

EC-Lab[®] Express Software User's Manual

Version 5.5x – November 2011



Equipment installation

WARNING! The instrument is safely grounded 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,
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 - 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[®] Express software has been designed to control single channel potentiostats (SP-50, SP-150, SP-200, SP240 and SP-300). But it is also compatible with the other potentiostats of our range (VMP2(Z), BiStat, VMP3, VSP and VSP-300). Each channel board of our multichannel instruments is an independent potentiostat/galvanostat board that can be controlled by EC-Lab[®] Express software.

Once the techniques have been loaded and started from the PC, the experiments are entirely controlled by the instrument's on-board firmware. Data are temporarily buffered in the instrument and regularly transferred to the PC, which is used for data storage, on-line visualization and off-line data analysis and display. This architecture ensures very safe operation since a shutdown of the monitoring PC does not affect the experiments in progress. The computer can be connected to the instrument through an Ethernet connection or with an USB connection.

The application software package provides useful protocols for general electrochemistry, corrosion, electroanalysis and fuel cell testing.

Standard graphic functions such as re-scaling zoom, linear and log scales are available. The user can also overlay curves and make various data analyses (peak and wave analysis, Tafel, R_p , linear fits). An EIS data analysis tool is included in the package for full treatment of data recorded.

The aim of this manual is to guide the user in EC-Lab[®] Express software discovery. It is assumed that the user is familiar with Microsoft Windows[®] and knows how to use the mouse and keyboard to access the drop-down menus.

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

2. EC-Lab[®] Express software: settings

2.1 Starting the Program

Double click on the EC-Lab[®] Express icon on the desktop. The EC-Lab[®] Express software's **Device** window will be displayed:

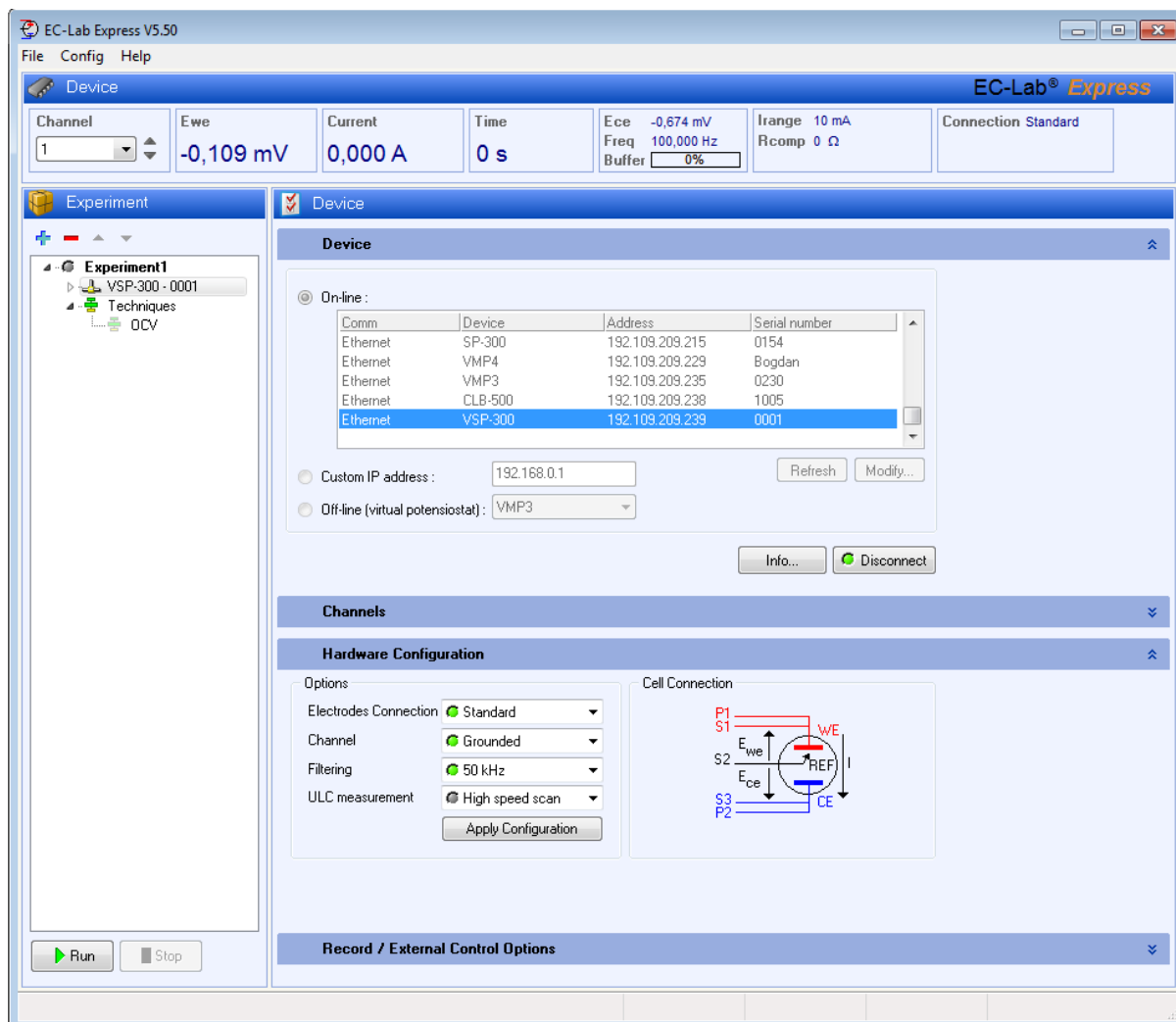


Fig. 1: Device EC-Lab[®] Express window.

2.1.1 Connection with the instrument

To see all the instruments present in the network, click on "**Refresh**" (of course only one is displayed in case of direct connection). The automatic search frame shows the name of the instruments detected with their serial numbers (#). A Mac address is given to each instrument at the factory. The Mac address is used to detect the instrument in a LAN even if its IP Address is not valid in the network. It is also used for the detection of instruments connected by USB.

It is why when the connection is done by USB, the kind and serial number of the instrument are displayed with the IP address equal to 0 like shown in Fig. 2; whereas when the

connection is done by Ethernet all the information (kind, serial number and IP address) are displayed.

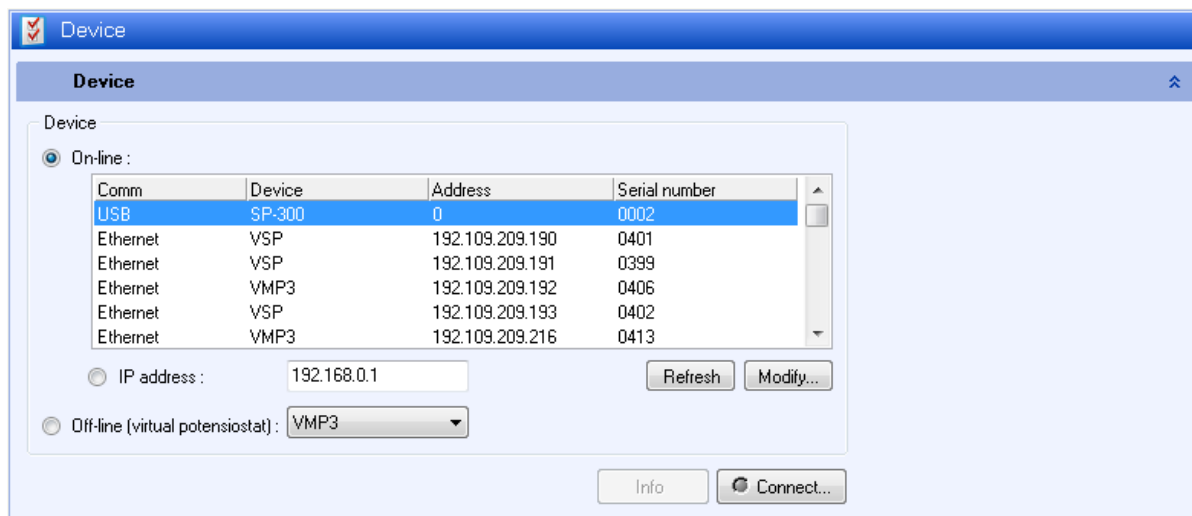


Fig. 2: Device selection window.

Choose one instrument in the list and click on “**Connect**”. The “Connect” button becomes a “Disconnect” button and the light on the button is green, the instrument is connected (Fig. 3).

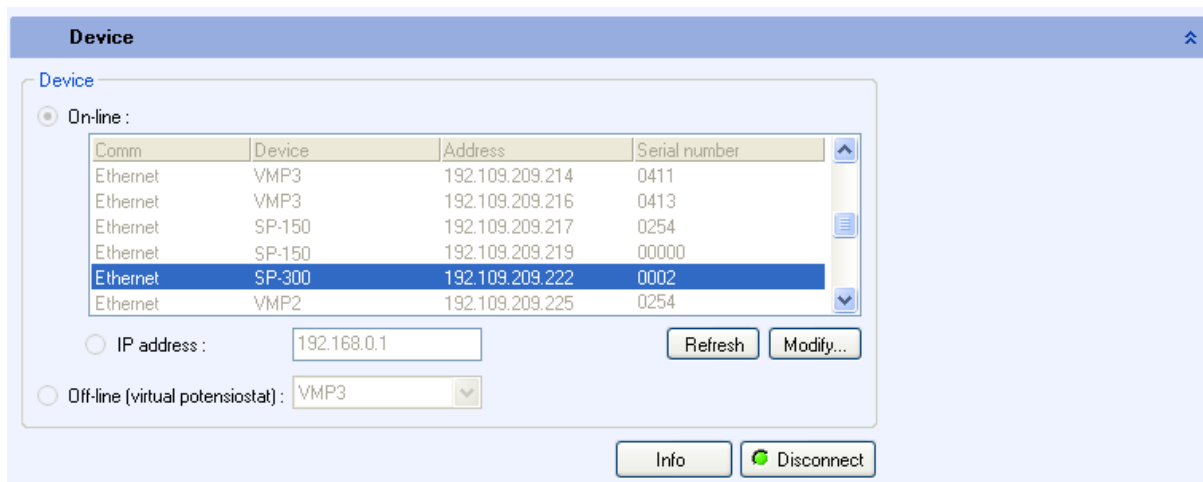


Fig. 3: Instrument connection.

To disconnect the instrument, click on the “Disconnect” button.

Note:

- Ethernet connection is possible only if the computer has a valid IP Address in the same network as the instrument,
- The user can work with EC-Lab[®] Express software off-line (without being connected). The software will work as if it was connected to a virtual potentiostat. The user just has to define the device he wants to simulate and click on the “**Connect**” button.

- The Info button give all the necessary information on the instrument like the serial number, the number of channels, the firmware version, the IP address,

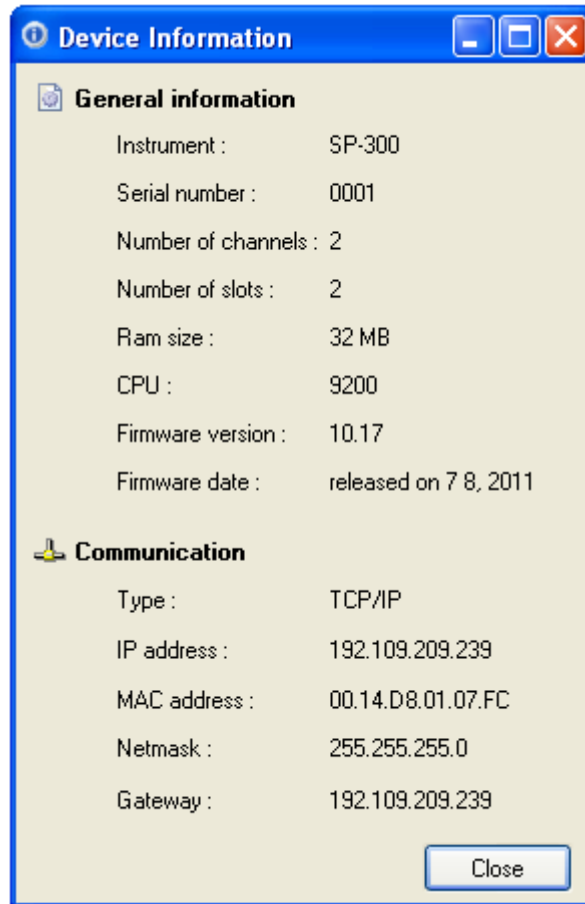


Fig. 4: Information window.

2.1.1.1 Instrument IP address and gateways change: network connection

If the default IP address of the instrument is not compatible with the network IP addresses, it is possible to change the IP address of the instrument. This change can be done in the Device window (Fig. 2):

- Select the desired instrument and click on "Modify". The following window then appears:

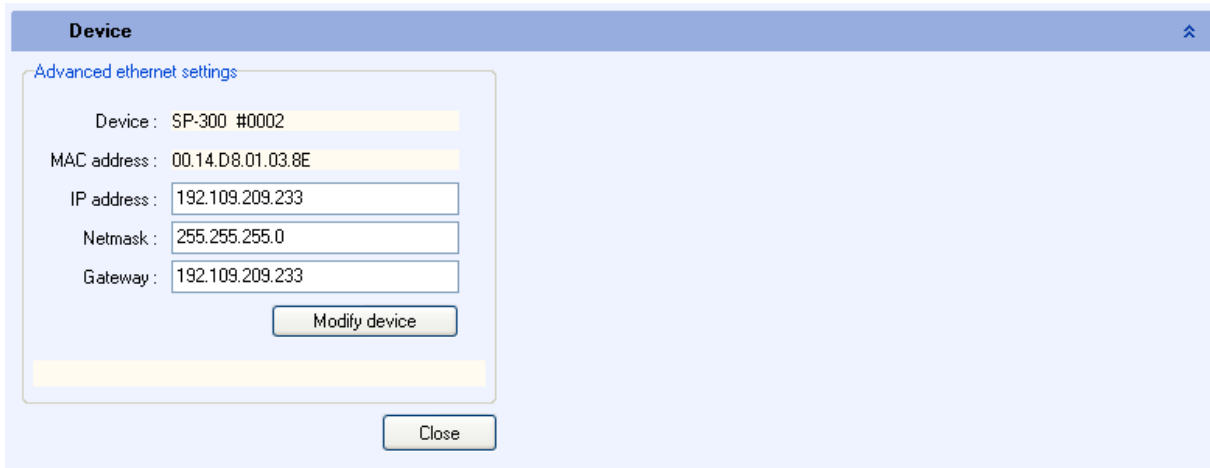
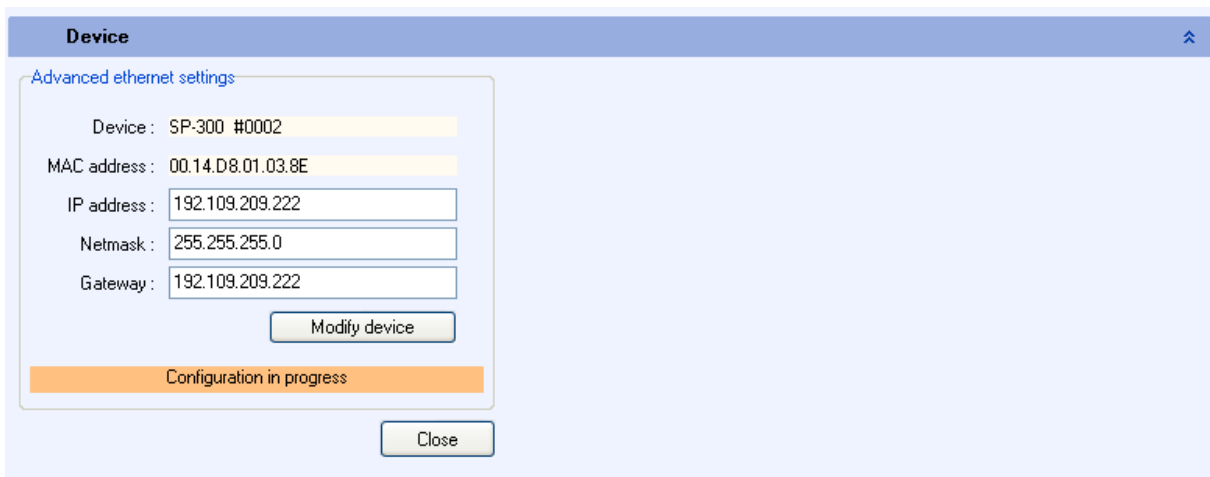
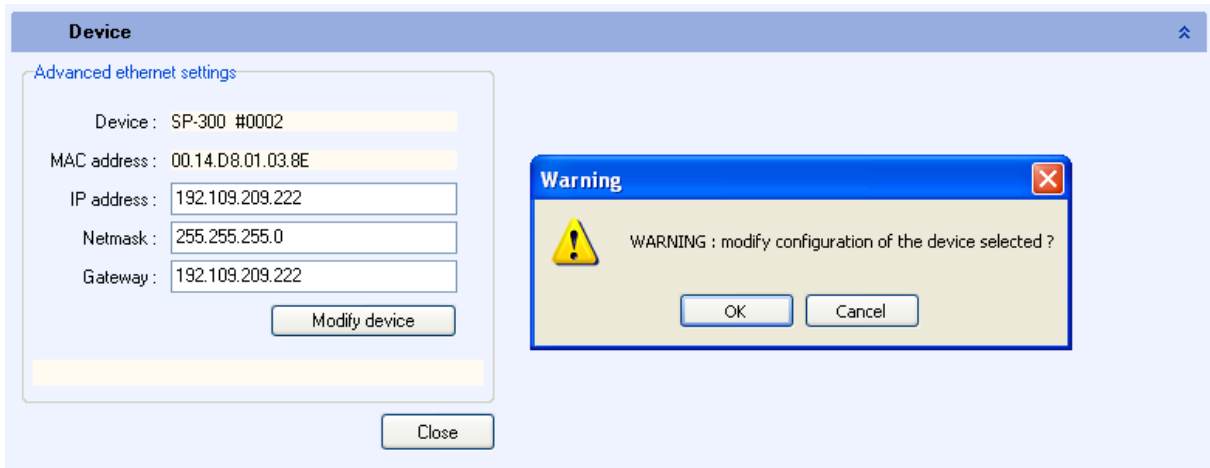


Fig. 5: “Modify” window of the “Device” window used to change the instrument IP Address.

Modify the IP Address to have a valid address in your network. Repeat this procedure with the Gateway and click on “Modify device”. A warning message is displayed, click on “OK”. When the process is in progress, an orange message is displayed and when the instrument receives the new IP address, a “configuration changed” message is displayed in green. Several “Bip” sounds are emitted indicating that the communication board is reinitialized with the new IP Address. “Configuration changed” appears at the bottom of this window.



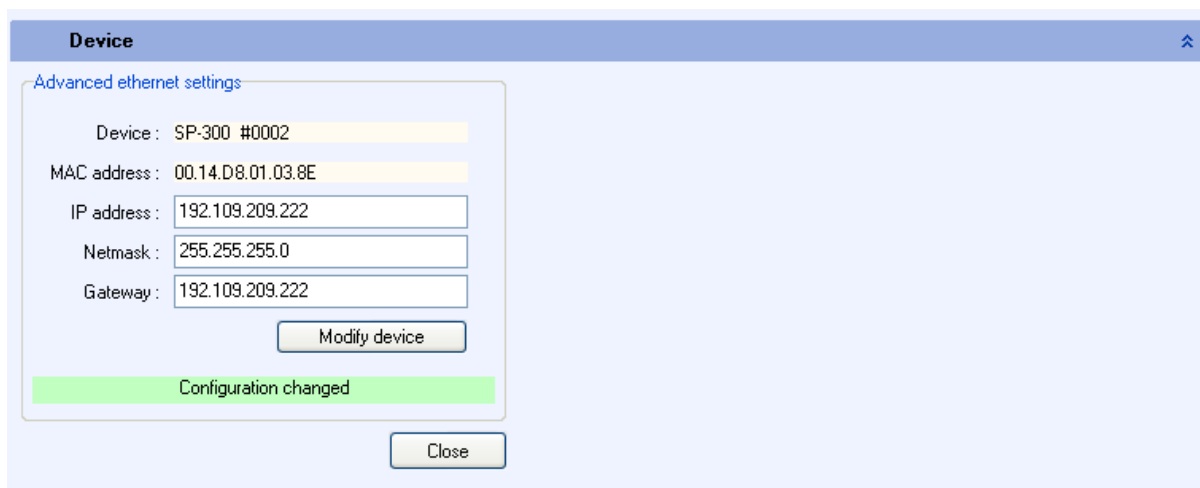


Fig. 6: Instrument new configuration.

Then click “**Close**” to display the “New Device” window where you have to click “**Refresh**” to refresh the window and select your instrument IP address.

Now the instrument is ready for use.

When connected to the web, the software automatically displays a newsletter announcing news about Bio-Logic Product range:



Fig. 7: Newsletter.

2.1.2 Selection of the channel

Once the connection with the instrument is done, the connection window is automatically closed. The Channels selection window is automatically opened as shown Fig. 8. Selecting a channel allows the user to select the hardware configuration. In case of a Bipotentiostat experiment the user has to define the master channel.



Fig. 8: Channels selection window.

2.1.3 Hardware configuration

Once a channel is selected, user can access the selection of:

- The electrodes connection
- The grounded or floating mode,
- The analog filtering,
- The ULC measurement option if a ULC option is connected to the select channel

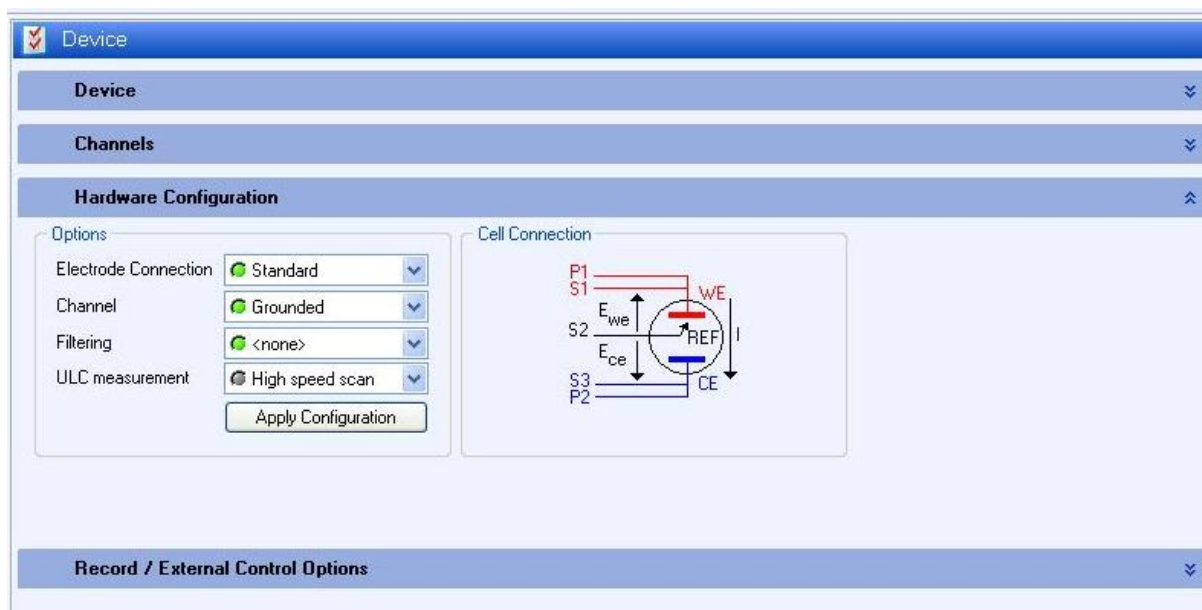


Fig. 9: Hardware configuration window.

2.1.3.1 Electrodes connection

Four connection modes can be used with EC-Lab[®] Express, the standard mode for general purpose, the CE to Ground mode more dedicated to special measurement such BiStat measurements, the +/-48 V control used with a booster 1 A/48 V and the WE to ground mode dedicated to experiments like hydrogen permeation.

To be easily identified, each lead has an associated color and label. For each mode of connexion, depending of the technology, labels on the leads are different.

For VMP3 technology (VMP2, VMP3, BiStat, VSP, SP-150, SP-50):

- **Ref1:** RED – Reference 1 for the control and measurement of the working electrode potential.
- **Ref2:** WHITE – Reference 2 for the control and measurement of the Reference electrode potential.
- **Ref3:** BLUE – Reference 3 for the control and measurement of the Counter electrode potential.
- **CA2:** RED – Control Booster for the current control and measurement flowing through the working electrode (in standard mode).
- **CA1:** BLUE – Control Booster for the current control and measurement flowing through the counter electrode (in standard mode).
- **GND:** BLACK – Ground.

For SP-300 technology (SP-200, SP-300, SP-240, VSP-300):

- **S1:** RED – Sense 1 for the control and measurement of the Working electrode potential.
- **S2:** WHITE – Sense 2 for the control and measurement of the Reference electrode potential.
- **S3:** BLUE – Sense 3 for the control and measurement of the Counter electrode potential.
- **P1:** RED – Power 1 for the current control and measurement flowing through the Working electrode.
- **P2:** BLUE – Power 2 for the current control and measurement flowing through the Counter electrode.
- **GND:** BLACK – Ground

2.1.3.1.1 Standard mode

This mode of connexion is the one used for most of the electrochemical applications. In the standard configuration, a measurement channel has 5 lead connections to the electrochemical cell: 4 are used in the cell control loop (2 for the current and 2 for the potential) while the 5th lead permits simultaneous recording of a supplementary cell potential.

For VMP3 technology:

Select Electrodes connection = Standard and connect the cell as follows:

- CA2 (WE) and Ref1 leads to the working electrode
- Ref2 lead to the reference electrode
- CA1 (CE) and Ref3 leads to the counter electrode

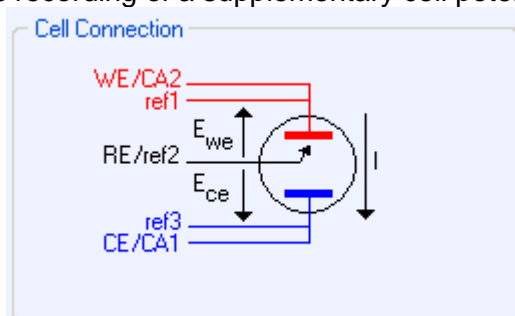


Fig. 10: Standard mode connection for VMP3 technology.

For SP-300 technology:

Select Electrodes connection = Standard and connect the cell as follows:

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

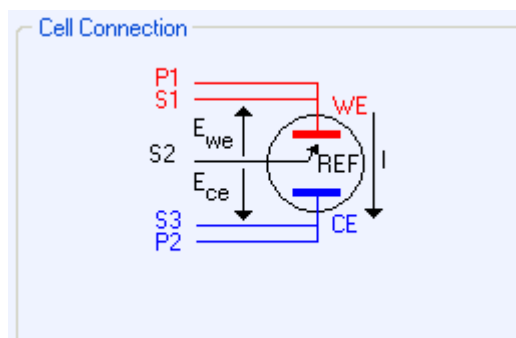


Fig. 11: Standard mode connection for SP-300 technology.

2.1.3.1.2 CE to Ground mode

This mode of connexion is dedicated to special applications such as for example bipotentiostat mode. In the bipotentiostat mode two working electrodes are present in the same bath whereas only one counter electrode and one reference electrode are used.

For VMP3 technology:

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

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

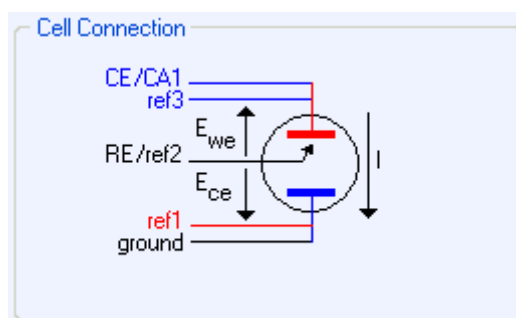


Fig. 12: CE to ground connection mode for VMP3 technology.

For SP-300 technology:

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 leads to the counter electrode

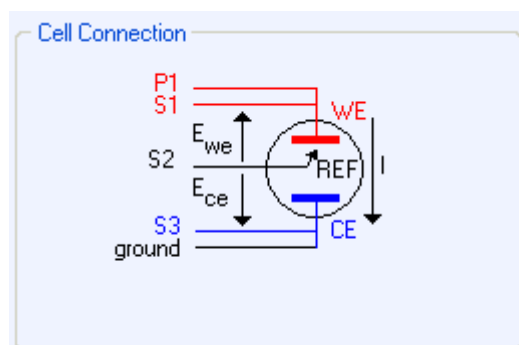


Fig. 13: CE to ground connection mode for SP-300 technology.

To set the standard connection, proceed in the same way: disconnect the electrodes from the cell, select Electrodes connection = standard and set the next connections:

- Ref1 and CA2 (WE) leads to the working electrode for VMP3 technology or P1 and S1 leads to the working electrode for SP-300 technology
- Ref2 lead to the reference electrode for VMP3 technology or S2 lead to the reference electrode for SP-300 technology

- CA1 (CE) and Ref3 leads to the counter electrode for VMP3 technology or S3 and P2 leads to the counter electrode for SP-300 technology.
Then click on Apply configuration button.

Refer to the “Installation and configuration manual” 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 ± 10 V.
The CE to ground option is not available with the ZRA protocol (Zero Resistance Ammeter).

2.1.3.1.3 +/- 48 V control mode

This connexion mode is only available with the SP-300 when a 1 A/48 V is present inside the chassis.

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

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

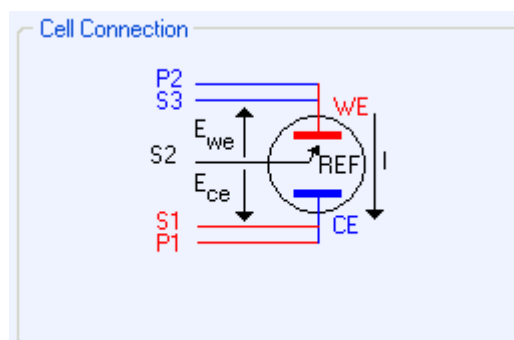


Fig. 14: +/- 48 V control mode for SP-300 technology.

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.

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

2.1.3.1.4 WE to Ground mode

This connection mode is only available with SP-300 and SP-200 instruments for special experiment such as Hydrogen permeation.

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

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

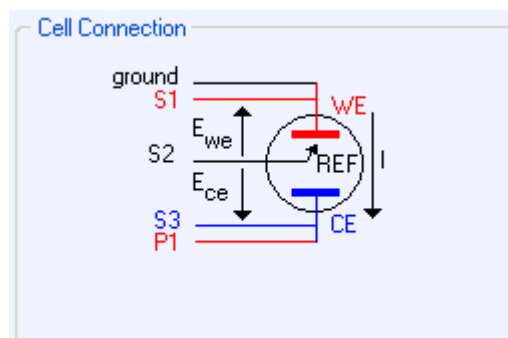


Fig. 15: WE to Ground mode for SP-300 technology.

To set the standard connection, proceed in the same way: disconnect the electrodes from the cell, 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.

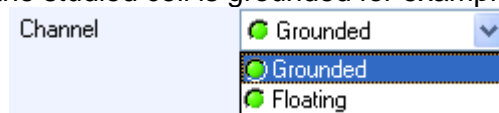
Then click on Apply configuration button.

Refer to the “Installation and configuration manual” for more details on the WE to Ground connection mode.

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.

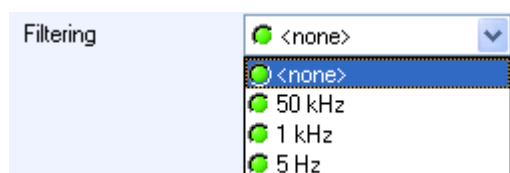
2.1.3.2 Channel

This menu is only available for the SP-300 technology. The Channel menu permits the selection between Grounded and Floating mode for the used channel. Floating mode is recommended only when the studied cell is grounded for example autoclaves, pipeline,



2.1.3.3 Filtering

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



2.1.3.4 Ultra Low Current (ULC) measurement

This option is only available with the SP-300 technology and more especially when the Ultra Low Current option is connected to the channel. Two modes are available Standard and High Speed Scan. This High Speed Scan option is necessary when low current ability at relatively

high speed is required. In these extreme conditions, measurements may be distorted. For instance, a loop appears at the vertex.

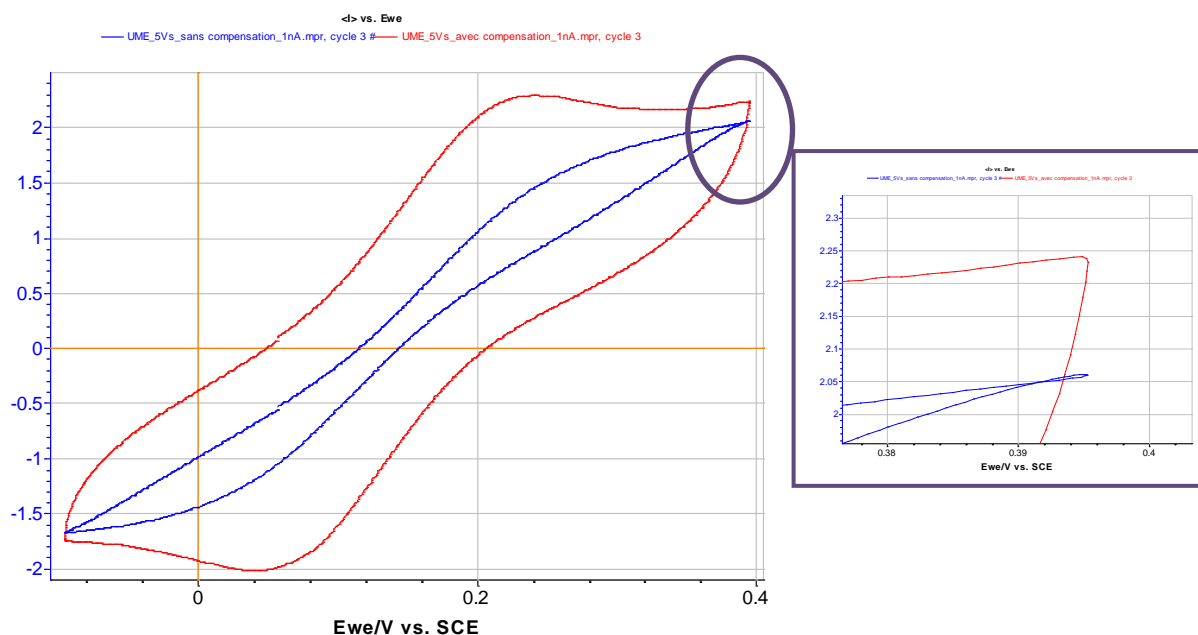


Fig. 16: CV carried out with Ultra Microelectrode of 10 μm in a solution of ferrocene in EtOH with TBAP as supporting salt. The range of current is 1 nA and scan rate is 5 $\text{V}\cdot\text{s}^{-1}$.

The value of current scan where the correction must be applied depends on the intrinsic characteristics of the cell (type of electrode, distance between electrodes, ...). A correction is offered in the “Hardware configuration” window in the menu “ULC measurement”. This option is automatically selected when Ultra Low current option is connected.



Note that, if the Ultra Low Current option box is selected, the data may be noisier especially for ranges below 1 nA (see figure below). It is possible to reduce the noise by filter the data (available in the “**Math**” menu of the “**Analysis**” menu).

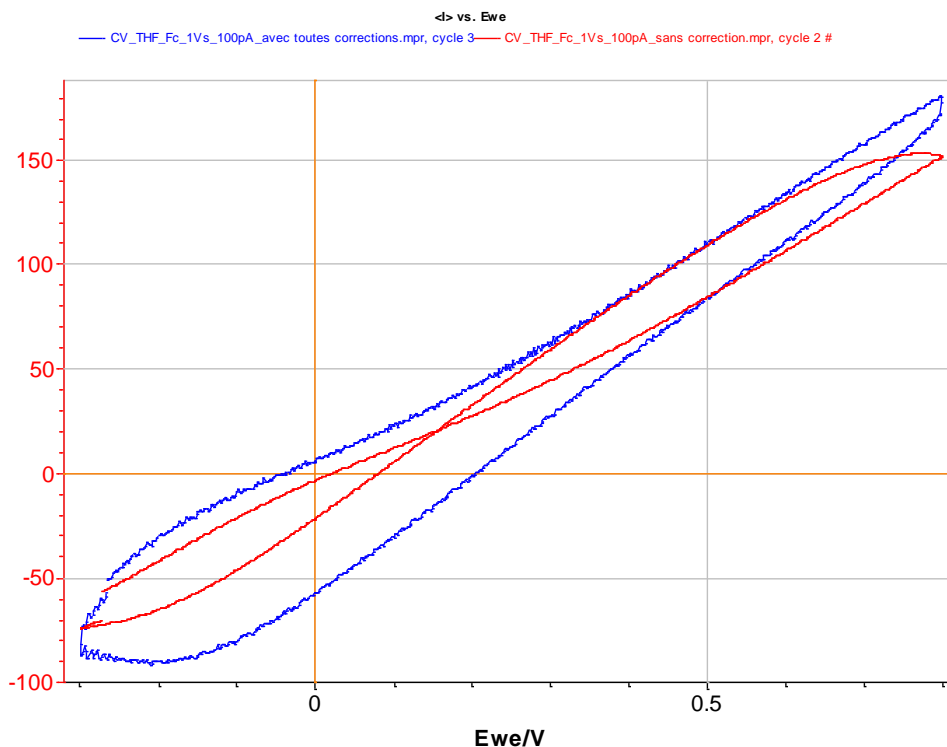


Fig. 17: CV carried out with Ultra Microelectrode of 10 μm in a solution of ferrocene in THF without any supporting salt. The range of current is 100 pA and scan rate is $1 \text{ V}\cdot\text{s}^{-1}$.

2.1.4 Recording options

This part of the device frame offers the possibility to the user to:

- record the potential of the counter electrode,
- record external signals (pH, T, P,...) using the analog input 1 and input 2,
- Add an external signal to the voltage or current control (connection is done via analog Input2). For the current control, the resistance of interest is defined in the table below.
- have an additional parameter corresponding to the control mode
- record the charge Q
- record the I range in the mpr file

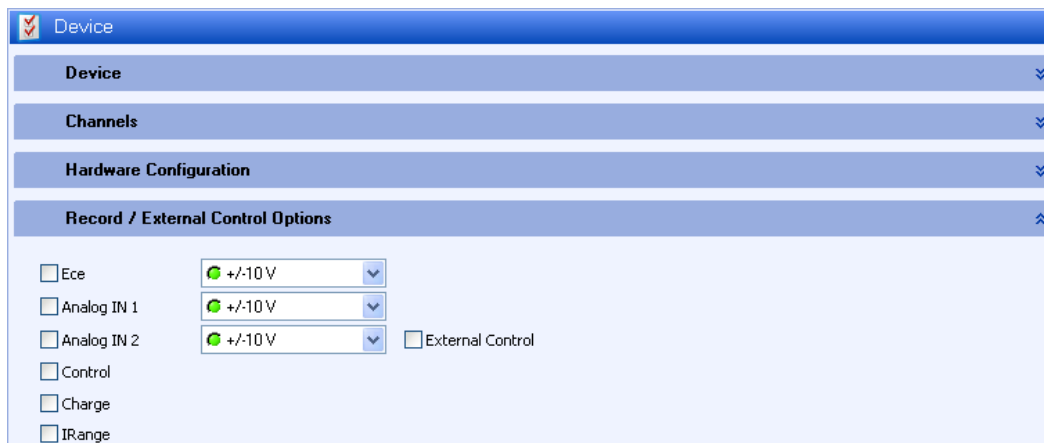


Fig. 18: Record/External control options window.

