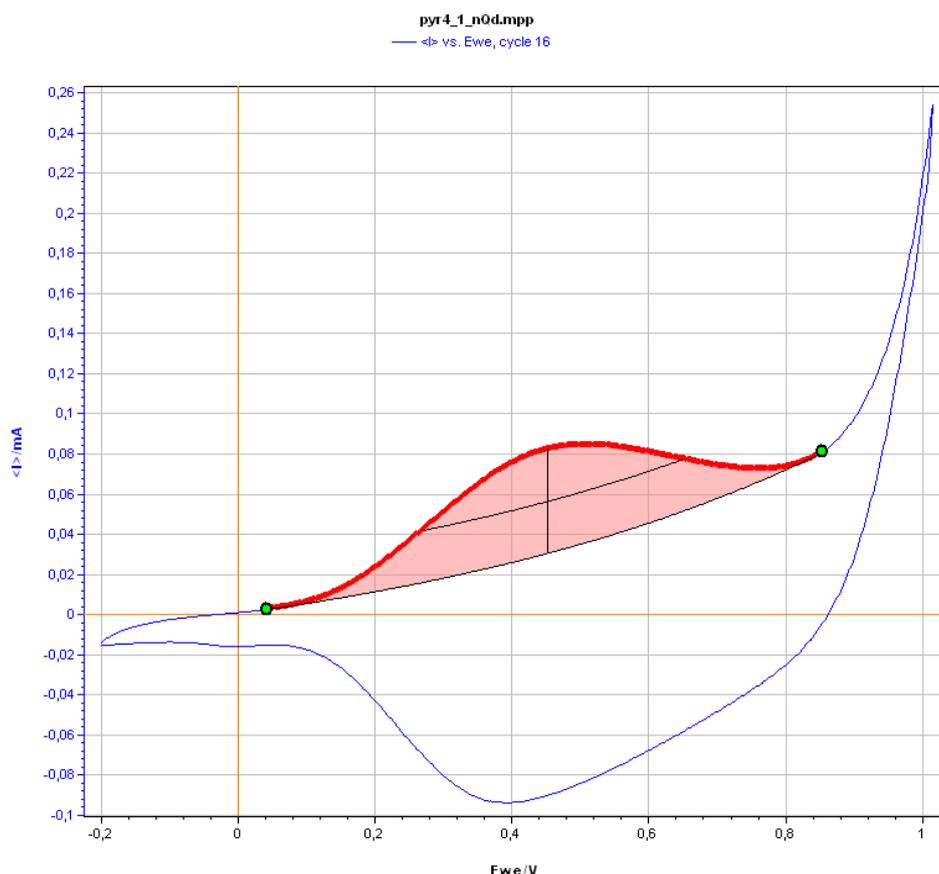


Fig. 146: Peak analysis on a cyclic voltammetry experiment using a polynomial baseline.

4.2.2 Wave analysis

The wave analysis  is the most useful tool for the analysis of experiments performed in a controlled hydrodynamic regime (for instance with a rotating disk electrode). When a data point zone is selected, clicking on “**Calculate**” will perform the analysis. The wave analysis is made according to two straight lines, defined using a linear regression fit. The software will automatically find the two parts of the curve with the shallowest slope for the fit. For the first regression the first 20 % of the selected data points are taken into account. The last 20 % of the selected data points are taken into account for the second regression. The data point zone for the analysis is shown in the **Selection** frame by the *extrema*.

The **Results** of the analysis are displayed in the **Results** frame. Several values for the wave are displayed: $E_{1/2}$ and the limit anodic and cathodic currents.

The results can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can also be saved in a text file.

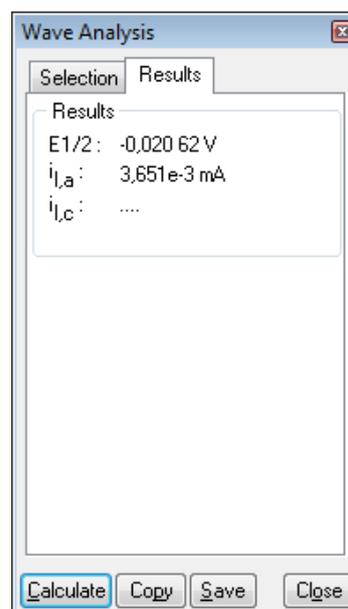


Fig. 147: Wave Analysis Results tab.

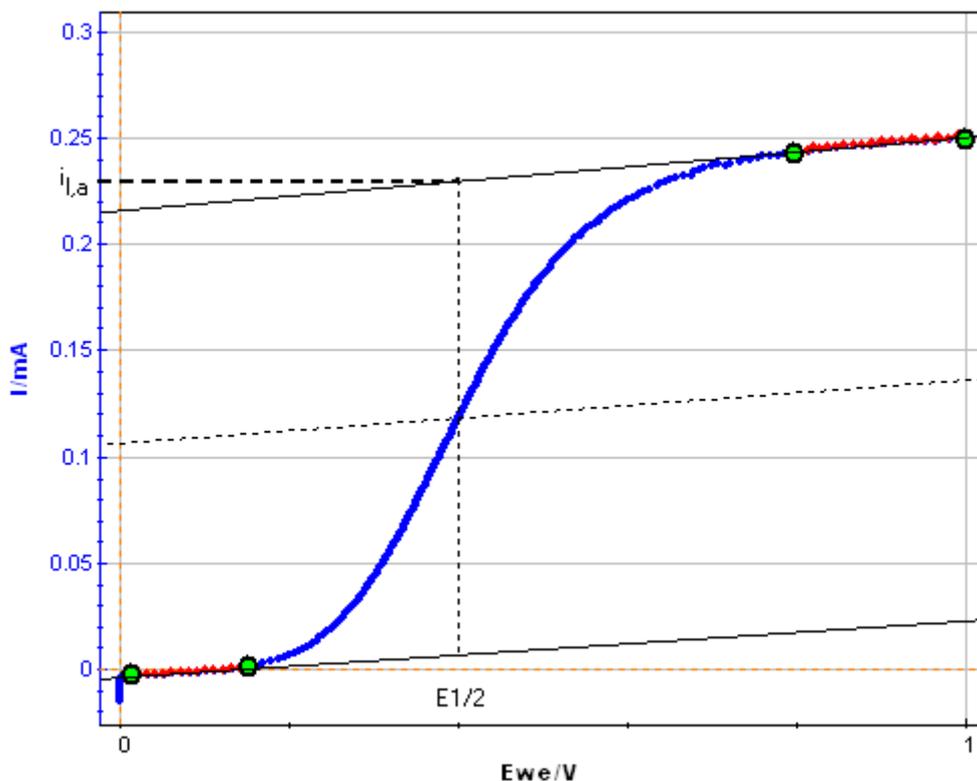


Fig. 148: Wave analysis on a curve resulting from a RDE experiment.

$E_{1/2}$ is the half-wave potential obtained by the intersection of the curve with the median between both linear regressions. $I_{1,a}$ is defined as the current value for $E = E_{1/2}$ on the anodic linear regression and $I_{1,c}$ is defined as the current value for $E = E_{1/2}$ on the cathodic linear regression.

4.2.3 CV Sim

CV Sim  is a tool designed for the simulation of cyclic voltammetry curves resulting from a voltammetry experiment.

It is a useful tool to elucidate the mechanism of an electrochemical reaction involving from one electron (E) to five electrons (EEEEEE).

To perform the simulation, it is assumed that the Initial current is equal to zero. The voltage sweep will start from E°

The user needs to define the number of electron transfer steps that are involved in the mechanisms *via* the combo box. E represents a mechanism with one electron transfer (E); and so on up to 5 electron transfer (EEEEEE). Depending on the number of electron transfers selected the corresponding number of tabs appears. The EC and CE electrochemical reactions are also available, C standing for bulk chemical reaction with no electron transfer.

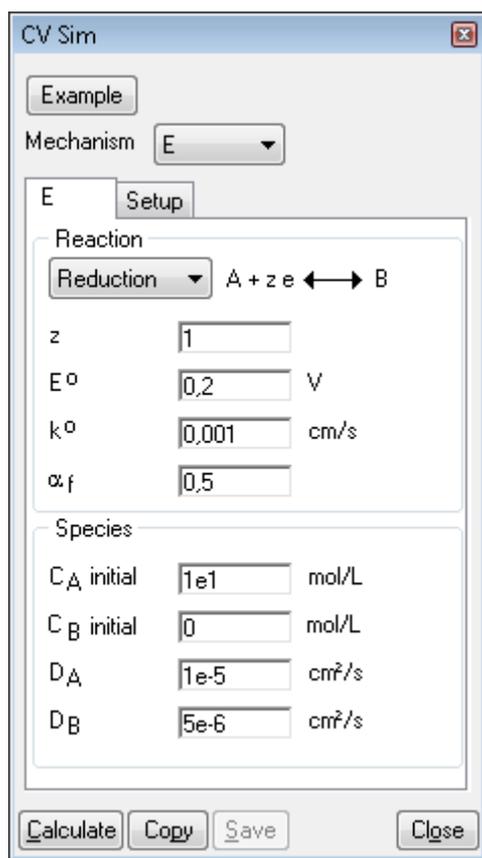


Fig. 149: CV Sim window with a single transfer.

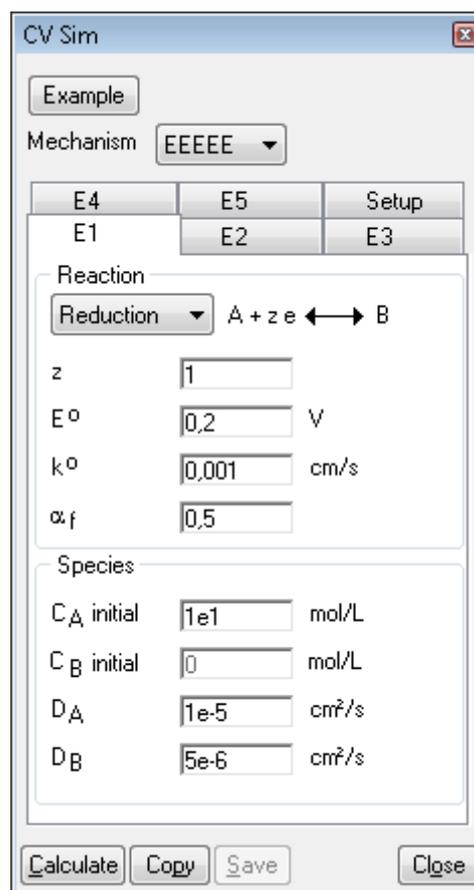


Fig. 150: CV Sim window with several transfers.

For each step, the type of reaction and the species characteristics are set in two different frames:

1. Reaction:
 - Reduction or oxidation has to be selected by the combo box
 - z represents the number of electron involved in the electron transfer
 - E° is the standard potential of the electron transfer step
 - k° is the heterogeneous rate constant
 - α_f is the charge transfer coefficient in the forward direction
2. Species:
 - C_x is the concentration of the species x .
 - D_x are the diffusion coefficients of the species x .

The experimental conditions are set in the “**Setup**” tab which is divided in five blocks:

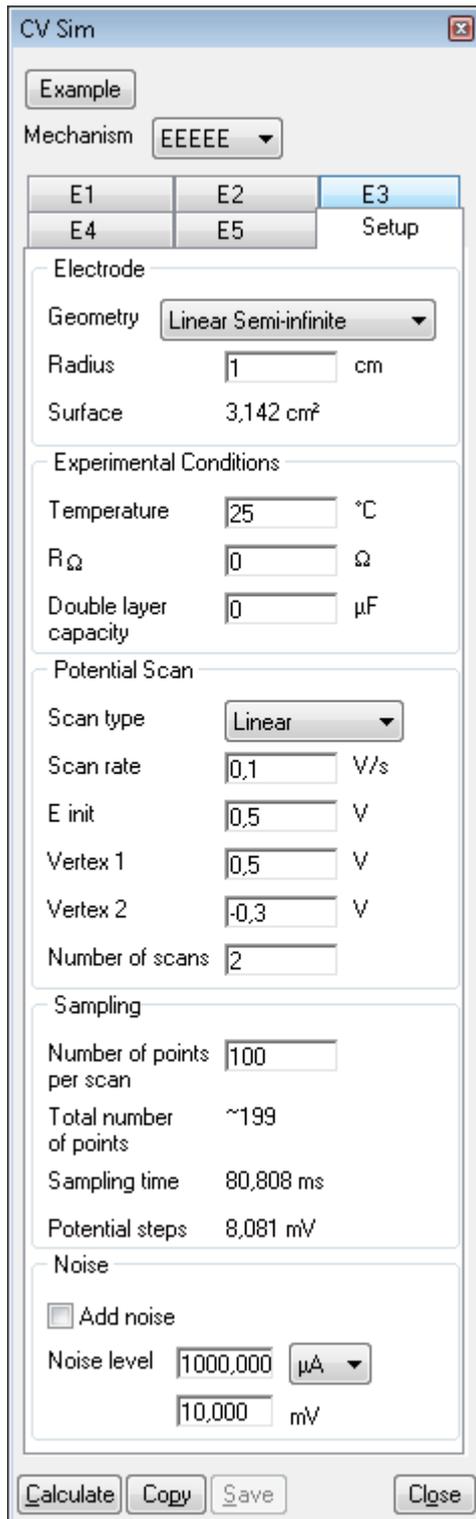


Fig. 151 : “Setup” tab of CV Sim

When all the parameters are set, the user has to click on the calculate button to display by default the simulated CV curve.

- Electrode
 - Geometry of the electrode can be linear semi-infinite or spherical semi-infinite
 - The surface area of the electrode is calculated from the value of the radius of the electrode
- Experimental conditions
 - Temperature in degree Celsius
 - R_{Ω} : the electrolyte resistance (ohmic drop) in Ohm
 - Double layer capacity in μF
- Potential scan
 - Scan type: linear or sinusoidal scan, respectively for CV or LASV simulation
 - Scan rate in V per second
 - The initial and the two vertex potential in V
 - Number of scans performed for the CV or LASV simulation
- Sampling

The user defines the number of points needed per scan to perform the simulation. The total number of points, the resolution in time and in voltage is indicated.
- Noise

Some noise in current or in voltage can be superimposed to the simulated curve.

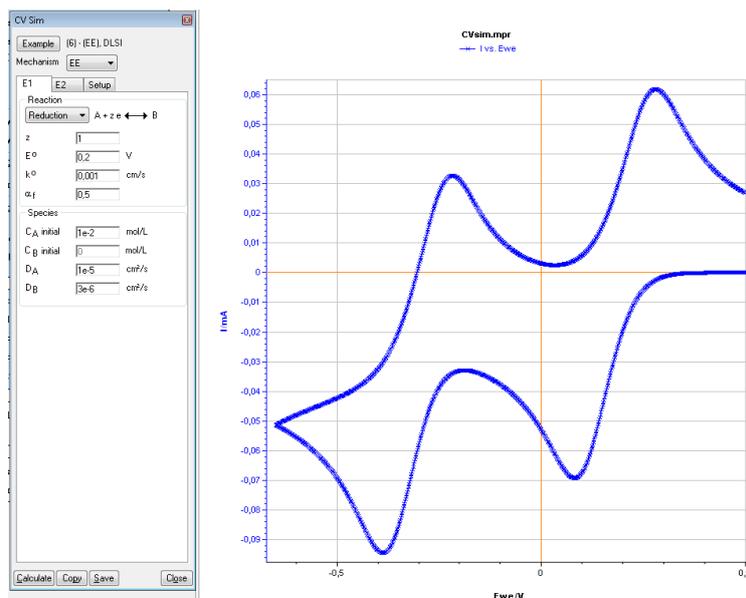


Fig. 152: CV simulation with two electron transfer.

It is also possible to display the interfacial concentration of the electroactive species involved in the mechanism. The resulting curve can be saved as mpr file.

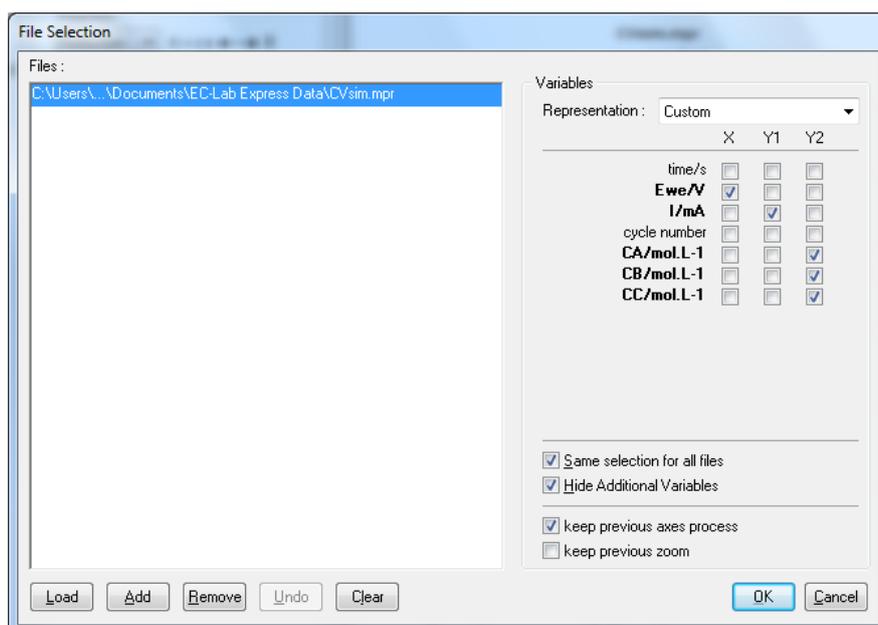


Fig. 153: Variable selection window to display concentrations

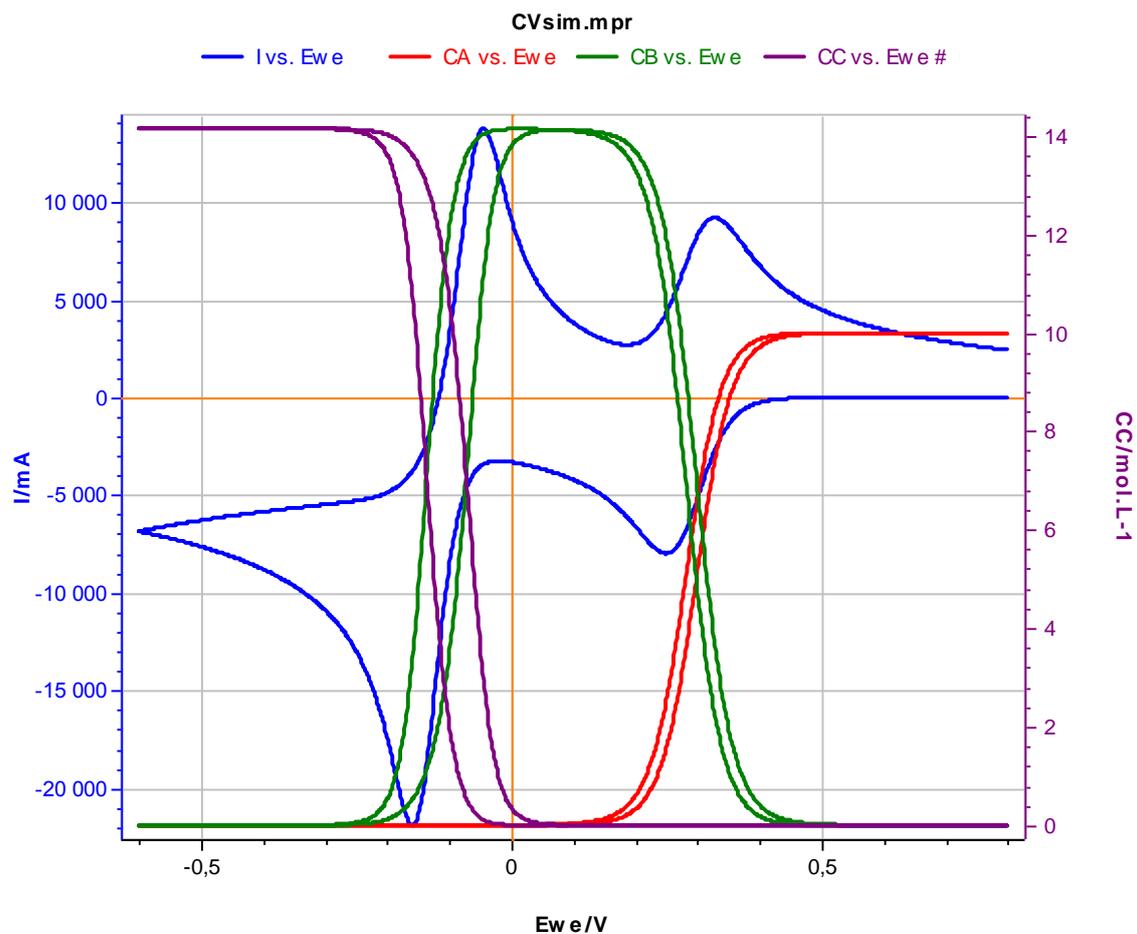


Fig. 154: Interfacial concentration variation versus electrode potential.

Several examples are available in the **CV Sim** window. To display an example, one has to click on the “**Example**” button on the top of the “**CV Sim**” menu. Then **CV Sim** examples window appears to select the mechanism of interest:

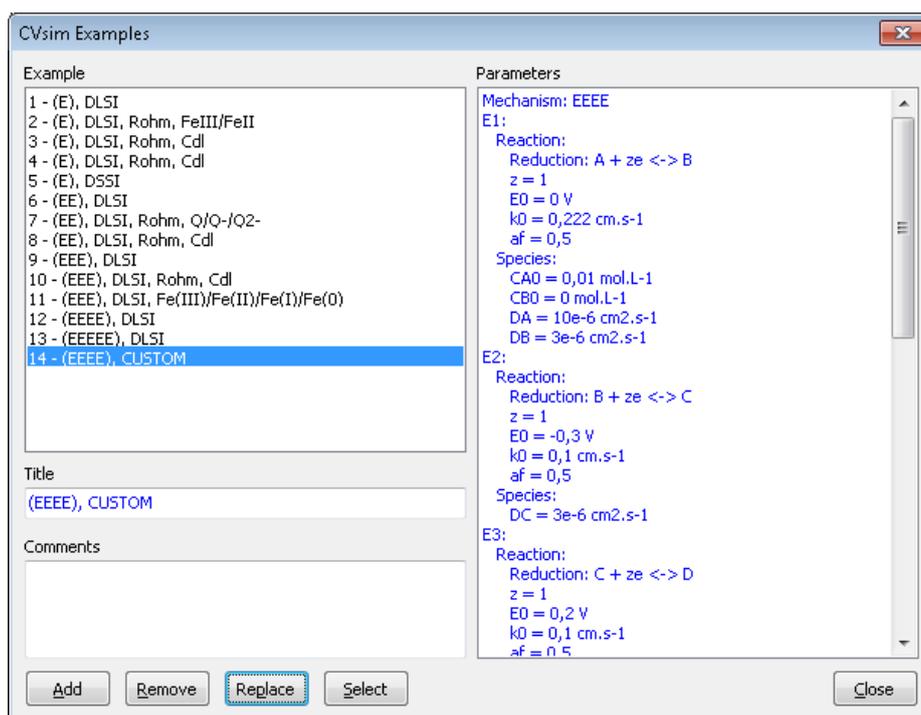


Fig. 155: CV Sim examples window.

13 predefined examples are available in this window. The corresponding parameters are displayed on the right column. Custom reactions can be added by the user by clicking on the “Add” button. The custom parameters must be entered in the parameters window, then needs to be added to the custom example by clicking on Replace.

4.3 Electrochemical Impedance Spectroscopy menu

Impedance analysis is a powerful tool to determine the mechanism involved in an electrochemical reaction and the values of the kinetic parameters of this mechanism. Electrochemical impedance data analysis allows the user to propose an electrochemical reaction mechanism to define the system. The expression of the faradaic impedance of a certain type of reaction can be represented by an equivalent circuit of resistors, capacitors, inductors and diffusion elements with specific values. Knowing these values and the type of equivalent circuit help interpreting the impedance data. The following section describes:

- the electrical components
- Z Sim, which is the EC-Lab® Impedance graph simulation tool,
- Z Fit which is the EC-Lab® impedance fitting tool,
- the Mott-Schottky fit dedicated to semi-conductor analysis and the
- Kramers-Kronig transformation, which helps determining that the impedance measurement was performed on a linear, stable, time-invariant system and is hence valid.

4.3.1 Electrical equivalent elements: description

The impedance analysis tool contains currently 13 different electric components. These components are:

- R: resistor,
- L: self/inductor,
- L_a : modified self/inductor,
- C: capacitor,
- Q: Constant Phase Element (CPE),

- W: Warburg element simulating the semi-infinite diffusion,
- W_d : Warburg diffusion element simulating the convective diffusion,
- M: restricted linear diffusion Element,
- M_a : modified restricted linear diffusion,
- M_g : anomalous diffusion,
- G: Gerischer element
- G_a : modified Gerischer element #1
- G_b : modified Gerischer element #2

4.3.1.1 Resistor: R

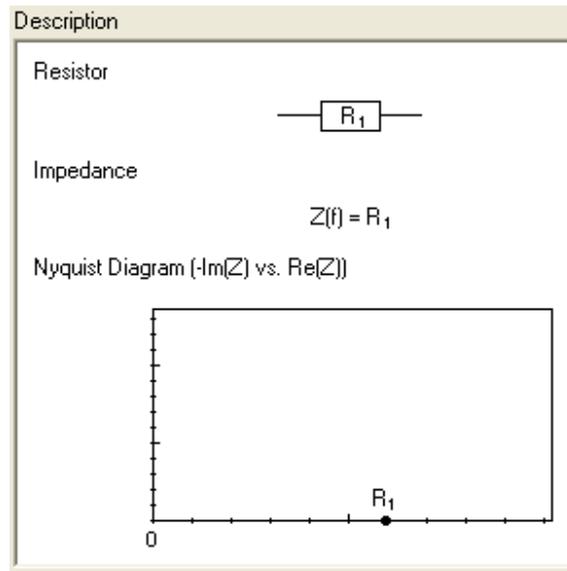


Fig. 156: Resistor element description.

The resistor element is defined as a passive component with a constant value when frequency varies. Fig. 156 describes the resistor with its symbol, its faradic impedance and a view of its Nyquist representation. The resistor element is characterized by a constant value that can be measured in the Nyquist diagram by the Real part ($Re(Z)$) for an imaginary part equal to zero ($-Im(Z)=0$)

4.3.1.2 Inductor: L

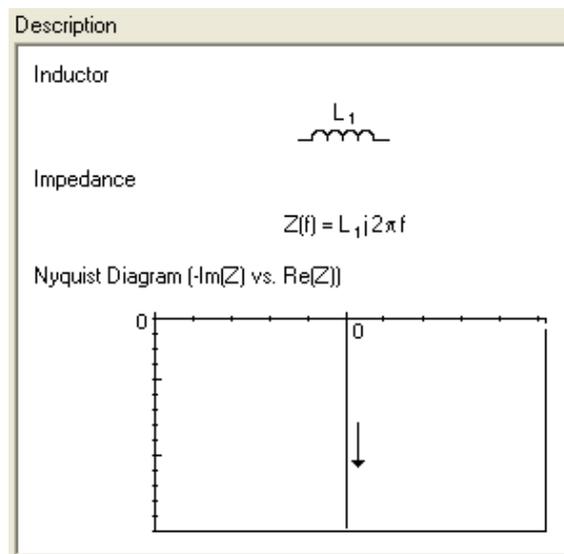


Fig. 157: Inductor element description.

The inductive element has impedance with a frequency dependency (as shown on the faradic impedance equation). The Nyquist plot of an inductance is a vertical straight line in the imaginary negative part ($-\text{Im}(Z) < 0$ ou phase = $\pi/2$).

4.3.1.3 Inductor: L_a

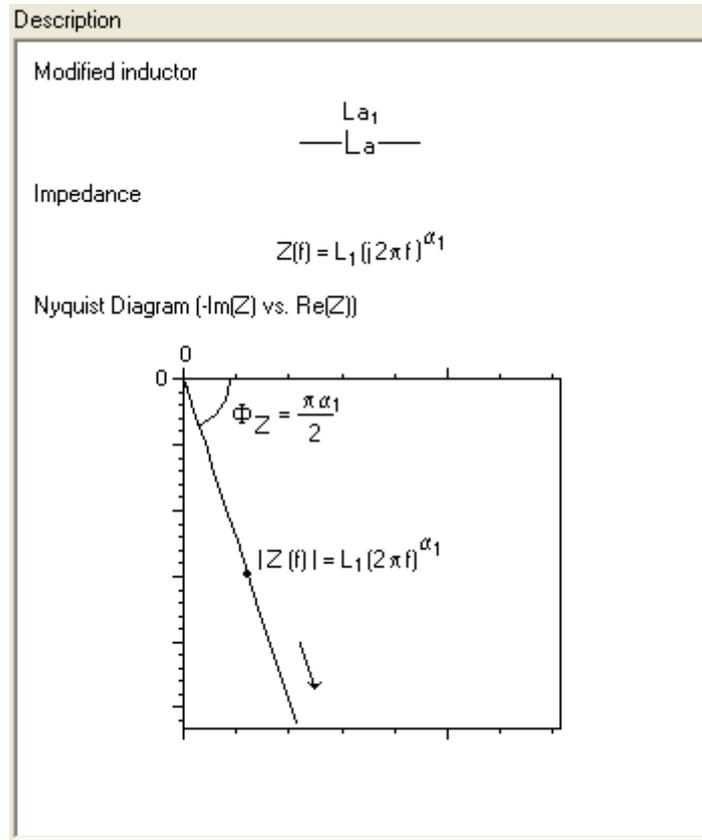


Fig. 158: Modified inductor element description.

The modified inductance L_a is an electric component defined on based on the inductance model L . The modified inductance can be used to represent the presence of an unusual inductance in the Nyquist diagram. It has an impedance with a frequency dependency similarly to the inductance but with an additional parameter α_1 (as shown on the impedance equation Fig. 156). The Nyquist plot of a modified inductance is a straight line in the imaginary negative part but not vertical ($-\text{Im}(Z) < 0$ with phase = $\alpha_1 \pi/2$). More info can be found in the corresponding Application Note #42.

4.3.1.4 Capacitor: C

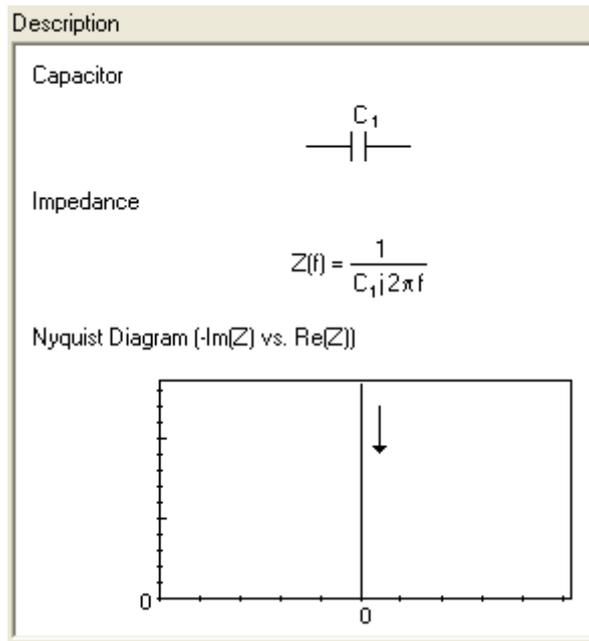


Fig. 159: Capacitor element description.

Capacitor C is a common electrical element representing an ideal capacitor. Its impedance is frequency dependent. The Nyquist plot of such an element corresponds to a vertical straight line in the imaginary positive part: $(-\text{Im}(Z) > 0)$ or phase = $-\pi/2$. The faradaic impedance decreases when the frequency increases.

4.3.1.5 Constant Phase Element: Q

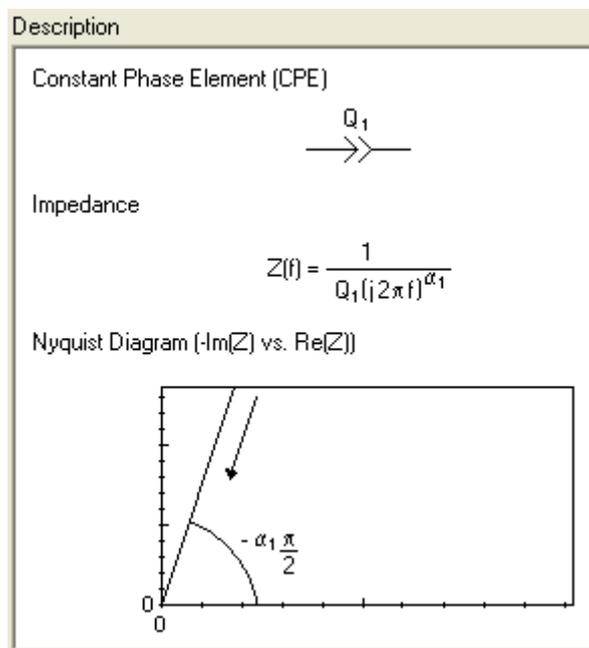


Fig. 160: Constant Phase Element description.

The CPE impedance is also frequency dependent. The Nyquist plot of such an element corresponds to a straight line in the imaginary positive part $(-\text{Im}(Z) > 0)$ with a $-\alpha\pi/2$ angle with the real axis. The faradaic impedance of the CPE decreases when the frequency increases.

4.3.1.6 Warburg element for semi-infinite diffusion: W

The Warburg element can be used to simulate a semi-infinite linear diffusion that is unrestricted diffusion to a large planar electrode.

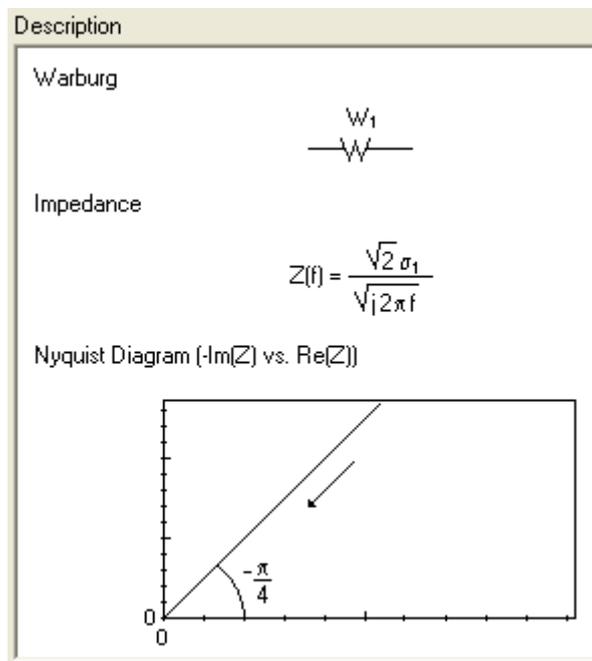


Fig. 161: Warburg diffusion element description.

The Warburg impedance is an example of a constant phase element for which the phase angle is constant $-\pi/4$ and independent of frequency. The Warburg is unique because absolute values of the real and imaginary components are equal at all frequencies.

4.3.1.7 Warburg element for convective diffusion: W_d

The Warburg element for a convective diffusion is an approximation mainly used in case of diffusion on a Rotating Disk Electrode in a finite length. The mass transport is supposed to happen only by diffusion in the Nernst diffusion layer and the solution is considered homogeneous outside this layer. The impedance when a species diffuses through the Nernst Diffusion Layer is described by W_d .

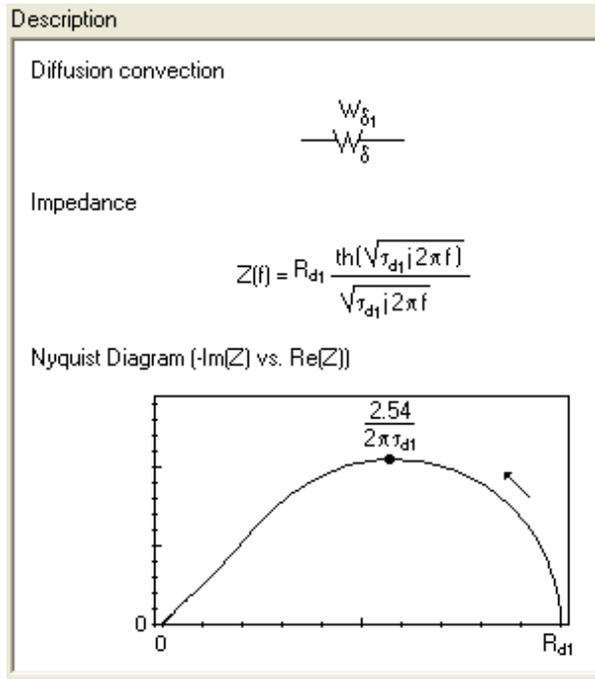


Fig. 162: Warburg element for convective diffusion.

The Warburg element for convective diffusion is equivalent to the Warburg element in the high frequency range ($f \gg 2.54/(2\pi\tau_{d1})$).

4.3.1.8 Restricted diffusion element: M

This diffusion element is used for finite length linear diffusion, for example in the case of insertion reactions.

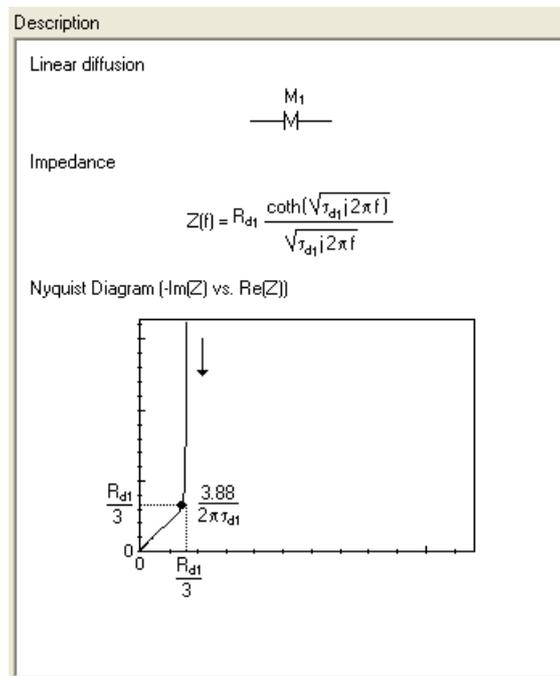


Fig. 163: Restricted Diffusion element.

The restricted diffusion element is equivalent to the Warburg element in the high frequency range ($f \gg 3.88/(2\pi\tau_{d1})$) and to an R and C in series circuit in the low frequency range.

4.3.1.9 Modified restricted diffusion element: M_a

This diffusion element is used for finite length linear diffusion, for example in the case of insertion reactions for which the element M is not suitable.

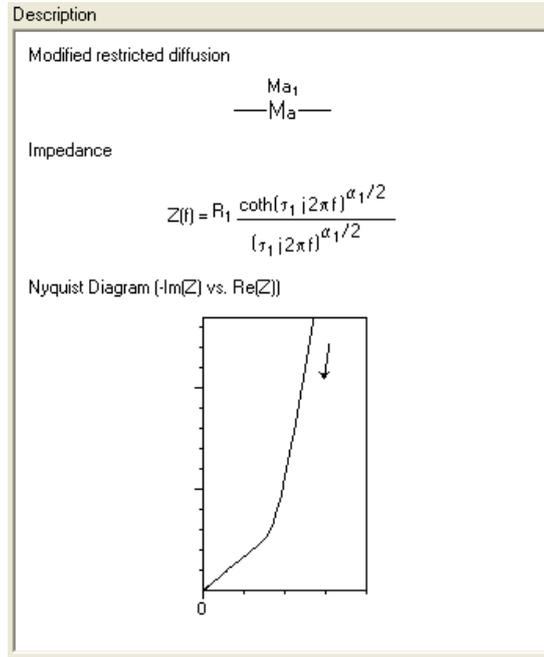


Fig. 164: Modified Restricted Diffusion element.

The modified restricted diffusion element is equivalent to the Warburg element in the high frequency range ($f \gg 3.88/(2\pi\tau_{d1})$) (see element M) but in the low frequencies, instead of being a vertical straight line, it has a phase of $\alpha_1\pi/2$.

4.3.1.10 Anomalous diffusion element or Bisquet diffusion element: M_g

A second modified diffusion element M_g has been used for models that do not match the restricted diffusion element M nor the modified restricted diffusion element M_a . This element is also called Bisquet element. The expression of its impedance is given below:

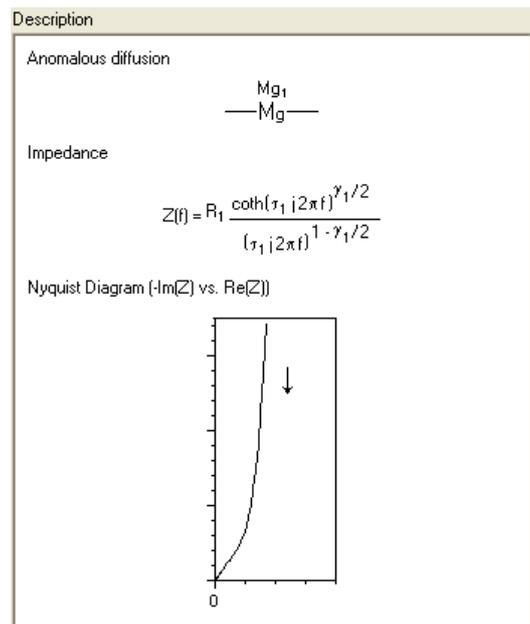


Fig. 165: Anomalous Diffusion element.

4.3.1.11 Gerischer element: G

The Gerischer circuit element arises when an electroactive species undergoes a chemical reaction in the bulk. A Gerischer element has also been used to model a porous electrode.

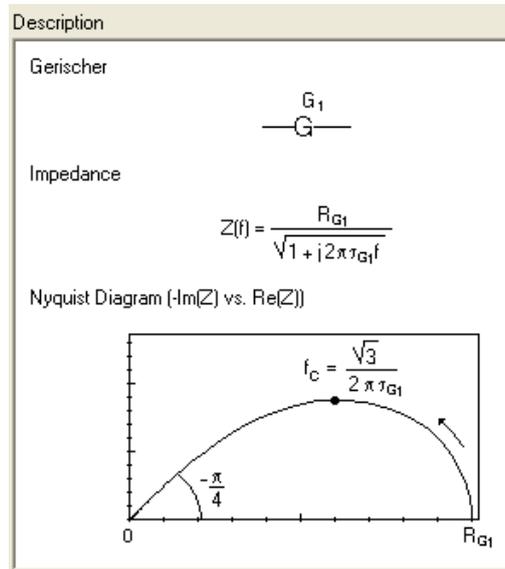


Fig. 166: Gerischer Diffusion element.

At high frequency the **G** circuit element presents a 45° line on the Nyquist plot.

4.3.1.12 Modified Gerischer element #1: Ga

The expression of the modified Gerischer circuit element derived from that of the Gerischer diffusion element expression by adding the parameter α .

The expression of the impedance of the modified Gerischer is given below.

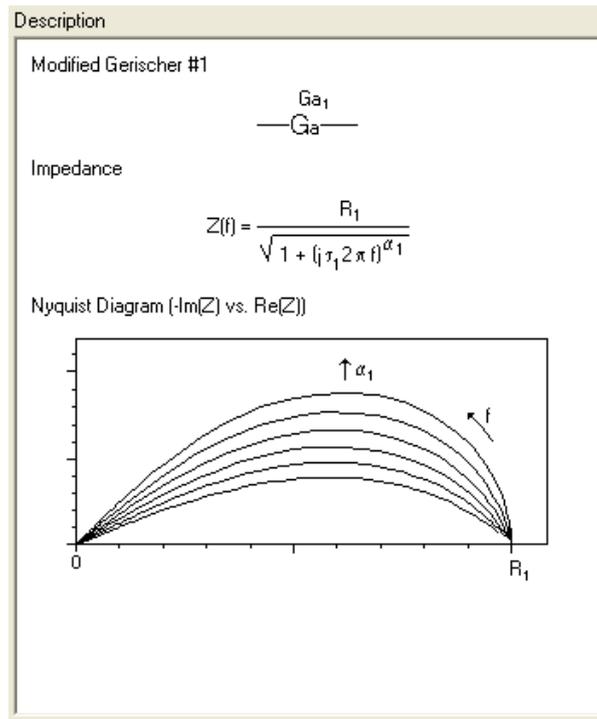


Fig. 167: Modified Gerischer diffusion element #1.

4.3.1.13 Modified Gerischer element #2: G_b

A second modified Gerischer circuit element G_b has been used for models that do not match the Gerischer element G nor the modified Gerischer element G_a . The expression of the impedance of the modified Gerischer G_b is given below:

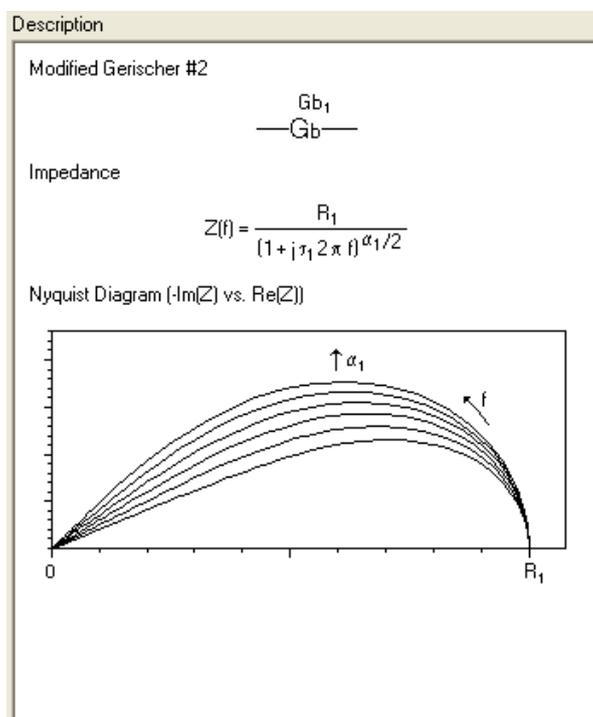


Fig. 168: Modified Gerischer diffusion element #2.

4.3.2 Simulation: ZSim

In order to define the equivalent circuit after an impedance experiment, the user can create an electrical circuit and plot the corresponding Nyquist impedance diagram in a given frequency range. To illustrate the capabilities of this tool, let us consider the ZPOT_Fe_basique.mpr data file that the user can find in the sample folder (c:\ECLab\Data\Samples). The aim of this section is to define the appropriate circuit for the fit.

The data file that will be used in the simulation section and the fitting section has been made from an iron solution on a gold disc-working electrode in a pure diffusion regime in the potenti mode at the open circuit potential. Open the "PEIS_Fe_basique.mpr" data file using the "Experiment" menu ("Load data file..."). The following window will be displayed:

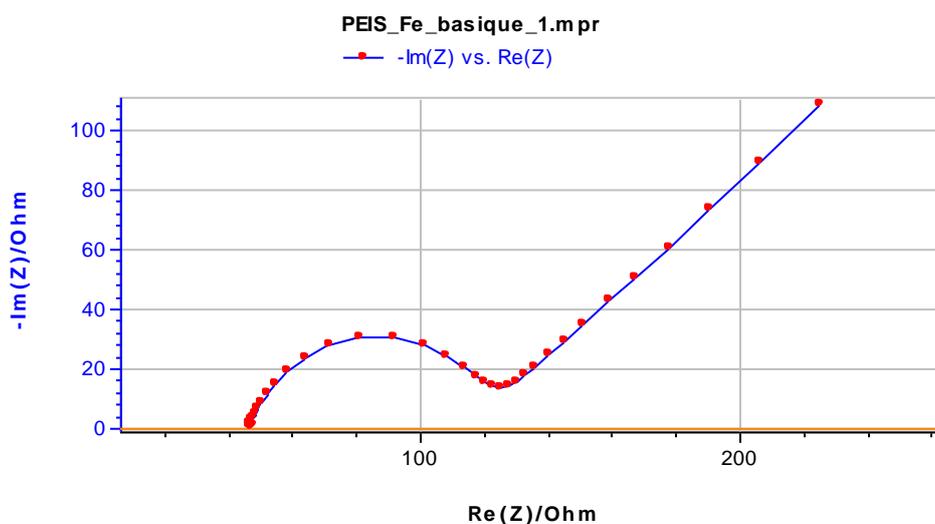


Fig. 169: Experimental Nyquist impedance data file.

This is a typical impedance data file performed in a pure diffusion regime in a solution containing both Ox and Red species of a redox system.

4.3.2.1 ZSim window

1st step:

To simulate a curve with the same shape as the previous experimental results, click on ZSim icon  or right-click on the graph and select "Analysis\ZSim". Then the ZSim selection window appears with the corresponding graphic window. This window shows the simulated graph of the circuit with the values selected.

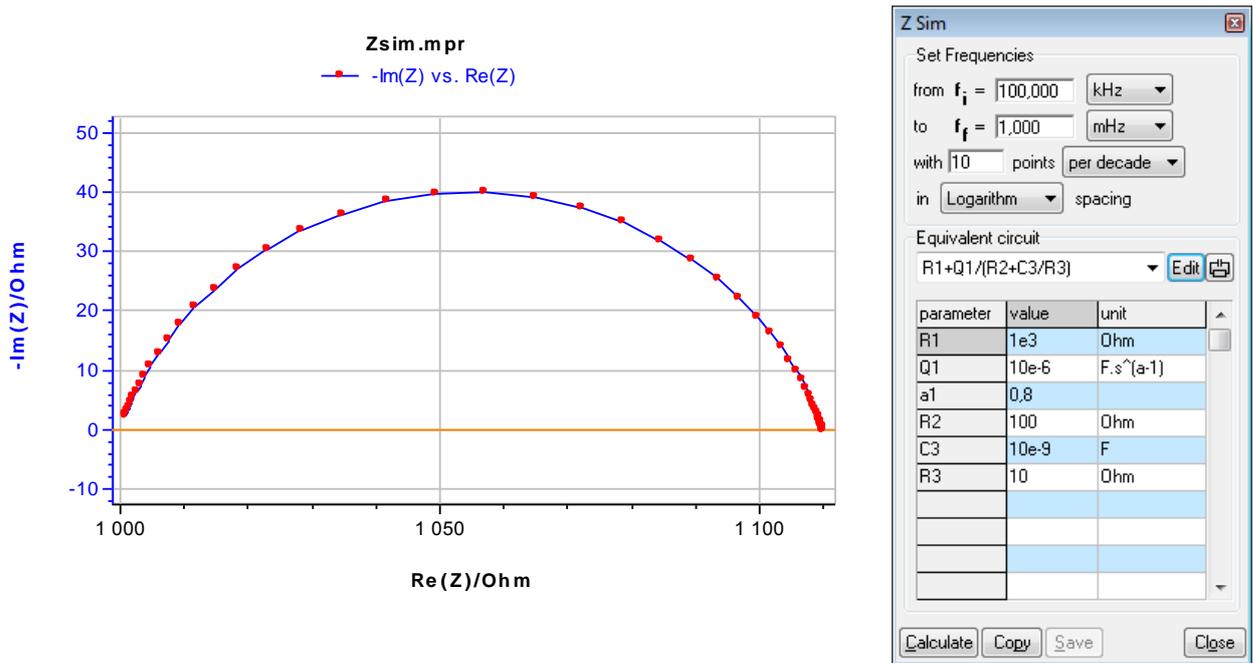


Fig. 170: ZSim menu and the graph corresponding to the selected circuit.

Note: the simulation circuit opened by default is the one used in the previous simulation.

2nd step:

In the frequency frame, set the frequency range (between 500 kHz and 10 μHz) with the number of points per decade and the spacing (logarithmic or linear). Select an equivalent circuit in the list. If the required circuit is not in the list, then the user can create a new circuit in the “Edit” window. Click on “Edit” to display this window.

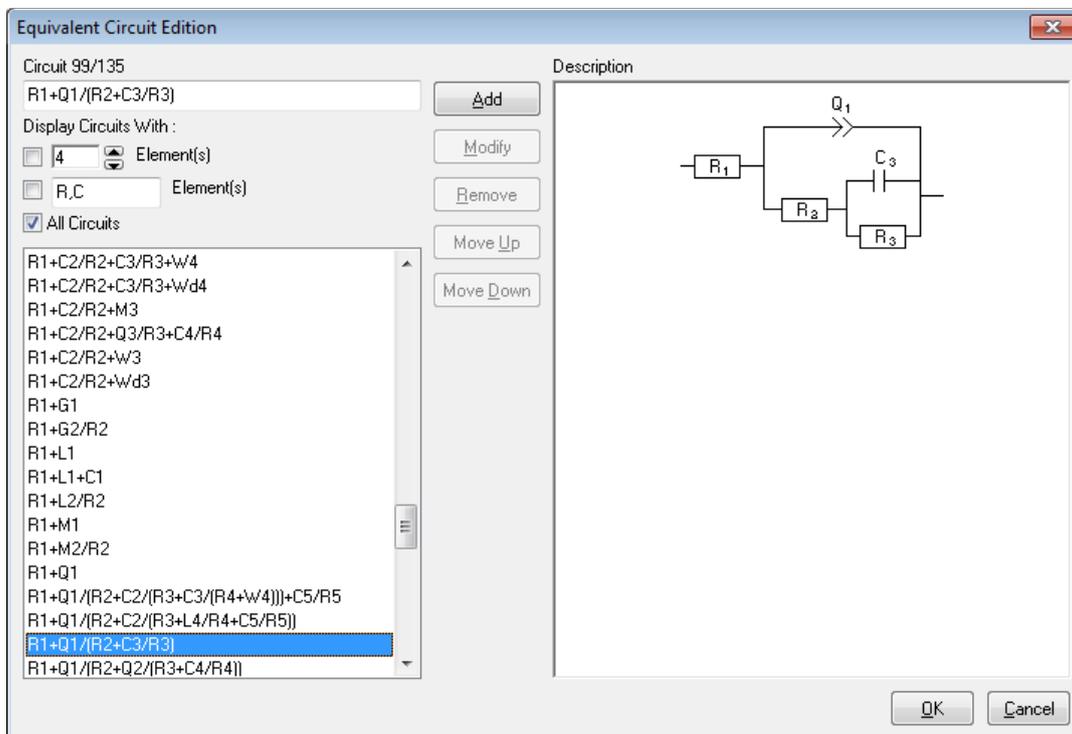


Fig. 171: ZSim/Zfit Equivalent Circuit Edition window.

The circuit base contains more than 130 circuits. The user can create new circuits to be added (in blue) to the list. The most usual circuits are described and explained on the right side

of the window. This description contains the circuit scheme, the faradaic impedance expression and the impedance Nyquist diagram.

4.3.2.2 Circuit selection

The user can pick a circuit in a list containing all the circuits or only some circuits according the number and type of elements desired in the circuit. To refine the list the boxes

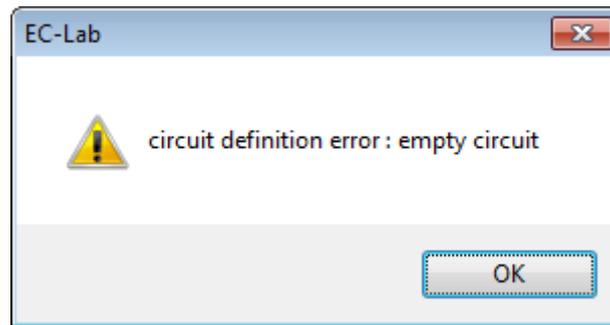


and must be checked. Please note that in the example above, all the circuits with 4 elements containing *at least* 1 R and 1 C will be displayed, which means the displayed circuits might contain L or W elements.

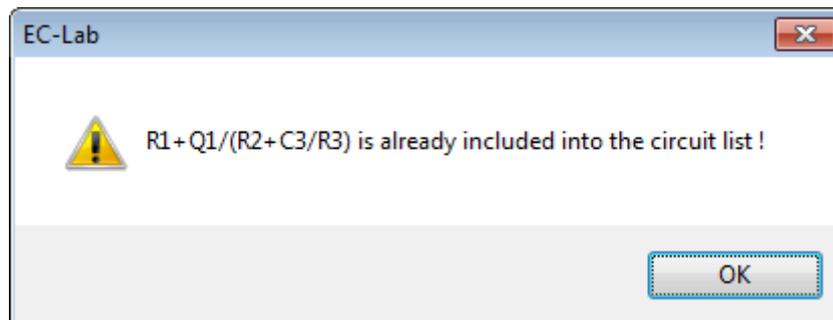
4.3.2.2.1 Circuit description

If the required circuit does not appear in the list, the user can create it. The new circuit can be written in the first frame (top) with several rules.

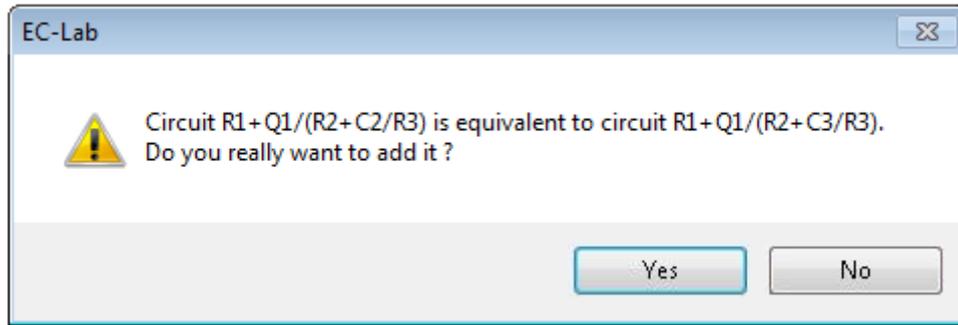
- 1- For elements in series the used sign is "+". For example for R in series with C the equivalent circuit will be "**R1+C1**".
- 2- For elements in parallel the sign is "/". For example for R in parallel with C the equivalent circuit will be "**R1/C1**".
- 3- If several elements are in series or parallel with each other, then the considered elements must be set between brackets. For example for R2 and C2 in series together and in parallel with R1, the equivalent circuit will be "**R1/(R2+C2)**".
- 4- To write circuits, it is necessary to give a number for each element to differentiate the elements. If the syntax is not correct, an error message will be displayed:



- 5- If the new circuit is already in the list, this message will be displayed:



- 6- If the new circuit is equivalent to an existing circuit the following message will be displayed :



- 7- Circuits created by the customer will be stored in the list in blue. They can be modified, removed from the list or moved in the list.
- 8- For the selected file (PEIS_Fe_basique.mpr), find the correct circuit (Randles Circuit):
 $R1+Q2/(R2+W2)$
- 9- Click on “Calculate” to show the corresponding curve on the graphic window.

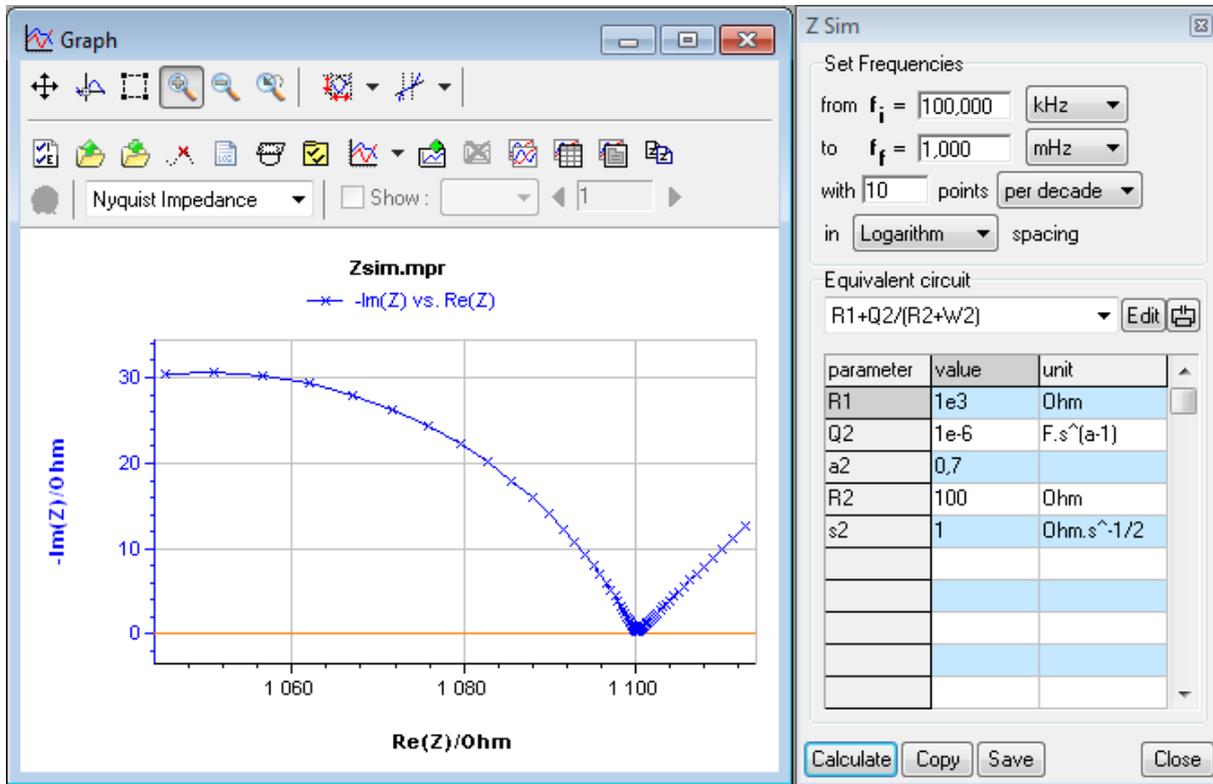


Fig. 172: ZSim Circuit Edition window.

- 10- To adjust this curve to the experimental one, the user must adjust values for each parameter as described in the window below and click on “**Calculate**”.

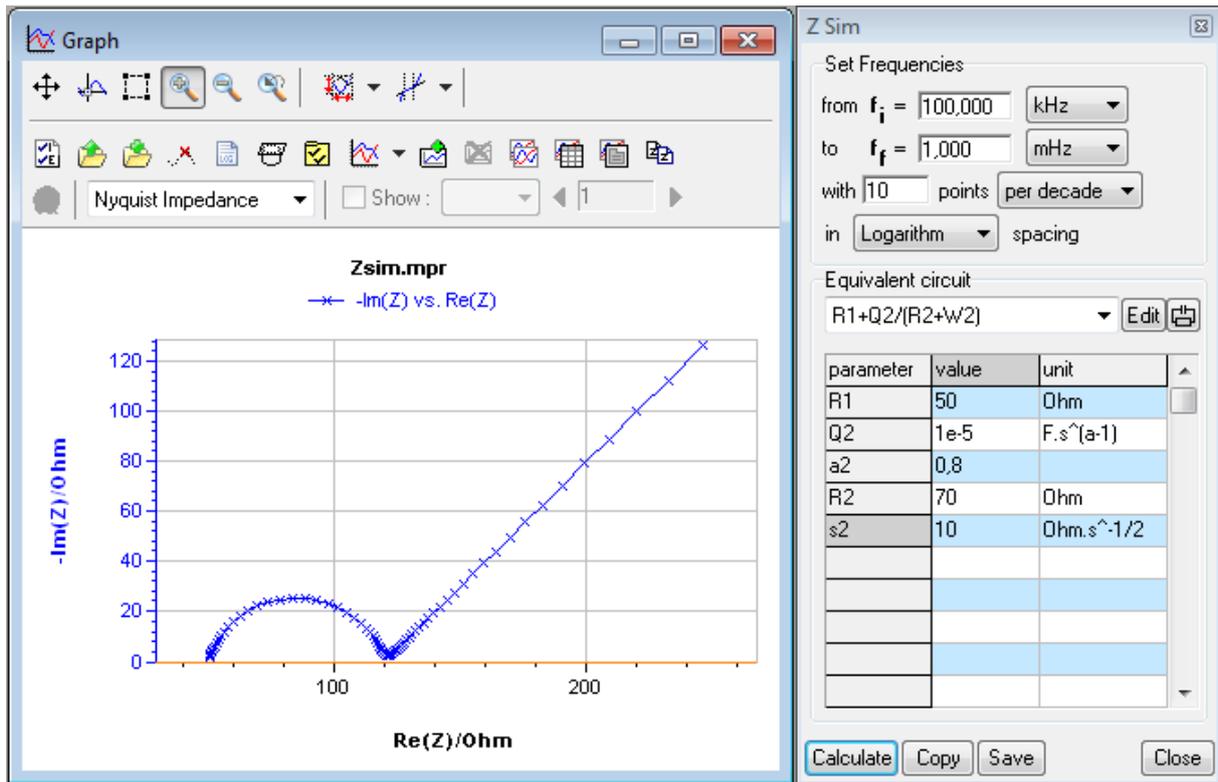


Fig. 173: ZSim Circuit Edition window with adjusted parameters.