Current range	resistance
1A	1 Ohm
100mA	10 Ohm
10 mA	100 Ohm
...	...
1 μ A	1 MOhm

2.2 Preparing and Running an Experiment with EC-Lab[®] Express software

This chapter is designed to guide users through the use of EC-Lab[®] Express software.

2.2.1 The Bar menu

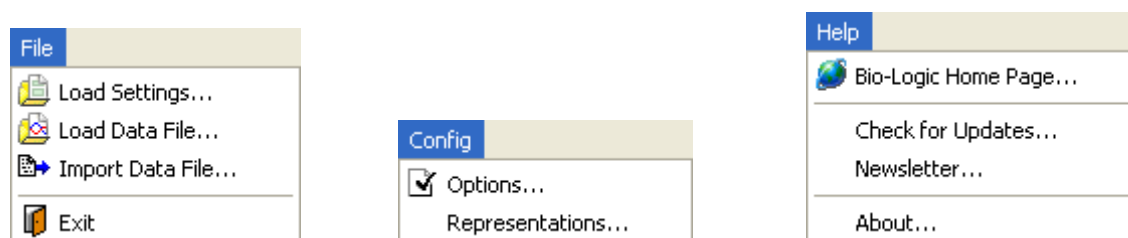


Fig. 19: The three menu items in the menu bar.

The menu bar offers the ability to load settings or data file previously stored and to import data file, but also to choose to use the advanced browser or specific graph Representations, but also to check for manuals and updates.

2.2.1.1 The File menu

The File menus offers the ability to load settings or data files previously stored and to import data files from other software such as FC-Lab, Power Suite, GPES, CONDECON, etc.

The import data file window is shown in Fig. 20. In a first time, the file to convert has to be loaded and the first lines of this file are displayed in the frame of the Input Text File part. To import data in a right way the user has to define, in the Importation parameters part, the file format, the columns separator and the format: number of column, columns type. Note that if the format file to export is already in the database of EC-Lab[®] Express, selection of the format is automatic. Then to finish push the Import button and the file will be exported in EC-Lab[®] Express format (.mpr file).

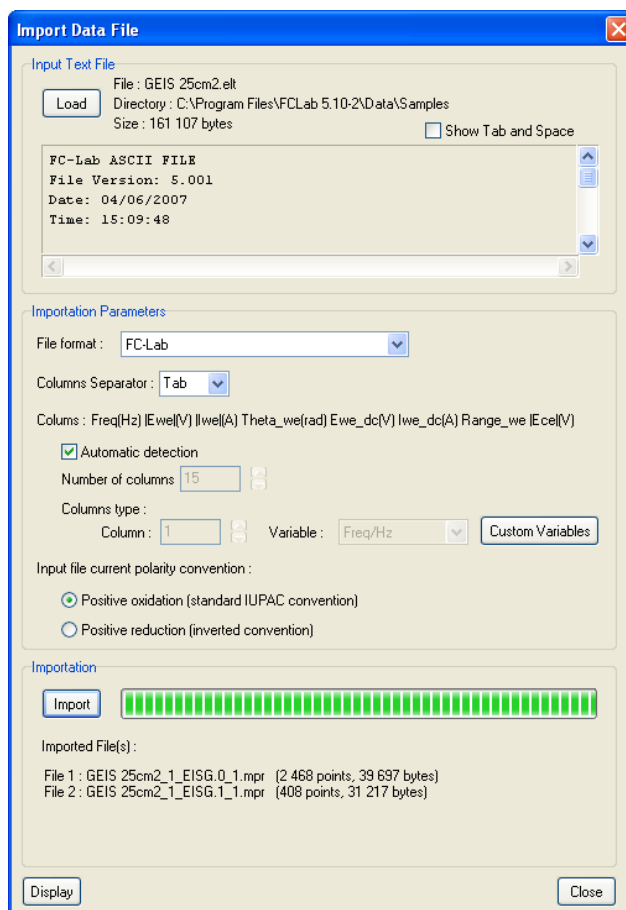


Fig. 20: Import data file window.

2.2.1.2 The config menu

This menu allows selecting Options like the Automatic reconnection at start-up or the interface. Two EC-Lab[®] Express interfaces exist (Fig. 22 and Fig. 23). Most of the menus are available in both interfaces. In standard interface only one experiment can be performed whereas in the advanced interface, two experiments can be settled simultaneously.

Note: if not connected to the instrument, all techniques are displayed even in the standard mode.

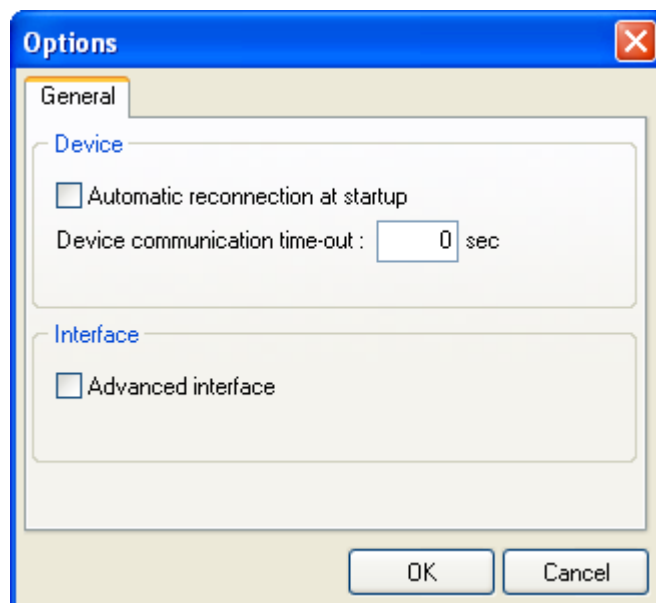


Fig. 21: Options window.

Two interface modes are available in EC-Lab Express: Standard interface mode and advanced interface mode. The figures below present the screenshot corresponding to each mode.

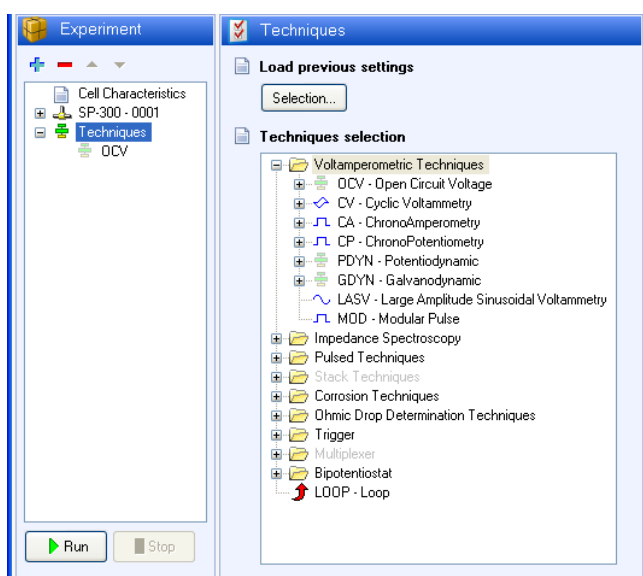


Fig. 22: Main window in standard interface mode.

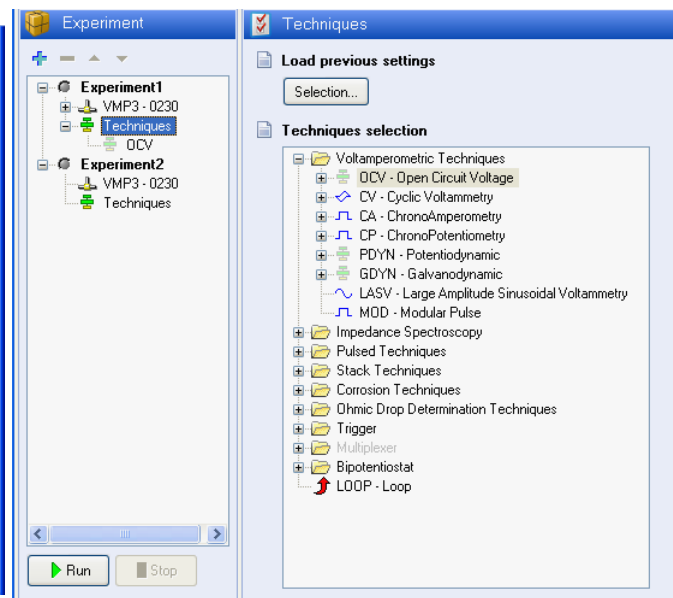


Fig. 23: Main window in advanced interface mode.

The “Representations” menu allows the user to define his own graphic display. More details are given in section 3.2.5 page 45.

2.2.2 EC-Lab[®] Express main window

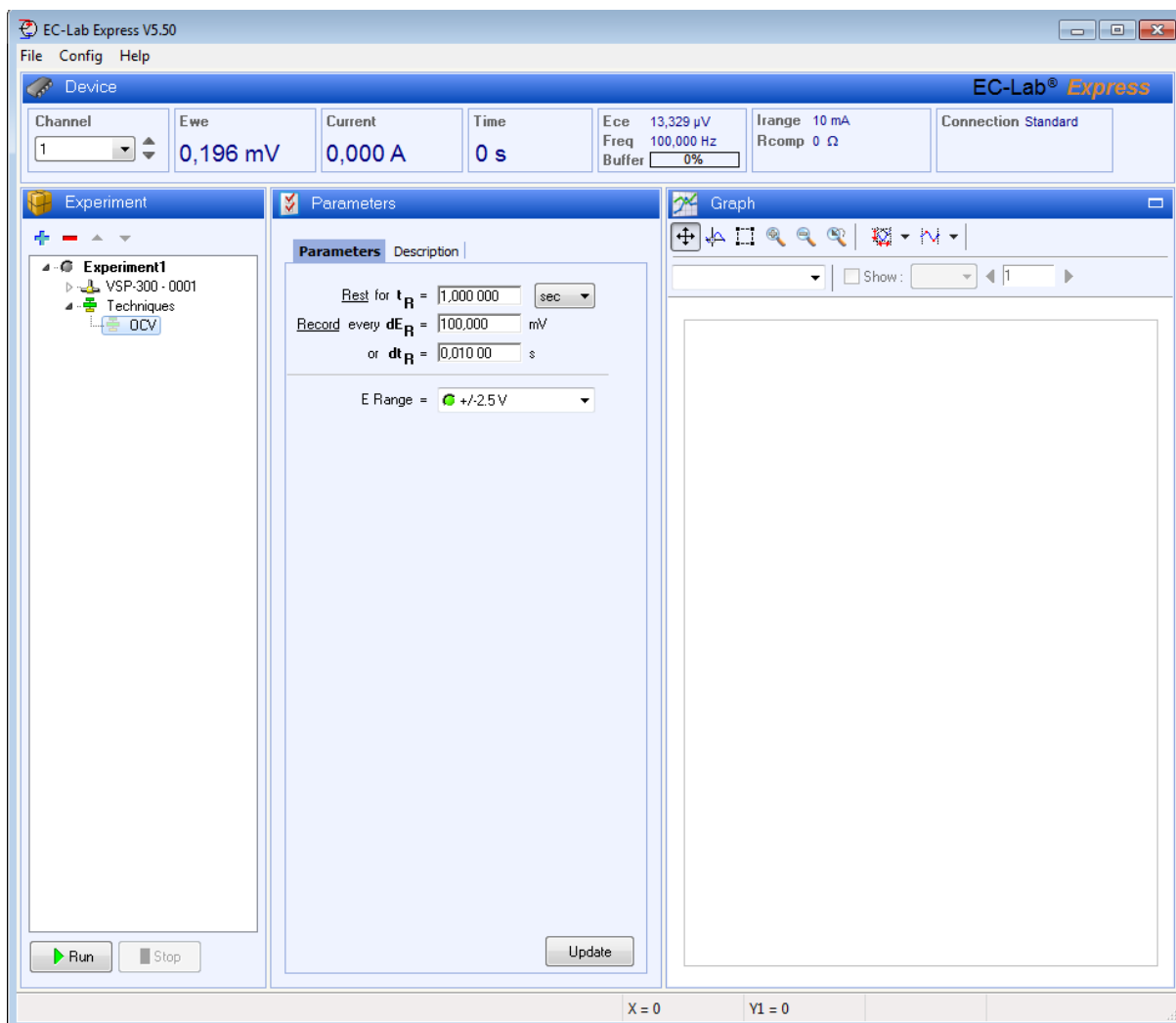


Fig. 24: Main window when EC-Lab[®] Express is connected to the potentiostat.

EC-Lab[®] Express displays only one mask. This software is recommended for electrochemistry teaching and new users. This window shows the menu bar with “File”, “Config” and Help” and 4 frames: **Device**, **Experiment**, **Parameters**, **Graph**.

2.2.2.1 Device frame



Fig. 25: Device frame.

In the Device frame, are displayed:

- the channel selected in the list displaying all the channels available in the instrument,
- the amplifier connected to this channel board,
- current values (time, E_{we} , I , Buffer filling, E_{range} , I_{range}),
- the connection mode (standard, CE to Ground, WE to Ground, ...).

2.2.2.2 Experiment frame


The experiment frame displays the instrument type (SP-200, SP-300, VMP3,..). It is used to build the experiment by linking techniques with the buttons at the top .



Fig. 26: Experiment frame (standard and advanced).

By clicking on the + button the user can either add a new technique to the existing experiment or add a new experiment labelled “experiment 2” to the existing experiment “experiment 1”. The – button will remove the selected technique or the selected experiment. The two arrows buttons are used to move up and move down techniques in the list.

2.2.2.2.1 Cell description part

In this part, you can either fill blank boxes, entering comments and values, or load them from a .mps setting file or a .mpr raw file using **Load Setting...** on the main 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 reference electrode used in the experiment. when defined these parameters are automatically used to calculate the corrosion rate after a Tafel Fit. They are also used for density plot.

Cell Properties

Cell description

Electrode material

Initial state

Electrolyte

Comments

Cell characteristics

Electrode surface area cm²

Characteristic mass g

Reference electrode

Offset potential vs. NHE : 0.000 V

Fig. 27: Cell properties window.

2.2.2.3 Parameters frame

This frame contains the parameters to be adjusted for the experiment. To display parameters for each technique the user has to select the technique in the experiment frame.

The parameters are described deeply in the “EC-Lab[®] Express Software Techniques and Applications” manual. For each selected technique a description is available. EC-Lab[®] Express software offers a classical right click on each box of the parameter window to copy, cut, paste and select values.

Note that parameters can be changed on-the-fly. Once it is done, click on the Update button to validate the changes.

The screenshot displays the 'Parameters' frame in the EC-Lab software, divided into two tabs: 'Parameters' and 'Description'.

Parameters Tab:

- Initial Potential E_i = 0,000 000 V Vs. Eref
- Vertex Potential E_1 = 1,000 000 V Vs. Eref
- Vertex Potential E_2 = -1,000 000 V Vs. Eref
- Final Potential E_f = 0,000 000 V Vs. Eref
- Scan with dE/dt = 100,000 mV/s
- Record every dE = 10,000 mV Average
- Measure I from 50 % of step to 100 % of step
- Repeat n_c = 0 times
- I Range = Auto range
- E Range = +/-2.5 V
- Bandwidth = 5 - Medium speed

An 'Update' button is located at the bottom right of the Parameters tab.

Description Tab:

The Description tab features a diagram of a cyclic voltammogram (CV) showing potential (E_{we}) on the y-axis and time (t) on the x-axis. The waveform is triangular, with vertices labeled E_i , E_1 , E_2 , and E_f .

The text below the diagram reads: "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."

Below this text, a second paragraph explains: "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: Parameter and description tab of the parameters frame.

2.2.2.4 Graphic frame

The graphic package is a complete tool. This is the same as EC-Lab® software. It will be described in a following section.

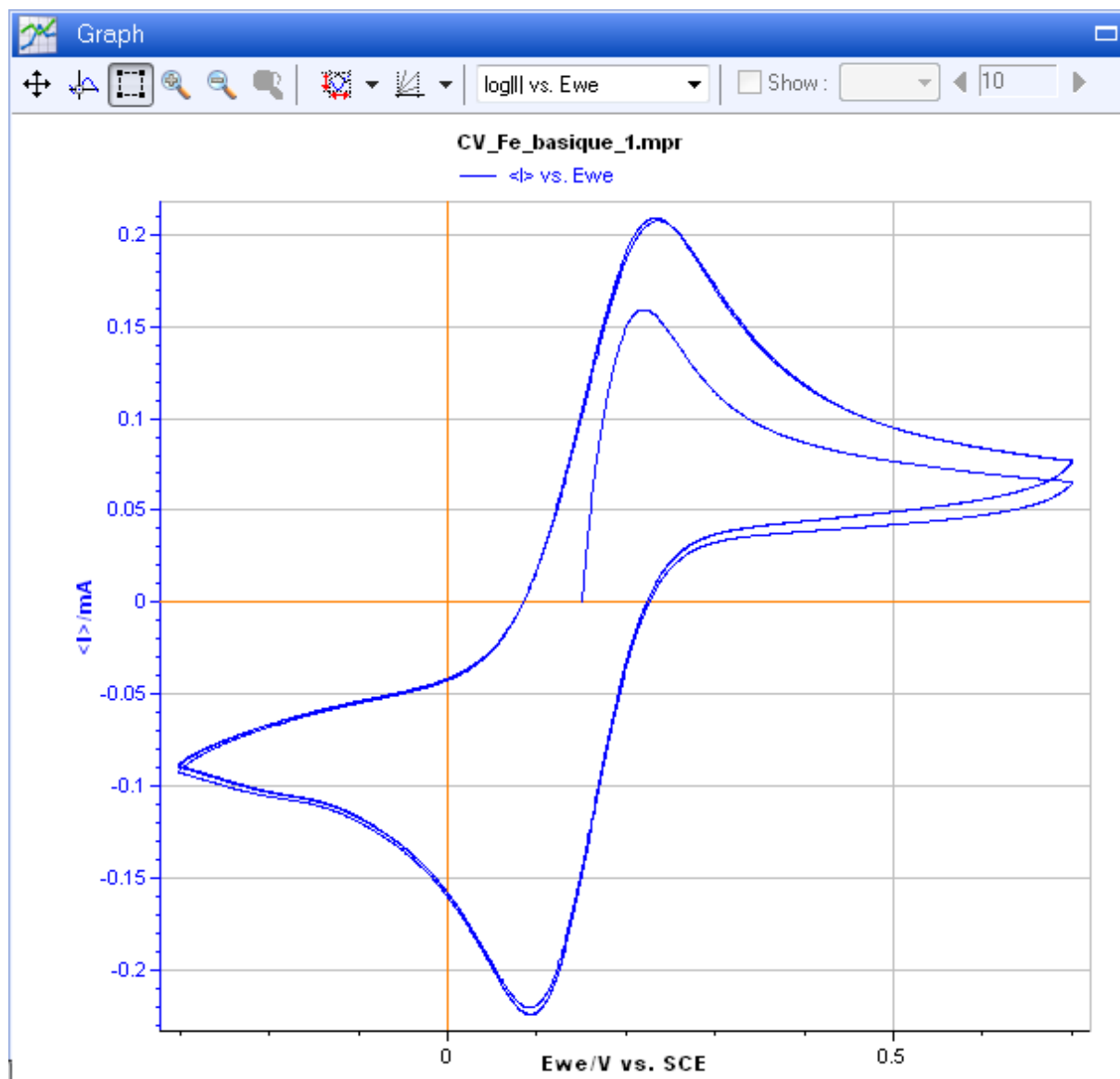


Fig. 29: Graph-displaying frame with tool bar.

2.2.3 Selecting a technique

When a channel is selected, the user can either select a new technique from the list of techniques (with default parameters) or load an existing setting previously built.

To select a new technique, click on the Techniques line. The technique selection window appears:

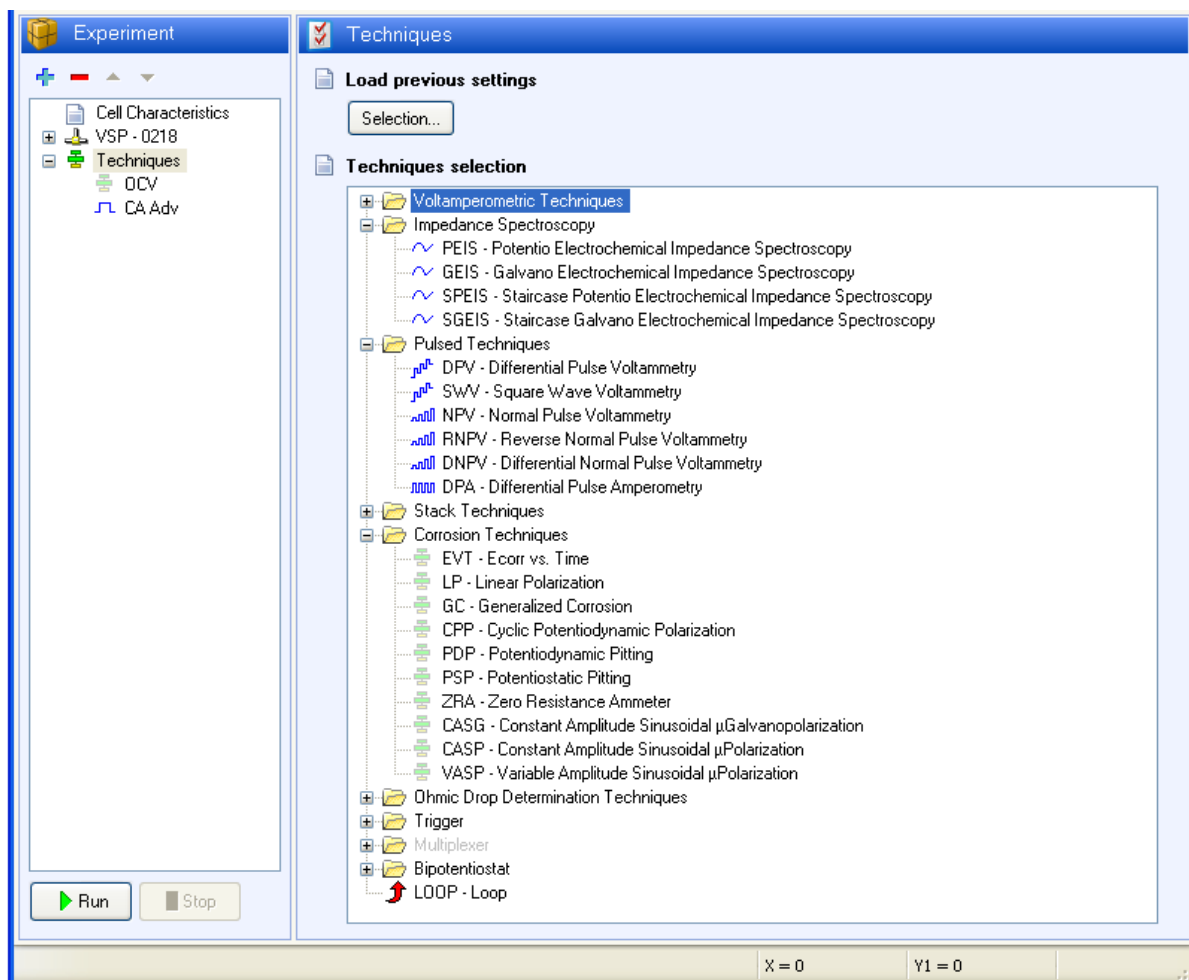





Fig.30: Techniques selection window.

To add a technique click on the  button and select the desired technique line on the Technique selection window and double click on it. To remove a technique select it in the Experiment tab and click on the  button.

Techniques available with EC-Lab® Express software have been separated in several fields: voltamperometric techniques, impedance spectroscopy, pulsed techniques, corrosion techniques, ohmic drop determination techniques and triggers techniques (stack, bipotentiostat and multiplexer techniques if the advanced interface is selected).

On the top of this window the user can choose to add a technique from file already used before (with parameters).

To select settings from an existing file the user can also click on the  **Load Settings** in the file menu and then select a **.mpr** raw file corresponding to the desired technique and click **OK**.

2.2.4 Parameter Settings: description

When a technique is selected the parameter frame displays the technique as boxes to complete.

Note: Most of the techniques use sequences  that can be added up to 100.

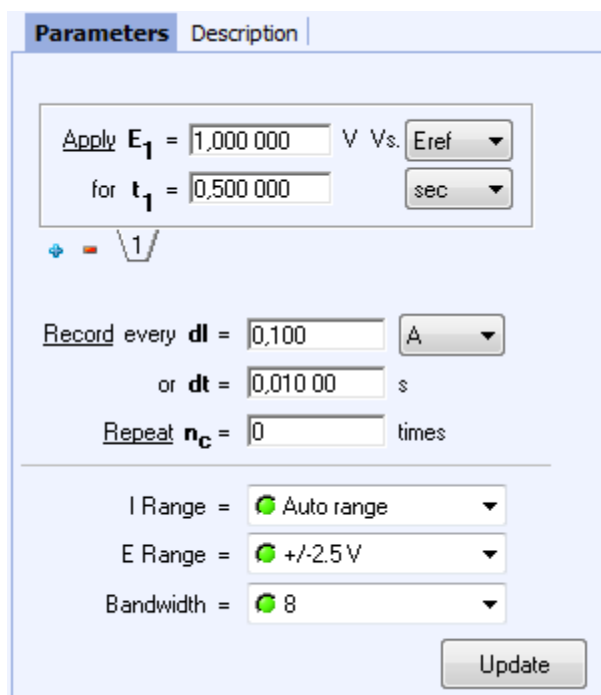



Fig. 31: Chronoamperometry parameters.

EC-Lab® Express software techniques are made of sequences in which the potential to apply and the duration can be changed. Other conditions can be added such as: recording conditions, repeat options and potentiostat parameters. These parameters are the same for all the sequences. To add sequences in the technique, click on the  button. Tabs with number are added.

The recording conditions are the same for all sequences and are defined either in time or in current when the control is in potential or in potential when the control is in current.

The instrument hardware parameters are defined as follows:

- I Range

The current range has to be determined by the user. When the current is measured, the measured values can be twice 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 $2.4 \times I$ 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.

- E Range adjustment

E Range can be defined by the user selecting three ranges of potential already defined (± 2.5 V, ± 5 V, ± 10 V) or the custom range. With the custom range, depending of the application, it is possible for the user to adjust carefully the potential range and then to increase the potential resolution from 305 μ V to 5 μ V for VMP3 technology and from 333 μ V to 5 μ V for SP-300 technology.

Note that two gains are available with the SP-300 technology allowing to reach voltages as small that ± 250 mV or ± 25 mV.

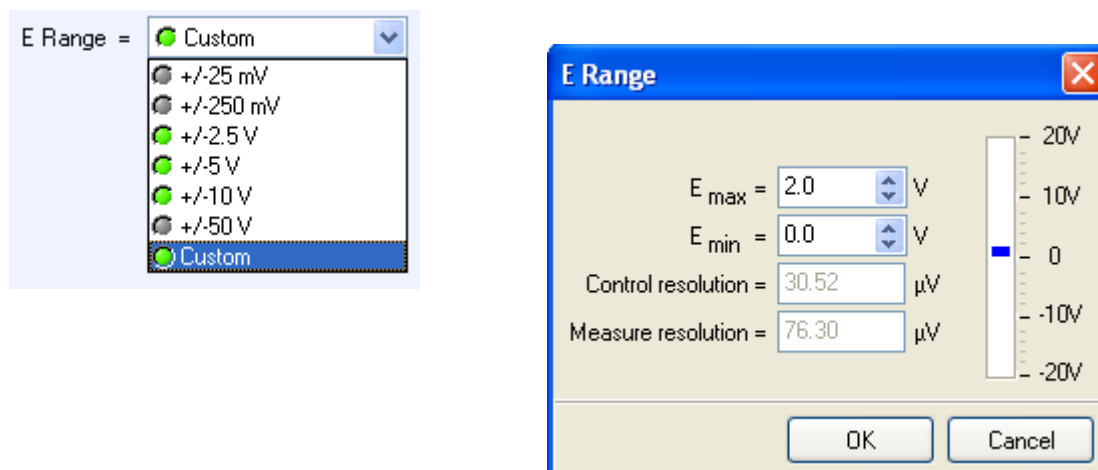


Fig. 32: E Range selection and Custom window.

- Bandwidth

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

The following table gives typical frequency bandwidths of the control amplifiers poles for the VMP3, VMP2/Z, VSP, SP-150, SP-50, HCP-803 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


Note:

- Refer to the SP-300, VSP-300, SP-200 or SP-240 installation and configuration manual for details about bandwidth definition for these instruments.
- When the mouse pointer stands for several seconds on a box a hint (see Fig. 33) 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 and the value that cancel the box.

max : 20
min : -20

Fig. 33: Hint.

2.2.5 Running acquisition

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

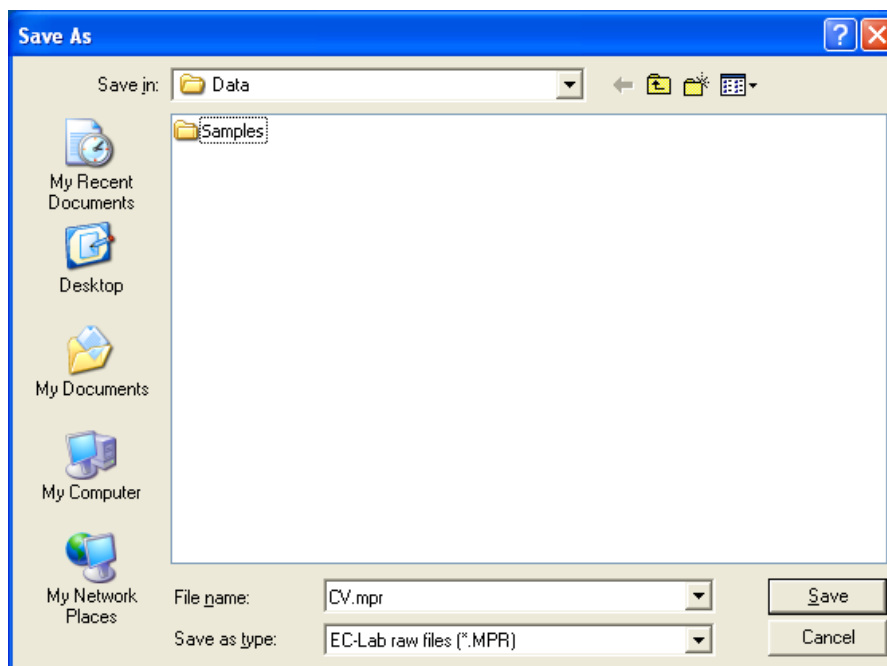


Fig. 34: Filename selection window.

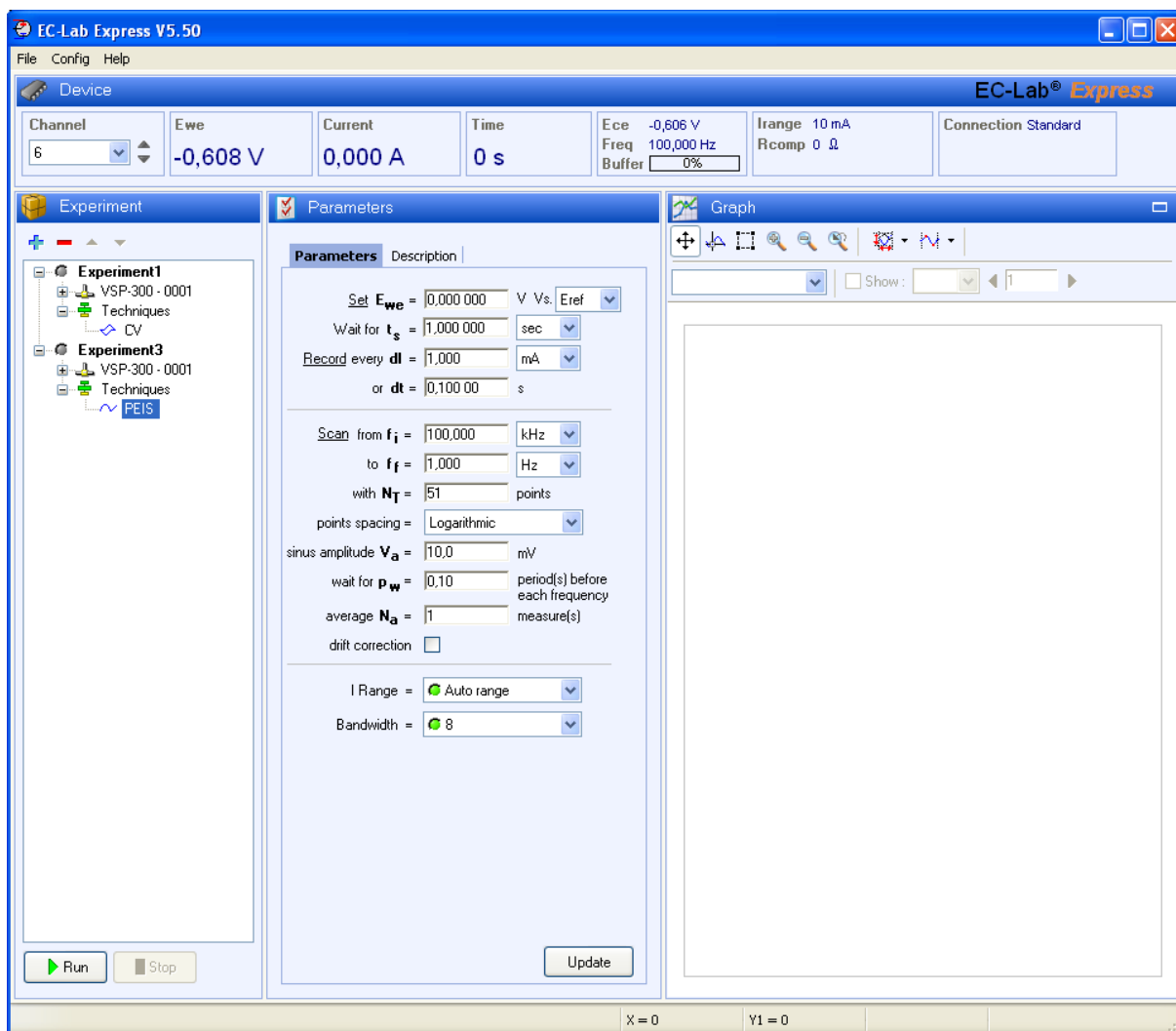
The default folder to save data in My document is called “EC-Lab[®] Express Data”. The user can choose and create another folder to save his data files.

Clicking on the **Save** button or pressing on the <ENTER> key will start the experiment. Two files are created when running the experiment: a binary raw data file, with a **.mpr** extension automatically added and a LOG file which is a reminder of the experimental settings and of the changes done during cycling.

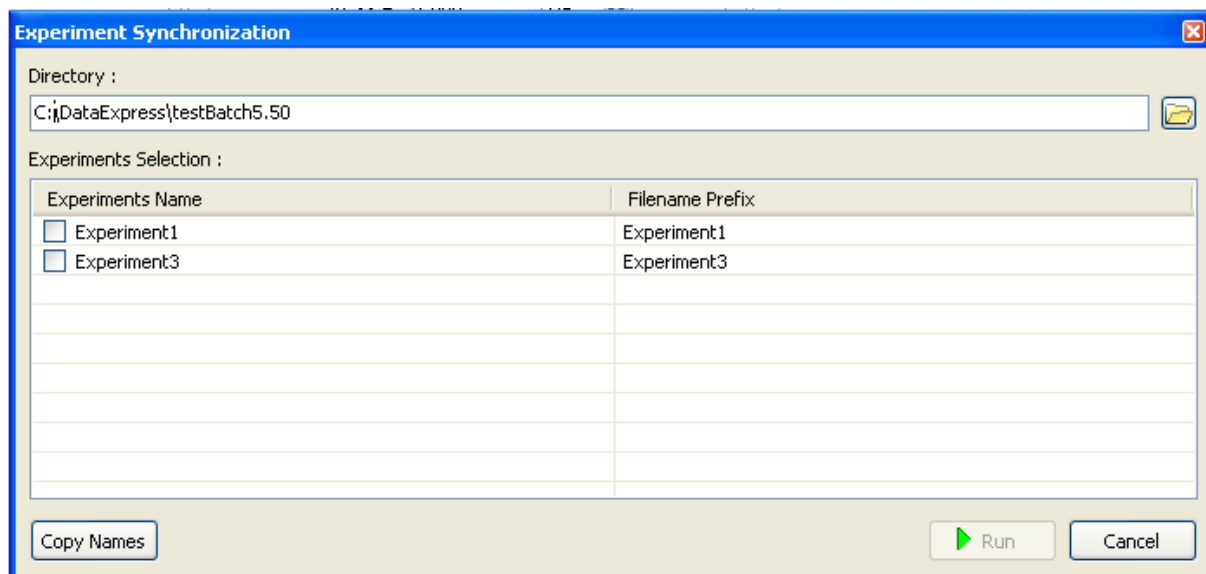
2.2.6 Running synchronized experiment

This option is available in the advanced interface. It is possible to synchronize several experiments together on different channels of an instrument, for example in a bipotentiostat experiment. The setup procedure is the following:

- Create several experiments (one for each channel) and select the related device for each of them. Automatically when more than one experiment is set, the software will offer the possibility to synchronize both experiments.



- Click on the “Run” button of the “Experiment” frame, “Experiment Synchronization” window appears. In this window, user selects the directory location and experiments (which should be synchronized) by ticking the corresponding box (name can be modified in the “Filename Prefix”). One file is saved for each experiment.



- Experiments are launched when the user click on the “Run” button on the window above.

2.3 Data properties

2.3.1 Type of data files

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

File extension	description
.mpr	Raw data binary file which contains the current parameter settings (refreshed at each modification) of the detailed flow-diagram and of the cell characteristic windows. This file includes all the information of the .mps file.
.mpp	Temporary binary file, available for particular protocols, derived from the .mpr file. This file is used for real time displaying of parameters obtained by raw data processing; e.g. the integrated charge since the starting of the experiment, the average current between two recordings (chronocoulometry).
.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 a .mpr or a .mpp data file. 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 open. Each fit result can be printed alone or with other fits.

During the experiment:

- Data from measurement results are appended to the .mpr file.
- Possible modifications of 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 unserviceable by the EC-Lab[®] Express software.

2.3.2 Variables description

Several variables are standard and common in every technique and application in 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 are processed.

Variable description	Variable name
Common variables	
Time (in s)	time/s
I: current (in mA)	I/mA
E _{we} : WE potential versus REF (in V)	E _{we} /V
E _{ctrl} : potential control (in V)	control/V
I _{ctrl} : current control (in mA)	control/mA
E _{ce} : CE potential versus REF (in V)	E _{ce} /V
State byte	
Mode = Intention/Potentio/Relax, State byte (bits n°1 and 2)	mode

variable description	Variable name
Additional variables	
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: in sweep pulsed techniques, potential step increment	E step/V

variable description	Variable name
Processed variables	
Cycle number	cycle number
Power: in CPW, calculated by $E.I$	P/W
Energy: in CPW calculated by $E.I.t$	Energy/W.h
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: Inverse of capacitance for Mott-Schottky plot	C (F)

variable description	Variable name
Impedance	
Frequency (in Hz)	freq/Hz
$ E_{we} $: module of E_{we} (V)	$ E_{we} /V$
$ I $: module of I (in A)	$ I /A$
Phase of Z (in degrees)	Phase(Z)/deg
$ Z $: module of Z (in Ω)	$ Z /\Omega$
Re(Z): real part of Z (in Ω)	Re(Z)/ Ω
-Im(Z): -imaginary part of Z (in Ω)	-Im(Z)/ Ω
Re(Z_{ce}): real part of Z (in Ω)	Re(Z_{ce})/ Ω
-Im(Z_{ce}): -imaginary part of Z (in Ω)	-Im(Z_{ce})/ Ω
$\langle E_{we} \rangle$: averaged E_{we} value for each frequency	$\langle E_{we} \rangle/V$
$\langle I \rangle$: averaged I value for each frequency	$\langle I \rangle/A$
Voltage fuel cell stack	E_{stack}/V
Current fuel cell stack	I_{stack}/A
$ E_{stack} $ magnitude of voltage fuel cell stack	$ E_{stack} /V$
$ I_{stack} $ magnitude of the current fuel cell stack	$ I_{stack} /A$
I Range: current range	I Range

2.3.3 Data recording

In all the technique sequences, the user is able to define different modes for data recording. The main mode corresponds to decide the recording resolution of the measured variable (potential, current, ...) with at least a recording every predetermined time interval dt (from 0.1 to 9999 s). This last condition gives a minimum of recorded points in the case where 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...).