The results can be copied to the clipboard and saved in a “Zsim.mpr” file. The user can modify parameters, which will be implemented when clicking on “Calculate”. To store this simulation the user will have to give another name to the data file because by default any simulation results are saved in a Zsim.mpr file.

4.3.3 Fitting: ZFit

When the correct equivalent circuit is defined with ZSim, the user can set it in the ZFit window to identify parameters of the elements with the experimental data points. Zfit works the same way as Zsim. If the user already knows what equivalent circuit to use it is not necessary to use Zsim. There are two tabs in the Zfit window: **Selection**, which shows the selected points and **Results**. The **Results** window contains two frames: Equivalent Circuit and Fit.

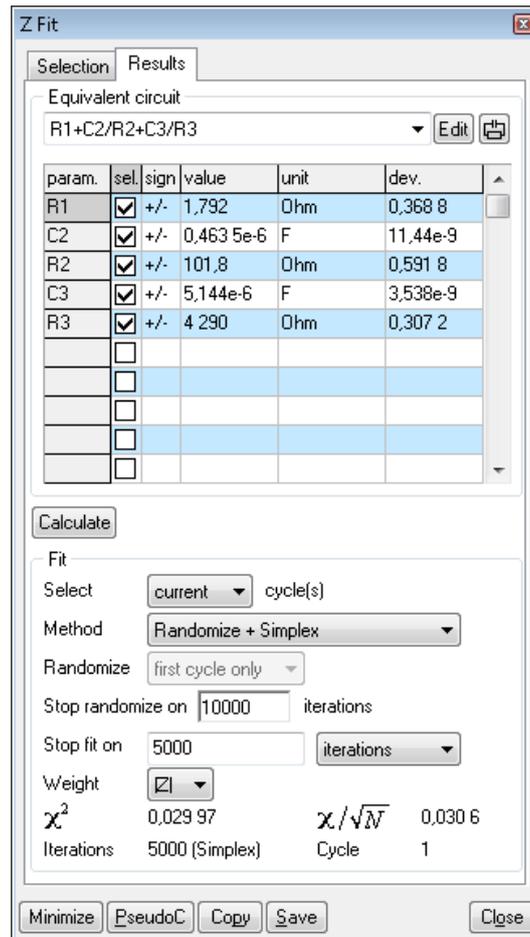


Fig. 174: ZFit Circuit selection window.

4.3.3.1 Equivalent circuit frame

As for the Zsim selection window, the Zfit selection window enables the user to edit and create a circuit. For more details about the circuit editing window please refer to the previous section. In the equivalent circuit frame, the table shows:

- the name of each parameter
- the sel box, that allows the user to choose if the parameter is taken into account in the minimization. If this box is not ticked the parameter value set in the cell is considered as the correct value and is not be modified during the minimization.
- the sign of the parameter value that can be changed by double clicking in the +/- box. If +/- is displayed, it means that the sign will be determined by the minimization
- the unit of the parameter
- a dev. parameter calculated using the Levenberg-Marquardt algorithm. This parameter can be assimilated to a standard deviation. The standard deviation is a confidence interval of the parameter. It gives an estimate of the relevancy of the parameter: if the dev. is very high it means that a great variation of the parameter will not affect very much the quality of the fit. Hence, the considered parameter is not critical in the minimization process.

The **Calculate** button will calculate and plot the data points for the parameter values set in the table without performing any minimization.

4.3.3.2 The Fit frame

- **Select current/cycles:** The ZFit tool can perform successive fits with the same model on successive curves in the same data file. The first thing to be defined by the user is the cycle for which the minimization is performed (either one single minimization performed on the cur-

rent cycle displayed on the graph or successive minimizations made on all the cycles of the experiment).

Minimization **Method**:

- Default values are set for every parameter but they rarely fit the real experimental values. Before fitting, in order to help the algorithm to find the best values, it is necessary to use initial values as close as possible to the real ones. A randomization is added before the fitting to select the most suitable set of parameter values. The most suitable set of parameter values are the values that yield the lower χ^2 value. χ^2 gives an estimation of the distance between the real data and the simulated data. Its expression is :

$$\chi^2 = \sum_{i=1}^n \frac{|Z_{meas}(i) - Z_{simul}(f_i, param)|^2}{\sigma_i^2}$$

with $Z_{meas}(i)$ is the measured impedance at the f_i frequency
 $Z_{simul}(f_i, param)$ is a function of the chosen model
 f_i is the frequency i
 $param$ is the model parameters (ex: R1, R2, C1, Q1, ...)
 σ_i is the standard deviation.

Considering that for each frequency the impedance has the same standard deviation then σ_i is equal to σ . In this case, minimizing χ^2 is the same as minimizing χ^2/σ .

Hence, the expression of the χ^2 criterion as it is used in Zfit is :

$$\chi^2 = \sum_{i=1}^n |Z_{meas}(i) - Z_{simul}(f_i, param)|^2$$

In this case the unit of χ^2 is Ohm.

If the user chooses to weigh the data points with $|Z|$ the impedance modulus, then the expression of χ^2 is :

$$\chi^2 = \frac{\sum_{i=1}^n |Z_{meas}(i) - Z_{simul}(f_i, param)|^2}{|Z|}$$

The available minimization algorithms are the following:

- *Randomize*: if this is selected, the software picks random values for all the parameters, calculate the χ^2 and keep for each parameter the value that yielded the lowest χ^2 . It should be mostly used to provide suitable initial values for a further minimization but can also be used as a minimization tool only slower and less powerful than the other two tools.
- *Simplex*: also called Downhill Simplex, is a minimization method *per se* mostly used to minimize linear functions.
- *Levenberg-Marquardt*: it is also a minimization method mostly used to minimize non-linear functions.

Using the parameters entered in the table as initial values, these two iterative methods that will provide the parameters yielding the lowest χ^2 . If the initial values are too far off, these two algorithms will not converge. It is the reason why two other minimization processes are offered.

- *Randomize+Simplex*: Randomize is first used to provide optimal initial values for the subsequent Simplex minimization.
- *Randomize+Levenberg-Marquardt*: Randomize is first used to provide optimal initial values for the subsequent *Levenberg-Marquardt* minimization.

- **Randomize**: if the experiment contains several cycles and **all cycles** are selected for the fit, the user has the possibility of selecting the **Randomization** on the first cycle only or on every cycle. The number of iterations for which the **Randomization** is stopped can be cho-

sen. The more iterations, the more likely it is that the optimal initial values will be found. The more parameters are used, the more iterations are needed.

- **Stop Fit:** it is possible to set a stop condition for the minimization iteration either on the number of iterations or on the relative error. The relative error is the difference between the value of a parameter at an iteration i and at an iteration $i+1$. The relative error is normalized, so that it can be applied to any type of parameter (R, C, L and so on).

- **Weight:** if $|Z|$ is chosen more importance are given, during the minimization process, to the points with a high impedance modulus. In this case χ^2 is divided by $|Z|$.

If 1 is chosen the same importance is given to all the data points and the expression of χ^2 is the same as defined above.

- χ^2 was defined above and is the criterion that needs to be minimized. The lower it is, the better the fit is. $\chi/(N)^{1/2}$ with N the number of points, is a normalized expression of χ^2 , whose value is independent on the number of points. It is equivalent to an error.

During the fitting process, the iteration number as well as the cycle number are displayed at the bottom of the window.

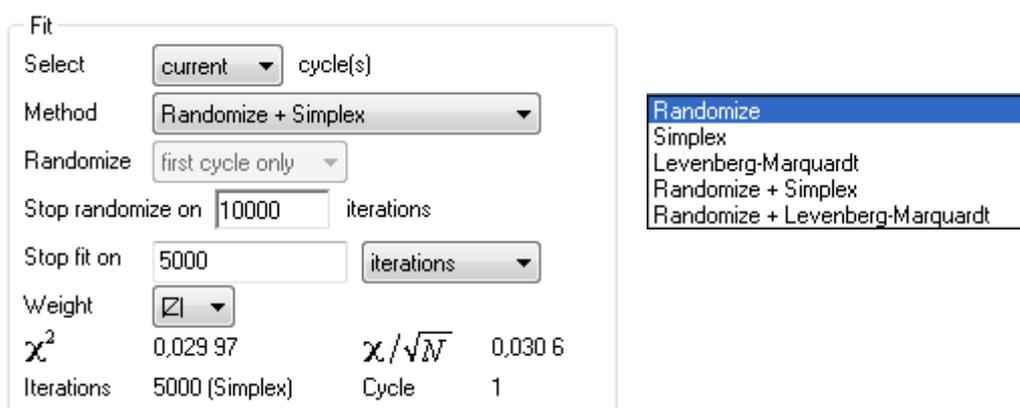


Fig. 175: Fitting method selection.

To perform the calculation, click on “**Minimize**”.

4.3.3.3 Application

Considering the previous example (ZPOT_Fe_basique.mpr), the following result may be obtained using the “**Randomize+Simplex**” option with the default parameter values:

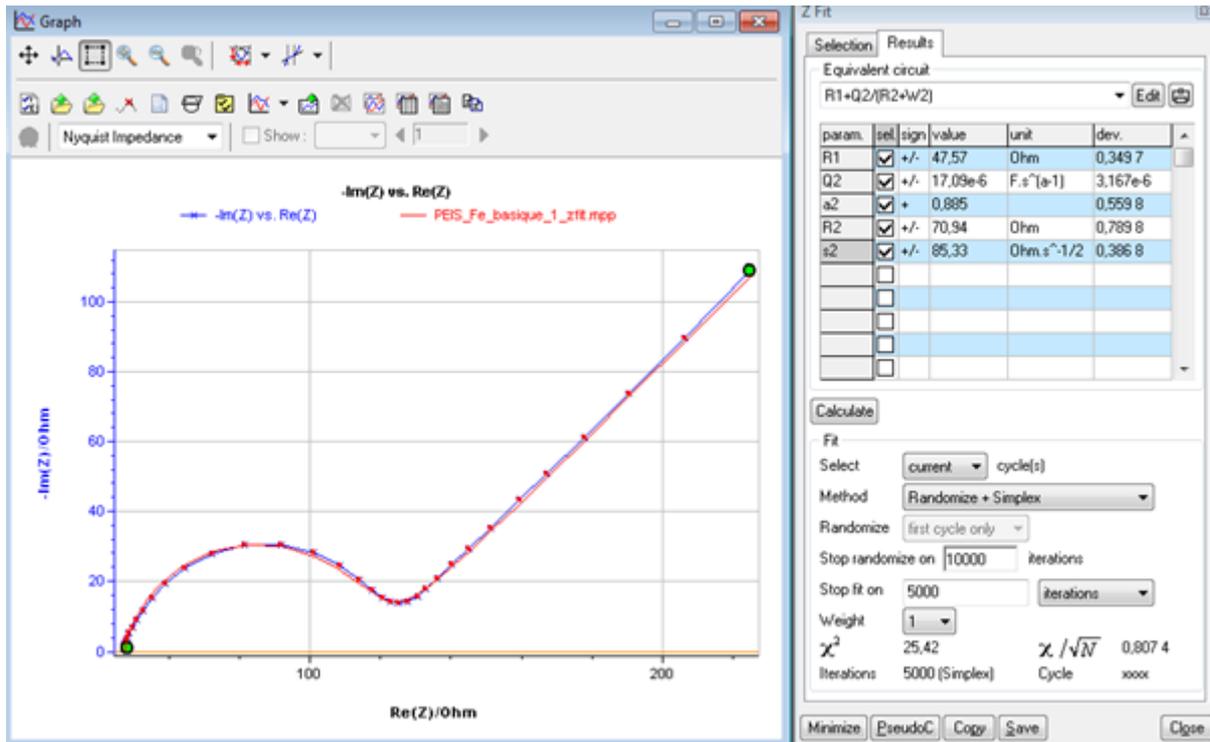


Fig. 176: Fit results with a combination Randomize+Simplex.

The randomization was stopped after 10000 iterations and the fit after 5000 iterations. In that case the χ^2 value is related to a weight 1 for each point. The more points are selected for the fit, the higher the χ^2 value will be. In case of a weight $|Z|$, the results are as follows:

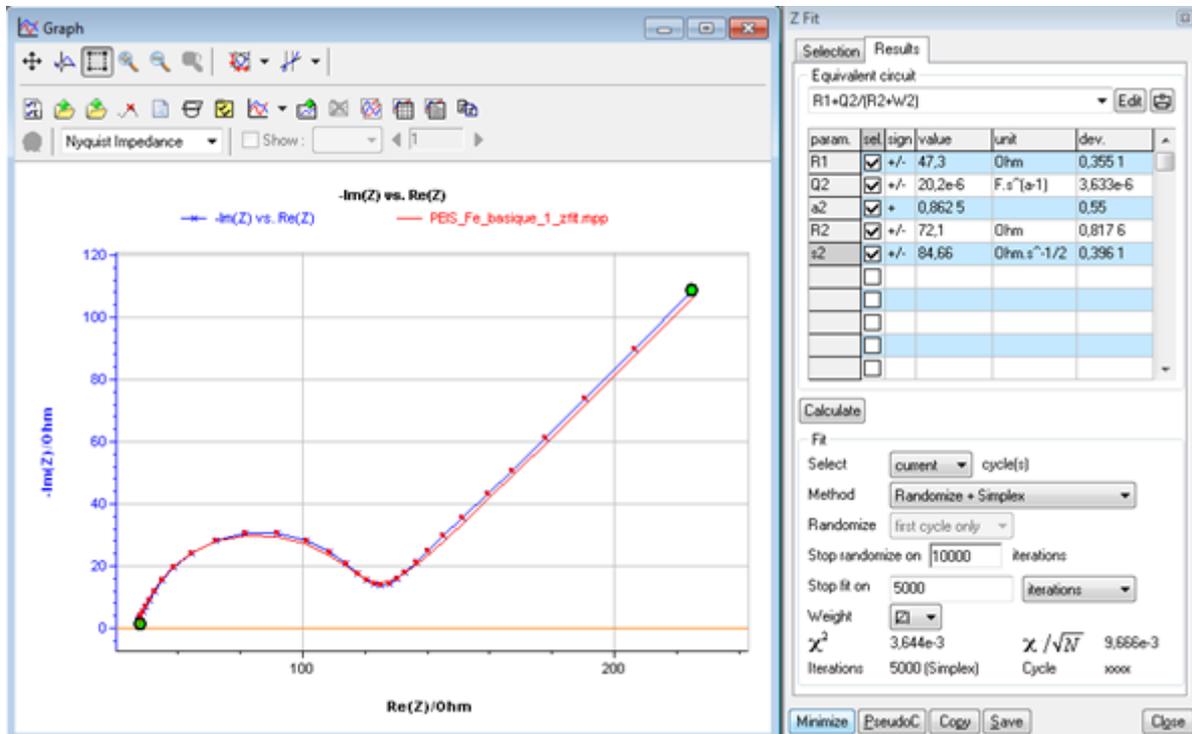


Fig. 177: Fit results with a combination Randomize+Simplex and $|Z|$ as weight.

In the case of a weight $|Z|$, the χ^2 value is much smaller than without weight and tends toward zero. It shows that weighing the data points with respect to the modulus of their impedance is

beneficial for the quality of the fit. The results can be copied to the clipboard or saved in a fit file (filename.fit). When the mpr file is displayed, the fit results can be reloaded with the “Show analysis results” button. Note that ZFit can be used with data represented with the Bode plot or the Nyquist plot.

Please note that it is now possible to stop the minimization before the number of iterations is

reached using the Stop button: 

4.3.3.4 Fit on successive cycles

ZFit tool includes an option to fit successive impedance cycles. For example, in the case of potential steps with EIS measurements on each step, we can make an automatic data fitting on each cycle successively without any action by the user. The EIS spectra obtained on each step can be seen on the graph in the left hand corner on the figure below. The potential was scanned from 0 to 1 V with 20 steps of 50 mV. We can see the 21 EIS spectra that can be fit one by one at the user’s convenience. Selecting all cycles for the fit and randomization on only the first cycle will lead to an automatic fit.

When the Minimization is launched a new graph is added in the bottom right corner. This graph will display the equivalent circuit parameters obtained by the fit (in this case R1, R2, R3, C2, C3) versus potential or time. The user can have a time evolution or a potential evolution of the desired parameter

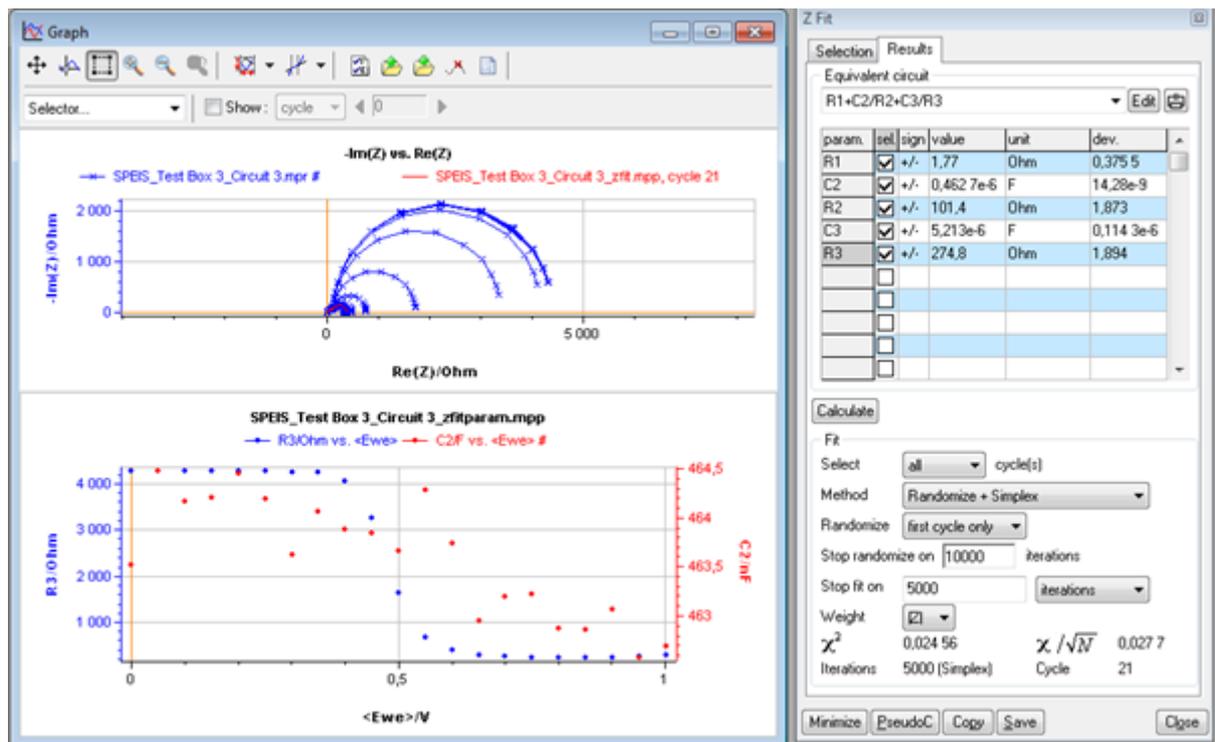


Fig. 178: Successive fits on cycles with randomization on the first cycle.

We can see the evolution with the DC potential of the resistance R3 and the capacitance C2. The parameters of the equivalent circuit components are stored for each cycle in the *File-name_Zfitparam.mpp* file.

References:

- W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, Numerical Recipes in C. The Art of the Scientific Computing, Cambridge University Press, Cambridge (UK), 2nd Edition, 1992.
- E. Walter and L. Pronzato, Identification of Parametric Models: from experimental data, Springer, 2006.
- J.-P. Diard, B. Le Gorrec, C. Montella, Cinétique électrochimique, Hermann, 1996.
- E. Barsoukov and J. Ross Macdonald, Impedance Spectroscopy: Theory, Experiment and applications, Wiley interscience, 2nd Edition, 2005.

4.3.3.4.1 Pseudo-capacitance

ZFit calculates the pseudo-capacitance associated with a CPE. This value can be calculated only for an equivalent circuit R1+(R/Q). This calculation corresponds to the determination of a capacitance value C at a frequency f_0 corresponding to the maximum imaginary part on the Nyquist circle obtained by fitting with the equivalent circuit R1+(R/Q). This value is the solution of the following equation

$$\frac{1}{2\pi(RQ)^{1/\alpha}} = \frac{1}{2\pi RC}$$

With α and Q the CPE parameters.

Considering the previous example from the first frequency down to 20 Hz, the equivalent circuit could be R1+(R2/Q2)

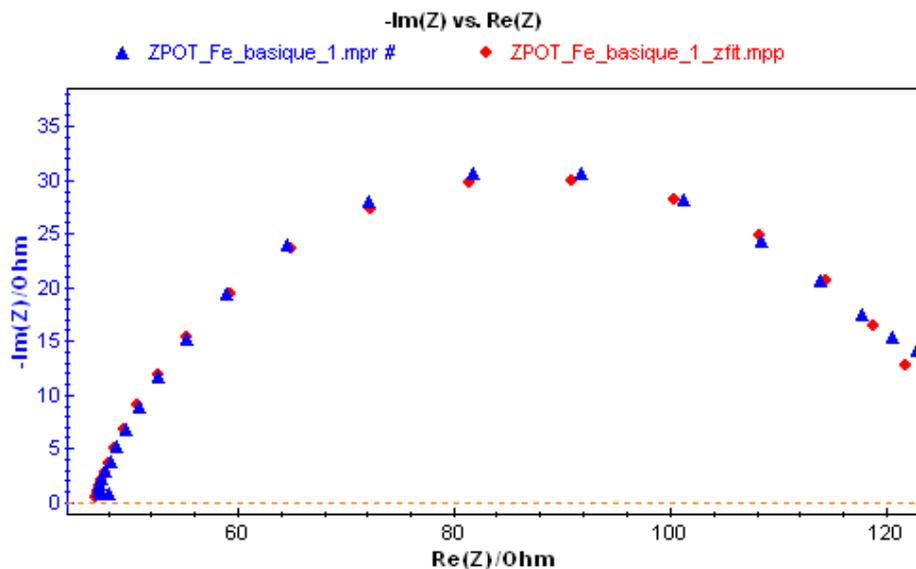


Fig. 179: Fit results with an R1+(R2/Q2) circuit.

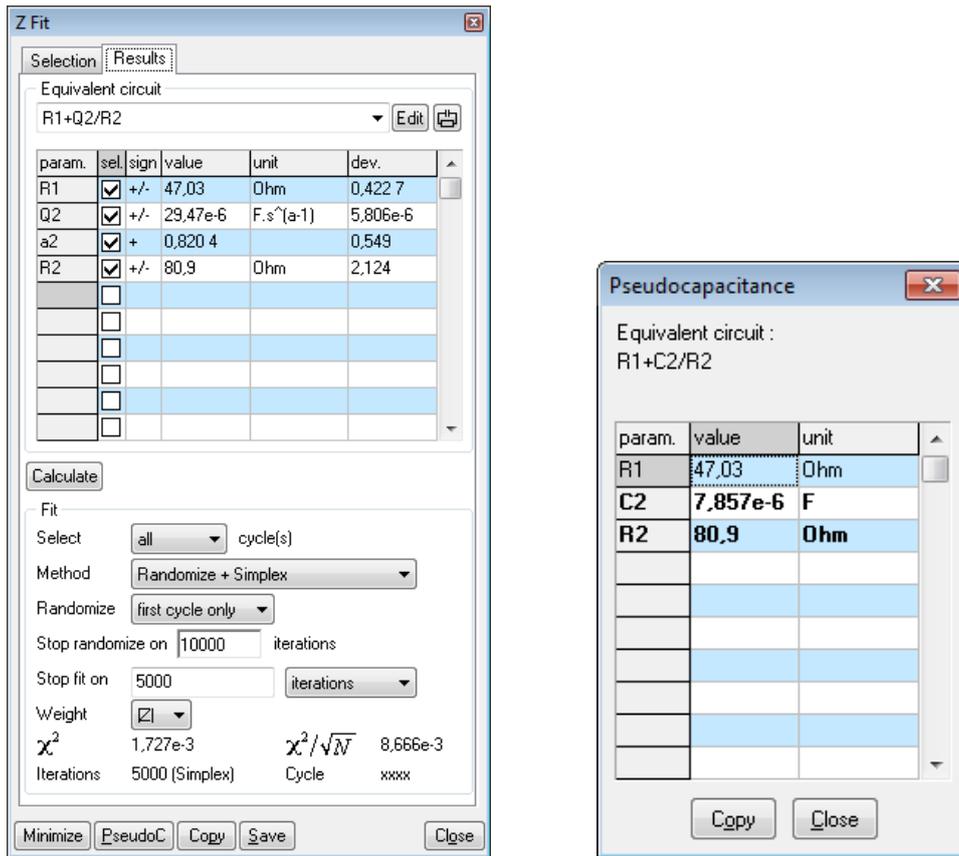


Fig. 180: Fit results and pseudo-capacitance calculation.

The results can be copied and pasted in another document.

4.3.3.4.2 Additional plots

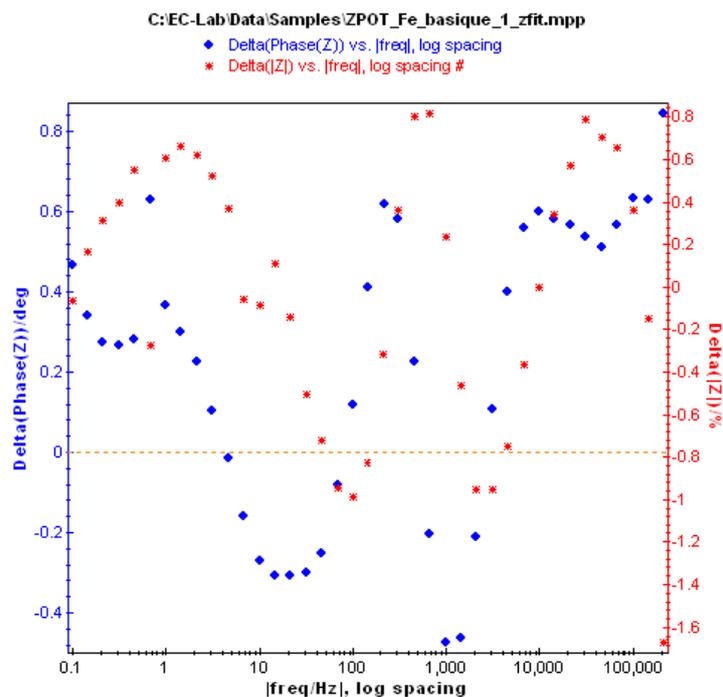


Fig. 181: Plot of the relative error on |Z| and phase vs. frequency (log spacing).

The equations used for this calculation are described below. The same error plot exists for the real part and the imaginary part of the impedance. The error is calculated for each frequency:

$$\Delta|Z|_{\%} = \frac{|Z|_{meas} - |Z|_{calc}}{|Z|_{meas}} \times 100 ; \quad \Delta|\varphi|_{\%} = |\varphi|_{meas} - |\varphi|_{calc} ;$$

$$\Delta|\operatorname{Re}(Z)|_{\%} = \frac{|\operatorname{Re}(Z)|_{meas} - |\operatorname{Re}(Z)|_{calc}}{|\operatorname{Re}(Z)|_{meas}} \times 100 ;$$

$$\Delta|\operatorname{Im}(Z)|_{\%} = \frac{|\operatorname{Im}(Z)|_{meas} - |\operatorname{Im}(Z)|_{calc}}{|\operatorname{Im}(Z)|_{meas}} \times 100$$

Right-click on the graph to see the menu and select “**Selector**” to display the following window offering the possibility to display the relative errors. The same window can be accessed from the rapid graphic selection bar (select “**Custom**”).

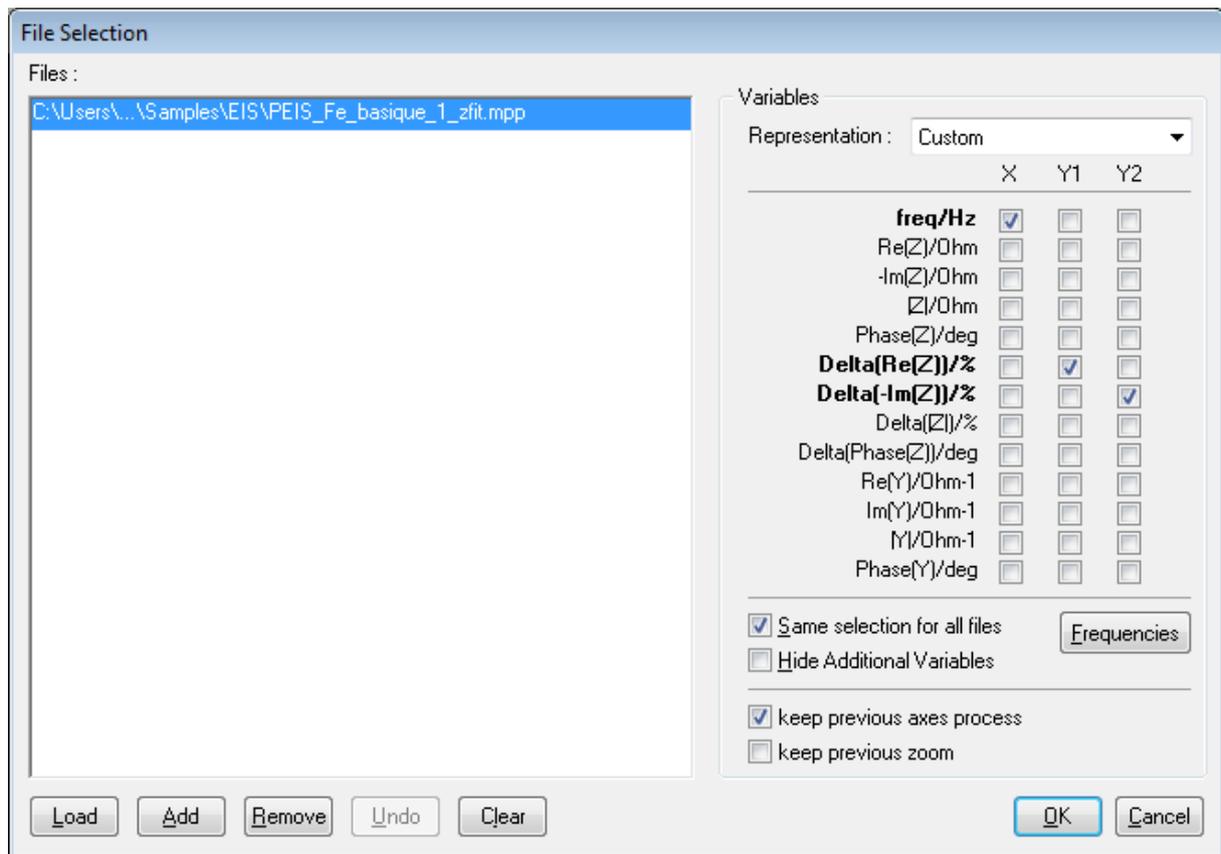


Fig. 182: Selector for the Zfit.mpp file offering the possibility to display the relative errors.

These additional plots may be very useful in evaluating the acceptability of the equivalent circuit selected and the relevance of the measured data points.