For open circuit voltage (OCV) period, nothing is controlled and 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 available on a time variation and/or an instantaneous current variation (dI)

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

If the user wants to force a periodic recording in time, he has to set a large value in the recording resolution of the variable.

2.3.4 Data Saving

Each channel has its own memory buffer to store data points. This memory can receive 40,000 data points. When the memory is full, data points are rejected until the memory is a little emptied and could receive data points.

3. EC-Lab[®] Express software: Graphic Display

3.1 The Graphic window

The EC-Lab[®] Express application includes a graphic facility to display experiments on-line and off-line. The user has also the ability to add graphs to an existing graphic window. In that case the window is divided in two or more graphs (depending on the number of graphs).

When an experiment is running, the graphic window is automatically opened to display the corresponding result file(s). Default graphic parameters have been chosen (for example plot I vs. E for the CV technique). The user can replace the default graphic parameters by his own parameters. To do so, he has to select the menu Representations in the Options menu and define his custom settings.

In case of linked techniques, two different graphic windows will be displayed, one for all voltamperometric techniques (plot versus time) and one for the impedance spectroscopy (plot versus frequency).

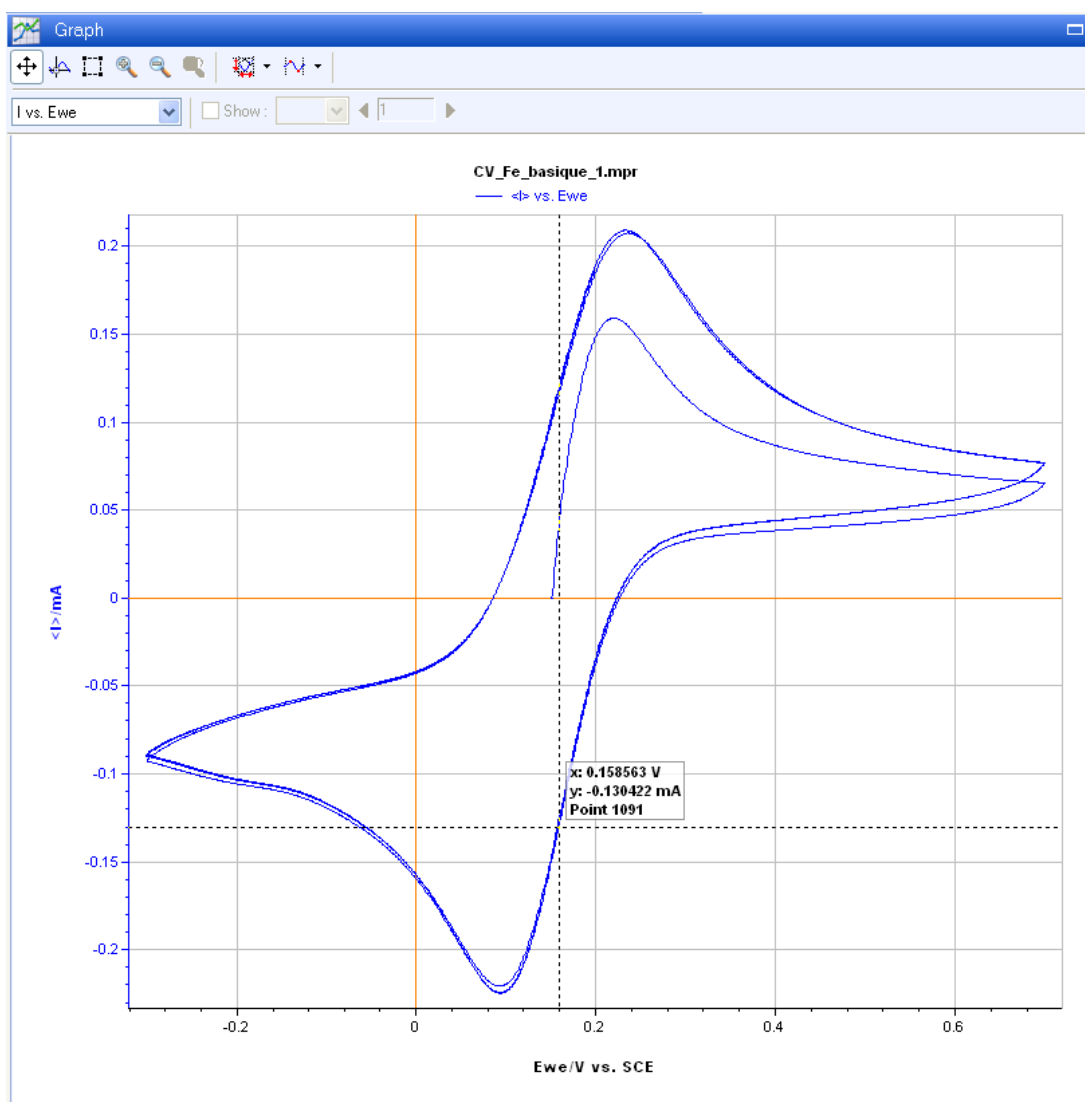

















Fig. 35: Graphic window.

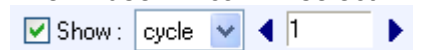
On the top of this graphic frame, the classical tools are displayed:


- The **scroll**  is used to move the curve on the graphic window .
- The **cursor**  allows the user to display for each point its coordinates and the number of the point. When you right click on the mouse, a comment is added on the graph given the coordinates of the point .
- The **selection**  allows the user to select a zone of the curve (data points) either before a fit or analysis or to hide bad data points .
- **Zoom +**  and **Zoom -**  are used either with a zone selection (smoothing) or by left clicking on the part of the curve that you want to zoom .
- **Zoom Back**  is very useful when you have zoomed in an undesired zone. It is not limited in the number of actions.
- The Mouse Rescale is made of different scaling functions according to each axis. These buttons allow rescaling on X axis , Y1 axis , Y2 axis  and every axes  at the same time .

Five section of fitting tools are available:

- Maths tools section  including Min-Max determination, linear and circle fit, linear interpolation, file subtraction, integral, Fourier Transform, Filter, Multi-exponential Sim and Multi-exponential Fit
- General Electrochemistry section  including Peak Analysis, Wave Analysis and CV Sim.
- Electrochemical Impedance Spectroscopy section  including Z Fit, Z Sim and Mott-Shottky Fit and Kramers-Kronig analysis
- Photovoltaic/Fuel Cells section  including Photovoltaic Analysis
- Corrosion analysis tools section  including Tafel Fit, Rp Fit, Corr Sim, VASP Fit, CASP Fit, Electrochemical Noise Analysis Fit.

The user can select the cycle to display with the “Show” option



This graph window can be maximized using the top right corner button .

Note that the user can also have all the point coordinates by hovering the mouse over a point while holding the **SHIFT** key of the keyboard. A comment box is displayed.

3.1.1 The graphic window right click menu

The graphic menu window can be obtained by clicking on the right button of the mouse.

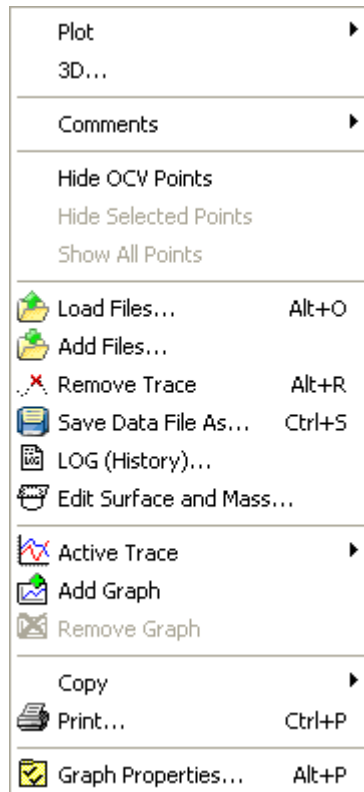
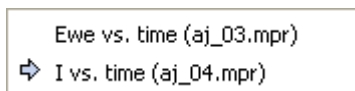


Fig. 36: Mouse right click on the graphic window.

On this right click, several frames are displayed:

- 1st for plot and Graph type selection.
- 2nd for the addition of comments on the graph with the possibility to Add and delete a comment zone and to paste a comment from the clipboard.
- 3rd for showing or hiding OCV points and artefact data points that the user wants to remove before an analysis or a print.
- 4th for file selection with **Load files...**, **Add files...**, **Remove trace**, **Save Data Files as**, **LOG (history)...**
- 5th for the graphic display with the **Active trace...**, **Add graph** and **Remove graph**.



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

- 6th for “**Copy** and **Print...**” tools.
- 7th for the **Graph properties....**

3.1.2 Loading a data file

With the EC-Lab® Express software the user can reload data files previously recorded following the link **File\Load Data File...** or in the graphic window with the mouse right click menu item **Load Files....** The following window appears:

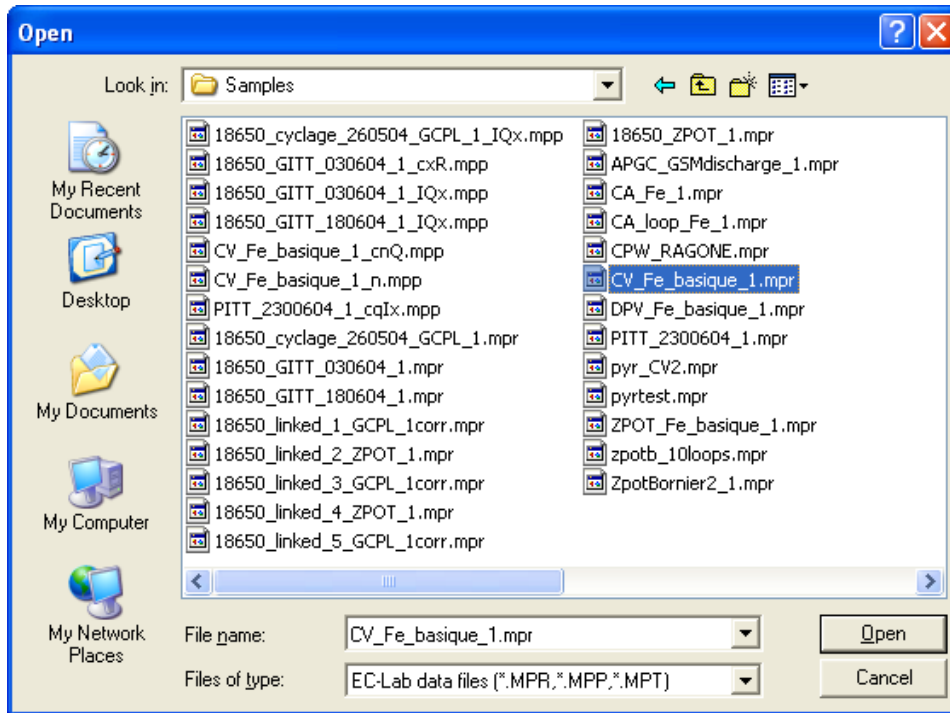


Fig. 37: Open file window.

Select the data file you want to open and click on **Open**.

3.1.3 The data file and plot selection window

Right click on the mouse, the following menu appears.

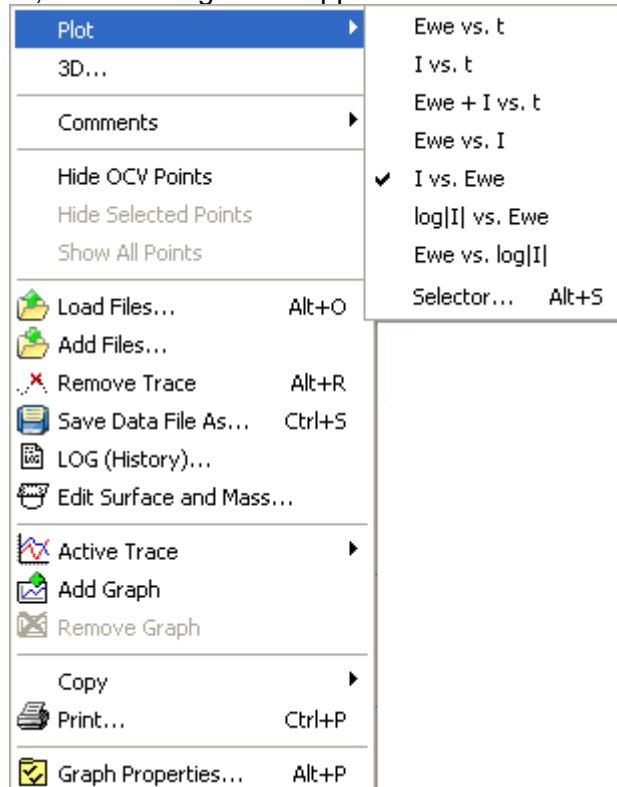


Fig. 38: Plot menu.

In the **Plot** menu, select “**Selector...**”. The following window will be displayed:

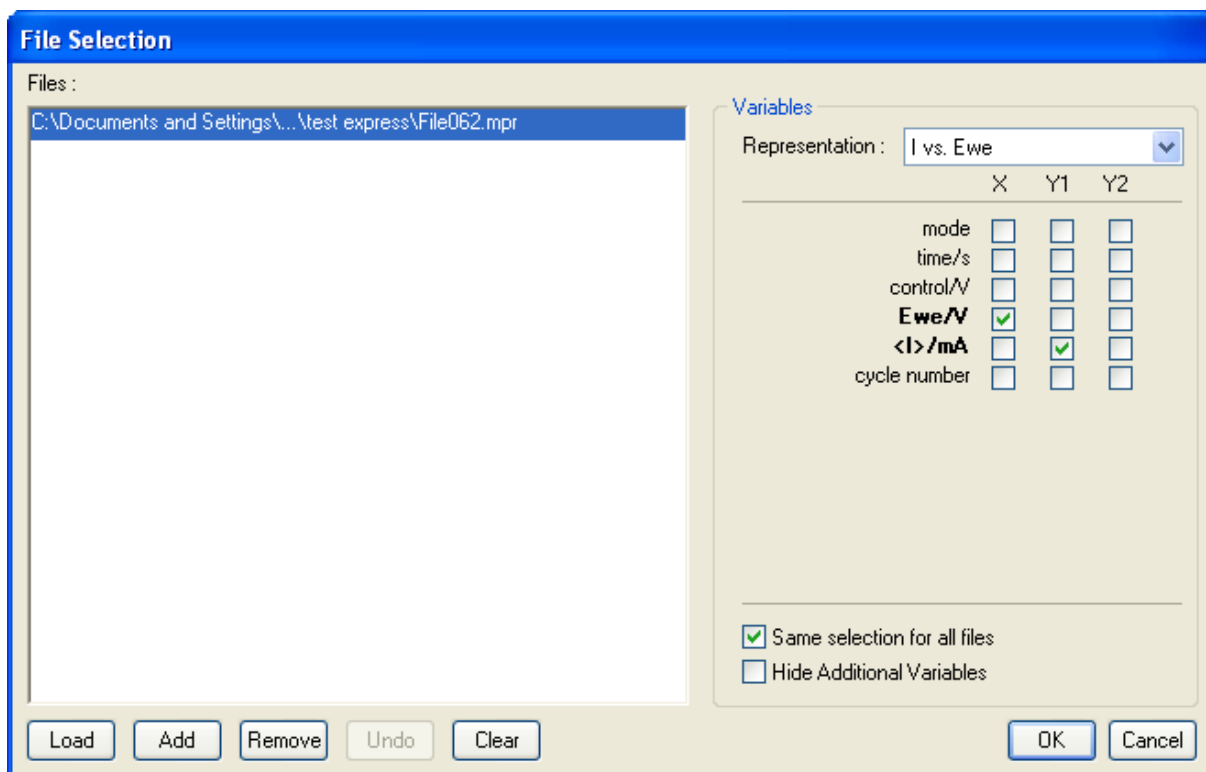


Fig. 39: File selection window.

The user can choose to plot another visualization (for example: time/s for X, E_{we}/V for Y1 and $\langle I \rangle/\mu A$ for Y2). 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, $\langle I \rangle/\mu A$) 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 indicate different statuses 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). So the option **Hide Additional variables** is checked by default. Unchecking the option will add the variables to the file selection window.

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® Express 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 for quick selection of the graph plot.

When a data file is displayed in the graphic window the user can modify the graph properties for a better representation of the curve. The graphic parameters are automatically saved in a

graphic file. Then when the user reopens the same data file in the graphic window, the graphic parameters defined before will be kept.

3.2 Graphic facilities

3.2.1 Show/Hide points

The EC-Lab[®] Express software is equipped with a show/hide option on the right click menu. Aberrant points can now be hidden on the graph in order to perform data processing without any troubling points. The hidden data points are not removed from the data file. They are only graphically hidden for better processing. The data points must be selected with the selection mouse mode  before being hidden. Then click on **Hide selected points** to mask the points.

3.2.2 Add comments on the graph

The graphic package offers the ability to add comment zones on the graph. The number of comment zones that can be added on the graph is not limited.

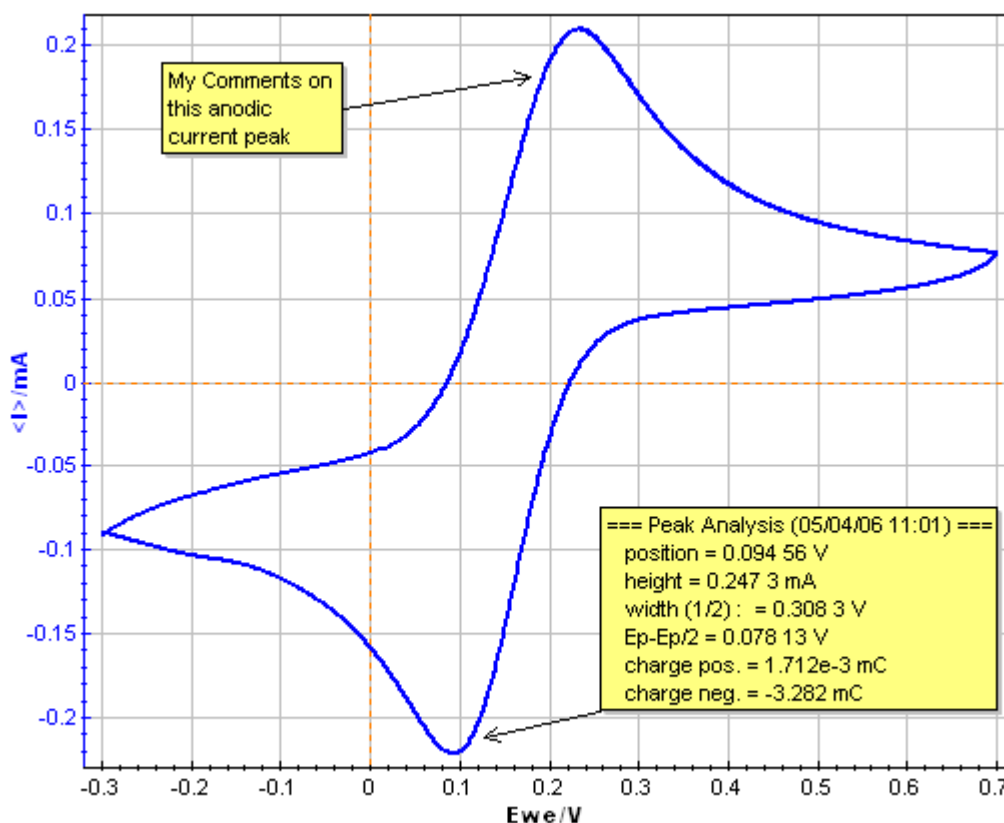


Fig. 40: Comment zones on the graph.

To add Comment zones to 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 is displayed:

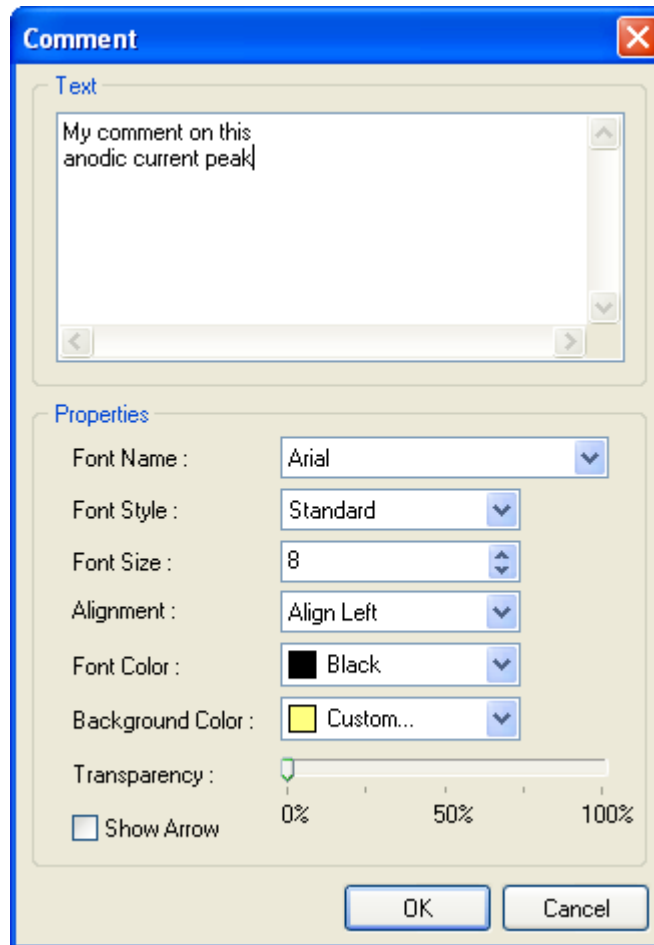


Fig. 41: Edit Comment zone.

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 to the desired part of the curve.

To remove comment zones, right click on the zone and select "Delete comment".

Note: The comment zone is automatically printed on the graph.

With the Suppr. button of the keyboard it is possible to delete the comments.

3.2.3 Three-Dimensional graphic

A 3D representation is available by right clicking on the graph menu. 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 in Fig. 42.

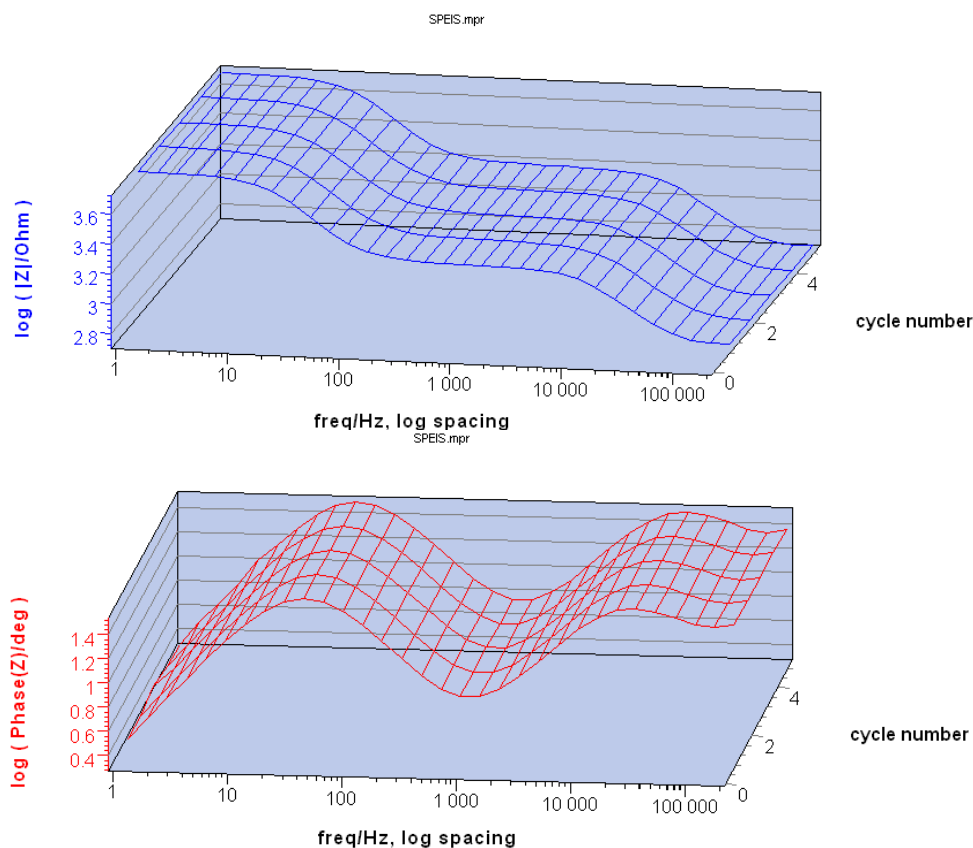


Fig. 42: Bode diagram displayed in the 3D representation.

Once on the 3D representation, it is possible to reach the 3D menu by right clicking on the graph (Fig. 43). Thanks to this menu, it is possible to come back to the 2D representation or to display simultaneously 2D and 3D graphs. As for the 2D representation, it is possible to copy and print the graph as explained in section 3.2.7 page 51. The Graph properties menu for the 3D representation is the same that the Graph properties menu for the 2D graph and this menu is detailed in the following paragraph.

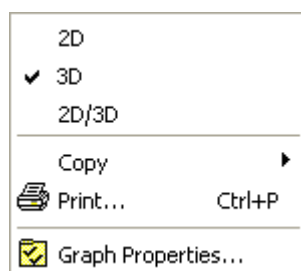
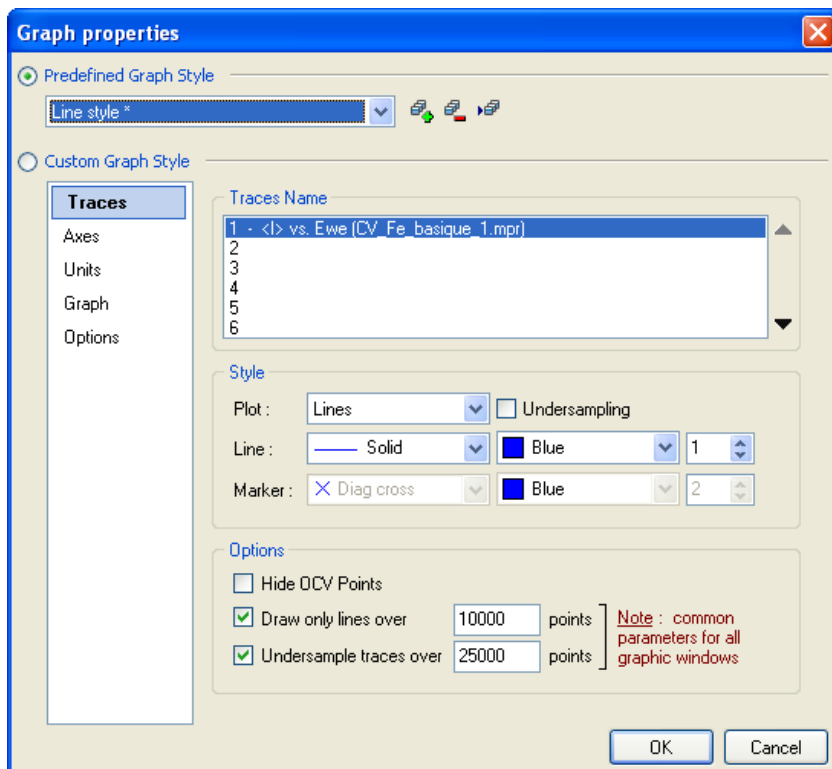


Fig. 43: 3D menu.

Note that to display a data file with the 3D function, the number of points should be inferior to 15000 points.

3.2.4 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.



The Traces window allows the user to define all the properties of the selected traces. Select the trace you wish to modify in the Trace 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 lines are plotted (not with markers).

Fig. 44: Traces window.

In the Options window, it is possible to choose to hide OCV point or to draw only lines over a number of points or to undersample traces over a number of points or to scroll graph over a number of point. Note that the two last possibilities should be the same for all the traces. The undersampling traces over and the scroll graph over are incompatible options. The user must choose one of the two options.


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 (when the mouse becomes a hand with a pointed

finger ).

It is also possible to select between four styles already defined:

- 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.

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.

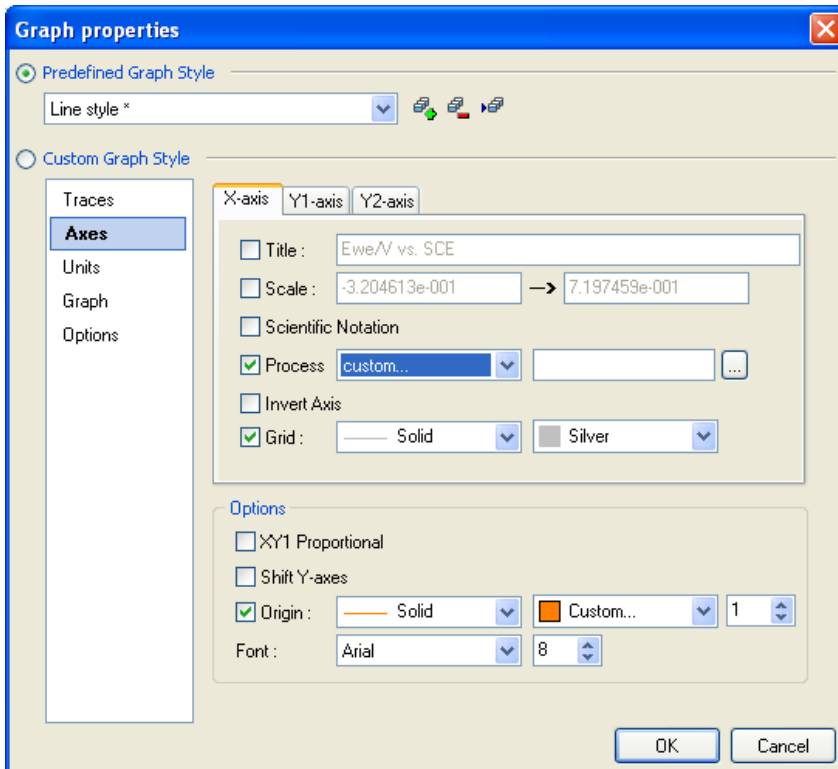



Fig. 45: Axes window.

In the option 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.

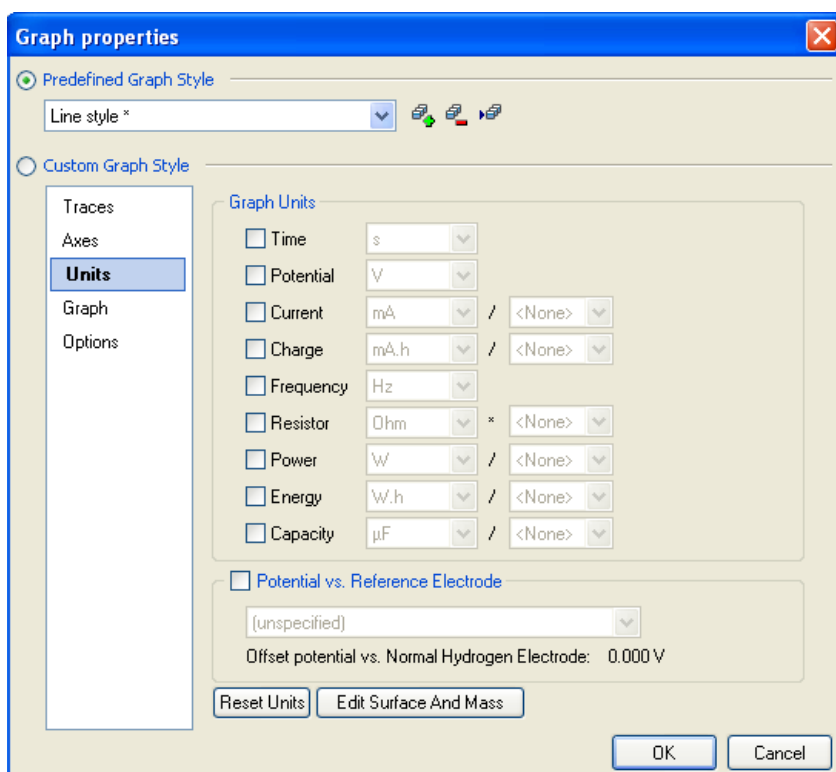
Note: - On the graph the user can move one of the Y axes with the mouse (left click) in order

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.



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, he must activate his choice by ticking the box corresponding to the represented variable. 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 select a current density or a charge density according to the electrode area or to the electrode characteristic mass.

Fig. 46: Units window.

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:

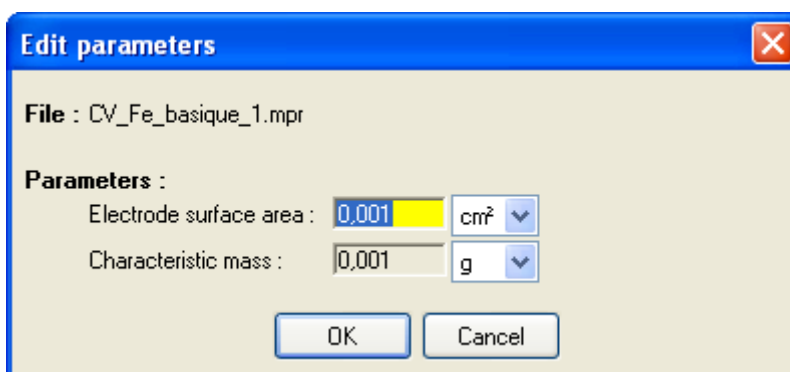


Fig. 47: Electrode Surface Area and Characteristic Mass window.

The Electrode Surface area and Characteristic Mass window is used in the unit window for area charge 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. Click on **Save to file** to save the surface in the raw data file.

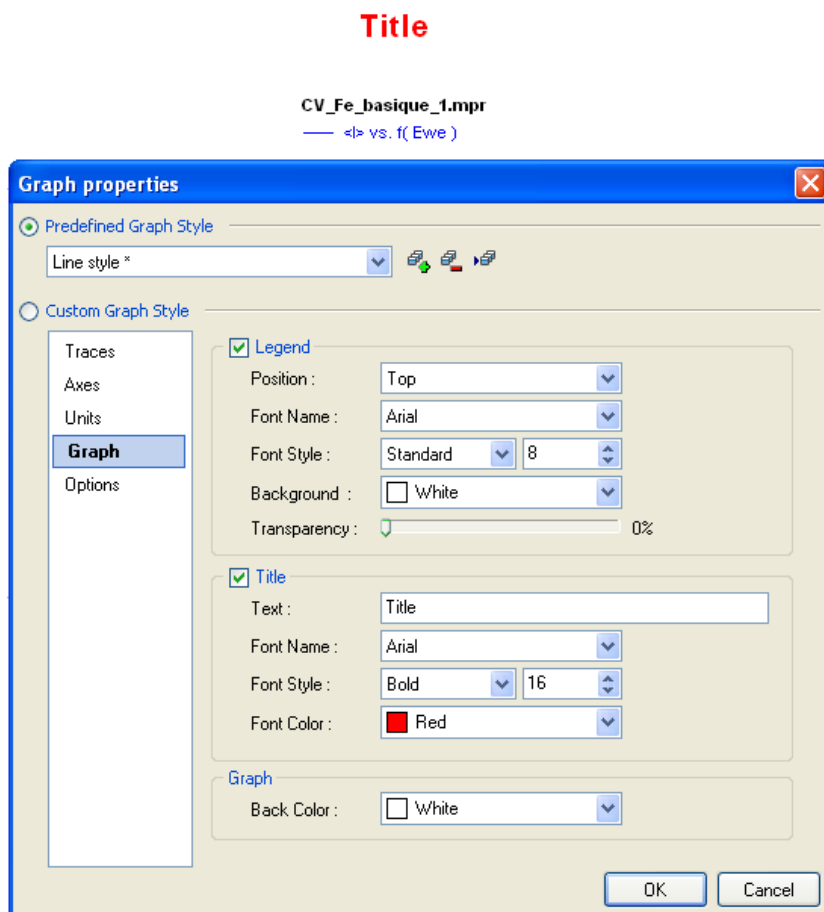


Fig. 48: Graph window.

The user can show or hide the graph legend. He can define the position, the font name, style and size, the background color and the transparency of this background.

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.

Note: When several traces are plotted on a graph, the user can select the active trace by clicking on the corresponding legend.

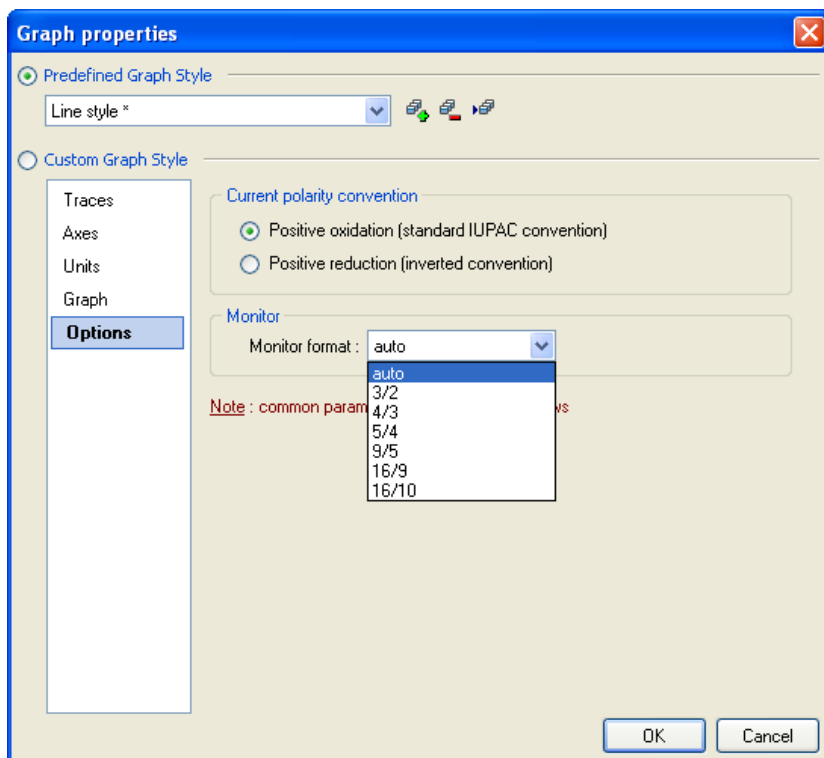


Fig. 49: Options window.

This window allows the user to choose to work in inverted convention for the current polarity.

It is also possible to adjust the graph size to the monitor format.

3.2.5 Graph Representation menu

It is possible for the user to define fast graphic displaying modes with the Representation tool in the Config 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. 50, 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.