4.3.4 Mott-Schottky Fit

Only the instruments equipped with the EIS measurement option have the capability of Mott-Schottky fitting.

4.3.4.1 Mott-Schottky relationship and properties of semi-conductors

The Mott-Schottky relationship involves the apparent capacitance measurement as a function of potential under depletion condition:

$$\frac{1}{C_{SC}^2} = \frac{2}{e\epsilon\epsilon_0 N} \left(E - E_{FB} - \frac{kT}{e} \right)$$

where

C_{SC} is the capacitance of the space charge region,

ϵ is the dielectric constant of the semiconductor,

ϵ_0 is the permittivity of free space,

N is the donor density (electron donor concentration for an n-type semi-conductor or hole acceptor concentration for a p-type semi-conductor),

E is the applied potential,

E_{FB} is the flatband potential.

The donor density can be calculated from the slope of the $1/C^2$ vs. E_{we} curve and the flatband potential can be determined by extrapolation to $C = 0$. The model required for the calculation is based on two assumptions:

a) Two capacitances have to be considered: the one of the space charge region and the one of the double layer. Since capacitances are in series, the total capacitance is the sum of their reciprocals. As the space charge capacitance is much smaller than the double layer capacitance, the double layer capacitance contribution to the total capacitance is negligible. Therefore, the capacitance value calculated from this model is assumed to be the value of the space charge capacitance.

b) The equivalent circuit used in this model can be either:

- a resistor and a capacitance (the space charge capacitance) in series. The capacitance is calculated from the imaginary component of the impedance ($\text{Im}(Z)$) using the relationship:

$$\text{Im}(Z) = -\frac{1}{2\pi f C_s}$$

- a resistor and a capacitance (the space charge capacitance) in parallel. The capacitance is calculated using the following relationship:

$$C_p = \text{Im}(Z)/(2\pi f |Z|^2)$$

This model is adequate if the frequency is high enough (on the order of kHz).

The C_s variable is available for all the impedance techniques. The C_p variable is available only for the SPEIS technique.

4.3.4.2 The Mott-Schottky plot

The Mott-Schottky plot presents the capacitance (C_s or C_p) or the inverse of the square of the capacitance ($1/C_s^2$ or $1/C_p^2$) as a function of the potential E_{we} (see Fig. 181).

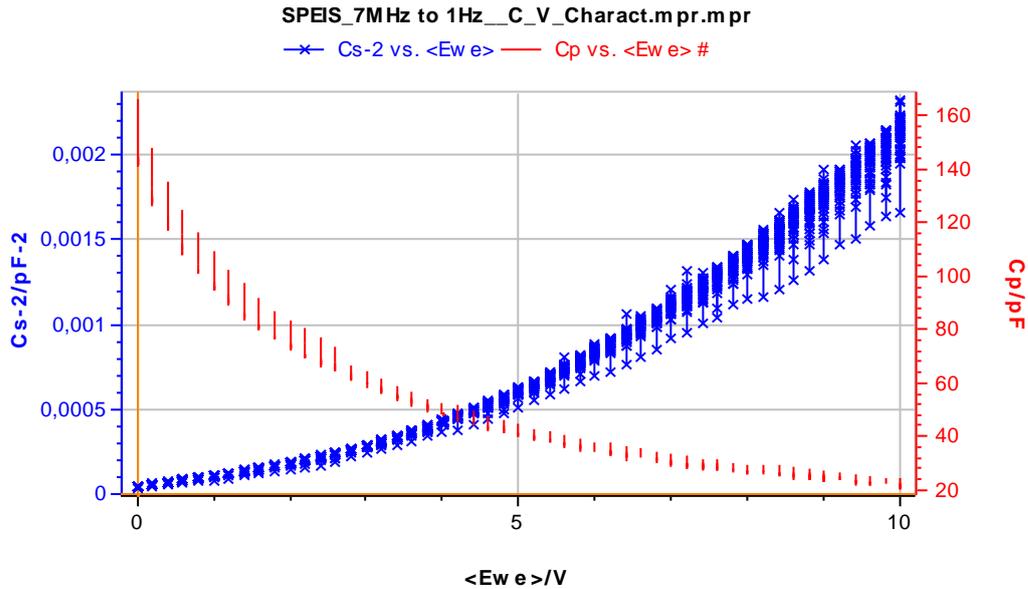


Fig. 183: Mott-Schottky plot.

4.3.4.3 The Mott-Schottky Fit

Once the Mott-Schottky plot is chosen, the frequencies must be selected. If they are not, the warning message will be seen. A window will allow the user to select the frequencies. The user can select several or all frequencies (see Fig. 182). Click on Ok to display the Mott-Schottky curves. The selection is the same for the time evolution of the impedance or of the phase. Then, the graphic window shows one trace per frequency (see Fig. 183). Use the shift key to display the frequency.

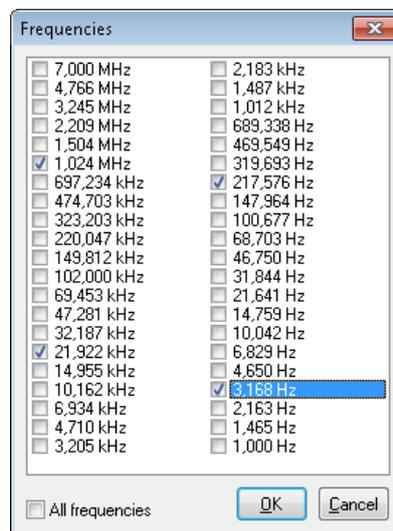


Fig. 184: Frequency selection window.

It is possible to set the surface area and plot a capacitance related to the surface.

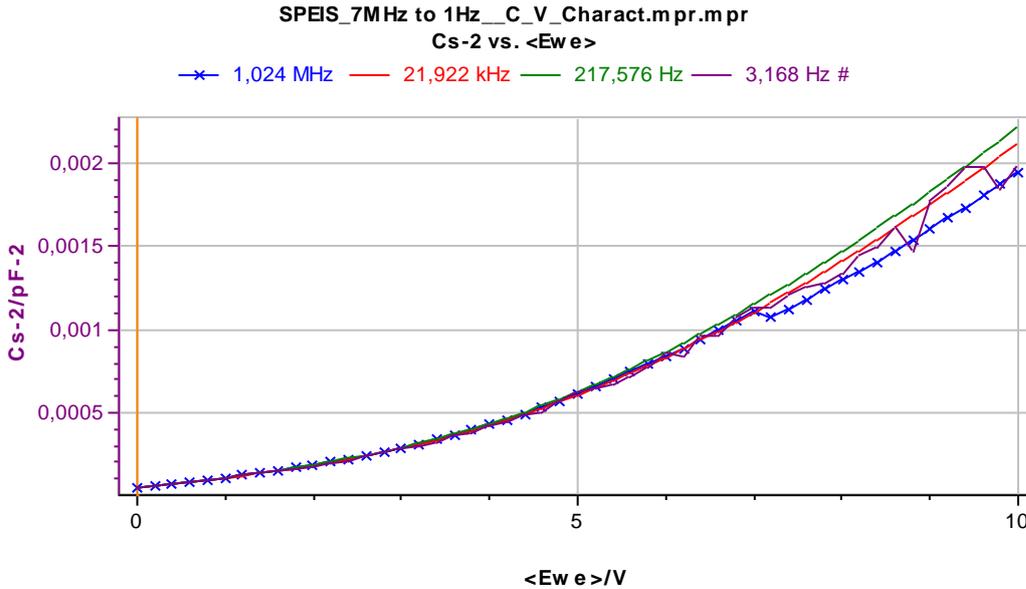


Fig. 185 : Mott-Schottky plot for several frequencies

The Mott-Schottky Fit is a graphic tool introduced with the SPEIS technique to determine semi-conductors parameters (flatband potential and donor density based on the Mott-Schottky relationship) from a Mott-Schottky plot. Before using this fit a Mott-Schottky plot ($1/C_s^2$ vs. E_{we}) of the experiment must be displayed on the graph. This plot shows one trace for each selected frequency. Note that only C_s can be used for the fit.

The Mott-Schottky Fit corresponds to a linear fit for each trace (one trace for each selected frequency). The same potential range is used for every trace. When a data point zone is selected click on “**Calculate**”.

A straight line for each trace is displayed as a result of the linear regression between two green circles with the Least square method fit. Move the circles with the mouse (by holding the mouse left button) to modify the range of data points selected for the fit. The new linear regression is automatically calculated upon moving a circle.

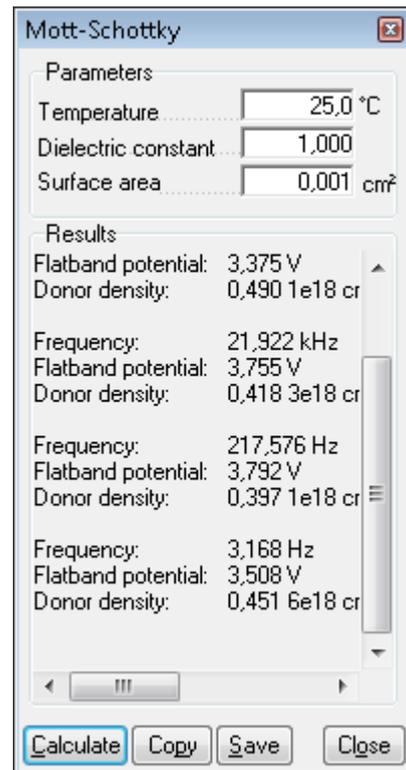


Fig. 186: Mott-Schottky results window.

The potential range used for the analysis is shown in the **Results** frame. For each selected frequency the flat band potential is determined by extrapolation of the linear regression to $C = 0$. The donor density is calculated from the slope of the linear regression at 25°C according to the dielectric constant of the material and the surface area of the semi-conductor defined in the **Parameters** frame.

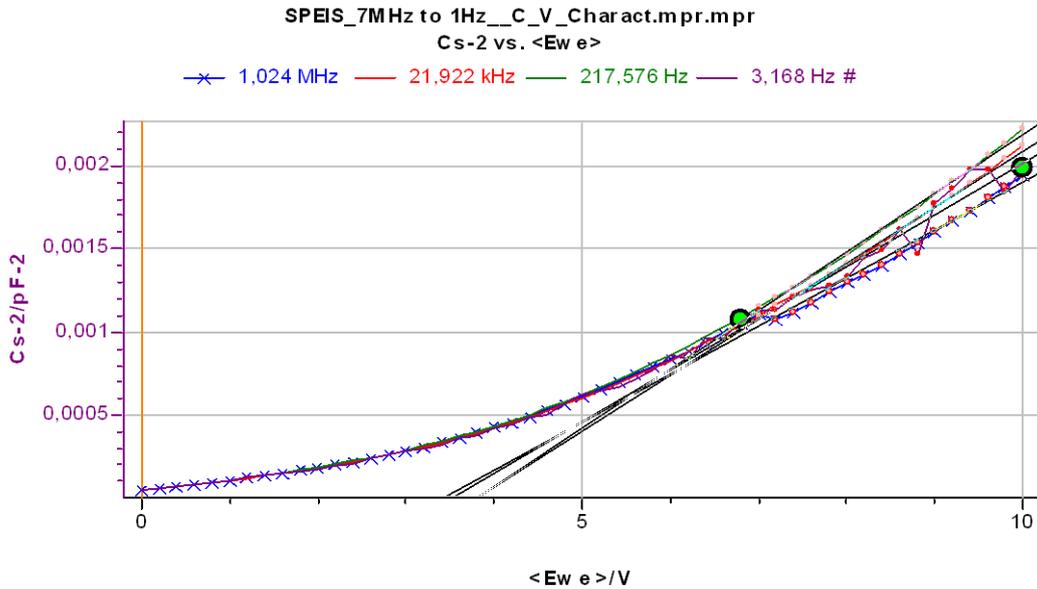


Fig. 187: Mott-Schottky Fit.

The results of the fit (flatband potential, donor density) can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can be saved in a text file.

4.3.4.4 Saving Fit and analysis results

All the fits described above can be saved in a text file. Click on “save” to create a fit file (*.fit) in the same folder as the raw data file. When the data file is displayed a function “**Show Analysis Results ...**” is available on the right-click menu. Select this function to display the fit results window:

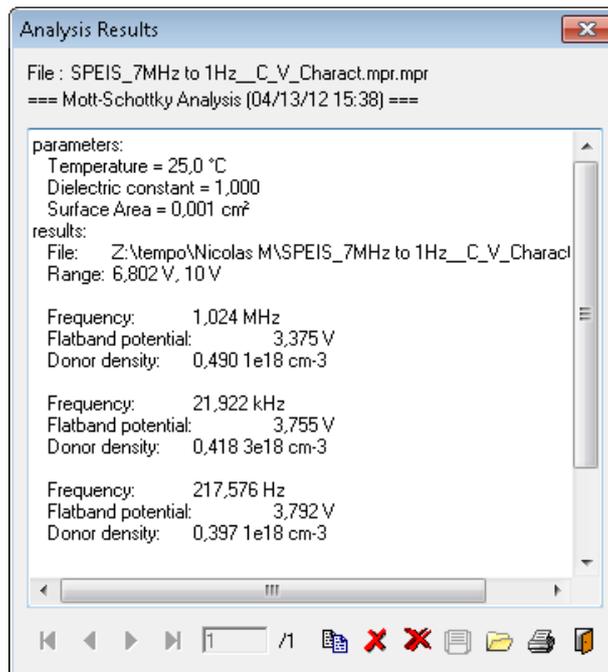


Fig. 188: Analysis Results window.

This text file shows the file name and the analysis performed on the curve with the date and time at the top. If several fits were made successively on the curve, the user can display every analysis one after the other using the “Next” button. The results can be printed, edited to be copied, or deleted.

4.3.5 Kramers-Kronig transformation

It is possible to determine the imaginary part of the impedance from the real part and *vice versa*. The system must be causal, stable, linear and invariant in time and the impedance must be finite when $\omega \rightarrow 0$ or $\omega \rightarrow \infty$. The Kramers-Kronig transformation is sometimes used in electrochemistry for the validation of experimental results. The impedance imaginary part can be calculated from the real part (or conversely) with the equation:

$$\text{Im}(Z_{KK}(\omega)) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{\text{Re}(Z(x)) - \text{Re}(Z(\omega))}{x^2 - \omega^2} dx$$

The Kramers-Kronig transformation can also be verified in an admittance plot. If we consider the previous data file (ZPOT_Fe_Basique.mpr), the Kramers-Kronig transformation applied to the whole point series gives the following results:

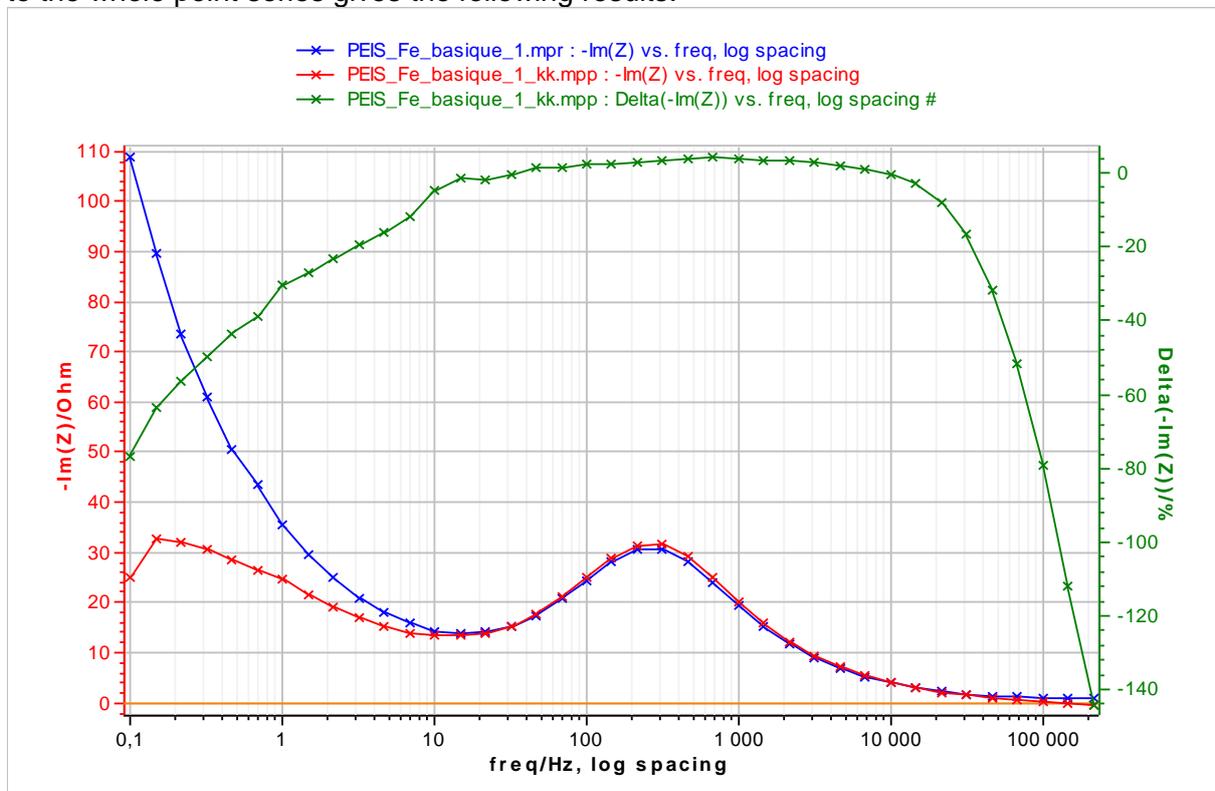
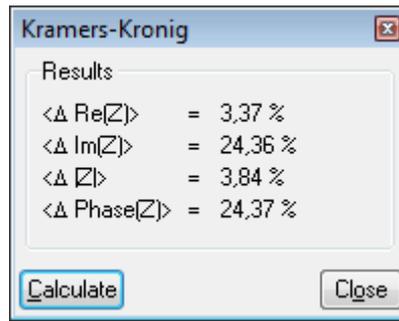


Fig. 189: Result of the Kramers-Kronig criterion applied to the data points with the experimental $\text{Im}(Z)$ part, the calculated one and the relative error.

One can see that the system does not fulfill the Kramers-Kronig conditions because in the low frequency range the impedance does not tend towards 0. For the high frequency range, the imaginary part tends to 0, so the precisions given below are not significant.



The results of this test are displayed as an averaged relative error for each parameter (Re, Im, |Z| and phase).

References:

- H.W. Bode, Networks Analysis and feedback Amplifier design, Van Nostrand, New York, 1945.
- R.L. Van Meirhaeghe, E.C. Dutoit, F. Cardon and W.P. Gomes, Electrochim.Acta, 21 (1976), 39.
- D.D. MacDonald, Electrochim. Acta, 35 (1990), 39.
- J.-P. Diard, P.Laudaud, J.-M. Le Canut, B. Le Gorrec and C. Montella, Electrochim. Acta, 39 (1994), 2585.

4.4 Batteries menu

This menu is only composed of process tools and these processes are described in the part 5.

4.5 Photovoltaic/fuel cell menu

The photovoltaic analysis provides characteristic values of a solar cell.

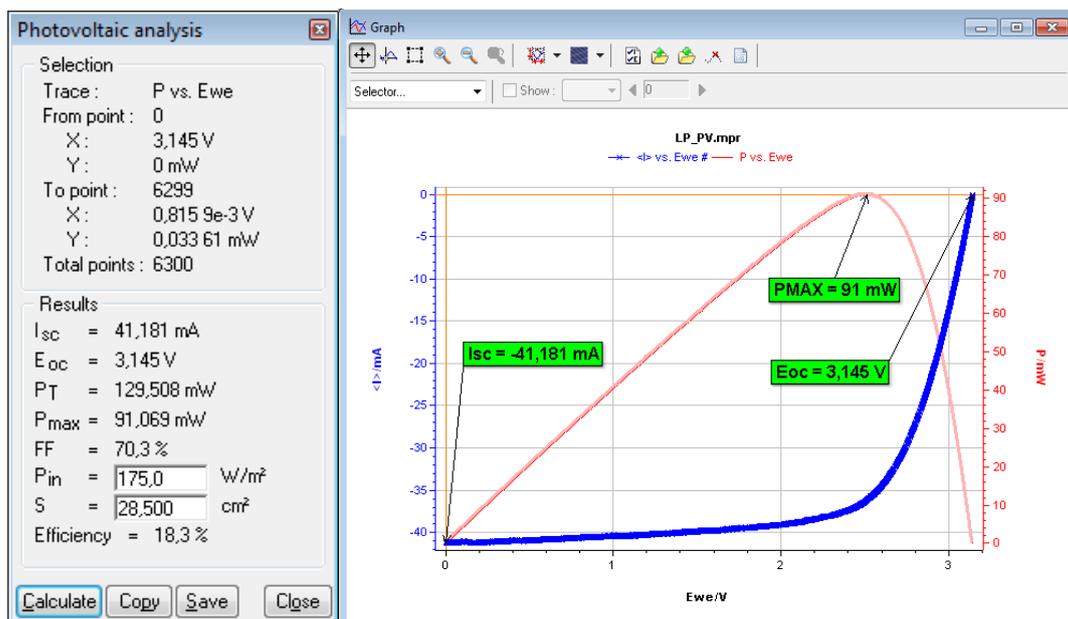


Fig. 190: Typical I vs E curve for a photovoltaic cell.

The resulting I - V characterization shows a typical I vs. E and P vs. E curves. Several parameters can be drawn from this curve with the “Photovoltaic analysis” tool:

- Short Circuit Current (I_{sc}), which corresponds to the maximum current when $E = 0$ V, $I_{sc} = 41$ mA in this example,
- the Open Circuit Voltage (E_{oc}), which is the potential at which the current is equal to 0, $E_{oc} = 3.145$ V,
- the theoretical power (P_T), which is defined by the following relationship $P_T = |I_{sc}| \times E_{oc}$, $P_T = 129$ mW,
- the maximum power, $P_{max} = 91$ mW,
- the Fill Factor (FF), which is P_{max}/P_T ; $FF = 70.3\%$,
- the efficiency can also be calculated: It is assumed that the solar power is equal to 175 W/m², which gives 499 mW for our photovoltaic cell of 28.5 cm². The efficiency of the photovoltaic cell is $91/499 = 18\%$.

4.6 Corrosion menu

Several techniques such as Linear Polarization (LP), Constant Amplitude Sinusoidal microPolarization (CASP) and Variable Amplitude Sinusoidal microPolarization (VASP) measurements are used to characterize the corrosion behavior of metallic samples. These measurements are used to determine the characteristic parameters such as:

- the corrosion potential, E_{corr} ,
- the corrosion current, I_{corr} ,
- the Tafel constants β_a (metal oxidation) and β_c (oxidizing species reduction) for the anodic and cathodic reactions, respectively, defined as positive numbers. The Tafel constants can be given as b_a and b_c where $b_a = \ln 10/\beta_a$ and $b_c = \ln 10/\beta_c$.
- The polarization resistance R_p

Please note that these techniques are built upon the assumption that the electrochemical systems are tafelien i.e. that the current flowing in the electrode is only limited by the electron transfer and not by mass transport. In this case the potential-current relationship is described by the Stern or Wagner-Traud equation :

$$I = I_{corr} \exp \frac{\ln 10(E - E_{corr})}{\beta_a} - I_{corr} \exp \frac{-\ln 10(E - E_{corr})}{\beta_c}$$

Also please note that all the techniques are valid for a negligible ohmic drop. Please refer to the [application notes on corrosion measurements](#) for more information.

4.6.1 Tafel Fit

The Stern equation predicts that for $E \gg E_{corr}$ the anodic reaction predominates and that for $E \ll E_{corr}$ the cathodic reaction predominates. This is known as the Tafel approximation:

$$I \approx I_{corr} \exp \frac{\ln 10(E - E_{corr})}{\beta_a}, \quad \text{for } E \gg E_{corr}$$

$$I \approx -I_{corr} \exp \frac{-\ln 10(E - E_{corr})}{\beta_c}, \quad \text{for } E \ll E_{corr}$$

This can be written :

$$I \approx I_{corr} 10^{\frac{(E - E_{corr})}{\beta_a}}, \quad \text{for } E \gg E_{corr}$$

$$I \approx -I_{corr} 10^{\frac{-(E-E_{corr})}{\beta_c}}, \quad \text{for } E \ll E_{corr}$$

So, in a $\log|I|$ vs. E representation, one should see two linear parts for $E \gg E_{corr}$ and $E \ll E_{corr}$:

$$\log|I| \approx \frac{E - E_{corr}}{\beta_a} + \log I_{corr}, \quad \text{for } E \gg E_{corr}$$

$$\log|I| \approx \frac{E_{corr} - E}{\beta_c} + \log I_{corr}, \quad \text{for } E \ll E_{corr}$$

4.6.1.1 Tafel Fit window

The **Tafel Fit** window allows the user to find the anodic and cathodic Tafel coefficients using a $\log(|I|)$ vs. E representation (Tafel Graph).

On a linear polarization trace, select the **Tafel Fit** with the **Tafel Fit** button  or the mouse right-click and the data points for which the fit will be performed. A warning message pops up to switch to the $\log(|I|)$ versus E_{we} graph representation in case it was not the selected representation.

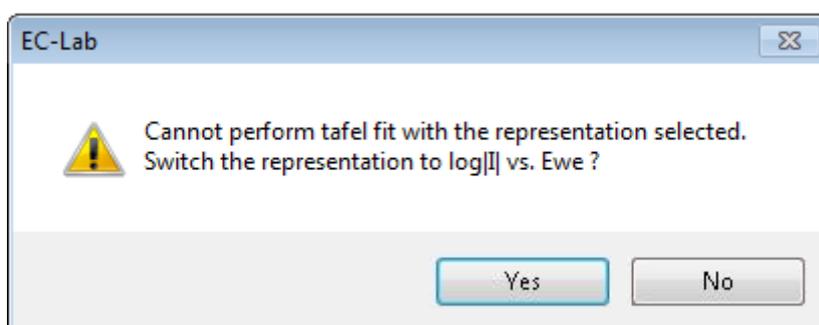


Fig. 191: Tafel Fit warning message to switch the graph representation.

Answer **Yes** to the previous message. The **Tafel Fit** analysis window appears. The fit can be minimized with a Simplex method. The results can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can also be saved in a text file.

Note: - One can manually select the $\log(|I|)$ versus E representation. In **Graph Properties/Axis/Axis Processing**, select “**log |I|**” for Y1.
- The equivalent weight, the density and the surface area used for the corrosion rate calculation can be defined before the beginning of the experiment in the “**Cell Characteristics**” window (see part 2.5.2).

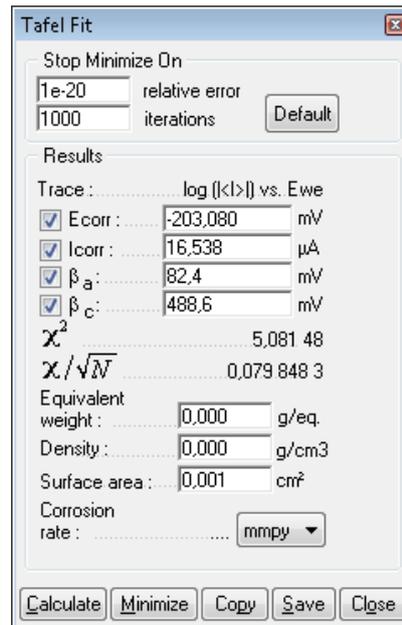


Fig. 192: Tafel Fit Window.

The Tafel graph (Fig. 193) is displayed in $\log |i|$ vs. E_{we} . Two linear regressions are automatically made using the least square method. Each linear fit is limited with two circle markers that can be moved.

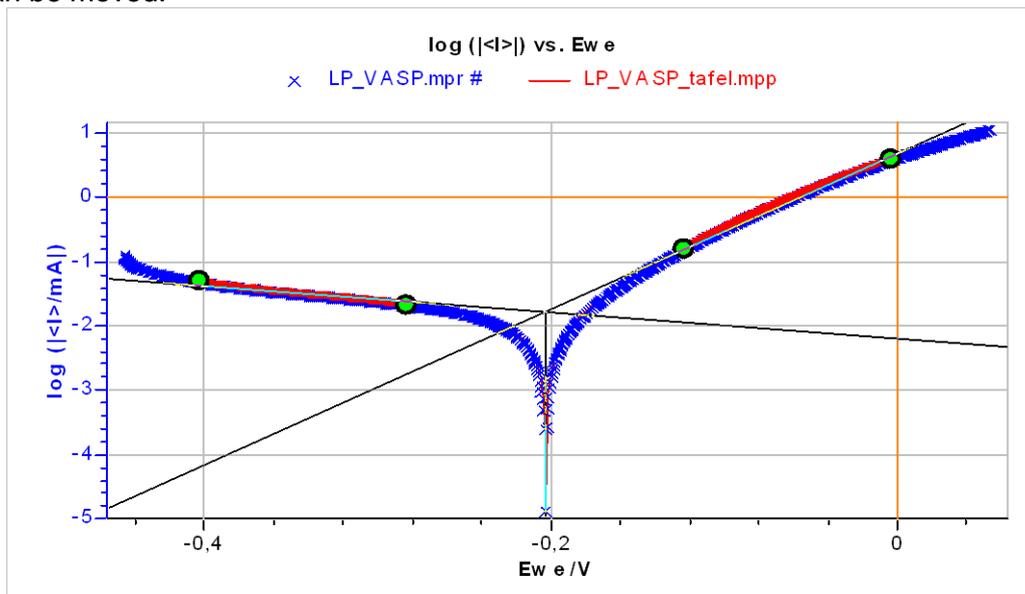


Fig. 193: Tafel graph.

The results of the Tafel Fit are recalculated whenever a marker is moved. The default positions of the markers are ± 80 mV and ± 200 mV around E_{corr} . Thanks to the intersection of the linear regressions, the software calculates the corrosion potential (E_{corr}), the corrosion current value (I_{corr}) and the Tafel constants (β_a and β_c). The Fit accuracy can be estimated with the χ^2 or the χ/\sqrt{N} . The Tafel Fit can also be performed on the E_{we} vs $\log|i|$ plot.

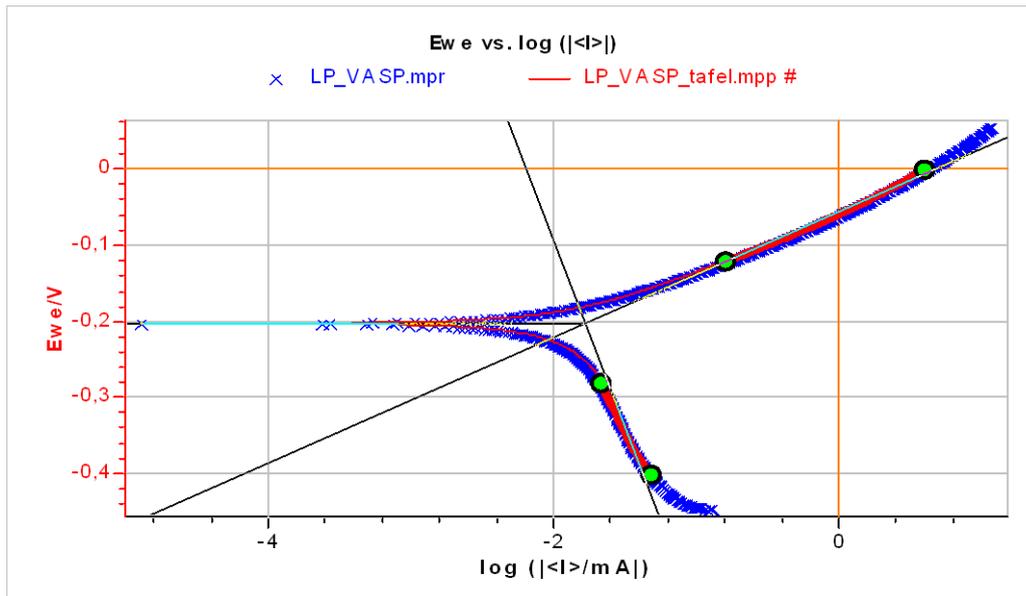


Fig. 194: Tafel Fit on the Ewe vs log|| graph.

4.6.1.2 Corrosion rate

Finally the corrosion rate (CR) is calculated according to the following equation:

$$CR = \frac{I_{corr} \cdot K \cdot EW}{d \cdot A}$$

CR is in millimeter per year (mmpy) or milliinch per year (mpy)

I_{corr} corrosion current (in A).

K constant that defines the units of the corrosion rate.

EW equivalent weight (in g/equivalent). It is defined as the molar mass of the oxidized metal divided by the number of electrons involved in the dissolution reaction. For instance, for the corrosion of iron $Fe \rightarrow Fe^{2+} + 2e^-$ $EW = 55.85/2 = 27.925$ g/equivalent. the equivalent weight can be set up in the Cell Characteristics tab (see 2.5.2).

d density (in g/cm^3).

A sample area (in cm^2).

K	CR units
3272 mm/(A cm year)	mm/year (mmpy)
1.288×10^5 milliinch/(A cm year)	milliinch/year (mpy)

4.6.1.3 Minimize option

In some cases the calculation of the Tafel parameters and corrosion parameters may not yield a satisfying fit because for instance within the default potential ranges chosen, the material does not exhibit a “Stern” behaviour but more a mass transport limited behaviour or a passivation. In these cases, it is possible to numerically find satisfying parameters and reduce the error between the model $I_{calc,i}$ and the measured data $I_{meas,i}$ by minimizing the following value:

$$X^2 = \frac{1}{N} \sqrt{\frac{\sum_{i=1}^N (I_{meas,i} - I_{calc,i})^2}{I_{meas,i} + 10^{-9}}}$$

This is obtained by clicking on the **Minimize** button. The Nelder and Mead Simplex method (ref [2]) is used to minimize the χ^2 value. Keep the button pressed (<Enter> or <Alt+M> keys) until the Stern and Geary parameters E_{corr} , I_{corr} , β_a and β_c have stabilized. Then a simulated Tafel graph is displayed, this graph is displayed in agreement with the parameters obtained with the Minimize button. Note that the Simplex method may not converge if the initial values are too much different from the minimum ones (it may fall into a local minimum of χ^2 (E_{corr} , I_{corr} , β_a , β_c)) or if the $I(E_{we})$ curve is linear around E_{corr} . In that case the following message will be displayed:

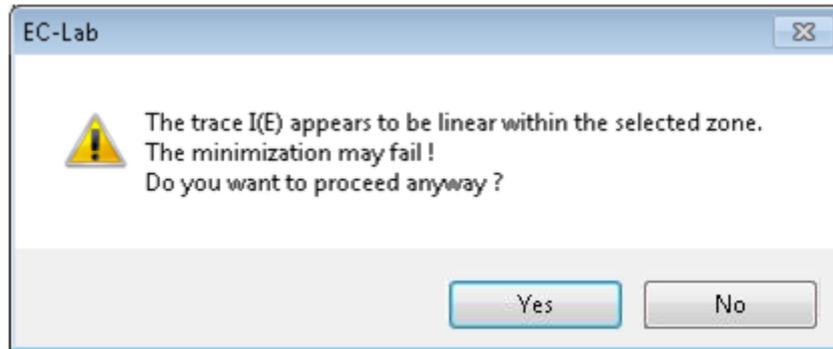


Fig. 195: Tafel Fit minimization message.

For this reason, it is possible to enter directly E_{corr} , I_{corr} , β_a and β_c values and then start the minimization. Unchecking the boxes around E_{corr} , I_{corr} , β_a and β_c will remove the corresponding parameter from the minimization. At any time, one can restart the calculation from the linear fits by clicking on the **Calculate** button.

Reference:

- [1] Stern M. and Geary A.L., J. Electrochem. Soc., 104, (56), 1957.
 [2] Press W.H., Teukolsky S.A., Vetterling W.T., Flannery B.P., Numerical Recipes in C, second edition, Cambridge University Press, section 10.4, 408-412, 1999

4.6.2 R_p Fit

For E sufficiently close to E_{corr} , it is possible to simplify the Stern equation, so that:

$$I = I_{corr} (E - E_{corr}) \frac{\beta_a + \beta_c}{\beta_a \beta_c} \ln 10$$

This equation is commonly presented with E as function of I :

$$E = \frac{I \beta_a \beta_c}{I_{corr} (\beta_a + \beta_c) \ln 10} + E_{corr}$$

When expressed this way, it is easy to see that $E = E_{corr}$ for $I = 0$. The slope of this equation dE/dI is named the *polarization resistance* because it has the unit of a resistance (if the current is used) and is commonly abbreviated R_p :

$$\left(\frac{dE}{dI} \right)_{E_{corr}} = R_{p, E_{corr}} = \frac{\beta_a \beta_c}{I_{corr} (\beta_a + \beta_c) \ln 10}$$

This relationship is commonly named the Stern-Geary relationship.

For the **R_p Fit**, the user has to select the data points and the fit (with the R_p fit button  as described before). By clicking on **Calculate**, the software will automatically find a potential value E₁ on the curve for I = 0. Two circle markers are set in a ± 25 mV potential range around E₁ as well as default values for β_a and β_c. This range and β_a and β_c values used for the fit are defined in the **Parameters** frame.

The **R_p Fit** calculates the polarization resistance (R_p) and the open circuit potential (E_{corr}) by a linear regression around E₁ (± 25 mV) on I vs. E plot. All the data points in the potential range are used for the linear regression.

R_p is given by the inverse of the linear fit slope and E_{corr} by the potential value calculated from the linear equation for I = 0.

The correlation coefficient shows the accuracy of the linear regression.

It is also possible to determine I_{corr} by adjusting the Tafel coefficients β_a and β_c previously determined by the Tafel Fit.

The results can be copied to the clipboard to be pasted in the print window comment zone or in a text file. They can also be saved in a text file.

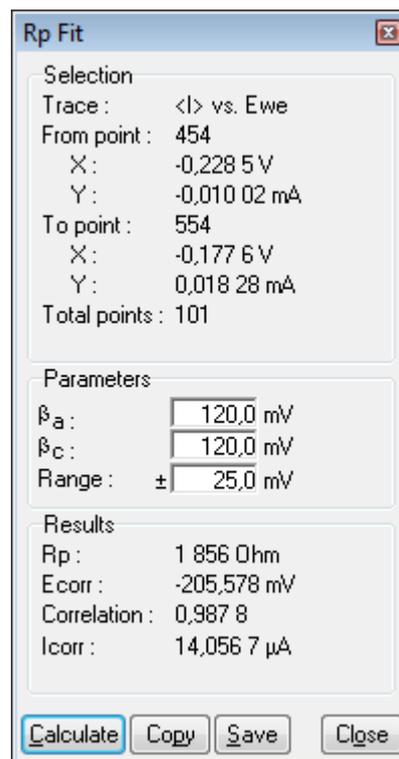


Fig. 196: R_p Fit window.

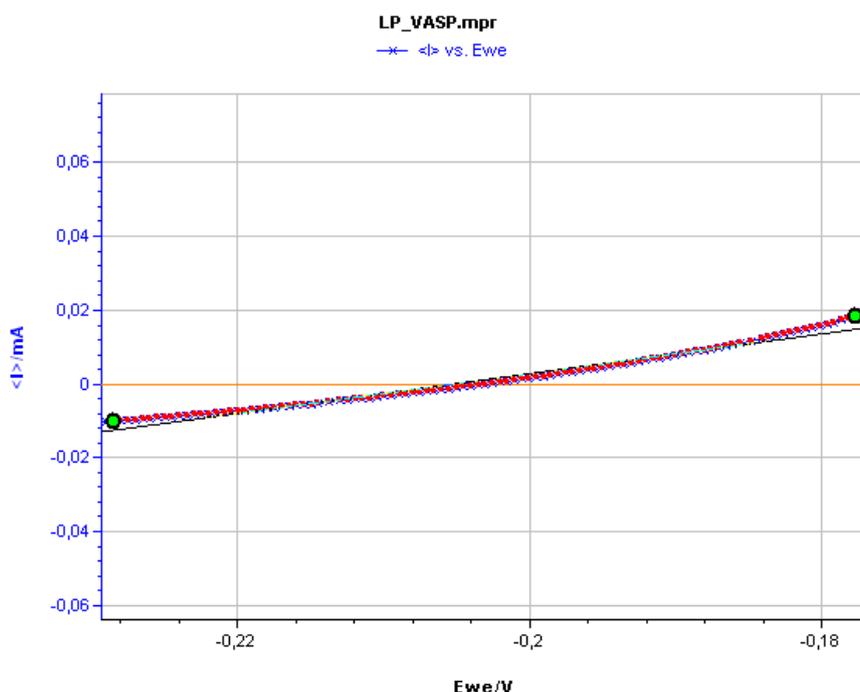


Fig. 197: Linear polarization curve of an iron electrode in H₂SO₄ (0.1 M).

Note: - The user can adjust the R_p Fit by grabbing and moving markers. The fit result is automatically updated.

- One could use the Linear fit to get the same results, but the R_p fit is more convenient for the R_p calculation.

4.6.3 Corr Sim

The “Corr Sim” tool allows the user to simulate data in the same way as ZSim (see 4.3.2). According to the parameters contained in the Stern (or Wagner-Traus) equation i.e. E_{corr} , I_{corr} , β_a , β_c , CorrSim generates the response corresponding to the technique chosen in the Output: LP, VASP or CASP (see Fig. below).

Clicking on the “Calculate” button gives the simulated curve according to the parameters set. The output plot depends on the type of the techniques used. The results can be copied in the clipboard to be pasted in the print window comment zone or in a text file. They can be saved in a text file.

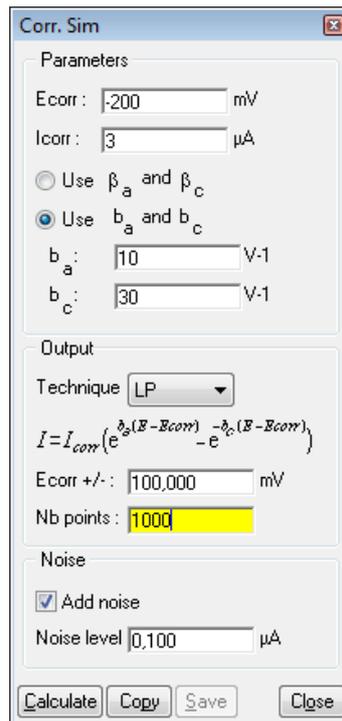


Fig. 198: Corr Sim window for Linear Polarization.

The results provided by CorrSim are used to present the CASP and VASP fitting tools.

4.6.4 Variable Amplitude Sinusoidal microPolarization fit (VASP Fit)

A potential sine wave of constant frequency and increasing amplitude from V_a min to V_a max is applied to the system. The frequency is chosen such that the impedance shown by the system is its polarization resistance. The amplitudes must be large enough such that the non-linear behaviour of the system is reached. The R_p determination is performed at each amplituden δE (see Fig. 190).

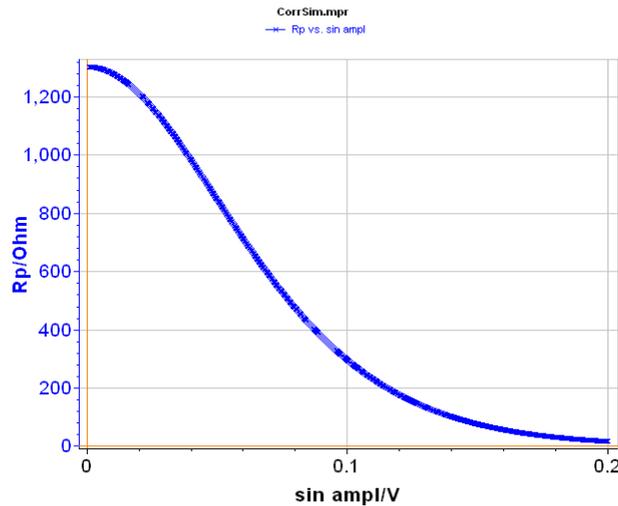


Fig. 199: Output data for VASP simulation.

Please refer to the [Application Note on VASP](#). For a non-linear system, the inverse of the polarization resistance of the system can be calculated using a Taylor series [3-4]:

$$\frac{1}{R_p} = I_{corr} \sum_{k=0}^K \frac{(b_a^{2k+1} + b_c^{2k+1}) \delta E^{2k}}{2^{2k} k! (k+1)!}$$

This shows that, by plotting R_p as a function of δE , one can obtain the corrosion parameters I_{corr} , b_a and b_c .

VASP Fit allows the user to fit data from VASP measurements. The output parameters can be given as β or b constant. The χ^2 is defined by the following equation:

$$\chi^2 = \frac{1}{N} \sqrt{\sum_{i=1}^N (X_{meas,i} - X_{calc,i})^2}$$

[3] K. Darowicki, Corrosion Science, Vol. 37, n°6, 913-925 (1995)

[4] J.-P. Diard, B. Le Gorrec, C. Montella, Comments, Corrosion Science, 40, 495 (1998)

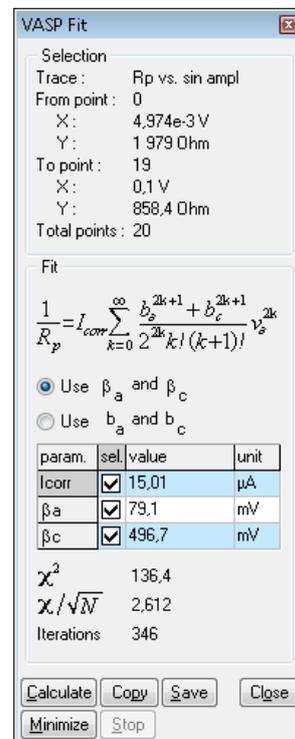


Fig. 200: VASP Fit window.

4.6.5 Constant Amplitude Sinusoidal microPolarization fit (CASP Fit)

For more information, please refer to the [Application Note on CASP](#). A sinusoidal potential perturbation $\Delta E(t) = E(t) - E_{corr} = \delta E \sin(2\pi f_s t)$ of a single frequency f_s is applied to the system, which is considered to be a Tafelian system. The frequency is low enough such that the system is considered steady - state, in which case the current response with time can be described using the Stern equation.

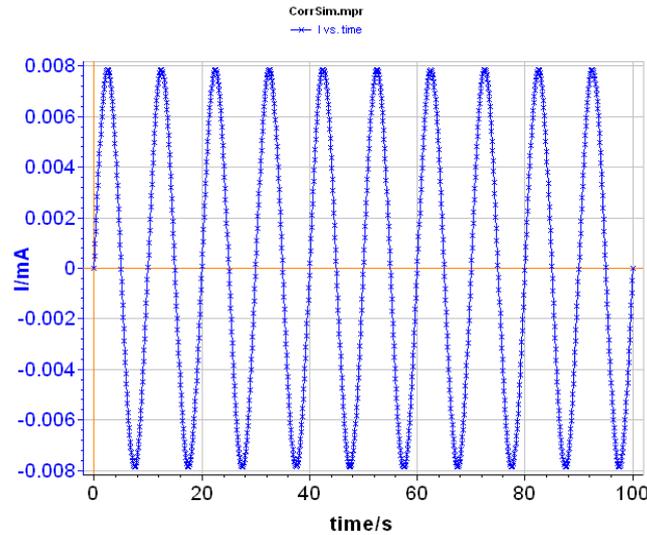


Fig. 201: Output data for CASP simulation.

The current response can be expressed using a Fourier series expansion, which results in the following equation [5-6]:

$$I(t) = \delta I_0 + \delta I_1 \sin(\omega t) + \delta I_2 \cos(2\omega t) + \delta I_3 \sin(3\omega t) + \dots$$

where the fundamental is δI_1 and the two first harmonics are δI_2 ; δI_3 respectively:

$$\delta I_1 = I_{corr} \left((b_a + b_c) \delta E + \frac{b_a^3 + b_c^3}{8} \delta E^3 + \frac{b_a^5 + b_c^5}{8} \delta E^5 + \dots \right)$$

$$\delta I_2 = I_{corr} \left(\frac{b_a^2 - b_c^2}{4} \delta E^2 + \frac{b_a^4 + b_c^4}{48} \delta E^4 + \dots \right)$$

$$\delta I_3 = I_{corr} \left(\frac{b_a^3 - b_c^3}{24} \delta E^3 + \frac{b_a^5 + b_c^5}{384} \delta E^5 + \dots \right)$$

It is assumed that the harmonics superior to 3 are not significant, so they are neglected in the calculation of I_{corr} , β_a and β_c . To validate the fit, δI_1 , δI_2 and δI_3 are given in the window. This method leads to valid results only if δI_1 is positive, δI_2 positive or equal to 0 and δI_3 negative.

The corrosion current is then:

$$I_{corr} = \frac{1}{4\sqrt{3}} \frac{(\delta I_1 + 3\delta I_3)^2}{\sqrt{-\delta I_2^2 - 2\delta I_3(\delta I_1 + 3\delta I_3)}}$$

$$b_a = \frac{2}{\delta E} \frac{\sqrt{3} \sqrt{-\delta I_2^2 - 2\delta I_3(\delta I_1 + 3\delta I_3)} - \delta I_2}{\delta I_1 + 3\delta I_3}$$

$$b_c = \frac{2}{\delta E} \frac{\sqrt{3} \sqrt{-\delta I_2^2 - 2\delta I_3(\delta I_1 + 3\delta I_3)} + \delta I_2}{\delta I_1 + 3\delta I_3}$$

The error gives an information about the quality of the chosen amplitude and the quality of the fit.

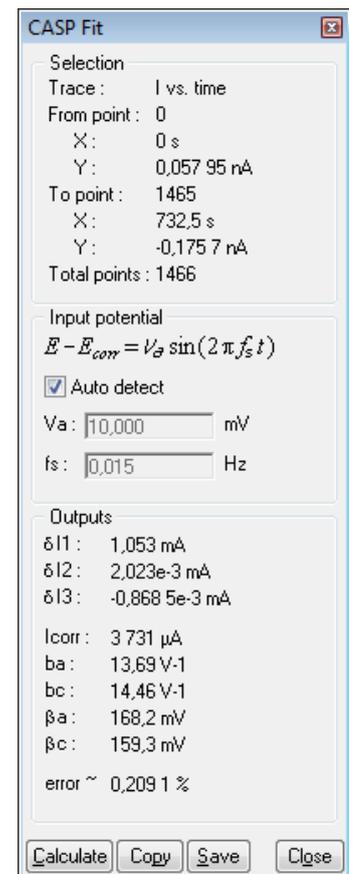


Fig. 202: CASP Fit window.

[5] L. Mészáros, G. Mészáros, B. Lengyel, J. Electrochem. Soc. 141, 8, (1994)

[6] J.-P. Diard, B. Le Gorrec, C. Montella, Comments, J. Electrochem. Soc. 142, 3612, (1995)

4.6.6 Electrochemical Noise Analysis

The Electrochemical Current Noise (ECN) is defined as the spontaneous current fluctuations occurring between two dissimilar or identical electrodes held at the same potential. These current fluctuations are due to a galvanic activity between either two dissimilar electrodes or two electrodes of the same material with microstructural differences. ECN is usually measured using a Zero Resistance Ammeter (ZRA), which connects the two working electrodes. A reference electrode or a pseudoreference electrode of the same material as the working electrodes can be used to measure the potential fluctuations, which are called Electrochemical Potential Noise (EPN) of the pair of electrodes. To analyze these fluctuations, the tool

Electrochemical Noise Analysis  was introduced. This tool is used to calculate the noise resistance of the system R_n .

Three methods are available to calculate the electrochemical noise:

- **Standard deviation.** With the two standard deviation values (current and potential) it is possible to apply the Ohm's law relationship and to obtain the parameter (R_n): $R_n = \frac{\sigma_{Ewe}}{\sigma_I}$ with

σ_{Ewe} and σ_I obtained with the formula

$$\sigma_x = \sqrt{\frac{1}{N-1} \sum_{i=0}^{N-1} (x - \bar{x})^2}$$

where $\bar{x} = x$ is the average.

- **PSD with DFT.** It is also possible to calculate the standard deviation from the Power Spectral Density (PSD), indeed according to the Parseval theorem it is possible to link variance σ_x and Power Spectral Density of the x variable $P_{xx}(f)$:

$$\sigma_x^2 = \int_{-\infty}^{\infty} P_{xx}(f) df.$$

Note that $P_{xx}(f) = X^2(f)$ where $X(f)$ is the Fourier transform of $x(t)$.

- **PSD with MEM.** The Maximum Entropy Method (MEM) is an estimation of the PSD suggested by information theory. Calculation of the PSD can be done with the following relationship:

$$P_{xx}(f) = \left| \frac{\Delta t \sigma_u}{1 + \sum_{k=1}^p a_k \exp(-2i\pi f \Delta t)} \right|^2$$

In the Parameters part of the window, two choices are available:

- doing the analysis on the cycle displayed on the graph selecting "**Current cycle(s)**",
- doing the analysis on all the cycles selecting "**All cycle(s)**". In this case, the analysis will be performed in all the cycles in a sequential way; the result of each cycle will be saved automatically.

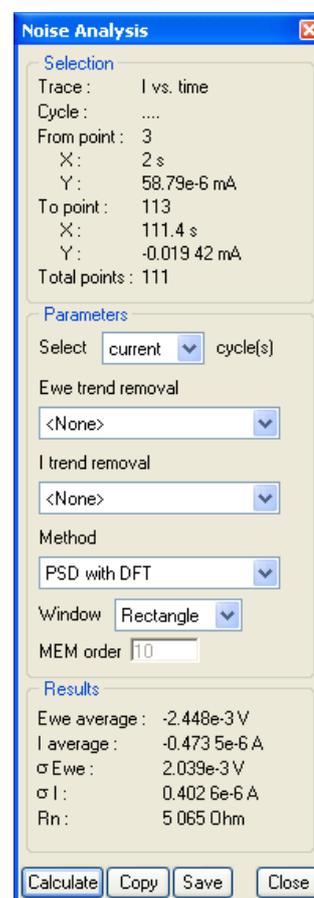


Fig. 203: Electrochemical Noise Analysis window.

Before to perform the analysis it is possible to remove the trend of the signal (potential and current) by using a **linear fit** or second order **polynomial fit**.

A description of the analysis windows that can be used is detailed in the section Fourier transform 4.1.7 page 96.

Example of electrochemical Noise Analysis is given in Fig. 204.

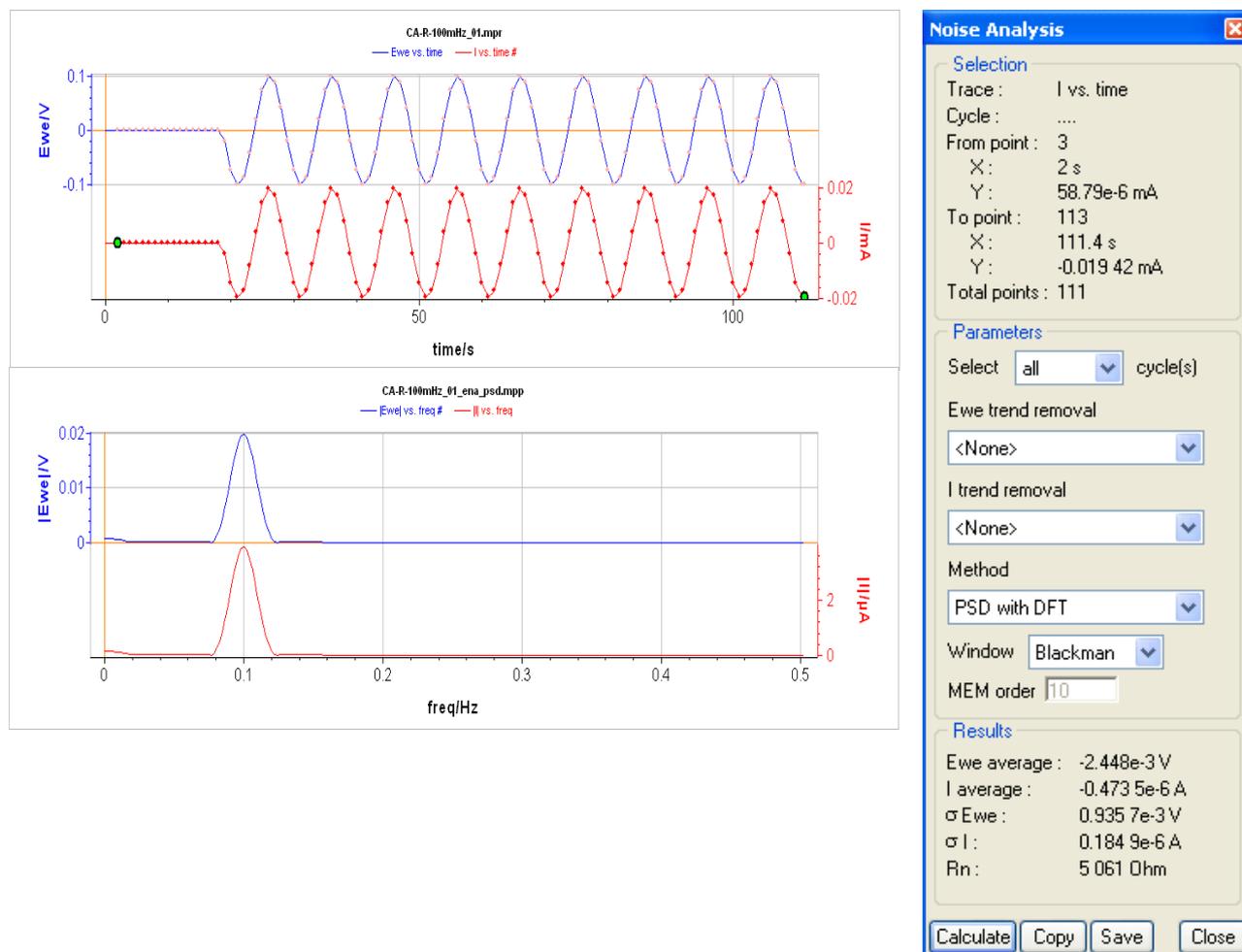


Fig. 204: Electrochemical Noise Analysis on system with a 100 mHz electrochemical noise.

References:

- Bertocci, U., Frydman, J., Gabrielli, C., Huet, F., and Keddad, M., Journal of. Electrochemical Society, 145 (1998), 2780–2786.
- Mansfeld, F., Sun, Z., and Hsu, C. H., Electrochim. Acta, 46 (2001), 3651–3664.
- Lee, C.C. and Mansfeld, F., Corrosion Science, 40 issue 6 (1998), 959-962.

4.6.7 Other corrosion processes

Two additional processes are available with the corrosion techniques: **Polarization Resistance** and **Multi-Pitting Statistics**. They are both described in the section below.

5. Data and file processing

General variables can be processed with the process data function. From the EC-Lab[®] menu choose the **Analysis** menu and for each of the analysis category, a list of processing functions can be applied to raw .mpr data files. Hereafter are summarized all the processes:

- Process Data
- Capacity and energy per cycle and sequence
- Summary per protocol and cycle
- Constant power protocol summary
- Polarization Resistance
- Multi-pitting Statistics.

All these functions are available off-line after the experiment. They create new binary files (.mpp) based on .mpr files with additional or removed variables. These files can be created during the experiment at a given time or after.

The structure of the raw files (.mpr) is defined to store all variables of interest and also be as compact as possible (with no variable redundancy). Nevertheless other variables obtained from the raw file may be of interest. For example, in potentiostatic mode, the instrument acts as a coulometer that performs charge recordings at periodic interval in charge or time. In practice it is more usual to display the current. Thus in such a case, data processing proposes calculating a charge increments between two recordings. From battery experiments several variables are of interest such as resistance. They can be extracted from raw data files in a compacted file.

5.1 Data processing

5.1.1 Process window

Select **Analysis, Batteries, Process Data** to load the processing window

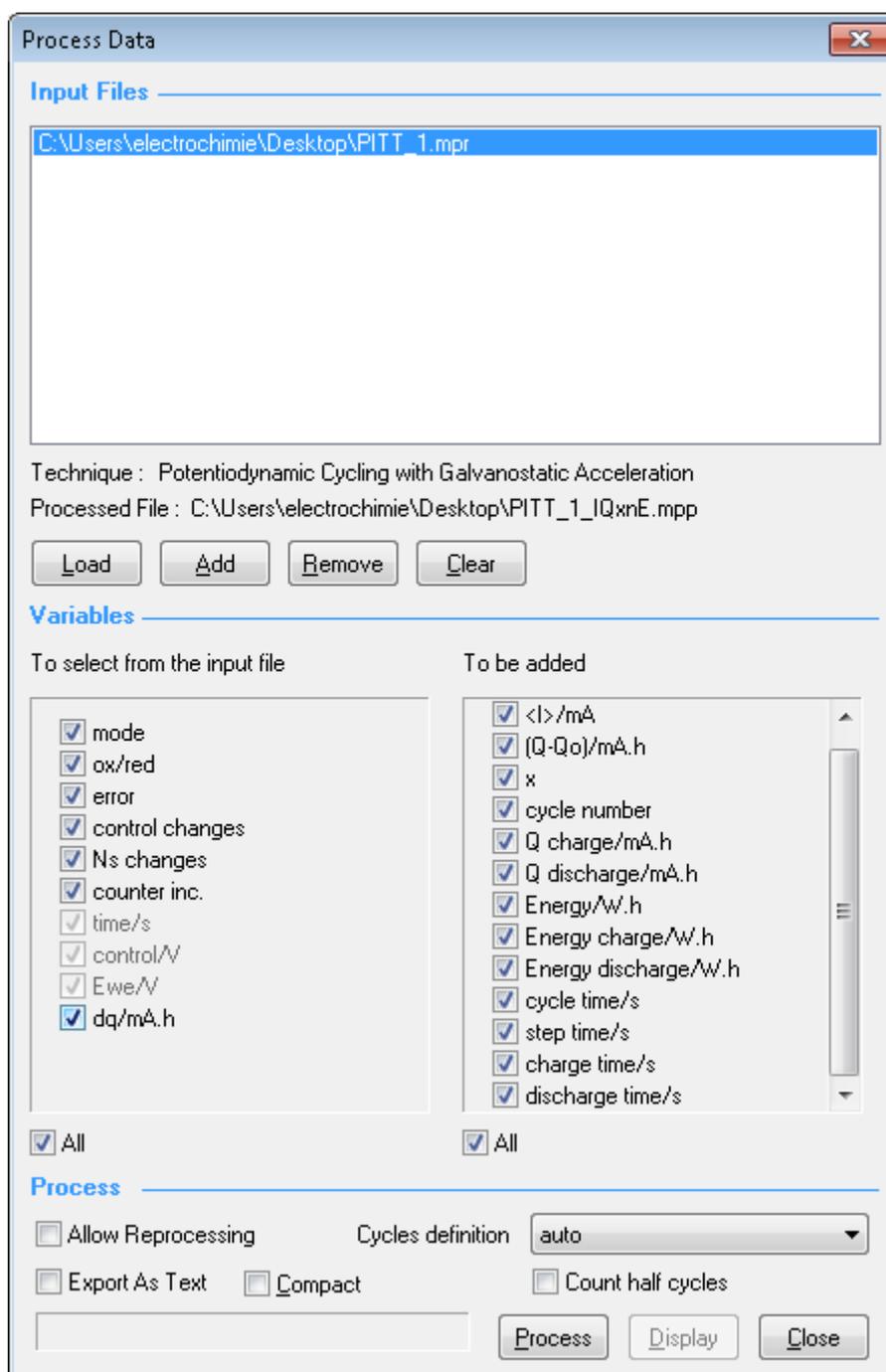


Fig. 205: PCGA Process window

This window is separated in 3 parts:

- in the first part “Input File” on the top of the window, the user will add the raw data files to process. Click on the **L**oad button to load a raw data file (in our example a PCGA file).
- The second part “Variables”, is dedicated to the variable selection generated the processed file. The left section is for the variable selection (from the native raw file) and the right section for those to be added to the processed file (calculated into either the firmware such as $\langle I \rangle$, $(Q-Q_0)$ or in the computer as processed variables.
- The bottom section is for additional options in the process. It is possible to:
 - o Allow reprocessing to be able to process again a mpp file
 - o Export as text a batch of data files

- Define the cycle as Auto / loop increment / every charge discharge alternance,
- Compact file for PCGA to add the dQ variable,
- Keep only values at the end of every Eoc period or I on period for GCPL
- Count half cycles

Select the variables you want to add and click on the **Process** button. This will create the processed file with the same name as the raw file, but with the addition of letters corresponding to the selected new variables and the .mpp extension instead of .mpr.