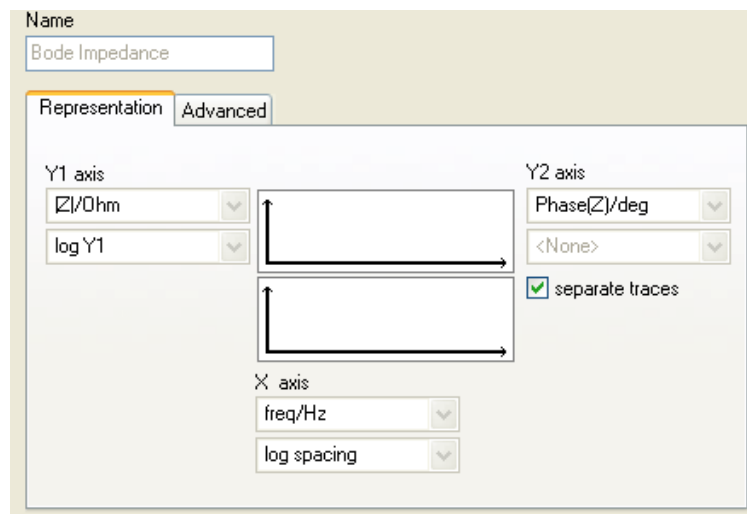
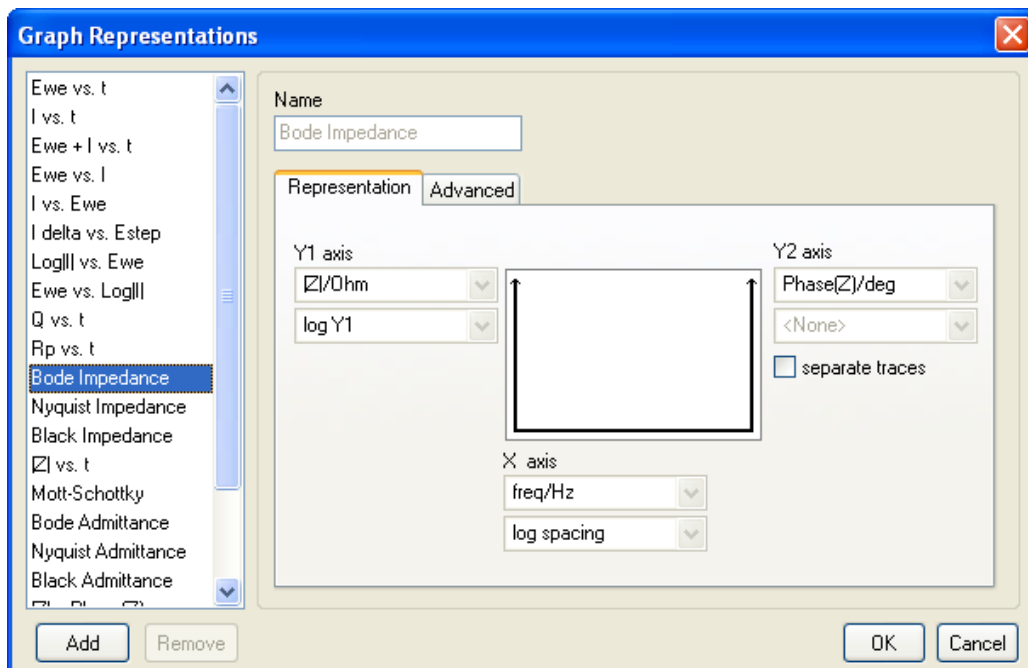
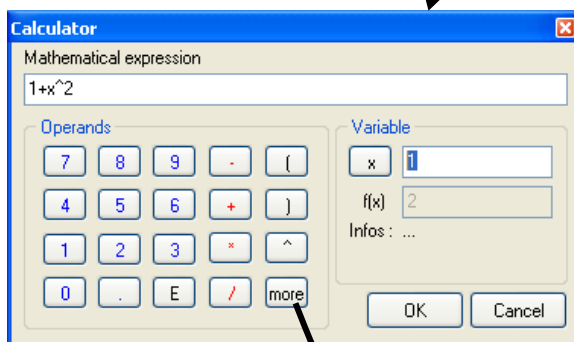
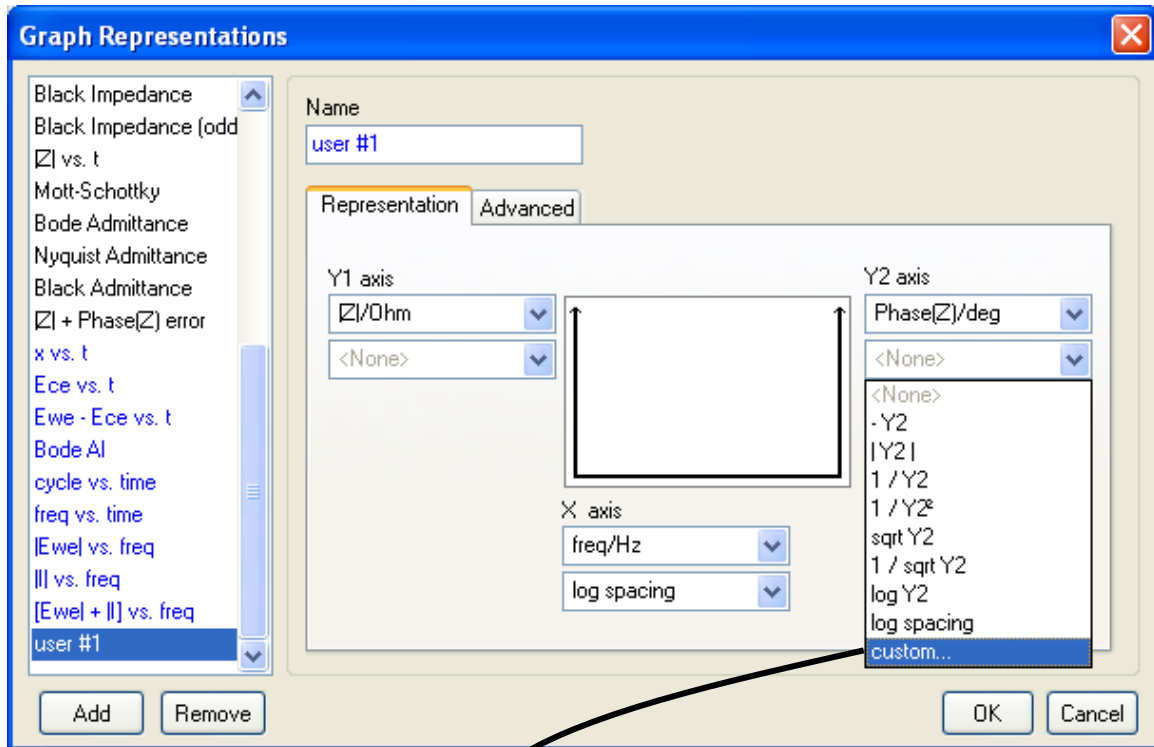


Fig. 50: Graph representations window.

3.2.5.1 Axis processing

As shown previously, it is possible to apply a mathematical function to each axis. By default standard functions such as $\log X$, $-X$, $|X|$, $1/X$ are proposed (Fig. 51). Nevertheless it is possible for the user to define his own processing function using the **Custom** menu.

Then in the window given Fig. 51, 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.



exp()	exponential of a number
sqr()	square of a number
sqrt()	square root of a number
abs()	absolute value
round()	round to the nearest integer
trunc()	truncates a real number to an integer
ln()	natural logarithm
log10()	logarithm base 10
logN(,)	logarithm for a specified base : LogN(Base, X)
sin()	sine of an angle in rad
cos()	cosine of an angle in rad
tan()	tangent of an angle in rad
arcsin()	inverse sine in rad
arccos()	inverse cosine in rad
arctan()	inverse tangent in rad
sinh()	hyperbolic sine of an angle in rad
cosh()	hyperbolic cosine of an angle in rad
tanh()	hyperbolic tangent of an angle in rad
arsinh()	inverse hyperbolic sine in rad
arcosh()	inverse hyperbolic cosine in rad
artanh()	inverse hyperbolic tangent in rad
PI	3.1415926535897932385
degtorad()	conversion of degrees to radians
radtodeg()	conversion of rad to degrees

Fig. 51: Axis processing window and available mathematical functions.

3.2.5.2 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. He must select variables to be displayed on X-axis and on Y1 and Y2 axes in the **Representation** window. He can also define a processed display for each axis in the **Advanced** window.

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. 52. 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 by selecting the **Edit** menu, see following paragraph for more details about the Graph Style creation.

Clicking on the second **Edit** button allows the selection of the desired technique. Once the selection done, techniques are displayed in the Selected techniques box as shown in the Fig. 52.

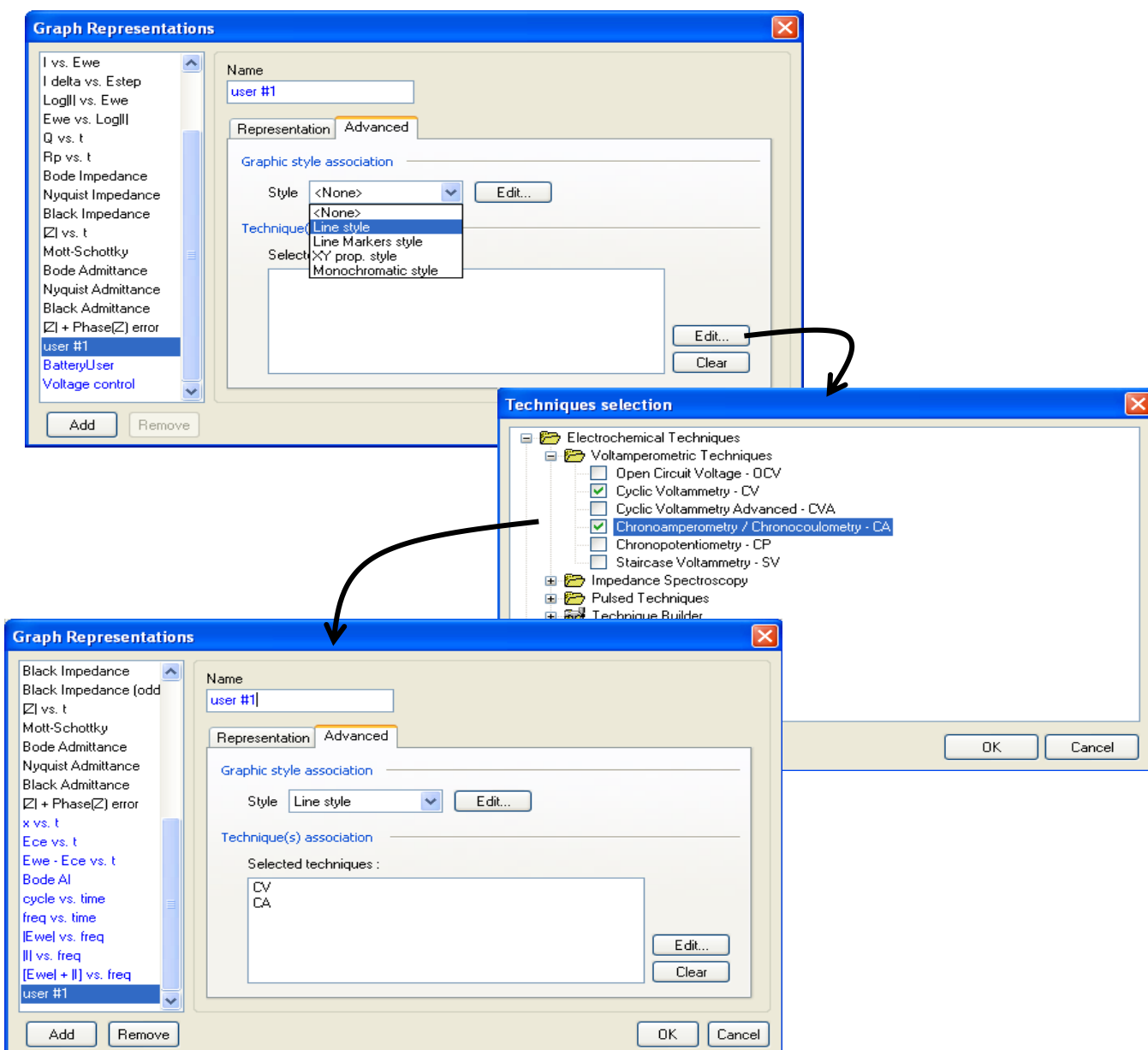


Fig. 52: Graph Style and technique selection.

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.

3.2.5.3 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[®] Express to create a Graph Style. In the menu bar, 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. 53). To define your own Graph Style, click on the **Edit...** button, the window **Graph Properties** will be displayed as shown Fig. 54.

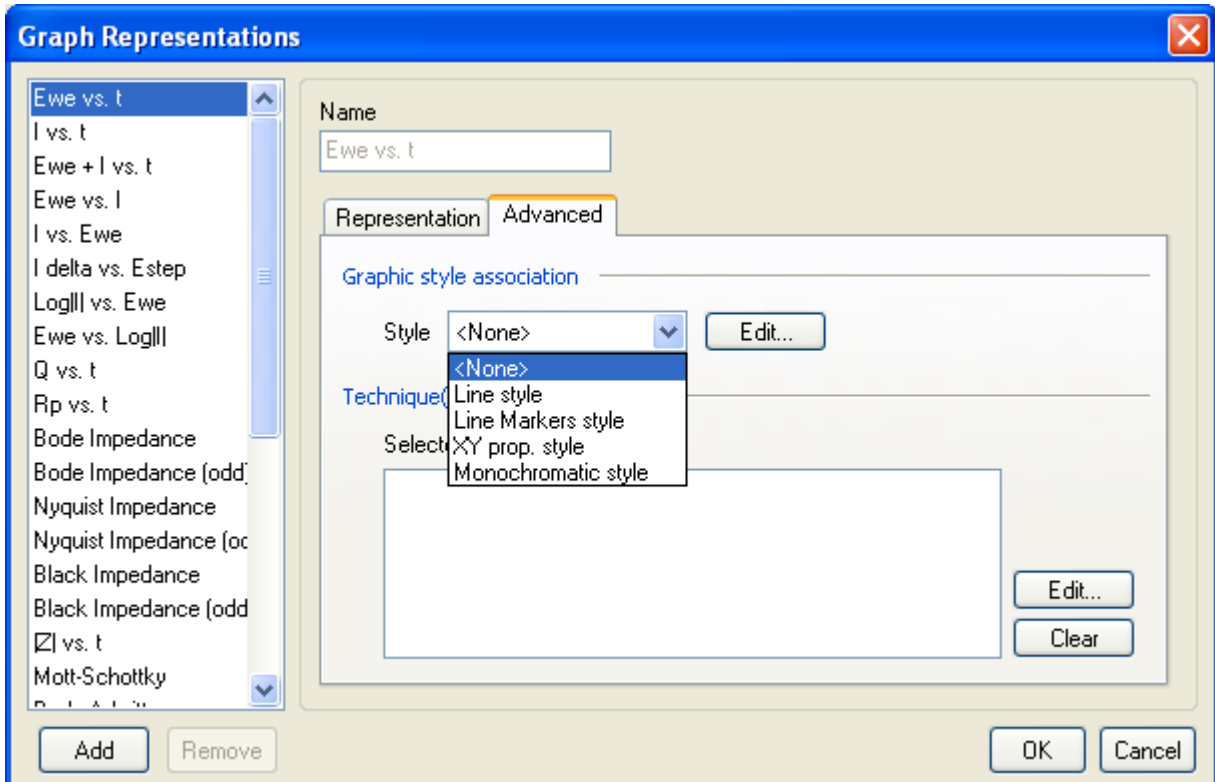


Fig. 53: Graph Style selection.

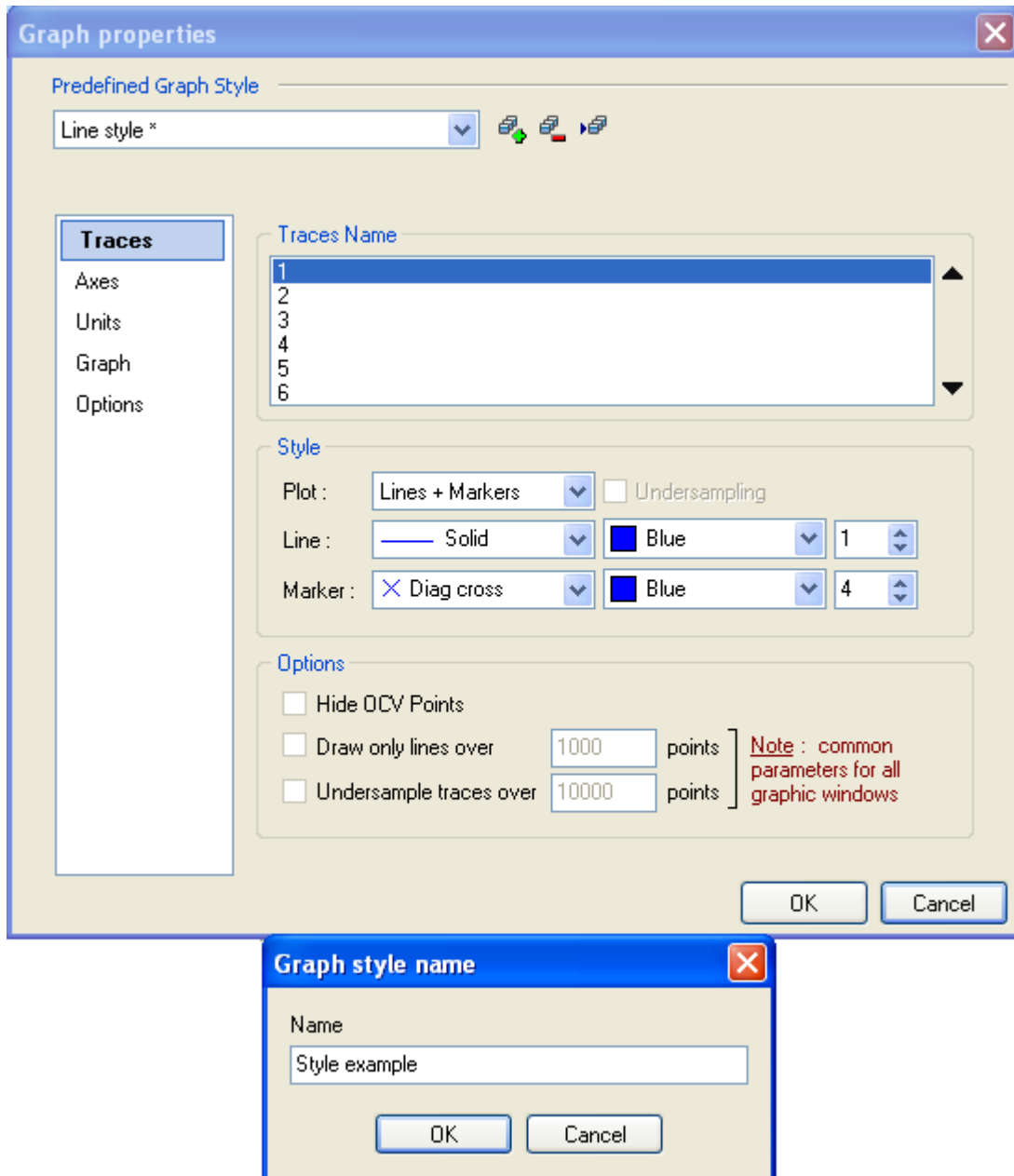



Fig. 54: Graph Properties window in the Graph Style creation.

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 fushia triangles markers and the curve 2 is defined as blue solid lines and blue sky diag cross marker (Fig. 55).

The Graph Style definition includes all the graph properties. These properties were previously defined in the section 3.2.4.

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

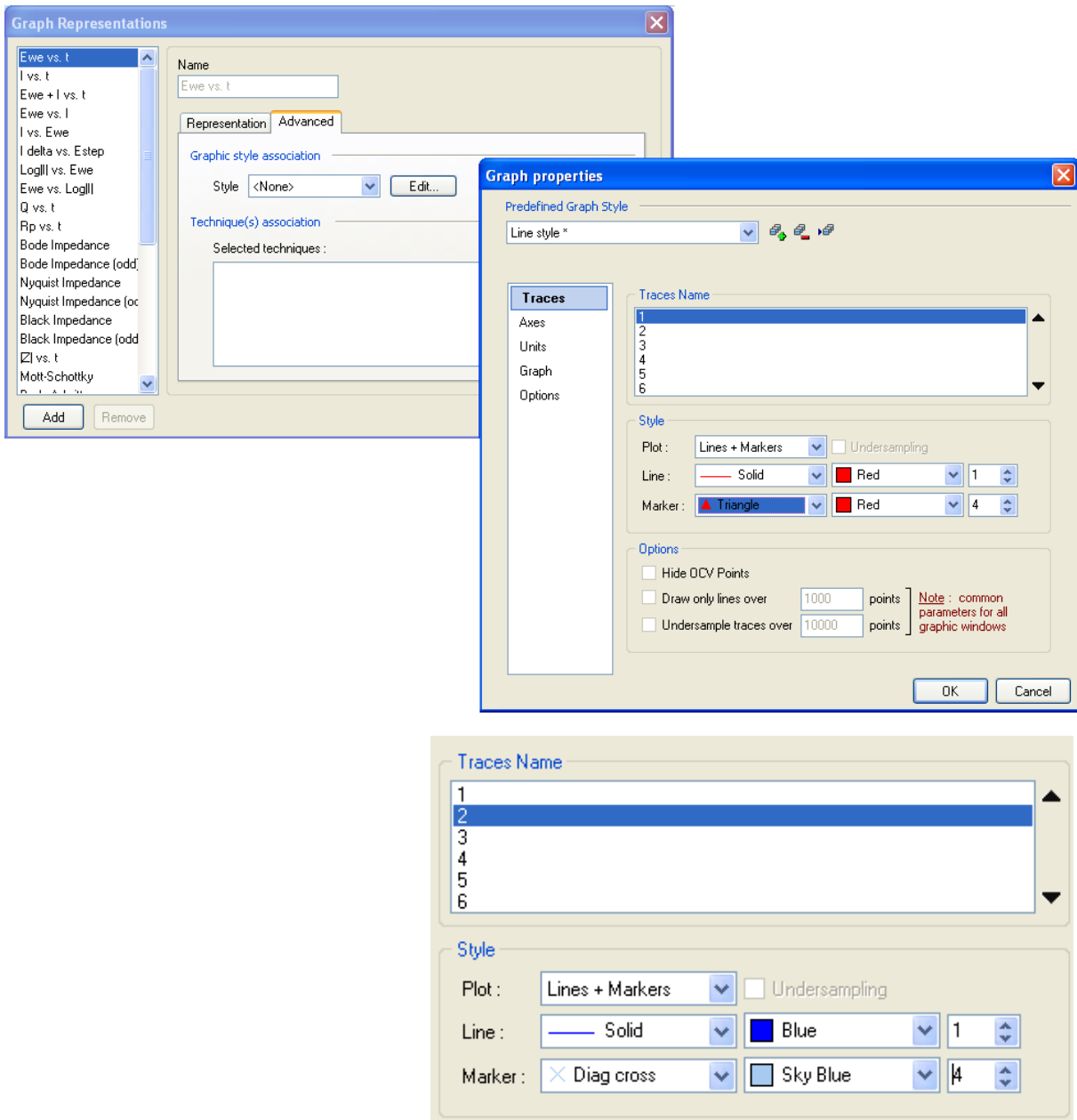



Fig. 55: Definition of traces properties in Graph style definition.

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.

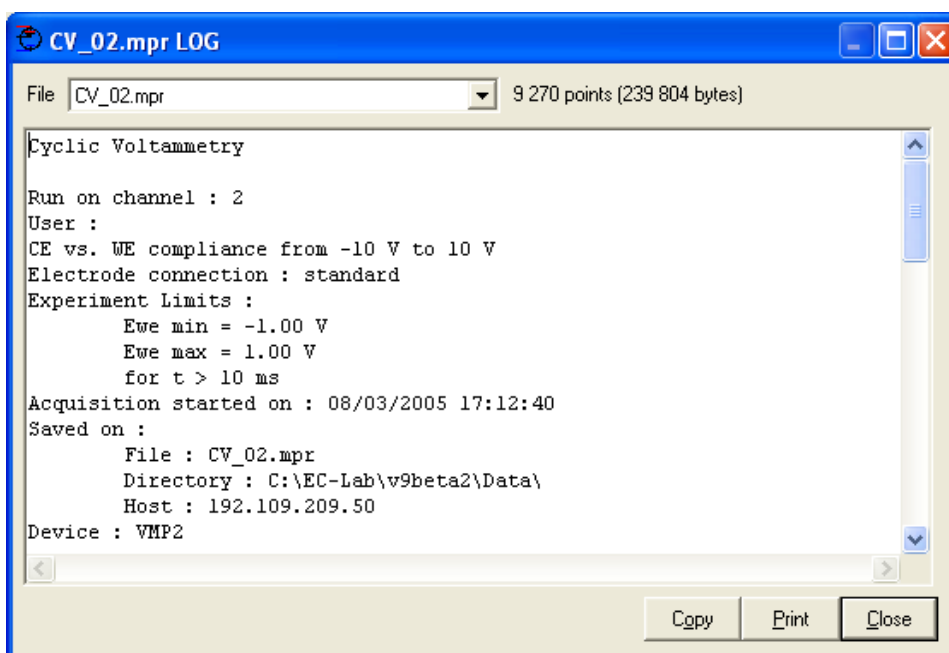


Fig.56: Experiment history window.

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.

3.2.7 Copy options

On the graphic display several copy options are available. When the user right clicks on the mouse the following copy options can be found in the "copy" menu:

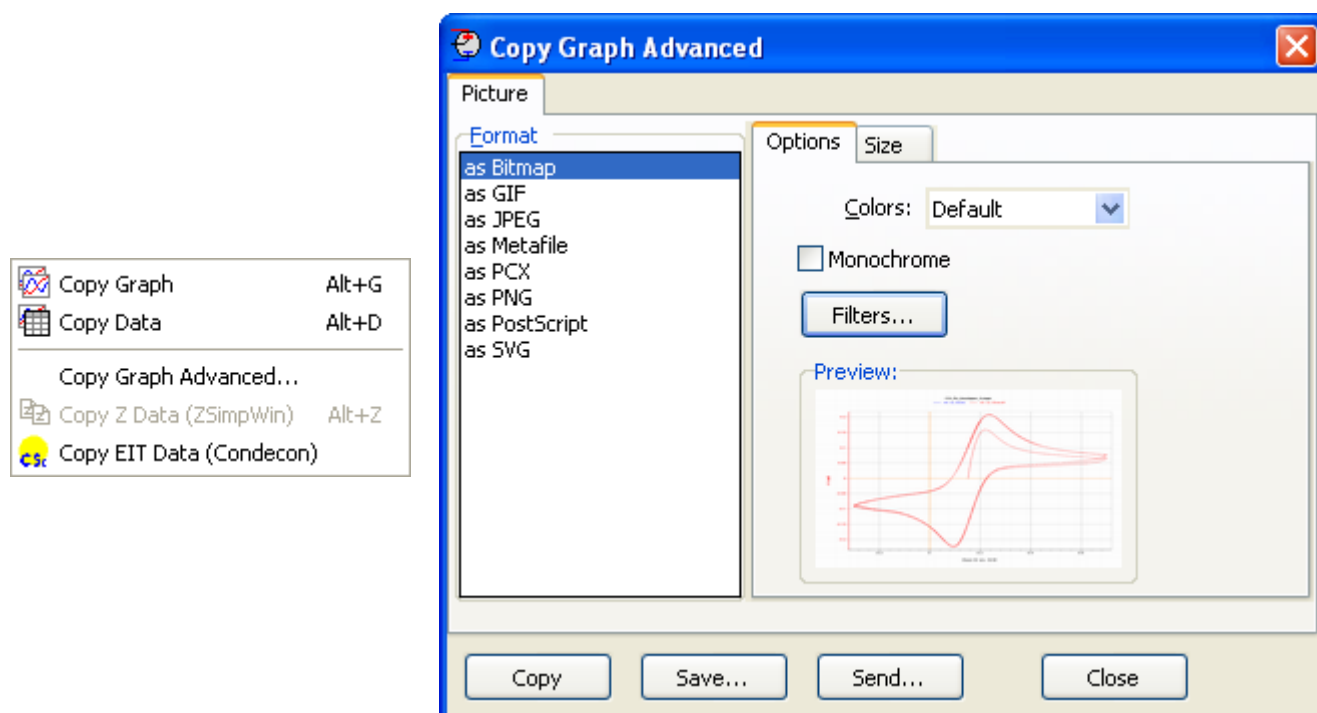


Fig.57: Copy option and copy graph advanced menu.

3.2.7.1 Standard copy options

On the top of the menu, two standard options either copy the graph or copy the data. The “**Copy Graph**” option will copy the graph in the clipboard as displayed on the computer screen in an enhanced metafile format (*.emf). The user can paste the file in the software he wants. 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 be directly pasted into 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: Bitmap, enhanced metafile, PostScript, SVG, PCX, PNG, GIF and JPEG 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 in 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 menu displays the print window. The user can print only the graph. He can also choose to print the log file and some comments added by the user in the comments tab. All will 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.

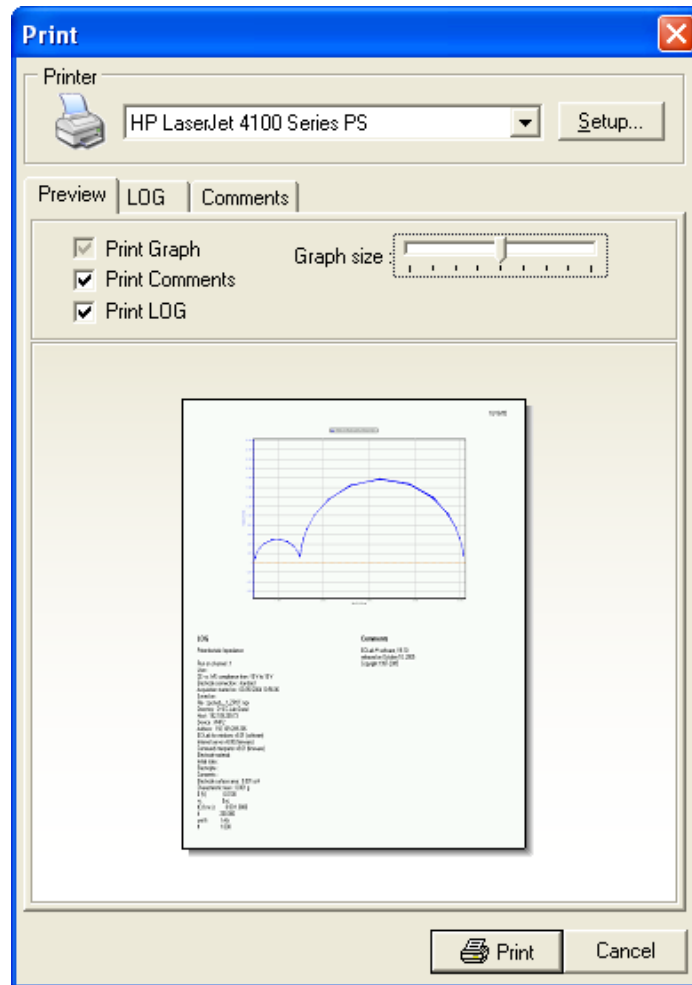


Fig. 58: Print window.

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

3.2.9 Multiple graphic in a window

The EC-Lab[®] Express software graphic window is capable of displaying several different and independent graphs. Four graphs can easily be displayed in the same window.

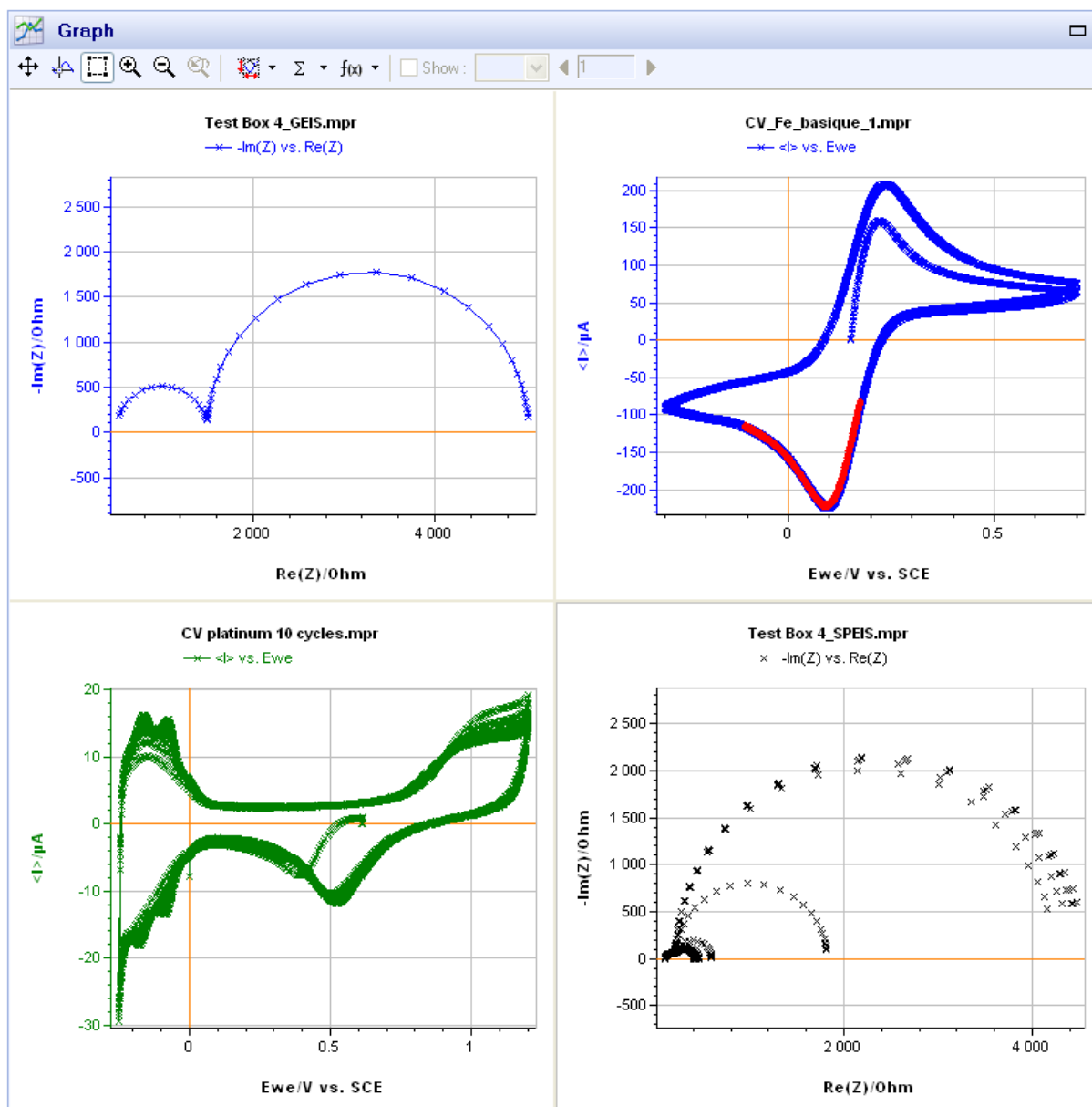


Fig. 59: Multigraph window.

To display several graphs in 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). Other graphs are not active. 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.

3.3 Graph Tools: Analysis tools

EC-Lab® Express software contains powerful analysis tools. These analysis tools are divided into five sections: Math, General Electrochemistry, Electrochemical Impedance Spectroscopy, Photovoltaic/Fuel cells and Corrosion. Each section contains its specific analysis tools or process. For example, in the corrosion section, it is possible to perform, **Linear Fit**, **Circular Fit**, **Tafel Fit**, **R_p Fit**, corrosion data can also be analyzed with efficient simulating program (Corr Sim). The analysis tools will be detailed in the following paragraphs.

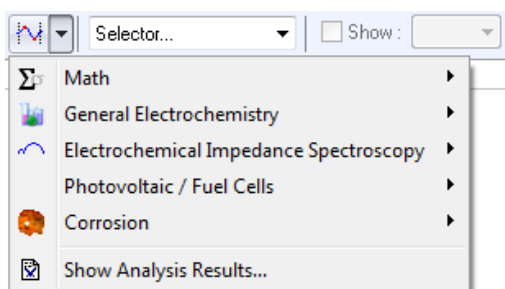


Fig. 60: Analysis tools menu.

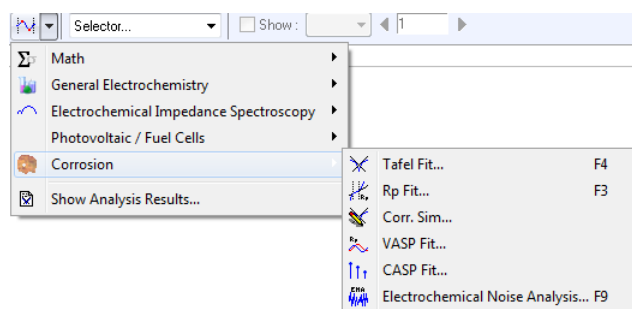



Fig. 61: Corrosion section of Analysis tools menu

First of all, before any analysis, select the trace to fit (if several traces are displayed on the graphic window) or the cycle (if the trace contains several cycles). There are two different ways to make a fit on a trace with EC-Lab[®] Express software. Two steps must be considered: the zone selection and the fit choice. One can be made before or after the other. The two ways to proceed are as follows:

- 1) Click directly on the selection button  of the graphic tool bar. On the graphic window select the zone that needs to be analyzed by holding the left mouse button. The cursor will draw a rectangle around the chosen zone. Once it is done, release the mouse button. The part of the curve selected should be highlighted in red and ready for analysis. Then select the required tools with the mouse right click
- 2) In the Analysis menu select one of the analysis tools. The mouse selection mode is automatically selected. The user has just to start a zone selection as described above.

Now a zone is selected on the trace and a fit window is displayed.

3.3.1 Zone selection

On the graphic display the zone selection can become very complex when several cycles or loops have been made during the experiment or when several zones are selected at the same time. In such a case, the software will ask you to select only one trace before doing a fit.

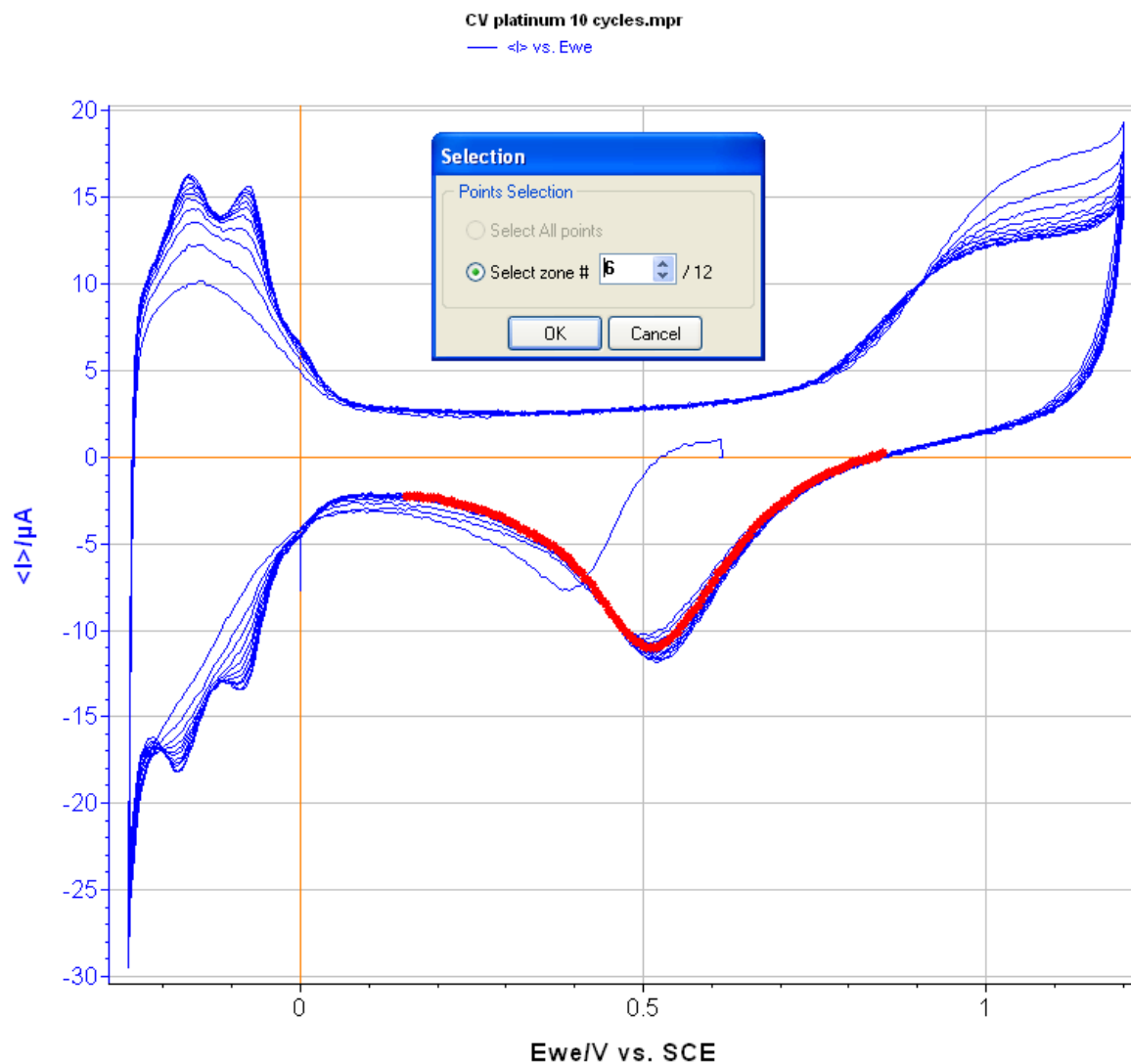



Fig. 62: Zone selection on the graph

In this example, the selection has to be done between 12 zones. To select the zone on which he wants to work, the user has to visualize all the zones and select the good one, for example the sixth zone (displayed in red). Then the user has to accept the selection by clicking on **OK**.

3.3.2 Math section

3.3.2.1 Min and Max determination

On the graphic display, select **Min/Max** with the Min/Max button  or with the mouse right click and the data points where the fit will be performed. The Min/Max analysis window is displayed. Select the zone to fit on the trace and click on **“Calculate”**. The Min and Max values are automatically detected. The minimum and maximum coordinates are displayed in the fit window. The minimum and maximum points are highlighted in red on the trace.

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.

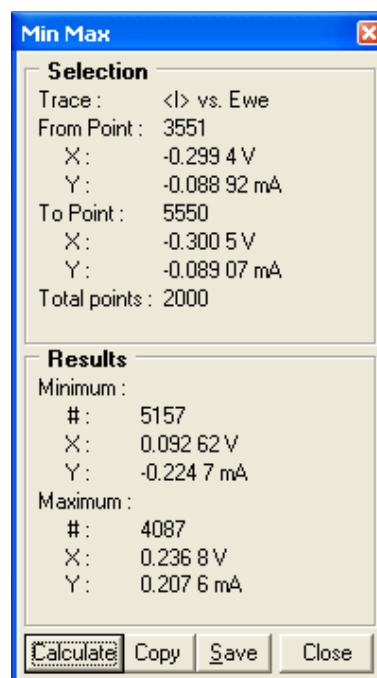


Fig. 63: Min/Max fit window.

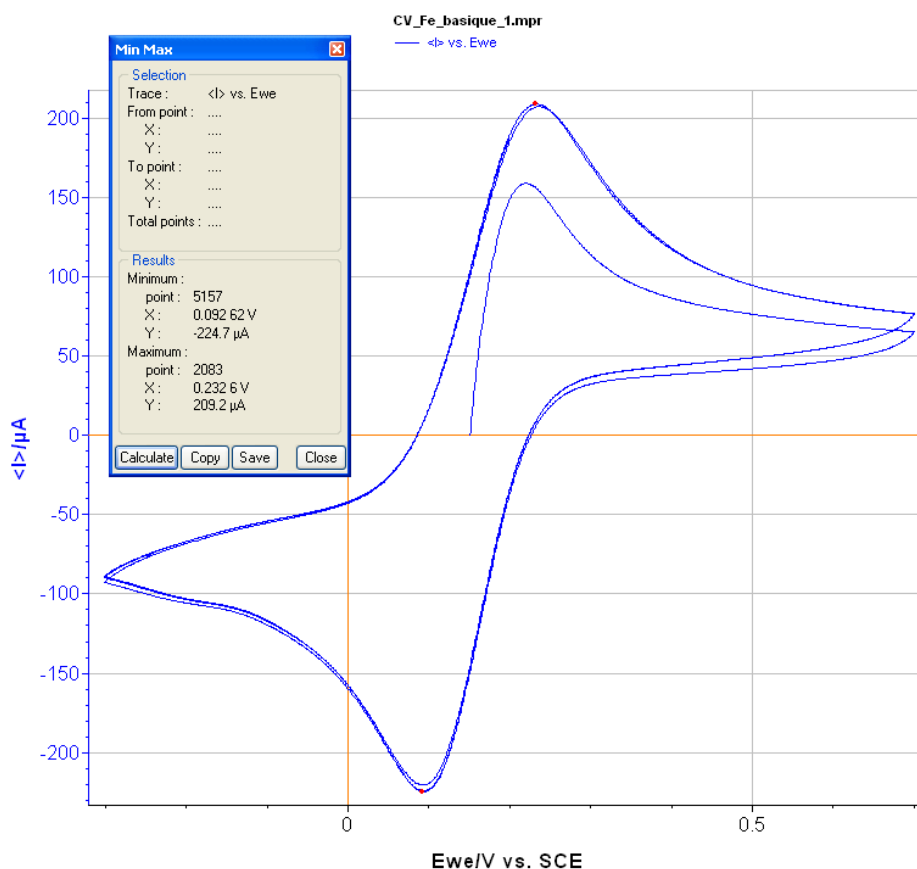


Fig. 64: Min/Max determination on the graph.

3.3.2.2 Linear Fit

When the zone to fit is selected click on “**Calculate**” in the linear fit window (Fig. 65). A straight line is displayed as a result of the linear regression between two green circles with the least square method fit (Fig. 66).

Move the circles with the mouse (by holding the left mouse button) to modify the range of data points selected for the fit. The new linear regression is automatically calculated when one of the circles 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 to be pasted in the print window comment zone or a text file. They can also be saved in a text file.

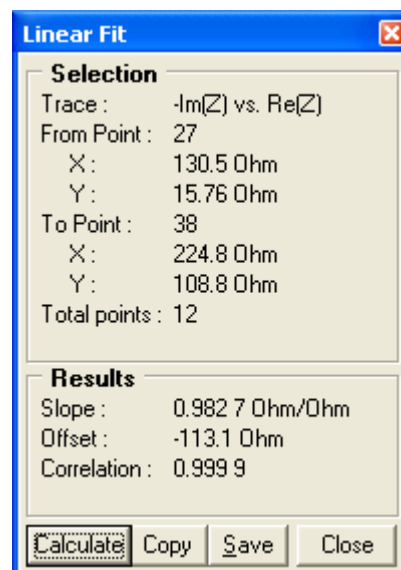


Fig. 65: Linear Fit window.

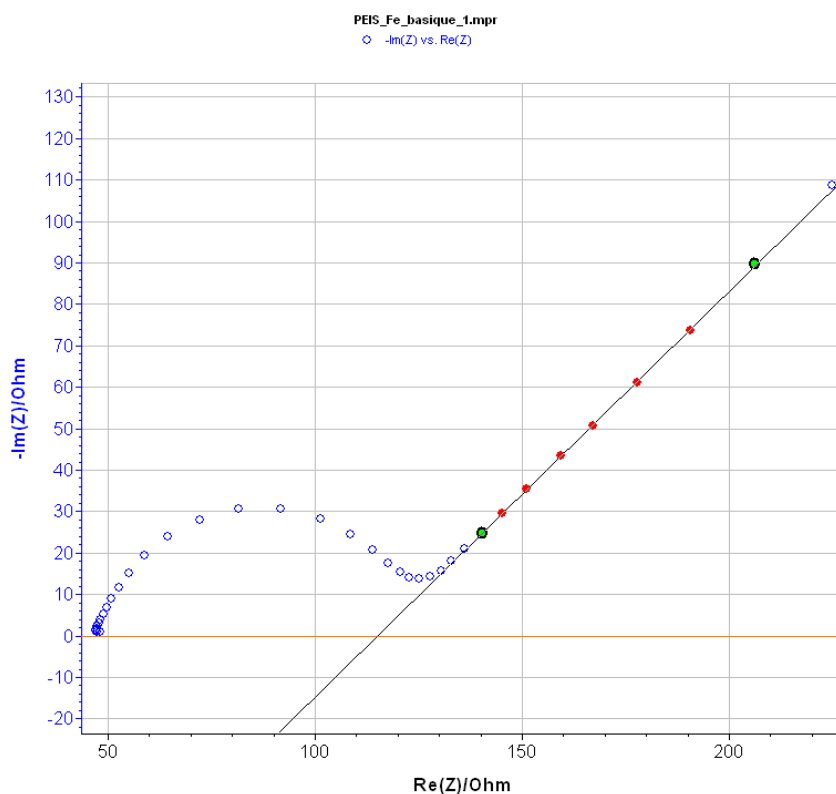


Fig. 66: Linear Fit on the graph.

3.3.2.3 Circle Fit

When the zone to fit is selected click on “Calculate” in the Circle Fit window (Fig. 67). 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. 68).

Move the cursors with the mouse (by holding the left mouse 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 for 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 the high X-intercept and low X-intercept. C is the capacitance determined for the experimental point in the selected zone where $-\text{Im}(Z)$ is the maximum ($Rc\omega = 1$).

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

Circle Fit

Selection

Trace : $-\text{Im}(Z)$ vs. $\text{Re}(Z)$

From point : 0

X : 48.15 Ohm

Y : 0.963 5 Ohm

To point : 23

X : 120.6 Ohm

Y : 15.33 Ohm

Total points : 24

Parameters

Iterative algorithm

Results

Center, X : 87.35 Ohm

Center, Y : -11.2 Ohm

Diameter : 83.71

Std Deviation : 0.305 2

Depression : -16°

Low x-intercept : 47.02 Ohm

High x-intercept : 127.7 Ohm

R : 80.66 Ohm

C : $6.254e-6$ F

Calculate Copy Save Close

Fig. 67: Circular Fit window.

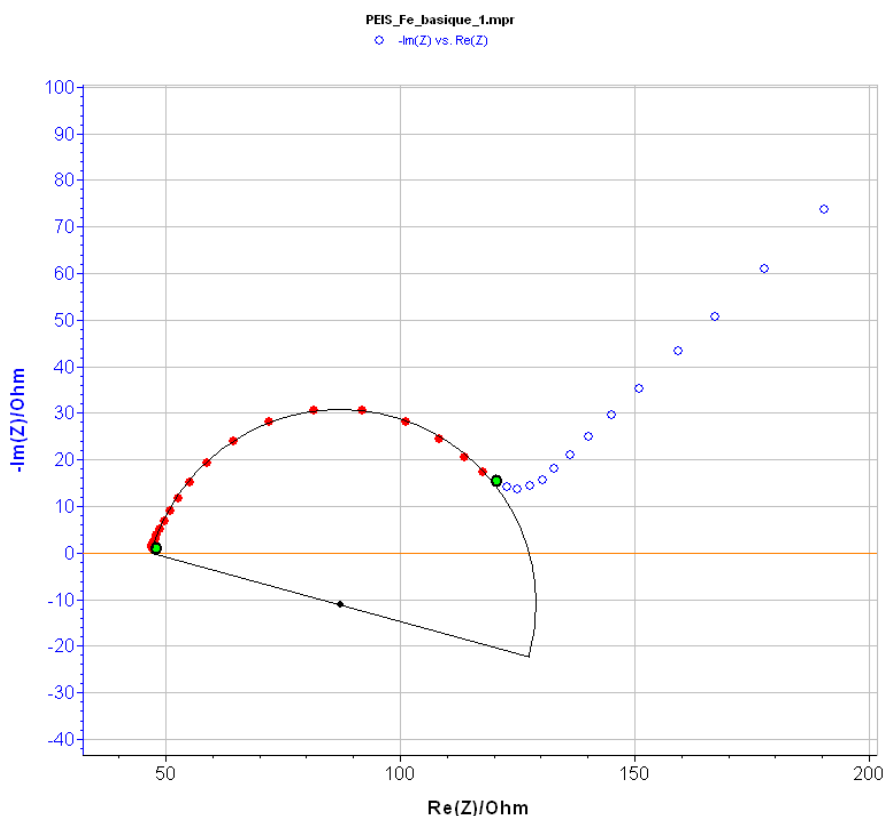



Fig. 68: Circular Fit on the graph.

3.3.2.4 Linear interpolation

An interpolation tool  is available in math section of Analysis tools menu. 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 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. Then a processed interpolated data file is created with the following name: filename_intpl.mpp.

This tool is very useful to subtract two data files. Indeed subtraction between two file is only possible when the files present the same regular distancing between each point.

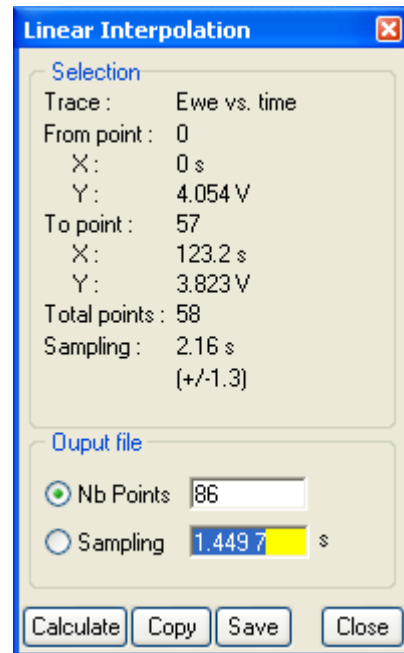



Fig. 69: Linear interpolation window.

3.3.2.5 Subtract files

A tool  for subtracting curves is available in math section of analysis tools menu. The raw data files are not changed after this analysis.

Indeed for some applications, it could be interesting to subtract two curves. The **“Subtract Files”** tool is available in the **“Math”** section.

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.

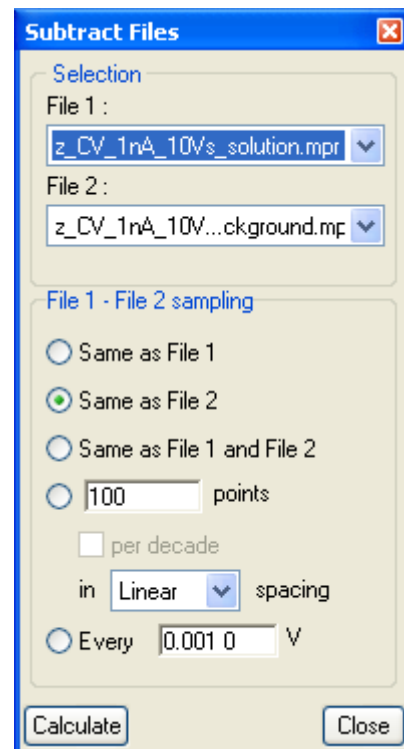


Fig. 70: Subtract files window.

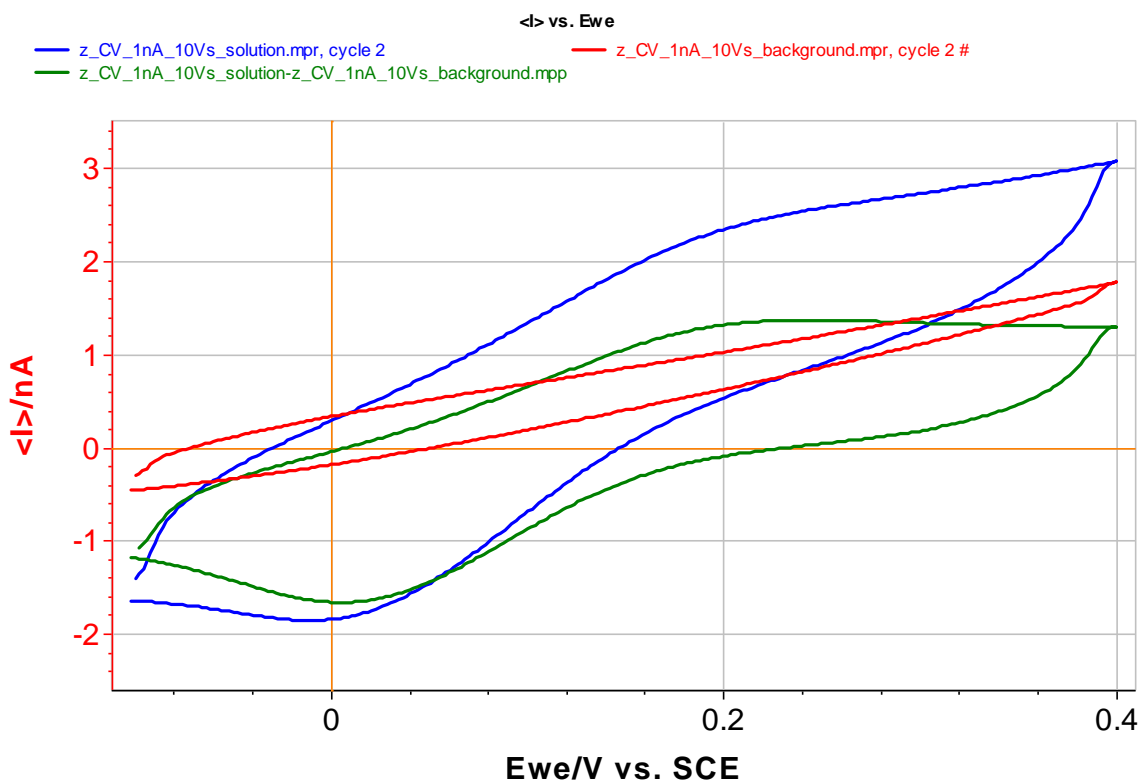



Fig. 71: Use of the Subtract Files tool on the blue and red curves. The Obtained curve is given in green color.

3.3.2.6 Integral

In the same way as the Linear Fit method, the user can calculate the integral value of a selected trace between two markers.

On the graphic display, select the **Integral** with the Integral button  in the math section and with the mouse right click on the data points where the fit will be performed. The Integral analysis window is displayed. Click on **Calculate**. Two markers delimit the integrated trace. The markers can be moved to adjust the selected fit zone. The fit is updated automatically. The integral is calculated according to X-axis. A pinkish area is displayed on the integrated zone.

The units of the integral fit result depend on the plotted data points. For a cyclic voltammetry the units will be A.V.

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.

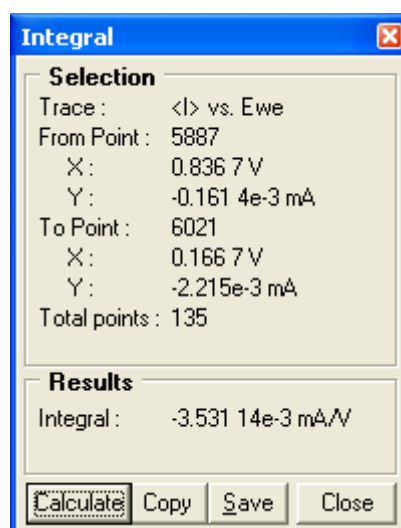


Fig. 72: Integral window.

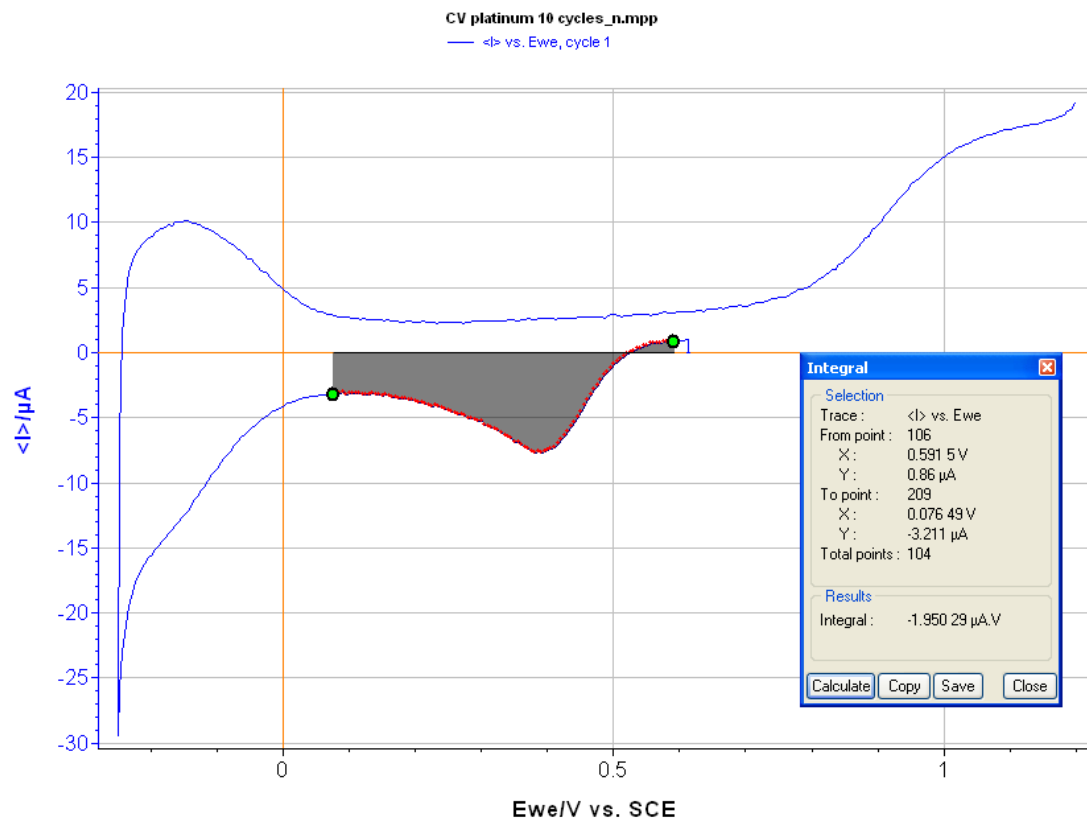


Fig. 73: Integral determination on a trace.

3.3.2.7 Fourier transform

This mathematical tool $\mathcal{F}\{\}$ allows the user to calculate the discrete Fourier transform (DFT), which is a specific kind of Fourier Transform. It transforms one function into another, which is called the frequency domain representation, or simply the DFT, of the original function. But the DFT requires a discrete input function and whose non-zero values have a limited duration.

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 selected, it is possible to choose the shape of the window where the calculation will be done. 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 another function or a signal (data) is multiplied by a window function, the product is also zero-valued outside the interval.

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

Rectangle: $w(t) = 1$

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

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

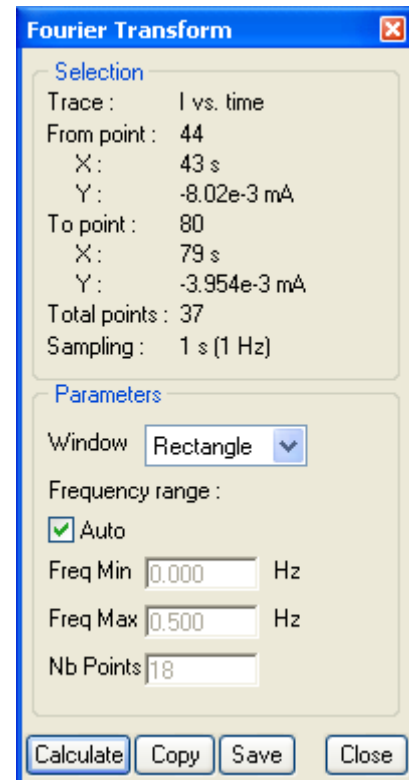
Hamming: $w(t) = 0.54 + 0.46\cos(\pi t)$

Blackman: $w(t) = 0.42 + 0.5\cos(\pi.5t) + 0.08\cos(2\pi t)$

Welch: $w(t) = 1 - \sqrt{|t|}$

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.



Rectangle
 Rectangle
 Barlett
 Hann
 Hamming
 Blackman
 Welch

Fig. 74: Fourier Transform window.

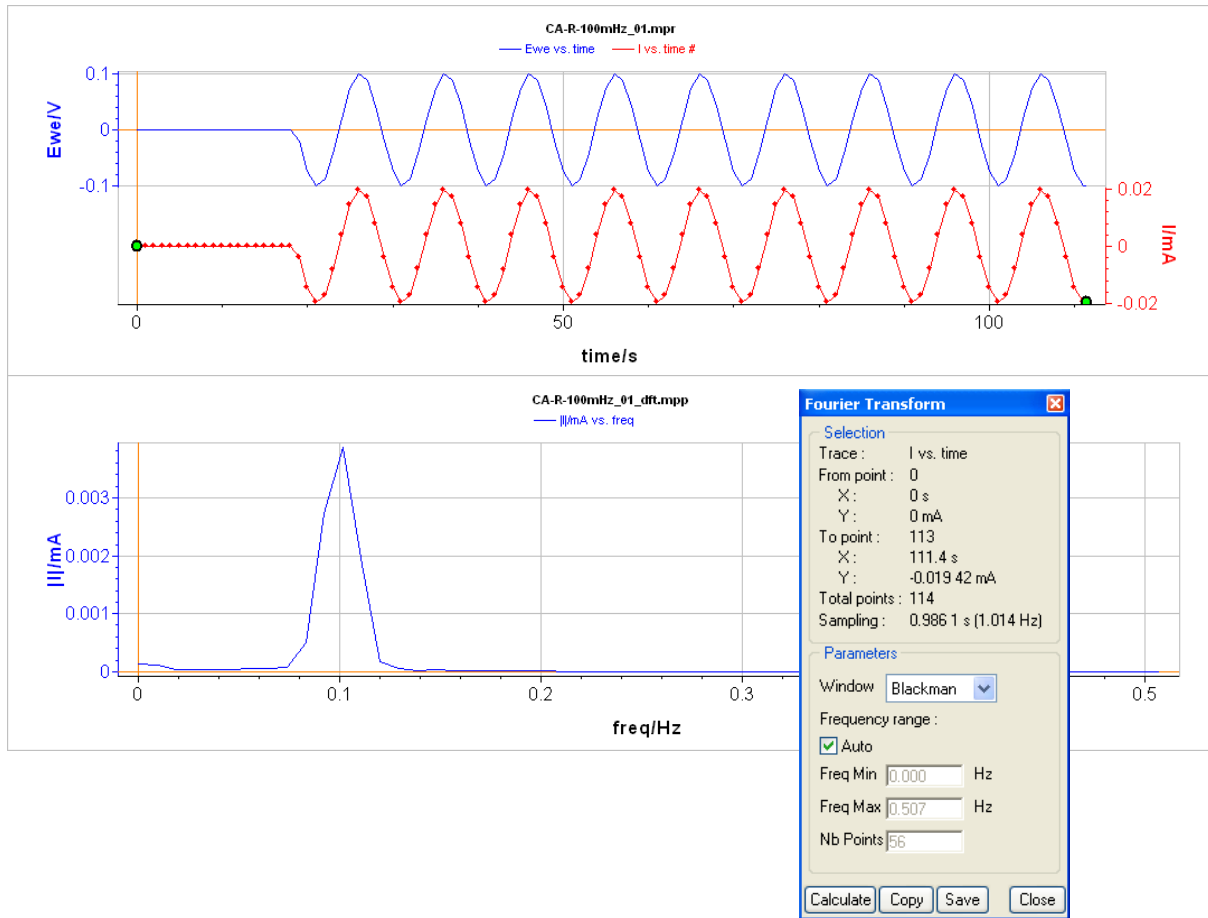



Fig. 75: Fourier transform analysis.

3.3.2.8 Filter

Data may be distorted by external perturbation, for instance the 50 or 60 Hz frequency signal coming from the electrical grid. The “**Filter**” tool  available in math menu allows the user to remove this additional signal and then yield to smoother results.

Several filtering methods can be set:

- Moving average method. For this method, the window size must be defined.
- Savitzky-Golay method. This method is based on polynomial calculation in a defined window. The window size and the polynomial order have to be set.
- 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) have to be defined (please refer to the Fourier transform part for more details on this point).

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.

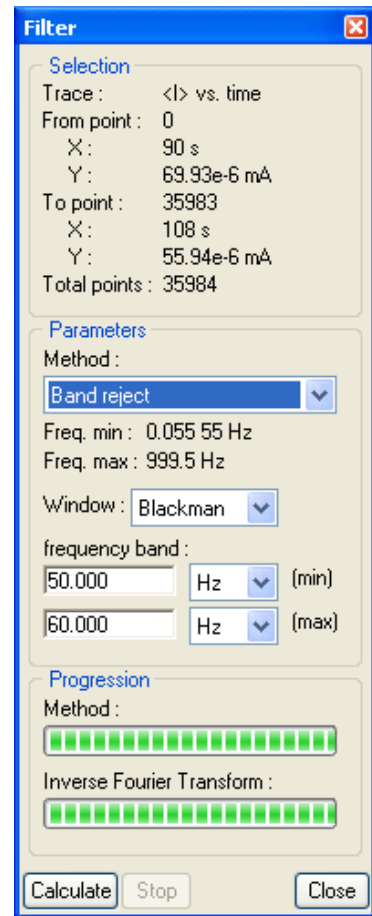


Fig. 76: Fourier Transform window.

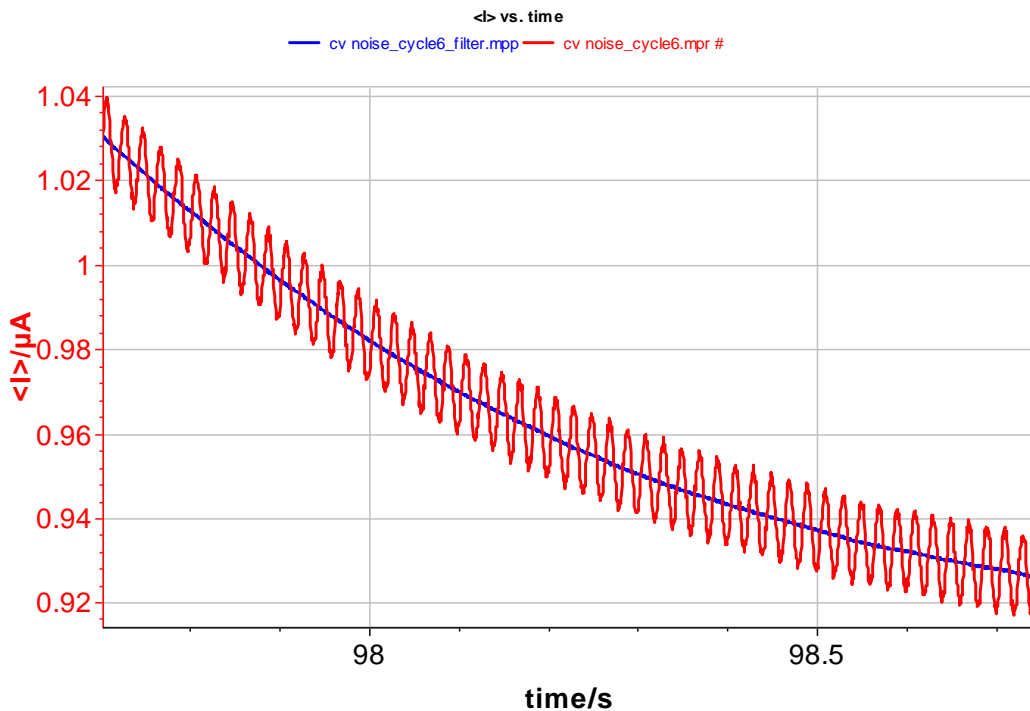


Fig. 77: Filter result. Red curve is the raw data file and the blue one is the filtered curve.

It is possible to model data with multiexponential behavior (up to order 6) with EC-Lab[®]-Express 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 section of “**Analysis**” tools menu.

3.3.2.9 Multi-Exponential Sim

The Multi-Exponential Sim tool allows user to plot a curve from a multi exponential equation. First of all, order of the multiexponential equation is selected (up to 6). Several units for x- 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.

3.3.2.10 Multi-Exponential Fit

As previously, the user can select the order of the exponential (up to 6). In the table (Fig. 99), a line is created for each parameter. Clicking on “Calculate”, the calculation without randomization or fit 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.

The “**Multi-Exponential Fit**” is able to perform a fit on every 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 x0 value cannot be fit and must be set manually by the user.

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.

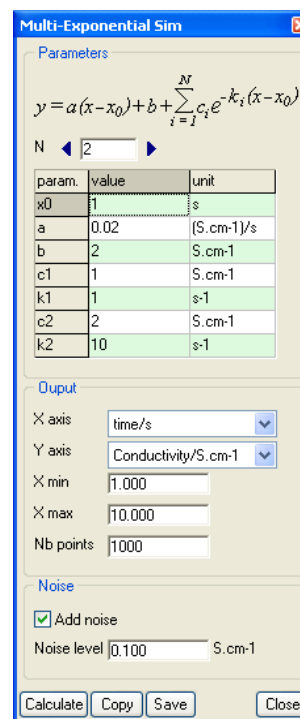


Fig. 78: Multiexponential Sim window.

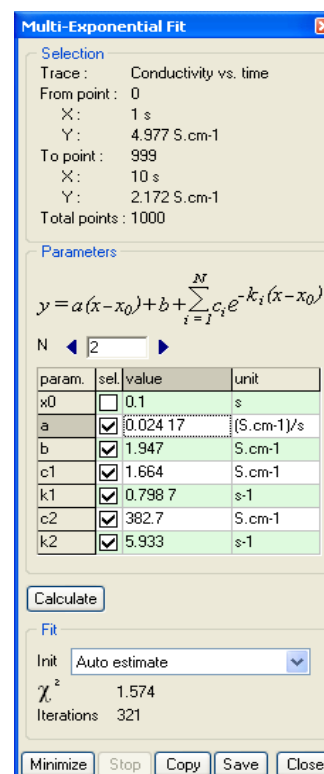


Fig. 79: Multiexponential Fit window.

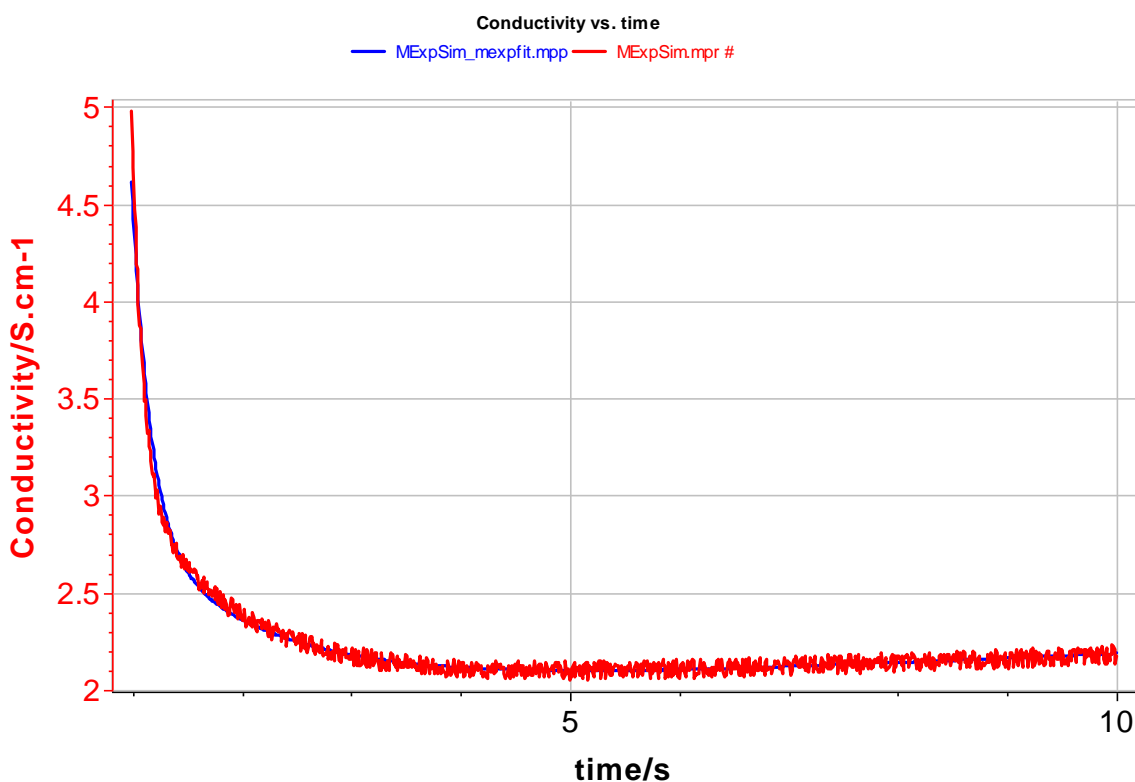




Fig. 80: Multi-Exponential fit result.

3.3.3 General Electrochemistry section

3.3.3.1 Peak Analysis

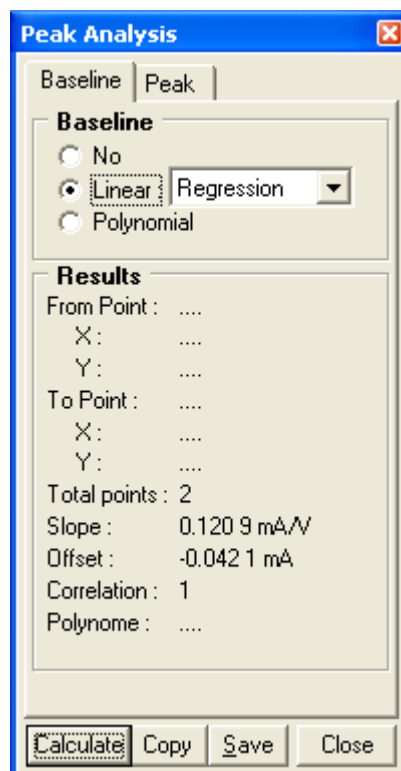
A peak analysis tool  is available with the EC-Lab[®]-Express software. Like other analyses with the EC-Lab[®]-Express software, the user has to select the analysis and then select the data points to fit or select the data points before choosing the fit. To select the peak analysis click on the  button 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. First the user must choose the baseline and second click on calculate to have the results.

3.3.3.1.1 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: A **manual** mode (with markers locked on the curve) or **regression** mode (with a linear regression made on the capacitive part of the curve before the peak) or in a **free** mode (two cursors defining a straight line unlocked to the curve).

If the user selects **Polynomial** type a polynomial baseline is plotted and adjusted to the data points in the following way: two data zones are used for the polynomial fit at the beginning and at the end of the selected zone (twenty first points and twenty last points of the selected data zone). The selected data zone and the polynomial fit are limited by two cursors that can be adjusted for a better fit. The polynomial fit used is defined as follows: $y = ax^3 + bx^2 + cx + d$. The results of the fit are automatically calculated when a cursor is moved.



7. Fig. 81: Baseline selection tab.

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 regression straight line determination is made with the least square method. Data points used for the regression are automatically selected in the 25 first percentage of the total point number between the beginning of the selected zone and the point corresponding to the max current value.