5.1.2 Additional processing options

At the user's convenience, the processed file can contain only a part of the native variables of the raw file. In that case the processed file will not be processable again. But for a later process of the processed file, the "**Allow Reprocessing**" box must be ticked on. This option will automatically select all the variables of the native raw file.

An "**Export as text**" option has been added in this window to automatically generate a text file processed file (*.mpt) that may be used in other software.

Different ways exist to define cycles in the processed file in order to plot Q and energy during the charge and discharge steps. The cycle for the process can be defined **automatically** or **every loop increment** or every **charge/discharge alternation**.

For the battery applications, specific process options "**Keep only values at the end of every OC period, I on period**" and "**Compact**" are available for the compacting process (for more details see the description below).

A "**Count half cycle**" process is available to separate half cycles especially for discharge measurements in battery testing.

Additionally, a process is also available for QCM experiment and especially for the determination of Mass variations. Using the auxiliary inputs of our instruments and a good setting to record the frequency changes, the software is able to process the mass variations. This feature is described in details in the application note #13.

5.1.3 The derivative process

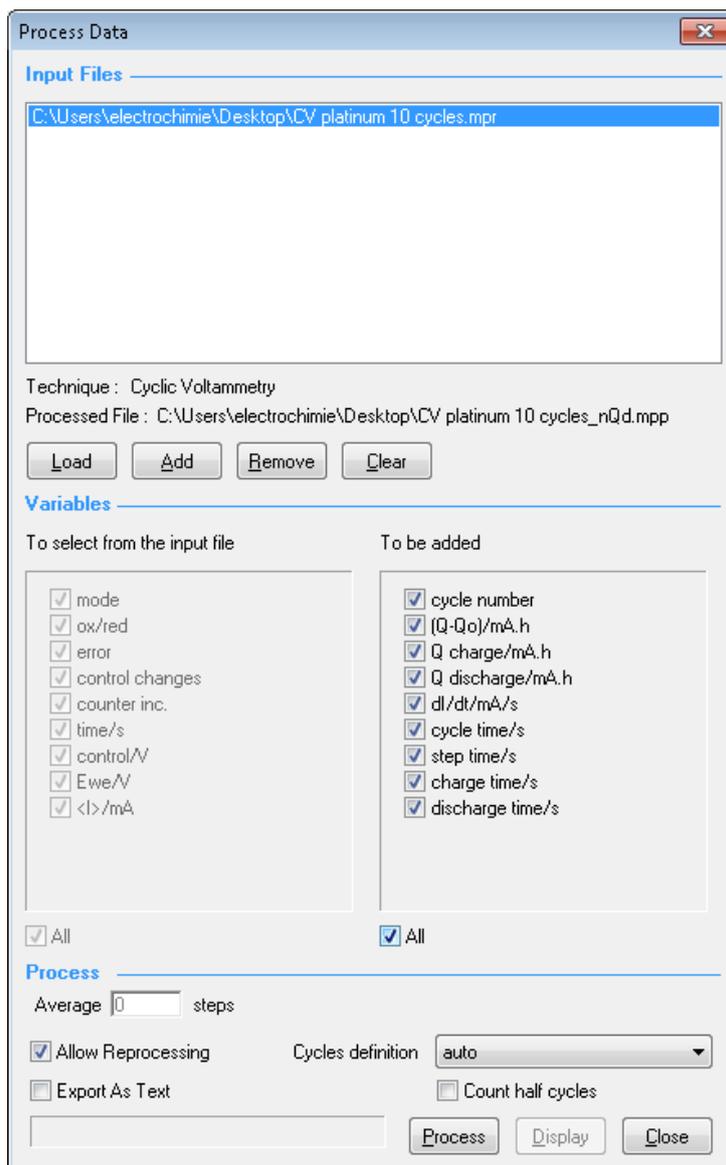


Fig. 206: Cyclic voltammetry processing window.

For techniques resulting in a current measurement (when the potential is controlled), the user can process the data file to create a new variable dl/dt , the derivative of the current versus time. Click on Display to automatically display the processed variable on the graph. The example below shows the Current derivative curve plotted versus the potential overlaid with the native cyclic voltammetry.

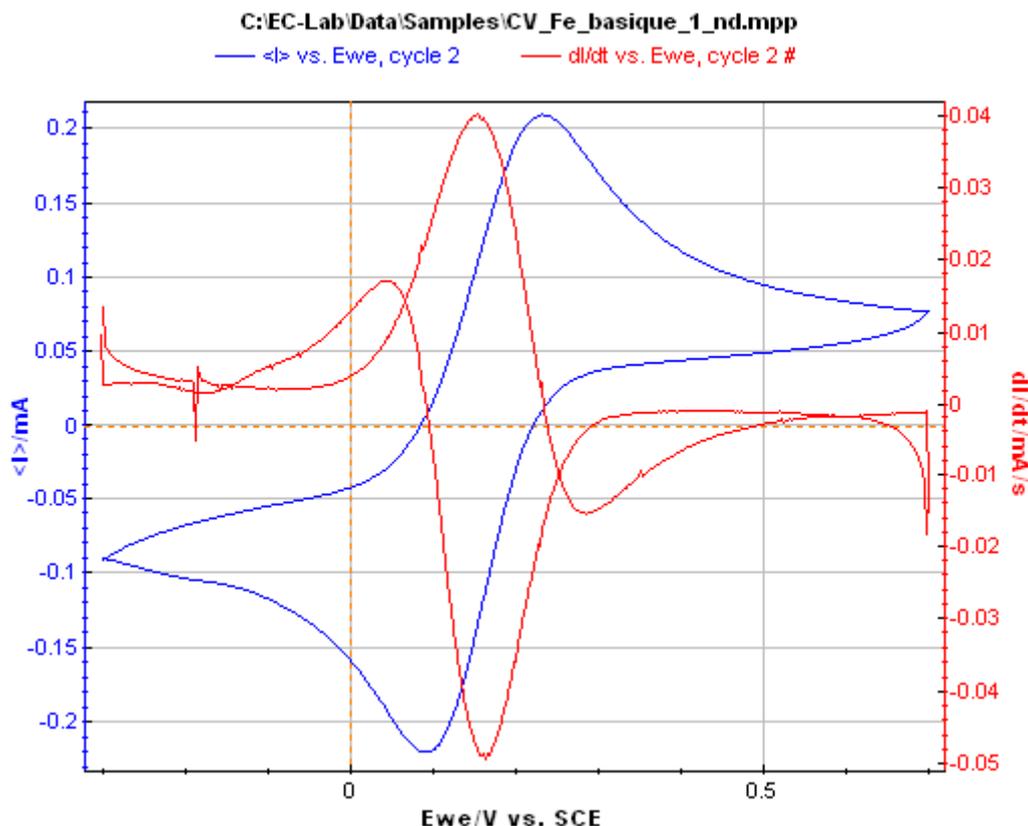


Fig. 207: Overlay Cyclic voltammetry with derivative curve.

All the graphic tools and fits can be applied to the derivative curve.

5.1.4 The compact process

The **Compact** function or “**Keep only values at the end of every OC period, I on period**” function can be used in GCPL and PCGA protocols. In the GCPL protocol, this function results in the determination of the apparent resistance “**Ri**” of the material studied (see the next section about GCPL). In the PCGA protocol, this function results in the determination of one average value of the variables for each potential step. Selecting **Compact** compresses the data resulting from the raw data file. All the points of each potential step are replaced by their average (current, potential, x or Q) taken at the end of the potential step. One consequence is an important decrease in the number of points in the compacted file compared to the raw file. The figure below shows the effect of the compact function on the current plot

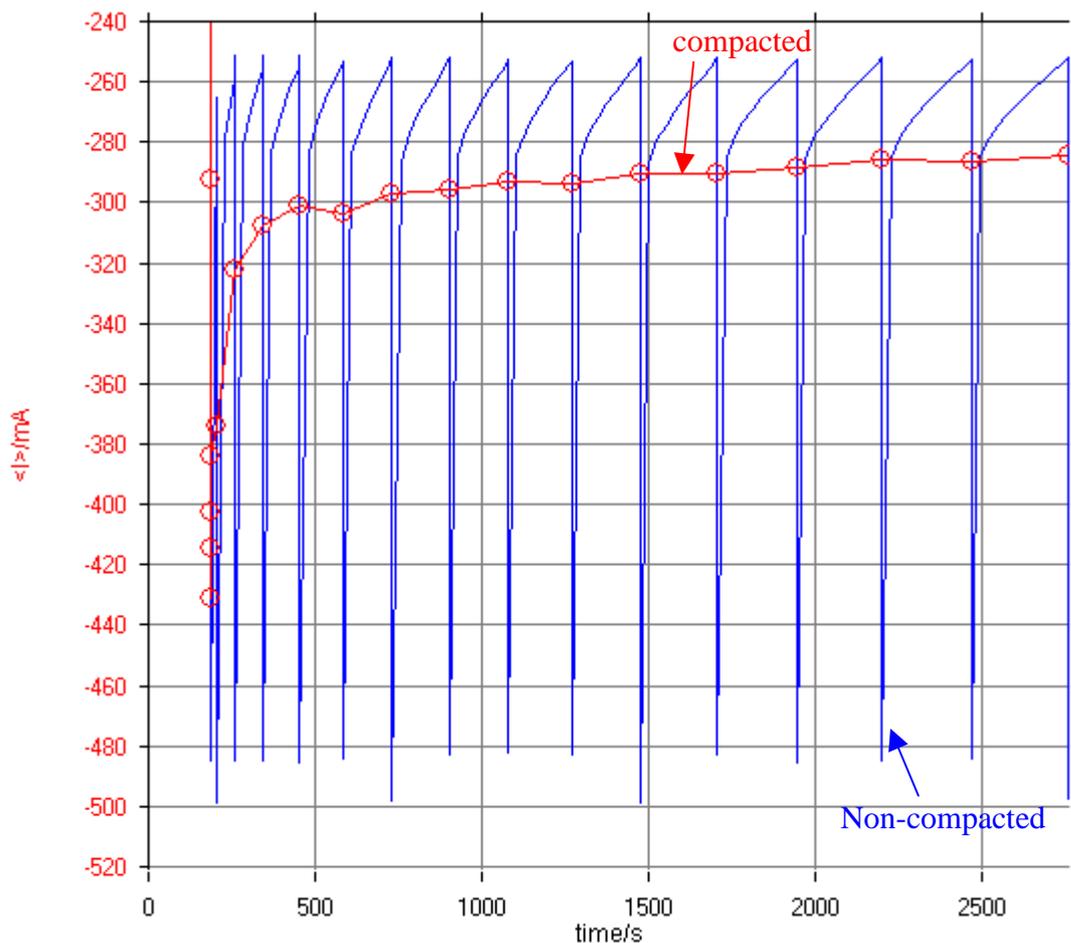


Fig. 208: Overlaid compacted and non-compacted current curves.

The variables that can be obtained from compacted files appear when the boxes at the bottom of the process window are ticked: **“keep only values at the end of every open circuit period and/or I on period.”**

5.1.5 Capacity and energy per cycle and sequence

Capacity and energy per Cycle and sequence... Calculates the capacity, energy and capacitance per cycle for the Galvanostatic Cycling with Potential Limitation (GCPL), Chronoamperometry / Chronocoulometry (Chrono I/Q), Cyclic Voltammetry (CV) and Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA) files. The values are calculated for both the charge and the discharge. The generated file is a compacted file. The user can define the frequency for which the data points are recorded (every sequence (a) or every cycle (b)). The cycle definition can be performed automatically or every loop or every charge/discharge alternance.

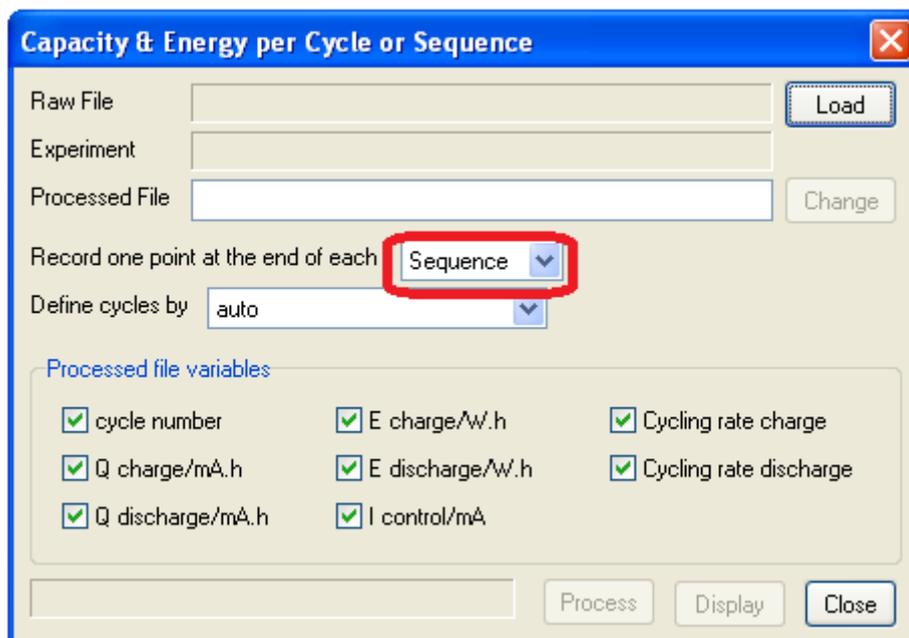


Fig. 209: Capacity and energy per sequence processing window.

The result of the calculation is a compacted processed file that contains several columns depending on the selected variables. The values can be processed as densities using the electrode surface area or the characteristic mass.

Qcharge, Q discharge and Energy are calculated by using the following formula:

- $Q_{\text{charge/discharge}} = i \cdot t / 3600$ (A.h)
- $E_{\text{charge/discharge}} = E \cdot i \cdot t / 3600$ (A.h)
- $\text{Cycling rate charge} = I(\text{control}) / Q_{\text{charge}}$
- $\text{Cycling rate discharge} = -I(\text{control}) / Q_{\text{discharge}}$
- $\text{Efficiency} = Q_{\text{discharge}} / Q_{\text{charge}}$

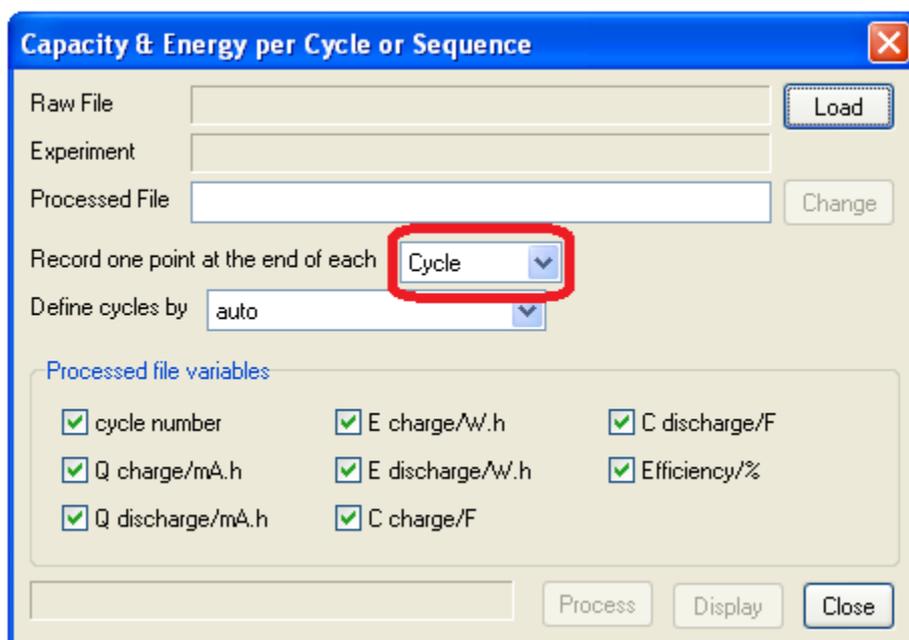


Fig. 210: Capacity and energy per cycle processing window.

The capacitance calculation is done as follows:

$$C = Q / \Delta E \text{ (Farad)}$$

$$C = i \cdot t / (3600 \cdot \Delta E)$$

Where ΔE is the potential difference between the first point of the sequence and the last point of the sequence.

5.1.6 Summary per protocol and cycle

This process allows the user to analyze CV, CA, CP, GCPL, GCPL2, GCPL3, GCPL4, GCPL5, GCPL6, GCPL7 and PCGA linked experiments in calculating Q_{anodic} , Q_{cathodic} and X_{min} and X_{max} (X being I_{anodic} , I_{cathodic} ...) for each cycle and linked experiment loop. Select this tool in the General electrochemistry analysis:

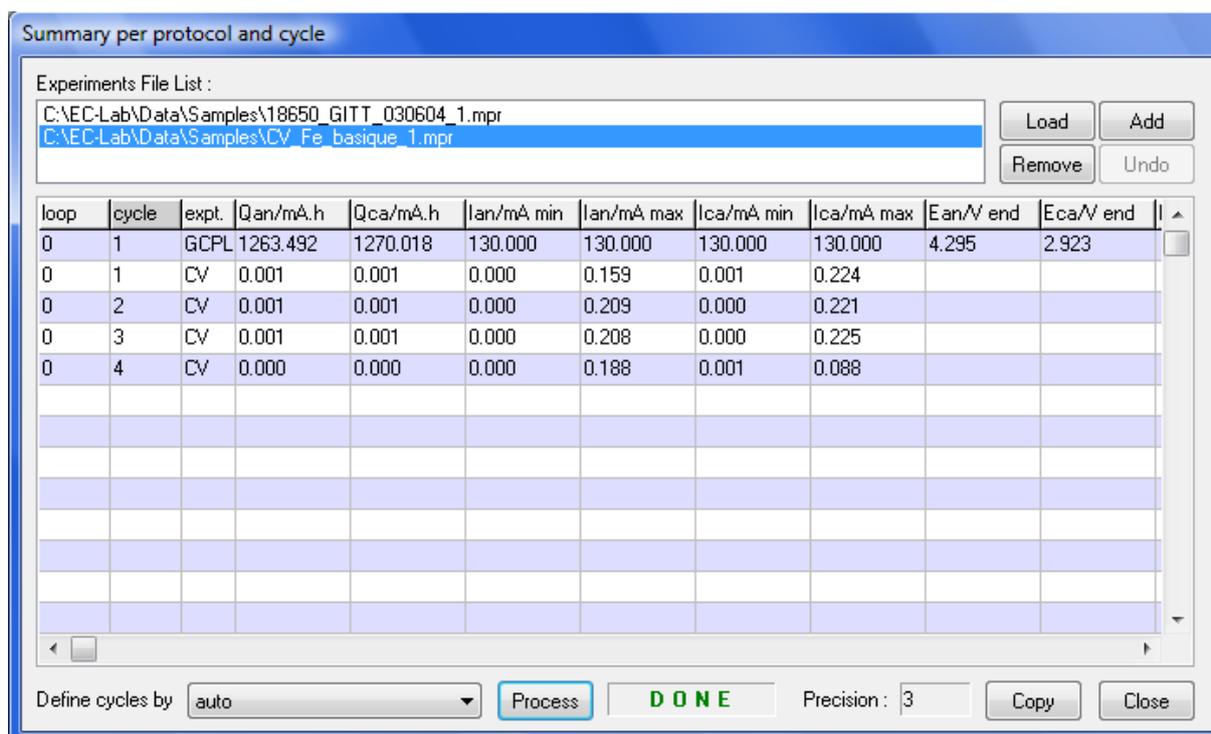


Fig. 211: Summary per protocol window.

Then, select the raw data files that correspond to two experiments, with the **L**oad (**A**dd, **R**emove and **U**ndo) buttons. In the example above:

- 18650_GITT_030604.mpr.mpr
- CV_Fe_basique_1.mpr

correspond to a GCPL and a CV run with cycles in each technique.

Click the **P**rocess button to start the calculation. This will create one processed file per raw file that contains the results (in the example: 18650_GITT_030604.mpr.mpp, CV_Fe_basique_1_cnQ.mpp) and displays the results in the Linked experiment window grid.

Notice that the linked experiment loops and the electrochemical cycles are both displayed and that the Summary per protocol and cycle window can be resized to full screen to display more values in the grid.

The grid can be copied to the clipboard (and pasted into a spreadsheet...) with the **C**opy button.

If one requires more accuracy, it is possible to increase the grid precision (up to 10 digits) by the following operations:

- change the **Precision** value,
- click again on the **Process** button.

Note that if the processed files are already calculated, this is not necessary to rebuild them (respond **Cancel** when the program asks you to rewrite them). Then the grid values will be reloaded from the existing processed files with the new precision.

The processed files are not deleted after the process and can be displayed in an EC-Lab® graph, or exported one by one into ASCII format.

5.1.7 Constant power protocol summary

A process called "Constant Power technique summary" has been especially designed for Ragone plot representation. It is associated with the CPW technique in battery applications. To use this data process, click on "process" in the graphic window or choose "Batteries\Constant Power Protocol Summary" in the **Analysis** menu. Then the following processing window will be displayed:

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

Fig. 212: 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):

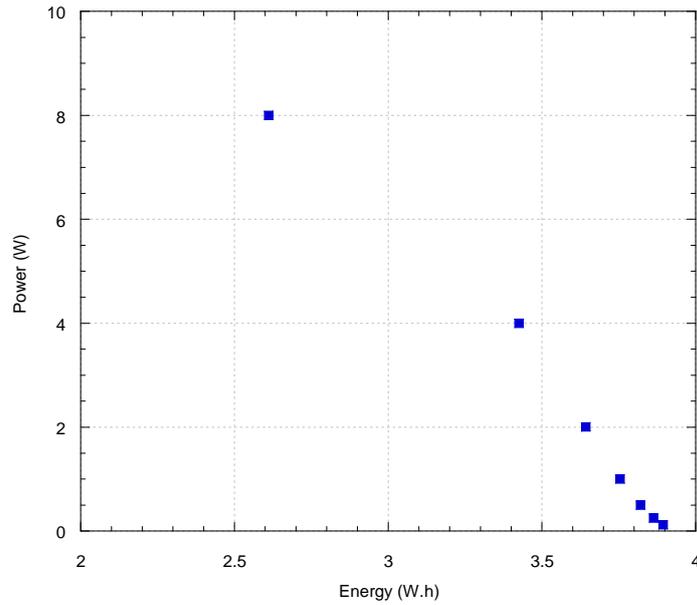


Fig. 213: Ragone plot for a Li-ion cell (1.35 A.h).

5.1.8 Polarization Resistance

Polarization Resistance... determines the R_p and I_{corr} values from a Polarization Resistance files. Select **Analysis/Corrosion/Polarization Resistance** to load the following window. 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 $\Omega \cdot \text{cm}^2$ calculus) here.

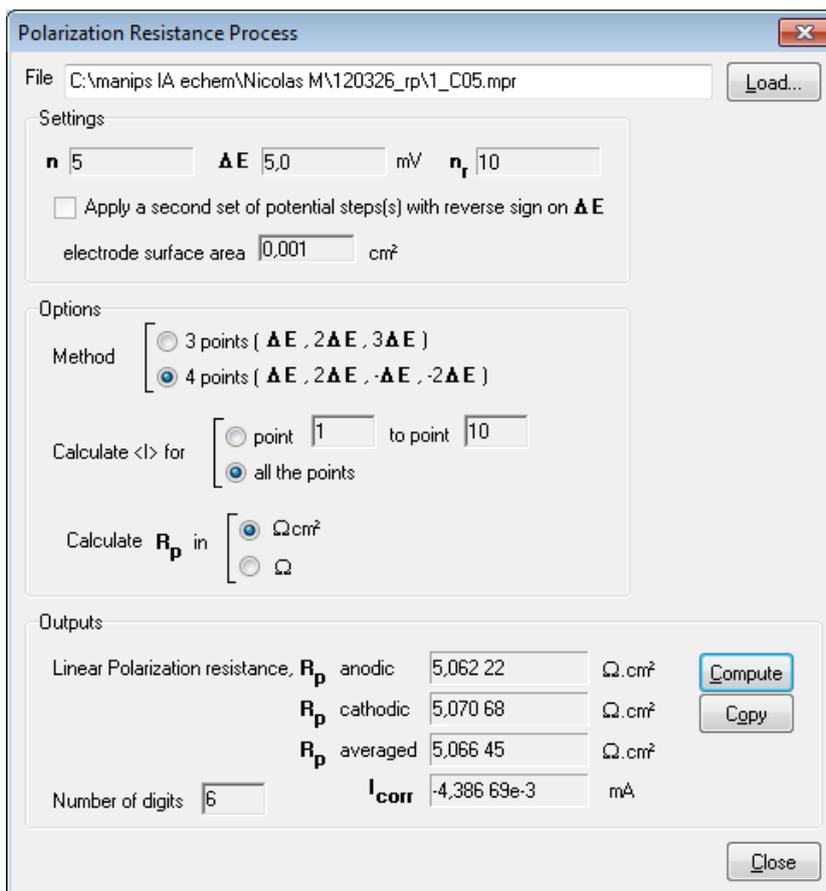


Fig. 214: Polarization Resistance process.

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:

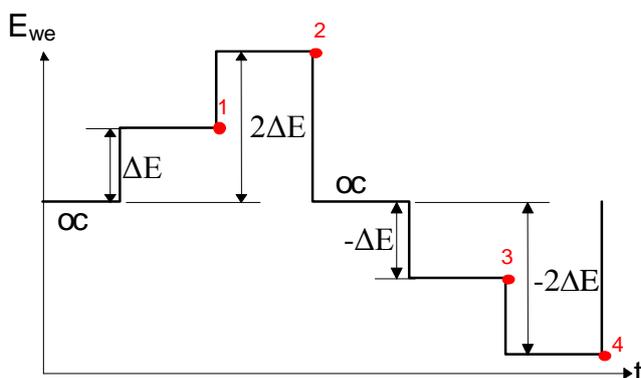


Fig. 215: 4 points method.
(n = 2, reverse steps)

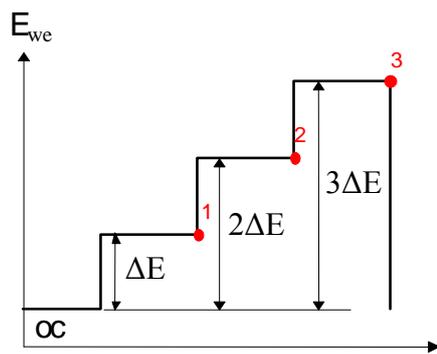


Fig. 216: 3 points method.
(n = 3, do not reverse steps)

The 4 points method gives more accuracy, so it is proposed by default. Nevertheless, it is not always possible to make a reduction after an oxidation, so then chose the 3 points method.
Note: one can perform more than the 4 points and 3 points method with the Polarization Resistance technique, but the process here accepts only these two.

If several points have been recorded per potential steps ($n_r > 1$), it is possible to exclude some points for the calculus. For example, selecting Calculate <I> for point 3 to 10 will exclude the first two points.

Choose the R_p unit ($\Omega \cdot \text{cm}^2$ or Ω) and click on **Compute** to calculate the next values:

$$R_{p_{anodic}} = \frac{e_2 - e_1}{i_2 - i_1}, \dots R_{p_{cathodic}} = \frac{e_4 - e_3}{i_4 - i_3} \dots \text{ and } R_{p_{averaged}} = \frac{R_{p_{anodic}} + R_{p_{cathodic}}}{2}$$

3 points method: $I_{corr} = \frac{i_1}{\sqrt{|4r_2 - 3r_1^2|}}$ with $r_1 = \frac{i_2}{i_1}$, and $r_2 = \frac{i_3}{i_1}$

4 points method: $I_{corr} = \frac{i_1 i_3}{\sqrt{|i_2 i_4 - 4i_1 i_3|}}$ 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.

5.1.9 Multi-Pitting Statistics

Multi-Pitting Statistics... is a process which can be applied to Multi-Pitting experiment files. It gives the mean value $\langle E \rangle$ and the mean quadratic deviations σ of the final open circuit potentials (E_{oc}) and pitting potentials (E_p) of a set of electrodes, or of a set of selected files. Note that the E_p value corresponds to the potential measured for $I = I_p$.

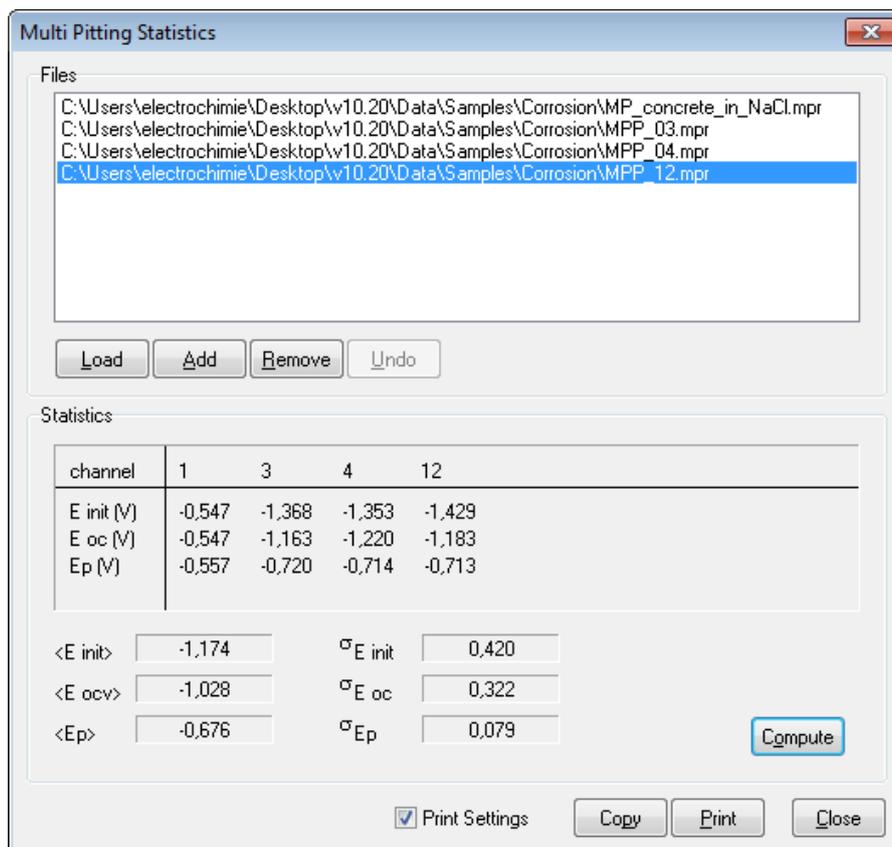


Fig. 217: Multi pitting statistics window.

5.2 Data File import/export functions

5.2.1 ASCII text file creation and exportation

For file exportation to other software (Kaleidagraph, Origin, Excel,...), it is possible to create text files from .mpr and .mpp files. Choose **Experiment, Export as Text...** in the EC-Lab® menu bar. This will load the window below.

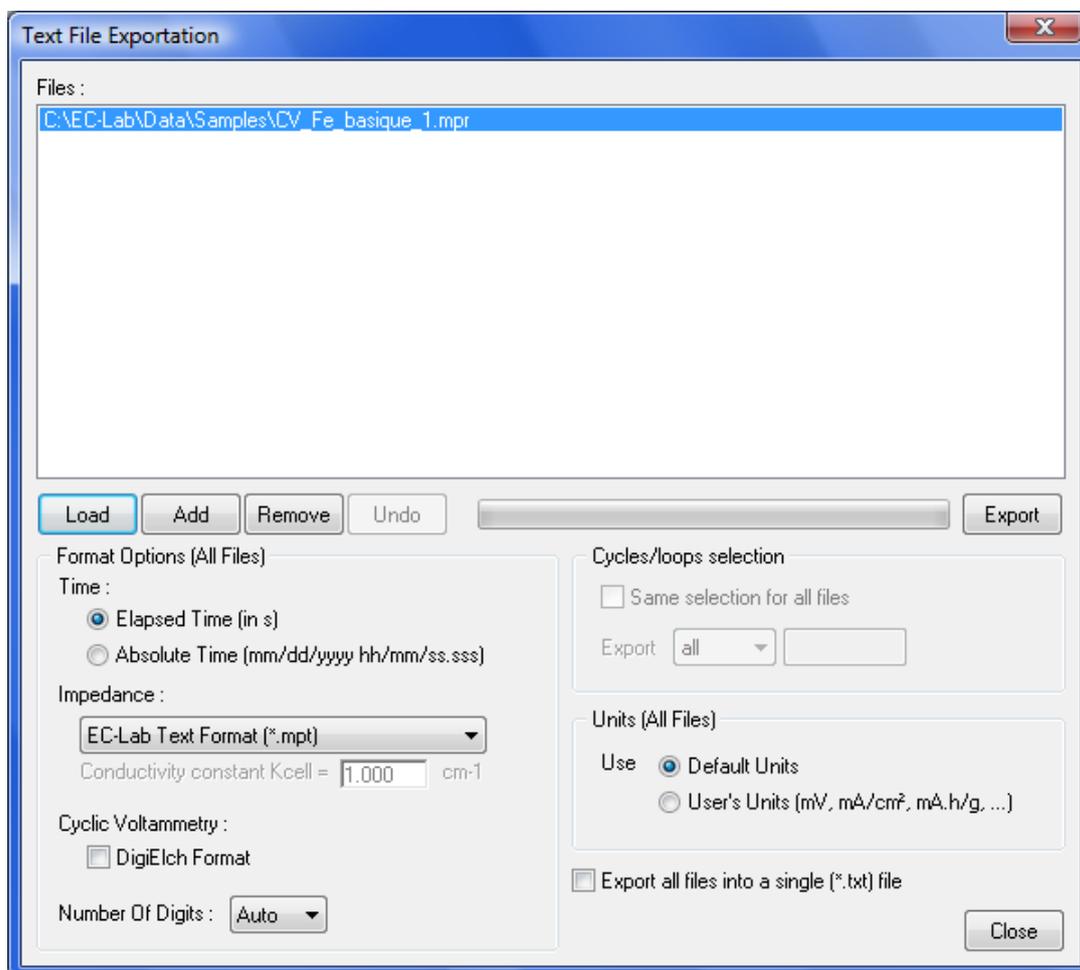


Fig. 218: Text File exportation.

Select one or more files (with the **L**oad and **A**dd buttons). Note that it is possible to select files from different directories. Click on the **E**xport button to export all the selected files into the selected text format. The resulting text file(s) are created in the same folder as the original file and differs only by the **.mpt** extension.

Several text formats can be created by EC-Lab® software depending on the importing software. For time files one can display the relative time from the beginning of the experiment e.g. $t = 0$ s for the first point (**E**lapsed Time (in s) option, default) or the absolute time in year, month, day, hours, minutes and seconds format (**A**bsolute Time (mm/dd/yyyy hh/mm.ss.sss option)). For impedance data files, an export text in ZSimpWin or Zview formats is available and allows to paste directly data into ZSimpWin or Zview software. An export text in Bio-Kine conductivity Ascii file is also available. For cyclic voltammetry files, an export option in DigiElch format is available. A *.use file is created in that case.

While running experiment, it is possible to export files. To do so, the user must check the **Text export** option into the "Cell Characteristics" window before starting the experiment.

Loops / cycles text exportation:

If the selected file contains linked experiments loops or the cycle number variable (processed files only), then one can export specific loops or cycles.

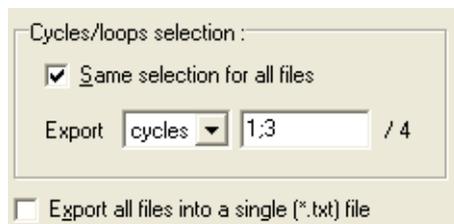


Fig. 219: Loops/cycles text exportation.

Proceed in the same way as with the **Selector**: check **Same selection for all files** if you want to apply the loop/cycle selection to all the selected files. If unchecked, each selected file will have its own loop/cycle selection. Select loop or cycles (if present) with the **Export** box and edit the selection list with the following rules:

- separate each single item by a ';' : <item1>;<item2>;<item3>;...
- use '-' to generate a list of consecutive items : <first item>-<last item>;...

The example above: '1;3' will select the cycles number 1, and 3.

Once the loops or cycles have been selected the text exportation will create one file per loop or cycle selected with the loop or cycle number added to the text file.

Note: the user can copy data in text format. Right-click with the mouse and select copy data. The displayed variables will be copied to the clipboard.

Unit selection

On the graphic window, EC-Lab[®] software is capable of plotting variable density (for example normalized current with mass or surface). These new variables are not stored in the data file and cannot be exported as text. To allow exportation of densities, the user can select the unit. The default one will not include the density and the user's units will include densities. :

Note: A text data file can be generated automatically during the experiment if the box "Text export" is checked in the "Advanced Settings" window.

5.2.2 ZSimpWin exportation

It is possible to export data directly into ZSimpWin through the Clipboard. To proceed, open an impedance data file, right-click with the mouse, and select **Copy Z Data (ZSimpWin)**, or click directly on the **Copy Z Data (ZSimpWin)** button in the Edit menu. Then the data points will be copied into the clipboard and can be pasted directly into ZSimpWin.

Warning: For good compatibility, the text file exported into ZSimpWin must contain between 16 and 199 points.

5.2.3 ASCII text file importation from other electrochemical software

EC-Lab[®] software allows the user to load every text file generated by other electrochemical software. All text formats can be loaded directly from the "**Load data file**" function in the **Experiment** menu. If the software recognizes the data file, EC-Lab[®] will be able to open it directly. If not the user can import the text file with the "**Import from text**" function in the **Experiment** menu. This can be done either automatically when it is possible (the format is known by the software) or manually with a definition by the user of the number of columns and of each variable.

In the “**Experiment**” menu select “**Import from text...**” or click on the import icon  to display the following window:

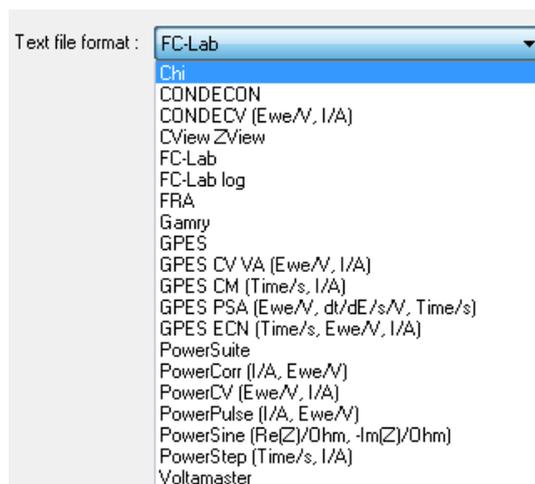
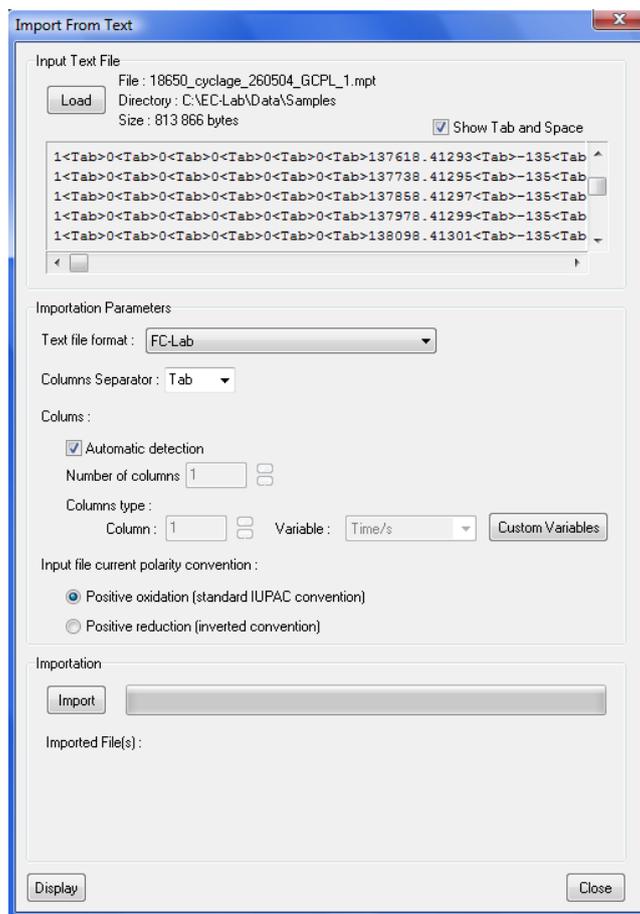


Fig. 220: Text file importation into EC-Lab[®] and available importation file formats.

To proceed to text file importation, click on the “**Load**” button and select the file to import. Now the file name, directory and size are displayed near the top of the window in the “**Input Text File**” frame.

The second frame defines the parameters for importation. In order to select the good separator, click in the “**Show tab and space**” box to display separators in the file. You can try with an automatic detection. In most of the cases the user will have to use a manual detection

while unchecking the box. Then define the number of columns and for each of them select the variable. The user can add his own labels and units to be displayed in the data file and the graphic window.

Then click on the “**Import**” button to import the file into the EC-Lab® .mpr format. The mpr file is created in the same folder as the text file. Several details are displayed when the file is created such as the name, the number of points and the size.

Finally the user can display the .mpr file quickly and easily with the “**Display**” button. Every analysis of EC-Lab® is available with the new generated files.

5.2.4 FC-Lab data files importation

FC-Lab® data files can also be imported and analyzed in EC-Lab® using the “**Text file format**” function. The FC-Lab® data file format is particular as all the data files for each technique are in the same file. So EC-Lab® software will separate every file of every technique used in the experiment.

5.3 Reports

A report file can be associated with each EC-Lab® data file to add all kinds of additional information. The data file and the report file have the same name but with different extensions: .mpr for the data file, and .rep for the report file. Note that the report file must be in the same directory as the corresponding data file in order to be recognized.

For instance:

- Data file: *c:\vmp\files\XXXX.mpr*
- Report file: *c:\vmp\files\XXXX.rep*

Reports are called from the Graphic Display window. Right-click with the mouse on the graphic window and select “**Report**” to call the report associated with the current data file. If the report does not exist, a message box appears to let the user create a new report:

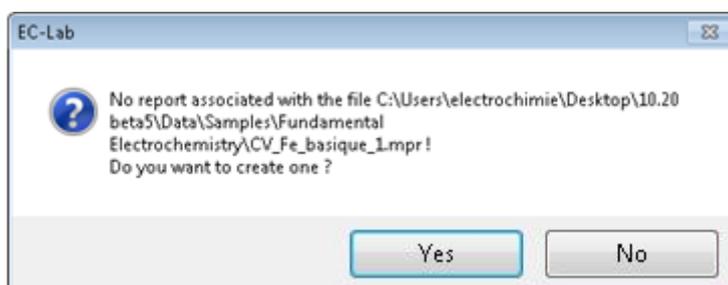


Fig. 221: Message window.

Here is an example of a report. The user can define the project, material and results.

Report : C:\Users\electrochimie\Desktop\v10.20 Beta 8...

Project Material Result

Project No.

Report-No.

User

Notes

Delete Print OK Cancel

Fig. 222: Report window.

OK saves modifications done to the report.

Cancel discards modifications done to the report.

Delete automatically sends the report to the recycle bin.

Report configuration

The structure of each new report is based on the read-only text file "*DefaultReport.rep*" (in the same directory as the EC-Lab® software), which is given as an example. However, the user can change the sections and keys to customize the report to his needs.

For example the changing of the content of "*DefaultReport.rep*" into:

```
[Section1]
Info1=
Info2=
[Section2]
Info10=
Info20=
```

will result in the new report:

Report : C:\Users\electrochimie\Desktop\10.20 beta5\...

Section1 Section2

Info1

Info2

Delete Print OK Cancel

Report : C:\Users\electrochimie\Desktop\10.20 beta5\...

Section1 Section2

Info10

Info20

Delete Print OK Cancel

Fig. 223: New Report.

6. Advanced features

6.1 Maximum current range limitation (2.4 A) on the standard channel board

6.1.1 Different limitations

VMP2, BiStat, VMP3, VSP are designed to accept a maximum continuous current of 400 mA (*) on the 1 A current range for each channel and for a room temperature of 25°C. Note that the maximum current that can be reached in continuous by the SP-50 and SP-150 is 800 mA and 500 mA the SP-200, SP-240, SP-300, VSP-300 and VMP-300.

In particular conditions of current and time, this limit can be passed. Then, the following message is displayed:

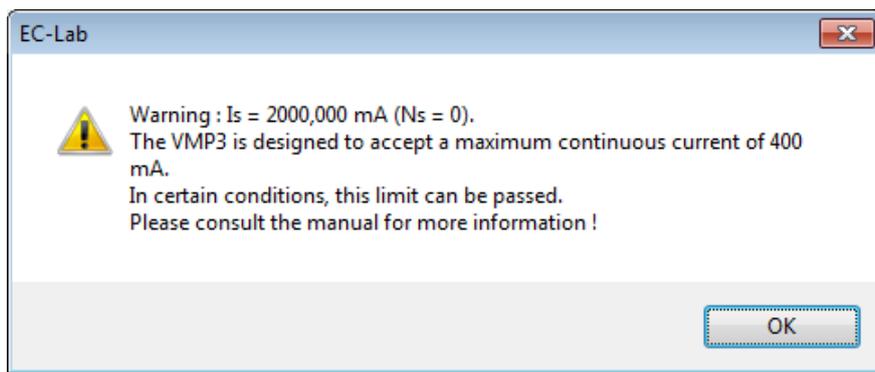


Fig. 224: Warning message for the current limitation.

To go over 400 mA (*), one must respect three limits that depend on the maximum continuous current duration, the average current, and the power supply:

- 1) The maximum continuous current (I) is limited to 2.4 A for a maximum duration (t) of 2 ms and must respect $It \leq 4.8 \times 10^{-3} \text{ A.s}$ (**).
For example, one can apply 2.4 A for only 2 ms and 1 A for 4.8 ms (see below). Beyond these limits a protection mode sets up in the instrument.

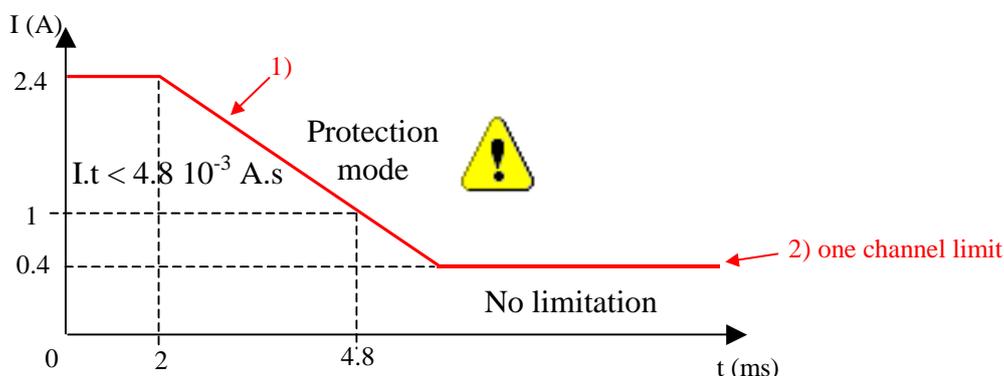


Fig. 225: Safe operating area.

- 2) The maximum average current $\langle I \rangle$ recommended during the experiment is 400 mA for one channel. For example in the protocol described on the following figure, two

different currents (I_1 and I_2) are applied for two durations (t_1 and t_2 respectively). The average current on a period is defined by:

$$\langle I \rangle = \frac{I_1 t_1 + I_2 t_2}{t_1 + t_2}$$

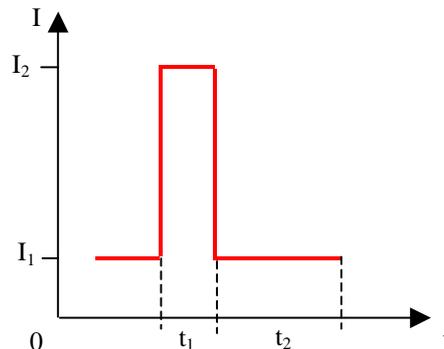


Fig. 226: Example of a current pulse protocol.

- 3) The power supply has a limit of 10 A. To avoid having the instrument enter the protection mode, the user must respect the following equation:

$$\sum_{1}^{Nb} I_{inst} \leq 10 \text{ A}$$

where Nb is the number of channels used simultaneously in the experiment and I_{inst} is the current measured for each of those channels.

For example, the number of channels used simultaneously in a 2.4 A current pulse protocol is limited to 4. It can increase to five if the maximum current is 2 A.

(*) for the instruments sold after **April 2004**. For the others, the limit is 250 mA.

(**) for the instruments sold after **April 2004**. For the others, the limit is $2.4 \cdot 10^{-3}$ A.s.

Note that the same principle is applied on all the I Range values (except the 1 A range) of SP-200, SP-240, SP-300, VSP-300 and VMP-300.

6.1.2 Application to the GSM battery testing

A specific current pulse profile is used for GSM battery testing. The GSM pulse protocol (see next figure) consists of applying a current pulse (I_1 between 1 and 2 A) for a short time ($t_1 \leq 1$ ms) followed by a step to a lower current (I_2) for a longer period (t_2).

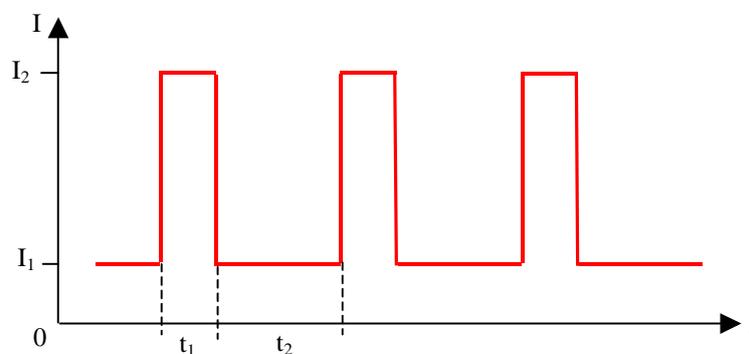


Fig. 227: Theoretical GSM pulse waveform.

This theoretical pulse waveform can be easily programmed into EC-Lab® with the chronopotentiometric protocol. The sequences are presented in the table below:

- Ns = 0: OCV
- Ns = 1: apply 1.4 A for 1 ms
- Ns = 2: apply 0.3 A for 10 ms

The sequence is repeated few times. The period is 11 ms and <I> never exceed 400 mA.

Ns	Is	unit Is	dIs	unit dIs	ts (h:m:s)	EM (V)	dQM (mA.h)	dEs (mV)	dts (s)	I Range
0	0.000	mA	0.000	mA	0:00:0.0000	pass	0.000000	0.00	0.0000	1 A
1	1.400	A	0.000	mA	0:00:0.0010	pass	0.000389	0.00	0.0002	1 A
2	0.300	A	0.000	mA	0:00:0.0100	pass	0.000833	0.00	0.0002	1 A

Fig. 228: Table of the experiments for GSM battery testing.

The result is represented on the following figure.

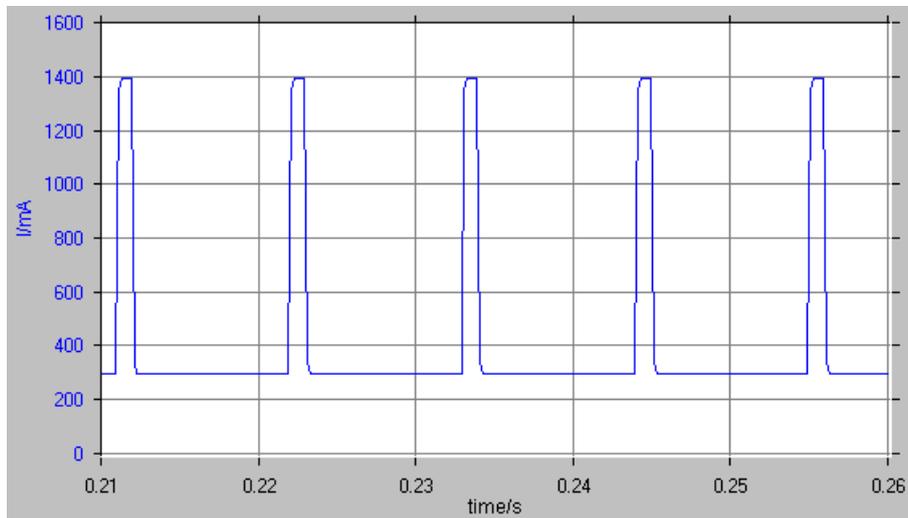


Fig. 229: GSM pulse waveform generated by chronopotentiometric protocol.

6.2 Optimization of the potential control resolution

6.2.1 Potential Control range (span)

Our potentiostats/galvanostats are digital instruments. The potential is applied to the cell via a 16 bit DAC (Digital to Analog Converter). The DAC delivers a potential in the ± 10 V range for VMP3, VSP, SP-150 and in the ± 10.9 V range for the SP-300 technology with a resolution equal to its LSB (Least Significant Bit) that corresponds to the smallest potential step available, and is defined as:

$$LSB = \frac{20 \text{ V}}{2^{16} - 1} = \frac{20 \text{ V}}{65535} = 305.18 \text{ } \mu\text{V} \text{ for VMP3 family,}$$

$$\text{and as } LSB = \frac{21.8 \text{ V}}{2^{16} - 1} = \frac{21.8 \text{ V}}{65535} = 333.33 \text{ } \mu\text{V} \text{ for SP-300 technology.}$$

When the user enters in EC-Lab® a potential value E_{ctrl} , the value sent to the DAC is a 16-bits value corresponding to an integer number of LSB, i.e. defined as:

$$E_{cell} = N \cdot LSB \text{ with } N = \text{round}\left(\frac{E_{ctrl}}{LSB}\right)$$

where "round" is the function that returns the nearest integer of the variable.

Usually, experiments do not require 20 V potential ranges.

So in EC-Lab®, the potential control resolution can be adjusted to the required experimental potential range, in order to have potential values as close as possible to the set values, and in potential sweeps, to be as close as possible to a linear sweep with the smallest potential step.

This is obtained by adjusting of the DAC output from ± 10 V (± 10.9 V) to the required potential range, through a programmable attenuator and a programmable offset.

This optimization is available in the "**Parameters Settings**" window (see below).

Given the E_{max} and E_{min} limits, the potential range is reduced to $E_{max} - E_{min}$ and the potential resolution becomes:

$$\frac{E_{max} - E_{min} + 0.2}{65535}$$

Adding the 0.2 V value is a hardware constraint to allow reaching E_{max} and E_{min} .

Thus the theoretical maximum resolution is $\sim 3 \text{ } \mu\text{V}$ ($200 \text{ mV} / 65535$).

In EC-Lab®, we have chosen to have a set of fixed resolution values adjusted to the potential range in a 1-2-5-10 scale.

This leads to the table below, for the maximum potential range values at which the resolution changes.

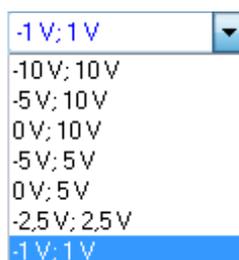
Table 1: Resolution values according to the E_{we} potential range.

$E_{max} - E_{min}$ (V)	Resolution (μ V)
20	305.18 or 333.33
19.46	300
12.9	200
6.3	100
3.0	50
1.1	20
0.4	10
0.12	5

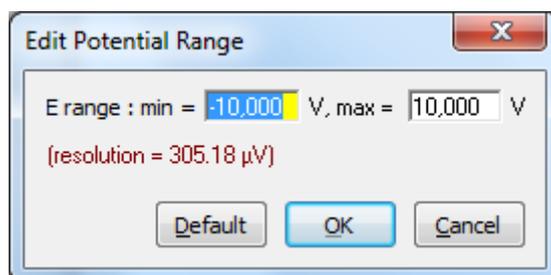
Note that the potential control resolution is available with low current boards delivered from 1st June 2004. For the other low current boards (delivered before 1st June 2004), a technical modification is necessary.

6.2.2 Settings of the Working Potential window

If no experiment limits are defined the potential resolution is 305.18 μ V (or 333.33 μ V), corresponding to the ± 10 V (± 10.9 V) range. E Range is located in the setting of each technique.

**Fig. 230: E Range selection.**

Using the “Edit” button opens a window to define the potential range manually. Entering the required E_{we} min and E_{we} max the corresponding value of the potential control resolution appears. For example entering 0 V and 1 V leads to 20 μ V resolution.

**Fig. 231: Edit potential range window.**

Application

Optimization of the potential resolution is particularly interesting when trying to perform protocols based on potential scan, such as CV, in order to approach linear scans as much as possible.

For example, after choosing the above 1 V potential window and loading a CV a 20 μV potential step value is automatically proposed when entering a scan speed dE/dt , as shown in Fig. 232 below.

Scan E_{WE} with $dE/dt = 10$ mV/s ($\sim 20 \mu\text{V} / 2.0 \text{ms}$)

Fig. 232: CV experiment, potential scan with 20 μV steps.

6.3 Measurement versus control current range

Our potentiostats are designed to work either in the potentiostatic (static or dynamic) mode or in the galvanostatic (static or dynamic) mode. In the potentiostatic mode, the potential between the working and the reference electrode is controlled. The current resulting from the redox processes at the applied potential is measured. On the contrary, in the galvanostatic mode the current is controlled, and the potential is measured. In both cases, one variable is controlled and the other one is measured. The current and the potential dimensions always have to be adjusted while choosing the range in which the experiment is performed. In fact, the result accuracy will be better if the range is chosen closer to the experiment's limits.

6.3.1 The potentiostatic mode

The potential control range can be adjusted for the experiment with the experiment limits E_{max} and E_{min} (see the installation and configuration manual for more details). The result of this adjustment is the potential resolution increase (from 300 μV to 5 μV). In this control mode, the user must define the measurement current range. The closer to the experiment the current range is, the better the measurement accuracy. The maximum current value that can be measured corresponds to 2.4 times the chosen current range. In other words, for the 10 μA range on the figure below, the user can apply potentials from -10 to $+10$ V and currents going from -24 to $+24$ μA can be measured with no restrictions.

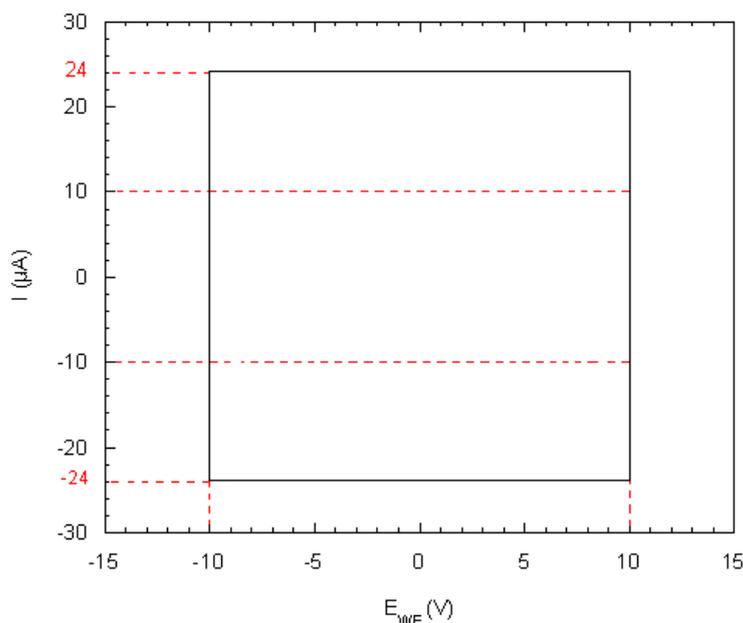


Fig. 233: Current versus Potential available domain in the potentiostatic mode.

6.3.2 The galvano mode

In this mode the current range must be adjusted to the controlled current. In that case, the user must distinguish the 1 A current range (which will be discussed in the following part) from the others (please refer to the part 6.1 page 164 for more details). Usually the controlled current value cannot bypass the range. If the user wants to apply 15 μA current to the cell, the 100 μA current range must be chosen.

With all the instrument of the Bio-Logic range, the user can bypass the current range in the control mode in a limit of 2.4 times the range with several conditions on the potential. In the galvano mode, when the controlled current value is higher than the range, the measured potential range is reduced to ± 8.6 V instead of ± 10 V whatever is the chosen current range (see figure below).

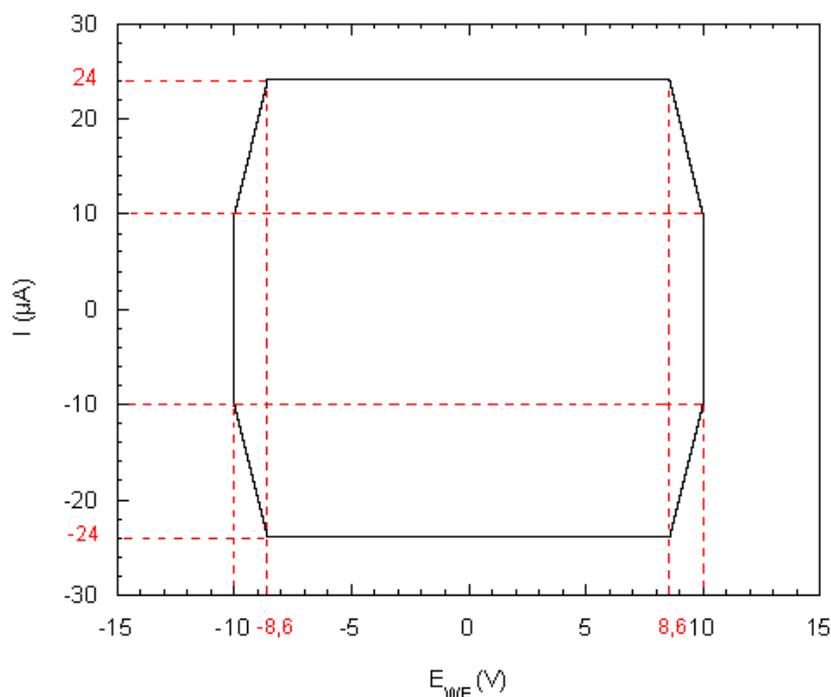


Fig. 234: Current versus Potential available domain in the galvano mode.

6.3.3 Particularity of the 1 A current range in the galvano mode

The 1 A current range is a very special range. The label (1 A) of this range has been chosen according to the control in the galvano mode and the measurement in the potentiometric mode. In the galvano or potentiometric mode, the channel board structure limits the maximum continuous applied or measured current to 400 mA (800 mA for SP-50, SP-150 and 500 mA for SP-300, SP-200, SP-240, VSP-300 and VMP-300). In certain cases the user can bypass this value to apply or measure current pulses up to 2.4 A (corresponding to 2.4 times the 1 A range, see 6.1). The average current for either measurement or control must not bypass 400 mA (800 mA for SP-150 and SP-150 and 500 mA for SP-300, SP-200, SP-240, VSP-300 and VMP-300). This is especially used for GSM battery testing (Please refer to the part 6.1 page 164 for more details)

Warning: the low current board cannot accept more than 400 mA in potentiometric and in galvano mode. We advise the users to be mindful of the maximum current when using low current boards.

6.3.4 Multiple current range selection in an experiment

The EC-Lab[®] software offers a facility to select different current ranges in either galvano or potentio mode for an experiment. The experiment can be made with only one technique but with several sequences in the technique or with linked techniques. In both cases, the user can choose different current ranges between sequences or between techniques if an OCV period is set between them.