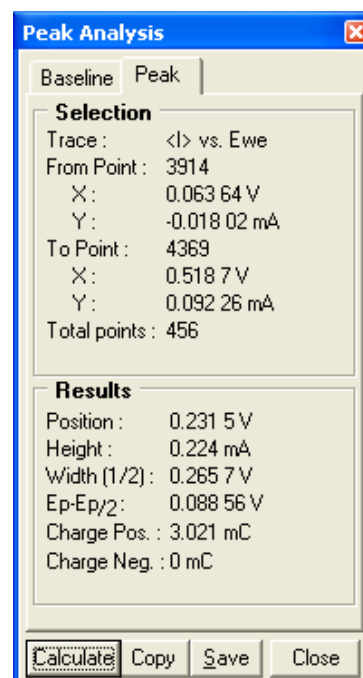
The results frame displays the baseline equation and the data point zone used for the regression.

3.3.3.1.2 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 in the peak analysis are selected by default from 35 % of the beginning of a zone (starting at the beginning of the selected zone and ending at the max current value), to the end of the zone. The data point zone for the analysis is shown in the **Selection** frame by the extreme points.

The results of the analysis are displayed in the **Results** frame. Several values for the peak are displayed: the position (E_p), height, width (1/2), $E_p - E_{p/2}$, charge pos. and charge neg. These values are explained below.

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.



7. Fig. 82: Peak results tab.

3.3.3.1.3 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.

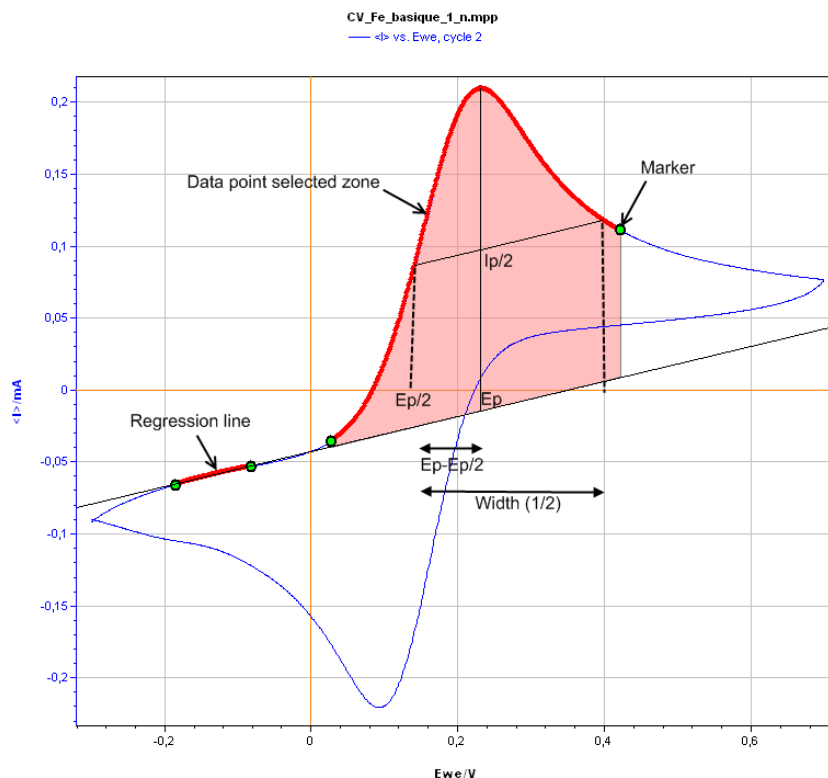


Fig. 83: Oxidation peak analysis on a cyclic voltammetry experiment using a linear regression baseline.

The different values in the result 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 potential peak 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 growing part of the peak.
- **Charge Pos.** is the charge corresponding to the integration of the peak versus time according to and above the baseline (in the case of an oxidation peak). The part of the peak considered for the calculation of the charge is limited to the green circle markers. This zone can be adjusted by moving the markers.
- **Charge Neg.** is the complementary part of the charge in the case where the selected zone crosses the baseline (below the baseline for an oxidation peak).

Note: it is possible to save the results of the analysis to a text file using the copy option. The results are copied to the clipboard and can be pasted in notepad or other software.

3.3.3.1.4 Results of the peak analysis using a polynomial baseline

In fact, it is often difficult to apply a linear regression to simulate the capacitive part of a curve or remove the beginning increasing part of a second current peak. A polynomial baseline could lead to a more significant fit. On the following figure a polynomial baseline has been used to do a peak analysis. The oxidative 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.

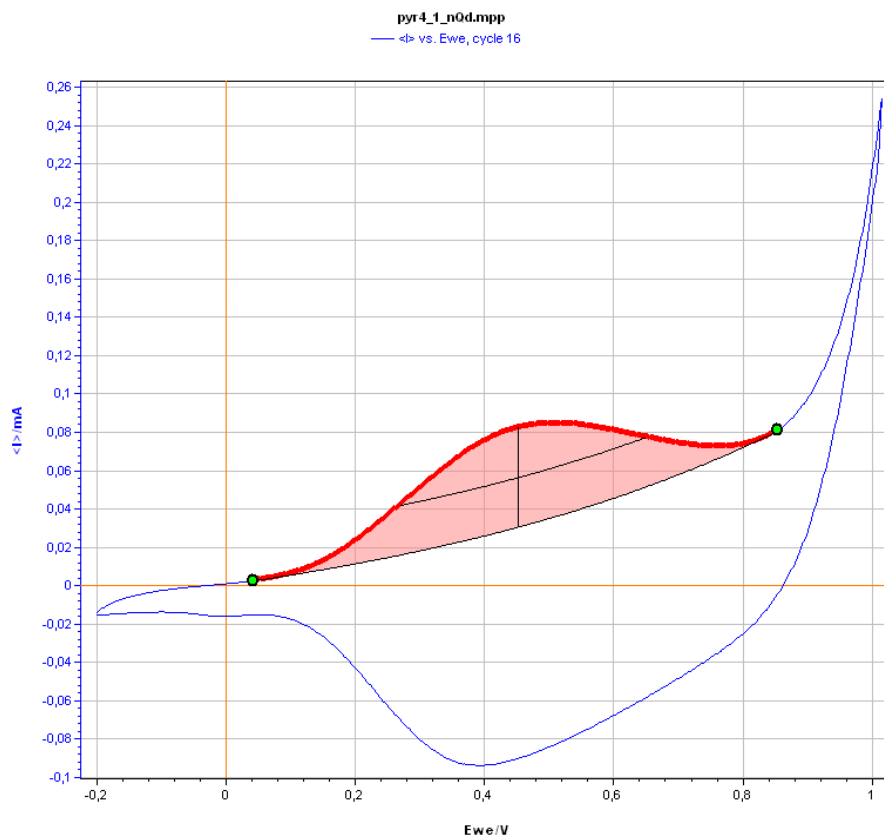



Fig. 84: Peak analysis on a cyclic voltammetry experiment using a polynomial baseline.

3.3.3.2 Wave analysis

The wave analysis  is the most useful tool for the analysis of experiments performed in a hydrodynamic regime (specially a rotating disk electrode).

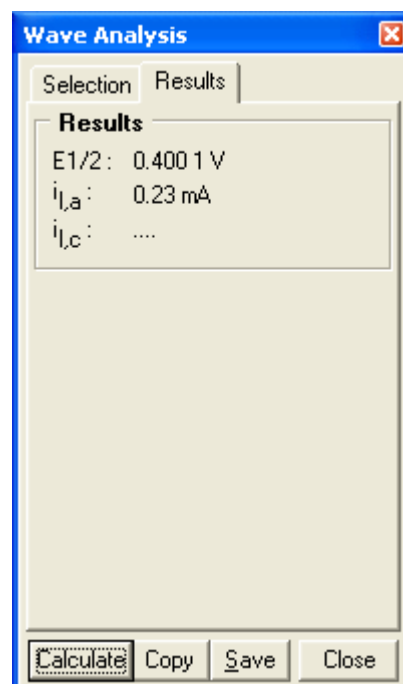
When a data point zone is selected click on “**Calculate**”.

The wave analysis is made according to two straight lines. These lines are defined using a linear regression fit. The software will automatically find the two parts of the curve with the weakest 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 extreme points.

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.



7. Fig. 85: wave results tab.

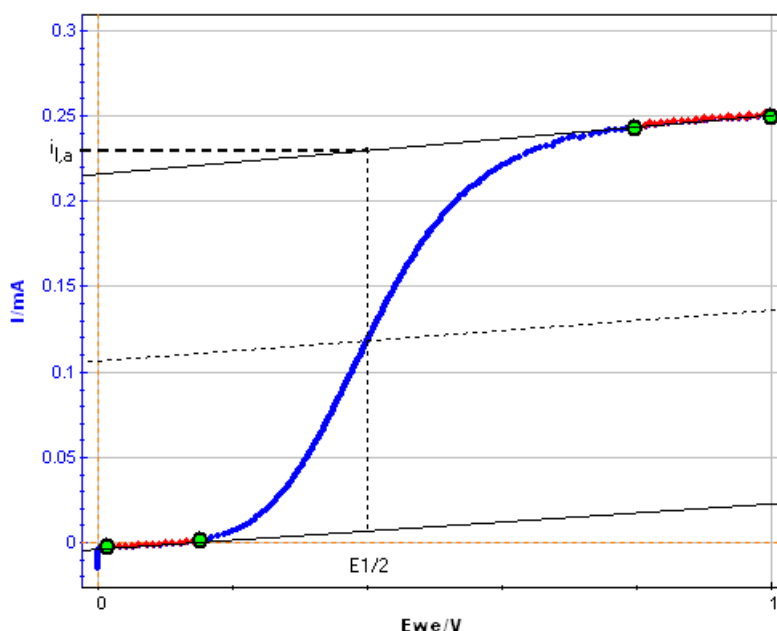



Fig. 86: Wave analysis on a curve resulting from a RDE experiment.

$E_{1/2}$ is the half-wave potential obtained by the intersection of the curve with the median between both linear regressions. $i_{l,a}$ is defined by the current value for $E = E_{1/2}$ on the top linear regression (for the oxidation reaction).

3.3.3.3 CV Sim

CV Sim  is a tool designed for the simulation of cyclic voltammetry curves. It is a useful tool to elucidate the mechanism of an electrochemical reaction.

To perform the simulation, it is assumed that:

- Only one specie (Red or Ox) is initially in the solution
- The Initial current is equal to zero. So the voltage sweep will start from the open circuit voltage.

First to perform the simulation, the user has 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 (EEEE). Depending on the number of electron transfers selected the corresponding number of tabs appears.

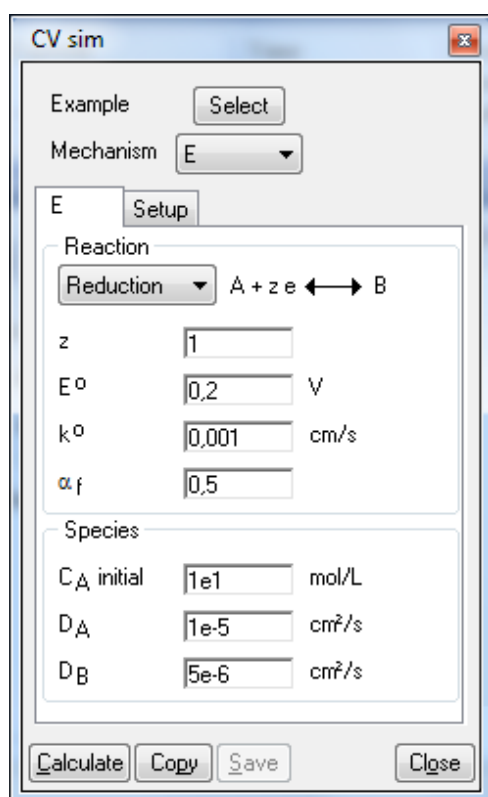


Fig. 87: CVSim window with a single electron transfer.

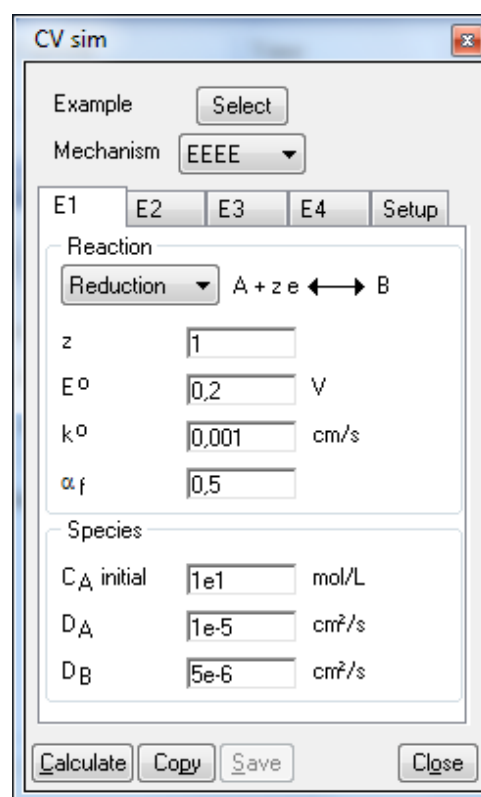


Fig. 88: CVSim window with several electron transfers.

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 electrons 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 specie x. As it is assumed that only one specie is initially in the solution, concentration is only set in the first step of the mechanism.
- D_x are the diffusion coefficients of the specie x.

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

Fig. 89: “Setup” tab of CV sim.

- 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 resistance 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

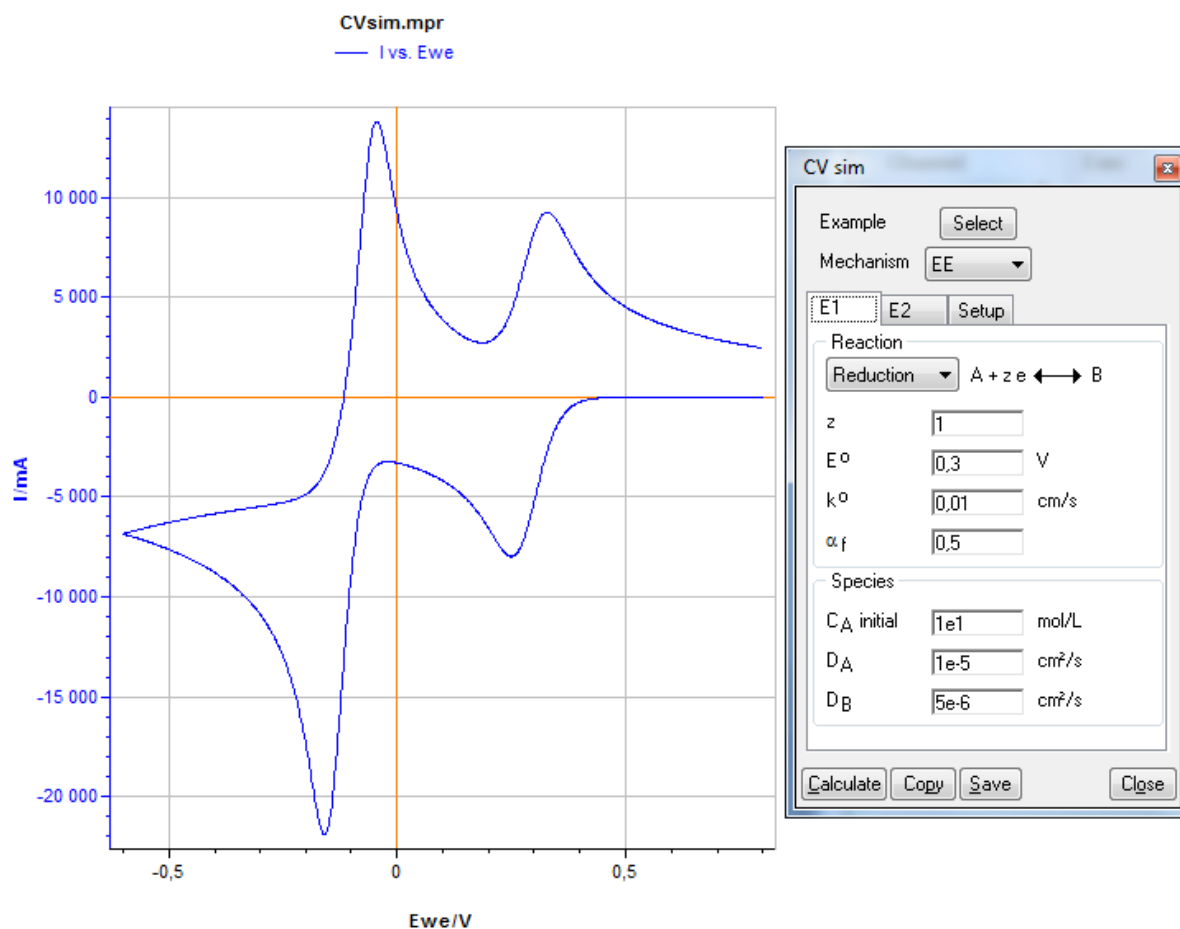
- Sampling

- 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.

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



7. Fig. 90: 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.

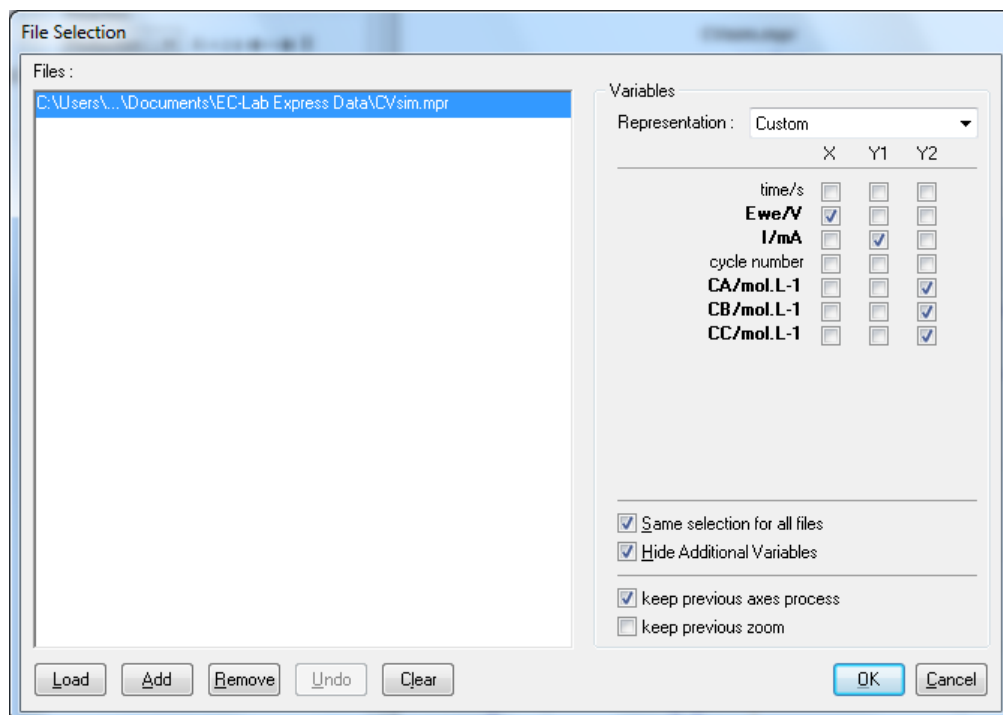
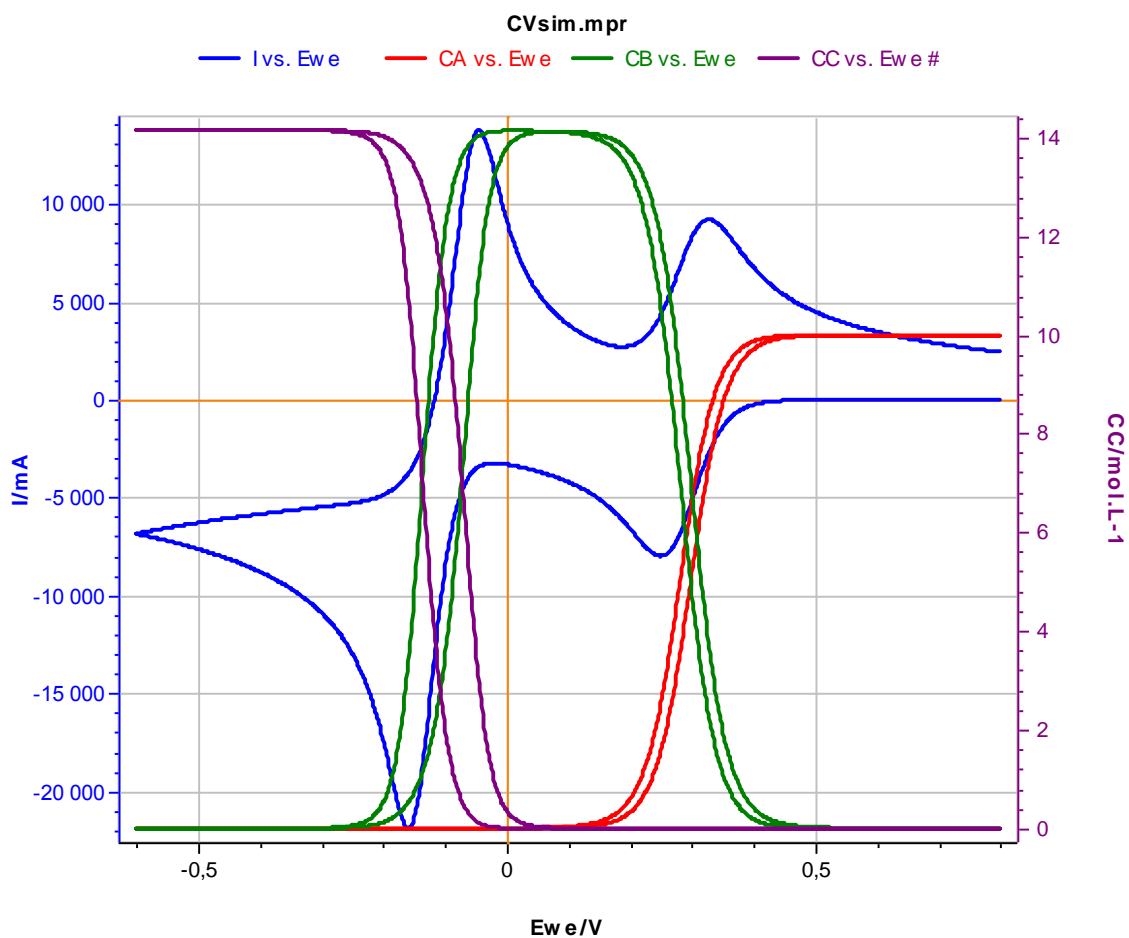


Fig. 91: Variable selection window to display concentrations.



7. Fig. 92: Interfacial concentration variation versus electrode potential.

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

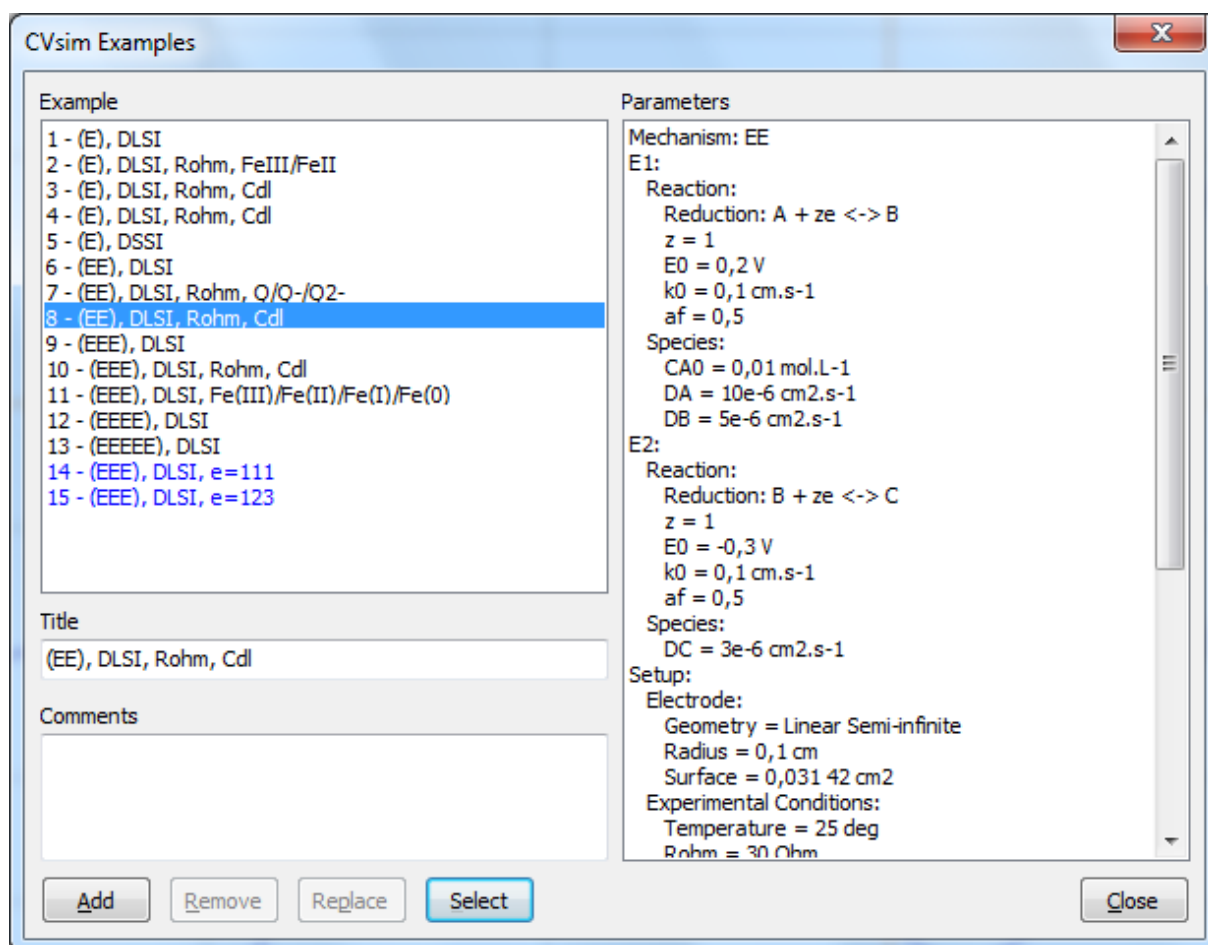


Fig. 93: CVsim examples window.

15 examples are available in this window. The corresponding parameters are displayed on the right column. When clicking the “Add” button, the corresponding curve is displayed.

3.3.4 Electrochemical Impedance Spectroscopy section

3.3.4.1 Z Fit

EIS analysis tools are powerful tools to determine the kinetic of an electrochemical reaction and values of the kinetic parameters. Electrochemical impedance data analysis allows the user to propose an electrochemical reaction mechanism. To be interpreted, electrochemical impedance data points need a comparison with an electrical circuit simulating the electron and electroactive species at the electrode surface/solution interface. Indeed, this process is assumed to be represented by an equivalent circuit of resistors, capacitors, inductors and diffusion elements. The total current is, in most cases, the sum of distinct contributions from the faradic process and double layer charging.

3.3.4.1.1 Electric equivalent elements: description

The impedance analysis tool contains currently 8 different electric components. These components are:

- R: resistor,
- L: self/inductor,
- C: capacitor,
- Q: constant Phase Element (CPE),
- W: Warburg Element simulating the semi-infinite diffusion,
- Wd: Warburg Diffusion Element simulating the convective diffusion,
- M: restricted Linear Diffusion Element,
- G: Gerischer Element.

3.3.4.1.2 Resistor: R

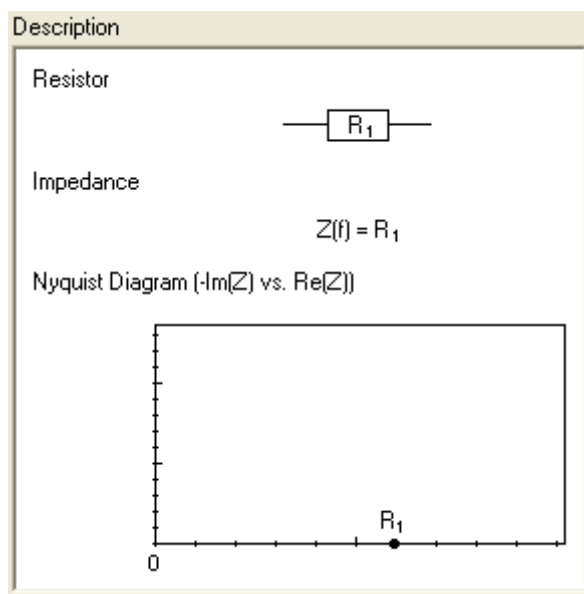


Fig. 94: Resistor element description.

The resistor element is defined as a passive component with a constant value when frequency varies. The Fig. 102 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 ($\text{Re}(Z)$) for an imaginary part to zero ($-\text{Im}(Z) = 0$).

3.3.4.1.3 Inductor: L

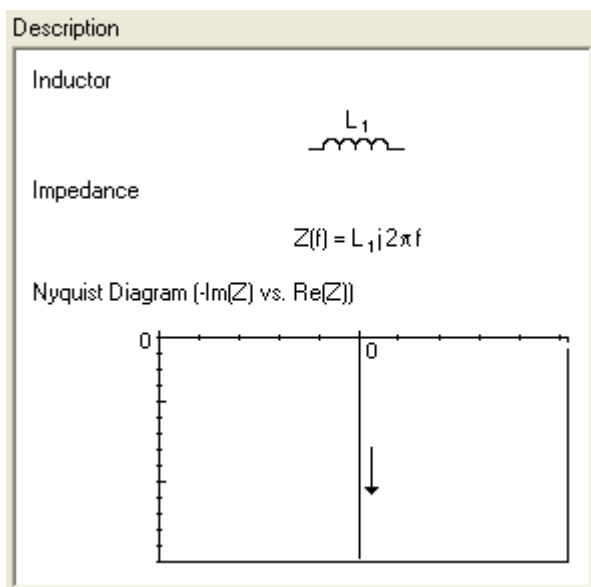


Fig. 95: Inductive element description.

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 ($-\text{Im}(Z) < 0$).

3.3.4.1.4 Capacitor: C

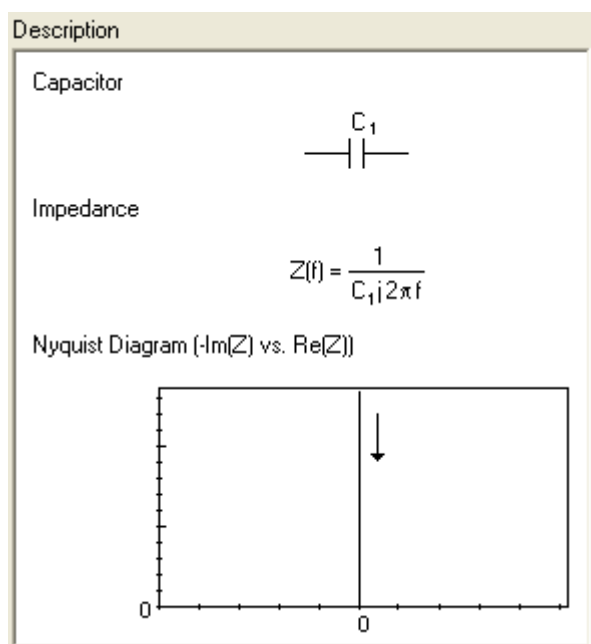


Fig. 96: Capacitor element description.

The capacitor impedance is also frequency dependent. The Nyquist plot of such an element corresponds to a vertical straight line in the imaginary positive part ($-\text{Im}(Z) > 0$). The faradic impedance decreases when the frequency increases.

3.3.4.1.5 Constant phase element: Q

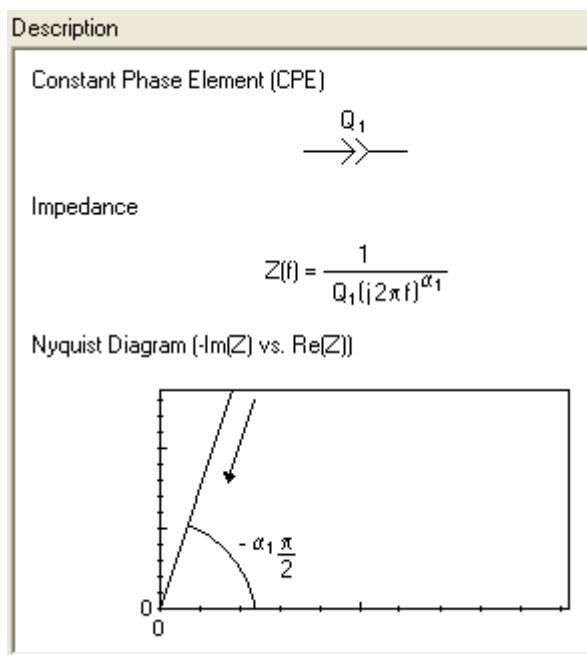


Fig. 97: Constant Phase Element description.

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 faradic impedance of the CPE decreases when the frequency increases.

3.3.4.1.6 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.

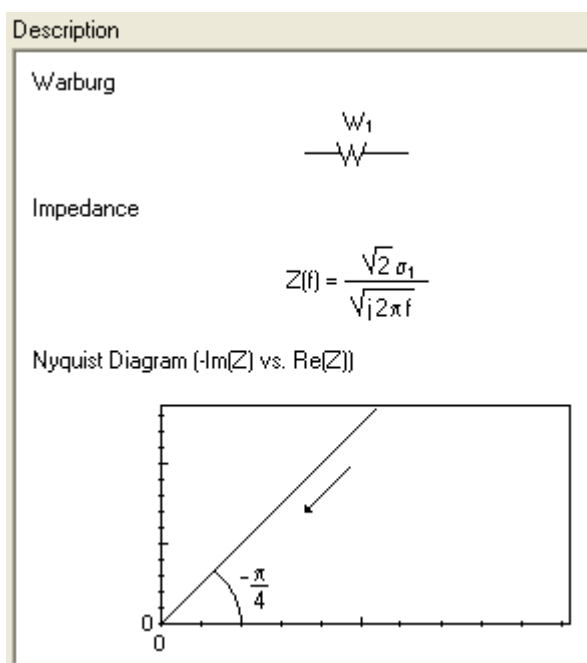


Fig. 98: Warburg diffusion element description.

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.

3.3.4.1.7 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 the material diffuses through the Nernst Diffusion Layer is described by W_d .

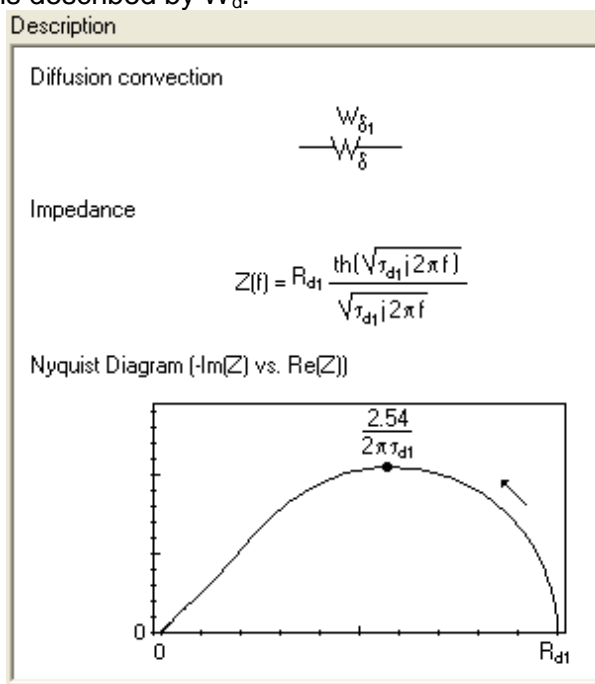


Fig. 99: Warburg element for convective diffusion.

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

3.3.4.1.8 Linear diffusion element: M

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

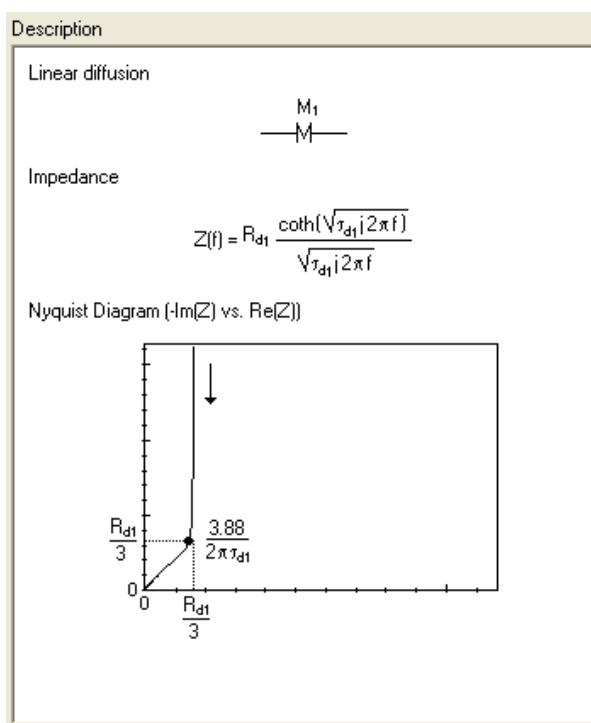


Fig. 100: Linear Diffusion element.

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

3.3.4.1.9 Gerischer element: G

The Gerischer circuit element arises when an electroactive species undergoes a chemical reaction in the bulk.

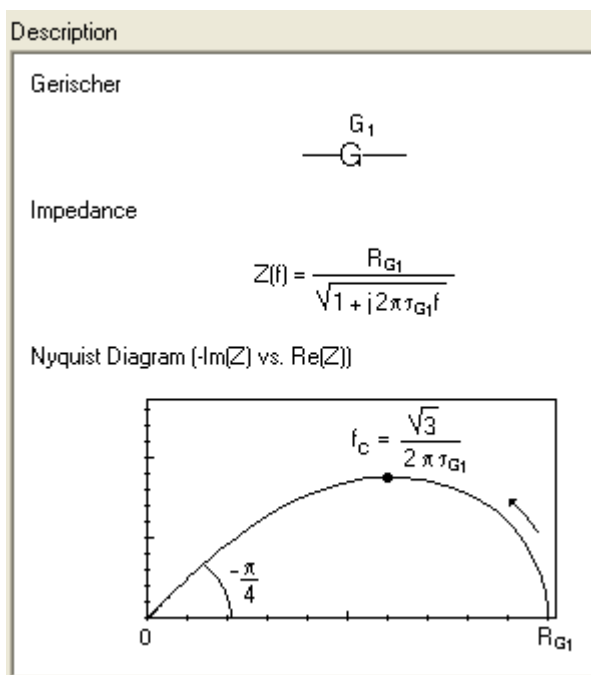


Fig. 101: Gerischer Diffusion element.

Note: This list can be continued by new electric elements whenever our customers define a significant one.

3.3.4.1.10 Z Fit selection window

The Z Fit 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 presents each parameter in row and for each of them, offers the ability to select it in order to be adjusted during the fitting, the ability to define the sign of the value (between +, -, +/-) by double clicking in the box, the unit and the standard deviation calculated when the Levenberg-Marquardt algorithm is used. When the selection box is not ticked the parameter value set in the cell will be considered as the correct value. It will not be modified during the minimization. The **Calculate** button will calculate and plot the data points for the parameter values set in the table without to randomizing or fitting.

3.3.4.1.11 Fitting methods

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 to do the minimisation (either one fit made on the **current** cycle displayed on the graph or the successive fits made on **ALL** cycles of the experiment). Default values are set for every parameter, but they never fit properly with the real experimental values. Before to do the fit and in order to help the algorithm to find the best values it is necessary to find a couple of values, as close as possible to the real one. Default values too far off will result in a divergence of the algorithm. A randomization has been added before the fitting to select the most suitable couple of parameter values (with the lower χ^2 value). The χ^2 equation used in this method is defined as follows:

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

with $Z_{meas}(i)$ is the measured impedance at the f_i frequency,

$Z_{model}(f_i, param)$ is 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. It can be assimilated to the weight of the impedance data points. It can be selected by the user to be 1 or $|Z|$.

Moreover, two fitting algorithms are available and the user can select between the Downhill simplex algorithm and the Levenberg-Marquardt algorithm. Both of them can be tried successively to choose the best results.

In the fitting method the user can select between different combinations:

- only Randomize,
- only Simplex fitting,
- only Levenberg-Marquardt fitting,
- combination of randomize followed by Simplex fitting,
- combination of randomize followed by Levenberg-Marquardt fitting.

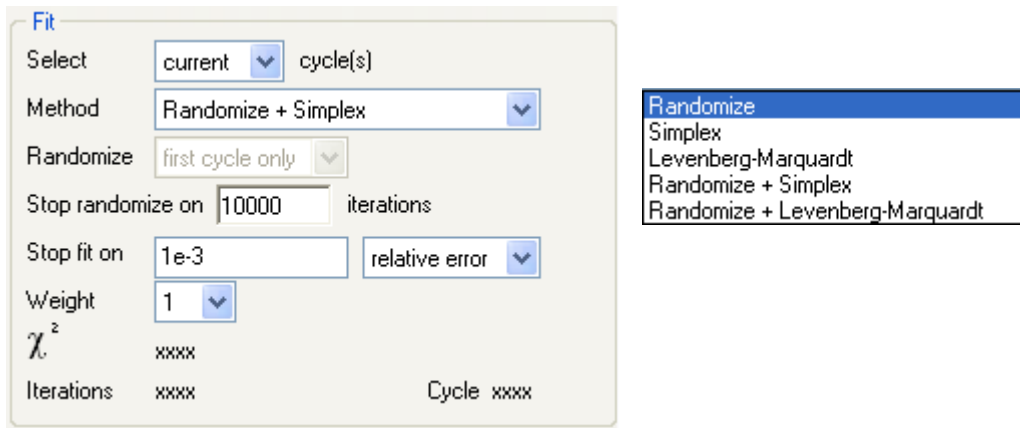


Fig. 102: Fitting method selection.

If **ALL** cycles are selected for the fit, the user will have the possibility of selecting the randomization on the first cycle only or on every cycle.

For both randomisation and fitting, the user can define the **number of iterations** and for the fit he can also select a **relative error**.

Another option, “**Weight**”, is available with two choices: either **1** or **|Z|** resulting in a different weight of data points at high and low frequencies. During the fitting process, the iteration number is displayed at the bottom of the window.

To start the operation, click on “**Minimize**”.

3.3.4.1.12 Application

Considering the data file (PEIS_Fe_basique.mpr) below. The following result may be obtained using the “**Randomize+Simplex**” option with the default parameter values:

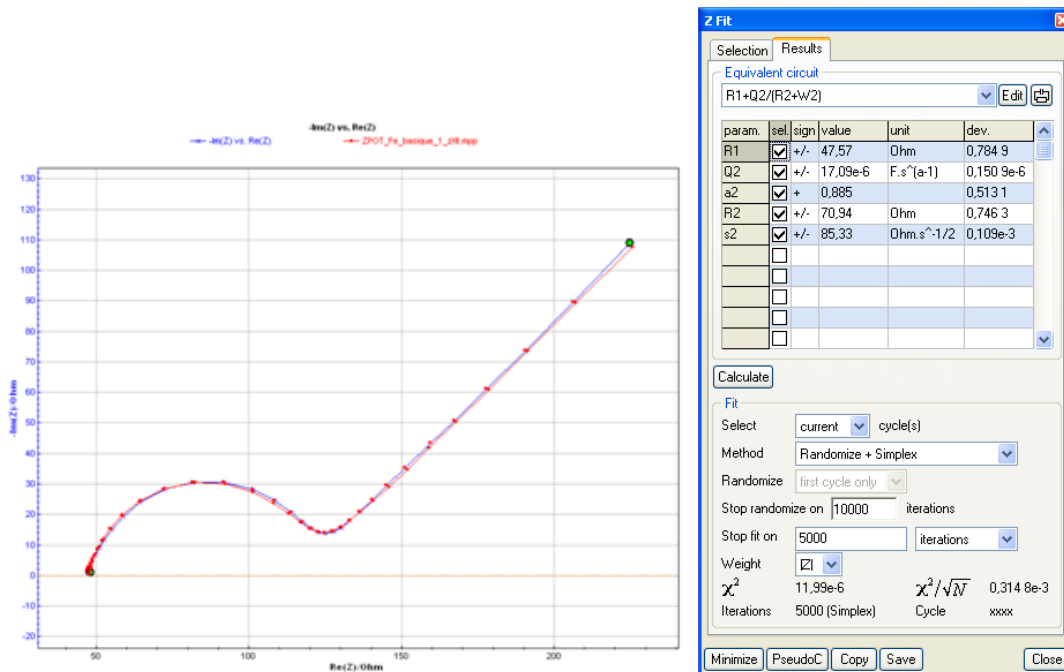


Fig. 103: Fit results with a combination Randomize+Simplex.

The randomization was stopped after 2000 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 the number of points selected for the fit, the higher the χ^2 value will be.

In the case of a weight $|Z|$ considered, the χ^2 value tends toward zero. In any case the value must be the smallest possible. 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.

3.3.4.1.13 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 at 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 randomisation on only the first cycle will lead to an automatic fit.

When the Minimization is launched a new graph is added at the bottom right hand 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.

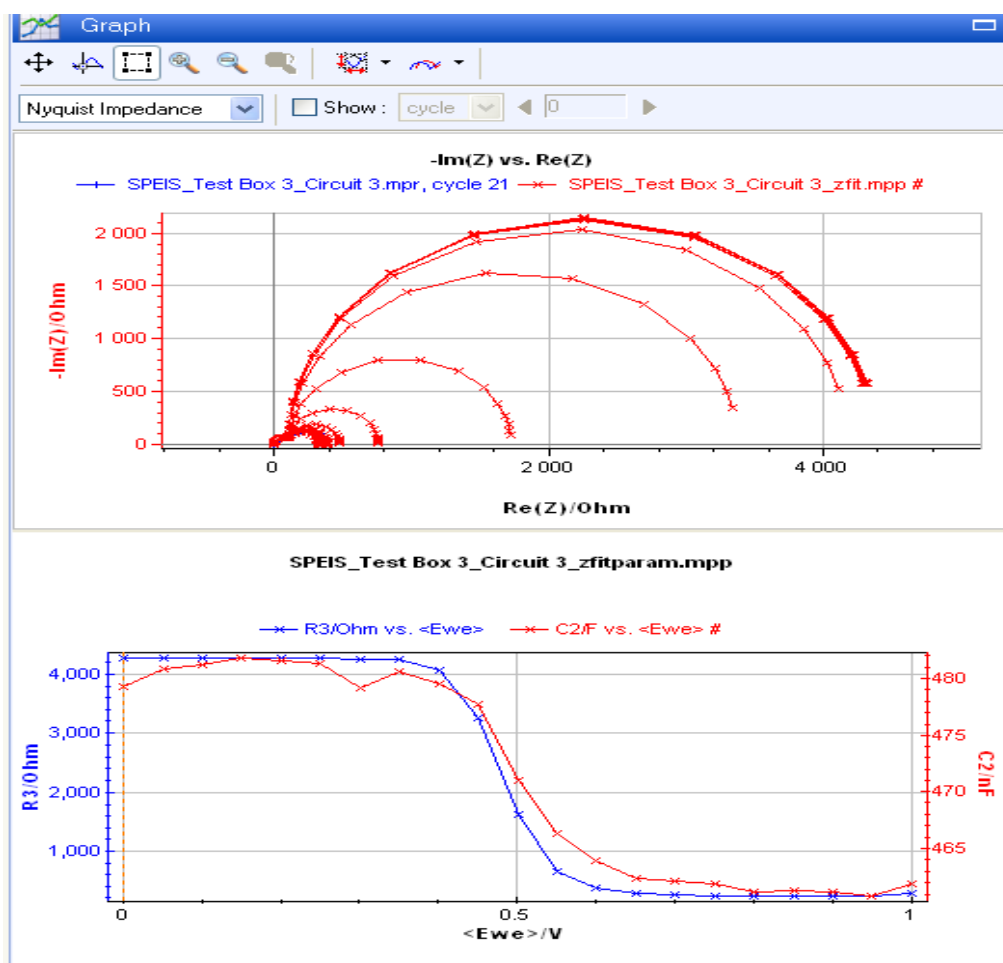


Fig. 104: Successive fits on cycles with randomization on the first cycle.

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

Note that the fit results are automatically saved in case of multi cycles treatment.

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.

3.3.4.1.14 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)

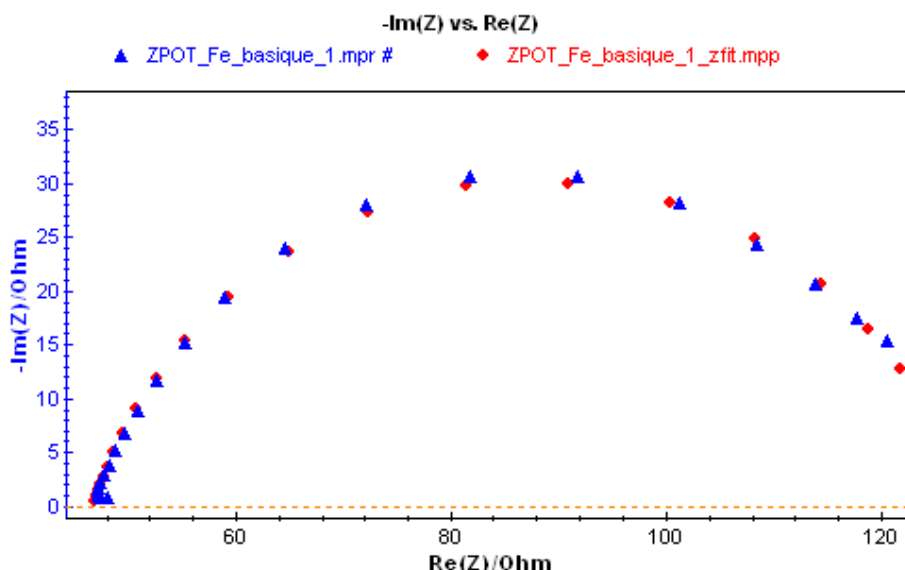


Fig. 105: Fit results with an R1+(R2/Q2) circuit.

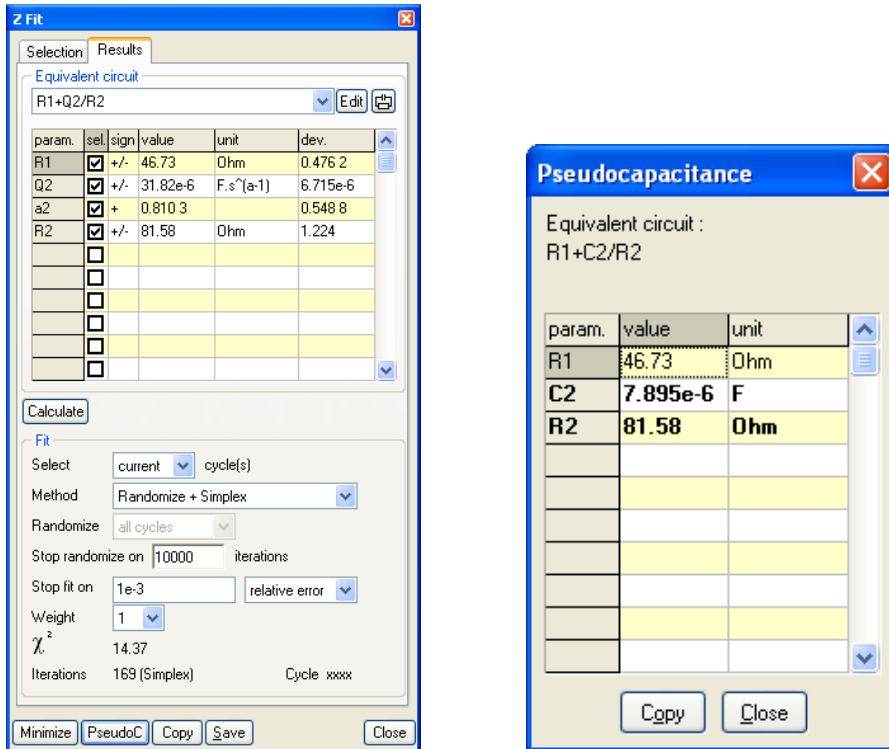


Fig. 106: Fit results and pseudo-capacitance calculation.

The results can be copied and pasted in another document.

3.3.4.1.15 Additional plots

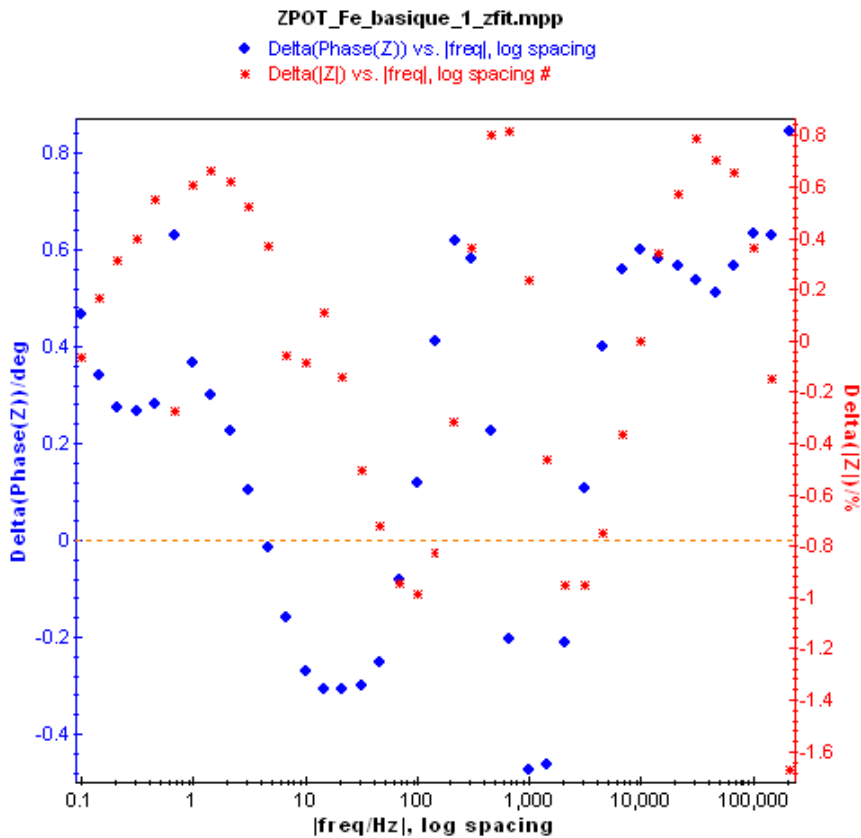


Fig. 107: Plot of the relative error on |Z| and phase vs. frequency (log spacing).

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:

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

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

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**”).

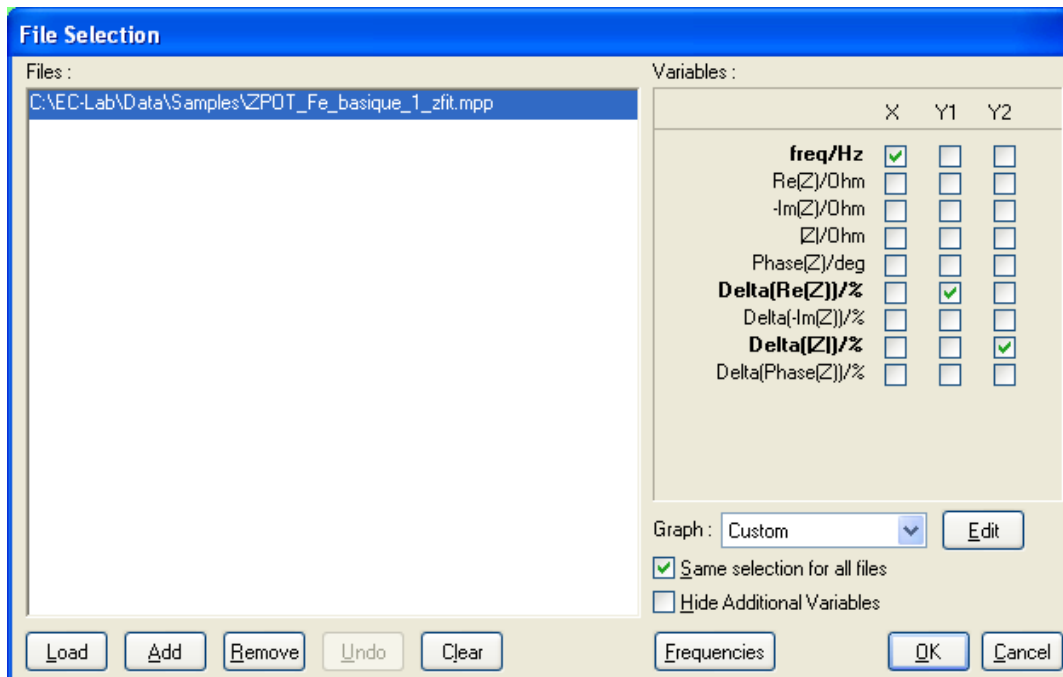


Fig. 108: Selector for the Zfit.mpp file offering the possibility to display the relative errors.

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

3.3.4.2 Z Sim

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's consider and fit the PEIS_Fe_basique.mpr data file below.

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 in the "File" menu ("Load data file..."). The following window will be displayed:

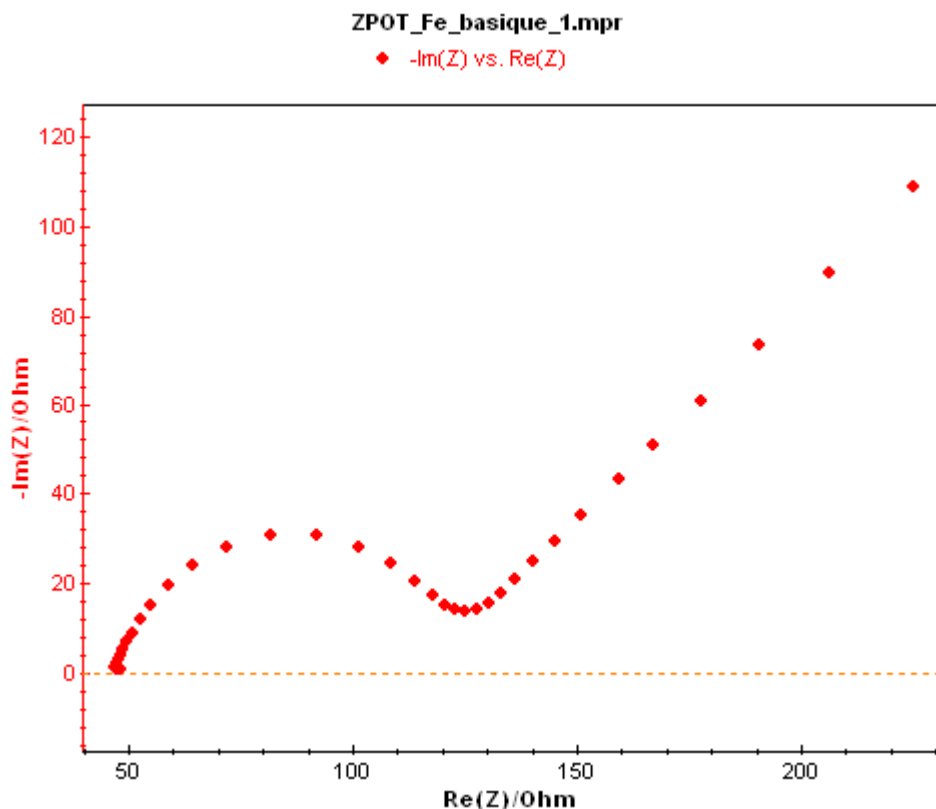



Fig. 109: Experimental Nyquist impedance data file.

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.

3.3.4.2.1 Z Sim window

1st step:

To simulate a curve with the same shape as the previous experimental results, click on ZSim icon  in the Analysis tools menu. Then the ZSim selection window appears with the corresponding graphic window. This window shows the simulated graph of the circuit with the values selected.

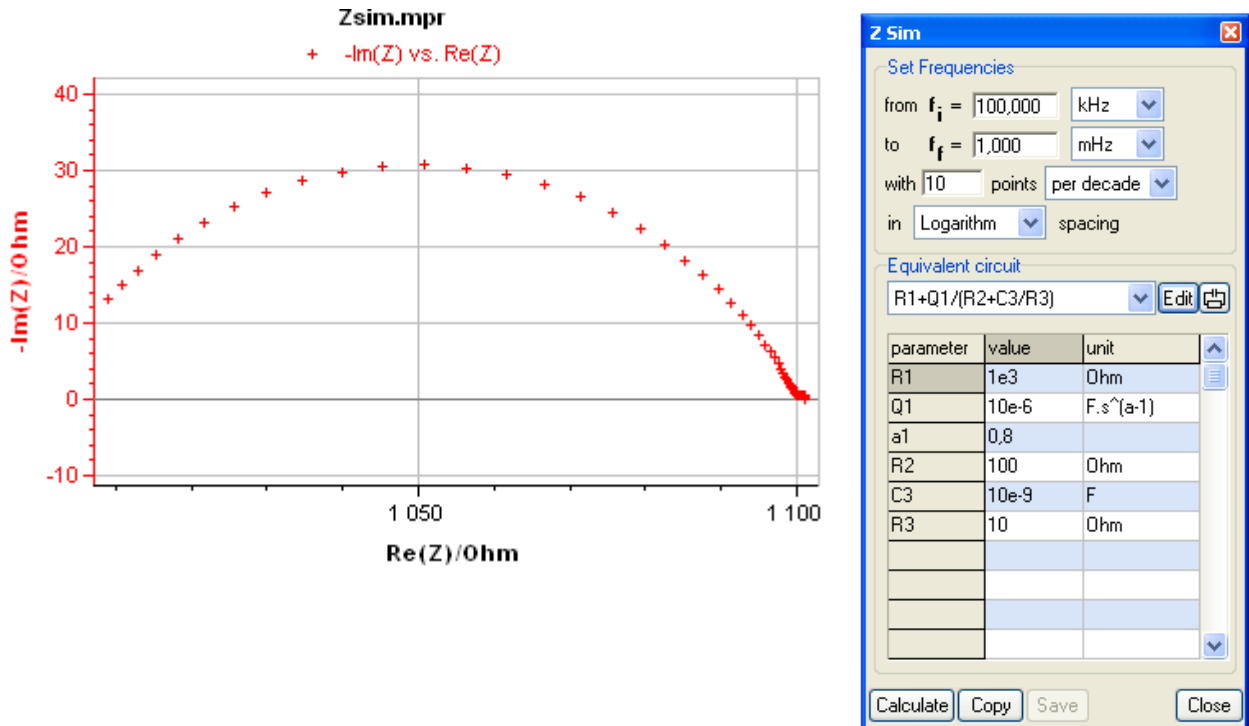


Fig. 110: ZSim menu and the graph corresponding to the selected circuit.

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

2nd step:

In the frequency frame, set the frequency range (between 500 kHz and 10 μ Hz) 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 his circuit in the "Edit" window. Click on "Edit" to display this window.

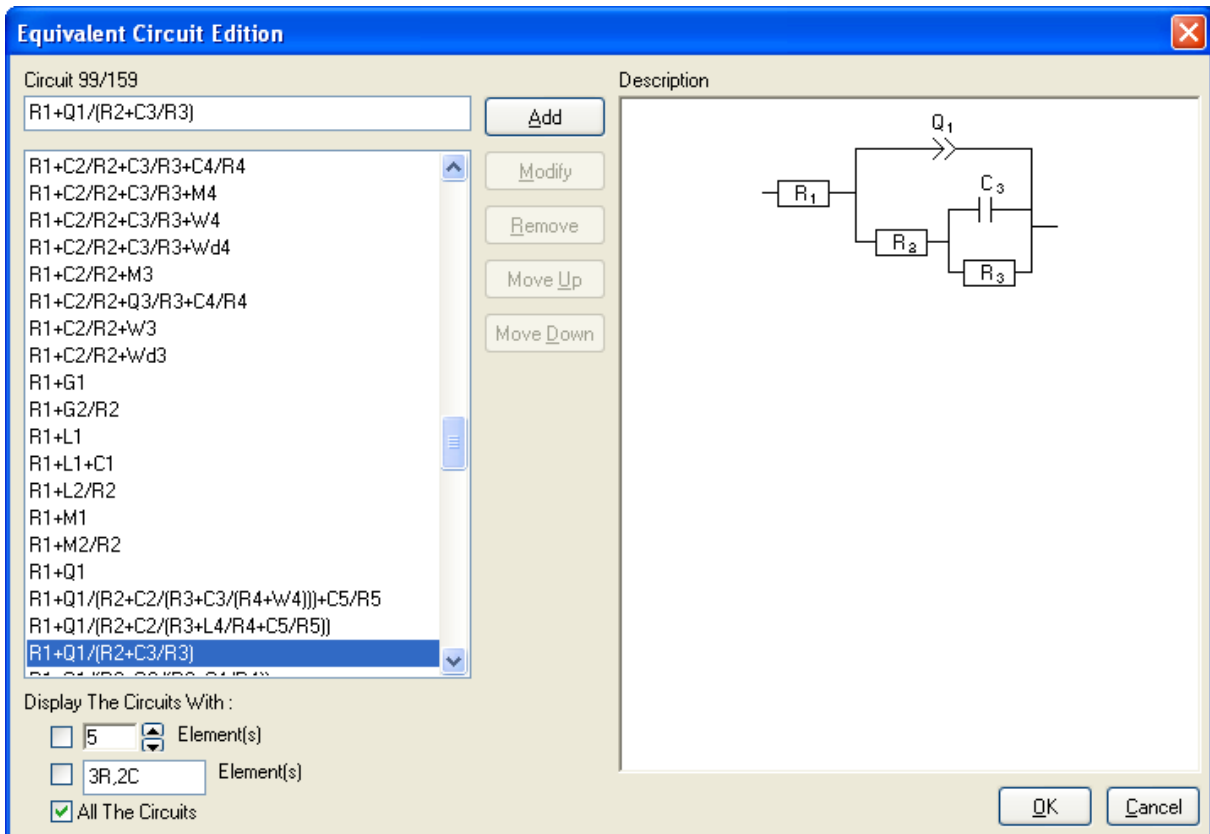


Fig. 111: ZSim/ZFit Circuit Edition window.

The circuit base contains more than 130 circuits. The user can create his circuits to be added (in blue) to the list. The main circuits have been described on the right side of the window (circuit scheme, faradic impedance equation and impedance Nyquist diagram).

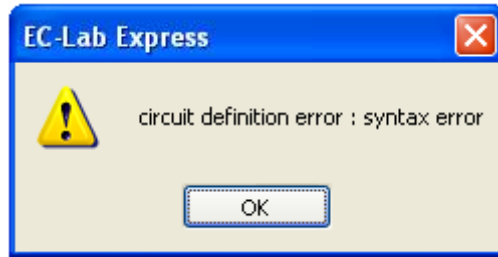
3.3.4.2.2 Circuit selection

To select a circuit in the list the user can select the displayed circuits according to the number of elements or the specific elements in the circuit (number of resistances, number of capacitors, ...).

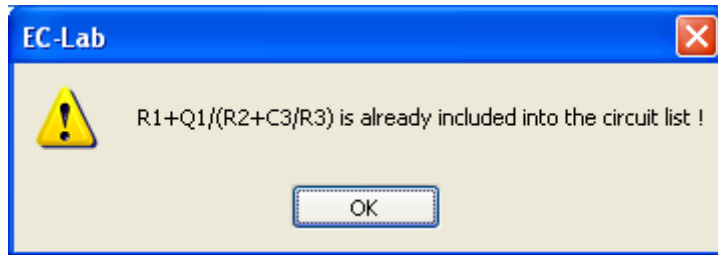
3.3.4.2.3 Description code

If the required circuit doesn't appear in the list, the user can create it. He must write it 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 separate the different 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 appear:



6- 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.

7- For the selected file (ZPOT_Fe_basique.mpr), find the correct circuit (Randles Circuit):

$$R1+Q2/(R2+W2)$$

8- Click on “Calculate” to show the corresponding curve on the graphic window.

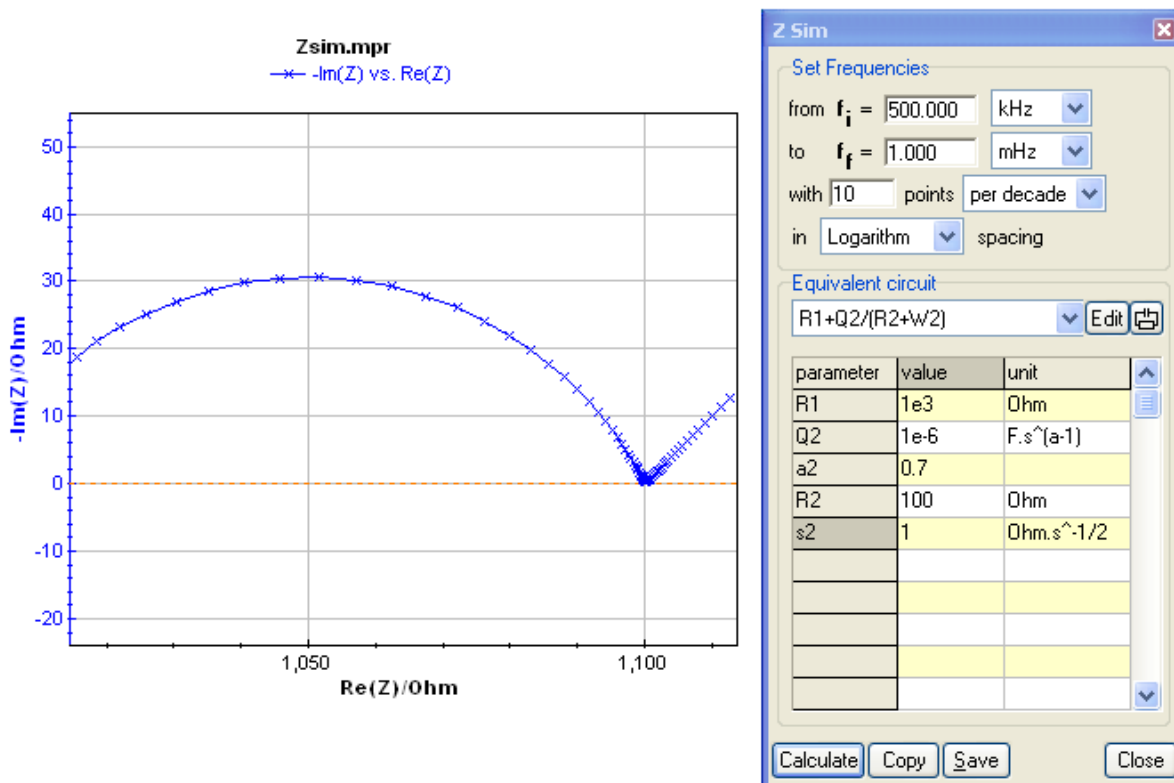


Fig. 112: ZSim Circuit Edition window.

- 9- 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**”.

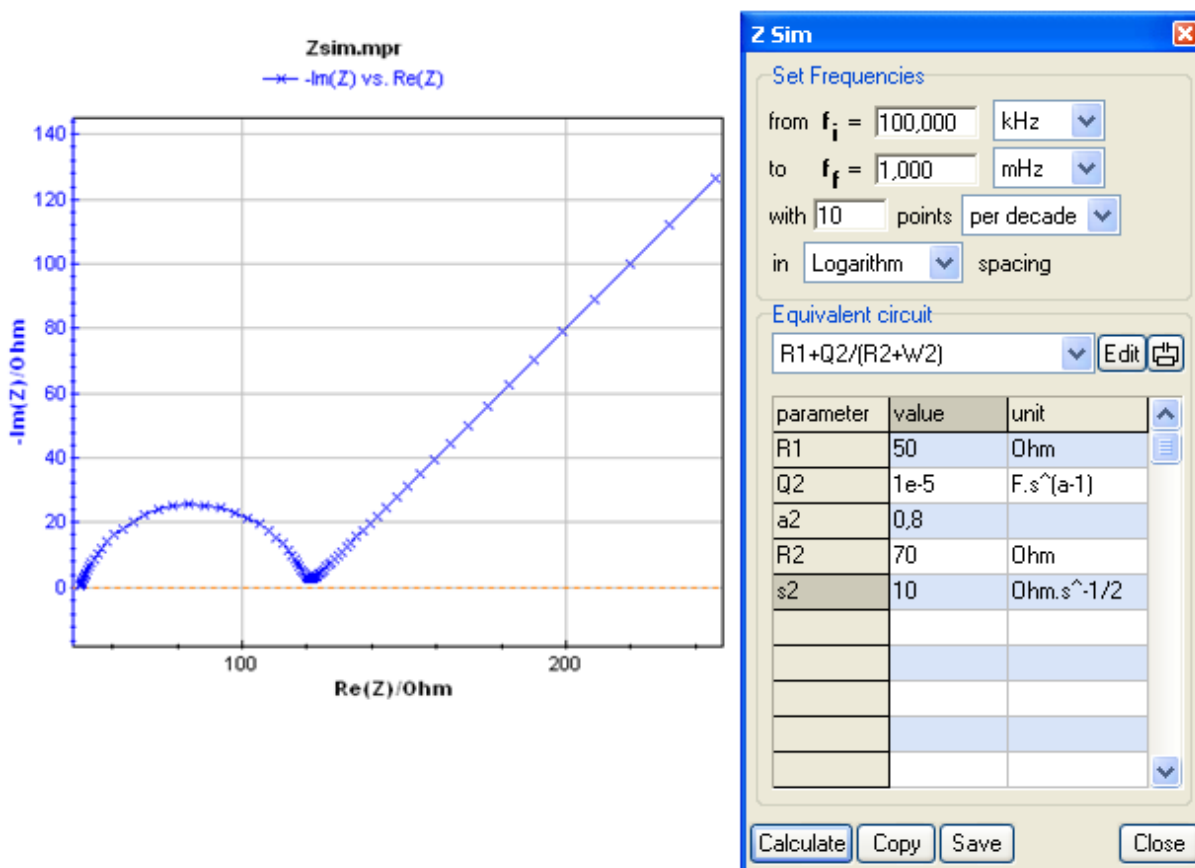


Fig. 113: ZSim Circuit Edition window with adjusted parameters.

The results can be copied to the clipboard and saved in a “Zsim.mpr” file. The user can modify parameters as much as he wants in the table. The new parameters will be implemented when clicking on “Calculate”. To store this simulation the user will have to give another name to the data file because a simulation is always created in the Zsim.mpr file.

3.3.4.3 Mott-Schottky Fit

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

3.3.4.3.1 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:

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

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

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

3.3.4.3.2 The Mott-Schottky plot

The Mott-Schottky plot presents $1/C^2$ versus E_{we} or $1/C$ versus E_{we} for each frequency with C calculated from the previous relationship: $\text{Im}(Z) = -\frac{1}{2\pi \cdot f \cdot C}$.

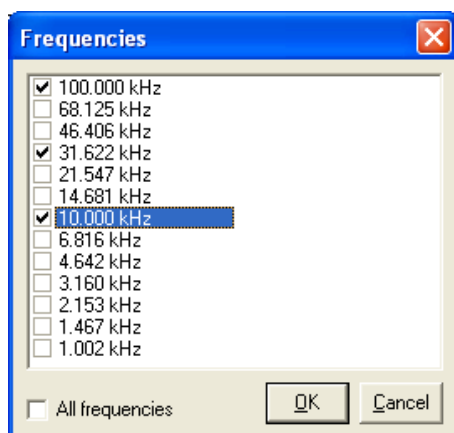


Fig. 114: Mott-Schottky frequency selection window.

When this plot is selected, the window on the left is displayed to select the frequencies. The user can select several or all frequencies. 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. Use the shift key to display the frequency.

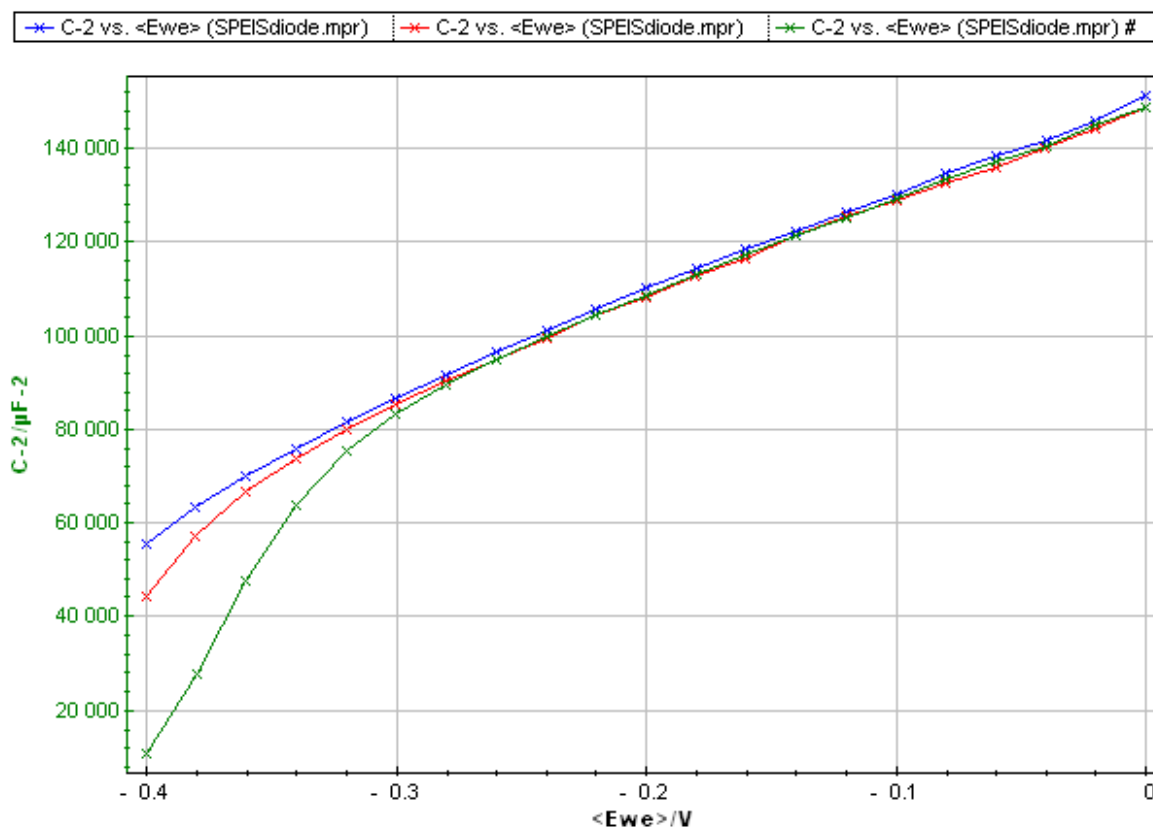



Fig. 115: Mott-Schottky plot.

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

3.3.4.3.3 The Mott-Schottky Fit

The Mott-Schottky Fit  is a graphic tool introduced with the SPEIS technique to determine semiconductor 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 ($1/C^2$ vs. E_{we}) of the experiment must be displayed on the graph. This plot shows one trace for each selected frequency.

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.