For example, in a GCPL experiment with 10 sequences, the user can select 10 different current ranges if the third block of OCV is activated into every sequence. Then a warning message is displayed:

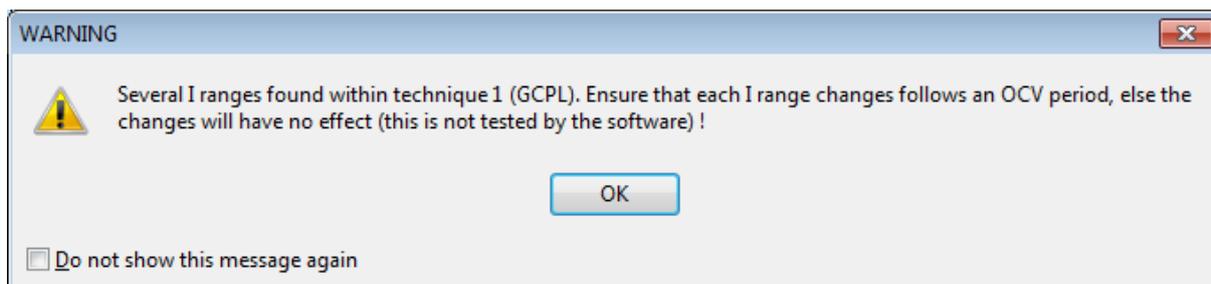


Fig. 235: Warning message on different current ranges into a setting.

Note: when several current ranges are selected in a setting the software will not test if some OCV periods are set between sequences. It is the user's responsibility.

6.4 External device control and recording

6.4.1 General description

EC-Lab[®] software enables the user to control external devices such as rotating electrodes and thermostatic baths and record external analog signals through the auxiliary DB9 connector. The user must configure the output to control an external device and configure Analog In1 and Analog In2 inputs to record external signals. Our instruments can control and record analog signals from -10 to $+10$ V. Most of the external devices work in a 0 to $+5$ V range. The figure below shows the external device window where the user sets parameters. Many instruments are already configured in the software to be controlled by our potentiostats. The list will be completed in the future versions of EC-Lab[®] software. To configure external devices, select "**External Devices**" in the "**Config**" menu. The following window is displayed:

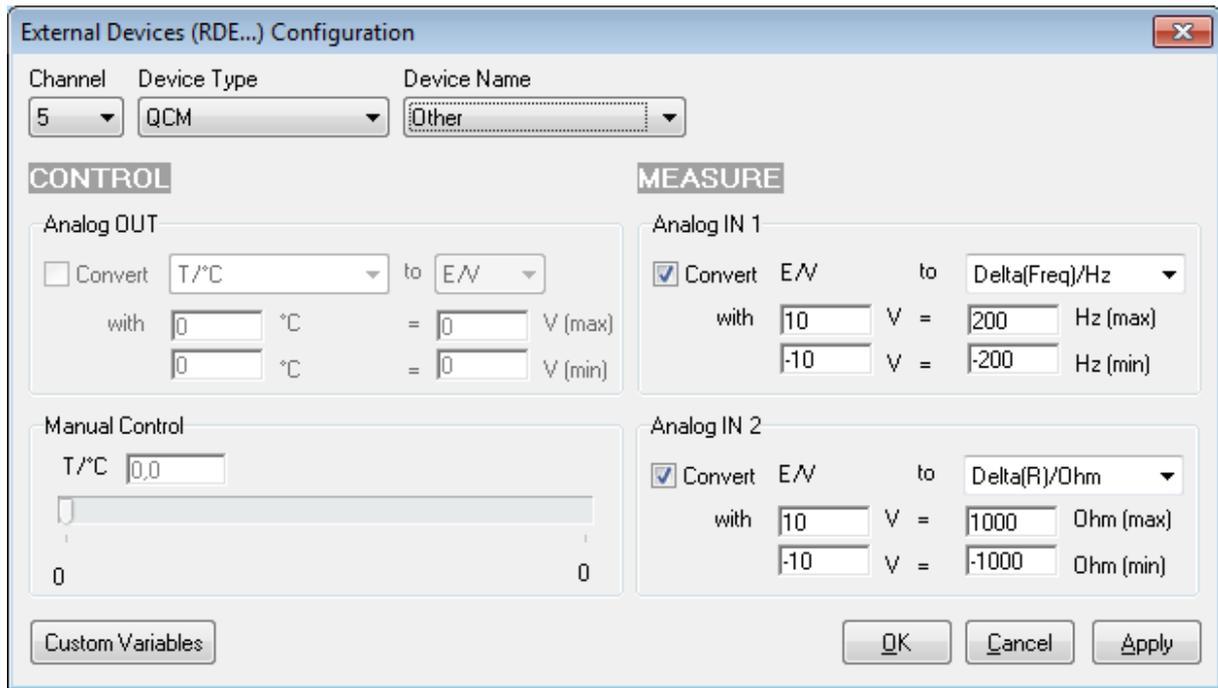


Fig. 236: External device configuration window.

The user must define several parameters to configure the external device to either be controlled via the analog output (left column) or record/measure data via analog input 1 and 2 (right column). The procedure for the configuration of the auxiliary inputs/outputs is described below:

- 1- Choose the channel to configure. Each channel can be configured for a specific device. One channel can control one device and the other one another device.
- 2- Select the Device Type in the list between None, Thermostat, RDE, QCM and other. One or several device names are available according to the selected device type.
- 3- Among the available devices, some can be controlled with the analog output and some of them can only be used to record values with analog inputs 1 and 2. The user must tick the box to activate the input/output.
- 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 variables. Click on **"Custom Variables"**. The figure below is displayed:



Fig. 237: 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 appears in the list in blue (as a custom variable) and can now be selected as the recorded variable for the analog inputs.

- 6- Finally, click on “**Configure**” to configure the selected channel to record the auxiliary input signal

The new selected variables for Analog In1 and Analog In2 are automatically displayed in 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 protocols 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.
- The configuration of external devices that can be controlled by the potentiostat (Analog output) are described in detail in the corresponding sections of the manual.
- A manual control of external devices is also available on the right of the panel.
- When a channel has been configured to control an external device, this device can be seen in the global view.

6.4.2 Rotating electrodes control

The standard instrument equipped with channels delivered since November 2004, with or without boosters can control a rotating electrode such as a ALS-RRDE-3A RRDE Rotating Disk electrode model with the auxiliary input/output. A specific control panel has been designed to control the rotating speed. Note that no measurement of the rotating speed is available. This model of rotating electrode is designed to work either one or two working electrodes (ring-disk electrodes). A bipotentiostat is necessary for the measurement of the working electrode potential of both electrodes. The VMP3 (using two channels), VSP, SP-300, VSP-300, VMP-300 or the BiStat are appropriate instruments for this kind of experiment.



Fig. 238: RRDE Rotating Disk electrode ALS RRDE-3A.

6.4.2.1 Control panel

Before running any experiment with a rotating electrode, one must first choose the rotating unit. Select **Config \ External Device (RDE...)...** in the EC-Lab® main menu:

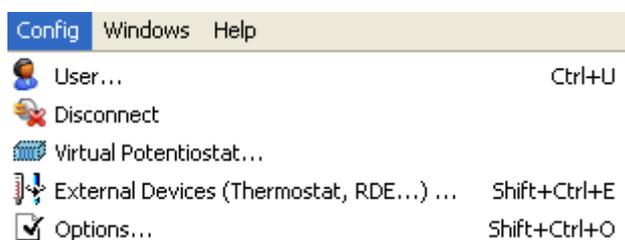


Fig. 239: Menu to choose for rotating electrode control.

Note: this menu is available only if channels designed to drive a RDE are connected with the RDE electrode rotator. Then the following window is displayed:

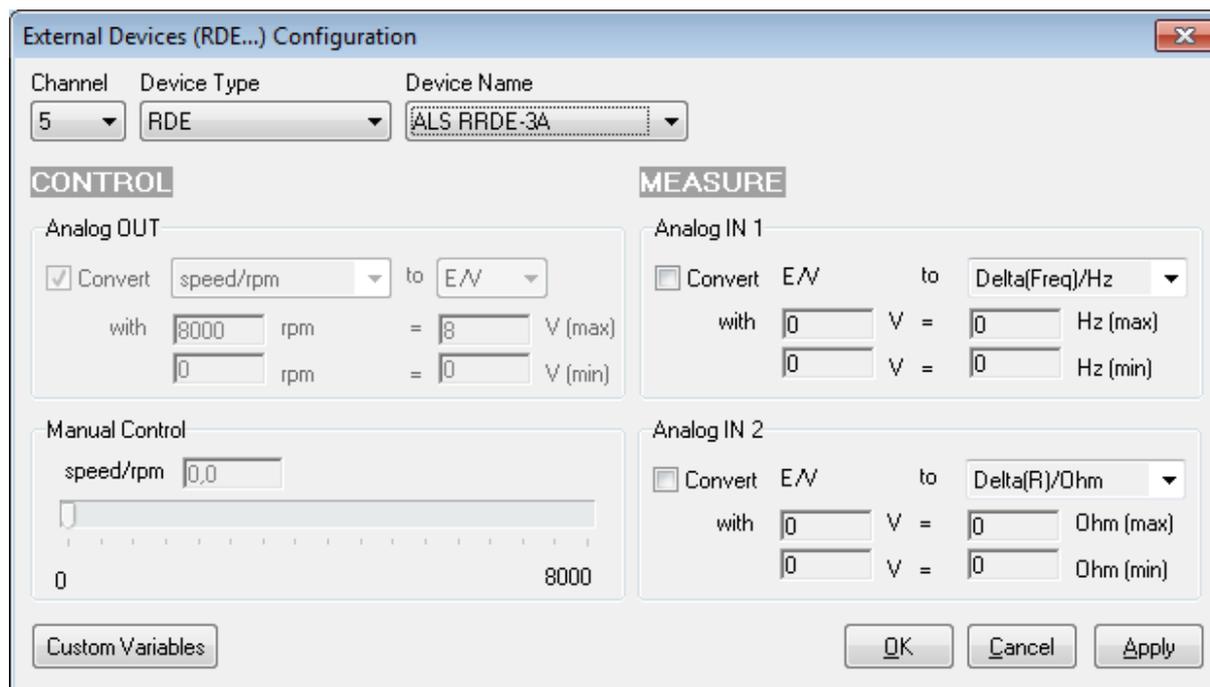
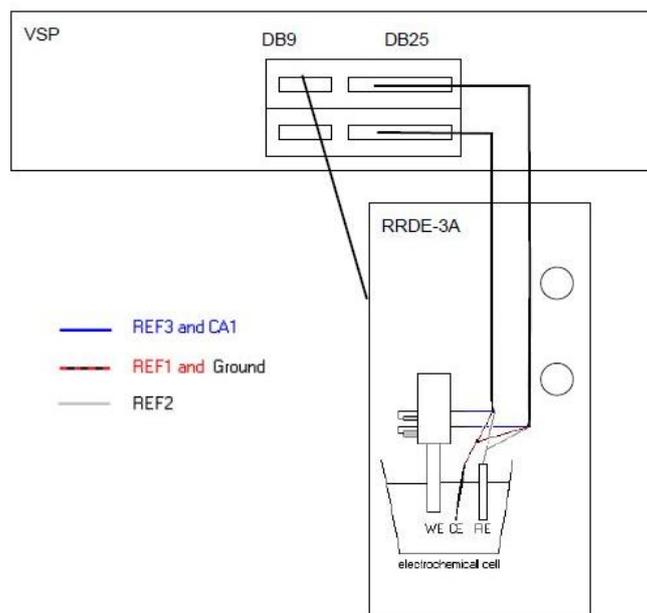


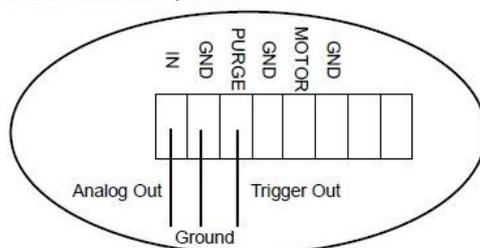
Fig. 240: Rotating electrode control configuration.

Under **Speed control unit**, one can select the standard supplied ALS RRDE-3A or PINE RRDE or RADIOMETER CTV101 electrodes rotator. For these devices, the calibration parameters are factory set. Other external systems can be used but are not available. They will be added to the list upon request. Note that calibration parameters for an already selected device are not available. Nevertheless if you select another device, it is possible in the “**Analog OUT**” window to define the control parameters. Click on the **Apply** button to validate the settings. Note that this menu can be activated without any rotating electrode unit, but will only have effects for the electrochemical instruments equipped with a rotating system.

In order to use two potentiostat/galvanostat channels and some rotating ring-disk electrode (with two working electrodes), it would be useful for the user to synchronize both channels together in order to start the experiment on both channels at the same time. Report to the corresponding part in the manual for more information about the synchronize option.



Focus on the rear panel:



6.4.3 Temperature control

Temperature control is possible with the auxiliary inputs/outputs of our potentiostats with a voltage control. Several thermostats have already been configured such as Julabo series and Haake Phoenix series.

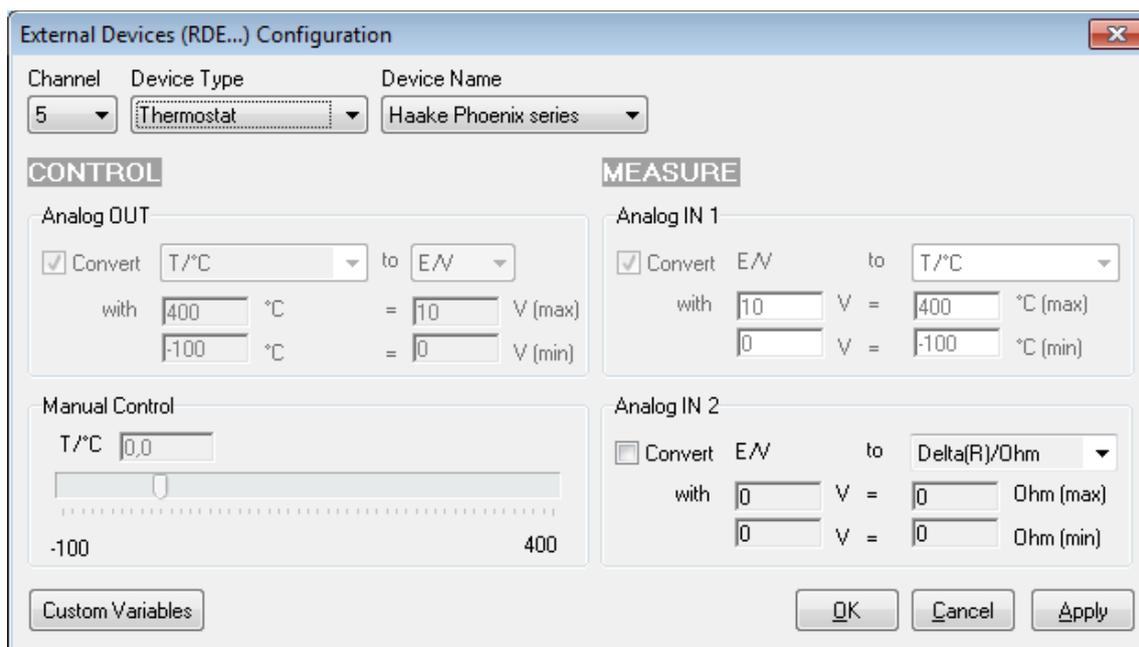


Fig. 241: Haake Phoenix series thermostat control configuration with a VMP3.

The user can configure other thermostats to only record temperatures (Analog in) or both control (Analog Out) and record (Analog In) temperature.

6.4.4 Electrochemical Quartz Crystal Microbalance coupling

The SEIKO EG&G QCM 922 quartz crystal microbalance has been coupled with our potentiostat/galvanostat to record both the frequency variation and the resistance variation. The configuration for the EQCM coupling is described in the figure below:

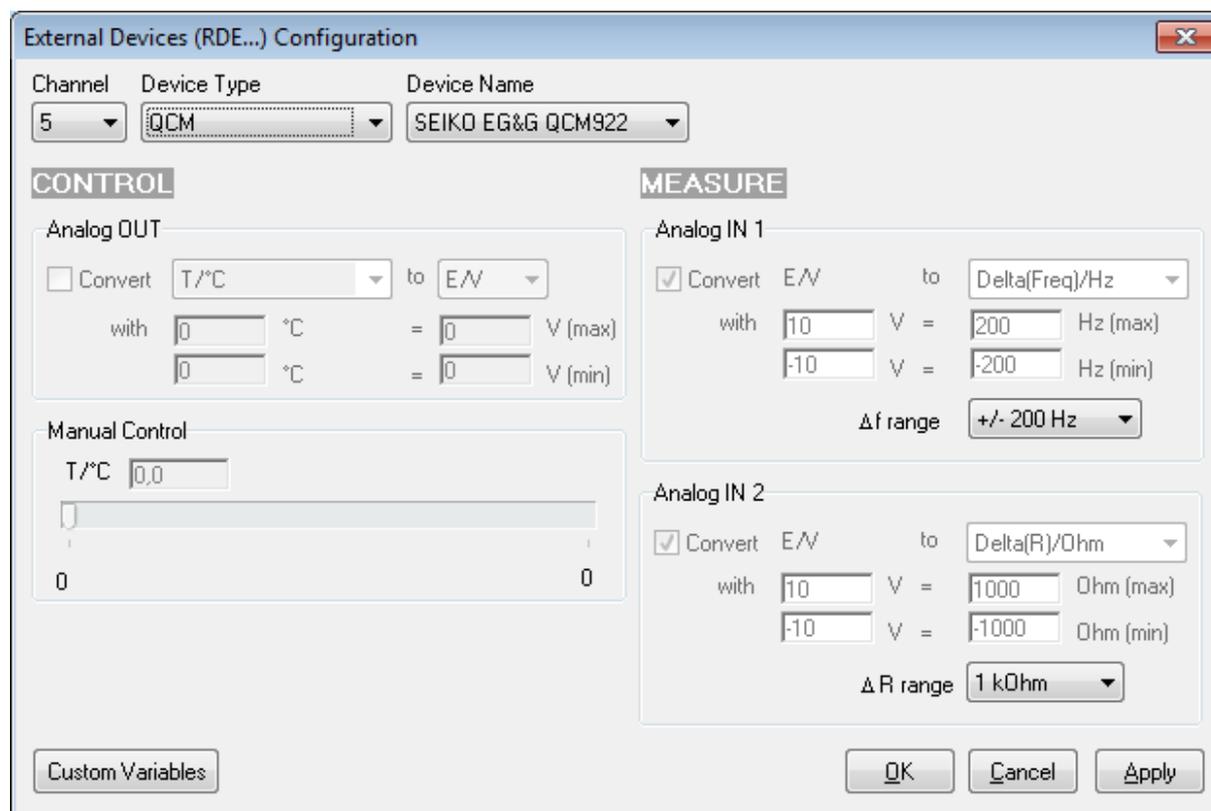


Fig. 242: SEIKO EG&G QCM 922 configuration window.

One can see that both frequency and resistance variations are recorded on the potentiostat analog inputs. The user must define both the frequency range and the resistance range. The results of this experiment are displayed below (Fig. 241):

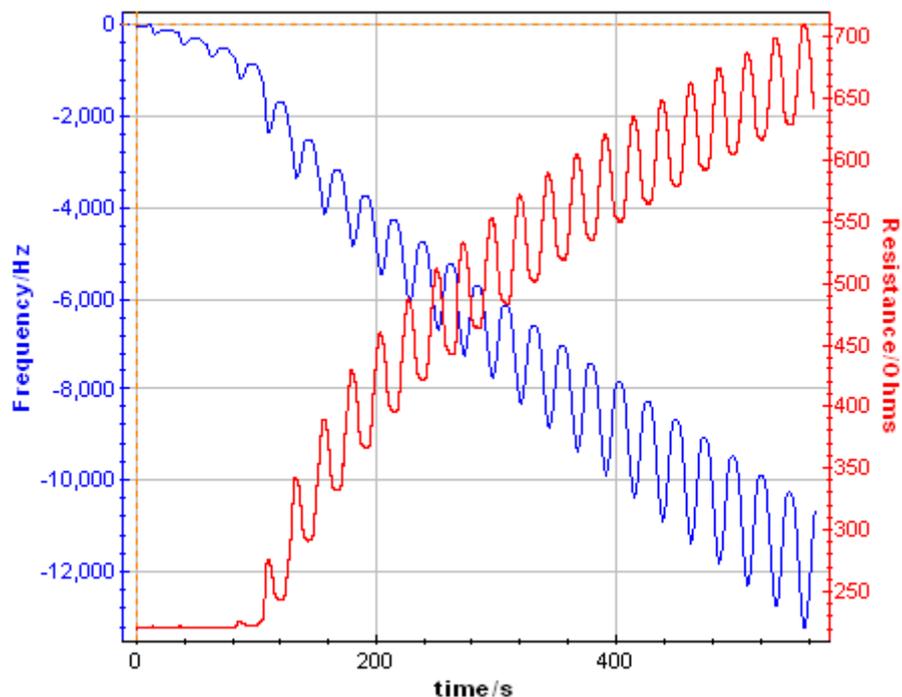


Fig. 243: Frequency and resistance variations recorded from the analog inputs for a VMP3 coupled with a SEIKO EG&G QCM 922.

A process is also available to calculate the amount of a species electro-disposed on the quartz. To use this process, select the process data option in the Analysis menu.

7. Troubleshooting

7.1 Data saving

Problem: Data cannot be saved from a given channel (this channel appears in yellow into EC-Lab®, and the program displays an error message while attempting to save data):

Solution(s):

- ensure that the saved file has not be moved, destroyed, opened by another application.
- if the saved file is on a network drive, ensure that you have the right to write data into the same directory (create and destroy a text file). Else see your network authorizations...
- in EC-Lab®, select **Tools, Repair...** Then select the saved file and click on the **Repair** button.
- ensure that the computer IP Address has not been modified since the beginning of the experiment.
- if the problem persists, contact us.

7.2 PC Disconnection

Problem: The PC is disconnected from the instrument ("Disconnected" is displayed in red on the EC-Lab® status bar):

Solution(s):

- check the PC – instrument connection:
 - direct connection: verify that the crossed Ethernet cable is plugged from both ends.
 - network connection: verify that the yellow led is blinking on the instrument front panel and that you can access to your network directories from the PC.
- check that the green LED is blinking (this assumes that the multichannel potentiostat is always running properly).
- in the Tera Term Pro window type "r" or "R" : this will restart the Ethernet connection program that is a part of the instrument firmware.
WARNING: this operation is not a simple task, so proceed like this only in case of trouble.
- if the problem persists, contact us.

7.3 Effect of computer save options on data recording

Electrochemical experiments can often have a long duration (more than 24 hours). During the experiment, the computer should always be able to record the data points. If the user enables the power save option for his hard disk, data saving can be disabled. In order to avoid this, we advise the user to remove the power save option from the computer in the settings panel.

8. Glossary

This glossary is made to help the user understand most of the terms of the EC-Lab[®] software and the terms mentioned in the manual. The terms are defined in the alphabetical order.

Absolute value: mathematical function that changes the negative values in positive ones.

Accept: button in EC-Lab[®] software that switches to "Modify" when the user clicks on. "Modify" must be displayed to run the experiment.

Booster: current power booster that can be added to each channel individually.

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 galvanostatic mode and vice versa.

ASCII file exportation: exportation of the raw data files or the processed data files to ASCII text format in order to use them with other software (new format: .mpt).

Axis: graphic function used to define the axis range, the logarithmic spacing and the grid lines.

Bandwidth: represents the frequency of the regulation loop of the potentiostat. It depends on the electrochemical cell impedance. The bandwidth's 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}).

Capacity per cycle: processing function that calculates the capacity per cycle for the galvanostatic with potential limitation, the chronocoulometry / chronoamperometry, the cyclic voltammetry, and the potentiodynamic cycling with galvanostatic acceleration protocols.

CASP Fit: tool available with the graphic display used to fit a curve obtained with the Constant Amplitude Sinusoidal microPolarization technique. This tool is used to determine the current corrosion and the coefficients of corrosion.

Channels: each one of the boards corresponding to an independent potentiostat/galvanostat.

Characteristic mass: total mass of the species in the electrochemical cell in most of the cases. It is different from the mass of electroactive material. This mass is used in the graphic display to represent mass current density, or mass charge density.

Circle Fit: tool available with the graphic display used to fit a circular curve.

Compact: mathematical function allowing the user to compress data points from the raw data file. Compact functions are available with the GCPL and PCGA protocols. 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 compared to the raw file.

Compliance: correspond to the potential range of the counter electrode versus the working electrode potential. This option is used in molten salt electrochemistry where the potential decreases a lot between the counter and the reference electrode.

CE to ground connection: also called N'Stat connection, this mode allows the user to lead measurements on eight working electrodes with one or eight reference electrodes and one counter electrode connected to the ground. It is a very useful tool for biosensors study. This mode can be activated in the "Advanced settings" window.

Corr. Sim.: this tool simulates corrosion curves obtained with the Linear polarization, Constant Amplitude Sinusoidal microPolarization or Variable Amplitude Sinusoidal microPolarization techniques.

Cycle: inside a protocol, 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 voltammetry (CV): this protocol consists of scanning the potential of the working electrode linearly and measuring the current resulting from oxydoreduction reactions. Cyclic voltammetry provides information on redox processes, electron transfer reactions, and adsorption processes.

Default settings: settings defined and saved as default by the user and automatically opened when the corresponding protocol is selected.

Description: tab in the experiment selection window, which describes the chosen protocol.

Device: EC-Lab® software window in the "Config" menu used to add new instrument IP address to be connected to the computer.

EC-Lab®: software drives the multichannel potentiostats/galvanostat.

Electrochemical Noise Analysis: this tool is dedicated to analysis corrosion data and to determine the electrochemical noise presents on the data.

Electrode characteristics: in the "cell characteristics" window in EC-Lab®, the user can set all parameters about the electrode.

Electrode surface area: geometric surface of the working electrode. It is a value that is used to represent current density or charge density.

Experiment limits: in the "advanced settings" window, these limits can be used in two different ways and concern potential, current and charge. The first one is to protect the cell against damages. These limits must be higher than the limits set in the experiment. The second way to use these limits is the control potential resolution. It corresponds to smallest potential step that can be made according to the full potential range.

File-Export as text: function that converts the raw data file (.mpr) to a text format file (.mpt). The new created file is located in the same directory as the raw file.

File-Import as text: function that converts an ASCII file (.txt) created by other software into an EC-Lab® raw data file (.mpr). The new created file is located in the same directory as the text file.

File- Load: the "load" function allows the user to load a data file (.mpr), a settings file (.mps), a linked experiment settings file (.mpls) or a report file.

Filter: this filter can be used as off-line filter many times after the experiment but also just after the recording of the data by ticking a box on the Advanced Setting window. Many methods and windows are available.

Fit: graphic tool used to determine kinetic or experimental parameters.

Fourier Transform: tool used to apply a Fourier transform to recorded data, many windows are available.

Global view: EC-Lab[®] software window where all the channels are shown with the user, the experiment, the state (relax, oxidation, reduction), and the booster or low current board.

Group: option used in a multichannel mode to start different experiments on the selected channels at the same time.

Hint: small box appearing under the box pointed by the mouse. It indicates the min and the max values accepted in the box.

I range: current range used in the experiment. It is related to the current resolution.

Impedance: defined by the ratio E/I .

Info: tab in the graphic display that gives the number of points and the size of the raw data file.

Integral: tool available with the graphic display used to integrate curves.

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.

Limits: in the "advanced settings" window, the experiment limits are used in two ways, first to protect the electrochemical cell from damages during the experiment and second for the potential control resolution.

Linear Fit: tool available with the graphic display used to fit a curve as a straight line.

Linear Interpolation: the linear interpolation allows the user to space out regularly each point of the data file. The user can select to interpolate data by a defined number of points or a regular time between each point.

Linked experiments: EC-Lab[®] offers the ability to link up to ten different experiments with the protocol 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.

LOG: function of the graphic display that opens the log file (.mpl) containing details and settings of the experiment but no data points.

Loop: protocol available in the linked experiments and used to repeat one or more experiments. It is different from the cycle in an experiment.

Low current: option providing a sub-pA resolution that can be added to each channel. This option extends the current range down to 1 nA. This option can be added both to standard and Z option channel boards.

Min/Max: graphic tool to determine the min and max values on a selected zone of the curve.

Modify: button of the EC-Lab® main window allowing the user to select a protocol, change the experiment parameters (before or during the experiment). This button switches to "Accept" when the user clicks on.

Mott-Schottky: graphic display of $1/C^2$ vs. E_{we} curve and corresponding linear fit to determine slope and offset.

MultiExponential Sim: this tool can be used to simulate curves with multiexponential functions.

MultiExponential Fit: this tool can be used to analyze curves with multiexponential functions.

Multi pitting statistics: off-line processing function of the MPP and MPSP protocols that gives the mean values and the mean quadratic deviations of the final rest potentials and the pitting potentials obtained from all the channels used in the experiment.

N'Stat: connection mode used to work with several working electrodes, one counter and one reference electrode in the same electrochemical cell. This mode must be used with special connections (see the user's manual).

N'Stat box: accessory provided for measurement in the N'Stat mode. This box has been designed for multielectrode cell applications to simplify the potentiostat to cell connection.

Open Circuit Voltage (OCV): protocol 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.

Option: EC-Lab® software window in the "Config" menu used to choose general parameters of the software such as automatic data saving or warning messages.

Pause: button of the EC-Lab® main window that leads to a suspension of the progress of the protocol and the measurement recording. The cell is disconnected (OCV period). The "Pause" button switches to "Resume" when clicked.

Peak analysis: graphic tool used on an I(E) curve to determine the peak current, the peak potential, exchanged charge quantity, and several other parameters.

Preconditioning: previous part of the electrochemical experiment that consists of the equilibrium state establishment, deaeration period, accumulation of electroactive species on the electrode surface or pretreatment of the electrode surface.

Process: function in EC-Lab® software made to calculate or extract values of the raw files (.mpr). The new values (in the .mpp file) can be displayed on the graph. The possibilities of processing depend on the protocol used. Please see the description of each protocol in the application part of the user's manual to know the processed values.

Protocol linker: tool of EC-Lab[®] software used to link protocols in order to build a complete experiment with or without open circuit period between protocols.

Record: in each protocol, the command to define the number of points in the data file. The user can define several recording conditions with potential or charge variation (depending on the galvanic or potentiometric mode) and with time frequency. These data recording options reduce the number of points without losing any interesting changes in the curve.

Reference electrode: in EC-Lab[®] software, the user can choose a reference electrode in the list or add his own reference electrode.

Report: file that can be associated with the data file to add additional information.

R_p Fit: tool available with the graphic display used to calculate a polarization resistance.

Run: button that starts the experiment.

Save data: button in the experiment frame that forces the data transfer of the selected channel buffer.

Scan rate: speed of the potential sweep defined with the smallest possible step amplitude.

Selector: window in the graphic display allowing the user to load, add or remove a data file from the graph and to choose the axis parameters.

Specifications: characteristics of the instrument such as cell control or current and potential measurement.

Stern and Geary model: model of corroding systems based on the Tafel equation.

Stop: button used to stop the experiment.

Style: graphic function used to define the plot style and color.

Subtract files: this tool allows the subtraction of two curves, for example to subtract a background from a curve.

Summary per protocol and cycle: off-line processing function giving a table of the maximum and minimum charge, current and potential value for each cycle or loop both in the anodic and cathodic side.

Synchronize: option used in a multichannel mode to start the same experiment at the same time on all the selected channels.

Tafel Fit: tool available with the graphic display used to determine the corrosion current, the corrosion potential and the polarization resistance with a fit.

Tafel graph: off-line processing function allowing the user to display on the graph the logarithm of the current (Tafel plot).

Technique builder: section of the selection technique window including the tools and techniques used to create linked experiments.

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.

Units: graphic function used to modify the axis units.

VASP Fit: tool available with the graphic display used to fit a curve obtained with the Variable Amplitude Sinusoidal microPolarization technique. This tool is used to determine the current corrosion and the coefficients of corrosion.

Wave analysis: graphic tool used on curves obtained in a convective regime and returning the limit current and the half wave potential.

ZsimpWin: software delivered by PAR and used to fit impedance curves with electrical circuits.

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