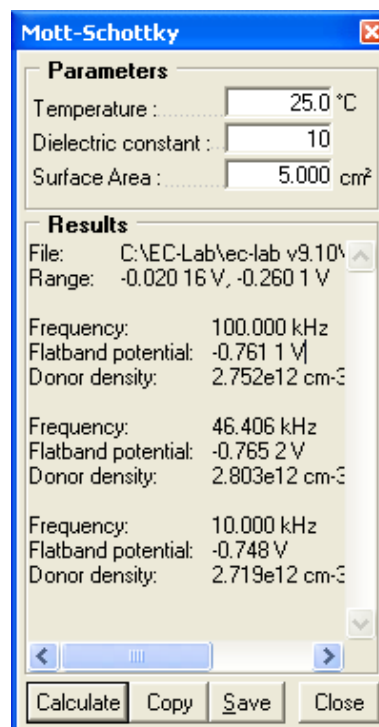


Fig. 116: Mott-Schottky results window.

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 semiconductor defined in the **Parameters** frame.

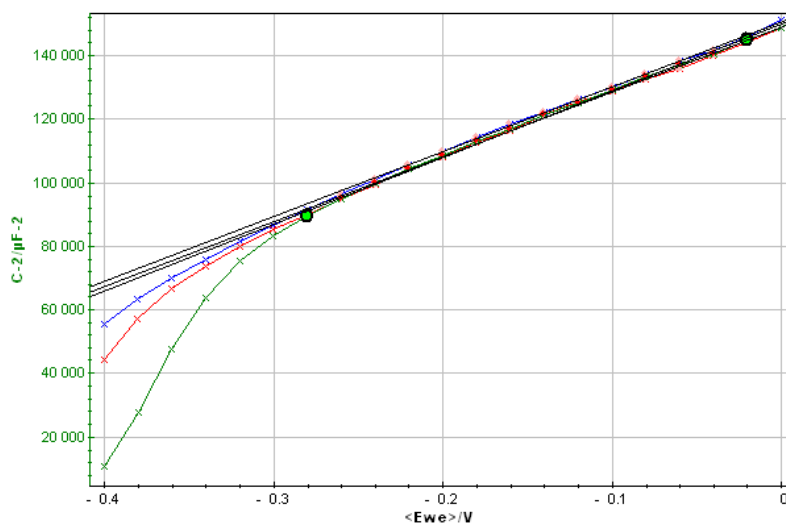


Fig. 117: Mott-Schottky Fit.

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.

3.3.4.3.4 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:

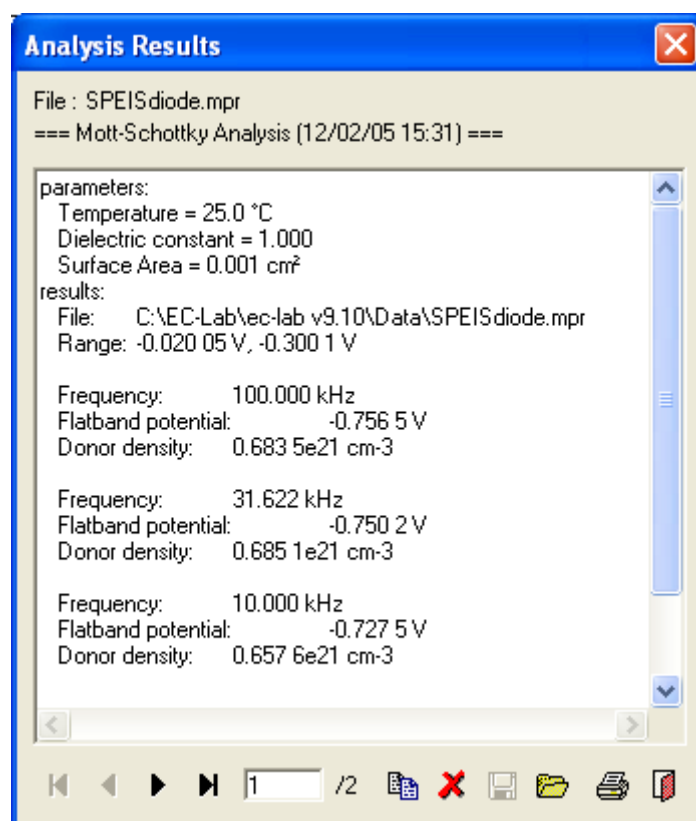


Fig. 118: Analysis Results window.

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.

3.3.4.4 Kramers-Kronig transformation

According to several conditions on the studied system, 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 $\omega \rightarrow \infty$. This transformation is sometimes used in electrochemistry for the validation of experimental results. For example 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:

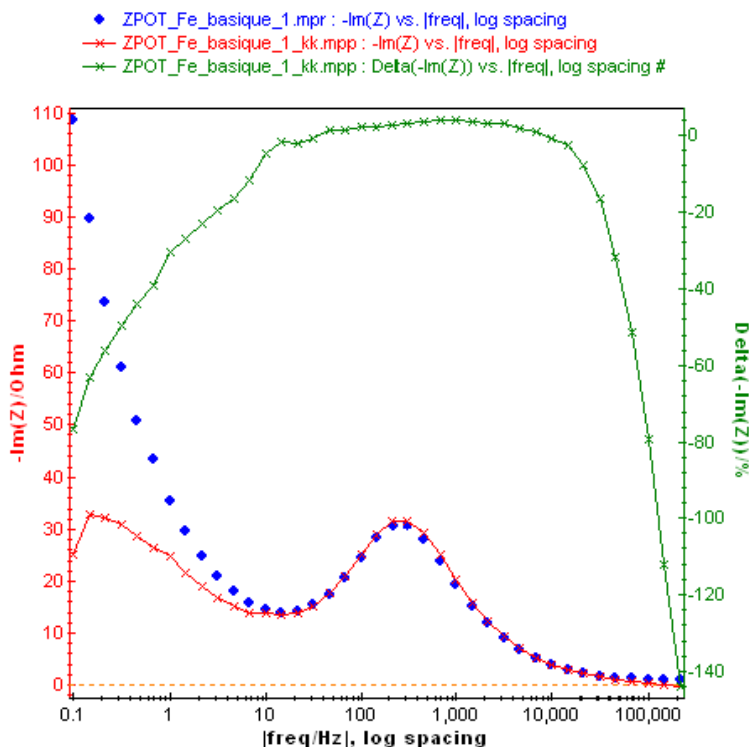
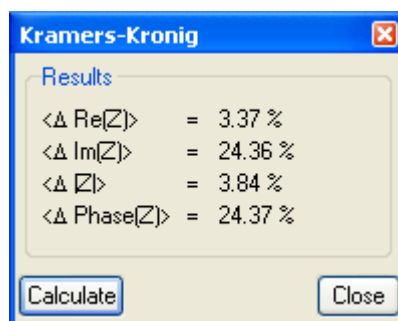


Fig. 119: Result of the Kramers-Kronig criterion applied to the data points with the experimental $\text{Im}(Z)$ part, the calculated one and the relative error.

One can see that the Kramers-Kronig criterion is not applicable to this system because in the low frequency range the impedance doesn't tend towards 0. For the high frequency range, the imaginary parts tend to 0. So the precision is 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.

3.3.5 Corrosion section

The **Tafel Fit** and the **R_p Fit** are both based on the Stern and Geary equation developed here. Stern and Geary (ref. [1]) proposed a model of a corroding system that involves two electrochemical reactions, an oxidation process and a reduction process. This model is based on the Tafel equation that predicts that the logarithm of the current observed in an electrochemical process is directly related to the difference between the applied potential and the open circuit potential.

The Stern and Geary equation can be expressed as follow:

$$I(E) = I_{corr} \left(10^{\frac{E - E_{corr}}{\beta_a}} - 10^{\frac{E - E_{corr}}{\beta_c}} \right)$$

where $I(E)$ is the total current at a specific applied potential E . E_{corr} is the open circuit potential of the system. β_a and β_c are the Tafel constant for the anodic (oxidation) and cathodic (reduction) reactions and are defined as positive numbers.

I_{corr} is the corrosion current corresponding to the anodic and cathodic current at $E = E_{corr}$. The total current $I(E_{corr})$ results from the difference of the anodic and cathodic current being null as expected.

- Stern M. and Geary A.L., J. Electrochem. Soc., 104, (56), 1957.

3.3.5.1 Tafel Fit

The Stern and Geary equation predicts that for $E > E_{corr}$ the anodic reaction predominates and that for $E < E_{corr}$ the cathodic reaction predominates:

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

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


So, in a $\log|I|$ versus E representation, one should see two linear parts for $E > E_{corr}$ and $E < E_{corr}$:

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

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

Tafel Fit window

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

On a linear polarization trace, select the **Tafel Fit** with the Tafel Fit button  in the corrosion section of the Analysis menu. In the $\log(|I|)$ versus E representation, the user has to select the data points centered around E_{corr} (Point for $I = 0$) then click on “**Calculate**”. The software will automatically find β_a and β_c values used for the calculation of the corrosion current I_{corr} . The Tafel Fit analysis window is displayed (Fig. 80). Note: The user will receive a warning message to switch to the $\log(|I|)$ versus E_{we} graph representation.

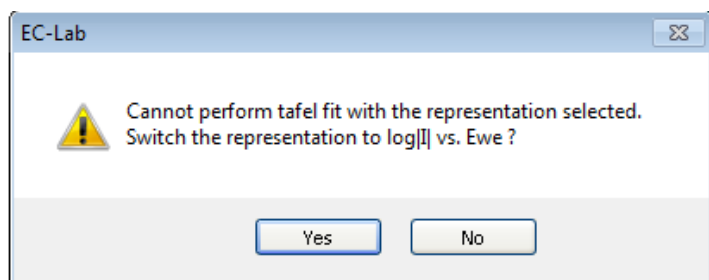


Fig. 120: warning message to switch the graph representation

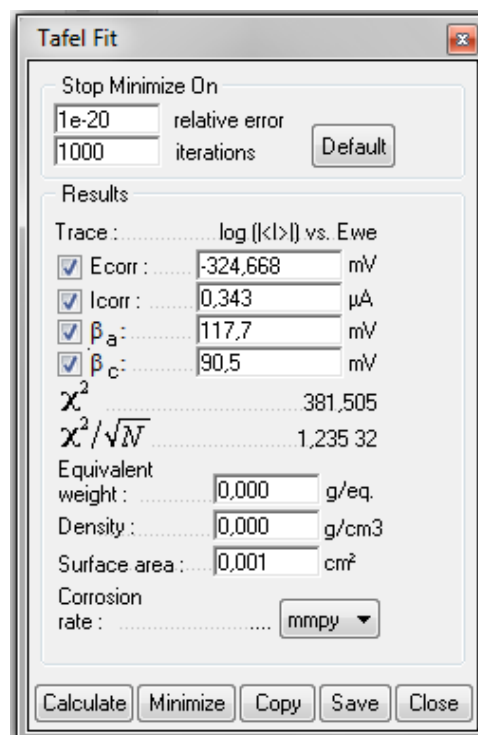


Fig. 121: Tafel Fit window.

Answer **Yes** to the previous message. The fit can be minimized with 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, density and surface area used for the corrosion rate calculation can be defined before the beginning of the experiment in the “**Cell characteristics**” window.

The Tafel graph (Fig. 122) 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.

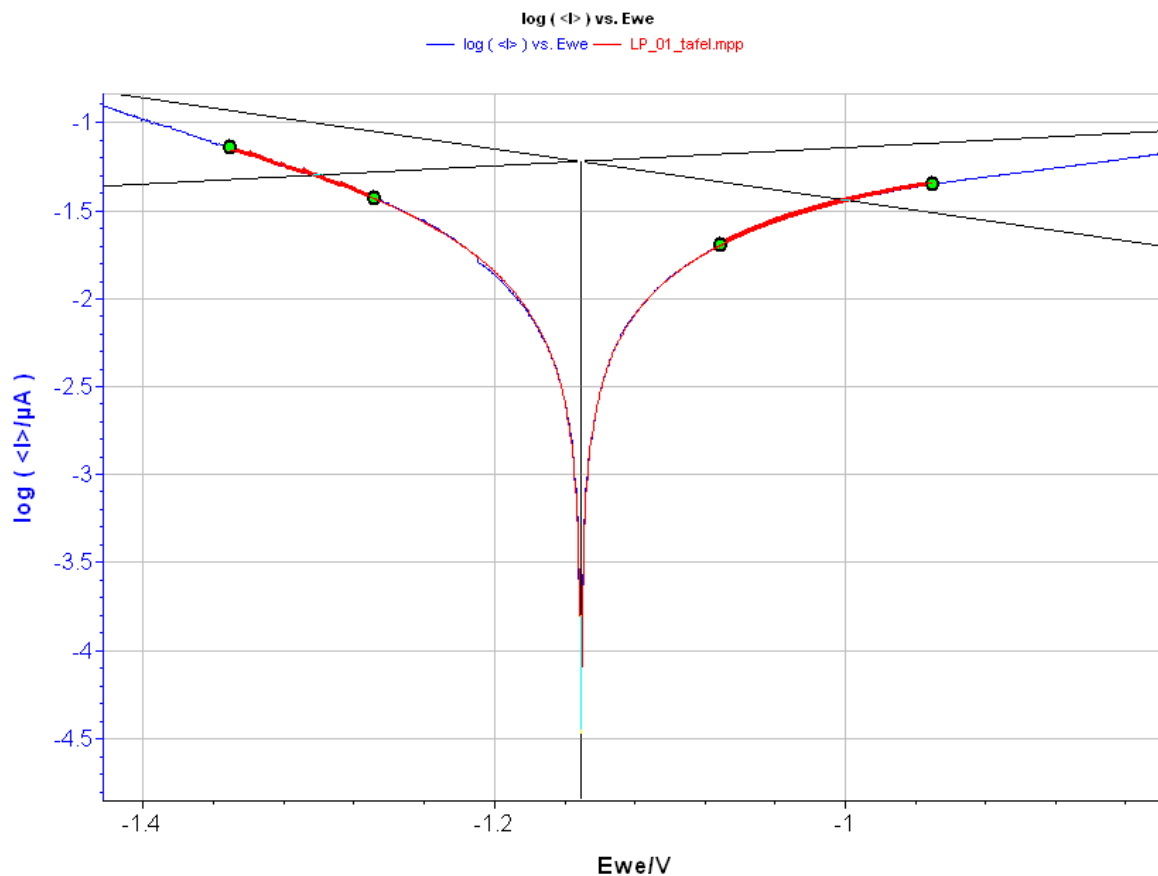


Fig. 122: Tafel graph.

Results of the Tafel Fit are calculated whenever a marker is moved. The default positions of the markers are ± 80 mV and ± 200 mV around $E_{l=0}$. The software deduces the open circuit potential (E_{corr}) from the linear regressions intersection, 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 . The Tafel Fit also works with the plot Ewe vs log||

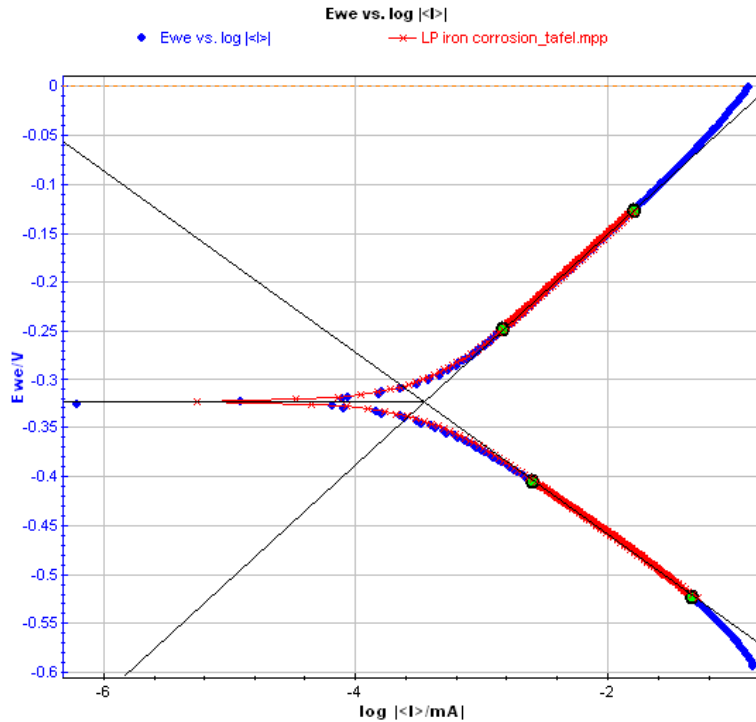


Fig. 123: Tafel Fit on the Ewe vs log|I| graph.

3.3.5.2 R_p Fit

For E sufficiently close to E_{corr} , it is possible to simplify the Stern and Geary equation, such as


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

This equation is commonly presented with E as a 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 is termed the *polarization resistance* because it has the unit of a resistance and is commonly abbreviated R_p :

$$\text{Polarization resistance} = R_{p,E_{corr}} = \frac{\beta_a \beta_c}{I_{corr} (\beta_a + \beta_c) \ln 10}$$

For the **R_p Fit**, the user has to select the data points and then fit (with the R_p fit button  as described before). Then click on “**Calculate**”. The software will automatically find a potential value E_1 on the curve for $I = 0$. Two circle markers are set in a ± 25 mV potential range around E_1 . 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 E_1 (± 25 mV) on an 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 a text file. They can also be saved in a text file.

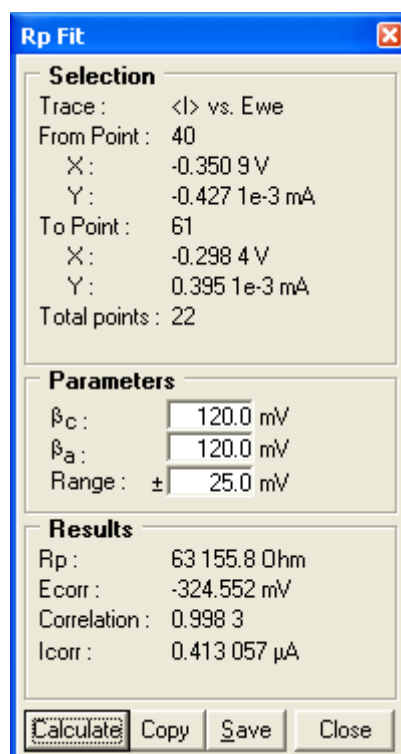


Fig. 124: R_p Fit window.

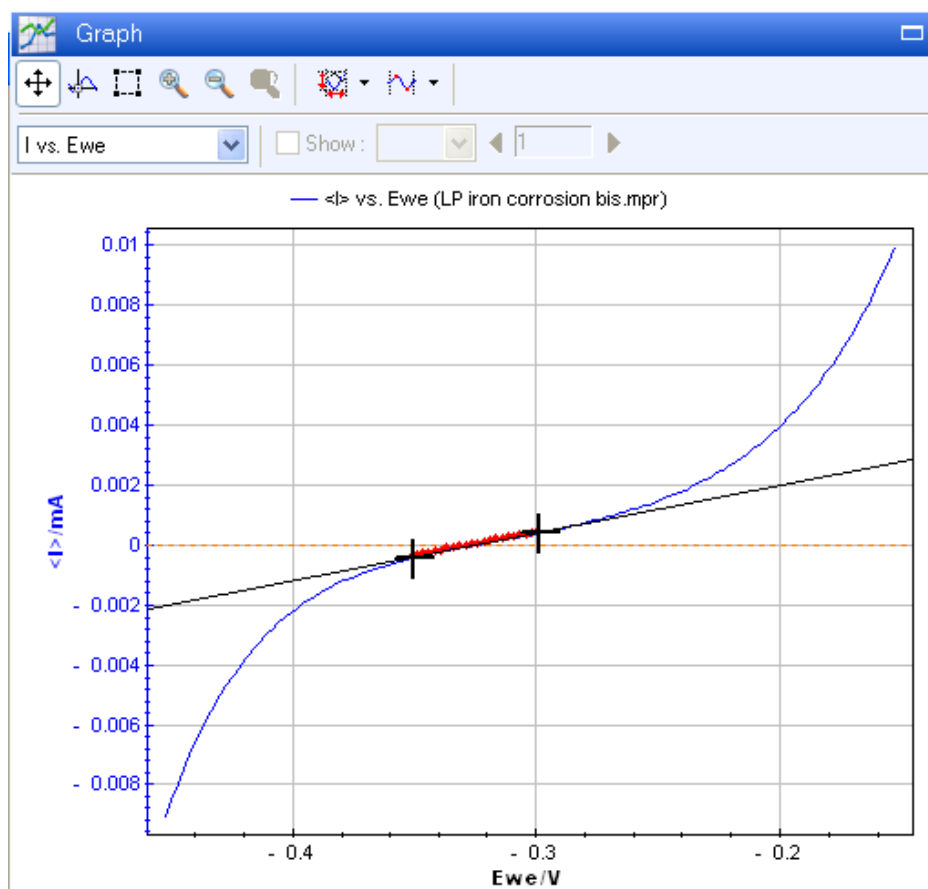


Fig. 125: Linear polarization curve of an iron electrode in H_2SO_4 (0.1 M).

Note: - the user can adjust the R_p Fit. He must grab and move markers. The fit result is automatically updated. It is not necessary to click on "Calculate" another time.

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

3.3.5.2.1 Corrosion rate

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

$$CR = \frac{I_{corr} \cdot K \cdot EW}{d \cdot A} \text{ in millimeter per year (mmpy) or milliinch per year (mpy)}$$

I_{corr}	corrosion current (in A).
K	constant that defines the units of the corrosion rate.
EW	equivalent weight (in g/equivalent).
d	density (in g/cm ³).
A	sample area (in cm ²).

K	CR units
3272 mm/(A-cm-year)	mm/year (mmpy)
1.288x10 ⁵ milliinch/(A-cm-year)	milliinch/year (mpy)

3.3.5.2.2 Minimize option

Nevertheless, results may be different from what is expected for two reasons:

- 1) The linear parts of the plot are not recorded.
- 2) The potential scan range is too large and an additional electrochemical reaction appears that does not fit the Stern-Geary model.

In these cases, it is possible to reduce the error between the model $I_{calc,i}$ and the measured data $I_{mes,i}$ by minimizing the following value:

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

This is obtained in clicking on the **Minimize** button. The Nelder and Mead Simplex method (cf. ref) was used to minimize the χ^2 value. Keep the button pushed (<Enter> or <Alt+M> keys) until the Stern and Geary parameters E_{corr} , I_{corr} , β_a and β_c are stabilized. Then a "theoretical" Tafel graph is displayed, this graph is displayed in agreement with parameters obtained with minimize button.

Note that the Simplex method may not succeed 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:

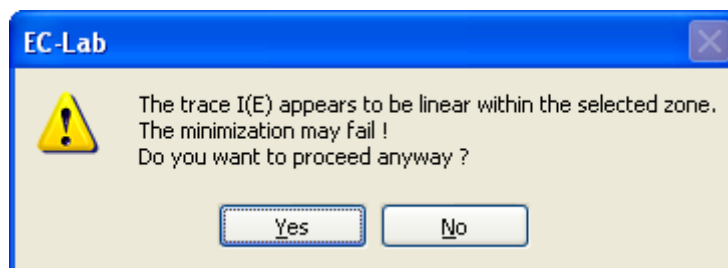


Fig. 126: Tafel Fit minimization message.

For this reason, it is possible to enter directly E_{corr} , I_{corr} , β_a and β_c values and then continue the minimization. Unchecking the boxes around E_{corr} , I_{corr} , β_a and β_c will remove the

corresponding value from the minimization. And at any time, one can restart the calculus from the linear fits by clicking on the **Calculate** button.

Reference:

- 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

3.3.5.3 Corr Sim

The “Corr Sim” tool allows user to simulate data. All these methods are based on the Stern and Geary model. Stern and Geary (ref. [1]) proposed a model of a corroding system that involves two electrochemical reactions, an oxidation process and a reduction process. This model is based on the Tafel equation that predicts that the logarithm of the current observed in an electrochemical process is directly related to the difference between the applied potential and the open circuit potential.

The Stern equation can be expressed as follow:

$$I(E) = I_{corr} \left(10^{\frac{E-E_{corr}}{\beta_a}} - 10^{-\frac{E-E_{corr}}{\beta_c}} \right)$$

where $I(E)$ is the total current at a specific applied potential E . E_{corr} is the open circuit potential of the system. β_a and β_c are the Tafel constant for the anodic (oxidation) and cathodic (reduction) reactions and are defined as positive numbers.

I_{corr} is the corrosion current corresponding to the anodic and cathodic current at $E = E_{corr}$. The total current $I(E_{corr})$ resulting into the difference of the anodic and cathodic current being null as expected.

Fig. 1: Corr. Sim. window.

The three proposed methods are presented hereafter. The appropriate method has to be selected in the combo box of the output frame.

Noise in current, in potential or in resistance depending on the technique can be superimposed to the resulting simulated data.

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.

Reference:


- [1] Stern M. and Geary A.L., J. Electrochem. Soc., 104, (56), 1957.

3.3.5.4 Variable Amplitude Sinusoidal microPolarization (VASP)

Variable Amplitude Sinusoidal micro Polarization (VASP) is a non linear EIS technique used as a corrosion technique to determine the corrosion current and the Tafel parameters. In this technique a potential sinusoidal wave is applied around the corrosion potential (E_{corr}) with N amplitudes increasing from V_{amin} to V_{amax} . For each amplitude, the polarization resistance (R_p) is determined and R_p versus applied potential amplitude is plotted.

For a negligible Ohmic drop $R_e \sim 0$, the R_p parameter can be expressed by the relation below [5,6]

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

The “**VASP Fit**” allows user to fit data from VASP measurements by clicking on the VASP Fit button  in the corrosion section of the analysis tools menu.

The software deduces the current corrosion I_{corr} , and the Tafel parameters β_a and β_c .

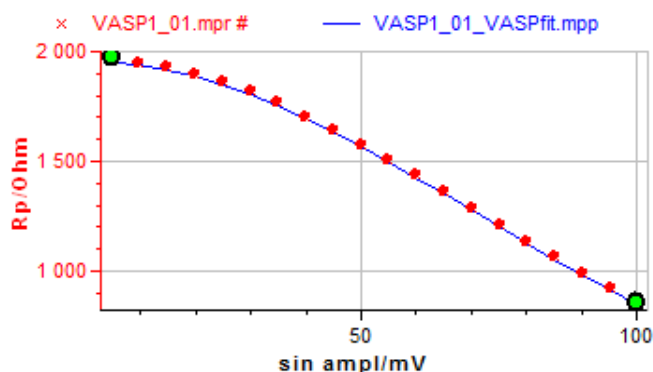
The results can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can also be saved in a text file.

The Fit accuracy can be estimated with the χ^2 parameter according the following equation:

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

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

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



7. Fig. 127: VASP plot and VASP Fit window.

VASP Fit

Selection

Trace : Rp vs. sin ampl
 From point : 0
 X : 4,974e-3 mV
 Y : 1 979 Ohm
 To point : 19
 X : 0,1 mV
 Y : 858,4 Ohm
 Total points : 20

Fit

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

Use β_a and β_c
 Use b_a and b_c

param.	sel.	value	unit
I_{corr}	<input checked="" type="checkbox"/>	11,9	μA
β_a	<input checked="" type="checkbox"/>	74,73	mV
β_c	<input checked="" type="checkbox"/>	190,4	mV

χ^2 3 059
 Iterations xxxx

Calculate Copy Save Close
 Minimize Stop

3.3.5.5 Constant Amplitude Sinusoidal microPolarization (CASP)

The relationship describing the potential modulation vs. the sinus of the frequency is given by:

$$E - E_{corr} = \delta E \sin(2\pi f_s t)$$

Then, by applying a Fourier Transform to the former relationship, the resulting current can be described by the following equation [3-4]:

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

Where the fundamental is δI_0 and the three first harmonics are δI_1 , δI_2 ; δI_3 respectively:

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

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

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

In order to prevent the polarization of the sample, the intensity of the sinusoidal excitation (V_a) has to be chosen so as to have a value of the three first harmonics δI_2 ; δI_3 and δI_3 not null and the rest of harmonics equal to 0. The (f_s) is determined by EIS technique. The simulated harmonic plot is given in I vs. Time.

The CASP fit tool allows the user to find the corrosion current and the anodic and cathodic tafel parameters into a I versus time presentation.


In the analysis menu, select the CASP Fit tool . The CASP Fit window is displayed. The user could receive a warning message to switch to the I versus time graph representation (Fig. 84).



Fig. 128: CASP Fit warning message

Answer Yes to the warning message. The Fit can be done by clicking on calculate button.

The CASP graph (Fig. 85) is displayed in I vs time representation.

The software deduces the current corrosion I_{corr} , and the Tafel parameters β_a and β_c .

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

The Fit accuracy can be estimated with the χ^2 parameter.

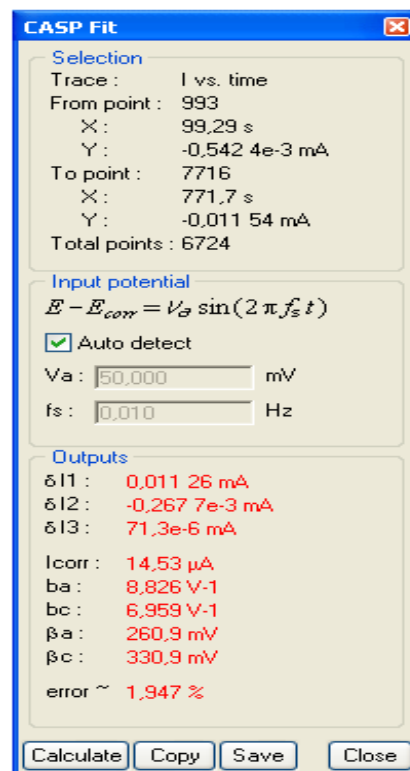


Fig. 129: CASP Fit window.

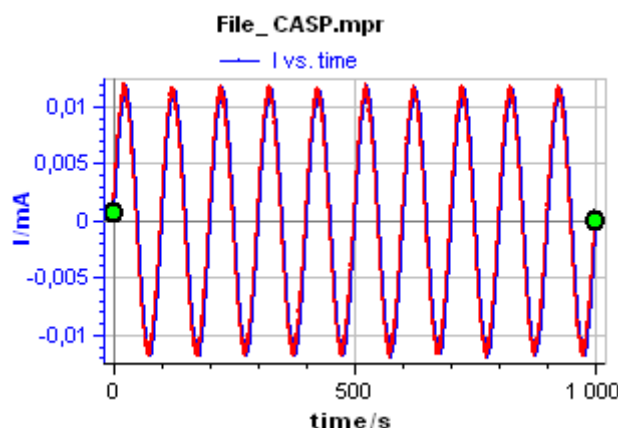



Fig. 130: CASP graph.

3.3.5.6 Electrochemical Noise Analysis

The study of corrosion phenomena by electrochemical noise involves the analysis of random current or potential fluctuations. To study these fluctuations the tool Electrochemical Noise Analysis  was introduced into EC-Lab® in the version 10.00.

Electrochemical noise method requires three electrodes to establish a parameter known as the noise resistance R_n . Two of these are working electrodes and current is measured between them at regular intervals. Fluctuations in current and potential are called current and potential noise.

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

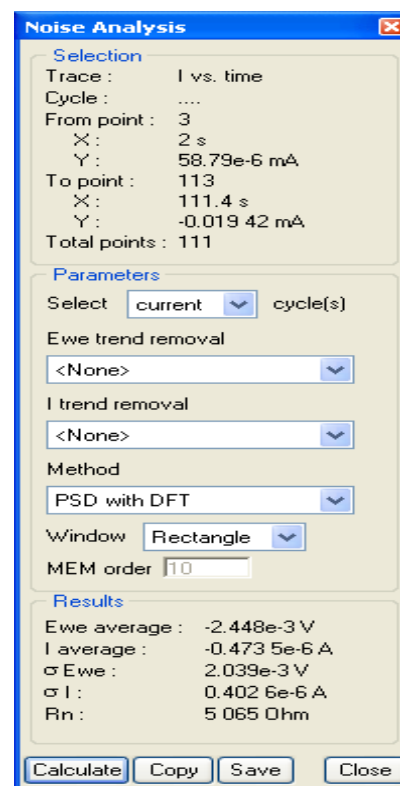
where $\bar{x} = \bar{x}$ is the average.

- **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:



7. Fig. 131: Electrochemical Noise Analysis window.

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

In the Parameters part of the window (Fig. 84), 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.

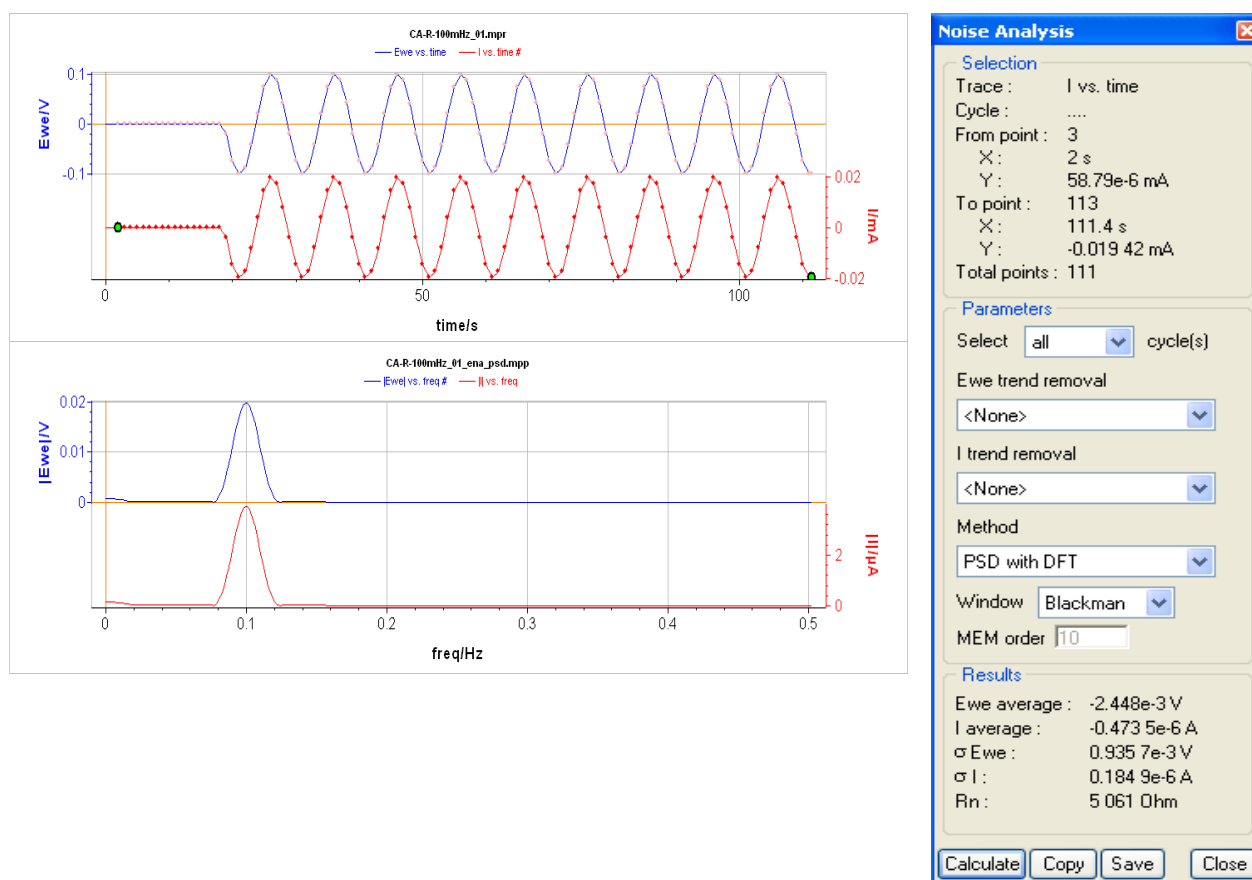
Before to perform the analysis it is possible to remove the trend of the signal (potential and current) by using a **linear fit** or a second order **polynomial fit**.

A description of the analysis windows that can be used is detailed in the section Fourier transform 3.3.2.7 page 63.

Example of electrochemical Noise Analysis is given in Fig. 132.

References:

- Bertocci, U., Frydman, J., Gabrielli, C., Huet, F., and Keddam, 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.



7. Fig. 132: Electrochemical Noise Analysis on system with a 100 mHz electrochemical noise.

4. Glossary

This glossary is made for the user to understand most of the terms of EC-Lab[®] Express software and the terms mentioned in the manual. Classification is done in the alphabetical order.

Absolute value: mathematical function that changes the negative values in positive ones.

Amplifier: current power booster that can be added to each channel individually.

Bandwidth: represents the frequency of the regulation loop of the potentiostat. It depends on the electrochemical cell impedance. The bandwidths values are going from up to 8 with increasing frequency.

CASP Fit: tool available in the Analysis tool menu. It allows user to determine corrosion current and Tafel parameters.

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.

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.

Cell connection: connection of the instrument channel board to the electrochemical cell with five leads.

Circular fit: tool available with the graphic display used to fit a curve and to determine the parameters of the circle such as the capacitance.

Cycle: inside a protocol, this term is used to describe a sequence repeated with time.

Cycle number: processed 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 in scanning linearly the potential of the working electrode and to measure the current resulting from oxydo-reduction reactions. Cyclic voltammetry provides information on redox processes, electron transfer reactions and adsorption processes.

Description: tab in the experiment selection window that describes the chosen protocol.

Device: EC-Lab[®] Express software window in the "Config" menu used to add new instrument IP address to be connected to the computer.

E range: potential range used in the experiment. It is related to the potential resolution.

Electrode surface area: geometric surface of the working electrode. It is a value that is used to represent current density or charge density.

File-Load: the "load" function allows the user to load a data file (.mpr), a setting file (.mps), a linked experiment setting 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.

General Settings: window in EC-Lab[®] Express in which the user can set all parameters about the electrode.

Graph Type tab: tab which contains 3 themes: graph properties, representation and techniques and allows to define the graph parameters and to attribute to each technique a special representation.

Group: option used in a multichannel mode to start at the same time different experiments on the selected channels.

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 give the number of points and the size of the raw data file.

Integral: tool available with the graphic display used to integrate curves.

Kramers-Kronig transformation: tool very helpful to validate impedance measurements done on electrochemical systems.

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.

LOG: function of the graphic display that open the log file (.mpl) containing details and settings of the experiment without any 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 or Z option channel boards.

Min/Max: graphic tool to determine the min and max values on a selected zone of the curve

Mott-Schottky: graphic display of $1/C^2$ vs. E_{we} or $1/C$ vs. E_{we} curve and corresponding linear fit to determine slope and offset.

Option: EC-Lab[®] Express software window in the "Config" menu used to choose the automatic reconnection of the software to the device.

Peak analysis: graphic tool used on a I(E) curve to determine the peak current, the peak potential, exchanged charge quantity and several other parameters.

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[®] Express software, the user can choose a reference electrode in the list or add its own reference electrode.

R_p Fit: tool available with the graphic display used to calculate a polarization resistance.

Run: button that starts the experiment.

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.

Smooth: option that calculates and displays sliding averaged values with n previous values.

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 that stops the experiment.

Subtract files: this tool allows the subtraction of two curves, for example to subtract a background from a curve.

Tafel fit: tool available with the graphic display used to determine with a fit the corrosion current, the corrosion potential and the polarization resistance.

Tafel graph: off-line processing function allowing the user to display on the graph the logarithm of the current (Tafel plot).

Traces processing: tool allowing to apply a mathematical function to the axes.

Units: graphic function used to modify the axis units.

VASP Fit: tool available in the Analysis tool menu. It allows user to determine corrosion current and Tafel parameters.

Wave analysis: graphic tool used on curves obtained in a convective regime and returning the limit current and the half wave potential.

Zfit: once the equivalent circuit defined, the Zfit tool allows to identify parameters of the elements with experimental data points.

ZSim: Simulation tool uses to define the equivalent circuit after an impedance experiment.

ZsimpWin: software delivered by PAR and used to fit impedance curves with electrical circuits.

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